ELECTRONIC EXCITATION AND DISSOCIATION OF GLOBAL WARMING AND OZONE DEPLETING MOLECULES

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Abstract

The research described in this thesis covers a wide range of experimental techniques used to characterise the excitation and dissociation processes of molecules relevant to atmospheric studies, with a particular emphasis on a newly discovered greenhouse gas, trifluoromethyl sulphur pentafluoride, SF$_5$CF$_3$. Since the excitation, dissociation and ionisation processes, together with their subsequent chemical reactivity are particularly important in the upper region of the Earth's atmosphere (e.g., in the stratosphere and ionosphere), the research aimed to provide accurate VUV absorption cross sections for a selected set of atmospheric trace gases.

The spectroscopy of such molecules has been investigated by high resolution photo-absorption and, in the particular case of SF$_5$CF$_3$, electron energy loss spectroscopy (EELS) was also used. High resolution photo-absorption spectra were obtained in a new apparatus assembled at the Institute for Storage Ring Facilities, University of Aarhus, Denmark, where synchrotron radiation with photon energies from 3 eV up to 11 eV has been used with a FWHM resolution better than 0.1 nm. Electronic excitation into both valence and Rydberg states has been studied and assigned for dimethylsulphide and acetaldehyde, trifluoromethyl sulphur pentafluoride, dichlorodifluoromethane, acetonitrile and acrylonitrile. The present results are compared, wherever possible, with previous data.

A photo-electron experiment carried out at the University of Liège to investigate trifluoromethyl sulphur pentafluoride is also described. The ionisation energies obtained were then used to assign the Rydberg series observed in the VUV studies.

At stratospheric altitudes, local chemistry and physics are strongly influenced by the formation of ices and dust surfaces and therefore in this thesis we also present, for the first time, results on the reactivity of gaseous SF$_5$CF$_3$ on ice surfaces.
Acknowledgements

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And last, but not least, my dear and loving Parents, for always being there, for their encouragement and support throughout these years and for making my stay in London possible.
## Symbols and acronyms

The following list of symbols and acronyms appears according to their alphabetical order (Arabic and Greek), where other quantities are formerly presented.

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<td>origin of vibrational transition series</td>
<td>(0-0), $v_{00}$</td>
</tr>
<tr>
<td>degrees Celsius</td>
<td>°C</td>
</tr>
<tr>
<td>electron-dipole spectroscopy</td>
<td>$(e,e)$</td>
</tr>
<tr>
<td>peak assignment uncertainty; no assignment</td>
<td>$(?);?$</td>
</tr>
<tr>
<td>First electronic excited state</td>
<td>$\tilde{A}$</td>
</tr>
<tr>
<td>Angstrom ($10^{-10}$ m)</td>
<td>$\bar{A}$</td>
</tr>
<tr>
<td>appearance energy</td>
<td>AE</td>
</tr>
<tr>
<td>Argon; $n^\text{th}$ order Argon clusters</td>
<td>Ar, Ar$_n$</td>
</tr>
<tr>
<td>Aarhus Storage Ring in Denmark</td>
<td>ASTRID</td>
</tr>
<tr>
<td>gold</td>
<td>Au</td>
</tr>
<tr>
<td>Albedo of the Earth (=0.31)</td>
<td>$a$</td>
</tr>
<tr>
<td>atomic mass units</td>
<td>amu</td>
</tr>
<tr>
<td>arbitrary units</td>
<td>a.u.</td>
</tr>
<tr>
<td>$C_{2v}$ symmetry species</td>
<td>A$_1$, A$_2$, B$_1$, B$_2$</td>
</tr>
<tr>
<td>$C_s$ symmetry species</td>
<td>A', A&quot;</td>
</tr>
<tr>
<td>Second electronic excited state</td>
<td>$\tilde{B}$</td>
</tr>
<tr>
<td>Chlorofluorocarbons</td>
<td>CFCs</td>
</tr>
<tr>
<td>Trichlorofluoromethane</td>
<td>CFC-11</td>
</tr>
<tr>
<td>Third electronic excited state</td>
<td>$\tilde{C}$</td>
</tr>
<tr>
<td>$n$-fold rotation of $(2\pi/n)$ radians</td>
<td>$C_n$</td>
</tr>
<tr>
<td>velocity of light in the vacuum, $\sim 2.998 \times 10^8$ ms$^{-1}$</td>
<td>$c$</td>
</tr>
<tr>
<td>calorie</td>
<td>cal</td>
</tr>
<tr>
<td>direct current</td>
<td>d.c.</td>
</tr>
<tr>
<td>Dissociative Electron Attachment</td>
<td>DEA</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>DMS</td>
<td>dimethylsulphide</td>
</tr>
<tr>
<td>DOS</td>
<td>Differential Oscillator Strength</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>e.g.</td>
<td>for example (exempli gratia)</td>
</tr>
<tr>
<td>eq(s).</td>
<td>equation(s)</td>
</tr>
<tr>
<td>et al.</td>
<td>and others</td>
</tr>
<tr>
<td>eV</td>
<td>electron-Volt</td>
</tr>
<tr>
<td>Fig.; Figs.</td>
<td>Figure; Figures</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-Width Half Maximum</td>
</tr>
<tr>
<td>HCFCs</td>
<td>Hydrochlorofluorcarbons</td>
</tr>
<tr>
<td>He, HeI</td>
<td>Helium; Helium I photo-electron</td>
</tr>
<tr>
<td>HFCs</td>
<td>Hydrofluorocarbons</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>h</td>
<td>Planck's constant</td>
</tr>
<tr>
<td>IP</td>
<td>ionisation potential</td>
</tr>
<tr>
<td>IR</td>
<td>Infra-Red</td>
</tr>
<tr>
<td>J(λ)</td>
<td>actinic flux of solar radiation</td>
</tr>
<tr>
<td>km</td>
<td>Kilometre</td>
</tr>
<tr>
<td>Kr</td>
<td>Krypton</td>
</tr>
<tr>
<td>k</td>
<td>rate constant; (10^3)</td>
</tr>
<tr>
<td>k_{OH}</td>
<td>hydroxyl radical rate constant</td>
</tr>
<tr>
<td>k_p</td>
<td>photo-dissociation rate constant</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Un-occupied Molecular Orbital</td>
</tr>
<tr>
<td>l/s</td>
<td>litres per second</td>
</tr>
<tr>
<td>l_λ</td>
<td>Rydberg series, ( l = 3, 4, \ldots ) and ( \lambda = \sigma, \pi, \delta )</td>
</tr>
<tr>
<td>M</td>
<td>Electronic ground state of molecule M</td>
</tr>
<tr>
<td>M^*</td>
<td>Ionic electronic excited state of molecule M</td>
</tr>
<tr>
<td>Mb</td>
<td>Mega barn (10^{-18} cm²)</td>
</tr>
<tr>
<td>MeV</td>
<td>Mega electron-Volt (10^6 eV)</td>
</tr>
<tr>
<td>ML</td>
<td>Mono-Layer</td>
</tr>
<tr>
<td>MPI</td>
<td>Multi-Photon Ionisation</td>
</tr>
<tr>
<td>m</td>
<td>meter</td>
</tr>
<tr>
<td>mA</td>
<td>mili-Ampères (10^{-3} A)</td>
</tr>
<tr>
<td>mbar</td>
<td>mili bar (= 100 Pa)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>mol</td>
<td>unit of elementary mass</td>
</tr>
<tr>
<td>mT</td>
<td>mili-Tesla ($10^{-3}$ T)</td>
</tr>
<tr>
<td>$N; N$</td>
<td>number of atoms; number of magnetic poles</td>
</tr>
<tr>
<td>NIR</td>
<td>Negative Ion Resonance(s)</td>
</tr>
<tr>
<td>NOx</td>
<td>Nitric oxide radicals</td>
</tr>
<tr>
<td>$n$</td>
<td>lone pair electrons; principal quantum number</td>
</tr>
<tr>
<td></td>
<td>gas number density</td>
</tr>
<tr>
<td>$n\sigma; n\nu$</td>
<td>vibrational series</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometre ($10^{-9}$ m)</td>
</tr>
<tr>
<td>n*</td>
<td>Rydberg reduced term energy coefficient</td>
</tr>
<tr>
<td>ODPs</td>
<td>Ozone Depletion Potentials</td>
</tr>
<tr>
<td>OH</td>
<td>Hydroxyl radical</td>
</tr>
<tr>
<td>Pa</td>
<td>Pascal</td>
</tr>
<tr>
<td>PES</td>
<td>Photo-Electron Spectroscopy</td>
</tr>
<tr>
<td>PSCs</td>
<td>Polar Stratospheric Clouds</td>
</tr>
<tr>
<td>$p$</td>
<td>sample pressure (Pa)</td>
</tr>
<tr>
<td>ph</td>
<td>photons</td>
</tr>
<tr>
<td>p.; pp.</td>
<td>page; pages</td>
</tr>
<tr>
<td>ppb; ppbv</td>
<td>part per billion; part per billion by volume</td>
</tr>
<tr>
<td></td>
<td>$\sim 2.5 \times 10^{10}$ molecules cm$^{-3}$, $T = 298K$, $p = 1$ atm</td>
</tr>
<tr>
<td>ppm; ppmv</td>
<td>part per million; part per million by volume</td>
</tr>
<tr>
<td></td>
<td>$\sim 2.5 \times 10^{13}$ molecules cm$^{-3}$, $T = 298K$, $p = 1$ atm</td>
</tr>
<tr>
<td>ppt; pptv</td>
<td>part per trillion; part per trillion by volume</td>
</tr>
<tr>
<td></td>
<td>$\sim 2.5 \times 10^{7}$ molecules cm$^{-3}$, $T = 298K$, $p = 1$ atm</td>
</tr>
<tr>
<td>$R; R$</td>
<td>monochromator resolution; universal gas constant; one Rydberg (13.6 eV)</td>
</tr>
<tr>
<td>$R_c$</td>
<td>crossing radius of two potential energy surfaces</td>
</tr>
<tr>
<td>RPD</td>
<td>Retarding Potential Difference</td>
</tr>
<tr>
<td>RTM</td>
<td>Race Track Microtron</td>
</tr>
<tr>
<td>Ru</td>
<td>Ruthenium</td>
</tr>
<tr>
<td>R(Y - X)</td>
<td>Internuclear separation of species X and Y</td>
</tr>
<tr>
<td>ref.</td>
<td>reference</td>
</tr>
<tr>
<td>S; S</td>
<td>Sulphur; solar constant</td>
</tr>
<tr>
<td>$S_n$</td>
<td>n-fold improper rotation</td>
</tr>
<tr>
<td>Symbol</td>
<td>Acronym/Description</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------</td>
</tr>
<tr>
<td>SR</td>
<td>Synchrotron radiation</td>
</tr>
<tr>
<td>S₀, S₁</td>
<td>singlet ground and first excited states</td>
</tr>
<tr>
<td>T, Tₑ</td>
<td>absolute temperature (K); Earth’s temperature</td>
</tr>
<tr>
<td>TEM</td>
<td>Trochoidal Electron Monochromator</td>
</tr>
<tr>
<td>T₁</td>
<td>first triplet excited state</td>
</tr>
<tr>
<td>TNI</td>
<td>Temporary Negative Ion</td>
</tr>
<tr>
<td>TPEPICO</td>
<td>Threshold Photo-Electron–Photo-Ion COincidence</td>
</tr>
<tr>
<td>TPES</td>
<td>Threshold Photo-Electron Spectroscopy</td>
</tr>
<tr>
<td>Tg, Tgy⁻¹</td>
<td>Tera grams (10¹² g); Tera grams per year</td>
</tr>
<tr>
<td>torr</td>
<td>= 133.3 Pa</td>
</tr>
<tr>
<td>UCL</td>
<td>University College London</td>
</tr>
<tr>
<td>UVI</td>
<td>Ultra-Violet 1</td>
</tr>
<tr>
<td>V; V</td>
<td>sample cell volume; Volt</td>
</tr>
<tr>
<td>V(R)</td>
<td>Potential energy</td>
</tr>
<tr>
<td>VOCs</td>
<td>Volatile Organic Compounds</td>
</tr>
<tr>
<td>VUV</td>
<td>Vacuum Ultra-Violet</td>
</tr>
<tr>
<td>ν</td>
<td>electron’s velocity in a synchrotron ring</td>
</tr>
<tr>
<td>X</td>
<td>Electronic ground state</td>
</tr>
<tr>
<td>yr</td>
<td>Year</td>
</tr>
<tr>
<td>α₀</td>
<td>intercept coefficient of the yy axis</td>
</tr>
<tr>
<td>β₀</td>
<td>Gradient</td>
</tr>
<tr>
<td>Γₜₖₜ</td>
<td>total number of vibrational modes</td>
</tr>
<tr>
<td>Γ(R)</td>
<td>Energy width of an ionic state</td>
</tr>
<tr>
<td>Γ(ψₗ)</td>
<td>Irreducible representation for the wavefunction</td>
</tr>
<tr>
<td>ΔE</td>
<td>energy difference</td>
</tr>
<tr>
<td>Δνᵢ</td>
<td>vibrational energy difference of mode νᵢ</td>
</tr>
<tr>
<td>ΔS</td>
<td>total spin momentum</td>
</tr>
<tr>
<td>δ</td>
<td>quantum defect; delta orbital</td>
</tr>
<tr>
<td>ε</td>
<td>kinetic energy of the incident electron</td>
</tr>
<tr>
<td>θ'</td>
<td>vector velocity angular component</td>
</tr>
<tr>
<td>λ</td>
<td>wavelength</td>
</tr>
<tr>
<td>μ</td>
<td>electric dipole operator</td>
</tr>
<tr>
<td>μ'; μm</td>
<td>velocity in a moving frame χ'; 10⁻⁶ m</td>
</tr>
</tbody>
</table>
Symbols and acronyms

\( \nu, \nu_i \)  
\( \nu, \nu_i \) vibrational state; vibrational mode, \( i = 1 - \infty \)  
velocity of a particle

\( \pi \)  
pi orbital

\( \pi^* \)  
pi anti-bonding molecular orbital

\( \sigma(\lambda) \)  
photo-absorption cross section

\( \sigma \)  
\( \sigma \) sigma orbital; reflection plane of symmetry  
\( \sigma^* \) Stefan-Boltzmann constant

\( \sigma^* \)  
sigma anti-bonding molecular orbital

\( \sigma^\sigma, \sigma_u, \pi_u, \pi^u, \delta_u \)  
C_{\text{e}h} symmetry species

\( \nu \)  
frequency

\( \chi, \chi' \)  
stationary reference frame; reference moving frame

\( \varphi \)  
angle between normal incidence and plane

\( \varphi(\lambda) \)  
primary quantum yield

\( \psi_i \)  
electronic wavefunction of state \( i \)
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True sciences are those which have penetrated through the senses as a result of experience and thus silencing the tongues of disputants, not feeding investigators on dreams but always proceeding successively from primary truths and established principles, in a proper order towards the conclusion.

Leonardo da Vinci, (1452-1519), *in Codex Urbinas Latinus*
Chapter 1

Atmospheric environmental physics: an overview

*Take nothing on its looks: take everything on evidence.*

Charles Dickens (1812 – 1870)

1.1 Introduction

Environmental science is a rapidly emerging discipline with major political and social consequences. Accurate analysis of the composition of the terrestrial atmosphere is crucial in understanding many modern environmental issues and assessing whether remedial actions are successful. Many of the techniques to study the physics and chemistry of the terrestrial atmosphere are based on spectroscopy. This is due to the fact that every atom, molecule or molecular cluster is uniquely characterised by a set of energy levels. Transitions between levels, by the absorption or emission of electromagnetic radiation, result in highly specific spectroscopic features. Moreover, since each atom or molecular species directly interacts with its local environment, the relevant energy levels and transition intensities may be perturbed by their surroundings, hence by probing the spectroscopy of each atom or molecule it is possible to probe its local environment. Atomic/molecular spectroscopy thus allows both the identification and the quantification of trace amounts of species in the atmosphere and provides an accurate assessment of their physical and chemical environment.

In order to develop accurate models of the physico-chemical processes in the terrestrial atmosphere large amounts of spectroscopic data must be collected for a vast number of compounds. For example a detailed knowledge of the visible and ultra-violet photo-absorption spectra of a molecular system enables an estimation of the atomic / molecular lifetime in the sunlit atmosphere. Infrared photo-absorption spectra determine how effective a molecule will be at absorbing radiation emitted by the Earth and hence determine the atmospheric energy balance and surface temperatures.
Currently, there are a few specific spectroscopic techniques used to monitor the atmosphere. These include laser techniques and remote sensing techniques from satellites for example NASA’s Upper Atmosphere Research Satellite (UARS) monitors the global ozone layer, while the Meteosat series of satellites monitors weather patterns by IR measurement of clouds. Other satellites probe carbon dioxide emissions, or SO$_2$ plumes from industry and volcanoes. All these observations rely upon having an accurate spectroscopic data base. The work in this thesis aims to provide a detailed spectroscopic study of the VUV spectra of several atmospheric molecules and to investigate mechanisms by which they are removed from the terrestrial atmosphere. Before describing the experiments and results obtained it is necessary to briefly review the structure, composition and physical and chemical processes prevalent in the Earth’s atmosphere.

1.2 The Earth’s atmosphere

The Earth’s atmosphere is a gaseous envelope, retained by gravity, surrounding the planet. Most dense at its surface, 90% of the mass is contained in the first 20 km and 99.9% of the mass within the first 50 km. The atmosphere becomes thinner with increasing height until at around 1000 km it merges indistinguishably with interstellar space. The Earth’s atmosphere can be divided into layers characterised by their temperature (curved line, Figure 1.1). Each layer is called a sphere (troposphere, stratosphere, mesosphere, ionosphere, thermosphere and magnetosphere) and the boundary between layers is called a pause (tropopause, stratopause, mesopause) [1.1].

It is generally believed that the solar system condensed out of an interstellar cloud of gas and dust, about 4.6 billion years ago. The atmospheres of the Earth and the other planets, such as Venus and Mars, are thought to have formed as a result of trapped volatile compounds from the planet itself. The early atmosphere of the Earth is believed to have been a mixture of carbon dioxide, nitrogen, and water vapour, with trace amounts of hydrogen, a mixture similar to that emitted by present day volcanoes.

The Earth’s atmosphere is now composed primarily of ~78% N$_2$, ~21% O$_2$ and ~1% Ar, whose abundances are controlled over geologic time scales by the biosphere, uptake and release from crustal material, and degassing of the interior. Water vapour is the next most abundant constituent. It is found mainly in the lower atmosphere and its concentration is variable, reaching values up to 3%. The remaining gaseous constituents, known as trace gases, comprise less than 1% of the atmosphere. However,
Chapter One

these trace gases play a crucial role in the Earth’s radiative balance and drive most of the chemistry of the atmosphere.

Present-day measurements coupled with analyses of ancient air trapped in bubbles in ice cores provide a record of dramatic, global increases in the concentrations of gases such as ozone ($O_3$), carbon dioxide ($CO_2$), methane ($CH_4$), nitrous oxide ($N_2O$), and various halogen-containing compounds. These gases act as atmospheric thermal insulators. They absorb infrared radiation from the Earth’s surface and re-emit a portion of it back to the surface (see section 1.2.2).

Carbon dioxide in the Earth’s atmosphere accounts for just 0.03 % – 0.04 % of its mass, while water vapour, varies in amount from 0 to 2%. Carbon dioxide and some other minor gases present absorb some of the thermal radiation leaving the surface and emit radiation from much higher and colder levels out to space. These radiatively active gases known as greenhouse gases act as a partial blanket for the thermal radiation from the surface ensuring the Earth is substantially warmer than it would be otherwise. Indeed without these greenhouse gases, the Earth's average surface temperature would be roughly $-20^\circ C$ [1.1]. To understand this it is necessary to review laws of radiation.

Figure 1.1 – The structure of the Earth’s atmosphere.

1.2.1 Solar radiation and atmospheric heating

A black-body is defined as a hypothetical body consisting of a sufficient number of molecules absorbing radiation and emitting electromagnetic radiation in all parts of
the electromagnetic spectrum, so that all incident radiation is completely absorbed and the maximum possible emission is realised at all wavelengths bands and isotropically.

The active role played by the atmosphere in the regulation of the Earth's temperature is best appreciated by looking at the effects of not having an atmosphere. These consequences can be seen by taking a simple radiative balance model where the Sun emits radiation in all directions, the Earth absorbs solar radiation, warming its surface and then re-emits energy isotropically. Assuming the Earth as a spherical blackbody with radius $R_E$ and temperature $T_E$, Stefan-Boltzmann's law states that the power output, $P$ is:

$$P = 4\pi R_E^2 \sigma T_E^4$$

with $\sigma$ the Stefan-Boltzmann constant ($5.67 \times 10^{-8} \text{ Wm}^2\text{K}^{-4}$). The rate of solar energy arising at the Earth is given by $S(1 - \alpha) \pi R_E^2$, where $\alpha$ is the albedo of the Earth ($= 0.31$), and $S$ the solar constant (1353 Wm$^{-2}$). The magnitude of this constant changes slightly as the radiation reaching the Earth will have variations with season and the 11 year solar cycle as well as some shorter term variations, e.g. sunspots. The terrestrial energy balance then requires that:

$$S(1 - \alpha) \pi R_E^2 = 4\pi R_E^2 \sigma T_E^4$$

with the result that the Earth's "effective temperature" is given by:

$$T_E = \sqrt[4]{\frac{S(1-\alpha)}{4\sigma}}$$

Using eq. (1.3), the effective temperature of the Earth is ~ 253 K, or -20°C. However, the average temperature of the Earth's surface is well above this (288 K, 15°C). We have neglected those atmospheric absorption/emission processes discussed above and in effect considered the space-atmosphere interface, not the atmosphere-ground interface [1.1]. The 35°C elevation in surface temperature is due to the greenhouse effect (see section 1.2.2).

The majority of the energy entering the Earth's atmosphere is coming from the Sun, produced in the photosphere, which acts as a blackbody of approximately 6000 K. Radiation is mainly emitted at visible, infrared and ultra-violet wavelengths with the peak occurring in the yellow part of the visible region.
Figure 1.2 shows the intensity of incident radiation at the top of the atmosphere represented by the blue curve, and the black curve is the intensity of the radiation observed at the Earth’s surface. It is clear that there is a general attenuation (green colour area) of the radiation due to passing through a gas and in accordance to the Beer-Lambert law:

\[ I = I_0 \exp(-n \sigma x) \]  \hspace{1cm} (1.4)

with \( I_0 \) the incident intensity, \( I \) the transmitted intensity, \( n \) the gas number density, \( \sigma \) the photo-absorption cross section and \( x \) the path length.

![Figure 1.2 – Energy budget of the Earth’s atmosphere.](image)

The red areas in Fig. 1.2 indicate the presence of infrared absorbing bands in the water (H₂O), oxygen (O₃) and carbon dioxide (CO₂) atmospheric molecules, in addition to the general attenuation. On average, about one third of the solar radiation that hits the Earth is reflected back to space (Figure 1.3), some is absorbed by the atmosphere but most is absorbed by the land and oceans.

The total energy arriving at the top of the Earth’s atmosphere per unit area per unit time is \( \sim 1353 \text{ Wm}^{-2} \). Due to geometrical arguments, the effective solar flux incident to a level surface at the top of the atmosphere is given by \( \frac{1}{4}S \), which means 343 Wm\(^2\) [1.2] (Figure 1.3). The numerical values in Fig. 1.3 show how the radiation...
interacts with the Earth’s atmosphere and surface, and the power associated with each process (measured in Wm$^{-2}$). The absorption value at the Earth’s surface is given by 168 Wm$^{-2}$ minus the reflection from the surface, with a net value of approximately 140 Wm$^{-2}$. The values entering (absorbed by surface, 140 Wm$^{-2}$, and atmosphere, 100 Wm$^{-2}$) total 240 Wm$^{-2}$) and leaving the atmosphere (240 Wm$^{-2}$) are the same so the system is in thermal equilibrium.

![Energy budget of the Earth's atmosphere](image_url)

Figure 1.3 – Energy budget of the Earth’s atmosphere.

### 1.2.2 Greenhouse effect

The Earth not does not only absorb and reflect radiation, but is also an emitter. The emission is that of a blackbody at 288 K and therefore peaks far in the infrared. The energy balance (Fig. 1.3) is based on the emission and partial absorption of this infrared radiation and any change in any of these processes may disturb the balance.

When the Earth has absorbed the solar radiation it heats up and then re-emits at longer wavelengths (in the infrared). The increase in the global temperature is due to retention of some of the outgoing terrestrial radiation flux. Hence, the atmosphere must be more efficient at absorbing infrared radiation than it is at absorbing the visible / UV solar radiation. The principle that some molecules are strong infrared absorbers and thus
retain terrestrial thermal energy is the basis of global warming that raises Earth’s temperature from 253 K to 288 K.

The transmittance of the Earth’s atmosphere in the infrared region is shown in Figure 1.4 together with the main molecular absorption bands. The transmittance in this region of the spectrum may be of the order of 60% – 80% but there are regions where most of the radiation is absorbed. These absorptions are due to the presence of infrared active bands of atmospheric molecules such as \( \text{O}_3 \), \( \text{CO}_2 \) and \( \text{H}_2\text{O} \). While the effect of these absorptions on the solar flux is small (because it is mainly peaked in the visible regions), the effect in the Earth’s infrared emission spectrum is much larger. In fact, of the infrared energy emitted by the Earth, only 8% is directly transmitted to space with the other 92% undergoing several absorptions and re-emissions before being emitted to space at altitudes of \( \sim 6 \) km near the top of the troposphere. This cycle leading to retention of thermal energy is known as greenhouse effect.

**Figure 1.4 – Transmittance of the Earth’s atmosphere in the infrared.**

Molecules that absorb effectively in the infrared but have little or no absorbance in the visible are generically designated as greenhouse gases. The effectiveness of a greenhouse gas is defined as radiative forcing, and is a measure of the change in the Earth atmosphere system’s radiation budget (in \( \text{W m}^{-2} \)) when the atmospheric concentration of that certain molecule is changed \([1.3]\).
Chapter One

The most important anthropogenic greenhouse gases present in the Earth's atmosphere are those that absorb in the regions of Fig. 1.4, where the Earth's transmittance is not usually high, in particular between ~ 7.5 μm – 14 μm. These molecules, then absorb radiation that would otherwise escape onto space and thus enhance the natural global warming.

1.2.3 Enhanced greenhouse effect

The retention of thermal energy by the greenhouse effect is a natural phenomenon with the magnitude of the effect relying on the equilibrium of production and destruction of the absorbing gases. However, anthropogenic emissions are causing greenhouse gas levels in the atmosphere to increase.

Table 1.1 lists some of the main greenhouse gases and their concentrations in pre-industrial times (compared with 2000), their atmospheric lifetimes, anthropogenic sources, and Global Warming Potentials (GWP) [1.4, 1.5].

<table>
<thead>
<tr>
<th>Greenhouse gases</th>
<th>Chemical formula</th>
<th>Pre-industrial concentration</th>
<th>Concentration in 2000</th>
<th>Atmospheric lifetime (years)</th>
<th>Anthropogenic sources</th>
<th>Rate of change (increasing)</th>
<th>GWP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>CO2</td>
<td>280 ppmv</td>
<td>368 ppmv</td>
<td>5 to 200</td>
<td>Fossil combustion</td>
<td>31 ± 4%</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Land use conversion</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cement production</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>CH4</td>
<td>700 ppbbv</td>
<td>1750 ppbv</td>
<td>12</td>
<td>Fossil fuels</td>
<td>151 ± 25%</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Waste dumps</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Livestock</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>N2O</td>
<td>270 ppbv</td>
<td>316 ppbv</td>
<td>114</td>
<td>Fertilizer</td>
<td>17 ± 5%</td>
<td>296</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Industrial processes</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Combustion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CFC – 12</td>
<td>CCl3F2</td>
<td>0</td>
<td>503 pptv</td>
<td>100</td>
<td>Liquid coolants</td>
<td>increased globally</td>
<td>9300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Foams</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCFC – 22</td>
<td>CHClF2</td>
<td>0</td>
<td>70 pptv</td>
<td>12</td>
<td>Liquid coolants</td>
<td>increased globally</td>
<td>1300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>increased globally</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perfluoromethane</td>
<td>CF4</td>
<td>40 pptv</td>
<td>80 pptv</td>
<td>&gt; 50000</td>
<td>Production of</td>
<td>50 ± 2%</td>
<td>5700</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>aluminium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur hexafluoride</td>
<td>SF6</td>
<td>0</td>
<td>&gt; 4 pptv</td>
<td>3200</td>
<td>Dielectrics</td>
<td>increased globally</td>
<td>22200</td>
</tr>
<tr>
<td>Trifluoromethyl sulphur pentafluoride</td>
<td>SF3CF3</td>
<td>0</td>
<td>0.125 ppt</td>
<td>~ 1000</td>
<td>Unknown</td>
<td>~6%</td>
<td>17600 - 19100</td>
</tr>
</tbody>
</table>

Table 1.1 – The main greenhouse gases.

These gases include halocarbons, chlorofluorocarbons (CFCs), sulphur hexafluoride (SF6), and trifluoromethyl sulphur pentafluoride (SF3CF3). All are present in only small quantities but possess large radiative forcings and in some particular cases long lifetimes, which leads to substantial contributions to the global radiation budget.
SF3CF3 has been included because it has been recently discovered in the atmosphere (Chapter 5) and its effect on global warming and ozone depletion could become important, especially with its current rate of increase at ~ 6% a year [1.4]. The GWP is an index defined as the cumulative radiative forcing between the present and some chosen time horizon (usually 100 years) caused by a unit mass of gas emitted, expressed relative to a reference gas such as CO2, (section 3.2.5.3).

Since the beginning of the industrial revolution, atmospheric concentrations of carbon dioxide have increased nearly 30%, methane concentrations have more than doubled, and nitrous oxide concentrations have risen by about 15% [1.5]. These increases have enhanced the heat-trapping capability of the Earth's atmosphere. Atmospheric CO2 has increased from concentrations of about 280 ppmv to about 368 ppmv at present. The smooth curve in Figure 1.5 is based on a hundred year running average [1.6]. It is evident that the rapid increase in CO2 concentrations has been occurring since the onset of industrialization, following the increase in emissions from fossil fuels.

![Figure 1.5 - Global atmospheric concentrations of CO2 (after [1.6]).](image)

The plot in Figure 1.6 is an example of the recent (1990 – 1999) and future (2000 – 2010) trends in the total greenhouse gas emissions of six greenhouse gases: carbon dioxide (CO2), methane (CH4), nitrous oxide (N2O), HFCs, PFCs and sulphur hexafluoride (SF6), for the United Kingdom and Portugal [1.6]. Actual emissions of CO2, CH4, N2O have been used to calculate the evolution trending, while PFCs and SF6
were included only in the 1995 calculation. Projected emissions are obtained taking into account emissions from CO$_2$, CH$_4$, N$_2$O for 1990 and 2010 [1.6].

The plots are expressed in million tonnes of CO$_2$ equivalent emissions versus time - 1990 (base year) to 2010 (or Kyoto target period 2008 – 2012). The white lines represent actual data for the period 1990 – 1999.

![Graph showing greenhouse gas emissions as a function of the year](image)

**Figure 1.6 – Total greenhouse gas emissions as a function of the year (after [1.6]).**

The orange lines delineate the binding reduction commitments or emissions targets for the 2008 – 2012 period, and are expressed in percentages of decrease or increase from the base year according to what has been requested or allowed for in the Kyoto Protocol$^1$. The intervals between the black and the orange lines highlight the percent differences difficulty in meeting the proposed emissions levels by 2010. In this thesis we present results on greenhouse gases (SF$_5$CF$_3$, CCl$_2$F$_2$ both produced by industry) dimethylsulphide and acetaldehyde (naturally occurring greenhouse gases).

**1.3 The ozone filter**

Ozone (Fig. 1.7) is a minor constituent of the Earth’s atmosphere, forming only 0.2% of the atmospheric mass. If all the atmospheric ozone were collected at the Earth’s surface, it would form a layer just 3 mm thick at standard temperature and pressure. However, at altitudes ~ 30 km the ozone layer defines a region of locally high ozone

---

$^1$ The main target is a global reduction of the emissions of six greenhouse gases (Carbon dioxide (CO$_2$), Methane (CH$_4$), Nitrous oxide (N$_2$O), Hydrofluorocarbons (HFCs), Perfluorocarbons (PFCs), Sulphur hexafluoride (SF$_6$)) to a level 5% below that of 1990. The richer countries should have reductions of 6% - 8% while the poorer are allowed to increase their emissions in order to catch up in their development with the richer countries. A clean development mechanism should also help the poorer in sustainable development, mitigating the emissions of greenhouse gases during their growth.
concentration of ~ 10 km in thickness [1.7] that protects life from the sun's harmful ultraviolet radiation.

In the upper atmosphere (stratosphere), oxygen atoms are created as a result of the breakdown of the oxygen molecule (O$_2$) by ultraviolet radiation.

In the lower atmosphere, where natural ozone levels are low, additional ground-level ozone is formed as a result of anthropogenic emissions of VOCs and nitric oxide radicals. Indeed when the ozone levels are too high (> 180 µg m$^{-3}$ of air) bronchial asthma and other health effects may be induced.

![Geometry of an ozone molecule.](image)

The atmospheric ozone absorbs essentially all the radiation below a wavelength of 295 nm due to a strong optical transition at ~ 225 nm which extends into the mid-UV region. Figure 1.8 shows the absorption spectrum of ozone between 190 nm and 330 nm, with a maximum cross section of ~ 11.5 Mb at ~ 225 nm.

![Absorption spectrum of ozone in the wavelength region 190 nm – 330 nm.](image)
Ozone is constantly formed in the upper layer of the atmosphere through the combination of molecular oxygen (O\(_2\)) and atomic oxygen. The latter is formed through the photo-dissociation of O\(_2\) in the 100 km region by light with wavelengths shorter than 175 nm. Sunlight UV radiation excites the electronic transition between the triplet ground state of O\(_2\) (\(^3\Sigma_u^-\)) and a triplet excited state (\(^3\Sigma_g^-\)). Once excited, the O\(_2\) may dissociate into two oxygen atoms, one in the ground triplet state O (\(^3\Sigma_P\)) and one in a metastable excited state O (\(^1\Delta\)), according to equation 1.5:

\[
O_2(3\Sigma_u^-) + h\nu (\lambda < 175 \text{ nm}) \rightarrow O_2(3\Sigma_g^-) \rightarrow O(^3\Pi) + O(^1\Delta)
\]

Once formed, atomic oxygen reacts with O\(_2\) to form O\(_3\):

\[
O + O_2 + M \rightarrow O_3 + M
\]

where M is any atom or molecule capable of absorbing the excess of energy released by the exothermic formation of ozone.

The efficiency of O\(_3\) formation by UV radiation is sensitive to a large number of factors, amongst which are the availability of O\(_2\), changes in stratospheric temperature, chemicals and dust from volcanic eruptions [1.7]. Most of the ozone is produced above the equator, where the amount of incident solar UV light is maximum. Ozone formed at these latitudes then diffuses towards the pole, where it is accumulated. The effective thickness of the ozone layer may increase from 3 mm at the equator to more than 4 mm above the pole at the end of winter. The ozone concentration displays daily and seasonal fluctuations and tends to be higher in late winter and early spring.

Any decrease in the thickness of the stratospheric ozone layer, leads to higher levels of UV radiation from the sun reaching the Earth's surface. Increased UV can lead to more cases of skin cancer, cataracts, and impaired immune systems. Ocean phytoplankton could also decrease, leading to a decline in populations of higher organisms in the marine food chain. Also, increased UV radiation can be instrumental in forming more ground-level ozone, leading to increased numbers of cases of asthma and other health effects.
1.3.1 Stratospheric ozone depletion

Under natural conditions, ozone in the stratosphere is continuously produced and destroyed, but at equal rates such that a stable ozone layer is maintained. There are basically two pathways for the destruction of ozone and the re-formation of $O_2$:

\begin{align*}
O + O_3 &\rightarrow 2O_2 \\
O_3 + O_3 &\rightarrow 3O_2
\end{align*}

These reactions are the result of a complex set of reactions catalysed by various gases and radicals, such as, atomic chlorine Cl, nitric oxide NO and hydroxyl radicals OH, the pathways along which they operate is shown in Fig. 1.9. If one looks at Cl radical, it reacts with an O atom from $O_3$ (right-hand side), forming $ClO$; then loses an O atom to a free O atom and returns to the radical Cl state again, with the net effect given by eq. (1.7). The scheme requires free O atoms to be present at altitudes of 25 km or more.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{breakdown_ozone}
\caption{Breakdown of ozone to molecular oxygen by means of Cl, NO and OH free radicals.}
\end{figure}

$N_2O$ is partly anthropogenic in origin and is released from the soils and waters where it has been formed as fertiliser waste product. Like CFCs, the $N_2O$ released at the Earth’s surface may eventually photo-decomposed and NO is formed. These radicals, together with the OH radical, remove 99% of the stratospheric ozone [1.7]. So, how are the free radicals NO, Cl and OH produced? The OH radical is a product of the breakdown of $H_2O$ vapour, for instance produced in the exhaust of aeroplanes. Although part of Cl radical may be formed from HCl released by volcanoes, the major contribution into the stratosphere is from chlorofluorocarbons, CFCs, once widely used as refrigerants and foam-blowing agents (e.g. see Chapter 6), halons used in fire
extinguishers, refrigerants, propellants, and certain solvents such as carbon tetrachloride. Under the Montréal Protocol, an international agreement ratified by most nations in 1987, the production of CFCs, halons, and other ozone depleting substances has been phased out. However since it can take years for ozone depleting chemicals to reach the stratosphere, some of the ozone depleting substances that were released in past years are still present in the atmosphere and may affect the ozone layer for many years to come.

Certain anthropogenic chemicals, referred to as ozone depleting substances, can disturb this natural balance. These ozone-depleting substances degrade slowly and can remain intact for many years as they move through the lower atmosphere until they reach the stratosphere. There they are broken down by the intensity of the sun's ultraviolet rays and release chlorine and bromine molecules, which react and destroy the ozone. One chlorine or bromine molecule can destroy up to 100 000 ozone molecules, causing ozone to disappear much faster than nature can replace it [1.8]. Presently, satellite observations indicate a worldwide thinning of the protective ozone layer. The most noticeable losses occur over the North and South Poles, because ozone depletion accelerates in extremely cold conditions [1.4].

### 1.3.2 Antarctic ozone hole

The stratosphere is very dry and generally cloudless. The long polar night produces temperatures as low as −90°C (183 K) at heights around 15 − 20 km, cold enough to condense even the small amount of water vapour present to form *Polar Stratospheric Clouds* (PSCs). The lowest temperatures are more prevalent in the Antarctic, where the polar vortex is more stable than in the Arctic. The exceptional stability of the vortex at the South Pole may be a result of the almost symmetric distribution of ocean around Antarctica. The less stable Arctic polar vortex tends to mix with surrounding air and does not attain the isolation and low temperatures achieved at the South Pole.

The stratosphere contains a natural aerosol layer at altitudes of 12 to 30 km and is composed of small sulphuric acid droplets with a size of the order of 0.2 μm in diameter and present in concentrations of 1 to 10 cm⁻³. In the mid-altitude lower stratosphere (∼ 15 km) the temperature is about −53°C (220 K), and the particles in equilibrium with 5 ppm water have compositions of 70 to 75% weight of H₂SO₄ [1.7]. Despite the composition of PSCs still being uncertain, they have been classified into
two types: Type I and Type II (Table 1.2) [1.9]. Type I are further sub-divided into Ia and Ib. Type Ia have traditionally been identified as crystals of nitric acid trihydrate, that form once temperatures fall below ~ 195 K. Type Ib consist of super cooled ternary solutions of HNO₃/H₂SO₄/H₂O, also forming at about the same temperature threshold. Type II PSCs are largely frozen water ice, non-spherical crystalline particles, that are formed at temperatures below the ice frost point, where e.g., at 3 x 10⁴ Torr, H₂O ice frost point is 191 K [1.9].

The chemical environment near and inside the Arctic polar vortex is predominantly affected by the heterogeneous (surface) processes on the ice particles that form these clouds. Such processes may be induced by either solar UV photons or those secondary electrons produced by photo-ionisation of adsorbed molecular species (e.g., CFCs and nitric oxides).

<table>
<thead>
<tr>
<th>Classification</th>
<th>Composition</th>
<th>Structure</th>
<th>Temperature threshold for formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type Ia</td>
<td>HNO₃·3 H₂O (NAT)*</td>
<td>non-spherical, crystalline</td>
<td>~190 – 195 K</td>
</tr>
<tr>
<td>Type Ib</td>
<td>HNO₃/H₂SO₄/H₂O</td>
<td>spherical, liquid</td>
<td>~190 – 195 K</td>
</tr>
<tr>
<td>Type II</td>
<td>H₂O ice</td>
<td>non-spherical, crystalline</td>
<td>~188 – 190 K</td>
</tr>
</tbody>
</table>

* - nitric acid trihydrate

Table 1.2 – Classes of Polar Stratospheric Clouds (PSCs).

These in turn may lead to the liberation of reactive (radical) species enhanced chlorine and NOₓ catalysis, which leads to rapid ozone loss. Recently an interesting correlation between cosmic rays flux and ozone depletion has been shown, with those winters experiencing largest cosmic flux having the most ozone loss (largest ozone hole). A new and novel explanation has therefore been suggested by Sanche and co-workers (see Chapter 6, and references therein) in which low energy solvated electrons on ice surfaces in the PSCs are released by cosmic ray bombardment enhancing dissociation of co-adsorbed CFCs (and nitric oxides), producing large numbers of ozone depleting radicals.

1.4 Replacements for CFCs – the HCFCs / HFCs

The discovery of the stratospheric ozone-depleting potential of CFCs in the 1970s led to a ban in the United States (announced in 1976 and effective in 1978) on the use of CFCs as aerosol propellants and similar restrictions in Canada and Scandinavia.
followed. When the Antarctic ozone hole was discovered in 1982, an international protocol outlining proposed actions to protect the stratospheric ozone layer was signed in Montréal in September 1987. The so-called Montréal Protocol specifies a 20% reduction from 1986 levels of fully halogenated CFCs by 1994 and a further 30% reduction by 1999. A turn-down in emission rates has been observed, reflecting the results of the Montréal Protocol, but further regulations and amendments now require the use of CFCs in industry to be totally phased out and alternatives found within the next decade.

A rapid phase out of production - and hence of consumption and release - of CFCs is necessary to reverse the trends of increasing concentrations of atmospheric chlorine and increasing ozone depletion. The international scientific and technical experts conducting assessments for the United Nations Environment Programme (UNEP) have stated that availability of HCFCs and HFCs is necessary to allow a rapid global phase out of CFCs. This, however, depends on the extent of recycling and technical feasibility of equipment, on the availability of HCFC and HFC replacements and on their toxicological and environmental acceptability [1.10]. HCFCs are technically and economically necessary for the transition in the majority of refrigeration and air conditioning, manufacture of insulating foams, selected and limited solvent applications, and certain fire protection applications.

HCFCs and HFCs are considered environmentally superior to CFCs because they are largely destroyed in the lowest region of the atmosphere and HFCs do not contain chlorine and have no potential to deplete ozone [1.5]. HCFCs, however, do contain chlorine, but only a small percentage of that chlorine can reach the ozone layer, this is because most of the HCFCs released at ground level are destroyed in the lower atmosphere before they reach the stratospheric ozone layer [1.5]. In this thesis we have studied dichlorodifluoromethane (CCl2F2) and other atmospheric relevant molecules such as dimethylsulphide ((CH3)2S) and acetaldehyde (CH3CHO), trifluoromethyl sulphur pentafluoride (SF5CF3), acetonitrile (CH3CN) and acrylonitrile (C2H3CN).

1.5 Conclusions

In this thesis the spectroscopy of several aeronomic molecules playing an important role in the Earth’s atmosphere has been studied. In particular we have studied their photolysis and hence derived the atmospheric lifetime and reactivity. Molecules studied include dimethylsulphide ((CH3)2S) and acetaldehyde (CH3CHO),
trifluoromethyl sulphur pentafluoride (SF$_3$CF$_3$), dichlorodifluoromethane (CCl$_2$F$_2$), acetonitrile (CH$_3$CN) and acrylonitrile (C$_2$H$_3$CN). (CH$_3$)$_2$S and CH$_3$CHO play an important role as intermediate species in the oxidation mechanism of tropospheric hydrocarbons. SF$_3$CF$_3$ is a newly discovered greenhouse gas with a long lifetime in the atmosphere. CCl$_2$F$_2$ is an important stratospheric ozone depletor. CH$_3$CN is a product of both natural and industrial processes and may be a potential tracer gas for monitoring biomass burning, and C$_2$H$_3$CN is produced industrially and used in the manufacture of acrylic fibres and as a raw material in the fabrication of plastics, rubbers and resins. To complement these studies, electron impact and photo-electron studies have been made to further characterise the electronic spectroscopy and dissociation processes, both in the gas-phase and on simulated atmospheric ice surface.
1.6 References


Chapter 2

Molecular spectroscopy

Knowing is not enough; we must apply. Willing is not enough; we must do.

Johann Wolfgang von Goethe (1749 – 1832), German poet, dramatist.

2.1 Introduction

This chapter describes the molecular spectroscopy underlying the study of excitation and dissociation of a molecular system by photon and electron impact. Dissociative processes play an important role in atmospheric chemistry and in plasma physics because the resulting fragment species are often found to be more chemically reactive than the parent molecules. The absorption of light by a molecule reveals particular patterns, which correspond uniquely to the energy levels within the molecule. So, the resulting molecular spectrum is used as a fingerprint in the identification and characterisation of a compound.

2.2 Molecular spectroscopy

The study of the interactions between molecular systems and electromagnetic radiation is the topic of molecular spectroscopy. Spectroscopy can change dramatically from an isolated atom to a molecule. For the former, the interactions can occur only on the basis of a change in motion of an electron with respect to the nucleus, while for the latter, such interactions may also occur and may change the electric dipole moment of the molecule (neglecting high order effects such as changes in quadrupole moment). However molecules can change their dipole moments by changing the internuclear positions which in turn makes the spectroscopy more complicated.

Nuclear motions are classified as translation (experienced by atoms as well), rotation and vibration. Taking into account the kinetics of a molecule’s centre of mass, i.e., it moves as a free particle with no net change in the electric dipole moment, translations can be separated from the other motions. Assuming that there is no
appreciable change in the internuclear distance, molecular rotations cause the orientations of any dipole moments to change, thus allowing interactions with radiation to take place. Molecular vibrations disturb the electronic cloud of the molecule due to the motion of the nuclei with respect to each other. The change in the electron cloud distribution brought about by transitions between electronic states may also change the electric dipole moment of a molecule.

The way that these three mechanisms can interact may be simplified since they can be treated separately due to the different molecular time scales over which they occur: over the time a molecule takes to complete one rotation it may go through several vibrations, whereas electronic transitions occur so fast, that according to the Franck-Condon principle, the nuclear positions do not change appreciably during a transition between two electronic states. However, the energies involved for each of these mechanisms are also quite different. Rotational energy levels are typically separated by a few meV, vibrational levels have separations of the order of tens to hundreds of meV, and electronic transitions range from a few to tens of eV. Molecules can experience these different types of motion simultaneously, but due to the fact that the energies of the motions are so different they can be treated separately, such that the total energy is the summed contribution of each of them:

$$E_{\text{total}} = E_{\text{rotation}} + E_{\text{vibration}} + E_{\text{electronic}}$$  \hspace{1cm} (2.1)

This is known as the Born-Oppenheimer approximation.

### 2.2.1 Rotational excitation

The pure rotational motion of molecules is studied using microwave spectroscopy. In order to calculate the expected rotational levels of a molecule the assumption is made that the internuclear distances are fixed, and the rigid-rotor approximation applies [2.1]. However, pure rotational spectra are not relevant to the work presented in this thesis, therefore no further analysis or discussion will be given.

### 2.2.2 Vibrational excitation

Vibrational spectroscopy concerns the motions of nuclei relative to one another within a molecule, where the equilibrium positions of the vibrations are determined by the balance of the repulsive forces between positively charged nuclei, the repulsive
forces between inner shell electrons surrounding each nucleus and the attractive forces between the nuclei and the electrons throughout the molecule.

When all these forces are balanced to obtain a state of minimum energy, the equilibrium internuclear distances are then defined as bond lengths. For a molecule containing $N$ nuclei, the positions and motions of them can be described by a set of $3N$ coordinate values. The number of vibrational modes is given by $3N - 6$ (or $3N - 5$ for linear molecules), since nuclear translations and rotations along the axes do not affect the vibrational motion.

Molecular vibrations can be evaluated by taking into account several approximations or models such as the simple harmonic oscillator model [2.1] and ending up on a more real Morse potential function, where solving the time independent Schrödinger equation one can get the selection rules for the vibrational transitions [2.1]. However, such theory is well known and therefore no further discussion is given here but reference made to introductory atomic and molecular physics books (e.g. [2.1]).

### 2.2.3 Electronic excitation

Electrons fill orbitals in a molecule according to its internal energy. If a molecule absorbs a photon of the required energy an electronic transition will occur and the electron is moved to an upper orbital. The photon is then said to be resonant with the electronic state. The processes referred in this thesis are only due to absorption, so emission will not be taken into account. The energies required to excite electronic transitions are typically between 1 eV and 15 eV, depending on the molecule, and the observed electronic spectra are in the ultra-violet and visible energy regions of the electromagnetic spectrum.

Neglecting changes in rotational state, an electronic transition may be accompanied by a change in the vibrational state of a molecule. In photo-absorption investigations conducted at room temperature the original state is usually the ground electronic state with most of the population in the lowest vibrational state ($v'' = 0$). However there may also be a small population in the first few vibrational levels as predicted by the Boltzmann distribution:

$$\frac{N_v}{N_{v''}} = \exp \left( \frac{-\Delta E}{k_B T} \right)$$  \hspace{1cm} (2.1)
where \( N_{v''} \) and \( N_{v'} \) are the number of molecules in the states \( v'' \) and \( v' \), \( \Delta E \) is the energy difference between the states, \( k_B \) the Boltzmann’s constant and \( T \) the absolute temperature.

The vast majority of the population is thus in the lowest energy state \( (v'' = 0) \), and the absorption spectrum is characterised by transitions from this level. However, contributions from higher lying vibrational states can lead to photo-absorption and produce small structures shifted to the low energy side of the main absorption bands by an amount equivalent to the energy of the vibrational mode involved above the ground state. These structures are known as hot bands.

Transitions between two electronic states can easily be described if one considers that they occur so rapidly that the internuclear distances of the molecule do not have time enough to change appreciably their position of equilibrium. This is known as the Franck-Condon principle. Hence an electronic transition between two states may be represented by a vertical line joining the potential energy surfaces, originating from the most probable internuclear separation in the ground state.

In these transitions there is a possibility the molecule may also dissociate, as shown in Figure 2.1.

![Figure 2.1 - Examples of dissociative excitations.](image)

In a), the molecule is excited into a repulsive state which leads directly to dissociation (fragmentation). The amount of energy above the lower dissociation limit is defined as the Kinetic Energy Release (KER) of the fragments. However, in b) the molecule is first excited into a vibrational level of a bound state, and the molecule begins to vibrate such that the internuclear separation \( (r) \) increases to a maximum. At
this position, the bound state potential energy surface can cross a repulsive potential curve and it is possible for the molecule to undergo a radiationless transition into this state and hence dissociate. This process is known as pre-dissociation.

The probability of a transition between two states can be a rather complicated calculation. However, the problem can easily be simplified by just considering whether a transition probability is zero or non-zero. In this case, they are defined as forbidden or allowed, respectively, and obey a series of selection rules. For all molecules experiencing optical transitions (resulting from photon absorption), the total spin quantum momentum $\Delta S$ of the system is zero. For polyatomic molecules, other selection rules are given by symmetry considerations, where an excited state can be characterised by multiplying the symmetry types of the occupied orbitals together. Hence, once the state symmetries are known it can be determined whether the transition is allowed or forbidden.

There are two different types of excited electronic states to which a ground state molecule can be promoted; valence and Rydberg states. Generally speaking, the atomic orbitals that combine to form the molecular orbitals define the valence shell of a molecule. Excitations into the remaining unfilled orbitals generated by the valence shell orbitals are known as valence transitions. However, excitations into orbitals corresponding to higher values of the principal quantum number $n$ are Rydberg transitions, although the lowest Rydberg states can be found to sometimes overlap with the valence states (e.g. $(\text{CH}_3)_2\text{S}$ & $\text{CH}_3\text{CHO}$ - chapter 4 and $\text{C}_2\text{H}_3\text{CN}$ - chapter 7).

In most cases, the orbital classifications fall into one of three categories: $\sigma$, $\pi$ and $n$ orbitals (non-bonding). In general, electrons in the $\sigma$ orbitals are the most firmly bound to the nuclei, and hence require more energy to undergo transitions than the less strongly bound $\pi$ and $n$ electrons. The $n$ electrons are usually (but not always) less weakly bound than the $\pi$ electrons (Figure 2.2). The next figure shows the corresponding classification of electronic transitions abbreviated as $(\sigma \rightarrow \sigma^*)$, $(\pi \rightarrow \pi^*)$, $(n \rightarrow \sigma^*)$, $(n \rightarrow \pi^*)$.

Rydberg states can be seen as an electron in an orbital with large radius, travelling around a cationic core consisting of the nuclei and the remaining occupied molecular orbitals. All Rydberg states containing the same molecular ion core are related since their energy surfaces are determined by that of the molecular ion. The absorption band profiles of these states resemble that of the corresponding ionisation band in a photoelectron spectrum. The fact that Rydberg states containing the same core
are related to the corresponding molecular ion is exemplified by the Rydberg formula (section 3.2.5.1). Generally speaking transitions into Rydberg states are observed above \(~ \sim 7\) eV, and also series converging to a particular ionic state, the relative intensities of the members are found to decrease as \(n^3\) [2.2].

Figure 2.2 – Classification of electronic transitions.

### 2.2.4 Ionisation

When a molecule absorbs sufficient energy to remove an electron from a bound state, it becomes ionised. Typical ionisation energies for molecules are greater than \(~ \sim 8\) eV, and a series of Rydberg states comprising a remote electron bound to the molecular ion core found converging on each ionisation potential according to appropriate symmetry selection rules.

The transition into a molecular ionic state is governed by the Franck-Condon principle, and the properties of the ion depend on the type of electron that is removed from the neutral molecule: (i) if a non-bonding electron is removed, the bond strengths of the ion remain virtually the same as those of the neutral molecule, hence the bond lengths and vibrational spacing are also similar; (ii) if an anti-bonding electron is removed, the bonds become stronger, the ion bond lengths are generally shorter than those in the neutral and the vibrational spacing increases; (iii) if a bonding electron is removed, the bonds become weaker, thus the ionic bond lengths become larger than those of the neutral and the vibrational spacing decreases.

Molecular ionisation is usually observed experimentally using photoelectron spectroscopy, in which the molecules are ionised by photons of a particular energy and
the liberated electrons are recorded as a function of their kinetic energy (section 3.4). In practice there are two types of experimentally determined ionisation energies, adiabatic and vertical. An adiabatic ionisation energy may be defined as the energy difference between the zero vibrational levels of the two electronic states involved [2.1], the lower state being the ground state of the neutral molecule. However, in molecules where significant changes in geometry are experienced on ionisation, the zero-zero transition may not be observed since the ion is vibrationally excited, hence the adiabatic ionisation energies of many polyatomic molecules remain unobserved. On the other hand, the vertical ionisation energy is defined as the energy difference between the ground state of the molecule and the excited molecular ionic state with the nuclear positions identical to those of the neutral ground state [2.1]. Such a transition corresponds to a vertical line drawn through the potential energy surfaces, and is usually assumed to correspond to the point of maximum intensity in an experimental spectrum.

No spin-orbit coupling should be observed in the ionic state of molecules with less than a three-fold symmetry axis, as such molecules contain no orbitals that are degenerate because of symmetry [2.3]. The Jahn-Teller effect can play an important role in the photoelectron spectroscopy of polyatomic molecules. It states that a symmetric, non-linear molecule in a degenerate electronic state distorts in such a way as to reduce the symmetry and hence remove the degeneracy if it contains at least a three-fold axis of symmetry [2.3]. Thus if an electron is removed from a degenerate state, a distortion of the ion removes the degeneracy and splits the energy levels resulting in separate bands in the spectrum. However, if the magnitude of the split between the energy levels is small, it may just be observed as a broadening of the appropriate band in the spectrum. For two molecular species studied in this thesis, CH$_3$CN has $C_{3v}$ symmetry (Chapter 7) and SF$_5$CF$_3$, $C_{4v}$ (Chapter 5), no such effect has been observed.

2.3 Electron-molecule scattering

2.3.1 Electron-molecule interactions

Electron scattering processes differ from photo-absorption in two important ways. First, electron scattering is a non-resonant process, it means that the incident electron can transfer any amount of its kinetic energy to the molecular target. Secondly, the incident electron may simultaneously excite a molecule and exchange some of its quantum numbers with those of a bound electron within the target. This process is known as exchange interaction and is essentially a quantum mechanical effect; it allows
an electron impact to excite a forbidden state of a molecule by changing the total spin momentum of the target, which cannot be done by the absorption of a single photon, where selection rules force $\Delta S = 0$. In fact, with photons such a process has a high probability of not occurring (but is not totally forbidden) because there is no appreciable transverse momentum impinged by the oscillating electric field.

In electron-molecule collisions the following process are defined as open channels. The electron may collide with the molecule and the collision occurs in such a way that all energies are conserved, e.g.:

\[ e'(\varepsilon) + AB \rightarrow e'(\varepsilon) + AB, \text{ elastic scattering} \quad (2.1) \]

The scattering process is also possible with an already excited molecule imparting its excess energy to the colliding electron:

\[ e'(\varepsilon) + AB^* \rightarrow e'(\varepsilon') + AB, \varepsilon' > \varepsilon, \text{ super elastic scattering} \quad (2.2) \]

Alternatively, the electron may impart some of its energy to excite the molecule to a higher state and then continue with decreased energy in the process of inelastic scattering. If the excitation is to a repulsive state, the excited molecule may then decay to its ground state by a radiative process (not represented here) or may dissociate into fragments:

\[ e'(\varepsilon) + AB \rightarrow e'(\varepsilon'') + AB^*, \text{ electron impact excitation} \quad (2.3) \]

\[ e'(\varepsilon) + AB \rightarrow e'(\varepsilon'') + A + B^*, \text{ dissociative excitation} \quad (2.4) \]

\[ e'(\varepsilon) + AB \rightarrow e'(\varepsilon'') + e'(\varepsilon_1) + AB^+, \text{ electron impact ionisation} \quad (2.5) \]

\[ e'(\varepsilon) + AB \rightarrow e'(\varepsilon'') + e'(\varepsilon_1) + A + B^+, \text{ dissociative ionisation} \quad (2.6) \]

\[ e'(\varepsilon) + AB \rightarrow [AB]^* \rightarrow A^+ + B^*, \text{ dissociative electron attachment} \quad (2.7) \]

Here, $\varepsilon$ is the kinetic energy of the incident electron, $\varepsilon''$ ($\varepsilon'' < \varepsilon$) the energy lost/gained by the electron, $\varepsilon_1$ is the kinetic energy of an ejected electron.

**2.3.2 Resonance formation**

Another way to get information on the energies, symmetries, and spatial charge distributions of low-lying unoccupied molecular orbitals is the study of the negative ion resonances (NIR). Many of them decay by auto-detachment of the temporarily trapped incident electron and lead to the population of vibrational levels of the neutral species in its electronic ground state. In electron-molecule scattering negative ions are formed at
well-defined incident energies (typically below 20 eV). These resonances are formed by the temporarily attachment of an incident electron to the target molecule for a period of time in between 10 – 1000 times longer than the collision time (\( \sim 10^{-16} \) s), and they are usually defined as temporary negative ion resonances. They are divided in two categories: shape resonances and core excited (shape) resonances.

When a low energy electron approaches a neutral molecule, the polarisation force can become significant. This interaction between the electron and the charge distribution of the molecule may induce an electric dipole moment within the neutral. Shape resonances may thus arise due to an interaction between the charge of the extra electron and the permanent and induced dipole moments of the neutral molecule, leading to an effective potential which supports a bound state of the negative ion \([2.4]\). The lifetimes of shape resonances are typically of the order of \( 10^{-16} \) s – \( 10^{-14} \) s, and their subsequent decay may leave the neutral molecule in a vibrationally (or rotationally) excited state. Thus in low energy scattering experiments, the intensities of vibrational peaks may be observed to increase by several orders of magnitude at energies where shape resonances are excited.

Core excited resonances may be classified as core excited (shape) resonances and Feshbach resonances. Both types arise from the attachment of an electron to an excited state of the molecule (Figure 2.3). Core excited (shape) resonances lie slightly higher than the parent state. The configuration of such a resonance is essentially that of an excited neutral molecule with an extra electron in the upper orbital, slightly rising its internal energy. If the extra electron is subsequently ejected, the configuration becomes identical to the excited state of the neutral. Therefore, since they can decay into the neutral parent state by single electron detachment, core excited (shape) resonances have shorter lifetimes (\( \sim 10^{-15} \) s). These resonances are thus usually observed as broad peaks with little or no vibrational structure. On the other hand, Feshbach resonances lie energetically below the parent state of the neutral (\( \sim 0.5 \) eV), and tend to have long lifetimes (\( 10^{-14} \) s – \( 10^{-12} \) s) since they can only decay by a two electron transition into the ground state of the neutral. One electron is ejected whilst the other drops back into the ground state configuration. Since these resonances have long lifetimes they may be observed to support vibrational structure.
2.3.3 Dissociative electron attachment

2.3.3.1 Gas-phase

Rather than decaying into the neutral molecule, a temporary negative ion resonance may also undergo dissociation to produce a stable negative ion and neutral fragments (eq. 2.7). This process is known as dissociative electron attachment (DEA). For a particular molecule (M) there will be several fragmentation pathways, leading to a set of different negative ions and excited states of the neutral fragments. Fig. 2.4 shows a schematical potential energy curves for the neutral and DEA ionic channel (Y + X'). DEA processes can be monitored experimentally by analysing both the mass and energy of the negative ion fragments as a function of the incident electron energy. The recorded ion signal, plotted as a function of both electron energy and ion energy, reveals the energies of the resonances involved for each DEA process. The observed DEA processes may be identified by measuring of the threshold energy and the relation between the ion energy and the incident electron energy. This is best explained with the aid of a specific example and is discussed in detail for acetonitrile, CH₃CN, in Chapter 7, section 7.3 of this thesis.

The threshold energies (minimum incident electron energy required) for each DEA processes can be predicted from:

$$ AE(M - X)^{-} = D((M - X) - X) - EA(M - X) + \Delta E $$  (2.8)
where $AE$ is the appearance energy for the fragment anion $(M - X)^-$, $D$ the bond dissociation energy, $EA$ the electron affinity for the fragment $(M - X)$ and $\Delta E$ the excess energy of the process.

2.3.3.2 Condensed phase

Any environment, in particular a surface provides an effective means to dissipate energy via intermolecular collisions. For a NIR on a surface one consequently expects a considerable reactivity (bond cleavage via DEA) in favour of associative attachment yielding an un-dissociated anion.

The electron may collide with the molecule $(M)$ adsorbed (ad) on a surface and the collision occurs in such a way that the exit possible channels are:

\[ e^- (\varepsilon) + M_{ad} \rightarrow (M_{ad}^*)^- \rightarrow R_{ad} + X^- \]  
(2.9)

\[ e^- (\varepsilon) + M_{ad} \rightarrow (M_{ad}^*)^- \rightarrow R + X_{ad}^- \]  
(2.10)

\[ e^- (\varepsilon) + M_{ad} \rightarrow (M_{ad}^*)^- \rightarrow R_{ad} + X_{ad}^- \]  
(2.11)

\[ e^- (\varepsilon) + M_{ad} \rightarrow (M_{ad}^*)^- \rightarrow M_{ad}^- \]  
(2.12)

where $R$ is a radical and $X$ a fragment.
However, there are also mechanisms where the medium can enhance DEA. The mechanism for such an enhancement is based on the effect of the medium on the auto-detachment rate, i.e., the lifetime of the resonance towards energy loss. Any change in the rate must be counterbalanced by the two competing processes, namely associative attachment or DEA, both keep of which the additional electron in a bound state within the system.

Another mechanism involves electronically excited states where also appreciable enhancements are observed. An unfavourable orientation of the molecule at the surface may additionally be responsible for the lack of any desorption signal al low electron energies (Chapter 5, section 5.6.2). What is the mechanism for such a dramatic effect? For a core excited resonance it may no longer be adequate to describe its decay by the competition between dissociation and auto-detachment along a repulsive potential energy surfaces. At those energies the appreciable density of electronic states leads to many curve crossings and hence direct electronic dissociation processes are exceptional cases. In addition, the auto-detachment lifetime depends strongly on the character of the core excited state. An open channel resonance is located in energy above the associated electronically excited state of the neutral and can effectively decay via one electron transition into the associated neutral molecule. A closed channel (or Feshbach) resonance is located below the excited neutral and can only decay into the neutral molecule via a two electron process. Therefore Feshbach-type resonances have much longer auto-detachment lifetimes. With respect to solvation this means that an open channel resonance in the gas phase can be converted into a Feshbach-type resonance in an environment. The increased auto-detachment lifetime will result in an enhancement of the DEA cross section (Chapter 5, section 5.6.2). Figure 2.5 illustrates the situation schematically in an energy diagram. The vertical arrows on the left side (open channel resonance) describe effective auto-detachment via one electron process.
2.4 Molecular symmetry

The scope of this section is just to provide the reader with some guide references on molecular symmetry and group theory (e.g., [2.8]) necessary to characterise the molecular states. A molecule can be assigned to a "point group": a fingerprint which describes its symmetry properties, and where symmetry arguments are extremely important in the determination of allowed and forbidden transitions. However, no such detailed description will be given except a general view for the symmetry of the molecules studied in this thesis.

A symmetry operation always has a corresponding symmetry element, which is the point, line or plane with respect to which operation is carried out. Disregarding translational symmetry operations, there are five types of symmetry operation, which are described in Table 2.1.

<table>
<thead>
<tr>
<th>Symmetry operation</th>
<th>Symmetry element</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identity</td>
<td>Whole body</td>
<td>$E$</td>
</tr>
<tr>
<td>n-fold rotation</td>
<td>n-fold axis of symmetry</td>
<td>$C_n$</td>
</tr>
<tr>
<td>Reflection</td>
<td>Plane of symmetry</td>
<td>$\sigma_v, \sigma_h, \sigma_d$</td>
</tr>
<tr>
<td>Inversion</td>
<td>Centre of symmetry</td>
<td>$i$</td>
</tr>
<tr>
<td>Improper rotation</td>
<td>Axis of improper rotation</td>
<td>$S_n$</td>
</tr>
</tbody>
</table>

Table 2.1 – Symmetry elements and their operations.
Chapter Two

\(E\) is the identity operation which reflects the act of doing nothing to the object. The symmetry element is the object itself; \(C_n\) represents an \(n\)-fold rotation of \((2\pi/n)\) radians, and the element is an axis of symmetry; \(\sigma\), is a reflection and the element is a mirror plane. When the mirror plane includes the principal axis of symmetry the plane is defined a vertical plane, \(\sigma_v\), if it is perpendicular to that axis is termed horizontal plane, \(\sigma_h\), and if the mirror plane bisects the angle between two \(C_2\) axes it is defined as dihedral plane \(\sigma_d\). \(i\) is defined as inversion and the element is a point called the centre of symmetry. Inversion is an operation where each point of the object is taken on a straight line through the centre of symmetry to an equal distance on the other side; \(S_n\) is the \(n\)-fold improper rotation and the element is an axis of improper rotation. The operation consists of a \(n\)-fold rotation followed by a reflection in plane perpendicular to the \(n\)-fold axis.

Each point group has a character table containing information relating the symmetry operations of the group to the geometric properties of the molecule [2.7]. Each point group has it own irreducible representations, which reflect particular geometric properties pertaining to the point group. Since the molecules studied in this thesis have only \(C_s\), \(C_{2v}\), \(C_{3v}\) and \(C_{4v}\) symmetries, Table 2.2 gives the ordering of the symmetry species. When a molecule experiences an electronic or vibrational transition the symmetry may be affected. For the irreducible representations, and in the particular case of a molecule with \(C_{2v}\) point group (e.g., \((CH_3)_2S\) and \(CCl_2F_2\), chapter 4 & 6 respectively), Table 2.3 shows that the first row with the sets of “1” means that \(A_1\) is the dominant symmetric mode.

<table>
<thead>
<tr>
<th>Point group</th>
<th>Symmetry species</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_s)</td>
<td>(A', A'')</td>
</tr>
<tr>
<td>(C_{2v})</td>
<td>(A_1, A_2, B_1, B_2)</td>
</tr>
<tr>
<td>(C_{3v})</td>
<td>(A_1, A_2, E)</td>
</tr>
<tr>
<td>(C_{4v})</td>
<td>(A_1, A_2, B_1, B_2, E)</td>
</tr>
</tbody>
</table>

Table 2.2 – Ordering of symmetry species (after Shimanouchi [2.9]).

The last two columns of table 2.3 show the representations to which some of the basic geometric features belong. In the particular case of a \(C_{2v}\) molecule, the zz-axis (vertical) has \(A_1\) symmetry, whereas rotation about the zz-axis (\(R_z\)) has \(A_2\) symmetry.
For a particular orbital on the xx-axis (e.g., px lobular orbital), its symmetry is B₁ as the sign of the wavefunction is changed as a result of the C₂ and the σₓ′ (yz) operations. The “A” symmetry means a singly degenerate orbital while a “B” means a single degenerate but anti-symmetric with respect to the major rotational axis [2.7, 2.8].

Symmetry arguments can be used to determine allowed and forbidden transitions. The probabilities of a single photon electronic transition between molecular orbitals of different symmetries are determined through the probability integral, I, where a formally allowed transition results on a finite value for that integral:

$$I = \left| \langle \psi_1 | \mu | \psi_2 \rangle \right|^2$$  \hspace{1cm} (2.9)

where μ is the electric dipole operator, ψ₁ and ψ₂ are the initial and final states, respectively. For the particular case of a molecule with C₂ᵥ symmetry, μ is obtained from the representation of x, y and z having A₁+B₁+B₂ symmetry (Table 2.3). The transition probability integral is then given by the product of the irreducible representation of the symmetries of the two states involved and the operator:

$$I = \langle \Gamma(\psi_1) \times \Gamma(\mu) \times \Gamma(\psi_2) \rangle$$  \hspace{1cm} (2.10)

The integral is evaluated over all space and has to be symmetric for an allowed transition, i.e., it must include a contribution from a totally symmetric representation (A₁) to be non-zero, otherwise the transition is strictly forbidden. Table 2.4 shows an example for a transition from an A₁ orbital into orbitals A₂ and B₂ symmetry in the C₂ᵥ point group.

**Table 2.3 – C₂ᵥ character table (after Gingell [2.5]).**

<table>
<thead>
<tr>
<th>C₂ᵥ</th>
<th>E</th>
<th>C₂</th>
<th>σₓ (xy)</th>
<th>σₓ′ (yz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A₂</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>B₁</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>B₂</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

$$\begin{align*}
&= z, x^2, y^2, z^2 \\
&= R_x, x y \\
&= x, R_y, x z \\
&= y, R_z, y z
\end{align*}$$
Thus we can conclude that for C$_2v$ point group, all transitions are allowed with the exception of A$_1$ ↔ A$_2$ and B$_1$ ↔ B$_2$ which are forbidden by symmetry. The importance of molecular symmetry is that any transition, which is not allowed by symmetry, tends to have very low photo-absorption cross sections for single photon absorption (e.g., CH$_3$CHO, Chapter 4, section 4.3).

### 2.5 Conclusions

In this chapter a description of the different types of spectroscopy (rotational, vibrational, electronic and ionisation) have been summarised. The Born-Oppenheimer approximation and Franck-Condon principle have been introduced. Electron-molecule scattering in both gas and condensed phases were also described as is appropriate for the experimental work presented in this thesis.

Molecular symmetry considerations on the basis of the molecular systems studied have been presented and examples given. Overall, this chapter is intended to give a few basic ideas on how the experimental data presented in the later chapters has been evaluated.
2.6 References

Chapter 3

Experimental apparatus

Nothing ever becomes real till it is experienced
even a proverb is no proverb to you till your life has illustrated it.

John Keats (1795 – 1821)

3.1 Introduction

This chapter is devoted to the description of the apparatus used to study VUV photo-absorption spectroscopy using synchrotron radiation, electron energy loss spectroscopy, photo-electron spectroscopy and dissociative electron attachment. Each of these techniques is briefly described and the methodology relevant for data analysis resulting from those experiments discussed.

Ultraviolet and visible radiation is important to characterise and study the molecular spectroscopy. The energy of the photons in these wavelength regions is higher than a few eV and sufficient enough to cause electronic excitation, where the region of the electromagnetic spectrum below 180 nm (above 6.9 eV) is known as the vacuum-ultraviolet (VUV) region of the electromagnetic spectrum.

Interactions between molecules and electrons also provide relevant information on the type of molecular bonds and electronic symmetries. In fact, electrons, as a probing source of electronic state spectroscopy, complement results obtained by photo-absorption. Electron attachment measures the yield of negative ions as a function of the impact energy. The electrons attach to the molecules through resonant processes at specific kinetic energies, forming a temporary negative ion (TNI). This TNI may subsequently decay fragmenting the molecule.

3.2 Synchrotron radiation

The use of synchrotron radiation (SR) in the study of molecular spectroscopy is extremely important because it is possible to obtain coherent intense, highly collimated
and highly polarised radiation in the plane of the storage ring with very high spectral resolution. This high intensity and broad spectral range when combined with other properties such as high degree of polarization and collimation makes SR a powerful tool for basic and applied research in physics, chemistry, biology and medicine, as well as for finding applications in such technologies as X-ray lithography, materials characterisation and micromechanics. In the present studies the UV radiation used provided results on the molecular system's spectroscopy, which in turn yields information on the related valence and Rydberg states. Knowledge of photo-absorption cross sections is also extremely necessary if we are to evaluate the role of these molecular systems in the atmosphere where they undergo photolysis.

3.2.1 ASTRID synchrotron radiation, Denmark

The synchrotron radiation facility used for the molecular systems studied in this thesis is the ASTRID - UV1 beam line (Figure 3.1) at the Institute for Storage Ring Facilities, University of Aarhus, Denmark - www.isa.au.dk

![Synchrotron radiation schematic layout](image)

Figure 3.1 – ASTRID Synchrotron radiation schematic layout.

When a magnetic field is applied normal to an electron beam travelling at relativistic speeds, deflection from its straight line path will occur (curved trajectories),
the electrons will lose energy, and synchrotron radiation is emitted (Figure 3.2). In its electron storage mode, ASTRID operates as a synchrotron radiation (SR) source. A 100 MeV Race-Track Microtron (RTM) is used to accumulate up to 250 mA of electrons which are then accelerated to 580 MeV to produce SR from either bending magnets or an undulator magnet. Lifetimes up to 15 hours are possible with stored electron currents of ~ 150 mA. In general, three kinds of magnets are used to make the necessary magnetic fields: bending magnets, wigglers and undulators. In bending magnets, a simple dipole structure is used to constrain the electrons in a curved path (Figure 3.2).

![Figure 3.2 – Synchrotron radiation schematic diagram.](image)

The radiation emitted is extremely intense and extends over a broad wavelength range from the infrared through the visible and ultraviolet and into the soft and hard X-ray regions of the electromagnetic spectrum.

High-field wiggler magnets are often used as sources in order to increase the flux at shorter wavelengths. A wiggler is a sequence of bending magnets of alternating polarities (Figure 3.3) which gives a 2N enhancement in the flux, where N is the number of poles, forcing the electron beam path to undulate about its mean path. The properties of wiggler SR are thus very similar to that of dipole radiation with a reduction in the critical wavelength as a consequence of the higher field. For superconducting wiggler magnets a value of 6 Tesla, as opposed to around 1.2 Tesla for conventional dipoles, would be typical. The emitted radiation (photons) in each curved trajectory superposes coherently with high resultant intensity. The emitted radiation continua produced by the bending and wiggler magnet types is in contrast to the almost
monochromatic radiation produced by the undulator. Undulators, consisting of periodic magnetic arrays, cause small electron deflections comparable in magnitude to the natural emission angle of the SR (Figure 3.4).

![Figure 3.3 – Synchrotron wiggler magnet schematic diagram.](image)

The radiation emitted at the various poles interferes coherently resulting in the emission of a pencil-shaped beam (headlight effect) peaked in narrow energy bands at the harmonics of the fundamental energy. For N poles, the beam's opening angle is decreased by $N^{1/2}$ and thus the intensity per solid angle increases as $N^2$. The coherence superposition means that the radiation produced by the undulator is discrete and practically monochromatic for the high energy regions of the electromagnetic spectrum.

![Figure 3.4 – Synchrotron undulator magnet schematic diagram.](image)
The headlight effect is an inherent result of the relativistic motion of the electrons that confines the highly collimated synchrotron radiation into a narrow beam in the direction of electron motion (Appendix I). For 1 MeV – 5 MeV electrons all the radiation lies within 90 degrees of the velocity vector. For higher energies the radiation is contained in a narrower pencil-shaped beam with angular distribution confined within 17.5 degrees and 13 degrees for 75 MeV and 100 MeV, respectively. The resulting pattern from an isotropically emitting electron observed in an inertial referential is, for electron energies close to the speed of light, \( c \), a pencil-shape beam and the radiation is essentially confined to a collimated beam.

At the ASTRID facility, the electron injector is a 100 MeV Race-Track Microtron (RTM). The power for the klystron (resonant cavity) and electron gun acceleration voltage is delivered from the same pulse transformer; the klystron is fed with about 100 kV / 100 A, while the electron gun receives about 70 kV. This power comes from a high-energy pulse supply by discharging a capacitor/inductor network. The 70 kV electron pulse enters the linear accelerator (LINAC), where it receives a 5.3 MeV energy gain (Figure 3.5). The pulse then reverses direction via a small loop after the LINAC, and re-enters it. Since this is a standing wave type, it can accelerate particles in both directions.

![Figure 3.5 – Schematic diagram of the Race-Track Microtron (RTM).](image-url)
After 17 additional turns through the LINAC, with increasing orbit diameter in the main dipoles, the beam is extracted and directed towards the storage ring injection system.

The UV1 beamline (Figure 3.6) has been designed to operate in the wavelength range of 100 nm to 700 nm (1.8 eV – 12.4 eV), and is capable of providing a typical flux of $2 \times 10^{11}$ photons s$^{-1}$. In order to be able to perform meaningful spectroscopic experiments it is necessary to be able to select a single wavelength of radiation from the continuous spread of wavelengths and for that a monochromator is needed.

![Figure 3.6 - The UV1 beamline assembly.](image)

### 3.2.2 UV1 monochromator

The monochromator has been designed to provide a high flux of photons with a moderate resolution ($1000 < R < 5000$) while preserving the high degree of linear polarisation of the source synchrotron radiation. A sketch of the beamline UV1 that is located on a bending magnet source is shown in Figure 3.7. The beamline consists of
only two optical elements: a toroidal pre-mirror, which provides independent horizontal and vertical focusing and a toroidal concave curved grating to disperse the synchrotron radiation. Two gratings are required to cover the proposed wavelength range (Table 3.1) whilst maintaining sufficient resolution. The entrance and exit slits are of fixed but selectable sizes in order to choose between different photon bandwidths. In order to maintain the correct focus at the exit slit as the grating rotates, it is necessary to translate the exit slit. This translation is mechanically linked to the experimental platform upon which the experiments are mounted. The range of this movement is about 65 cm over the full wavelength range.

![Figure 3.7 - Schematic diagram of the UV1 beamline.](image)

<table>
<thead>
<tr>
<th>Optics</th>
<th>Major radius (m)</th>
<th>Minor radius (m)</th>
<th>Active area (mm²)</th>
<th>Photon energy range (nm), (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First mirror</td>
<td>3.947</td>
<td>0.3657</td>
<td>120 × 50</td>
<td></td>
</tr>
<tr>
<td>Grating 1</td>
<td>1.0</td>
<td>0.7755</td>
<td>40 × 40</td>
<td>700 nm – 200 nm (1.8 eV – 6.2 eV)</td>
</tr>
<tr>
<td>1000 lines/mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grating 2</td>
<td>1.0</td>
<td>0.7755</td>
<td>40 × 40</td>
<td>350 nm – 100 nm (3.5 eV – 12.4 eV)</td>
</tr>
<tr>
<td>2000 lines/mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1 – UV1 optical specifications.
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The monochromator used for the high resolution experiments throughout this thesis over the wavelength ($\lambda$) range 110 nm – 350 nm was grating 2, and it has been possible to achieve a full width half maximum resolution of 0.075 nm (at 248 nm, 5 eV). The reflection gratings consist of diffraction gratings superimposed upon reflective rather than a transparent surface. The principle of operation of such diffraction gratings is that a monochromatic plane wave incident upon the grating will be diffracted. At each slit the plane wave becomes a circular wave due to interference, that in turn means that each circular wave will interfere (constructively or destructively) with the other circular wave fronts such that at certain angles, where the path length difference is an integer number ($n$) of $\lambda$s, the pattern will be constructively and the intensity doubled. For path lengths with differences of half integer, the interferences are destructive with no observed intensity (Figure 3.8 - after Kendall [3.1]).

![Diagram of diffraction pattern order](image)

**Figure 3.8 – The action of two-slit grating on monochromatic light plane waves.**

The diffraction angle is related to the wavelength by $n\lambda = d\sin\theta$, where $n$ is the diffraction order, $\lambda$ the wavelength, $d$ the grating spacing and $\theta$ the diffraction angle.

Constructive interference has several orders where the first, $n = 1$, means that the path difference is one wavelength, the second, $n = 2$, two wavelengths, and so on (Figure 3.9), whereas for zero order, $n = 0$, there is no diffraction. The monochromator selects the necessary photon energy by rotating the grating until the required first order light is able to pass through.
Figure 3.9 – Diffraction of polychromatic light from a 2000 lines mm\(^{-1}\) reflection grating.

### 3.2.3 UV1 photo-absorption cell

All the high-resolution photo-absorption measurements performed in this thesis were obtained in a closed gas cell with a path length of 25 cm. The absorption cell is a commercially available six-way cross adapter with a ~ 1.2 litres capability and is shown schematically in Figure 3.10.

Figure 3.10 – The photo-absorption cell.
A Baratron pressure gauge (MKS 390HA - 00001, 1 torr range) is mounted on the top of the cell. On the lateral side a stainless steel \( \frac{3}{4}'' \) tube is connected to a DN40 CF flange for gas admission via two valves (Swagelok SS-4H-TH3 and Nupro SS-4H) in turn connected to the sample reservoir. The cell is evacuated by a Turbovac 50 litre/s backed by a Leybold D49 rotary pump. The exhaust from the rotary system is connected to the central laboratory’s exhaust system.

A lithium fluoride (LiF) transmission window and a calcium difluoride (CaF\(_2\)) transmission window, respectively, define the entrance and exit of the photo-absorption cell. A QL30F/RFI photo-multiplier (PMT) detector is placed behind the CaF\(_2\) window for photon detection.

A steady Helium flow is maintained between the outlet CaF\(_2\) window and the PMT to avoid absorption from molecular oxygen which could lead to errors in the measured photo-absorption cross section.

### 3.2.4 Calibration and data acquisition

The apparatus is calibrated using O\(_2\) and SO\(_2\). The Schuman-Rüngge absorption band of O\(_2\) (6.9 eV – 9.5 eV) [3.2] is used to calibrate the absolute cross section because its broad nature minimises the effect of any changes in energy resolution (Figure 3.11). SO\(_2\) is used to calibrate the energy scale as it has absorption bands with clearly defined sets of sharp absorption peaks in the ranges 3.8 eV to 5.1 eV [3.3] and 5.15 eV to 7.25 eV [3.4] (Figure 3.11).

Great care is taken to ensure there are no second-order light effects. The minimum and maximum wavelengths between which scans are performed, 113 nm to 320 nm (10.97 eV to 3.88 eV), are determined by the transmission windows of the gas cell and the grating energy range, respectively. The sample pressure is measured using a baratron capacitance manometer and varied to give maximum absorption whilst avoiding any saturation. The synchrotron beam ring current is monitored throughout the collection of each spectrum since the current circulating in the storage ring is directly proportional to the intensity of synchrotron radiation produced and decays slowly over a period of time. Therefore, recording the ring current will allow the flux intensity to be normalised.
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2.018 16 14 12 10 8 6 4 2 0
Photon energy [eV]

Figure 3.11 – The photo-absorption spectrum of O\textsubscript{2} and SO\textsubscript{2}.

3.2.5 Data analysis

The photo-absorption cross section spectrum of a molecule is energy dependent and may be analysed through the use of the Beer-Lambert law:

\[
I_d(E) = I_o(E) \exp \left(- n \sigma(E) x\right) \\
\sigma(E) = \ln \left(\frac{I_d(E)}{I_o(E)}\right) \times n x
\]  

(3.1) \hspace{1cm} (3.2)

where \(I_d(E)\) is the radiation intensity transmitted through the gas sample at energy \(E\), \(I_o(E)\) is the radiation intensity through the evacuated cell at energy \(E\), \(n\) the molecular number density of the sample gas \((pV=nRT)\), \(\sigma(E)\) the absolute photo-absorption cross section of the molecular species at energy \(E\), and \(x\) is the absorption path length.

High pressure measurements on the photo-absorption cross sections can lead to observation of the line saturation effect. For high-resolution experiments it is not possible to attain zero bandwidth (or infinite energy resolution), causing some systematic errors which propagate through the cross sectional values obtained via equation (3.2). Line saturation arises mainly for high pressure measurements where large peak intensities can be underestimated. One way to overcome this problem is to repeat the experiment over a series of pressures determining where the photo-absorption cross section becomes pressure-independent. Even allowing for line saturation, the
measured cross sections are of course subject to errors, arising from the determination of \( I_0/I \), and becoming very large as this ratio approaches 1, i.e., as \( n \) approaches 0. The accuracy of the cross sectional values reported in this thesis have been estimated to be of the order of ± 5%.

### 3.2.5.1 The Rydberg equation

In assigning Rydberg states we may use the Rydberg formula:

\[
E_n = E_i - R(n - \delta)^2
\]

where \( E_i \) is the molecule’s ionisation energy, \( n \) is the principal quantum number of the Rydberg orbital of energy \( E_n \), \( R \) is the Rydberg constant and \( \delta \) is the quantum defect.

The values of the quantum defect varies for each series (s, p, d, …) and the most common are summarised in Table 3.2 (after [3.5, 3.6]). The quantum defect is thus a correction term that reflects a degree of the “shielding” of the nucleus by lower orbitals.

<table>
<thead>
<tr>
<th>atomic elements</th>
<th>( \delta ) quantum defect values</th>
</tr>
</thead>
<tbody>
<tr>
<td>B, C, N, O, F</td>
<td>~1.0, ~0.7, ~0 – 0.1</td>
</tr>
<tr>
<td>Al, Si, P, S, Cl</td>
<td>~2.0, ~1.4 – 1.7, 0.3 – 0.5</td>
</tr>
<tr>
<td>Te, I</td>
<td>3.9 – 4.2, 3.5 – 3.9, 1.8 – 2.7</td>
</tr>
</tbody>
</table>

Table 3.2 – Rydberg series and their related \( \delta \) quantum defect values according to the atomic element [3.5].

However if the obtained values from the experimental data do not exactly match those in Table 3.2 it is possible to conclude that there is some mixed valence-Rydberg in the observed absorption features.

When more than one atom from each row on the periodic table are involved in electronic excitation into a Rydberg orbital, e.g. OCS, the quantum defect evaluation is not straight forward and the \((n - \delta)\) quantity should be replaced and evaluated as the reduced term energy coefficient \( n^* \), and the analysis should follow via the Elden’s plots.

### 3.2.5.2 Elden’s plots

In order to help the interpretation and classification of the Rydberg series, Elden’s diagrams should be established. The variation of the quantum defect (\( \delta R \)) with the reduced term energies \((n^*)^{-2} \) should follow the commonly accepted Rydberg-Ritz equation [3.6]:

---

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with $\alpha_\delta$ and $\beta_\delta$ being the coefficients of the linear equation and $(n^*)^2 = (n - \delta)^2$. Diagrams of $\delta_\delta$ as a function of $(n^*)^2$ should give straight lines analogous to atomic Elden's plots [3.7]. In the present work Elden's plots were used in the assignment of most of the Rydberg series observed in the photo-absorption spectra presented.

### 3.2.5.3 Actinic fluxes and photolysis rates

During the last two decades, special attention has been devoted to the environmental importance of global warming molecules. Understanding molecular photolysis in the atmosphere is crucial if we are to determine the lifetime and chemical importance of such compounds. Having determined the absolute photo-absorption cross sections for each molecule, we have evaluated the photolysis using a computer model developed by Kendall [3.1]. The photolysis rates for each molecule are calculated as a function of altitude up to the stratopause (50 km). The program has been recently upgraded and allows the user to compute these rates from 0 up to 1000 km in the Earth's atmosphere.

Photolysis rates, $J$, are calculated as a product of the Solar Actinic Flux, $F(z, \lambda)$, [3.8] (at a given wavelength (Figure 3.12), $\lambda$, and altitude, $z$), the molecular photo-absorption cross section, $(\sigma(\lambda)$, at the same wavelength) and the quantum yield of dissociation, $\phi(\lambda)$:

$$J(z, \lambda) = \sigma(\lambda) F(z, \lambda) \phi(\lambda)$$  \hfill (3.4)
In general, the quantum yield for primary photolysis depends on both wavelength and total air pressure, and has been found to be much smaller than unity in some cases. Rate constants calculated assuming $\phi(\lambda) = 1$ therefore represent upper limits for the rate constant for photo-dissociation under atmospheric conditions.

For each altitude a total photolysis rate is then calculated by summing over the individual photolysis rates for that altitude. The reciprocal of the total photolysis rate for a given altitude in a sunlit, clear sky atmosphere gives the local photolysis lifetime at that altitude, i.e. the time taken for the molecule to photo-dissociate at that altitude if the solar flux remains constant.

The lifetime of a molecule can be then used to calculate its Global Warming Potential (GWP) using the GWP equation defined by the International Panel on Climate Change [3.9]. GWP values are used to calculate the molecule’s contribution to the greenhouse effect compared to CO$_2$ gas over a certain period of time:

$$ GWP_x = \frac{m_{CO_2}/m_x}{(\alpha_x/\alpha_{CO_2}) \times (\tau_x/\tau_{CO_2}) \times [(1 - \exp(-t/\tau_x))/(1 - \exp(-t/\tau_{CO_2}))]} \times GWP_{CO_2} \tag{3.5} $$

where $m$ is the mass of the molecule, $\alpha$ is the radiative forcing, $\tau$ the lifetime in the atmosphere, $t$ the timescale over which the GWP is considered. The subscript $x$ refers to the molecule of interest and CO$_2$ to carbon dioxide, which is the reference gas used.

Similarly, an index named Ozone Depletion Potential (ODP) has been adopted for regulatory purposes under the Montreal Protocol. The ODP of a compound is an estimate of the integrated total ozone depletion due to 1 Kg of the compound divided by the total ozone depletion due to 1 Kg of CFC-11 (CCl$_3$F) over a chosen time scale. Thus, the ODP shows relative effects of comparable emissions of the various compounds. Calculated values for ODPs of individual compounds change as the basic understanding of their interaction with the ozone layer changes. The general expression can be written as [3.10]:

$$ ODP_x = \frac{F_x}{F_{CFC11}} \times \frac{m_{CFC11}}{m_x} \times \frac{\tau_x}{\tau_{CFC11}} \times \frac{n_x}{3} \times \zeta \times \beta \tag{3.6} $$

where $F_x/F_{CFC11}$ denotes the fraction of the species $x$ reaching the stratosphere that is dissociated compared to that of CFC-11, $m_{CFC11}$, $m_x$, $\tau_x$ and $\tau_{CFC11}$ indicate the molecular
weights and atmospheric lifetimes of species \( x \) and CFC-11, respectively, while \( n_x \) is the number of potentially ozone depleting atoms (note that CFC-11 has 3 chlorine atoms per molecule). \( \zeta \) reflects the enhanced efficiency of the atoms for ozone loss as compared to chlorine. \( \beta \) represents the fraction release (at the surface) that reaches the stratosphere. For molecules with lifetimes of the order of several months, it is reasonable to assume a value for \( \beta \) close to unity. However for compounds with very short tropospheric lifetimes, the assumption that the distribution is nearly well mixed in the troposphere is not valid and \( \beta \) must be explicitly evaluated.

### 3.3 The Electron Energy Loss (EEL) Spectrometer, UCL, UK

Energy Loss Spectroscopy (EELS) is a very adaptable technique that has been used to measure the spectroscopy of atomic and molecular targets in both gas and solid phases and may be used to produce pseudo photo-absorption spectra. The EEL spectrometer used at University College London (Figure 3.13) has been described in detailed elsewhere [3.11]. Briefly, the configuration used in this gas phase work uses electrons with an impact energy of 150 eV. The electrons that are detected are constrained to those that have travelled undeflected from their pre-collision trajectory (i.e., scattering angle \( \sim 0^\circ \)). These particular criteria are selected as electron impact excitation then closely follows optically allowed selection rules. This occurs as an electron with sufficiently high incident energy, \( T \), (\( > 100 \) eV) scattered at small angles (\( \sim 0 \) degrees) will induce an electric field at the molecule very similar to that of a photon pulse. The electric field interacts with the transition dipole of the molecule with electric dipole transitions being predominantly excited [3.11]. Under such experimental conditions, the momentum transfer is negligible and electric-dipole transitions have been found to dominate the electron energy-loss (EEL) spectra. This technique is known as dipole \((e,e)\) spectroscopy.

Hence, in this configuration, the produced energy loss spectrum will closely approximate a photo-absorption experiment. This is useful as it means that results obtained in the EELS experiment will have direct relevance in modelling the molecule’s behaviour in a sunlit atmosphere. The EELS experiment also has certain advantages over photo-absorption experiments, mainly for the fact that a wide energy range from visible to VUV wavelengths is easily accessible without the need to change optical lamps or filters.
A current of around 2.3 A is passed through the filament to generate the electrons. The electron gun is then used to accelerate the electron beam into the hemispherical electrostatic mono-chromator, which reduces the energy spread of the beam from around 0.5 eV to 50 meV. The quasi-monochromatic energy beam is then accelerated to an energy of 150 eV, by a set of electron lenses for imaging and energy control of the electron beam, before colliding at right angles with a perpendicularly travelling effusive gas beam in the interaction region. The gas leaving the interaction region flows directly into a diffusion pump thus eliminating multiple scattering from recycling molecules. Those electrons whose path is undeflected after the interaction region then pass through the aperture in the front of the analyser section and are decelerated into the second hemisphere, with an acceptance angle of ~1°. This hemisphere acts as an energy loss selector and the voltage is set according to the energy loss required. The energy loss is determined by the incident energy minus the pass energy of the analyser section. Thus setting the analyser voltage to 140 Volts will let through only electrons with an energy loss of 150 – 140 = 10 eV. Thus the only electrons to reach the channeltron detector will fulfil the criteria specified to simulate photo-absorption. By varying the analyser voltage by up to ±5 V it is possible to detect electrons with an energy loss range of up to 10 eV. A Multi Channel Analyser (MCA) cumulatively adds the electron counts over a number of sweeps over the voltage range and hence builds up an EEL spectrum. The analyser can rotate about the interaction region.
region to allow detection of electrons scattered at different angles covering an angular range (θ) from -10° to 130° with respect to the incident electron beam. The angular resolution is ± 1.5°. The energy loss scale is calibrated by measuring the spectrum of nitrogen, N₂, which has a very well known energy loss peak at 12.92 eV peak. The apparatus is encased in a stainless steel vacuum chamber and is shielded by mu-metal casing to minimise magnetic fields.

3.3.1 EELS data conversion to photo-absorption cross sections

The inelastic scattered intensity (I(E)) may be converted to a relative differential oscillator strength (DOS) distribution, df/dE by:

\[ \frac{df}{dE} = \frac{E_n}{R} \Delta \theta \frac{1}{\ln[1 + (\theta / \gamma)^2]} I(E) \]  
(3.7)

\[ \gamma = \frac{E^2}{4RT(E)} \]  
(3.8)

where df/dE is the DOS, T is the incident electron energy, E is the energy loss, Δθ is the acceptance angle (~ 1°), R is the Rydberg constant. The DOS values are directly proportional to the photo-absorption cross sections but are relative values as they are only proportional to the intensity losses of the electron beam so the data must be normalised at one wavelength to a measured optical cross section using:

\[ \frac{df}{dE} = \frac{\sigma}{109.75} \]  
(3.9)

where σ is in Mb and df/dE in units of eV⁻¹. Comparison of the EELS cross section values with those recorded using the synchrotron radiation source provides a test for any systematic error in the optical values arising from the line saturation effect and second order light from the light source and beam line. For all the molecules studied in this thesis these effects were found to be negligible, e.g. for SF₅CF₃ (see Chapter 5).

3.4 Photo-Electron (PE) Spectrometer, Liège, Belgium

3.4.1 Photo-electron spectroscopy

Photo-electron spectroscopy involves the measurement of the kinetic energy of emitted electrons from atoms or molecules which have been photo-ionised (section
2.2.4). If a molecule is ionised by photons of energy \( hv \), the kinetic energies of the emitted electrons \( (E_k) \) are given by:

\[
E_k = hv - E_I
\]

(3.10)

where \( E_I \) is an ionisation energy. For a polyatomic molecule there will be many ionisation energies as there are several molecular orbitals each of which will lead to a band structure observed for the molecular ion. Therefore an energy analysis of the emitted electrons will reveal information on the band structures of the molecular ion, and give the ionisation energies of the neutral molecule, which can be either the adiabatic or the vertical ionisation energies (section 2.2.4).

3.4.2 The University of Liège photo-electron spectrometer

A typical photo-electron spectrometer used to investigate valence shell orbitals consists of an interaction region where a beam of UV photons is incident upon a target molecule and an electron energy analyser to detect the photo-emitted electrons. In this work, we used a traditional photo-electron spectrometer at the University of Liège. The helium, 21.22 eV (HeI, 21.2182 eV), photo-electron spectrometer has been described in detail previously [3.12]. Briefly, the spectrometer consists of a 180° cylindrical electrostatic analyser with a mean radius of 5 cm (Figure 3.14). The analyser is used in constant energy pass mode and is fitted with channeltron detector.

![Figure 3.14 – Schematic of PES apparatus.](image)

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The incident photons are produced by a d.c. He discharge in a two-stage differentially pumped lamp. Spectra are recorded by sweeping the retarding voltage in steps of 1 meV between the ionisation chamber and the entrance slit of the hemispherical selector analyser.

The apparatus is evacuated by a diffusion pump such that the base pressure of the system is \( \sim 10^{-6} \text{ torr} \) (1.333 \( \times 10^{-4} \) Pa), rising to \( \sim 5 \times 10^{-6} \text{ torr} \) (6.666 \( \times 10^{-4} \) Pa) during gas admission.

The energy scale is calibrated using the well-known xenon peaks, \( ^2P_{3/2} = 12.130 \text{ eV} \) and \( ^2P_{1/2} = 13.436 \text{ eV} \) [3.13] with a resolution estimated (from the full width half maximum of the Xe peaks) to be \( \sim 25 \text{ meV} \).

The data obtained was subsequently de-convoluted employing the ratio method of Van Cittert [3.14] with Grimm's algorithm [3.15] to remove instrumental dependencies from the recorded signal, and precise ionisation energies are therefore obtained as well as relative ionisation cross-sections.

The measured photo-electron spectra can be used to aid in the assignment of Rydberg states in the photo-absorption spectra. For certain molecules the photo-electron transition may involve vibrational excitations in the final state, reflecting the bonding properties of the orbitals. Ionisation from strongly bonding orbitals often leads to long vibrational progressions in spectra, where a given vibrational mode is observed to be excited in a number of different quanta. In other cases, electrons may be emitted from orbitals which have only little influence on the molecular geometry.

In all cases the outgoing electron leaves the system in a more or less strongly excited vibrational state. If this internal energy is high, corresponding to a highly excited vibrational state, the kinetic energy of the electron will be low, and conversely, if the vibrational energy is low, the kinetic energy is high. Thus, the vibrational states are directly displayed in the spectrum. The energy spacing is typically in the order of a hundred or a couple of hundreds of meV, which means that the vibrational excitations can be readily studied in UV photo-electron spectra.

### 3.5 Dissociative Electron Attachment (DEA) apparatus

Electron attachment spectroscopy (EAS) is a technique used to measure negative ion yields as a function of the electron collision energy. If the electron beam energy is resonant with the empty molecular energy level, the extra captured electron will be trapped and a temporary negative ion (TNI) will be formed. In most of the molecular
systems studied the TNI dissociate into fragments, a process known as dissociative electron attachment (DEA). Studying the product anions therefore probes the fragmentation dynamics of the anion.

In electron attachment investigations a monochromatic electron beam is accelerated to the required kinetic energy and directed onto a molecular beam target. The product negative ions are easily detected by mass spectrometric techniques if their lifetimes are long enough in comparison to the time-of-flight. Since all, the DEA processes are resonant, the electron energy resolution is very important in these experiments and the resolution achieved is always limited by the quality of the monochromator.

3.5.1 The Innsbruck apparatus for measuring DEA

The experimental apparatus used provides low energy free electrons with kinetic energies in the range from 0 up to 10 eV. The anions and fragment radicals formed in the attachment process can initiate ion-molecule or radical-molecule reactions in which new molecular species may be formed. Hence it is possible not only to probe fundamental properties of the molecular target species but study complex chemical reactions induced by fragmentation of molecular systems in different phases of matter.

Experiments are performed in an interaction chamber, in which a neutral effusive molecular beam is crossed at right angles with a monochromatic electron beam produced by a Trochoidal Electron Monochromator (TEM) [3.16].

3.5.1.1 The trochoidal electron monochromator

The whole monochromator, Figure 3.15 (after Sailer [3.16]), is placed in a magnetic field of variable strength (< 5mT) produced by a pair of Helmholtz coils (70 cm diameter).

Thermally emitted electrons from a tungsten filament with energy spread ≈ 700 meV pass through the dispersive element that only transmits electrons with a narrow energy spread of ∼ 50 meV. Slow electrons are rejected by a retarding electric field, allowing the resolution of the monochromator to be increased up to 30 meV. After this stage, the monochromated electrons are accelerated to the desired collision energy. After passing the interaction region the electron beam is collected by a Faraday cup detector.
Figure 3.15 – Diagram of trochoidal electron monochromator used in Innsbruck.

The electron monochromator can routinely be operated with a resolution of 45 meV – 50 meV and electron currents of ~ 5 nA. This type of TEM is particularly effective in low energy beam experiments where stray electrostatic fields cause a loss of current at low energies as is prevalent in traditional hemispherical monochromators.

3.5.1.2 Detection system

Anions formed in the collision region are extracted by a weak electric field formed by two ion extraction lenses placed at opposite sides of the collision region, Figure 3.16 (after Sailer [3.17, 3.18]).

Ions are then accelerated up to 20 eV and focussed into a quadrupole mass spectrometer where they are selected according to their mass to charge ratio. After leaving the quadrupole mass filter the ions are deflected by a semicircular ion-deflector electrode and accelerated into a channeltron electron multiplier detector. The electrical signal is then passed through a discriminator and fed into a computer-based data acquisition system.
3.5.2 The electron Stimulated Desorption (ESD) apparatus in Berlin

Understanding the mechanisms that can affect stratospheric ozone depletion when greenhouse or ozone depleting molecules are co-adsorbed in the polar stratospheric clouds, is extremely important. Recent studies have shown that electron trapping in dielectric media can occur via several mechanisms, such as resonance stabilisation and dissociative electron attachment (DEA), leading to dissociative states of the relevant molecule. We therefore undertook a collaborative project to study electron stimulated desorption from condensed layers to characterise the effect of charge transfer.

The ESD apparatus in the Freie Universität Berlin, consists of a low energy electron gun (0 – 18 eV) a TEM, a cryostat, a mono-crystalline Au (111) surface target (assembled on a 3D manipulator), a quadrupole mass spectrometer and a secondary electron multiplier detector, schematically represented in Figure 3.17 [3.19].
The working base pressure is \( \sim 10^{-10} \) mbar \((10^{-7} \) Pa) and the system is pumped by two pumps in parallel. One is a turbo pump (Leybold Turbvac 360) with a pumping speed of 360 l/s, and the second is an Ion getter pump with pumping speed of 270 l/s. The adsorbing molecules are condensed on the Au (111) crystal kept at a temperature of around 30 K – 35 K. The crystal may also be heated, by a resistive wire to 473 K to evaporate condensed layers and keep surface clean prior to gas deposition.

### 3.5.2.1 The electron gun and monochromator

The trochoidal electron monochromator is schematically represented in Figure 3.18 and has been described in earlier publications [3.16]. Electrons emitted thermionically from the cathode are collimated into a beam and focussed by the off axis molybdenum lenses \( B_1, B_2 \) and \( B_3 \). The electron beam enters the energy selector in the region between \( C_1 \) and \( C_2 \) where a perpendicular electric field, \( \vec{E} \), and a parallel magnetic field, \( \vec{B} \) (30 Gauss), to the beam trajectory are applied. Typically nanoamp electron beams with a resolution of \( \sim 50 \) meV – 60 meV are produced.

The beam then passes through accelerating and retarding lenses, \( S_1, S_2, S_3 \) and \( S_4 \), to impinge upon the adsorbed molecules. The ions formed are then extracted by a system of lenses towards the entrance of a commercial mass analyser filter and detected by a secondary electron multiplier (section 3.5.2.3).
3.5.2.2 Cryostat and target surface

The target crystal surface is cooled down by a means of a two stage Helium cryostat (CRYODYNE, CTI Cryogenics, 2W), reaching a temperature of ~ 20 K. The crystal holding is made of a copper wire and is connected with the second head of the cryostat by a thick copper wire in order to assure good thermal connection (Figure 3.17). The temperature is monitored using a thermocouple sensor. The crystal surface is dosed via a small 40 ml volume chamber, where the pressure is measured with the MKS baratron manometer capacitor. This gas preparation chamber is connected to the main chamber through a sapphire fine gate valve.

The position of the crystal may be adjusted with a manipulator in order to place it close to the gas sample inlet (~ 0.7 cm from the capillary) (Figure 3.19).
In the present experiments the sample has been placed in the same position and the same pressure (in the main chamber) used to ensure a constant dosage velocity and reproducible thickness of adsorbate. The typical uncertainty using this procedure is around 20% – 30%.

**3.5.2.3 Analysis and detection system**

The low energy electron monochromator and mass spectrometer are computer controlled via a National Instruments MCS card. When the electron beam hits the condensed substrate, desorbing ions are drawn to the entrance of a commercial quadrupole mass spectrometer (QMS, Balzers QMG 311) by a weak electric field.

One of the most important features of an electron stimulated desorption experiment is the electron beam energy resolution. For the present studies on the reactivity of gaseous SF$_5$CF$_3$ with water and xenon sub-monolayers co-adsorbed on an Au (111) surface (Chapter 5) the electron current transmitted through the condensed film to the Au (111) surface is measured (Figure 3.20, black line) and then differentiated (Figure 3.20 red line) in order to get the electron beam resolution of the monochromator. For each measurement scan, the zero energy is defined as being at the beginning of the current onset (0 eV, vacuum level). This calibration procedure has an estimated error of ± 0.5 eV.

![Figure 3.20 - Electron beam transmitted current and energy profile in ESD experiments.](image)
3.6 Conclusions

In this chapter, the apparatus used in the course of this thesis have been discussed. In particular, the experimental apparatus used to obtain high resolution (~0.75 Å) VUV photo-absorption cross sections by means of a synchrotron radiation facility has been described. The UCL EEL spectrometer has been used to obtain the first data on SF₅CF₃ which may be directly compared to photo-absorption spectra. A photo-electron spectrometer has been used to obtain information on the ionisation potentials of some the studied molecules, and this data has also been used to assign the Rydberg state spectroscopy of the molecular systems in particular SF₅CF₃. A dissociative electron attachment spectrometer has been used to study the formation of negative ions in electron-molecule collisions. Finally, a electron stimulated desorption experiment, used to perform the first heterogeneous studies and the reactivity of gaseous SF₅CF₃ with water and Xenon sub-monolayers co-adsorbed on Au (111) surface (Chapter 5) has also been presented.
3.7 References


Chapter 4

High resolution VUV photo-absorption cross sections for (CH$_3$)$_2$S and CH$_3$CHO

*Imagination is more important than knowledge.*
Albert Einstein (1879 – 1955)

4.1 Introduction

This chapter describes experimental studies on the spectroscopy of dimethylsulphide (DMS), (CH$_3$)$_2$S, and acetaldehyde, CH$_3$CHO, and discusses how these may be used to quantify their role in stratospheric chemistry.

Due to their importance as air pollutants, research into oxidation reactions has intensified over the last twenty years. (DMS) and CH$_3$CHO, have been found to play an important role as intermediate species in the oxidation mechanisms of tropospheric hydrocarbons. Moreover, the photo-dissociation products of these compounds play an important role in the chemistry of several other trace compounds in the lower atmosphere.

High-resolution VUV photo-absorption spectra of both (CH$_3$)$_2$S and CH$_3$CHO compounds were recorded using the ASTRID synchrotron radiation facility (Chapter 3). The cross sections recorded for both molecules revealed absorption features ascribed to Rydberg states, some of them observed for the first time. Absolute photo-absorption cross sections are compared with previous measurements, obtained with an accuracy of ± 5%.

4.2 VUV photo-absorption of dimethylsulphide, (CH$_3$)$_2$S

4.2.1 Introduction

Dimethylsulphide (DMS), (CH$_3$)$_2$S, is the most abundant dissolved compound found in sea water and plays an important role in the global sulphur cycle. Therefore,
DMS has been identified as being the dominant gas, accounting for more than 50% of the global sulphur emissions from natural sources. It is a product of biodegradation of organosulphur compounds in marine environments, which upon release into the atmosphere may be changed into different sulphur species, e.g. sulphur dioxide, methane-sulphonic acid, sulphate and sulphuric acid, all of which can contribute to the acidity of rain. DMS is central to the coupling between the marine atmospheric sulphur cycle and atmospheric cycles [4.1]. Moreover, such sulphur containing gases are known to be precursors of sulphate aerosol particles and cloud condensation nuclei over remote parts of the oceans and could also act as a feedback mechanism in climate regulation, which affects the Earth’s radiative balance by direct scattering of solar radiation [4.2]. It has recently become clear that the natural sulphur cycle has been seriously disturbed by anthropogenic gaseous emissions. Recent studies indicate that the total anthropogenic sulphur (S) flux from fossil fuel combustion is estimated to be about 80 ± 20 TgSyr\(^{-1}\) and it is approximately equal in magnitude to the natural flux of reduced sulphur compounds in the atmosphere. Studies on (DMS) and its oxidation products in marine atmosphere, production and release in local estuaries and distribution in surface waters have therefore recently become the subject of intense research [4.1, 4.3, 4.4]. It is therefore necessary to understand quantitatively the factors that regulate DMS emissions both in the ocean and in the atmosphere.

![Figure 4.1 – Dimethylsulphide, \((\text{CH}_3)_2\text{S}\) molecule spatial orientation diagram.](image)

### 4.2.2 Experimental review

The absorption spectrum of (DMS) was taken using the photo-absorption cell set-up described in Chapter 3, section 3.2.3 with an absorption path length of 25 cm. The spectrum was recorded in 11 nm sections, in 0.1 nm steps. The sample used in this investigation was obtained from Sigma Aldrich, with a purity of 99+%. No further purification was undertaken except for freeze-thaw-pump cycles.
The dimethylsulphide spectrum was recorded over the sample pressure range 0.015 torr - 0.900 torr (see Table 4.1), with typical attenuations of 10%. High pressure was used in order to observe the low intensity features at 5.0 eV - 5.5 eV. \((\text{CH}_3)_2\text{S}\) molecule has seven totally symmetric ground-state vibrational modes [4.5] and belongs to the \(C_{2v}\) point group. The results presented in the following sections are a definitive series of measurements to determine both the absolute photo-absorption cross section and to classify its electronic spectroscopy over the energy range from 5.0 eV to 11.0 eV.

<table>
<thead>
<tr>
<th>Energy range (eV)</th>
<th>Wavelength (nm)</th>
<th>Pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.59 - 5.39</td>
<td>270 - 230</td>
<td>0.900</td>
</tr>
<tr>
<td>4.68 - 5.82</td>
<td>213 - 265</td>
<td>0.375</td>
</tr>
<tr>
<td>5.79 - 7.17</td>
<td>173 - 214</td>
<td>0.150</td>
</tr>
<tr>
<td>7.13 - 8.11</td>
<td>153 - 174</td>
<td>0.075</td>
</tr>
<tr>
<td>8.05 - 10.08</td>
<td>123 - 154</td>
<td>0.023</td>
</tr>
<tr>
<td>10.00 - 10.97</td>
<td>113 - 124</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Table 4.1 - Photon energy (eV), wavelength (nm) and pressure (torr) ranges for dimethylsulphide photo-absorption measurements.

The electronic states have been studied previously [4.5 - 4.7] as have its photo-electron spectra, photo-ionisation spectra, electron momentum density distributions and transition polarisations, fluorescence excitation [4.8 - 4.16] and magnetic circular dichroism [4.17]. The vacuum-ultraviolet (VUV) absorption spectrum of \((\text{CH}_3)_2\text{S}\) in the wavelength range 190 nm to 250 nm (5.0 eV to 6.5 eV) was first reported by Thompson et al. [4.6] and subsequently discussed by Scott et al. [4.5]. Electronic spectra of a number of divalent sulphur compounds have also been reported [4.16 - 4.21] and may be compared to dimethylsulphide.

4.2.3 Results

The high resolution photo-absorption cross section spectrum of (DMS) is shown in Figure 4.2 in the energy range 5.0 eV - 11.0 eV and is in good agreement with that obtained recently by Tokue et al. [4.16]. The spectrum is composed of absorption bands with low cross sections, below 6.0 eV and a series of sharp, more intense peaks above 6.0 eV some of which contain rich vibrational structures. The dashed line marked IP represents the lowest ionisation potential, IP, and the dashed feature close to 11.0 eV is only partially recorded due to the cut-off in the transmission of the CaF₂ window.
(Chapter 3, section 3.2.3). The overall resolution of the obtained spectrum is ~ 0.075 nm FWHM.

(DMS) has nine atoms with $3N - 6$ vibrational modes, giving it twenty-one fundamental modes of vibration, which can be subdivided by symmetry properties into $7A_1, 4A_2, 6B_1$ and $4B_2$ [4.7]. However, the seven totally symmetric ground state vibrational modes are classified in the symmetry type as $I_{\text{vib.}} = 7A_1$ and are presented in Table 4.2.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Description</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>C – H stretching</td>
<td>0.369</td>
</tr>
<tr>
<td>$v_2$</td>
<td>C – H stretching</td>
<td>0.364</td>
</tr>
<tr>
<td>$v_3$</td>
<td>CH$_3$ deformation</td>
<td>0.178</td>
</tr>
<tr>
<td>$v_4$</td>
<td>CH$_3$ deformation</td>
<td>0.165</td>
</tr>
<tr>
<td>$v_5$</td>
<td>CH$_3$ rocking$^1$</td>
<td>0.127</td>
</tr>
<tr>
<td>$v_6$</td>
<td>C – S stretching</td>
<td>0.085</td>
</tr>
<tr>
<td>$v_7$</td>
<td>C – S – C deformation</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Table 4.2 – Dimethylsulphide totally symmetric ground state vibrational energies (eV).

$^1$ Parallel to CSC plane
Figure 4.2 – VUV photo-absorption spectrum of dimethyl sulphide in the energy region 5 eV to 11 eV.
For \((\text{CH}_3)_2\text{S}\) the outermost valence molecular orbitals may be represented in the independent particle model as: \((2b_1)^2 (7a_1)^2 (4b_2)^2 (1a_2)^2 (5b_2)^2 (8a_1)^2 (3b_1)^2\), with a configuration for the ground state as: \(\tilde{X}^1A_1\). The \(3b_1\) \(\approx np_z\) orbital, normal to the molecule's plane, is the HOMO and together with \(8a_1\) \(\approx np_z\) are the orbitals identified as sulphur non-bonding electrons \((n)\), \(5b_2\) the \(\sigma_{\text{CS}}\), \(4b_2\) the \(\pi_{\text{CS}}\), \(7a_1\) the \(\sigma_a\) and \(2b_1\) the \(\pi_{\text{CH}_3}\) [4.21]. The LUMO's are \(\sigma^* (2b_2)^0\), \(\sigma^* (3a_1)^0 (\text{(n+1)s})\) and \(\sigma^* (4a_1)^0 (\text{(n+1)s})\). The \((\text{n+1})p_{xyz}\) sulphur orbitals are labelled \(b_1\), \(b_2\), and \(a_1\), respectively [4.17]. Since the ground state is \(1^1A_1\), electric dipole transitions to \(1^1A_1\), \(1^1B_1\) and \(1^1B_2\) are symmetry allowed, while transitions to \(1^1A_2\) are forbidden.

The observed absorption bands can be classified as either members of Rydberg series or molecular valence transitions of the type \((nS \rightarrow \sigma^*)\), although for the low-energy members of the Rydberg series, a mixed Rydberg-valence character with the bands having characteristics of both types of transitions have been suggested [4.5, 4.6, 4.22]. However, until now, there has not been any agreement concerning these assignments. An even greater lack of accord is found for the assignment of the broad band at 6.126 eV [4.5, 4.6, 4.16, 4.18] with recent work on electronic absorption and magnetic circular dichroism [4.17] assigning this band as the \(3p(1b_1) \rightarrow \sigma^* (4a_1)\), \(3B_1\) \((nS \rightarrow \sigma^*)\) transition.

Features between 5.0 eV - 7.0 eV and above 7.0 eV have been interpreted as belonging to Rydberg series converging to the ionic ground state potential of \((\text{CH}_3)_2\text{S}\), 8.686 ± 0.010 eV [4.23], arising from transitions of a lone-pair sulphur \((nS)\) electron to the Rydberg orbitals. Pre-dissociation and mutual overlap between bands have been observed in the broader structures observed in the higher energy range band (\(>\) 7.5 eV) and for energies above 6.0 eV. Each of these bands is discussed in more detail below. Higher energy absorption bands are observed at \(~\) 9.6 eV and 10.534 eV, and tentatively assigned as originating from non-bonding sulphur orbital of \(a_1\) character, and it has been suggested [4.22] that they can be members of a \(nd\pi\) and \(nd\delta\) Rydberg series converging to the 11.30 eV [4.21] ionic electronic first excited state with quantum defects \((\delta)\) of \(0.17 < \delta < 0.21\) and \(\delta = 0\), respectively.

Photo-dissociation measurements of \((\text{DMS})\) [4.11, 4.12], have shown that upon electronic excitation, the \(C_{2v}\) symmetry of the molecule relaxes to \(C_s\) symmetry, and the photo-dissociation can then proceed via a superposition of the first excited electronic \(1^1A''\) and \(2^1A''\) states. These states correlate with the \(1^1B_1\) and \(1^1A_2\) \(C_{2v}\) states,
respectively, only if the S – C bond of the upper state is kept approximately the same as the ground state molecule. The $2^1A''$ state is bound and, unlike the $1^1A''$ state, it does not correlate adiabatically with ground state fragments $\text{CH}_3(\tilde{X}^2A_2'') + \text{CH}_3\text{S}(\tilde{X}^2E)$, but dissociation may occur via vibronic coupling with the lower $1^1A''$. It has been reported [4.11, 4.12] that theoretical calculations suggest that the $2^1A'' \rightarrow 1^1A''$ non-adiabatic transition involves significant geometrical changes that may induce a rich vibrational activity in the dissociating complex. This effect could clearly explain the observed pattern for the electronic excitation in the next two energy regions (5.0 eV - 6.0 eV and 6.0 eV - 7.0 eV).

4.2.3.1 The 5.0 eV - 6.0 eV photon energy region

In this energy region, the first dipole allowed electronic transition has been identified as $1^1B_1(9a_i \leftrightarrow 3b_1) \leftrightarrow \tilde{X}^1A_1$ in the $C_{2v}$ symmetry [4.12]. The present absorption spectrum (Figure 4.2) shows evidence of pre-dissociative vibronic structure followed by a series of more diffuse maxima. The low absorption feature centred at 5.443 eV (~ 228 nm) with a local maximum cross section of 2.47 Mb (Figure 4.3) is a result of the excitation to an anti-bonding orbital along the sulphur lone pair electrons ($n_S \rightarrow \sigma^*$) of the $(\text{CH}_3)_2\text{S}$ molecule, and assigned as the (0-0) transition of the electronic band.

![Figure 4.3 – Vibrational progressions in the 5.0 eV – 6.0 eV absorption band of dimethylsulphide.](image)
Chapter Four

The vibrational analysis (Table 4.3) in this region is in good agreement with the work of Thompson et al. [4.6]. The structure at 5.412 eV, 0.031 eV from the 5.443 eV (0-0) transition is tentatively assigned as a hot band resulting from a $\nu_7$ mode (0.035 eV in the ground state). For the observed structures at energies above 5.8 eV, despite their diffuseness, vibrational assignments have already been proposed [4.22]. The vibrational excitation in this energy region is mainly characterised by short progressions on the CH$_3$ deformation and rocking modes together with C – S stretching mode. The assignments in Table 4.3 are compared to previous work [4.6] where brackets denote possible degeneracy in energies for the vibrational mode involved. For some features the peak position is uncertain due to their width and low cross section so these have only been tentatively assigned and marked as (?

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Assignment</th>
<th>Energy (eV)</th>
<th>Assignment</th>
</tr>
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<tbody>
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<td>$\nu_{00}$</td>
<td>5.448</td>
<td>$\nu_{00}$</td>
</tr>
<tr>
<td>5.472</td>
<td>$\nu_7$</td>
<td>5.482</td>
<td>$\nu_7$</td>
</tr>
<tr>
<td>5.530</td>
<td>$\nu_6$</td>
<td>5.540</td>
<td>$\nu_6$</td>
</tr>
<tr>
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<td>$\nu_5$</td>
<td>5.581</td>
<td>$\nu_5$</td>
</tr>
<tr>
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<td>2$\nu_6$(or $\nu_4$)</td>
<td>5.619</td>
<td>2$\nu_6$</td>
</tr>
<tr>
<td>5.656</td>
<td>$\nu_5 + 2\nu_6$</td>
<td>5.670</td>
<td>$\nu_5 + \nu_6$</td>
</tr>
<tr>
<td>5.687</td>
<td>2$\nu_5$(or 3$\nu_3$)</td>
<td>5.699</td>
<td>2$\nu_5$ or 3$\nu_6$</td>
</tr>
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<td>5.724 (?)</td>
<td>$\nu_5 + 3\nu_6$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5.778</td>
<td>2$\nu_4$</td>
<td>5.789</td>
<td>2$\nu_5 + \nu_6$ or 4$\nu_6$</td>
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<tr>
<td>5.810 (?)</td>
<td>3$\nu_5$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5.873 (?)</td>
<td>2$\nu_4 + \nu_5$</td>
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</tr>
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</table>

Table 4.3 – Vibrational assignment in the 5.0 eV – 6.0 eV absorption band of (CH$_3$)$_2$S.

4.2.3.2 The 6.0 eV – 7.0 eV photon energy region

This energy region is displayed in Figure 4.4 and exhibits considerable vibrational structure, it has a remarkable resemblance to the 5.0 eV – 6.0 eV energy region. It is therefore possible to assign this band in terms of progressions and combinations of CS deformation, $\nu_7$ and stretching modes, $\nu_6$ and CH$_3$ rocking, $\nu_5$ and deformation, $\nu_4$ modes. The (0-0) transition lies at 6.348 eV (~ 195 nm) and is a result of the excitation to an anti-bonding orbital along the sulphur lone pair electrons ($n_S \rightarrow \sigma^*$) of the (CH$_3$)$_2$S molecule. Vibrational analysis has been carried out (Table 4.4). The structure at 6.259 eV, 0.089 eV from the 6.348 eV (0-0) transition has been
tentatively assigned as a hot band of the C – S stretching mode, ν<sub>6</sub>, (with 0.085 eV in the ground state). These new vibrational assignments may be compared to those in previous lower resolution work [4.6]. The main vibrational modes are those related to CH<sub>3</sub> deformation and rocking and C – S stretching (Table 4.4).

![Diagram](image)

**Figure 4.4 – Vibrational progressions in the 6.0 eV – 7.0 eV absorption band of dimethylsulphide.**

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Assignment</th>
<th>Energy (eV)</th>
<th>Assignment</th>
</tr>
</thead>
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<td>ν&lt;sub&gt;00&lt;/sub&gt;</td>
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<td>6.472</td>
<td>ν&lt;sub&gt;5&lt;/sub&gt;</td>
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<tr>
<td>6.508</td>
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<td>6.508</td>
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<tr>
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<td>6.554</td>
<td>ν&lt;sub&gt;5&lt;/sub&gt; + ν&lt;sub&gt;6&lt;/sub&gt;</td>
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<tr>
<td>6.595</td>
<td>2ν&lt;sub&gt;5&lt;/sub&gt; (or 3ν&lt;sub&gt;6&lt;/sub&gt;)</td>
<td>6.592</td>
<td>2ν&lt;sub&gt;5&lt;/sub&gt; or 3ν&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
<tr>
<td>6.634 (?)</td>
<td>ν&lt;sub&gt;5&lt;/sub&gt; + 2ν&lt;sub&gt;6&lt;/sub&gt;</td>
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<td>ν&lt;sub&gt;5&lt;/sub&gt; + 2ν&lt;sub&gt;6&lt;/sub&gt;</td>
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<tr>
<td>6.673</td>
<td>2ν&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>-</td>
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<tr>
<td>6.720</td>
<td>3ν&lt;sub&gt;5&lt;/sub&gt;</td>
<td>6.681</td>
<td>2ν&lt;sub&gt;5&lt;/sub&gt; + ν&lt;sub&gt;6&lt;/sub&gt; or 4ν&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
<tr>
<td>6.760</td>
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<td>6.810 (?)</td>
<td>3ν&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>6.900</td>
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</tr>
</tbody>
</table>

**Table 4.4 – Vibrational assignment in the 6.0 eV – 7.0 eV absorption band of (CH<sub>3</sub>)<sub>2</sub>S.**
4.2.3.3 Rydberg series converging to the $\tilde{X}^2B_1$ state

The cross section above 7.5 eV consists of sharp peaks superimposed on broad bands up to the lowest ionisation potential (IP) limit, 8.686 ± 0.010 eV [4.23] (Figure 4.2 and 4.5). The broad featureless bands are probably due to the excitation of high energy valence excited states which are dissociative in character. The following Rydberg series assignments were obtained using the Rydberg equation in chapter 3 (section 3.2.5.1). Following the notation of Wang et al. [4.24], the Rydberg orbitals are:

- \( ns: a_1 (\sigma_g), \) for \( n \geq 4 \) (4.1)
- \( np: b_2 (\sigma_u), a_1 (\pi_u), b_1 (\pi_u), \) for \( n \geq 4 \) (4.2)
- \( nd: a_1 (\sigma_g), a_2 (\pi_g), b_2 (\pi_g), a_1^* (\delta_g), b_1 (\delta_g), \) for \( n \geq 3 \) (4.3)

where the brackets' notation refer to \( C_{\infty h} \), with the \( yy \) axis being the \( C_{\infty h} \) symmetry axis. The transitions from the \( 3b_1 \) orbital to the Rydberg orbitals, are all symmetry allowed with the exception for the \( (3b_1)^1 (n^b_2) \uparrow A_2 \leftarrow \tilde{X}^1A_1 \). Thus, only one \( s \) series, two \( p \) series and four \( d \) series (in a total of seven) should be observed [4.16]. However, it has only been able to identify four series the present data.

The \( nsa \) Rydberg series

Figure 4.5 shows the absorption spectrum between 5.0 eV and 9.0 eV range revealing the four Rydberg series. The low intensity feature located at 5.443 eV has been assigned as the Rydberg transition to \( 1B_1 (2B_1, n^s(1b_1) \rightarrow 4s(3a_1)) \) state [4.16, 4.23], of \( n = 4 \) term \( 1b_1 \rightarrow nsa(a_1) \) series with a quantum defect \( \delta = 1.95 \) (Table 4.5). This electronic transition shows vibrational excitation of \( v_6 \) with a frequency of 0.074 eV.

The \( np\lambda \) Rydberg series

The first member of the \( np\lambda \) (\( np\sigma \) or \( np\pi \)) series, assigned as the Rydberg transition to \( 1A_1 (4A_1, n^s(1b_1) \rightarrow 4p(2b_1)) \) state [4.16, 4.17], is attributed to the 6.414 eV peak, the quantum defect being \( \delta = 1.55 \) (Table 4.5). Like the previous transition, this is accompanied by the vibrational excitation of the \( v_6 \) normal mode with a frequency of \( \sim 0.080 \) eV. The second and third terms of the series are observed at 7.546 eV and 8.004 eV, respectively, both with a quantum defect of \( \sim \delta = 1.55 \).
Figure 4.5 - Assignment of Rydberg series converging to the ionisation potential of 8.686 eV.
The \( \text{nd\sigma} \) Rydberg series

There are no agreements so far for the symmetry of the 3d orbital; however, Scott and Russel [4.14] have proposed either \( a_1 \) or \( a_2 \) symmetry according to their studies on electronic symmetries, dipole moments and polarisabilities in Rydberg states determined from electric-field effects on absorption spectra.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Quantum defect (( \delta ))</th>
<th>Assignment</th>
<th>Energy (eV)</th>
<th>Quantum defect (( \delta ))</th>
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</thead>
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<td>( n\sigma ) series</td>
<td></td>
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<td>( np\lambda ) series</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>4s\sigma</td>
<td>6.414</td>
<td>1.55</td>
<td>4p\lambda</td>
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<tr>
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<td>8.109</td>
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<td>6d\pi</td>
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<td>8.394</td>
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<td>7d\pi</td>
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<tr>
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<td>8.463</td>
<td>0.19</td>
<td>8d\pi</td>
</tr>
<tr>
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<td>9d\sigma</td>
<td>8.510</td>
<td>0.21</td>
<td>9d\pi</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
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<td>0.18</td>
<td>10d\pi</td>
</tr>
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<td>8.592</td>
<td>0</td>
<td>12d\pi</td>
</tr>
</tbody>
</table>

Table 4.5 – Energy values, quantum defect and assignment of Rydberg series converging to the ionic electronic ground-state \( \tilde{X}^3B_1 \) of dimethylsulphide.

The peak at 6.900 eV (Figure 4.5) has been interpreted as a \( n = 3 \) term of a \( nd\sigma \) series, with a calculated quantum defect \( \delta = 0.24 \) (Table 4.5). The second and third terms are at energies of 7.735 eV and 8.088 eV, respectively, both with a quantum defect \( \delta \sim 0.23 \). The higher members of this series for which relative intensity decreases abruptly, are hidden by bands due to the excitation of other Rydberg series states. The last observed series starting at 6.977 eV (Figure 4.5 and Table 4.5) has been assigned as
a \( n = 3 \) term of a \( nd\pi \) series, in agreement with a previous study [4.16]. The second and third terms of the series lie at 7.749 eV and 8.109 eV, with quantum defects \( \delta = 0.19 \) and 0.15 respectively. The bands due to the higher members are overlapped by those of the previous Rydberg series, which makes assignment difficult for higher energy members. The various Rydberg series that have been recorded are consistent with those observed even though the present resolution is higher than that of the earlier study [4.15].

The relatively small changes in the permanent dipole moments imply that, in each of the excited states, the Rydberg orbitals are localized about the atom from which the excited electron is coming from. Actually the changes in dipole moments due to intravalent transitions are large, and are considered to be more charge transfer in nature than the Rydberg transitions. Nevertheless, this corroborates the generally accepted view that Rydberg transitions are localised about their centre of origin, while larger movements of charge are linked to intravalent transitions involving non-bonding electrons. In order to help the interpretation and classification of the Rydberg series, Elden’s diagrams (see Chapter 3, section 3.2.5.2) have been established as shown in Figure 4.6.

![Figure 4.6 - Elden's diagrams for the variation of the quantum defect (\( \delta_{\text{nt}} \)) with the reduced term energies (\( n^{-3} \)) for the first terms of the Rydberg series converging to the ionisation limit (8.686 eV).](image)

A similar approach may be taken when performing a Rydberg analysis for the other molecules studied throughout this thesis. Therefore, the variation of the quantum
defect ($\delta_{\text{def}}$) with the reduced term energies $(n^*)^2 = (n - \delta)^2$ has been plotted. Diagrams of $\delta_{\text{def}}$ as a function of $(n^*)^2$ should give straight lines analogous to atomic Elden's plots [4.25].

4.2.4 Photolysis rates and local lifetimes

Using the absolute photo-absorption cross sections the photolysis rates for (CH$_3$)$_2$S can be calculated at 1 km altitude steps up to the stratopause (50 km), (Chapter 3, section 3.2.4.3). Photolysis rates were calculated as the product of the Solar Actinic Flux [4.23] at a given wavelength and altitude, and the molecular photo-absorption cross section at the same wavelength.

![Graphs showing photolysis rates and local lifetimes](image)

**Figure 4.7** – The photolysis rates (s$^{-1}$) and the lifetimes (Days) for dimethylsulphide as a function of altitude in Earth’s atmosphere.
At each altitude a total photolysis rates (Figure 4.7) may then be calculated by summing over the individual photolysis rates for that altitude (Figure 4.8). The reciprocal of the total photolysis rate gives the local photolysis lifetime at that altitude, i.e. the time taken for the molecule to photo-dissociate if altitude and solar flux remain constant. The results show that the local photolysis lifetime of this molecule varies from around one year near the ground to just over one hour at 50 km. The lifetime of (CH$_3$)$_2$S at the tropopause is therefore averaged at the order of a few weeks such that it may play a role in the local chemistry.

![Figure 4.8 - The photolysis rates (s$^{-1}$ nm$^{-3}$) vs. wavelength (nm) and photon energy (eV) for dimethylsulphide as a function of altitude (0 - 50 km) in Earth’s atmosphere.](image)

The fluorescence excitation measurements of Itokue at al. [4.16], give important information on the photo-dissociation processes. The dispersed fluorescence produced by the 153 nm (8.105 eV) photolysis of (DMS) has been assigned as the CH$_3$(A $-$ X) band, with the threshold wavelength for producing CH$_3$(A $^2$A$_1$) obtained at 190 nm (6.523 eV) and the related reaction pathway as:

$$\text{CH}_3\text{SCH}_3 \rightarrow \text{CH}_3\text{S}(\tilde{A}) + \text{CH}_3(\tilde{X})$$

(4.4)

In the photon energy region of 6.16 eV - 8.80 eV (200 nm $>$ $\lambda$ $>$ 140 nm), the process in eq (4.4) is predominant producing electronically excited fragments from (DMS). In fact, the maximum of the photolysis occurs at 50 Km (Figure 4.8), at 202 nm (6.11 eV)
with a rate of $\sim 1.11 \times 10^{-5} \text{ s}^{-1} \text{ nm}^{-1}$. From the point of view of the environmental evaluation of (DMS) (section 4.2.5) the production of the CH$_3$S radical is important since it can participate in the reaction with O$_2$ to form OCS, this with a estimated atmospheric lifetime of about 7 years.

4.2.5 Environmental evaluation

The ocean surface layer influences climate not only through exchange of greenhouse gases such as carbon dioxide and methane with the atmosphere, but also gases like dimethylsulphide which is thought to exert a cooling influence on the climate system. Climatic factors in turn influence the biogeochemical cycles of these trace gases, and there may then be feedbacks to the global climate system through the related habitats in the ocean surface. The contribution of sea and estuarine (DMS) emissions to the local sulphur budget is insignificant compared to anthropogenic emissions.

Sulphur is essential for all forms of life, and its oxidation-reduction conversions play a significant role in the biogeochemical cycle of sulphur. Disturbances in the natural sulphur cycle, as a result of increased anthropogenic activity, lead to imbalances in the sulphur flux, resulting in problems affecting all levels of the environment, including natural waters and waste-waters, the atmosphere, solid wastes, soils and sediments. Its adverse effects are well known: acid rain, odour nuisance at polluted rivers, landfills and treatment systems, corrosion of steel and concrete, release of heavy metals from oxygen-exposed sediments and mineral ores.

Once in the atmosphere, (DMS) reacts with OH at rate constant of $\sim 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, exceeding that with NO$_3$ by a factor of 4, to produce SO$_2$ and methane sulphonic acid (CH$_3$S(OH)O$_2$), among other products [4.26]. Sulphur dioxide, itself, reacts with OH to produce H$_2$SO$_4$, which can nucleate to produce H$_2$SO$_4$-H$_2$O particles. These once dissolved in the cloud droplets in the atmosphere may be returned to the ground in the form of acid rain. Whether H$_2$SO$_4$ formed from oxidation of (DMS) in the marine atmosphere nucleates homogeneously or condenses on existing particles depends on the surface area concentration of the existing particles. The SO$_2$ may also be absorbed into existing droplets, where it can be converted heterogeneously to sulphate. By these processes, sulphur emitted as DMS constitutes a major fraction of non-sea-salt sulphate (NSS) and of marine cloud condensation nuclei (CCN). (DMS) is a prime regulator of marine CCN concentrations and that a climate feedback mechanism could
exist in which temperature changes influence phytoplankton productivity and (DMS) emissions, thereby affecting marine cloudiness.

4.2.6 Summary

Dimethylsulphide emitted by marine phytoplankton, is the second most important source of atmospheric sulphur, after anthropogenic SO$_2$. In the atmosphere, DMS is transformed into condensable acidic sulphur products and, through gas-to-particle conversion, it becomes the most important natural source of atmospheric sulphate aerosols. Possible climatic effects have been suggested, linked to the negative radiative forcing due to scattering of solar radiation and especially to modification of cloud albedo over oceans by sulphate aerosol particles. These effects occur in addition to those derived from the superimposed anthropogenic component of the atmospheric sulphate.

The measured cross-sectional values are in excellent agreement with the earlier data over the range 210 nm > $\lambda$ > 110 nm (5.9 eV to 11 eV) [4.16] although the local maximum cross section of 44 Mb at 6.348 eV (Figure 4.4) is slightly lower than the photo-absorption data of Tokue et al. [4.16]. The present measurements appear to be the first absolute cross sections for $\lambda$ > 210 nm [4.22]. The experimental results presented therefore provide the highest resolution VUV photo-absorption spectrum of (CH$_3$)$_2$S in the range 5.0 eV to 11 eV (250 nm to 110 nm). Vibrational features at the higher energies are observed and assigned for the first time. The Rydberg bands in general exhibit vibrational structure, while the valence transitions tend to be broad and featureless. Among the low-energy members of the Rydberg bands, evidence has been presented suggesting mixed valence-Rydberg character, with the bands having characteristics of both types of transitions. Photolysis rates and local lifetimes of the molecule were calculated for various altitudes in the atmosphere, and the sulphur cycle has been evaluated with the implications arising from (DMS) oxidation and possible formation of acid rain.
4.3 VUV photo-absorption of acetaldehyde, CH$_3$CHO

4.3.1 Introduction

Acetaldehyde, CH$_3$CHO, is formed by photochemical degradation of other organic compounds, mainly by oxidation of tropospheric higher hydrocarbons. The photo-dissociation products of this compound may react with other trace compounds in the lower atmosphere, with both the hydroxyl radical, OH, nitrogen trioxide radical, NO$_3$, and peroxyacyl nitrates (RC(O)OONO$_2$), all of which are greenhouse gases. Reactions with NO$_3$ radicals are of minor importance as a consumption process for acetaldehyde, thus the major processes involve photolysis and reaction with OH radicals. Hydroxyl radical reactions with acetaldehyde involves H-atom abstraction to produce the corresponding acetyl radical (CH$_3$CO), that rapidly reacts with molecular oxygen to produce peroxyacyl radicals (CH$_3$C(O)OO), that in turn will react with NO and NO$_2$, the latter leading to peroxyacyl nitrates, e.g., CH$_3$C(O)OONO$_2$, CH$_3$CH$_2$C(O)OONO$_2$.

![Acetaldehyde molecule spatial orientation diagram.](image)

Acetaldehyde belongs to the group of aldehydes and is a precursor of ketones and has been seen as an important spectroscopic intermediate between formaldehyde (H$_2$CO) and acetone ((CH$_3$)$_2$CO). Actually, CH$_3$CHO is formed from formaldehyde with H substitution of an CH$_3$ radical. Ketones and aldehydes have been extensively studied by several theoretical and experimental techniques [4.27, 4.28], both of these compounds are found to possess an optically forbidden-transition weak absorption band at $\sim$ 4 eV assigned to the lowest n $\rightarrow$ $\pi^*$ transition [4.29]. Many vertical excitations and information on the geometries of the excited states and their related vibrational frequencies (ketones and aldehydes) have been assigned in the past.
4.3.2 Experimental overview

The photo-absorption spectrum of acetaldehyde was obtained using the static cell (Chapter 3, section 3.2.3) with an absorption path length of 15 cm. The spectrum was recorded from 113 nm (10.97 eV) up to 186 nm (6.67 eV) in sections of either 5.5 nm or 11 nm, with 0.025 nm or 0.1 nm steps, respectively. Above 184 nm (6.74 eV), data was collected in 36 nm section with 0.1 nm steps and from 200 nm – 350 nm, in 1.0 nm step (Table 4.6).

<table>
<thead>
<tr>
<th>Energy range (eV)</th>
<th>Wavelength (nm)</th>
<th>Pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.54 - 6.74</td>
<td>184 - 350</td>
<td>0.900</td>
</tr>
<tr>
<td>6.67 - 7.09</td>
<td>175 - 186</td>
<td>0.038</td>
</tr>
<tr>
<td>6.33 - 6.70</td>
<td>185 - 196</td>
<td>0.150</td>
</tr>
<tr>
<td>6.67 - 7.09</td>
<td>175 - 186</td>
<td>0.075</td>
</tr>
<tr>
<td>7.05 - 10.33</td>
<td>120 - 176</td>
<td>0.038</td>
</tr>
<tr>
<td>7.56 - 10.97</td>
<td>113 - 164</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Table 4.6 – Photon energy (eV), wavelength (nm) and pressure (torr) ranges for acetaldehyde photo-absorption measurements.

Acetaldehyde was obtained from Sigma Aldrich, with a stated purity of 99 %, and no further purification was undertaken except use of freeze-thaw-pump cycles. The spectrum was obtained for sample pressure ranges from 0.075 torr – 0.900 torr, with attenuation factors of ± 10%. Higher pressures were used in order to observe the low intensity band centred at 4.3 eV.

The acetaldehyde electronic states have been extensively studied previously and compared to several deuterated homologues in the vacuum-ultraviolet (VUV) absorption spectrum region around 6.8 eV [4.31 – 4.32], as well as with other small aliphatic aldehydes and ketones in the energy range of 3.0 eV – 6.0 eV [4.33]. Almost two decades ago, Moule and Ng presented the first electronic absorption system in the vapour phase at room temperature for energies around 3 eV [4.34] and a (2+1) REMPI spectrum of jet-cooled has been recorded over the energy range 3.4 eV - 5.5 eV (352 nm – 365 nm) [4.35]. Recently, time resolved UV spectroscopy has been used to evaluate the role of acetyl radical in the photolysis-initiated reaction with chlorine [4.36] and jet-cooled absorption spectra have been obtained for the 3s Rydberg electronic state [4.37]. Moreover, electron energy loss spectra have been reported by several groups.
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[4.38, 4.39 – 4.42] as has a detailed study of the electronic structure and decay channels of the acetaldehyde negative ion [4.43]. A HeI photo-electron spectrum of its three deuterated derivates has been also reported [4.44].

Detailed multi-photon ionisation (MPI) studies on its $n \rightarrow 3s$ Rydberg state and deuterated analogs have been presented [4.45, 4.46] as well as analysis on the positive ion fragmentation patterns by MPI mass spectrometry [4.47]. Laser induced fluorescence excitation on the first excitation band using a jet-cooled molecular beam and the dynamics of selected single rotational levels have been evaluated [4.48, 4.49]. Finally, other investigations have been carried out mainly on the mechanisms of atmospheric photo-oxidation [4.50] and theoretical studies on the excited states of carbonyl compounds, mainly formaldehyde and acetaldehyde [4.51]. They will be discussed and evaluated in section 4.3.5.

4.3.3 Results

The high resolution photo-absorption spectrum is shown in Figure 4.10, with a resolution ~ 0.075 nm FWHM, and is in good agreement with those obtained previously [4.30 – 4.33]. The 3.0 eV – 6.0 eV energy region has been magnified five hundred times and compared with the results of Martinez et al. [4.33] and the space science data base [4.52] (Figure 4.11). The spectrum is composed of absorption bands with low cross sections below 6.0 eV, with special attention being devoted to the first absorption band assigned as $\tilde{A} \leftarrow \tilde{X} (n \rightarrow \pi^*)$. A series of sharp, more intense peaks observed above 6.8 eV, some of which contain rich vibrational structures, and are mainly characterised as transitions into Rydberg states. The lowest ionisation potential (IP) has been plotted as a dashed line.

A featureless continuum above the ionisation limit is observed. The dashed feature close to 11.0 eV is only partially recorded due to the cut-off in the transmission of the CaF$_2$ window.
Figure 4.10 – VUV photo-absorption spectrum of acetaldehyde in the energy region 3 eV to 11 eV.
Before analysing the spectra in detail, a brief review of the structure, geometry and properties of CH$_3$CHO is useful. Acetaldehyde belongs to the C$_s$ symmetry point group and has fifteen normal modes of vibration classified in the symmetry type as $\Gamma_{vib} = 10A' + 5A''$ (Table 4.7), where the fundamental vibrational energies were summarised by Shimanouchi [4.53]; the outermost valence molecular orbitals electron configuration in the independent particle model can be represented according to reference [4.38] as: $(1a')^2 (2a')^2 (3a')^2 (4a')^2 (5a'')^2 (1a'')^2 (6a')^2 (2a'')^2 (7a')^2$, giving a configuration in the ground state: $\tilde{X}^1A'$.

7a' has been identified as representing the oxygen non-bonding electrons, 2a'' the CO $\pi$-bonding electrons, 6a' and 1a'' $\sigma$ orbitals and the position of 1a'' relative to the other orbitals is not known so far. According to Herzberg, the lowest ionisation potential is 10.229 eV [4.29].

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Description</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$ (a')</td>
<td>CH$_3$ degenerate stretching</td>
<td>0.373</td>
</tr>
<tr>
<td>$v_2$ (a')</td>
<td>CH$_3$ symmetrical stretching</td>
<td>0.362</td>
</tr>
<tr>
<td>$v_3$ (a')</td>
<td>CH stretching</td>
<td>0.350</td>
</tr>
<tr>
<td>$v_4$ (a')</td>
<td>CO stretching</td>
<td>0.216</td>
</tr>
<tr>
<td>$v_5$ (a')</td>
<td>CH$_3$ degenerate deformation</td>
<td>0.179</td>
</tr>
<tr>
<td>$v_6$ (a')</td>
<td>CH bending</td>
<td>0.174</td>
</tr>
<tr>
<td>$v_7$ (a')</td>
<td>CH$_3$ symmetric deformation</td>
<td>0.168</td>
</tr>
<tr>
<td>$v_8$ (a')</td>
<td>CC stretching</td>
<td>0.138</td>
</tr>
<tr>
<td>$v_9$ (a')</td>
<td>CH$_3$ rocking</td>
<td>0.114</td>
</tr>
<tr>
<td>$v_{10}$ (a')</td>
<td>CCO deformation</td>
<td>0.063</td>
</tr>
<tr>
<td>$v_{11}$ (a'')</td>
<td>CH$_3$ degenerate stretching</td>
<td>0.368</td>
</tr>
<tr>
<td>$v_{12}$ (a'')</td>
<td>CH$_3$ degenerate deformation</td>
<td>0.176</td>
</tr>
<tr>
<td>$v_{13}$ (a'')</td>
<td>CH$_3$ rocking</td>
<td>0.108</td>
</tr>
<tr>
<td>$v_{14}$ (a'')</td>
<td>CH bending</td>
<td>0.095</td>
</tr>
<tr>
<td>$v_{15}$ (a'')</td>
<td>Torsion</td>
<td>0.019</td>
</tr>
</tbody>
</table>

Table 4.7 – Acetaldehyde ground state vibrational energies (eV).

The observed absorption bands can be classified as members of Rydberg series and molecular valence transitions of ($n \rightarrow \pi^*$), ($\pi \rightarrow \pi^*$) and ($\sigma \rightarrow \pi^*$) type, although for the low-energy members of the Rydberg series, mainly at 6.655 eV, a mixed Rydberg-valence character has been suggested with the bands having characteristics of both types of transitions [4.43, 4.54]. ($\sigma \rightarrow \pi^*$) transitions have not been experimentally detected so far, although according to recent theoretical calculations on configuration interaction (CIS) method, its origin is tentatively assigned at 10.436 eV [4.54], and where the $^1(\sigma, \pi^*)$ valence transition, $^1B_j (3A'', \sigma \rightarrow \pi^*)$, has been reported at 10.34 eV.
The origin of the second excited electronic state, $\tilde{B} \rightarrow \tilde{X}$ ($> 6.6$ eV), has been identified as the $(n, 3s)$ Rydberg state by resonance-enhanced multiphoton ionisation [4.45], by VUV absorption spectroscopy [4.30] and a mixing of $(n, 3p)$ and $(n, 3d)$ transitions [4.43]. These features fit a series converging to the ionic ground state potential arising from transitions mainly of lone-pair localised oxygen electrons. Pre-dissociation does not seem to play a very important role and each of these bands are discussed in more detail below. The broad featureless band above 10 eV is probably due to the excitation to high-energy valence ionic excited states which are dissociative in character.

### 4.3.3.1 The 3.5 eV - 6.0 eV photon energy region

In this energy region, the $(7a')^{-1}$ electronic transitions have been identified as transitions to triplet $^3(n, \pi^*) \tilde{X} \rightarrow \tilde{A}^1A', \text{ and singlet states } ^1(n, \pi^*) \tilde{X} \rightarrow \tilde{X}^1A'$ having a mixing character [4.31, 4.39, 4.41]. This is a result of the excitation from the oxygen lone pair electrons to the CO $\pi^*$ character LUMO [4.30] ($n_O \rightarrow \pi^*$) of the CH$_3$CHO molecule, and the (0-0) transitions of the electronic bands assigned at 3.679 eV and 4.275 eV, respectively. The present data obtained in this energy region are in close agreement with the cross section profiles reported by Martinez et al. [4.33] and from the space science data base [4.51] (Figure 4.11).

![Figure 4.11 - Photo-absorption cross section in the 3.0 eV - 6.0 eV energy band of acetaldehyde.](image-url)
Despite the small differences in magnitude of the absorption cross section, the present results are \( \sim 1\% \) and \( 37\% \) higher for 4.881 eV and 4.732 eV, respectively, with much better resolved vibrational structure. A higher resolution can in part explain such cross sectional differences. Taking into account previous photo-absorption cross sections measurements and through comparison with earlier data obtained at Daresbury synchrotron facility, the accuracy of the cross section is estimated to be \( \pm 5\% \).

**The singlet – triplet transition, \( S_0-T_1 \) (3.6 eV – 4.9 eV)**

This energy region is characterised by a weakly C\(_s\) symmetry allowed transition, making the (0-0) assignment for the singlet-triplet transition \( S_0-T_1 \) often ambiguous and difficult. Actually, several values have been suggested [4.39] and Noble et al. [4.48, 4.49] shown that the origin lies at 3.692 eV, in close agreement with the present high-resolution data pointing to a value of \( \sim 3.679 \) eV (0.006 Mb). Although optically forbidden, singlet to triplet transitions can be observed with very low cross-sections by photo-absorption. The valence transition ends \( \sim 4.862 \) eV close to 4.89 eV reported by Walzi et al. [4.41]. Vibrational excitation assignments for this energy region (Figure 4.12) have been studied for the low energy region of the \( S_1 \) state by laser induced fluorescence in a supersonic jet expansion [4.49], and it is present here a more complete and extended set for the observed pattern. Assignments are given in Table 4.8, with brackets (?) denoting greater uncertainty.

---

**Figure 4.12** – Vibrational progressions in the 3.6 eV – 5.0 eV absorption band of acetaldehyde.
The carbonyl stretch $v_4$ vibrational mode, is the most Franck-Condon active vibration ($\sim 0.196$ eV), however the CH stretch $v_3$ and the CCO deformation modes $v_{10}$ seem to be very active as well. In fact, the long $v_4$ progression is associated with the lengthening of the $C=O$ bond under electronic excitation due to the lowering of the bond order [4.49]. Moreover, it can be seen that the vibrational excitation pattern extends over the singlet-singlet transition, giving the 3.5 eV – 6.0 eV energy region a mixing of vibrational structures (Figure 4.12 and 4.13). In fact, the $S_0$-$S_1$ transition should not be so rich in vibrational excitation (Table 4.8) which is in agreement to the present observed structures and Noble and Lee [4.49].

<table>
<thead>
<tr>
<th>$\tilde{\tilde{A}}^3A'' \leftarrow \tilde{\tilde{X}}^1A'$</th>
<th>$\tilde{\tilde{A}}^1A'' \leftarrow \tilde{\tilde{X}}^1A'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (eV)</td>
<td>[4.49] present work</td>
</tr>
<tr>
<td>3.692</td>
<td>3.696</td>
</tr>
<tr>
<td>$v_{00}$</td>
<td>$v_{14}$</td>
</tr>
<tr>
<td>4.275</td>
<td>4.305</td>
</tr>
</tbody>
</table>

Table 4.8 – Vibrational assignments in the 3.6 eV – 5.2 eV absorption band of CH$_3$CHO.

The singlet – singlet transition, $S_0$-$S_1$ (4.2 eV – 5.2 eV)

This electronic excitation transition has its origin at 4.275 eV with a local maximum cross section of 0.049 Mb (Figure 4.13), ending at 5.166 eV and in agreement with Walzi et al. [4.41].
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The vibrational excitation (Table 4.8) is tentatively assigned for the first time [4.54], despite their diffuseness, with mainly CH bending $\nu_6$ and CH$_3$ deformation $\nu_{12}$ vibrational modes. It is also remarkable that $\nu_{14}$ CH bend vibrational mode seems to be very active in both singlet and triplet transitions with an energy $\sim$ 0.026 eV. The energy splitting between triplet and singlet, $S_j$-$T_j$, states can be evaluated and is found to have an energy difference of $\sim$ 0.596 eV [4.54] in contrast to the 0.372 eV presented by Noble et al. [4.49].

![Figure 4.13 - Vibrational progressions in the 4.2 eV - 5.2 eV absorption band of acetaldehyde.](image)

4.3.3.2 The 6.3 eV - 7.4 eV photon energy region

This energy region is displayed in Figure 4.14, and exhibits considerable vibrational structure. The region is composed of one valence transition involving electrons from the CO $\pi$ orbital, $^3(\pi, \pi^*)$ [4.43], one Rydberg transition identified as $n(7a') \rightarrow 3s$ (B $^1A'$) [4.30, 4.31, 4.45 - 4.47] and a $^3ns$ newly assigned series in close agreement with previous suggestions [4.43]. It is however now possible to assign this band in terms of progressions and combinations of CH stretching and bending modes and CH$_3$ deformation modes.

For the valence transition, the energy of the band maximum has been reported before [4.28, 4.39, 4.41, 4.43, 4.51] and with the present data (Figure 4.14) has been estimated at $\sim$ 6.352 eV (0.013 Mb). The weakness of this band is due to its spin-
forbidden nature and has been proved by the flatness of the related characteristic in differential cross section as a function of the angle [4.41].

The (0-0) transition lies at 6.824 eV (~ 182 nm), with a local cross section of 39.708 Mb, and is a result of the excitation of an oxygen lone pair electron (n → 3s) to a Rydberg state, and is in good agreement with Crighton and Bell [4.30]. Vibrational analysis has been carried out (Table 4.9) with several structures that have been previously reported as hot bands of mainly CCO deformation, v_{10} and torsion, v_{15} modes [4.30, 4.37, 4.45, 4.46] and several new features are tentatively assigned for the first time below the (0-0) transition.

As the neutral ground states excitation energies for modes, v_6 and v_7 are very close compared to the resolution in this part of the spectrum, we do not suggest one or other as more probable. Therefore we adopted the v_{6,7} notation to describe the relevant assignments. In fact degeneracy has been reported for these modes in the B → A' state of acetaldehyde [4.30]. It is also remarkable, in Table 4.9, there is evidence of sequence bands for the torsional v_{15}, CCO deformation v_{10} and CH bend v_{14} modes.

Figure 4.14 – Valence-Rydberg transitions in the energy range 6.3 eV – 7.4 eV of acetaldehyde.
Table 4.9 – Vibrational assignments in the 6.3 eV – 7.4 eV absorption band of CH$_3$CHO.

### 4.3.3.3 Rydberg series converging to the $\tilde{X}^2A^-$ state

The excitation energy range above 6.7 eV consists of sharp peaks up to the ionisation potential limit, 10.229 eV [4.29] (Figure 4.10 and 4.15). The broad featureless band above 10.4 eV is probably due to the excitation of high-energy valence excited states which are dissociative in character. The series were obtained using the Rydberg equation from chapter 3 (section 3.2.5.1) and in the following tables, assignment within brackets (?) denotes higher uncertainty.
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The superscript ns Rydberg series

Figure 4.14 also shows an attempt to identify the 6.655 eV feature to a triplet Rydberg series, which fits very well a \((2\hat{A}', n\sigma(7\hat{a}') \rightarrow 3s)\), with a quantum defect \(\delta = 1.10\) (Table 4.10). Van Veen et al. [4.39] reported the origin for this transition at 6.62 eV, while the EELS data of Dressler and Allan [4.43] predict the origin at 6.65 eV both being in good agreement with the present results.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Quantum defect</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.655</td>
<td>1.05</td>
<td>3s</td>
</tr>
<tr>
<td>8.689</td>
<td>1.03</td>
<td>4s</td>
</tr>
<tr>
<td>9.336</td>
<td>1.10</td>
<td>5s</td>
</tr>
<tr>
<td>9.656</td>
<td>1.13</td>
<td>6s</td>
</tr>
<tr>
<td>9.848</td>
<td>1.03</td>
<td>7s</td>
</tr>
<tr>
<td>9.951 (?)</td>
<td>1.01</td>
<td>8s</td>
</tr>
<tr>
<td>10.003</td>
<td>1.25</td>
<td>9s</td>
</tr>
<tr>
<td>10.052</td>
<td>1.23</td>
<td>10s</td>
</tr>
<tr>
<td>10.084</td>
<td>1.32</td>
<td>11s</td>
</tr>
</tbody>
</table>

Table 4.10 – Energy values, quantum defect and assignment of the superscript ns Rydberg series converging to the ionic electronic ground state \(\bar{X}^2\Sigma^+\) of CH₃CHO.

The superscript 1ns Rydberg series

The low intensity feature located at 6.824 eV (Figure 4.15) has been assigned to the singlet Rydberg transition \(^1B_2\) \((2\hat{A}', n\sigma(7\hat{a}') \rightarrow 3s)\) state [4.27, 4.37, 4.38, 4.39, 4.41], of \(n = 3\) term series with a quantum defect \(\delta = 0.90\) (Table 4.11). The vibrational modes have been previously identified as a mixing with the second electronic singlet excitation (Table 4.9). However, Van Veen et al. [4.39] showed that mainly the alkyl groups' excitation are involved. The 4s band is broader than the other bands in the spectrum, which has been attributed to interaction with an underlying dissociative valence state [4.28].

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Quantum defect</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.824</td>
<td>1.00</td>
<td>3s</td>
</tr>
<tr>
<td>8.831</td>
<td>0.88</td>
<td>4s</td>
</tr>
<tr>
<td>9.421</td>
<td>0.90</td>
<td>5s</td>
</tr>
<tr>
<td>9.709</td>
<td>0.89</td>
<td>6s</td>
</tr>
<tr>
<td>9.864</td>
<td>0.90</td>
<td>7s</td>
</tr>
<tr>
<td>9.963</td>
<td>0.85</td>
<td>8s</td>
</tr>
<tr>
<td>10.023</td>
<td>0.88</td>
<td>9s</td>
</tr>
</tbody>
</table>

Table 4.11 – Energy values, quantum defect and assignment of the superscript 1ns \(^1B_2\) Rydberg series converging to the ionic electronic ground state \(\bar{X}^2\Sigma^+\) of CH₃CHO.
The $^1np_y$ Rydberg series

The first member of the $np_y$ series (Table 4.12), assigned as the Rydberg transition to $^1B_2 (3A', \nu(7a') \rightarrow 3p)$ state [4.38, 4.39, 4.41], is attributed to the 7.456 eV peak, the quantum defect being $\delta = 0.79$. This is accompanied by the vibrational excitation of the CH bend $v_6$ normal mode with a frequency of $\sim 0.123$ eV and CO stretching $v_4$ normal mode with a frequency of $\sim 0.207$ eV. The second and third terms of the series are observed at 8.971 and 9.497 eV, respectively, both with a quantum defect of $\delta = 0.70$.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Quantum defect</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.456</td>
<td>0.79</td>
<td>$3p_y$</td>
</tr>
<tr>
<td>7.579</td>
<td>-</td>
<td>$3p_y + v_6$</td>
</tr>
<tr>
<td>7.663 (?)</td>
<td>-</td>
<td>$3p_y + v_4$</td>
</tr>
<tr>
<td>8.971</td>
<td>0.71</td>
<td>$4p_y$</td>
</tr>
<tr>
<td>9.497</td>
<td>0.69</td>
<td>$5p_y$</td>
</tr>
<tr>
<td>9.751</td>
<td>0.67</td>
<td>$6p_y$</td>
</tr>
<tr>
<td>9.895 (?)</td>
<td>0.62</td>
<td>$7p_y$</td>
</tr>
<tr>
<td>9.979 (?)</td>
<td>0.62</td>
<td>$8p_y$</td>
</tr>
<tr>
<td>10.035 (?)</td>
<td>0.63</td>
<td>$9p_y$</td>
</tr>
<tr>
<td>10.072</td>
<td>0.69</td>
<td>$10p_y$</td>
</tr>
<tr>
<td>10.101</td>
<td>0.69</td>
<td>$11p_y$</td>
</tr>
<tr>
<td>10.121</td>
<td>0.78</td>
<td>$12p_y$</td>
</tr>
<tr>
<td>10.138</td>
<td>0.78</td>
<td>$13p_y$</td>
</tr>
</tbody>
</table>

Table 4.12 – Energy values, quantum defect and assignment of the $np_y (^1B_2)$ Rydberg series converging to the ionic electronic ground state $\bar{X}^2A^+$ of CH$_3$CHO.

The $^1np_x$ Rydberg series

The peak at 7.749 eV (Figure 4.15) has been interpreted as an $n = 3$ term of an $np_x$ series, with a calculated quantum defect $\delta = 0.66$ (Table 4.13). This series has been identified before [4.32, 4.39] with only 6 quantum numbers [4.32]. In our high resolution photo-absorption spectrum we have been able to identified up to $n = 16$ quantum numbers.

The origin of this series is in contradiction with 7.80 eV from Walzi et al. [4.41]. The second and third terms are at energies of 9.043 eV and 9.523 eV, respectively, both with a quantum defect $\delta \sim 0.61$. For $n = 4$, and as discussed before, these band is broader due to the interaction with a possible underlying dissociative valence state, which is characterised by $^1A_f (5A, \pi(2a^*) \rightarrow \pi^*)$.
Table 4.13 – Energy values, quantum defect and assignment of the \( np_x (^1A_1) \) Rydberg series converging to the ionic electronic ground state \( \tilde{X}^2A^+ \) of \( \text{CH}_3\text{CHO} \).

Another interesting feature at 9.043 eV appears broadened (Figure 4.15) and seems to be mainly due to the superposition of two states. In fact as it corresponds to a transition to a \( 4p_x \) series it has been pointed out [4.54] that the 9.057-9.063 eV energy position is due to the \( ^1(\pi, \pi^*) \) valence transition, \( ^1A_j (5A', \pi(2a') \rightarrow \pi^*) \), previously reported at 9.07 eV [4.51].

The \( ^1nd^2 \) Rydberg series

Another series starting at 8.434 eV (Figure 4.15 and Table 4.14) has been assigned as a \( n = 3 \) term of an \( nd^2 \) series, in agreement with a previous study [4.38, 4.32, 4.41, 4.51]. The feature at 8.580 eV, 0.146 eV above the origin is assigned to the CH bending \( v_6 \) mode and is in good agreement with the 0.153 eV value obtained by photo-electron spectroscopy [4.44], but in disagreement with a previous assignment [4.38]. The peak at 8.628 eV, 0.048 eV from 8.580 eV has been tentatively identified as a combination of \( v_6 \) and \( v_{10} \) modes, with the latter in good agreement with the 0.055 eV of Cvitaš et al.
[4.44]. The second and third terms of the series lie at 9.267 eV and 9.634 eV, with quantum defects $\delta = 0.24$ and 0.22 respectively.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Quantum defect</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.434</td>
<td>0.25</td>
<td>$3d_z^2$</td>
</tr>
<tr>
<td>8.580</td>
<td></td>
<td>$3d_z^2 + \nu_6$</td>
</tr>
<tr>
<td>8.628</td>
<td></td>
<td>$3d_z^2 + \nu_6 + \nu_{10}$</td>
</tr>
<tr>
<td>8.689</td>
<td></td>
<td>$3d_z^2 + 2\nu_6$</td>
</tr>
<tr>
<td>9.267</td>
<td>0.24</td>
<td>$4d_z^2$</td>
</tr>
<tr>
<td>9.634</td>
<td>0.22</td>
<td>$5d_z^2$</td>
</tr>
<tr>
<td>9.821</td>
<td>0.23</td>
<td>$6d_z^2$</td>
</tr>
<tr>
<td>9.935 (?)</td>
<td>0.20</td>
<td>$7d_z^2$</td>
</tr>
<tr>
<td>10.003</td>
<td>0.24</td>
<td>$8d_z^2$</td>
</tr>
<tr>
<td>10.052</td>
<td>0.23</td>
<td>$9d_z^2$</td>
</tr>
<tr>
<td>10.101</td>
<td>-0.31</td>
<td>$10d_z^2$</td>
</tr>
</tbody>
</table>

Table 4.14 – Energy values, quantum defect and assignment of the $nd_z^2 (^{1}B_2)$ Rydberg series converging to the ionic electronic ground state $\tilde{X}^2A^+$ of CH$_3$CHO.

The $^1nd_{xy}$ Rydberg series

The $nd_{xy}$ series (figure 4.15) with $n = 3$ (Table 4.15) is assigned to 8.707 eV and a quantum defect value, $\delta = 0.01$ in agreement with ref. [4.41]. The second and third terms are at 9.375 eV and 9.683 eV, respectively with quantum defects $\delta = 0.01$.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Quantum defect</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.707</td>
<td>0.01</td>
<td>$3d_{xy}$</td>
</tr>
<tr>
<td>9.375</td>
<td>0.01</td>
<td>$4d_{xy}$</td>
</tr>
<tr>
<td>9.683</td>
<td>0.01</td>
<td>$5d_{xy}$</td>
</tr>
</tbody>
</table>

Table 4.15 – Energy values, quantum defect and assignment of the $nd_{xy}$ Rydberg series converging to the ionic electronic ground state $\tilde{X}^2A^+$ of CH$_3$CHO.

The bands due to the higher members are overlapped by those of the previous Rydberg series, which makes assignment difficult for higher energy members. The various series that have been recorded are consistent with those observed previously [4.41] and the transition to the $^3ns$ Rydberg series at 6.655 eV is presented here for the first time.
Figure 4.15 – Assignment of Rydberg series converging to the ionisation potential of 10.229 eV.
The procedure for interpretation and classification of the Rydberg series has been performed according to Elden’s diagrams (Chapter 3, section 3.2.5.2) in Figure 4.16. As one should expect, the characteristics plotted give straight lines on the quantum defect with the reduced term energies for the first members of the series. Actually, it is clear from Figure 4.16 that the proposed previous assignments for the Rydberg series are in close agreement with this linear dependence.

![Figure 4.16 - Elden’s diagrams for the variation of the quantum defect ($\delta_{\text{eq}}$) with the reduced term energies ($n'^2$) for the first terms of the Rydberg series converging to the ionisation limit (10.229eV).](image)

It should be stressed that the linear dependence is only valid, on average, for the first four or five members of the series, as observed for both dimethylsulphide and acetaldehyde, because as one goes to higher energies and close to the ionization potential, there is always the effect of superposition of the different Rydberg states giving a mixing orbital character that tend to make the assignment difficult and in some cases ambiguous, which in turn gives quantum defect values varying quite a lot and observed lack of linearity in Elden’s plots.

### 4.3.4 Photolysis rates and local lifetimes

Using these absolute cross sections, the photolysis rates for CH$_3$CHO were calculated at 1 km altitude steps up to the stratopause (50 km) and are displayed in Figure 4.17. Photolysis rates were calculated as the product of the Solar Actinic Flux.
[4.23] at a given wavelength and altitude and the molecular photo-absorption cross section at the same wavelength (Chapter 3, section 3.2.4.3). At each altitude a total photolysis rate may then be calculated by summing over the individual photolysis rates for that altitude (Figure 4.18) and the reciprocal of the total photolysis rate for a given altitude gives the local photolysis lifetime at that altitude (Figure 4.17), assuming a constant solar flux. The results show that the local photolysis lifetime of this molecule varies from around two and a half hours near the ground to just over less than a minute at 50 km, pointing to an averaged lifetime of CH$_3$CHO at the tropopause of the order of a couple of minutes.

![Figure 4.17](image.png)

**Figure 4.17** – The photolysis rates (s$^{-1}$) and the lifetimes (Days) for acetaldehyde as a function of altitude in Earth’s atmosphere.
The information on the cross section, \(\sigma(\lambda)\), combined with the actinic solar radiation, \(J(\lambda)\), and the primary quantum yield for photolysis, \(\varphi(\lambda)\), to calculate the photo-dissociation rate constants, \(k_p\), have been evaluated previously for acetaldehyde [4.50] and assumed that the primary quantum yield for photolysis was unity at all wavelengths. In fact, \(k_p\) is obtained as:

\[
k_p = \int \sigma(\lambda)\varphi(\lambda)J(\lambda)d\lambda
\]  

(4.6)

Actually the quantum yield for primary photolysis depends on both the wavelength (\(\lambda\)) and total air pressure, and has been found to be smaller than one in some cases. Our values of \(k_p\), assuming \(\varphi(\lambda) = 1\), therefore represent upper limits for the rate constant for photo-dissociation under tropospheric conditions.

### 4.3.5 Environmental evaluation

The photo-dissociation rate constants have been reported and suggested that reaction of aliphatic carbonyl compounds with ozone, NO\(_x\) and HO\(_2\) are expected to be of minor importance in the troposphere due to the high rate constants with hydroxyl radicals [4.33, 4.50]. The calculations obtained for noon time photolysis rate constants for 1 January and 1 July under cloudless conditions at sea level and at latitude of 40° N,
have been compared with the pseudo-first order rate constants \( (k_{OH}) \) for reaction of acetaldehyde with hydroxyl radical at room temperature, assuming an average annual and diurnal OH concentration in the troposphere of \( 0.3 - 3.0 \times 10^6 \) molecules cm\(^{-3} \) [4.33]. \( k_p \) was found to be of the order of \( 1.2 \times 10^{-6} \) s\(^{-1} \) (1 January) and \( 4.3 \times 10^{-6} \) s\(^{-1} \) (1 July) in contrast to \( (5 - 50) \times 10^{-6} \) s\(^{-1} \) for \( k_{OH} \); hence the reaction with hydroxyl radical is 5-10 times as fast as photolysis. Thus the photo-dissociation process is a minor pathway for removal of acetaldehyde from atmosphere.

4.3.6 Summary

It has been possible to observe the low lying \( ^1 \), \( ^3(n, \pi^*) \) and \( ^3(\pi, \pi^*) \) transitions of CH\(_3\)CHO despite the low intensity photo-absorption signal. There is experimental evidence that the valence states, mainly the \( ^1(\pi, \pi^*) \) play an important role on the broadening of the 4p \( \pi^* \) and 4s Rydberg transitions, which has been previously observed for formaldehyde and acetone [4.28]. In fact the underlying dissociative valence state is in agreement with the background’s slightly broadening increase for this energy region.

The position for the \( ^1(\sigma, \pi^*) \) valence transition has been suggested for the first time [4.54] to lie at 10.436 eV and is in close agreement with the theoretical calculations obtained using the configuration interaction single excitations (CIS) method [4.51]. The experimental results presented provide the highest resolution VUV photo-absorption spectrum of CH\(_3\)CHO in the range 3.0 eV to 11.0 eV (413 nm to 113 nm). Vibrational features especially for the \( ^1 \)np\( _\pi \) Rydberg series are presented and evaluated for the first time.

While there has been much progress during the last few years in the understanding of the spectra of aldehydes and ketones, the field is still in its adolescence, and the VUV spectrum of acetaldehyde still continues to yield surprises and new insights into its spectroscopy.

4.4 Conclusions

The high resolution photo-absorption spectra of (CH\(_3\))\(_2\)S and CH\(_3\)CHO recorded using synchrotron radiation, have been presented and the electronic state spectroscopy discussed on the basis of previously reported results. Assignments of Rydberg and
valence states were made with particular attention to the former ones with new proposed assignments where possible. The role of these molecules in the Earth’s atmosphere has been evaluated and discussed.
4.5 References

[4.52] www.espsun.space.swri.edu/amop
Chapter 5

Electronic state spectroscopy of SF$_5$CF$_3$ by gas-phase and condensed phase conditions

Divide each difficulty into as many parts as is feasible and necessary to resolve it.

René Descartes (1596 – 1650)

5.1 Introduction

In this chapter an extensive study of the spectroscopy of trifluoromethyl sulphur pentfluoride has been carried out using VUV and IR photo-absorption, electron energy loss spectroscopy and photo-electron spectroscopy. In order to determine the possible mechanisms for removal of this molecule in the upper atmosphere, we have also studied the interaction of free electrons with SF$_5$CF$_3$ in both gas and condensed phases. Desorption from sub-monolayers of SF$_5$CF$_3$ on amorphous H$_2$O ice are compared to desorption from a Xe surface. The implications for the heterogeneous photochemistry of SF$_5$CF$_3$ adsorbed on ice or dust particles in the Earth’s atmosphere are discussed.

5.2 VUV photo-absorption of SF$_5$CF$_3$

5.2.1 Introduction

SF$_5$CF$_3$ has only recently been detected in the terrestrial atmosphere [5.1] and identified as a potent greenhouse gas. Although its origins are still unclear, it is believed to be purely anthropogenic in origin, probably being related to the plasma technology industry and gas dielectrics. It has been suggested that a likely source is as a breakdown product of SF$_6$.

Sulphur hexafluoride is a potent greenhouse gas and its atmospheric concentration has increased by two orders of magnitude since industrial production started in 1950s [5.2]. SF$_6$ is extremely stable with unique physical and chemical properties that make it ideal for some specialised applications, such as the plasma
industry. It is a heavy, inert and non-toxic and non-flammable gas. The dominant uses are in gas insulated switchgear and in blanketing or degassing molten aluminium and magnesium [5.2]. In 1953 its industrial production began as an insulated circuit breaker. Therefore it is expected that SF₂CF₃ may be formed while being used as a high voltage dielectric. Electrical discharges through SF₆ can cause electron attachment that leads to the production of SF₂⁺ radicals [5.3]. The electrical systems containing SF₆ are also likely to contain fluoropolymers as insulators. Therefore, SF₂⁺ radicals could react with these polymeric surfaces and scavenge CF₃ radicals to produce SF₂CF₃ which can be released into the atmosphere through natural leakage or release upon opening the installation for maintenance [5.1]. Indeed the trends for SF₆ and SF₂CF₃ track each other very closely over the past 30 years, suggesting that the production of SF₂CF₃ is connected directly to SF₆ [5.4]. However, the spectroscopy, dissociation dynamics and chemical reactivity of this compound are still poorly understood having only been the subject of research in the last two years.

5.2.2 Experiment overview

A high resolution photo-absorption spectrum of SF₂CF₃ was obtained in a closed cell (Chapter 3, section 3.2.3) with a path length of 25 cm. The spectrum was obtained in 11 nm sections, in 0.1 nm steps, with a resolution ~ 0.075 nm FWHM.

The sample used was obtained from Argo International Ltd. with a purity of 99%. The gas was used without further purification or treatment. SF₂CF₃ spectrum was recorded over the sample pressure range 0.075 torr - 0.750 torr (Table 5.1), with typical attenuation of 10%. High sample pressures were used for photon energies below 8 eV in order to guarantee no low absorption features were missed.

<table>
<thead>
<tr>
<th>Energy range (eV)</th>
<th>Wavelength (nm)</th>
<th>Pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.96 - 6.97</td>
<td>178 - 208</td>
<td>0.750</td>
</tr>
<tr>
<td>6.63 - 7.52</td>
<td>165 - 187</td>
<td>0.525</td>
</tr>
<tr>
<td>7.34 - 8.44</td>
<td>147 - 169</td>
<td>0.225</td>
</tr>
<tr>
<td>8.38 - 10.97</td>
<td>113 - 148</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Table 5.1 – Photon energy (eV), wavelength (nm) and pressure (torr) ranges for SF₂CF₃ photo-absorption measurements.
The first experimental measurements reported for this molecule concentrated upon its infrared properties. Sturges and co-workers [5.1] measured the room temperature IR photo-absorption cross sections and compared them to preliminary data reported by Eggers et al. [5.5] and subsequently refined and discussed by Griffiths [5.6].

The infrared spectra has been recently re-measured over a wave number range of 100 cm\(^{-1}\) – 4000 cm\(^{-1}\) with spectral resolutions of 0.01 cm\(^{-1}\) and 0.90 cm\(^{-1}\) [5.7] and the temperature dependence extensively studied between 203 K – 298 K over the range 600 cm\(^{-1}\) – 1500 cm\(^{-1}\) with a 0.03 cm\(^{-1}\) resolution [5.8].

There has been much speculation as to the mechanisms by which SF\(_5\)-CF\(_3\) is destroyed in the terrestrial atmosphere with current suggestions including by UV photodissociation in the stratosphere and mesosphere or by electron attachment and ion-molecule reactions in the mesosphere. Experiments have been performed to determine the ionisation and fragmentation of trifluoromethyl sulphur pentafluoride using threshold photo-electron photo-ion coincidence (TPEPICO) spectroscopy [5.9]. The role of bimolecular reactions with positive ions inherent in the upper atmosphere have been investigated to obtain rate coefficients and product ion distributions for the related reactions [5.10 – 5.12]. A comprehensive study of the electron attachment rate constant has been performed by Kennedy and Mayhew [5.13] and compared to low energy electron attachment at a high incident electron resolution by mass spectrometry [5.14]. Electron impact ionisation cross sections close to threshold have been reported [5.15] and the role of SF\(_5\)CF\(_3\) in the terrestrial atmospheric has been evaluated. Chim et al. [5.16] measured the fragmentation of the valence states of SF\(_5\)-CF\(_3\) over the energy range 12 eV – 26 eV by means of VUV synchrotron radiation and reported the energetics of important dissociation channels and ionisation energies. The first pseudo photo-absorption spectrum of SF\(_5\)CF\(_3\) in the energy range 5 eV - 23 eV was measured by Kendall and Mason [5.17] and has since been compared with photo-absorption cross sections measured recently in the VUV region [5.18, 5.19].

5.2.3 Results

Assignment of the valence state(s) of SF\(_5\)CF\(_3\) is difficult since there is still no agreement as to the symmetry type for this molecule, either \(C_{4v}\) \((a_1, a_2, b_1, b_2, e)\) or \(C_s\) \((a', a'')\) [5.6, 5.20]. Griffiths [5.6] concluded from his infrared and Raman spectra that the barrier to internal rotation is low or zero, and according to the observed patterns, \(C_{4v}\) suits the selection rules for those vibrational excitations. However recent calculations
have shown that the internal barrier potential energy surface and the internal torsion mode, C – S, have values at about 6.45 cm⁻¹ (77 J mol⁻¹) and 15 cm⁻¹, respectively [5.20], the latter being of the same order of magnitude of the energy necessary to overcome the barrier, suggesting the symmetry of SF₅CF₃ as Cₛ. Nevertheless, both symmetry types can be related to the irreducible representations and in Cₛ notation both b₂ and a₂ correlate with a′′, a₁ and b₁ correlate with a′, and e to the crossed product of a′ and a″ [5.21]. So, the twenty-four vibrational modes are classified in the Cₛ symmetry as \( \Gamma_{\text{vib}} = 15A' + 9A'' \) with their fundamental energies summarised by Griffiths [5.6] and Ball [5.20] in Table 5.2.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Description</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[5.6], [5.20]</td>
<td></td>
<td>[5.6] / [5.20]</td>
</tr>
<tr>
<td>v₁ (a₁, a')</td>
<td>CF₃ symmetric stretch</td>
<td>0.145 / 0.150</td>
</tr>
<tr>
<td>v₂ (a₁, a')</td>
<td>SF axial stretch</td>
<td>0.110 / 0.111</td>
</tr>
<tr>
<td>v₃ (a₁, a')</td>
<td>CF₃ symmetric deformation</td>
<td>0.094 / 0.093</td>
</tr>
<tr>
<td>v₄ (a₁, a')</td>
<td>SF₄ symmetric in-plane stretching</td>
<td>0.086 / 0.085</td>
</tr>
<tr>
<td>v₅ (a₁, a')</td>
<td>SF₄ out-of-plane deformation</td>
<td>0.076 / 0.074</td>
</tr>
<tr>
<td>v₆ (a₁, a')</td>
<td>C – S stretch</td>
<td>0.040 / 0.041</td>
</tr>
<tr>
<td>v₇ (b₂, a″)</td>
<td>Internal torsion</td>
<td>– / 0.002</td>
</tr>
<tr>
<td>v₈ (b₁, a')</td>
<td>SF₄ asymmetric in-plane stretch</td>
<td>0.078 / 0.080</td>
</tr>
<tr>
<td>v₉ (b₁, a')</td>
<td>F – S – F bending and CF bending</td>
<td>0.033 / 0.038</td>
</tr>
<tr>
<td>v₁₀ (b₂, a″)</td>
<td>SF₄ rocking</td>
<td>0.062 / 0.051</td>
</tr>
<tr>
<td>v₁₁ (e, a″)</td>
<td>CF₃ anti-symmetric stretch</td>
<td>0.156 / 0.161</td>
</tr>
<tr>
<td>v₁₂ (e, a″)</td>
<td>SF₃ anti-symmetric stretch</td>
<td>0.112 / 0.116</td>
</tr>
<tr>
<td>v₁₃ (e, a″)</td>
<td>SF₄ in-plane deformation</td>
<td>0.073 / 0.066</td>
</tr>
<tr>
<td>v₁₄ (e, a″)</td>
<td>CF₃ anti-symmetric deformation</td>
<td>0.069 / 0.070</td>
</tr>
<tr>
<td>v₁₅ (e, a″)</td>
<td>SF₄ in-plane deformation</td>
<td>0.053 / 0.058</td>
</tr>
<tr>
<td>v₁₆ (e, a″)</td>
<td>CF₃ wagging</td>
<td>0.040 / 0.040</td>
</tr>
<tr>
<td>v₁₇ (e, a″)</td>
<td>SF₃ rocking and CF₃ wagging</td>
<td>0.027 / 0.028</td>
</tr>
<tr>
<td>v₁₈ (e, a″)</td>
<td>SF₃ rocking</td>
<td>– / 0.026</td>
</tr>
<tr>
<td>v₁₉ (e, a″)</td>
<td>SF₄ out-of-plane deformation</td>
<td>– / 0.045</td>
</tr>
<tr>
<td>v₂₀ (e, a″)</td>
<td>SF₄ in-plane deformation</td>
<td>– / 0.050</td>
</tr>
<tr>
<td>v₂₁ (e, a″)</td>
<td>SF and CF wagging</td>
<td>– / 0.066</td>
</tr>
<tr>
<td>v₂₂ (e, a″)</td>
<td>CF₃ deformation</td>
<td>– / 0.070</td>
</tr>
<tr>
<td>v₂₃ (e, a″)</td>
<td>CF₂ anti-symmetric stretch</td>
<td>– / 0.117</td>
</tr>
<tr>
<td>v₂₄ (e, a″)</td>
<td>CF stretching</td>
<td>– / 0.162</td>
</tr>
</tbody>
</table>

Table 5.2 – SF₅CF₃ ground state vibrational energies (eV).

The total photo-absorption cross section spectrum is shown in Figure 5.1. The spectrum is composed of a single absorption band centred at 9.336 eV with a local maximum cross section of 17.078 Mb. The dashed feature close to 11.0 eV is only partially recorded due to the cut-off in the transmission of the CaF₂ window.
Figure 5.1 – VUV photo-absorption spectrum of SF\textsubscript{3}CF\textsubscript{3} in the energy region 4.0 eV to 11.0 eV.
Chapter Five

The present data was recorded over the energy range 4 eV to 11 eV, and reveals a broad band with a local maximum value of 17.078 Mb at 9.336 eV and a cross section value of 6.46 Mb at the Lyman-α wavelength (121.6 nm). These are considerably lower than the recent photo-absorption data reported by Chim et al. [5.18] who reported a cross section at 121.6 nm of 15 Mb. A similar spectrum recorded using the Daresbury Synchrotron facility, in a different cell configuration and with a different gas sample showed cross sections within 5% of the present cross section values. The present results therefore seem to be the most accurate and this data will be used to evaluate the SF₅CF₃ photolysis rates and local lifetime in the Earth's atmosphere (section 5.4.3).

5.3 EELS – Electron Energy Loss Spectroscopy of SF₅CF₃

In order to determine the lifetime in the Earth's atmosphere and study the spectroscopy of SF₅CF₃ above 11 eV, the first electron energy loss spectrum has been measured recently in pseudo-photo-absorption conditions (section 3.3) by Kendall and Mason [5.17] in the energy range of 5 eV to 23 eV and is shown in Figure 5.2. Hence it was applicable to use the conversion of EELS to differential oscillator strengths (DOS) presented in Chapter 3, section 3.3.1. The EELS spectrum has been energy scaled to the photo-absorption spectrum at 9.336 eV as shown in the Figure 5.2 inset.

Above 11 eV a series of broad bands are observed. A close and detailed analysis of both the EELS and VUV photo-absorption spectra reveals no evidence of vibrational features, Figure 5.2 and 5.1 respectively.

Assignment of the observed structure is not an easy task since there are no theoretical studies on the electronic configuration; only recent calculations on the geometry, vibrational frequencies, energies and reactions of SF₅CF₃ using high-level Gaussian-2 and Gaussian-3 methods have been reported [5.20]. However, with the knowledge of the photo-electron spectra we may explore some Rydberg assignments [5.22].
Figure 5.2 – EELS spectrum of SF$_5$CF$_3$ in the energy region 5.0 eV to 23.0 eV.
5.4 PES - Photo-Electron Spectroscopy of SF$_5$CF$_3$

In order to study the spectroscopy of SF$_5$CF$_3$ further we recorded a HeI photo-electron spectrum (Figure 5.3) to obtain precise values for the different ionisation potentials. The main goal of this work was to compare our PES results to the threshold photo-electron and photo-ion coincidence measurements of Chim et al. [5.16]. In fact, their data for the threshold of dissociative ionisation energies was obtained using an impulsive model and by extrapolating it to zero kinetic energy release. However, PES is a convenient and more accurate method.

![Figure 5.3 - HeI photo-electron spectrum of SF$_5$CF$_3$.](image)

The measured PES ionisation energies (Table 5.2) are in relatively close agreement with the vertical ionisation energies obtained by other workers [5.15, 5.16]. Gsir et al. [5.15] making use of a 60 meV resolution electron beam, detected several cations by mass spectrometry and the ionisation cross section was measured as a function of electron energy from the appearance energy to about 5 eV above.

The ionisation potentials values are summarised in Table 5.2 and compared to the data obtained by threshold photo-electron spectroscopy [5.16].
He! PES TPES [5.16]

<table>
<thead>
<tr>
<th>Hel PES</th>
<th>TPES [5.16]</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.960</td>
<td>14.13</td>
</tr>
<tr>
<td>14.699</td>
<td>-</td>
</tr>
<tr>
<td>15.632</td>
<td>15.68</td>
</tr>
<tr>
<td>16.147</td>
<td>-</td>
</tr>
<tr>
<td>16.461</td>
<td>-</td>
</tr>
<tr>
<td>16.845</td>
<td>16.94</td>
</tr>
<tr>
<td>17.199</td>
<td>-</td>
</tr>
<tr>
<td>17.894</td>
<td>17.86</td>
</tr>
<tr>
<td>18.721</td>
<td>-</td>
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<td>19.365</td>
<td>19.44</td>
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<tr>
<td>-</td>
<td>21.34</td>
</tr>
<tr>
<td>-</td>
<td>22.01</td>
</tr>
<tr>
<td>-</td>
<td>24.67</td>
</tr>
</tbody>
</table>

Table 5.3 – Ionisation energies observed in the Hel and in the TPE spectra of SF₅CF₃ (vertical values in eV).

5.4.1 Valence and Rydberg states

Using the PES ionisation potentials values summarised in Table 5.3 and the EELS data from Figure 5.2, a Rydberg series (section 3.2.5.1) evaluation was carried out. The assignments have been plotted in Figure 5.4 and summarised in Table 5.4.

![Figure 5.4](image)

Figure 5.4 – Assignment of the Rydberg series converging to the ionic potentials of SF₅CF₃.

The vertical ionisation energies may be due to bonding orbitals of mainly S – C character, and it seems reasonable to assign the absorption feature in the VUV absorption spectrum of Figure 5.1 as being due to transition from such an orbital.
Special attention has been devoted to VUV photo-dissociation studies of SF$_5$CF$_3$ because excitation in the energy region below the first ionisation potential, results in prompt dissociation along the S – C bond due to the strong repulsive nature of the σ* excited states [5.9, 5.16]. Though the low-lying valence excited states should arise from excitations of the σ HOMO to the σ* LUMO, a transition involving valence shell type orbital in the S – C bond. The feature at 9.336 eV has been tentatively assigned to the n = 4 member of a Rydberg series converging to the 13.960 eV ionisation limit (Table 5.4). The quantum defect value (δ) seems to be related to an ns Rydberg series. The n=5 and n = 6 members might be responsible for a feature around 12.420 eV and a partly resolved feature at 12.984 eV respectively (Fig. 5.4). The quantum defect values (Table 5.4) seem to be slightly higher for a series of this type mainly for the first and third terms. This might be attributed to a mixed Rydberg-valence character for the transition. The rather intense band centred at 11.431 eV (Fig. 5.4) corresponds to a state with a quantum defect value of 1.68 suggesting a 4p term (Table 5.4). The n = 5 and n = 6 terms are expected to have spectral bands at 12.740 eV and 13.228 eV. As the latter must be of lower intensity than the n = 4 band, they might be not well resolved from the features around 12.90 eV and 13.40 eV.

<table>
<thead>
<tr>
<th>IP (eV)</th>
<th>Energy (eV)</th>
<th>Quantum defect (δ)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.960</td>
<td>9.336</td>
<td>2.28</td>
<td>4s</td>
</tr>
<tr>
<td></td>
<td>12.420</td>
<td>2.03</td>
<td>5s</td>
</tr>
<tr>
<td></td>
<td>12.984</td>
<td>2.27</td>
<td>6s</td>
</tr>
<tr>
<td></td>
<td>11.431</td>
<td>1.68</td>
<td>4p</td>
</tr>
<tr>
<td></td>
<td>12.740 (?)</td>
<td>1.66</td>
<td>5p</td>
</tr>
<tr>
<td></td>
<td>13.228 (?)</td>
<td>1.69</td>
<td>6p</td>
</tr>
<tr>
<td>14.699</td>
<td>11.431</td>
<td>0.96</td>
<td>3d</td>
</tr>
<tr>
<td></td>
<td>13.228 (?)</td>
<td>0.96</td>
<td>4d</td>
</tr>
<tr>
<td>15.632</td>
<td>12.420</td>
<td>1.94</td>
<td>4s</td>
</tr>
<tr>
<td></td>
<td>14.185</td>
<td>1.93</td>
<td>5s</td>
</tr>
<tr>
<td>16.461</td>
<td>12.984</td>
<td>2.02</td>
<td>4s</td>
</tr>
<tr>
<td></td>
<td>14.878 (?)</td>
<td>2.07</td>
<td>5s</td>
</tr>
<tr>
<td>16.845</td>
<td>13.420</td>
<td>2.00</td>
<td>4s</td>
</tr>
<tr>
<td></td>
<td>15.425</td>
<td>1.90</td>
<td>5s</td>
</tr>
<tr>
<td></td>
<td>15.943</td>
<td>2.12</td>
<td>6s</td>
</tr>
<tr>
<td></td>
<td>16.294</td>
<td>2.03</td>
<td>7s</td>
</tr>
</tbody>
</table>

Table 5.4 – Peak energy values, derived quantum defects and assignment of the Rydberg series converging to the ionisation potentials of SF$_5$CF$_3$ (values in eV).
The 11.431 eV band might also be the first term of an \( nd \) series converging to the second ionisation limit with \( \delta \) of 0.96. Then the second member is expected to be around 13.228 eV (on the low energy side of the 14.185 eV band). The other three presented series, converging to the 15.632 eV, 16.461 eV and 16.845 eV ionisation limits respectively, have been assigned to \( ns \) series with \( \delta \sim 2.00 \). This is a tentative assignment as the \( n = 4 \) term of each series is of much lower intensity than the \( n = 5 \) member.

Additional experiments and calculations in the near future are necessary to clarify the type of transitions involved in this energy region.

In order to help interpretation and classification of the Rydberg series, Elden’s diagrams have been established as shown in Figure 5.5 (section 5.4.2), plotting the variation of the quantum defect (\( \delta_{\text{nl}} \)) with the reduced term energies \( (n^*)^2 = (n - \delta)^2 \). According to the commonly accepted Rydberg-Ritz formula (section 3.2.5.2), diagrams of \( \delta_{\text{nl}} \) as a function of \( (n^*)^2 \) should give straight lines.

### 5.4.2 Elden’s plots

The Elden’s plots obtained in Figure 5.5 give the variation of the quantum defect (\( \delta_{\text{nl}} \)) with the reduced term energies \( (n^*)^2 \) for the Rydberg series converging to the IPs.

---

**Figure 5.5 – Elden’s diagrams for the variation of the quantum defect (\( \delta_{\text{nl}} \)) with the reduced term energies \( (n^*)^2 \) for the first terms of the Rydberg series converging to the ionisation potentials.**
As shown in Figure 5.5 the experimental Elden’s diagrams for the $ns$, $np$ and $nd$ series converging to the different ionic states have been plotted for members with principal quantum numbers $n = 3 – 6$ and for the ionisation limit 16.845 eV up to 7. For each Rydberg series the variation of $\delta_\alpha$ with $(n^*)^2$ is quite smooth and linear, confirming the classification. However for the series converging to 14.699 eV, 15.632 eV and 16.461 eV IP we only have two points available from experimental data. The only relevant exception seems to occur for both the $ns$ series converging to 13.960 eV and 16.845 eV, where deviation from linearity suggests the valence-Rydberg mixing character assignment proposed in ref. [5.22].

5.4.3 Photolysis rates and local lifetime

Using the measured absolute photo-absorption cross sections the photolysis rates for SF$_3$CF$_3$ can be calculated at 1 km altitude steps up to the stratopause (50 km). Photolysis rates are calculated as the product of the Solar Actinic Flux at a given wavelength and altitude, and the molecular photo-absorption cross section at the same wavelength (Chapter 3, section 3.2.4.3).

Figure 5.6 – VUV photo-absorption cross section of SF$_3$CF$_3$ and stratospheric solar actinic fluxes in the lower and upper atmosphere.

It is remarkable that there is no overlap and an ~ 1 eV energy gap between the solar flux and the photo-absorption spectrum at altitudes lower than 50 km, meaning
that the SF₅CF₃ sink mechanisms at these altitudes must be other than direct gas phase photolysis.

In contrast at higher altitudes there is overlap, in particular the absorption close to the Lyman alpha peak (121.6 nm) at 10.2 eV where the solar UV flux at wavelengths lower than 180 nm is highest (Figure 5.6). Hence, it is likely that photo-dissociation of SF₅CF₃ will occur in the ionosphere or mesosphere regions of the atmosphere.

While there is a fairly substantial photolysis rate at the higher altitudes leading to a correspondingly short lifetime of a few days, at lower altitudes the lack of solar actinic flux at the absorption wavelengths of this molecule leads to an extremely long lifetime. Indeed, the height profiles of SF₅CF₃ through the stratosphere obtained by Sturges et al. [5.1] support this conclusion. It is this long lifetimes at low altitudes that makes SF₅CF₃ such a strong greenhouse gas.

5.5 IR – Infrared Spectroscopy

A molecule absorbing radiation in the atmospheric IR window (800 – 1300 cm⁻¹) is known as an effective greenhouse gas and contributes to the change in the Earth-atmosphere system’s radiation budget, i.e., the radiative forcing. This energy range is extremely important because natural greenhouse molecules (e.g., CO₂, CH₄) have little or no absorption. A molecule that absorbs in this region thus absorbs radiation that would otherwise escape to space and effective absorbers in this region can hence have a significant impact on global warming.

The first calculations on the radiative forcing of SF₅CF₃ have been reported by Sturges et al. [5.1] as 0.57 Wm⁻² ppb⁻¹ based upon an infrared spectrum measured at 296 K with a resolution of 0.5 cm⁻¹. Later, Nielsen et al. [5.7] also measured the photo-absorption spectrum in the 100 - 4000 cm⁻¹ energy range revealing new structures outside the original limits of Sturges spectrum, mainly at 613 cm⁻¹, increasing the radiative forcing to 0.59 Wm⁻² ppb⁻¹. However, recently Kendall et al. [5.8] re-measured the IR spectrum at different temperatures (Figure 5.7) and taking into account that the atmospheric temperature profile is not isothermal, because there is a large variation in temperatures, they observed that the peak cross sectional values increased as the temperature (203K - 298 K) was decreased and the shape of the band changed as well. Hence at 298 K the peaks of the bands are lower but broader while at lower temperatures the band peaks are higher but narrower. Table 5.5 shows the temperature
dependence of the cross sectional values for the two most intense peaks at 903 cm\(^{-1}\) and 1257 cm\(^{-1}\).

![Infrared photo-absorption spectrum of SF\(_5\)CF\(_3\) at 298 K.](image)

On average one can infer that the cross section values are \(\sim 1.45\) times higher for 203 K than for 298 K. So when evaluating the integrated absorption intensity as a function of the energy for the temperature ranges studied, it becomes clear that at lower temperatures SF\(_5\)CF\(_3\) becomes a more effective infrared absorber [5.7].

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>903 cm(^{-1}) Cross section (Mb)</th>
<th>1257 cm(^{-1}) Cross section (Mb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>203</td>
<td>11.6</td>
<td>9.58</td>
</tr>
<tr>
<td>213</td>
<td>10.9</td>
<td>8.83</td>
</tr>
<tr>
<td>233</td>
<td>10.0</td>
<td>8.40</td>
</tr>
<tr>
<td>253</td>
<td>9.17</td>
<td>7.77</td>
</tr>
<tr>
<td>273</td>
<td>8.28</td>
<td>6.88</td>
</tr>
<tr>
<td>298</td>
<td>7.67</td>
<td>6.99</td>
</tr>
</tbody>
</table>

*Table 5.5 - Temperature dependence of the 903 cm\(^{-1}\) and 1257 cm\(^{-1}\) IR peaks of SF\(_5\)CF\(_3\).*

Taking into account these results, a value for the radiative forcing of SF\(_5\)CF\(_3\) is derived as 0.60 Wm\(^{-2}\) ppb\(^{-1}\) [5.8], therefore the infrared absorbance of SF\(_5\)CF\(_3\) in the
Earth’s atmosphere is larger than initially thought, which in turn means that its global warming potential is increased by a few percent (section 5.8).

5.6 DEA with single molecules and clusters of SF₅CF₃

The experiments were performed in a crossed electron beam / molecular beam arrangement (single SF₅CF₃ molecules and homogeneous clusters). Single molecules were obtained by means of gas effusion through a capillary directed fitted to the collision chamber. Clusters were produced by adiabatic expansion of the gas (SF₅CF₃ seeded in Ar, mixing ratio 1:1000) at a stagnation pressure of 3 bar through an 80 μm nozzle at room temperature. After passing a skimmer, which separates the expansion chamber from the main interaction chamber, the molecular beam containing a distribution of clusters is crossed with an electron beam generated by a trochoidal electron mono-chromator (section 3.5). Negative ions formed are extracted from the interaction region by a small electric field (< 1 Vcm⁻¹) and subsequently analysed by a quadrupole mass spectrometer and detected by single pulse counting mode. For the gas phase experiments, the electron energy scale is calibrated using the well known zero eV resonance in SF₆.

5.6.1 SF₅CF₃ under single collision conditions

Figure 5.8 a) shows negative ion yields obtained from gas phase SF₅CF₃ under single collision conditions in the energy range 0.0 – 5 eV. Only fragment ions are observed appearing from pronounced resonance features reminiscent of dissociative electron attachment (DEA). By far the most dominant channel is the formation of SF₅⁻ from a very intense resonance peaking near zero eV and extending to about 2 eV. The present results are in reasonable agreement with those recently observed in a beam experiment [5.14]. Both studies detect the fragment ions SF₅⁻, CF₃⁻ and F⁻ with the heavy ion SF₅⁻ being by far the most dominant product ion. However, there are some differences concerning the relative intensity of the two remaining channels. In the present study, an intensity ratio SF₅⁻: F⁻: CF₃⁻ of ~ 1000:4:0.03 while it was 1000:1:4 in the Innsbruck experiment [5.14]. This difference is most likely due to different ion extraction conditions. The Innsbruck device is essentially field free in the ion source, it hence discriminates strongly towards fragment ions with excess kinetic energy. This also clearly demonstrates the limited accuracy that can be achieved when extracting absolute cross section data from beam experiments. In the present experiment the CF₃⁻
ion is only observed as a spurious signal in the vicinity of ~3.5 eV. The small contribution near zero eV is likely to be the result of electron capture to some impurity or decomposition product of the target molecule at the hot filament.

![Figure 5.8 a) – Formation of SF$_5^-$, F$^-$ and CF$_3^-$ from SF$_5$CF$_3$ as a function of the electron energy. Pressure of the gas $3 \times 10^4$ mbar at the ionisation gauge. Count rates in absolute units.](image1)

![Figure 5.8 b) – Formation of SF$_5^-$, F$^-$ from SF$_5$CF$_3$ in the extended energy range 0 – 15 eV on a log intensity scale.](image2)

From the logarithmic intensity representation extending to 15 eV (Fig. 5.8 b)), higher energy features (not reported in the recent beam study [5.14]) are visible in the F$^-$ DEA channel (weak resonances peaking near 3.5 eV and 11 eV). At this point we should mention that desorption of F$^-$ from condensed SF$_5$CF$_3$ is very effective via the resonance near 11 eV (see below). In the gas phase, electron attachment is strongly dominated by the SF$_5^-$ channel due to the DEA reaction:

$$e^{-}(e) + SF_5CF_3 \rightarrow SF_5CF_3^- \rightarrow SF_5^- + CF_3$$

(5.1)

with SF$_5$CF$_3^-$ the transient negative ion (TNI) formed upon electron attachment. The absolute cross section reaches values near $1 \times 10^{-14}$ cm$^2$ at energies approaching zero eV [5.14]. On the basis of the relevant bond dissociation energy $D(SF_5-CF_3) = 3.50$ eV and the electron affinity $EA(SF_5) = 3.80$ eV [5.14, 5.23, 5.24] process (5.1) is exothermic.
by -0.30 eV. It should be noted that the situation in the non-substituted compound SF₆ is completely different in the way that low energy electron attachment predominantly generates a long lived non-dissociated SF₆⁻ anion. This is essentially a consequence of the fact that dissociation into the energetically lowest channel (SF₆⁻ + F) is either endothermic or subjected to an activation barrier. In electron attachment to SF₅CF₃ under collision free conditions, we do not observe any un-dissociated anion SF₅CF₃⁻ within the time scale of the experiment (~ 50 μs). As will be discussed below, however, such a stabilised parent anion was observed from electron attachment to clusters. The DEA reaction leading to the energetically lowest F⁻ channels can be expressed as:

\[ \text{e}^-(e) + \text{SF}_5\text{CF}_3 \rightarrow \text{SF}_5\text{CF}_3^* \rightarrow \text{F}^- + \text{SF}_4\text{CF}_3 \]  \hspace{1cm} (5.2)
\[ \text{e}^-(e) + \text{SF}_5\text{CF}_3 \rightarrow \text{SF}_5\text{CF}_3^* \rightarrow \text{F}^- + \text{SF}_5\text{CF}_2 \]  \hspace{1cm} (5.3)

Although there are no explicit values available for the C – F or S – F bond dissociation energies in the present molecule, one can assume similar binding energies as in the non-substituted compounds (D(SF₅ – F) = 3.94 eV and D(CF₃ – F) = 5.56 eV [5.23, 5.24]). With the electron affinity of F (3.40 eV [5.23]) one expects the threshold for F⁻ formation at electron energies of about 0.5 eV and 2 eV for reaction (5.2) and (5.3), respectively. Thus it may be concluded that the low energy F⁻ feature is exclusively due to reaction (5.2). Regarding to the electronic structure of the presently observed resonances, it is likely that TNIs below 5 eV can be ascribed to single particle shape resonances, i.e., electronic states formed by accommodation of the extra electron into one of the virtual molecular orbitals (MOs) thereby leaving the electronic configuration unchanged. In contrast the feature near 11 eV is very likely to be a core excited resonance, i.e., an electronic state with at least two electrons in previously unoccupied MOs. The electronically excited states of the neutral molecule can be identified by electron energy loss spectroscopy (EELS) and optical absorption. Both EELS and VUV absorption by synchrotron radiation show two prominent absorption bands centred at 9.3 and 11 eV [5.17, 5.19]. The lowest ionization potential observed by photoelectron spectroscopy is located at 13.96 eV [5.22]. It is also remarkable that electron impact in gas phase SF₅CF₃ at energies above 13 eV leads to a variety of fragment cations but no detectable parent cation [5.15].
5.6.2 SF₅CF₃ clusters

Adiabatic expansion of SF₅CF₃ diluted in Ar leads to molecular aggregates including mixed SF₅CF₃/Ar clusters as can be seen by the negative ion mass spectrum (Fig. 5.9), recorded at impact energy close to zero eV. The cluster beam was generated by adiabatic expansion of an SF₅CF₃/Ar gas mixture at a ratio of 1/1000 and a stagnation pressure of 3 bar. In the mass spectrum the peak in the range 196/198 amu can be assigned to the un-dissociated parent negative ion indicating that SF₅CF₃ possesses a positive adiabatic electron affinity. The fine structure of all the mass peaks is due to the isotopes ^32S, ^33S, ^34S with the relative abundances of 95:0.8:4.2. The strongest signal in the mass spectrum is still SF₅'. It has to be kept in mind, however, that this signal can arise from both, electron attachment to clusters and to monomers (background gas and monomers travelling in the molecular beam).

![Figure 5.9 - Mass spectrum of negative ions from an expansion of SF₅CF₃ seeded in Ar (1:1000) at 3 bar and an electron energy close to 0 eV, M = SF₅CF₃.](image)

On the other hand, negative ions observed at mass numbers higher than the parent molecule must arise from reactions occurring in a cluster. Apart from SF₅' and SF₅CF₃' we observe in the mass range up to 300 amu the solvated fragment ions Arₙ SF₅' (n = 1, 2) and complexes of the form Arₙ SF₅CF₃' (n = 0 – 3) containing the un-dissociated negative parent anion. The mass spectrum also contains an SF₆' signal from the calibration gas. Formation of the parent negative ion is due to evaporative attachment, i.e., resonant capture of an electron by a cluster thereby generating an individual TNI within the target aggregate:

\[ e^-(\varepsilon) + (SF₅CF₃)_m Arₙ \rightarrow SF₅CF₃' (SF₅CF₃)_{m-1} Arₙ \]  

\[ (5.4) \]
which then decomposes. Since this reaction occurs close to zero eV, the excess energy is essentially comprised of the electron affinity of $\text{SF}_5\text{CF}_3$ which is used to evaporate the cluster according to:

$$\text{SF}_5\text{CF}_3^* (\text{SF}_5\text{CF}_3)_m \text{ Ar}_n \rightarrow \text{SF}_5\text{CF}_3^- + (m-1) \text{SF}_5\text{CF}_3 + n\text{Ar} \quad (5.5)$$

In (5.5) it is assumed that the initial aggregate completely evaporates into monomers. Formation of the un-dissociated parent anion $\text{SF}_5\text{CF}_3^-$ in electron attachment to clusters indicates that the reactivity of the target molecule is suppressed to some degree under aggregation, i.e., a fraction of attachment events is channeled into non-dissociative processes. A lower limit for the branching ratio between associative and dissociative processes can be given, assuming that the $\text{SF}_5^-$ signal completely arises from clusters. In this case, a lower limit for the branching ratio of $\text{AA}/\text{DEA} \geq 5\%$, where AA assigns associative attachment leading to un-dissociated product ions. Figure 5.10 shows ion yield curves on a log scale for the products $\text{SF}_5^-$, $\text{SF}_5\text{CF}_3^-$, and $\text{F}^-$ from electron attachment to clusters. As expected, the formation of the un-dissociated parent anion is concentrated in the low energy domain with a peak width broader than that from the calibration compound $\text{SF}_6^-$. Interestingly, from clusters one observes a surprisingly strong low energy $\text{SF}_5^-$ signal and considerable enhancement in the energy range of the second resonance feature above 1.5 eV.

Figure 5.10 – Ion yields for the stabilised parent anion $\text{SF}_5\text{CF}_3^-$ and the fragments $\text{SF}_5^-$ and $\text{F}^-$ on a log scale from electron attachment to clusters under the conditions of Fig. 5.9.
From gas phase molecules this resonance is only very weak in the SF$_5^-$ channel, but clearly visible in the F$^-$ yield (Fig. 5.8) and also the total attachment cross section. In clusters this second resonance is clearly visible on the SF$_5^-$ channel now peaking slightly below 3 eV. This shift principally mirrors the solvation energy of the TNI in the clusters. More precisely, the peak position of an ionic product is a convolution of the energy of the precursor ion (due to the initial Franck-Condon transition) with the energy dependent probability to decay into the channel under observation. The solvation shift can hence be counterbalanced to some degree by the energetics of the decomposition. In the F$^-$ channel (Fig. 5.10) this second feature is still weakly present near 3.5 eV.

On the basis of the high dilution of SF$_5$ in the carrier gas, the strong signal in the SF$_5^-$ channel is very striking and points towards an enhancement in low energy DEA. Since there is no direct access to the actual pressure in the collision region, it is impossible to extract absolute cross sections. The usual observation, however, is that the signal from electron attachment to the cluster beam is about one order of magnitude weaker compared to the effusive beam. Such a ratio is in fact observed in the F$^-$ count rates (Figs. 5.8 and 5.10) and supports the picture of a medium enhancement, particularly on the SF$_5^-$ fragment.

5.7 ESD - Electron Stimulated Desorption

This section is devoted to the study and interaction of low energy (0 – 18 eV) electron stimulated desorption (ESD) from adsorbed and condensed SF$_5$CF$_3$ in order to get information on the electron induced reactivity of the compound when is adsorbed with other molecules (e.g. water ice). The desorption of negative fragment ions as a function of electron energy is recorded from multilayers of SF$_5$CF$_3$ condensed directly on a Au (111) surface and from sub-monolayers of SF$_5$CF$_3$ adsorbed on a multilayer of Xe and H$_2$O ice as a spacer to the metallic substrate.

The electron stimulated desorption experiments were carried out in a UHV apparatus consisting of a trochoidal electron mono-chromator (TEM), a cryogenic cooled monocrystalline Au substrate mounted on a manipulator and a commercial quadrupole mass spectrometer with an ion extraction system (section 3.5.2). The substrate was cooled down to 40 K (measured by a thermocouple directly mounted at the crystal) by means of a closed cycle He refrigerator and resistively heated up to several hundred Kelvin. The material is deposited on the metallic substrate at 30 K by
exposing it to a volumetrically calibrated gas quantity effusing from a capillary located
0.7 cm from the crystal (section 3.5.2). In the case of SF$_5$CF$_3$ adsorption on Xe and H$_2$O
spacers, deposition is performed sequentially, i.e. adsorption of SF$_5$CF$_3$ on top of a
preformed Xe or H$_2$O layer.

The TEM operates with a weak homogeneous magnetic field (≈ 30 Gauss) which
prevents spreading of the beam at low energies. The instrument has thereby proven to
be particularly suited to study electron-induced processes in the low energy domain.
The base pressure in the chamber is in the 10$^{-10}$ mbar (10$^{-8}$ Pa) range. SF$_5$CF$_3$ was
obtained from Agro Ltd., Essex, and used as delivered.

5.7.1 Energy calibration

The energy calibration procedure has been already described in Chapter 3,
section 3.5.2. In the present studies keeping the energy resolution constant throughout
the measurements proved a difficult task because of the charging behaviour of the
SF$_5$CF$_3$ film after only a few minutes. For multilayer SF$_5$CF$_3$ coverage, charging of the
molecular film following electron beam exposition is inherently present as can be
observed by a shift of the injection onset with respect to the monochromator voltage
(Figure 5.11). This is due to the repulsive potential of the accumulated charge.

The electron energy is calibrated by the onset of electron transmission (the
electron injection curve into the substrate, 0 eV, vacuum level). From the steepness of
the onset curve, the FWHM energy resolution of the electron beam in the present
experiment was ~ 0.2 eV at a current of 10 – 20 nA.

![Figure 5.11 – Electron beam energy profile and effect of energy shift due
to film charging retarding potential from first to second scan.](image)
Exposure of the SF$_5$CF$_3$ film to the electron beam leads to accumulation of negative charges due to stabilized anions and possibly otherwise trapped electrons. This results in a shift of the electron injection curve with respect to the mono-chromator potential. All desorption spectra shown are calibrated with respect to the onset of the injection curve and represent first scans on a newly deposited adsorbate. Since charge accumulation is operative already within the first scan it is estimated from the general trend in charging that the accuracy in the location of the desorption peak is ± 0.5 eV (Figure 5.11).

### 5.7.2 Results and discussion

Figure 5.12 shows negative ion desorption from a 6 monolayer (ML) film of SF$_5$CF$_3$ directly condensed on the Au surface.

![Desorption of F and F$_2$ from a multilayer film of SF$_5$CF$_3$](image)

**Figure 5.12 – Desorption of F$^-$ and F$_2$ from a multilayer film of SF$_5$CF$_3$ condensed directly on the Au(111) substrate at 40 K.**

A remarkably strong F$^-$ desorption signal is observed peaking at 11 eV and also a comparatively weak F$_2$ contribution appearing at some higher energy. These two ions are the only negatively charged desorption products observed from SF$_5$CF$_3$. F$^-$ appears within an intense resonance feature which is reminiscent of dissociative electron attachment (DEA) followed by desorption of the fragment ion. In the gas phase the DEA cross section shows a small structure near 11 eV on both F$^-$ and SF$_5^-$ which is,
however, weak compared to the dominant low energy DEA process generating SF₅⁻. In SF₅CF₃ there is a slightly different situation where the gas phase molecule is effectively decomposed by low energy electrons while in the condensed phase the ion desorption channel is completely suppressed at these energies. On the other hand, a strong desorption signal appears from a resonance located at 11 eV where gas phase electron attachment is barely observable. From the non-observation of an ion desorption signal at low energies, however, it does not necessary follow that the DEA reaction at the surface is completely suppressed in that energy range. It may still be operative at low energy but with dissociation products remaining on the surface.

When proceeding from gas phase DEA to ion desorption from condensed phase molecules one has to consider two major points concerning how the surrounding medium will affect the process: (i) this concerns the primary step of electron interaction (and electron localization) and (ii) the subsequent decomposition. The first point is also relevant for clusters and has already been discussed before.

Low energy electron interactions with condensed molecules can usually be described by a molecular site that is the formation of an individual TNI coupled to the surrounding medium. The coupling of the TNI can be divided into the (classical) attractive polarization interaction of the excess charge with the surrounding molecules and the (quantum mechanical) repulsive electronic exchange interaction (Pauli repulsion) [5.25 – 5.27]. The latter may only contribute to any significant degree if the extra electron resides in a spatially extended orbital. In films composed of molecules the net interaction of the TNI is usually dominated by the attractive polarization interaction. A value of \( V_a \approx 1 \) eV was considered as a reasonable number for halogen compounds as discussed in a number of previous investigations [5.28 – 5.30]. For the present system this means that the dominant gas phase resonance (generating SF₅⁻ with strong contributions below 2 eV) is partly shifted to below the vacuum level thereby becoming partly inaccessible by free electrons. On the other hand, the charging behaviour of the SF₅CF₃ film indicates, that there is still some electron capture operative at low electron energies. To which degree these electron localization processes are associative or dissociative remains under question. In gas phase clusters the results point towards an increase of the attachment cross section under aggregation. In this case a measurable quantity of attachment events (> 5 %) was channelled into associative processes (see above).
The second point concerns the probability of desorption of an ionic fragment once a TNI is formed. Desorption probability is directly related to the orientation of the molecule at the surface, it is furthermore principally subjected to particular energy constraints. The negative fragment ion can only escape into vacuum if its kinetic energy exceeds the polarization interaction with the environment, i.e., the fragment ion must gain sufficient kinetic energy from the decomposition of the TNI. In the approximation of a unimolecular decomposition of the TNI at the surface and taking the same interaction energy \( V_a \) for the TNI and the fragment ion, the energy threshold \( E_d \) for desorption can be expressed as [5.28]:

\[
E_d = (m_i/m) V_a + \Delta H_0
\]  

(5.6)

with \( m_i \) and \( m \) the mass of the ionic and neutral fragment, respectively and \( \Delta H_0 \) the thermodynamic threshold of the corresponding gas phase DA process. Note that in this context \( V_a \) is a positive number. Expression (5.6) directly indicates that desorption of a heavy ionic fragment is energetically less favourable. This is a consequence of the principle of linear momentum conservation which results in more kinetic energy release to the light fragment ion. For the present system the desorption threshold for the light F' ion virtually coincides with that from the gas phase while the desorption threshold for the heavy SF\(_5^-\) ion is expected about 2 eV above the gas phase limit of the reaction (5.1). Taking into account some energy randomization in the decomposition of the precursor ion SF\(_5\)CF\(_3\)' it becomes immediately evident that desorption of SF\(_5^-\) is very unlikely, irrespective of the problem of the accessibility of the respective resonant state by free electrons.

For the channel (5.1) we may then conclude that in the condensed phase DEA is still operative, the heavy fragment ion, however will not be ejected into vacuum. Accordingly, the fact that desorption of F' is not observed at low energies is a mirror of the associated decomposition process which generates only slow F' ions, below the threshold for desorption.

In contrast to that, the TNI created around 11 eV dissociates in a way that F' is effectively ejected into vacuum. At that energy, the TNI must be associated with electronic excitation (core excited resonance). SF\(_5\)CF\(_3\) possesses a rich structure in the electron energy loss spectrum (EELS) in the energy range 8 eV – 15 eV [5.17], and the UV absorption spectrum shows two prominent peaks at 9.2 eV and 11.2 eV [5.18, 5.19].
The lowest ionisation potential occurs at 13.960 eV [5.22] and for the un-substituted compound SF$_6$ the ionisation energy is 15.3 eV [5.24]. The strong desorption signal suggests that the involved core excited resonance possesses appreciable S – F or C – F antibonding character, e.g., two electrons in antibonding $\sigma^*$ MOs.

Strong suppression of the low energy feature in the ion desorption channel together with appreciable medium enhancement of the reactivity for core excited resonances is frequently observed when comparing gas phase DEA and ion desorption [5.31 – 5.33]. A medium enhancement of dissociation can principally be explained by an enhanced lifetime of the resonant state towards auto-detachment. Within a medium, polarisation can shift the energy of an open channel core excited resonance to values below the energy of the excited neutral. It can then no longer decay via a one electron process into the associated excited neutral which results in a dramatic enhancement of its lifetime with respect to auto-detachment and consequently a dramatic enhancement of the DEA cross section (Figure 5.13). In the language of resonances, coupling to the medium converts a short lived open channel resonance into a long lived closed channel (Feshbach) resonance (Chapter 2, section 2.3).

![Figure 5.13 - DEA along a repulsive surface illustrating the effect of a medium on the DEA cross section (after Illenberger [5.33]).](image)

The enhancement can be illustrated by the two dimensional potential energy curve of Figure 5.13 where $V_i$ denotes the initial state (neutral) and $V_f$ the negative ion state. The dotted curves represent the condensed phase where ionic states are much more affected due to polarisation. $\Gamma(R)$ is the energy width of the ionic state due to auto-detachment. It is clear that in the solvated system the time the dissociating system spends in the area active for auto-detachment ($R < R_{\text{c,ad}}$) is reduced and therefore
electron loss is decreased in favour of dissociation. The effect becomes more pronounced the larger the auto-detachment width is. The example given in Figure 5.13 also describes DEA involving the electronic ground state of the anion where dissociation occurs along the lowest potential energy surface with no curve crossing.

Interestingly the molecular ion \( F_2^- \) is also observed in the vicinity of 13 eV (Figure 5.12). This ion was not detected in DEA from gas phase SF\(_5\)CF\(_3\). If it is generated via unimolecular decomposition of the TNI, the process involves the cleavage of two bonds in the target compound (C - F and / or S - F) and formation of the F – F bond. An alternative and more likely route would be formation via a secondary reaction, e.g. F' formation from DEA and reactive scattering creating F\(_2^+\).

5.7.3 SF\(_5\)FC\(_3\) sub-monolayer coverages on Xe and H\(_2\)O ice multilayers

Desorption behaviour of sub-monolayers of SF\(_5\)CF\(_3\) deposited on multilayers of Xe and H\(_2\)O ice has also been studied. Electron stimulated desorption from molecules embedded in an environment of polar molecules has attracted some attention since the previously reported giant enhancements of Cl' and F' desorption from CCl\(_2\)F\(_2\) at co-adsorption of ammonia or water following 250 eV electron impact [5.34, 5.35]. These enhancements were interpreted as transfer of electrons trapped by the polar medium to the molecule (CCl\(_2\)F\(_2\)) which then decomposes leading to desorption of Cl' and F'.

Different sub-monolayer coverages on Xe and H\(_2\)O are shown in Figs. 5.14 and 5.15 showing F' desorption sequences from SF\(_5\)CF\(_3\), and the absolute count numbers for the desorption intensity increases approximately linear with the coverage. Above one monolayer, the increase becomes gradually weaker until it levels off near 8 ML. By comparing the absolute count rates in Figs. 5.14 and 5.15 it can be seen that desorption from water ice is more effective than from Xe.

Although the accuracy in reproducing absolute count rates is within the difference seen between Xe and H\(_2\)O, the tendency during the runs always pointed towards a distinctly higher intensity from the water layer. The absolute count rate critically depends on the reproducibility of many parameters, the most sensitive is the position of the sample with respect to the electron beam and the quadrupole entrance. During condensation, the sample is moved off the position where desorption spectra are recorded.
This enhancement in desorption from water ice is a surprising result as ice films, grown by vapour deposition at substrate temperatures below 140 K (as in the present case) are amorphous. In the case of O\textsuperscript{−} desorption from O\textsubscript{2} it was shown that desorption intensity is appreciably suppressed when oxygen is deposited on amorphous ice [5.36, 5.37]. This was explained by the penetration of the molecules into the pores of the amorphous material which suppresses the probability for TNI formation and also the probability for fragment ion desorption. This is obviously not the case in the present system which may be an indication that SF\textsubscript{5}CF\textsubscript{3} does not penetrate in the water pores. One can then speculate why the desorption intensity from water exceeds that from Xe. The detailed problem is rather complex, it is mainly a question to which degree the water dipoles in the amorphous network respond to the negative charge during the lifetime of the TNI with the possibility to provide a polarization trap. In any case the high desorption intensity means that the associated decomposition is appreciably repulsive.

The water surface may further provide orientations of SF\textsubscript{5}CF\textsubscript{3} with respect to favourable desorption.
A second aspect concerns substrate mediated mechanism which can enhance the desorption intensity. Water possesses a series of resonances in the range $6 \text{ eV} - 12 \text{ eV}$ visible on the H$^*$ desorption spectrum (not shown here). Charge and energy transfer from these substrate resonances can enhance the desorption yield of the adsorbate molecule. Clear evidence for such substrate enhanced reactions was observed from molecules adsorbed on noble gas films [5.38]. Charge and energy transfer from the electron-exciton complexes of the noble gas then leads to sharp enhancements in the desorption yield from the adsorbate molecule as recently reported in the F$^*$ desorption profile [5.39]. We did not observe evidence for such substrate mediated desorption effects. Desorption at low coverage (0.25 ML) from the Xe spacer gives some additional contribution near 4 eV which may be viewed as the high energy tale of the second resonance seen in gas phase DEA peaking near 3.5 eV.

While a number for the absolute desorption cross section is very hard to extract under the present experimental conditions one can nevertheless give a very rough estimate of $10^{-17} \text{ cm}^2$ for the F$^*$ desorption cross section from sub-monolayers SF$_5$CF$_3$ on water ice at 11 eV. This results from a direct comparison of the absolute count rates with a system (CF$_3$I [5.31]) where an absolute desorption cross section was derived [5.40]. In summary, condensed phase SF$_5$CF$_3$ shows a very strong desorption signal at 11 eV due to impulsive dissociative attachment of the molecule.

5.8 Environmental evaluation

The measured atmospheric concentration level of SF$_5$CF$_3$ as 0.12 pptv has been reported by Sturges [5.1] with the tendency to increase at a level of $\sim 6\%$ per year. Hence even with the largest per molecule radiative forcing of any atmospheric molecule, SF$_5$CF$_3$ still constitutes a few hundredths of a percent of the total anthropogenic radiative forcing. Using recent IR absorption cross sections [5.8] has been possible to fix the radiative forcing of trifluoromethyl sulphur pentafluoride to a few percent ($\sim 1.7 \% - 5\%$) slightly above the previous obtained [5.1, 5.10], at around 0.6 Wm$^{-2}$ ppb$^{-1}$ [5.8], giving it the largest radiative forcing on a per molecule basis of all gases present in the atmosphere. Assuming a 1000 years limit for the mesospheric lifetime [5.22], a predictable GWP for SF$_5$CF$_3$ of around 18500 is reasonable, the second largest of any molecule and comparable with its un-fluorinated SF$_6$ (22200).
Hence it is important to identify current sources and prevent further emissions of this compound.

However, it has been shown that SF₅CF₃ is very effectively decomposed into SF₅⁻ + CF₃ [5.13, 5.14] by low energy dissociative electron attachment. This is in striking contrast to SF₆ which indeed possesses a very high cross section for thermal electron attachment (exceeding that of SF₅CF₃), the process, however, is virtually non-dissociative at ambient temperatures [5.41]. On the other hand, the existence of resonances of dissociative character as found in SF₅CF₃ is directly related to the heterogeneous photochemical activity of the molecule [5.42, 5.43]. Photo-induced decomposition of adsorbed molecules (involving weakly bound excess electrons) on dust or aerosol particles in the Earth’s atmosphere may readily occur at wavelengths where the gas phase molecule is photo-chemically inactive.

Recent studies of the reactions of SF₅CF₃ with positive ions in the stratosphere and/or ionosphere [5.10 – 5.12] have identified that ion-molecule interactions may remove this molecule from the Earth’s atmosphere. However, electron attachment studies strongly suggest that dissociative electron attachment is one of the dominant processes in the lower ionosphere [5.13, 5.14] and thus an atmospheric lifetime of around 1000 years seems reasonable.

5.9 Summary

The photo-absorption spectrum of SF₅CF₃, has been measured using synchrotron radiation in the range of 5.5 eV - 11 eV (225 nm > λ > 110 nm), and the lifetime due to photolysis will be long as there is no overlap with solar actinic fluxes at 50 km altitude or below. Dissociation by VUV radiation may be possible in upper regions but is more likely in the mesosphere and/or ionosphere where electron concentrations are high and fast electron attachment processes can happen.

An upper limit for the radiative forcing has been proposed from high-resolution IR spectrum obtained at a number of atmospheric relevant temperatures and the GWP evaluated. The overall lifetime of SF₅CF₃ will probably be of the order of a thousand years.

From the present observations the implications concerning the electron induced reactivity of condensed phase SF₅CF₃ may then be summarised as: the strong low energy dissociative gas phase resonance is completely suppressed in the ESD channel.
In clusters, low energy attachment is enhanced, however, part of the attachment events is channelled into associative attachment as it is obvious from the formation of the undissociated parent anion $\text{SF}_5\text{CF}_3^-$ and complexes of the form $\text{Ar}_n \text{SF}_5\text{CF}_3^-$. Surface charging, however, indicates that electron attachment is still operative in the low energy region. The question to which degree this process leads to decomposition of the molecule at the surface remains open. For the problem of $\text{SF}_5\text{CF}_3$ adsorption on dust or ice particles in the Earth's stratosphere we can conclude that UV radiation can liberate electrons which can induce dissociative electron attachment reactions at low energies. The dissociative state of $\text{SF}_5\text{CF}_3^-$ at 11 eV, strongly visible on the F$^-$ desorption channel, cannot be accessed by photoelectrons beyond the Lyman (α) line and may hence not play a significant role in the chemistry of the molecule in the atmosphere.
5.10 References

Chapter 6

Experimental studies of the global warming and ozone depleting characteristics of CCl₂F₂

*It doesn’t matter how new an idea is: what matters is how new it becomes.*


6.1 Introduction

Halocarbons were first synthesised in the late 19th century and their properties as refrigerants were recognised over fifty years ago. Chlorofluorocarbons, CFCs, have achieved widespread industrial use as refrigerants, propellants and solvents. Global anthropogenic emissions to the atmosphere grew from virtually negligible quantities in 1940 to about 2.5 Tg yr⁻¹ in 1990. The global average chlorine level in the atmosphere in 1945 was about 1 ppb, of which about 25% was man-made; by 1995 the total chlorine loading had increased to 3.5 ppb, 85% of which was anthropogenic (according to the recent 2001 report on the International Panel for Climate Change, IPPC – www.ippc.ch).

Among the halocarbons, dichlorodifluoromethane - CCl₂F₂, has attracted considerable attention as being important for the depletion of the stratospheric ozone layer and the increased absorption of infrared radiation. As it is chemically inert and has a low solubility in water, the most important atmospheric sink is photolysis by UV radiation (λ < 200 nm) in the stratosphere. Upon photolysis CCl₂F₂ releases chlorine (and/or fluorine) atoms, which initiates an extensive catalytic chain reaction leading to the net destruction of O₃ in the stratosphere. The cross sections for interaction with low energy electrons are several orders of magnitude larger than UV radiation, but the density of electrons is small in the stratosphere and electron interactions are generally not regarded as primary processes in the atmosphere. However surface induced dissociation by solvated electrons may play an important role in these processes.
6.2 VUV photo-absorption cross section for CCl$_2$F$_2$

6.2.1 Introduction

Dichlorodifluoromethane (CCl$_2$F$_2$ or CFC-12) is a halogenated hydrocarbon used extensively in refrigeration systems, as a foam blowing agent and as an aerosol propellant. It also plays an important role in the plasma etching industry [6.1, 6.2] for reactive ion etching (RIE) of GaSb as it can be readily dissociated in discharge plasma to produce Cl and F radicals [6.3].

Halogenated hydrocarbons or halocarbons such as CCl$_2$F$_2$ are (under photolysis) a source of atmospheric radicals and therefore are widely recognised to contribute significantly to stratospheric ozone depletion [6.4, 6.5] by Cl and/or F atoms release; moreover they are also strong greenhouse gases, and in particular CCl$_2$F$_2$ has a residence time in the atmosphere of about 100 years with an estimated global warming potential of 9000 in a 100-year period [6.6]. Thus, under the regulations of the Montreal Protocol and its amendments, the use of CFC-12 in industry must be phased out and alternatives found within the next decade.

The absorption spectrum was obtained in the closed cell photo-absorption set-up (Chapter 3, section 3.2.3) with a path length of 25 cm. The spectrum was obtained in 11 nm sections, in 0.1 nm steps. The sample used was from Fluorochem. with a purity greater than 99%. The gas was used without further purification or treatment. CCl$_2$F$_2$ spectrum was recorded over the pressure range 0.015 torr - 0.525 torr (Table 6.1), with typical attenuation of 10%. High sample pressures and 0.05 nm data acquisition steps were used between 7.75 eV and 9.25 eV in order to observe and resolve as much as possible the low intensity features.

<table>
<thead>
<tr>
<th>Energy range (eV)</th>
<th>Wavelength (nm)</th>
<th>Pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.51 – 8.73</td>
<td>142 – 225</td>
<td>0.075/0.375/0.525</td>
</tr>
<tr>
<td>8.55 – 9.25</td>
<td>134 – 145</td>
<td>0.015/0.150</td>
</tr>
<tr>
<td>9.19 – 10.97</td>
<td>113 – 135</td>
<td>0.015/0.023</td>
</tr>
</tbody>
</table>

Table 6.1 – Photon energy (eV), wavelength (nm) and pressure (torr) ranges for CCl$_2$F$_2$ photo-absorption measurements.

The electronic structure of this molecule has been studied previously [6.7 – 6.13] as have its photo-absorption, photo-ionisation and photo-fragmentation cross sections [6.4, 6.8, 6.10, 6.11, 6.14]. The vacuum-ultraviolet (VUV) absorption spectrum of CCl$_2$F$_2$ in the wavelength range 120 nm to 200 nm (10 eV to 6 eV) was first measured
during the 1950's by Zobel et al. [6.15] and subsequently discussed by Doucet et al. [6.10] together with a comparison with the photo-electron spectrum. An energy loss spectrum using 500 eV electrons was reported by King and McConkey [6.12] under experimental conditions that simulated optical absorption. Zhang et al. [6.7, 6.13] reported the absolute photo-absorption oscillator strengths using dipole spectroscopy between 8.5 eV and 200 eV, ionic photo-fragmentation branching ratios and the photo-ionisation efficiency at energies from the first ionisation threshold up to 70 eV. Recently, Au et al. [6.16] refined the data of Zhang et al. [6.7] reporting the absolute photo-absorption spectra from 5 eV to 60 eV by high-resolution dipole (e,e) spectroscopy. Photo-absorption cross sections have been compared with cross sections obtained from differential oscillator strength measurements using electrons with 100 eV and 8 keV, by Christophorou et al. [6.14]. A comprehensive study of the ultraviolet and visible emissions produced by dissociative electron impact on CCl$_2$F$_2$ was reported by Jabbour and Becker [6.17] with absolute photoemission cross sections reported for a variety of neutral, ionic fluorine and chlorine features as well as for diatomic CCl and CCl$^+$ bands. Mann and Linder [6.18] measured differential cross sections for both elastic and inelastic scattering from CCl$_2$F$_2$ in the electron energy range 0.5 eV to 10 eV and reported an excitation of the infra-red active CF$_2$ and CCl$_2$ stretching modes below 1 eV.

Until now, a complete high resolution VUV photo-absorption spectrum of CCl$_2$F$_2$ has not been reported, nor have the absorption bands been conclusively assigned to discrete valence and Rydberg transitions. Therefore, a definitive series of measurements to determine both the absolute photo-absorption cross section of CCl$_2$F$_2$ and to probe its electronic spectroscopy was recorded over the energy range from 5.5 eV to 11 eV (110 > $\lambda$ > 225nm) [6.19] with a resolution of ~ 0.075 nm FWHM.

6.2.2 Results

The total photo-absorption cross section spectrum of CCl$_2$F$_2$ is shown in Figure 6.1. The spectrum is composed of two absorption bands (each with low cross sections) between 6.0 eV and 8.5 eV and a series of sharp, more intense peaks above 9.5 eV. The dashed feature close to 11.0 eV is only partially recorded due to the cut-off in the transmission of the CaF$_2$ window. The energy region 5.5 eV – 9.0 eV is displayed as an insert in Figure 6.1.
Figure 6.1 - VUV photo-absorption spectrum of dichlorodifluoromethane in the energy region 5.50 eV to 11.00 eV.
A brief review of the structure, geometry and properties of CCl$_2$F$_2$ is helpful in the analysis and interpretation of the present data. The CCl$_2$F$_2$ molecule has C$_{2v}$ symmetry with two fold axis and consequently only non-degenerate symmetry. The nine non-degenerate fundamental vibrational modes have been classified in the symmetry types $\Gamma_{\text{vib}} = 4A_1 + A_2 + 2B_1 + 2B_2$ (Table 6.2).

The fundamental vibrational energies with their symmetries were summarised by Mann et al. [6.18] and are presented in Table 6.2. The electronic configuration of the outer shells of CCl$_2$F$_2$ may be written as [6.20]: $(3a_1)^2 (3a_2)^2 (3b_1)^2 (3b_2)^2 (4a_1)^2 (4a_2)^2 (4b_1)^2 (4b_2)^2$, giving a valence shell independent-particle configuration for the ground state as $\tilde{X}^1$A$_1$.

The four lowest ionisation potentials are 12.26 eV, 12.53 eV, 13.11 eV and 13.45 eV, for $^2$B$_2$, $^2$B$_1$, $^2$A$_2$ and $^2$A$_1$, respectively, and the highest ionisation potentials are due to bonding orbitals of mainly C-Cl character [6.8]. The lowest ionisation potentials are related to the molecular orbitals formed by the chlorine lone pair character [6.11], and the VUV absorption spectrum up to 9.92 eV is characterised by transitions from such orbitals [6.11].

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Description</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$ (a$_i$)</td>
<td>CF$_2$ symmetric stretch</td>
<td>0.136</td>
</tr>
<tr>
<td>$v_2$ (a$_i$)</td>
<td>CF$_2$ bending</td>
<td>0.083</td>
</tr>
<tr>
<td>$v_3$ (a$_i$)</td>
<td>CCl$_2$ symmetric stretch</td>
<td>0.057</td>
</tr>
<tr>
<td>$v_4$ (a$_i$)</td>
<td>CCl$_2$ bending</td>
<td>0.033</td>
</tr>
<tr>
<td>$v_5$ (a$_2$)</td>
<td>CF$_2$ twisting (torsion)</td>
<td>0.040</td>
</tr>
<tr>
<td>$v_6$ (b$_i$)</td>
<td>CF$_2$ asymmetric stretch</td>
<td>0.145</td>
</tr>
<tr>
<td>$v_7$ (b$_i$)</td>
<td>CF$_2$ plane rocking</td>
<td>0.055</td>
</tr>
<tr>
<td>$v_8$ (b$_2$)</td>
<td>CCl$_2$ asymmetric stretch</td>
<td>0.114</td>
</tr>
<tr>
<td>$v_9$ (b$_2$)</td>
<td>CCl$_2$ plane rocking</td>
<td>0.054</td>
</tr>
</tbody>
</table>

Table 6.2 – Dichlorodifluoromethane ground state vibrational energies (eV).

The lowest absorption features observed in Figure 5.1, in the range 6.0 eV to 8.5 eV, may be assigned to transitions involving valence shell type orbitals in the C-Cl bond, and may be characterised as (σ* → 4b$_2$). Features between 8.5 eV and 11 eV have been interpreted as belonging to a Rydberg series converging to the CCl$_2$F$_2^+$ ground state [5.10, 5.15], arising from the transition of a lone-pair chlorine electron to the Rydberg orbitals 4s and 4p. In general, the higher energy range band (> 10.2 eV) features exhibit no vibrational fine structure and are broadened due to pre-dissociation.
and mutual overlap between bands. Each of these bands is discussed in more detail in the following sections.

6.2.2.1 The 5.5 eV – 8.5 eV photon energy region

Special attention has been devoted to VUV photo-dissociation studies of CCl$_2$F$_2$ in this energy region because excitation results in prompt dissociation along the C-Cl bond due to the strong repulsive nature of the σ* excited states. Thus, Cl atoms that damage the ozone layer are released through solar photolysis from these electronic states (see section 6.2.3).

The broad and weak continuous absorption feature centred at 6.98 eV (~178nm) with a maximum cross section of 1.90 Mb is a result of the excitation to an anti-bonding orbital along the C-Cl bond (σ* → 4b$_2$) of the CCl$_2$F$_2$ molecule. At 8.14 eV (~152nm) there is a similar structure with a maximum cross section of 1.06Mb. This band has been assigned as one of the intervalence excitations (σ* → 4b$_2$) [6.20].

In agreement with Au et al. [6.16] the present data shows the 8.14 eV band with lower intensity than the 6.98 eV band, but this in contrast with the results of Ibuki et al. [6.20]. These weak absorptions can be described as C-Cl (σ* → n) transitions within the valence shell, where n is the outermost lone-pair orbital of Cl and σ* is the anti-bonding carbon chlorine σ molecular orbital [6.11].

6.2.2.2 The 8.5 eV – 11.0 eV photon energy region

A strong vibrational structure is observed between 8.50 eV and 9.25 eV superimposed upon a broader band repulsive state (Figure 6.2). Such structure was first reported by Zobel and Duncan [6.15] albeit at a lower resolution.

The higher resolution in the present results allows assignment of the structure to a vibrational progression in the CCl stretching mode, v$_9$ ($b_2$), with a frequency ~ 0.0323 eV of the excited state, in agreement with Ibuki et al. [6.20].

The present data also reveals a longer vibrational progression of v$_9$ CCl$_2$ rocking mode with 16 peaks being clearly identified with the lowest being assigned to n = 0 (Table 6.3). The weak feature at 8.574 eV may however be ascribed to a hot band of the v$_9$ ($b_2$) vibrational mode and in this case an alternative labelling, n' may be given with the first term in the series allocated to peak position at 8.607 eV.
Figure 6.2 – Vibrational progressions in the 8.50 eV – 9.25 eV absorption band of dichlorodifluoromethane.

<table>
<thead>
<tr>
<th>n</th>
<th>n'</th>
<th>$n\nu_9$</th>
<th>$\Delta E (\nu_9)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>8.574</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>8.607</td>
<td>0.033</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>8.640</td>
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</tr>
<tr>
<td>3</td>
<td>2</td>
<td>8.673</td>
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</tr>
<tr>
<td>4</td>
<td>3</td>
<td>8.704</td>
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</tr>
<tr>
<td>5</td>
<td>4</td>
<td>8.734</td>
<td>0.030</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>8.768</td>
<td>0.034</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>8.800</td>
<td>0.032</td>
</tr>
<tr>
<td>8</td>
<td>7</td>
<td>8.831</td>
<td>0.031</td>
</tr>
<tr>
<td>9</td>
<td>8</td>
<td>8.862</td>
<td>0.031</td>
</tr>
<tr>
<td>10</td>
<td>9</td>
<td>8.894</td>
<td>0.032</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>8.926</td>
<td>0.032</td>
</tr>
<tr>
<td>12</td>
<td>11</td>
<td>8.955</td>
<td>0.029</td>
</tr>
<tr>
<td>13</td>
<td>12</td>
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</tr>
<tr>
<td>14</td>
<td>13</td>
<td>9.024</td>
<td>0.036</td>
</tr>
<tr>
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</tr>
<tr>
<td>16</td>
<td>15</td>
<td>9.090</td>
<td>0.030</td>
</tr>
</tbody>
</table>

Table 6.3 – Vibrational progressions in the 8.50 eV – 9.25 eV absorption band of CCl$_2$F$_2$ (energies in eV).
6.2.2.3 Rydberg series converging to the four lowest ionisation potentials

The four assignment in Table 6.4 are the Rydberg series converging to the four lowest ionisation potentials, $12.26 \ (X^2B_2)$, $12.53 \ (\tilde{A}^2B_1)$, $13.11 \ (B^2A_2)$ and $13.45 \ (\bar{C}^2A_1)$ eV, respectively.

The 8.50 eV - 11.00 eV band has a mixing character attributed to valence and $(4s \rightarrow 4b_2)$ Rydberg transitions corresponding to the 12.26 eV ionisation potential [6.20]. Molecular excitation in this region arises from $(n \rightarrow 4s)$ and $(n \rightarrow 4p)$ Rydberg transitions of the Cl lone pair electrons relating to the four lowest ionisation potentials found in accordance with the molecule’s symmetry. However it is shown in Table 6.4 that for the feature at 10.472 eV, a transition to a 3d orbital is possible and is in agreement with the calculated quantum defect ($\delta$).

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Quantum defect ($\delta$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>this work</td>
<td>this work</td>
<td>[6.20]</td>
</tr>
<tr>
<td>8.926</td>
<td>8.940</td>
<td>1.98</td>
</tr>
<tr>
<td>9.801</td>
<td>9.802</td>
<td>1.65</td>
</tr>
<tr>
<td>10.472</td>
<td>10.473</td>
<td>0.24</td>
</tr>
<tr>
<td>9.360</td>
<td>9.380</td>
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<tr>
<td>9.871</td>
<td>9.904</td>
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<tr>
<td>9.641</td>
<td>9.612</td>
<td>2.02</td>
</tr>
<tr>
<td>9.717</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10.472</td>
<td>10.473</td>
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</tr>
<tr>
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<td>-</td>
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<tr>
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</tr>
<tr>
<td>10.781</td>
<td>10.783</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Table 6.4 – Peak energy values, derived quantum defects and assignment of the Rydberg series converging to the four lowest ionisation potentials of CCl$_2$F$_2$ (energies in eV).

A set of two broad bands appear at 9.360 eV and 9.641 eV (Figure 6.3). These features may be assigned as $4s$ Rydberg transitions, with ionisation potentials of 12.53 eV and 13.11 eV, respectively (Table 6.4).

The sharp peak at 9.801 eV (with a local maximum cross section of 116 Mb) has been assigned to a $4p$ Rydberg transition (ionisation potential of 12.26 eV) and is in good agreement with the absolute differential oscillator strengths reported by Au et al. [6.16], the photo-absorption data of Ibuki et al. [6.20] and Jochims et al. [6.21] all of
which are higher than the data of Doucet et al. [6.10]; the features at 9.871 eV and 9.935 eV have been assigned to the 4p and 4s transitions, (ionisation potentials of 12.53 eV and 12.26 eV), respectively [6.20] (Table 6.4).

The broad features at 10.472 eV and 10.781 eV may be interpreted as the 3d and 4p bands related to the 12.26 eV and 13.45 eV ionisation potentials, respectively. However, due to the cut-off in the transmission of the CaF\textsubscript{2} window the position of the latter feature’s maximum is unclear. In addition, two weak shoulders at 10.01 eV and 10.07 eV – 10.09 eV have been reported for the first time [6.19]. These electronic transitions are accompanied by the vibrational excitation of the \nu\textsubscript{2} normal mode with a frequency of \sim 0.075 eV, which is quite similar to that observed in the ionic electronic ground state, 0.074(4) eV (\sim 600 cm\textsuperscript{-1}) [6.8], and for the latter (10.08 eV) tentatively assigned as 4s0 + 2\nu\textsubscript{2} (Table 6.4).

![Figure 6.3- Assignment of Rydberg series converging to the four lowest ionisation potentials. Also shown the valence \sigma^* \leftarrow 4b_2 transitions.](image)

Absolute photo-absorption cross sections have been reported by several groups, these have been reviewed and recommended values for \lambda \geq 170 nm are listed in the NASA atmospheric data base [6.22]. Again our absolute cross section values are in good agreement with those derived by Au et al. [6.16], Ibuki et al. [6.20] and Gilbert et al. [6.11], but lower than those of Jochims et al. [6.21]. The NASA recommended values are plotted in Figure 6.3 and compared to the present results. The two data sets
are in excellent agreement, and recently, the present cross sectional values presented in this thesis have been recommended for use in the latest edition of NASA Chemical Kinetics and Photochemical Data for use in Atmospheric Studies [6.23].

6.2.3 Photolysis rates and local lifetimes

The photolysis rates of CCl₂F₂ may be evaluated as the product of the solar actinic flux [6.22] and the molecular photo-absorption cross section at different altitudes and wavelengths (chapter 3, section 3.2.5.3). The total rates shown in Figure 6.4 are the summations over the wavelength range of these partial rates (Figure 6.5) assuming that the quantum yield for photo-dissociation is unity.

Figure 6.4— The photolysis rates (s⁻¹) and the lifetimes (Days) for dichlorodifluoromethane as a function of altitude in Earth's atmosphere.
The local lifetime to photolysis at a given altitude, also shown in Figure 6.4, is thence simply reciprocal of the total photolysis rate. The lifetimes calculated are for a molecule with fixed altitude in a sunlit, clear sky atmosphere.

While there is a fairly substantial photolysis rate at the higher altitudes leading to a correspondingly short lifetime of a few days, at lower altitudes the lack of solar actinic flux at the absorption wavelengths of this molecule leads to an extremely long lifetime. It is this long lifetime at low altitudes coupled with its strong infrared absorption properties that make CCl$_2$F$_2$ such a strong greenhouse gas. However the fairly short lifetimes at 40 km and 50 km indicate that the molecule can be broken up fairly easily leading to liberation of the constituent halogens, which can then participate in ozone destruction in the stratospheric regions (see section 6.2.4).

![Figure 6.5 - The photolysis rates (s$^{-1}$ nm$^{-1}$) vs. wavelength (nm) and photon energy (eV) for dichlorodifluoromethane as a function of altitude (0 – 50 km) in Earth’s atmosphere.](image)

The photo-dissociation rates of $3 \times 10^8$ s$^{-1}$ at an altitude of 30 km reported by Molina and Rowland [6.26] are in good agreement with the present calculations at a wavelength $\lambda \approx 200$ nm (and 30 km altitude) predicting a value of $\sim 2 \times 10^8$ s$^{-1}$ (Figure 6.5). However with the inherent limitations of the present model (chapter 3, section 3.2.5.3), where e.g. diffusion and transport mechanisms are not taken into account, the
obtained profiles and their absolute values are however not far from those reported by Molina and Rowland [6.26].

6.3 Environmental evaluation

6.3.1 CCl₂F₂ photo-dissociation

Photo-dissociation of CFCs in the stratosphere produces significant amounts of halogen radicals (equation 6.1) which catalytically lead to the destruction of ozone (equation 6.2) [6.4, 6.5, 6.26].

\[ \text{CCl}_2\text{F}_2 + \text{hu} \rightarrow \text{CCIF}_2 + \text{Cl} \]  (6.1)

In addition, these molecules are efficient greenhouse gases, as they absorb thermal radiation in the spectral region of the atmospheric "window", between about 8 µm and 13 µm. CCl₂F₂ is an almost inert gas in the troposphere and consequently accumulates in the lower atmosphere and gradually penetrates into higher layers of the atmosphere. Halogen atoms (chlorine) thereby released convert odd oxygen species, O₃ and O, to molecular oxygen, O₂ through catalytic reaction cycles via a (Cl, ClO) chain (eq. 6.2 and eq. 6.3) [6.4, 6.26]:

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]  (6.2)
\[ \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \]  (6.3)

and under most conditions in the Earth's atmospheric ozone layer, (6.3) is the slower of the reactions because there is a much lower concentration of O than of O₃. Cl atoms are unable to remain permanently at stratospheric altitudes, either in the form of atoms or in some other chemical form, and are eventually removed by diffusion into the tropopause, below which they can undergo other reactions by the weather processes occurring there. This process of diffusion is presumed to occur with the various chlorine-containing species existing almost entirely in gaseous form. The competition between photolysis and upward diffusion reduces the relative concentration of CFCs at higher altitudes and the concentrations should be very low above 50 km. The peak rate of destruction and formation of Cl atoms, occurs at 25 km - 35 km, in the region of high ozone concentration.

Reactions with tropospheric OH radicals do not seem to be the primary sink for CFCs but rather a sink for hydrogen-containing compounds. As an example, the 0.82
ODPs for CFC-12, is considerably higher than 0.04 for CF$_2$HCl, the difference reflecting the more effective chemical removal in the troposphere [6.27].

The appearance energies (AE) of the ions formed following VUV photo-excitation of the transient parent ion, (CCl$_2$F$_2$)$^+$, were obtained by TPEPICO spectroscopy technique, showing considerable evidence of state-selective fragmentation at low energies. It is also well established that due to secondary effects such as electron-ion recombination resulting in the variation of ionisation cross section with energy close to threshold, energy thresholds are more accurately measured using photon sources [6.25]. Therefore, CF$_2$Cl$^+$, CFCl$_2^+$, CF$_2^+$, CFCI$^+$ and CF$^+$ fragment ions were detected, while neither the parent ion nor the fragments CCl$^+$ and CCl$_2^+$ were observed [6.24]; though the two most important reaction pathways are:

$$\text{CCl}_2\text{F}_2 + \text{hv} \rightarrow (\text{CClF}_2)^+ \left( \tilde{A}^2\text{B}_1 \right) + e^- \rightarrow \text{CF}_2\text{Cl}^+ + \text{Cl} + e^- \quad (6.4)$$

$$\text{AE} = (11.95 \pm 0.05) \text{ eV}$$

$$\text{CCl}_2\text{F}_2 + \text{hv} \rightarrow (\text{CClF}_2)^+ \left( \tilde{C}^2\text{A}_1 \right) + e^- \rightarrow \text{CFCl}_2^+ + \text{F} + e^- \quad (6.5)$$

$$\text{AE} = (14.2 \pm 0.3) \text{ eV}$$

Since the lowest dissociation threshold, CCl$_2$F$_2$ → CF$_2$Cl$^+$ + Cl + e$^-$, lies at 11.76 eV, the majority of the Franck-Condon region of the CCl$_2$F$_2^+$ $\tilde{X}^2\text{B}_2$ ground state, with an IP = 12.26 eV, is dissociative and, as a consequence is not detected. In fact this is not surprising since the absorption spectrum around 7.0 eV is structureless and the molecule photo-dissociates with a unit quantum yield [6.28], the major channel being Cl atom elimination.

### 6.3.2 Dissociative electron attachment to condensed CCl$_2$F$_2$

In the previous section the direct mechanisms by chemical reactivity or by the precursor molecule's previous photo-dissociation have been evaluated. Indirect processes that can lead to ozone depletion are close related to chemi-adsorption of molecules to the surface of ices as it has been discussed in Chapter 5 for SF$_3$CF$_3$.

In the Antarctic vortex (Chapter 1), the measured ClO abundance of the order of 1 ppbv is several hundred times greater than the usual concentration (0.01 ppbv) in the general stratosphere. It is known that the origin of the ozone hole is closely related to the existence of polar stratospheric clouds (PSCs) or polar stratospheric clusters consisting of water ice and nitric acid/water ice in the Antarctic stratosphere due to low temperatures. It has been accepted by the scientific community, that heterogeneous
chemical reactions occurring on the surfaces of PSCs play a dominant role, and for the particular case of chlorine molecules, the most important reaction is believed to be [6.29]:

\[ \text{HCl}(s) + \text{ClONO}_2(g) \rightarrow \text{Cl}_2(g) + \text{HNO}_3(s) \]  

(6.6)

which converts chlorine from the inactive compounds (HCl and ClONO\(_2\)) into reactive Cl\(_2\) (s, solid; g, gas phase). Upon photolysis, Cl\(_2\) releases Cl to destroy O\(_3\) via eq. (6.1). Recent experiments [6.29] show that the reaction mechanism is ionic in nature, which in turn means that solvated Cl\(^-\) (rather than molecular HCl) on PSCs surfaces plays a crucial role in the reaction to produce Cl\(_2\).

Lu and Madey [6.29] found that F\(^-\) and Cl\(^-\) yields produced by the impact of high energy electrons (250 eV) on CCl\(_2\)F\(_2\) adsorbed on a metal Ru surface were enhanced by several orders of magnitude when co-adsorbed with water and ammonia (precursors). They also postulated that, following the production of low-energy secondary electrons from the metal substrate and ice, the enhancement in anion desorption was due to the transfer of self-trapped electrons from the ice (H\(_2\)O or NH\(_3\)) to CCl\(_2\)F\(_2\) molecules that then dissociated, which has been observed to follow the same trend in experiments on water ices grown on Kr [6.30]; however experiments on condensed CCl\(_2\)F\(_2\) with 0 – 20 eV electrons did not show any enhancement in anion desorption upon co-adsorption of H\(_2\)O and NH\(_3\) but rather a decrease [6.31]. These contradictory results can be attributed to differences in the experimental technique and design, and the former data have been recently confirmed and verified using a charge trapping method [6.30].

There is a large probability for transfer of the electron from these precursors to CCl\(_2\)F\(_2\) to form a CCl\(_2\)F\(_2\)\(^-\) that dissociates or relaxes to stabilise the negative charge. In fact, stable dichlorodifluoromethane anion has been reported in cluster phase experiments by Langer et al. [6.31].

Illenberger and co-workers [6.30] have shown that electron-induced dissociation of CCl\(_2\)F\(_2\) molecules with low-energy electrons (~ 0 eV) is an extremely efficient process:

\[ e^-(e) + \text{CCl}_2\text{F}_2 \rightarrow \text{Cl}^- + \text{CClF}_2 \]  

(6.7)

On the other hand it is also known that the electron-induced dissociation cross section, (6.7), is \(\sim 10^4\) times higher than the photo-dissociation cross section, (6.1). Actually in the higher altitudes of the stratosphere, the free electron concentration drops sharply
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with decreasing altitude, from \(~ 10^3\) electrons cm\(^{-3}\) at \(~ 85\) km to less than 10 electrons cm\(^{-3}\) at \(\leq 60\) km [6.27]. Most free electrons are replaced by negative ions with increasing atmospheric density. The electron-induced dissociation processes are thus believed to be important for CFCs in the general atmosphere. However the case may be different in the winter Antarctic stratospheric vortex because of the existence of PSC ices [6.31].

In the stratosphere, the primary source of electrons is the ionisation of the atmospheric constituents by galactic cosmic rays or solar radiation. PSCs or polar molecular clusters are expected to contain self-trapped electrons that can cause CFC-12 dissociation to produce CI\(^-\) (6.7). The following reactions are known to be fast [6.34]:

\[
\text{OH} + \text{Cl}^- \leftrightarrow \text{HOCI}^- \\
\text{HOCI}^- + \text{H}^+ \rightarrow \text{Cl} + \text{H}_2\text{O} \\
\text{Cl}^- + \text{NO}_3 \rightarrow \text{Cl} + \text{NO}_3^- \\
\text{Cl}^- + \text{HOCI} + \text{H}^+ \rightarrow \text{Cl}_2 + \text{H}_2\text{O}
\]

(6.8) \hspace{1cm} (6.9) \hspace{1cm} (6.10) \hspace{1cm} (6.11)

Due to the abundances of OH, H\(^+\), NO\(_3\), and other radicals in the stratosphere, the Cl\(^-\) desorbing anion is rapidly converted to Cl atoms which then participate in (Cl, ClO) reaction cycles (eqs. 6.2 and 6.3) to destroy the ozone layer [6.34]. Cl\(^-\) ions which cannot desorb to an image/polarisation potential attraction are adsorbed at the surface of the PSCs. There is evidence that Cl\(^-\) ions adsorbed (solvated) at the surface of PSCs can react with other species to release photo-chemically reactive Cl\(_2\) or ClNO\(_2\) [6.29], by:

\[
\text{Cl}^- + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{NO}_3^- \\
\text{Cl}^- + \text{N}_2\text{O}_5 \rightarrow \text{ClNO}_2 + \text{NO}_3^- \\
\text{Cl}^- + \text{HNO}_3 \rightarrow \text{HCl} + \text{NO}_3^-
\]

(6.12) \hspace{1cm} (6.13) \hspace{1cm} (6.14)

where the reactions of eqs. (6.12) – (6.14) are fast with reaction rates of \(~ 10^{-9}\) cm\(^3\) s\(^{-1}\) at 300 K [6.35]. In sum, upon photolysis, Cl\(_2\) or ClNO\(_2\) releases reactive chlorine to destroy O\(_3\).

6.4 Summary

The photo-absorption spectrum of CCl\(_2\)F\(_2\), has been measured using synchrotron radiation in the range of 5.5 eV – 11 eV (225 nm > \(\lambda\) > 110 nm). Electronic state assignments have been suggested for each of the observed absorption bands
incorporating both valence and Rydberg transitions. The high resolution achieved has allowed vibrational series in one of these bands to be assigned for the first time. The measured VUV cross sections were used to derive the photolysis rate of CCl$_2$F$_2$ in the terrestrial atmosphere.

Implications for the atmospheric ozone depletion and related mechanisms were evaluated in the gas phase and condensed phase. Analyses of air sample from remote locations revealed that tropospheric chlorine attributable to anthropogenic halocarbons peaked near the beginning of 1994 and was decreasing at a rate of 25 ± 5 ppt yr$^{-1}$ by mid-1995; halogen concentrations were still increasing in mid-1995, but the total abundance decreasing. The amount of reactive chlorine will have maximized in the stratosphere between 1997 and 1999 and will decline thereafter if limits outlined in the adjusted and amended Montréal Protocol are not exceeded in future years [6.27].
6.5 References


Chapter 7

Electronic and vibrational excitation of CH$_3$CN and C$_2$H$_3$CN

It is by intuition that we discover and by logic that we prove.

Henri Poincaré (1854 – 1912)

7.1 CH$_3$CN & C$_2$H$_3$CN and their sources in the terrestrial atmosphere

This chapter reports the results of VUV photo-absorption experiments performed on acetonitrile, CH$_3$CN, and acrylonitrile, C$_2$H$_3$CN. Several previously unreported bands have been observed and assigned. The measured cross sections have been used to calculate the atmospheric lifetimes of both compounds. In addition dissociative electron attachment experiments on CH$_3$CN are reported.

Acetonitrile, also known as methyl cyanide and ethanenitrile, is an important industrial gas. Though also used to make pesticides, its major application lies in the extraction of inorganic and organic chemicals, most importantly butadiene [7.1]. Acetonitrile also has the potential to be a tracer for biomass burning, considered the dominant source of the compound in the atmosphere [7.2]. In 1999, the global emission of acetonitrile from biomass burning was estimated to be between 0.4 and 1.0 Tgy$^{-1}$ [7.3], compared to 0.02 Tgy$^{-1}$ from fossil fuel burning [7.4]. Chemically relatively inert, it has been observed in the stratosphere at concentrations of 110 pptv to 160 pptv [7.5]. CH$_3$CN is also an important molecular species observed in gas clouds of the interstellar medium [7.6] where it is believed to be synthesized by heterogeneous chemistry on interstellar dust grains. It is therefore recognised as a fundamental building block of the amino acids and thus an important precursor molecule in the study of the origins of life [7.7]. Hence it is important to study those mechanisms by which acetonitrile may be
dissociated through the interactions with photons [7.8], electrons [7.9] and surfaces [7.10].

Acrylonitrile, otherwise known as vinyl cyanide and 2-propenitrile, does not occur naturally but is produced in great quantities industrially [7.11]. World production in 2000 was estimated at 4.6 million metric tons [7.12]. The compound is used primarily in the manufacture of acrylic fibres and as a raw material in the fabrication of plastics, nitrile rubbers and barrier resins. It also has applications in microelectronics as electrochemically thin films of the molecule can be deposited onto metallic substrates [7.13]. Acrylonitrile is released into the environment as gas and in waste water during its production and use. Other sources include auto-exhaust and release from fibres and plastics [7.14]. Due to the carbon-carbon double bond, acrylonitrile is expected to show enhanced reactivity towards atmospheric photo-oxidation by hydroxyl radicals and other oxidants.

The roles of acetonitrile and acrylonitrile in the atmosphere are not well understood. In particular, the residence times of the species in the stratosphere are subject to large errors. The mechanisms for airborne destruction of CH₃CN and C₂H₃CN therefore need to be re-examined. The VUV photo-absorption spectrum of acrylonitrile presented in this thesis represents the highest resolution data yet published. Both results reveal new spectral detail and should allow a better estimate of the molecules' atmospheric lifetimes by photolysis.

7.2 VUV photo-absorption of acetonitrile, CH₃CN

7.2.1 Introduction

The absorption spectrum was taken using the closed photo-absorption cell (Chapter 3, section 3.2.3) with an absorption path length of 25 cm. The spectrum was recorded in 11 nm sections, in 0.1 nm steps. The sample used in this investigation was obtained from Sigma Aldrich, with a purity of 99.5%. No further purification was undertaken except for freeze-thaw-pump cycles.

The acetonitrile spectrum was recorded over the sample pressure range 0.008 torr - 0.375 torr (Table 7.1), with typical attenuations of 10%. Higher pressures were used in order to observe the low intensity features at 7.0 eV – 9.0 eV. The results presented in the following sections are a definitive series of measurements to determine
both the absolute photo-absorption cross section and to classify its electronic spectroscopy over the energy range from 7.0 eV to 11.0 eV [7.15].

Results are also compared to electron energy loss (EEL) spectra taken at the Université de Liège by Gochel-Dupuis et al. [7.16] with an overall energy resolution quoted to be around 30 meV.

<table>
<thead>
<tr>
<th>Energy range (eV)</th>
<th>Wavelength (nm)</th>
<th>Pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.88 – 5.64</td>
<td>220 – 320</td>
<td>0.900</td>
</tr>
<tr>
<td>5.39 – 8.00</td>
<td>155 – 230</td>
<td>0.038</td>
</tr>
<tr>
<td>7.13 – 8.11</td>
<td>153 – 174</td>
<td>0.150</td>
</tr>
<tr>
<td>8.05 – 8.67</td>
<td>143 – 154</td>
<td>0.150</td>
</tr>
<tr>
<td>8.61 – 9.32</td>
<td>133 – 144</td>
<td>0.075</td>
</tr>
<tr>
<td>9.25 – 10.97</td>
<td>113 – 134</td>
<td>0.008 / 0.015 / 0.038</td>
</tr>
</tbody>
</table>

Table 7.1 – Photon energy (eV), wavelength (nm) and pressure (torr) ranges for acetonitrile photo-absorption measurements.

7.2.2 Results

The high resolution photo-absorption cross section spectrum of CH$_3$CN is shown in Figure 7.1 in the energy range 4.0 eV – 11.0 eV and is composed of an absorption band with low cross section below 9.5 eV, followed by a series of sharp more intense peaks. Details of the energy region 8.00 eV to 8.75 eV (are also plotted in the inset) to show the presence of vibrational structure. The dashed feature close to 11.0 eV is only partially recorded due to the cut-off in the transmission of the CaF$_2$ window (Chapter 3, section 3.2.2).

The ground state geometrical configuration of acetonitrile is based on the analysis of rotational constants and X-ray diffraction spectra [7.17, 7.18]. The molecule has C$_3v$ symmetry. The methyl carbon is $sp^3$ hybridised, forming an $\sigma$ bond with each of the hydrogen atoms and with the nitrogen bonding carbon atom, hybridised $sp$ [7.19]. The nitrogen atom is similarly $sp$ hybridised and forms one $\sigma$ and two mutually perpendicular $\pi$ bonds (C – C $\equiv$ N). The two remaining nitrogen electrons form a lone pair directed away from the molecule.
Figure 7.1 - VUV photo-absorption spectrum of acetonitrile in the energy region 4.0 eV to 11.0 eV.
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The fundamental vibrational energies with their symmetries were summarised by Shimanouchi [7.20] and are presented in Table 7.2. The electronic ground state configuration of CH$_3$CN may be represented as $(1a_1)^2 (2a_1)^2 (3a_1)^2 (4a_1)^2 (5a_1)^2 (6a_1)^2 (1e)^4 (7a_1)^2 (2e)^4$, giving a independent-particle configuration $\tilde{X}^1 A'$ [7.21]. Within the present analysis, features are assigned to five vibrational modes of excitation: $v_1$, $v_2$, $v_3$, $v_4$ and $v_5$. Of these modes, all but $v_5$ are symmetric.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Description</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1 (a_1)$</td>
<td>CH$_3$ symmetric stretch</td>
<td>0.366</td>
</tr>
<tr>
<td>$v_2 (a_1)$</td>
<td>C = N stretching</td>
<td>0.281</td>
</tr>
<tr>
<td>$v_3 (a_1)$</td>
<td>CH$_3$ symmetric deformation</td>
<td>0.172</td>
</tr>
<tr>
<td>$v_4 (a_1)$</td>
<td>C - C(N) stretching</td>
<td>0.114</td>
</tr>
<tr>
<td>$v_5 (e)$</td>
<td>CH$_3$ degenerate stretch</td>
<td>0.373</td>
</tr>
<tr>
<td>$v_6 (e)$</td>
<td>CH$_3$ degenerate deformation</td>
<td>0.180</td>
</tr>
<tr>
<td>$v_7 (e)$</td>
<td>CH$_3$ rocking</td>
<td>0.129</td>
</tr>
<tr>
<td>$v_8 (e)$</td>
<td>C - C = N bending</td>
<td>0.045</td>
</tr>
</tbody>
</table>

Table 7.2 – Acetonitrile ground state vibrational energies (eV).

The present photo-absorption cross section is in good agreement with that obtained from Suto and Lee [7.9], Nuth and Glicker [7.22], and with the EELS results of Gochel-Dupuis et al. [7.16]. Suto and Lee report their spectral resolution as 0.08 nm, over the range 106 nm to 180 nm (11.7 eV – 6.9 eV) [7.9]. Nuth and Glicker [7.22] reported the absolute absorption cross section over the wavelength range 60 nm to 160 nm (20.7 eV – 7.7 eV) with a resolution of 0.05 nm. However, despite our resolution (~0.075 nm at FWHM) apparently being no better than Nuth and Glicker's, the present acetonitrile spectrum shows more detail. In particular, the peak at 10.501 eV is more clearly defined in the present work [7.15] than in that of Nuth and Glicker. The spectrum of Suto and Lee shows no feature at 10.401 eV, although it is visible both in the present work and in that of Nuth and Glicker.

From around 6.8 eV, a broad feature rises with a maximum cross section of 9.180 Mb occurring at 9.350 eV followed by a series of strongly absorbing narrow peaks. These sharp peaks are assigned to Rydberg transitions [7.9, 7.16, 7.22, 7.23]. However, as with acrylonitrile (section 7.4), the present analysis is complicated by some overlapping between valence and Rydberg states. The LUMOs have been identified to
be the $3e$ anti-bonding $\pi^*_{\text{CN}}$ and the $8a_1$ anti-bonding $\sigma^*_{\text{CC}}$ and/or $\sigma^*_{\text{CH}}$ valence orbitals [7.24]. Excitation of an electron from an $e$ to an $e$ or $a_1$ orbitals leads to $A_1$, $A_2$, $E$ or $E$ states, while transition from an $a_1$ to an $e$ or $a_1$ orbital leads to $E$ or $A_1$ states, respectively.

The low energy feature above 7 eV is associated with the two possible valence transitions occurring for $2e - 3e (\pi \rightarrow \pi^*)$ and $7a_1 - 3e (n_H \rightarrow \pi^*)$ superimposed on a background caused by pre-dissociation [7.16]. Although no absorption is observed in the present work below 7 eV, it should be noted that Gochel-Dupuis et al. [7.16] reported features at low energies, associated with optically forbidden excitations.

### 7.2.2.1 The 7.8 eV – 9.0 eV energy region valence excitation

The absorption cross section in this energy range is shown in detail in Figures 7.2 and 7.3. The structure is considered to be caused by the transition $2e - 3e (\pi \rightarrow \pi^*)$. Analysis of the peaks suggests the presence of $\nu_1$, $\nu_2$ and $\nu_3$ series beginning around 7.950 eV, the energy loss at which Gochel-Dupuis et al. [7.16] observe a small peak using incident electrons of 25 eV and a scattering angle of 30°, attributable to an optically forbidden excitation [7.25]. Therefore, the transition is tentatively assigned at 7.970 eV, the energy that appears to best match the pattern of vibrational structure observed in the present analysis.

![Figure 7.2 – Photo-absorption spectrum in the 7.8 eV – 9.0 eV band of CH$_3$CN.](image-url)
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Table 7.3 lists the energies of the features observed between 7.9 eV and 9.0 eV. Gochel-Dupuis et al. [7.16] propose the presence of $\nu_2$ progressions starting at 7.950 eV and 8.440 eV. Structure observed for the first time in this work leads us to suggest further sets of assignments in agreement with the symmetry-allowed components of the $\pi \rightarrow \pi'$ transition ($2e - 3e$).

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Assignment</th>
<th>Energy (eV)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>[7.16]</td>
<td>This work</td>
<td>[7.16]</td>
</tr>
<tr>
<td>7.970</td>
<td>$\nu_{00}$</td>
<td>8.510(?)</td>
<td>$2\nu_2 + 2\nu_8$</td>
</tr>
<tr>
<td>8.090 (?)</td>
<td>$\nu_3$</td>
<td>8.598</td>
<td>-</td>
</tr>
<tr>
<td>8.230 (?)</td>
<td>$2\nu_3$</td>
<td>8.640 (?)</td>
<td>$3\nu_2$</td>
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<td>8.321</td>
<td>$\nu_1$</td>
<td>8.713</td>
<td>$3\nu_2 + \nu_7$</td>
</tr>
<tr>
<td>8.460 (?)</td>
<td>$\nu_1 + \nu_3$</td>
<td>8.731</td>
<td>-</td>
</tr>
<tr>
<td>8.574</td>
<td>$\nu_1 + 2\nu_3$</td>
<td>8.818</td>
<td>$3\nu_2 + 4\nu_8$</td>
</tr>
<tr>
<td>8.660 (?)</td>
<td>$2\nu_1$</td>
<td>8.856</td>
<td>-</td>
</tr>
<tr>
<td>8.800</td>
<td>$2\nu_1 + \nu_3$</td>
<td>8.933</td>
<td>$4\nu_2 + \nu_7$</td>
</tr>
<tr>
<td>8.920 (?)</td>
<td>$2\nu_1 + 2\nu_3$</td>
<td>8.440 (?)</td>
<td>$\nu_{00}$</td>
</tr>
<tr>
<td>8.991</td>
<td>$\nu_{31}$</td>
<td>8.527</td>
<td>$2\nu_8$</td>
</tr>
<tr>
<td>8.060 (?)</td>
<td>$2\nu_8$</td>
<td>8.551</td>
<td>$\nu_3$</td>
</tr>
<tr>
<td>8.140 (?)</td>
<td>$4\nu_8$</td>
<td>8.620 (?)</td>
<td>$4\nu_8$</td>
</tr>
<tr>
<td>8.190 (?)</td>
<td>$\nu_2$</td>
<td>8.682</td>
<td>$\nu_2$</td>
</tr>
<tr>
<td>8.277</td>
<td>$\nu_2 + 2\nu_8$</td>
<td>8.756</td>
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<tr>
<td>8.366</td>
<td>$\nu_2 + 4\nu_8$</td>
<td>8.775</td>
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</tr>
<tr>
<td>8.411</td>
<td>$2\nu_2$</td>
<td>8.880 (?)</td>
<td>$\nu_2 + 4\nu_8$</td>
</tr>
<tr>
<td>8.490</td>
<td>$2\nu_2 + \nu_7$</td>
<td>8.933 (?)</td>
<td>$2\nu_2$</td>
</tr>
</tbody>
</table>

Table 7.3 - Vibrational assignments in the 7.9 eV - 9.0 eV absorption band of CH$_3$CN corresponding to the $(2e - 3e) \pi \rightarrow \pi'$ transition.

From 7.970 eV there appears to be two overlapping series of vibrational excitations. The first is associated with $\nu_1$, corresponding to C - H stretching, with a limited $\nu_3$ series beginning at each $\nu_1$ peak. The mode $\nu_3$ is symmetric and characterised by CH$_3$ deformation. The second series is attributed to vibrational excitation consistent with C $\equiv$ N bending, the $\nu_2$ mode. It has been proposed that double excitations of the anti-symmetric $\nu_8$ mode, corresponding to C - C $\equiv$ N bending, combine with the $\nu_2$ progression to give further small peaks [7.15]. In agreement with Gochel-Dupuis et al. [7.16], a $\nu_2$ excitation beginning at 8.440 eV is identified. The diffuse feature observed at 8.933 eV and attributed to a Rydberg transition (Figure 7.3) may include a $2\nu_2$
contribution from this series. As with the previous series, combinations of double $u_8$ excitations are suggested to account for further peaks and shoulders. The CH$_3$ rocking mode excitation ($u_7$) seems to be excited but coupled with the C = N stretching mode, $u_2$ ($a_1$).

7.2.2.2 The 8.9 eV – 9.5 eV energy region valence excitation

The valence transition ($7a_1 - 3e$) n$_N$ $\rightarrow \pi^*$ to the singlet state $^1E$ is considered to be responsible for the series of peaks beginning at 8.965 eV. The absorption spectrum for this energy range is shown in Figure 7.3. Gochel-Dupuis et al. [7.16] report three quanta of vibration with 0.110 eV mean spacing which they attribute to excitation of the $u_7$ mode, CH$_3$ rocking.

![Figure 7.3 – Photo-absorption spectrum in the 8.5 eV – 9.5 eV band of CH$_3$CN and first Rydberg series converging to 12.21 eV ionisation potential.](image)

At higher energies (> 9 eV), a structure is observed for the first time in the present work, which may be assigned to a $u_4$ series, corresponding to C – C stretching, combined with double excitations of the mode $u_8$ [7.15]. The observed peaks and their suggested assignments are listed in Table 7.4. The feature observed at 9.315 eV remains unassigned.
Table 7.4 - Vibrational assignments in the 8.9 eV - 9.5 eV absorption band of CH$_3$CN corresponding to the $(7a_i - 3e)$ $\eta_N \rightarrow \pi ^*$ transition.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Assignment</th>
<th>Energy (eV)</th>
<th>Assignment</th>
</tr>
</thead>
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<td>This work</td>
<td>[7.16]</td>
</tr>
<tr>
<td>8.965</td>
<td>$\nu_{98}$</td>
<td>9.301</td>
<td>$2\nu_4 + 4\nu_8$</td>
</tr>
<tr>
<td>9.103</td>
<td>-</td>
<td>9.315</td>
<td>-</td>
</tr>
<tr>
<td>9.063</td>
<td>9.07</td>
<td>9.340 (?)</td>
<td>-</td>
</tr>
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<td>9.123</td>
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<td>9.164</td>
<td>9.18</td>
<td>9.440 (?)</td>
<td>-</td>
</tr>
<tr>
<td>9.232</td>
<td>-</td>
<td>9.470 (?)</td>
<td>-</td>
</tr>
</tbody>
</table>

7.2.2.3 Rydberg series converging to 12.21 eV and 13.14 eV IPs

According to the symmetry elements for CH$_3$CN (section 7.2.2), the Rydberg series will be $nsa_i$, $npa_i$, $npe$, $nda_i$ and $nde$ corresponding to $n\sigma$, $np\sigma$, $np\pi$, $nd\sigma$ and $nd\pi$ series, respectively, in the pseudo-diatomic model with the $z$ axis on the CN internuclear axis [7.16].

Figure 7.4 shows the absorption observed between 9.5 eV and 11.0 eV where Rydberg transitions are known to occur. The suggested series converge to 12.21 eV and 13.14 eV, corresponding to the ionic electronic ground state and the ionic first excited state of CH$_3$CN, respectively [7.26].

The peak energies assigned to series converging to 12.21 eV are given in Table 7.5. The low energy, low intensity peak at 8.933 eV (shown in Figure 7.3) is assigned to the Rydberg transition $3\sigma$ as suggested by Nuth and Glicker [7.22]. The three peaks at 9.589 eV, 9.747 eV and 10.289 eV are attributed to the $n = 3$ transition of the $np\pi$, $n\sigma$ and $nd\sigma$ series converging to the ionic electronic ground state [7.16, 7.22]. In agreement with Gochel-Dupuis et al. [7.16], it has been suggested that vibrational progressions coupled with Rydberg peaks are responsible for further structure [7.15]. The vibrational modes suggested are $\nu_2$ and $\nu_4$, related to C = N stretching, and C - C stretching, respectively. This is consistent with the photoelectron work of Turner et al. [31] which shows the energy required for the excitation of $\nu_2$ and $\nu_4$ in the first ionic state to be 0.249 eV and 0.100 eV, very close to the energy differences observed in the present spectra. Table 7.6 gives the energies of the peaks assigned to Rydberg series converging
to the second ionisation potential, 13.14 eV. In accordance with Gochel-Dupuis et al. [7.16] the peaks at 10.489 eV and 10.772 eV are both attributed to the n = 3 transitions in the \( np\sigma \) and \( np\lambda \) series, respectively.

![Figure 7.4 - Assignment of the CH\(_3\)CN Rydberg series converging to the ionisation potentials 12.21 eV and 13.14 eV.](image)

### Table 7.5

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Quantum defect ( (\delta) )</th>
<th>Assignment</th>
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</thead>
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<td>This work</td>
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<td>[7.22]</td>
</tr>
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<td>-</td>
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<td>10.060</td>
<td>10.056</td>
</tr>
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<td>10.171</td>
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</tr>
<tr>
<td>9.747</td>
<td>9.745</td>
<td>9.678</td>
</tr>
<tr>
<td>9.786</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9.983</td>
<td>9.973</td>
<td>9.983</td>
</tr>
<tr>
<td>10.255 (?)</td>
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<td>10.286</td>
<td>10.292</td>
</tr>
<tr>
<td>10.401</td>
<td>10.415</td>
<td>-</td>
</tr>
<tr>
<td>10.534 (?)</td>
<td>10.531</td>
<td>10.501</td>
</tr>
<tr>
<td>10.643 (?)</td>
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<tr>
<td>10.735 (?)</td>
<td>-</td>
<td>10.744</td>
</tr>
</tbody>
</table>

Table 7.5 – Energy values, quantum defect and assignment of the Rydberg series converging to the 12.21 eV ionic electronic ground state of CH\(_3\)CN.
Previously unassigned features at 10.588 eV and 10.707 eV are attributed to vibrational excitations of the modes \( \nu_4 \) and \( \nu_2 \) combined with the Rydberg transition at 10.489 eV, noted as having symmetry \( a_1 \). The feature observed at 9.709 eV remains unassigned while that at 9.786 eV is proposed to be due to excitation of one quantum of \( \nu_8 \) despite its anti-symmetric nature (Table 7.5).

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Quantum defect (( \delta ))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.489</td>
<td>0.74</td>
<td>3p( \sigma )</td>
</tr>
<tr>
<td>10.588 (?)</td>
<td>-</td>
<td>3p( \sigma + \nu_4 )</td>
</tr>
<tr>
<td>10.707 (?)</td>
<td>-</td>
<td>3p( \sigma + \nu_2 )</td>
</tr>
<tr>
<td>10.772</td>
<td>0.60</td>
<td>3p( \lambda )</td>
</tr>
</tbody>
</table>

Table 7.6 – Energy values, quantum defect and assignment of the Rydberg series converging to the 13.14 eV ionic electronic first excited state of CH\(_3\)CN.

A more detailed analysis on the photo-absorption spectrum in Figure 7.4 reveals that the broad feature at 9.840 eV assigned to 3p\( \pi \) + \( \nu_2 \) is probably composed by the superposition of the \((2e - 3e) \pi \rightarrow \pi^*\) transition and in agreement with Gochel-Dupuis et al. [7.16] suggesting the \(^1\Sigma^+\) (in the C\(_{ov}\) symmetry point group) state at 9.8 eV.

Comparison is made between the photo-absorption cross section of acetonitrile reported in the present work with that of Suto and Lee [7.9]. The two sets of data are found to be in agreement to within the error of Suto and Lee. However, analysis of the three highest peaks, at 9.589 eV, 9.840 eV and 10.772 eV, shows the data in this work to be 10 to 20% higher than Suto and Lee. This may be due to higher energy resolution achieved for the present spectrum (~ 0.075 nm FWHM). The major peaks appear sharper in the present work and, importantly, absorption at 9.589 eV is greater than at 10.772 eV whereas Suto and Lee observe the opposite trend. The only other photo-absorption data for acetonitrile published for photon energies coinciding with the range presented in this thesis is the work of Nuth and Glicker [7.22]. Suto and Lee consider their result to agree with that of Nuth and Glicker to within the experimental uncertainties [7.9]. However, in agreement with the present data, Nuth and Glicker clearly show the cross section at 9.589 eV to be greater than at 10.772 eV. Thus, it can be concluded that the present spectrum is broadly consistent with previous photo-
absorption results although it reveals stronger absorption for narrow features, suggesting higher energy resolution in the present work.

### 7.2.3 Environmental evaluation for acetonitrile

Suto and Lee estimate the photolysis rate of acetonitrile to be very slow in the troposphere and less than $10^{11}$ s$^{-1}$ in the stratosphere [7.9]. Thus, low altitude destruction of acrylonitrile is dominated by reactions with atmospheric species. In particular, the stratospheric reaction rate of CH$_3$CN + OH is estimated to be $10^7$ s$^{-1}$ using the data of Kurylo and Knable [7.27] and Heicklen [7.28]. No meaningful result could be achieved using the model described in Chapter 3 (section 3.2.5.3) as the absorption of acetonitrile is extremely weak below 7 eV. Minimal solar radiation above 7 eV is observed in the stratosphere and troposphere (section 3.2.5.3). The Lyman α peak for solar radiation (121.6 nm), considered the key region for photolysis of acetonitrile in the upper atmosphere, is very close to the absorption peak at 9.840 eV, observed to be around 20% stronger in the present spectrum than in that of Suto and Lee. Thus it is predictable a slightly higher photolysis rate at high altitudes than that estimated previously whilst expecting that the overall atmospheric destruction of acetonitrile occurs dominantly through chemical reactions.

### 7.3 Low energy electron attachment to CH$_3$CN

#### 7.3.1 Introduction

To date there appears to have been only a few studies of electron attachment to CH$_3$CN, including the early work of Tsuda et al. [7.27] and Stockdale et al. [7.28]. Tsuda et al. [7.27] reported for three different electron energies (80, 40 and 9.5 eV) using a standard experimental set-up (with no means to reduce the electron energy distribution from the hot rhenium filament) relative anion abundances. At the energy of 9.5 eV which is of interest in the present study they observed only the presence of CN$^-$. Stockdale et al. [7.28] using a retarding potential difference electron gun (with an energy resolution of about 500 meV) in conjunction with a time of flight mass spectrometer reported relative attachment efficiency curves in the energy range from about 0 to 30 eV for the CH$_2$CN$^-\$ and the CN$^-$ ions. The position of the CH$_2$CN$^-$ peak at 4 eV is in agreement with an earlier observation and a mass 41 peak at the same energy can be accounted for in terms of the expected abundance of CH$_2$CN$^-$ containing one $^{13}$C
Chapter Seven

atom. Stockdale et al. [7.28] show that the mass 41 signal observed in the region above about 8 eV is too great to be accounted for in terms of CH$_2$CN containing one $^{13}$C atom and arrive at the conclusion that in this energy regime also the parent anion is being produced. A more comprehensive study of halogenic-nitrile compounds using a crossed beam arrangement with an energy resolution of 200 meV was reported by Heni and Illenberger [7.29] including relative attachment efficiency curves up to 16 eV for the five anions CH$_2$CN', CN', CHCN', C$_2$N' and CH$_3$'. It has been shown recently [7.30] that anions formed in electron impact with acetonitrile have virtually no kinetic energy ($< 0.1$ eV) and may therefore be detected with high efficiency with modest extraction fields. This fact should make it possible (see below) to measure absolute anion formation cross sections without discrimination.

A comprehensive study of the dissociation patterns of acetonitrile by low energy electrons using a high resolution crossed beam apparatus is reported here. The first absolute cross sections are reported and mechanisms for the formation of electron scattering resonances are discussed for CH$_2$CN', CN', CHCN', C$_2$N' and CH$_3$' fragment ions. In agreement with the work of Illenberger and co-workers the negative parent ion, CH$_3$CN', has not been detected, probably because the lifetime of the ion with respect to ejection of the extra electron (the auto-detachment lifetime) is shorter that the flight time of the ion from the interaction region to the detector.

7.3.2 Absolute cross section derivations

The current experiments have been performed using a high resolution trochoidal electron monochromator (TEM) in Innsbruck, in tandem with a quadrupole mass filter and channeltron secondary electron multiplier for ion analysis and detection. The TEM has been described in detail Chapter 3 and recent modifications to improve the energy resolution at high impact energies have been discussed in [7.30, 7.31]. With the improved monochromator an energy resolution of about 30 meV independent of incident electron energy can be obtained. However, due to the low cross sections of some fragmentation processes, larger electron currents, 45 nA (and hence lower resolutions, 140 meV) were used in some of the present experiments. The electron beam was perpendicularly crossed with an effusive gas beam emanating from an orifice 20 µm in diameter. In the present studies, gaseous samples of acetonitrile were prepared from liquid samples supplied by Sigma Aldrich with a quoted purity in excess of 99%.
Acetonitrile has a vapour pressure of 99 mbar at room temperature (20° C) thus, after some freeze/thaw distillation to remove any dissolved gases in the liquid sample, pure vapour samples were mixed with CCl₄ in a mixing ratio of 10:1. Cl⁻ production from electron impact of CCl₄ shows s-wave dissociative electron attachment (a strong resonance at zero electron energy) and therefore may be used to calibrate the electron energy scale in the experiment [7.32]. Pressures of the two admixtures were recorded on an absolute capacitance pressure gauge. The pressure in the experimental chamber was limited to a range from 1.0 to 2.0×10⁻⁶ mbar to ensure that there were few intermolecular collisions and hence reduce the probability of ion-molecule interactions occurring.

As mentioned above, the anions formed by electron impact with acetonitrile have a kinetic energy of less than 0.1 eV and may therefore be detected with high efficiency using modest extraction fields, such that it should be possible to measure absolute anion formation cross sections. Therefore only a modest symmetric extraction field (applying at maximum ± 1 Volt) was used in the interaction region to collect the anionic fragments and draw them into the quadrupole optics. The intensity of the anionic yields from acetonitrile was measured as a function of incident electron energy and compared with the Cl⁻ yield from CCl₄ under the same experimental conditions (taking into account the pressure ratios). The production cross section of Cl⁻ from CCl₄ exhibits a second resonance at 0.8 eV the magnitude of which has been accurately determined to be 5×10⁻²⁰ m² [7.33, 7.34] and may therefore be used to derive a measure for the cross section for the formation of each of the fragment anions produced by low energy electron impact of acetonitrile. It has been assumed constant transmission efficiency for each anion through the quadrupole optics and that the counting efficiency of the ion detector is mass independent.

7.3.3 Results

Electron attachment is shown to be a purely dissociative process with the production of the five anionic fragments in the order of their relative abundance CH₂CN⁻, CHCN⁻, CCN⁻, CN⁻ and CH₃⁻ (Figure 7.5). It is interesting to note that Hashemi and Illenberger reported the formation of the parent CH₃CN⁻ as a result of resonant attachment of free electrons to acetonitrile clusters [7.35]. This result is also in line with a study of the collisions between rare gas atoms in highly excited Rydberg
states giving evidence for the existence of stable CH$_3$CN$^-$ parent anions [7.28], this (i.e., the reaction sequence CH$_3$CN$^*$ + CH$_3$CN → CH$_3$CN$^-$) has also been invoked as a likely explanation for the observation of the CH$_3$CN$^-$ parent anion by Stockdale et al. [7.28] for electron impact above an energy of about 8 eV. As discussed by Illenberger and co-workers [7.29] the production in this case of the parent anion can be rationalized as a dipole bound state where the extra electron is extremely weakly bound in the field of the CH$_3$CN dipole. In the cluster case it seems that the cluster coupled bound state tends to stabilise this anion, allowing for the accommodation of an extra electron. In the case of the monomer however Heni and Illenberger [29] proposed a dissociative electron attachment process that is common to all nitriles namely electron capture into a $\pi^*_{CN}$ molecular orbital followed by a $\sigma$ bond cleavage.

![Diagram of dissociative electron attachment cross sections](image)

**Figure 7.5 – Absolute dissociative electron attachment cross sections for anions produced by electron impact on acetonitrile.**
7.3.3.1 Dissociative electron attachment at energies below 5.0 eV

The energetics of a dissociative electron attachment (DEA) process to a molecule M can be described as:

\[ AE(M - X^-) = D((M - X) - X) - EA(M - X) + \Delta E \]  

(7.1)

where \( AE \) is the appearance energy for the fragment anion \((M - X)^-\), \( D \) the bond dissociation energy, \( EA \) the electron affinity for the fragment \((M - X)\) and \( \Delta E \) the excess energy of the process.

The most intense fragment ion formed in DEA of acetonitrile is \( CH_2CN^- \) formed from the fragmentation of the parent anion by the loss of a single hydrogen atom. Assuming that the electron affinity \( EA(CH_2CN^-) = 1.560 \pm 0.006 \) eV [7.36] and the bond dissociation energy \( D(H-CH_2CN) \approx 4 \) eV [7.37], an appearance energy \( AE(CH_2CN) = 2.44 \pm 0.2 \) eV is predicted which is in good agreement with the experimental value of \( 2.35 \pm 0.1 \) eV. The maximum cross section for production of \( CH_2CN^- \) is \( \approx 4 \times 10^{-22} \) m\(^2\) at 3.2 eV.

An identical appearance energy and cross section profile is observed in the yield of \( CHCN^- \) formed by the abstraction of an \( H_2 \) molecule from the parent anion albeit with a cross section value two orders of magnitude lower than that of \( CH_2CN^- \).

The cross section profiles for \( CH_2CN^- \) and \( CHCN^- \) are characteristic of those arising from the capture of the scattered electron into the unoccupied molecular orbital of the target to form a temporary negative ion (TNI). Assuming \( EA(CHCN) = 0.8 \pm 0.4 \) eV [7.29], \( AE(CHCN^-) = 2 \times D(H-CH_2CN) - D(H-H) - EA(CHCN) \) [7.37, 7.38], the threshold for the AE of \( CHCN^- \) is estimated to be \( 2.3 \pm 0.6 \) eV which is in relatively good agreement with the value of \( 2.9 \pm 0.1 \) eV obtained from the present results [7.30].

Calculations have shown that the highest occupied molecular orbital (HOMO) of radical anions of the saturated nitriles is \( \pi^* \) anti-bonding with virtually all the additional charge localized at the CN group, leading to a reduction in the \( C \equiv N \) bond dissociation energy [7.29]. The formation of \( CN^- \) is therefore associated with energy transfer from the \( C \equiv N \) bond to the \( CH_3 - CN \) bond. Dissociation into \( CN^- \) and \( CH_3 \) radicals in their electronic ground state is symmetry forbidden (which is true as long as no distortions are occurring) and can only occur through pre-dissociation of the parent anion, thus the cross section for formation of \( CN^- \) is small at low energies peaking at \( \approx 4 \times 10^{-23} \) m\(^2\) at 1.8 eV with an appearance energy of \( 1.10 \pm 0.10 \) eV. Assuming the \( H_3C - CN \) bond dissociation energy is \( 5.36 \pm 0.03 \) eV [7.37] and the electron affinity of the cyano
radical is 3.82 eV [7.39], the threshold for the appearance energy of CN' becomes 1.54 ± 0.03 eV, close to the experimentally observed value of 1.10 ± 0.10 eV. Actually, in the work reported for acetonitrile by Illenberger and co-workers [7.29], the low energy resonance for CN' seems to be slightly energy shifted compared with the present experimental data showing an appearance energy of about 2.7 eV. In contrast, the data by Stockdale et al. [7.28] are supporting the present appearance energy. It is interesting to note that similar low energy patterns for CN' production have been observed in other CN containing compounds such as CH₃NO₂ [7.40]. It is also possible that these yields may arise from the excitation of vibrationally excited CH₃CN and future studies of anion yield as a function of temperature of the target should be taken into account.

### 7.3.3.2 Dissociative electron attachment at energies above 6.0 eV

At higher impact energies several anion fragments are observed, including the first yield of the bare backbone CCN'. The formation of CCN' requires the largest number of bonds in the parent to be broken, all three C – H bonds having to be severed. Consequently, there is high appearance energy for CCN', around 7.8 eV. In contrast to the observation of the CCN' ion at these high energies there is no evidence for the formation of the simplest dissociation product CH₂CN'.

The profiles of the CHCN', CCN', CN' and CH₃' cross sections above 6 eV suggest that these fragments ions may arise from a series of overlapping resonances. The data of Illenberger and co-workers [7.29] suggests (in accordance with the present data) that the high energy yield of CHCN' and CCN' is a composite of two resonance features peaking at about 8.3 eV and at 10.0 eV. The production mechanism for the CHCN' anion could proceed through an excited state of the TNI and may be associated with the formation of two separated hydrogen atoms (multi-fragmentation) rather than with the formation of a hydrogen molecule. The similarity of the cross section profiles of CHCN' and CCN' at these higher energies suggests that simple H abstraction from CHCN' may occur and that the two processes share common parent TNIs.

The complementary molecule-ion pair CN' + CH₃ or CN + CH₃' arises from cleavage of the central C – C bond. The appearance energy of CH₃' is obtained as 5.28 ± 0.03 eV since the methyl radical CH₃' possesses an electron affinity of 0.08 eV [7.41]. Both ion yields therefore have about the same appearance energy, 6.2 eV and 5.8 eV respectively, and peak at about the same position 7 eV. The CN' yield resonance is
composed of three overlapping peaks, one at about 7 eV, one at about 8 eV, and one centred around 9.2 eV. For the two higher resonances a multi-fragmentation pattern with formation of CH\textsubscript{2} and H is probable since there is no corresponding peak in the CH\textsubscript{3}\textsuperscript{-} yield.

**7.3.3.3 Quantum chemical and trajectory calculations**

In order to get information on the electronic structure and especially about the higher-lying molecular orbitals of acetonitrile that might be involved in the formation of the TN\textsubscript{1}\textsuperscript{1}, the electronic excitation spectrum has been calculated by means of a outer-valence Greens' function method [7.42, 7.45] (a more accurate alternative to Koopmans' theorem) together with the D–95V basis set [7.44]. It is known [7.45 – 7.47] that only such medium-sized basis sets reproduce semi-quantitatively the energies of transient negative ion states. All calculations were performed with the Gaussian 98 and 03 set of programs [7.48] and the corresponding results are given in Table 7.7. All EA's are negative, indicating that there is no thermodynamically stable anion state.

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<th>Orbital</th>
<th>Energy (eV)</th>
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</tr>
<tr>
<td>21, 22</td>
<td>-13.08</td>
</tr>
</tbody>
</table>

Table 7.7 – Calculated energies of the LUMO and the next orbitals of CH\textsubscript{3}CN.

We tried to obtain further qualitative insight into the fragmentation processes by performing a limited set of trajectory calculations. In these calculations, the CH\textsubscript{3}CN was described quantum chemically by the B3LYP [7.49, 7.50] density functional and the 6-31G* [7.51] basis set and the dynamics was generated by the ADMP (Atom centered Density Matrix Propagation) method [7.52, 7.53].

An encounter between a molecule of CH\textsubscript{3}CN and an incident electron was then simulated in the following way: (a) one electron was attached to the neutral CH\textsubscript{3}CN in its equilibrium geometry; (b) then Boltzmann-distributed velocities were assigned to the atoms of the CH\textsubscript{3}CN\textsuperscript{-} anion with a total kinetic energy equivalent to the energy of the

\textsuperscript{1}a useful ref. discussing temporary anion states in this and related molecules [J. Phys. Chem., 96 (1992) 7570] based on electron transmission spectroscopy locating the π\textsuperscript{*} resonance at 2.84 eV.
incoming electron (1 eV corresponds to a temperature of 1938 K). The individual
velocity components were created by appropriate scaling of random numbers; (c) this
process was repeated and 5 trajectories each for kinetic energies (0, 1, 2, 4, 8 and 10 eV)
were calculated; (d) each trajectory was propagated for about 500 time-steps of 0.1 fs
each. This trajectory calculation differs from the experimental situation mostly in the
respect that the kinetic energy of the electron is thermally distributed over the molecule
whereas in reality it will excite only certain vibrational modes that might lead to
dissociation before an equilibration takes place. Furthermore, 5 trajectories of 50 fs each
do not allow good-quality statistical sampling but it must be kept in mind that the
computational expense of the ab-initio molecular dynamics calculations is still very
high, even with the modest 6-31G* basis set.

Despite these limitations, it is interesting to compare the simulated
decomposition and the experimentally observed fragments [7.30] since the former ones
represent the limiting case of the anion in thermal equilibrium. An analysis of the
individual trajectories showed the following pattern: the abstraction of hydrogen is
always the first step and takes place very quickly within the first femtosecond,
sometimes even at energies < 1 eV. At slightly larger energy, a rather likely reaction is
that a second hydrogen is lost as well but in some cases this H later recombines again
with the CHCN fragment. The breaking of the C – C bond is much slower and occurs
only at higher energies, it has been observed in one of the trajectories at 8 eV after about
30 fs elapsed time [7.30].

7.3.3.4 Conclusions

In the present study dissociative electron attachment to acetonitrile has been
investigated from about zero to 10 eV. Intensity ratios of the product ions: \( \text{CH}_2\text{CN}^- \),
\( \text{CHCN}^- \),\( \text{CCN}^- \), \( \text{CN}^- \) and \( \text{CH}_3^- \) are 2000:35:7:50:1, these have been converted to absolute
cross sections by comparison with the known standard cross section for the production
of Cl\(^-\) from CCl\(_4\). With the exception of CH\(_2\)CN\(^-\) all anion cross sections are quite small.
In fact, CH\(_3\)\(^-\) exhibits the smallest cross section ever measured with the Innsbruck TEM
instrument, only 200 barn.

It is clear that dissociative electron attachment occurs via accommodation of an
extra electron into a \( \pi^*_{\text{CN}} \) character orbital. The most energetically favourable channel,
\( \text{CH}_3^* + \text{CN}^- \) is the result of a transition to the low-lying excited states having repulsive
adiabatic potential surfaces crossing with the electronic ground state above the
dissociation limit leading to pre-dissociation of the bond. The result is a low CN$^-$ cross
section at ~ 2 eV and an inter- and intramolecular energy transfer (or re-distribution)
with virtually no kinetic energy release.

7.4 VUV photo-absorption of acrylonitrile, C$_2$H$_3$CN

7.4.1 Introduction

The absorption spectrum of acrylonitrile (Figure 7.6) was obtained in the photo-
absorption set-up described earlier (section 3.2.3) with a path length of 25 cm. The
spectrum was recorded in 11 nm sections, in 0.1 nm and 0.05 nm steps. The sample
used was obtained from Sigma Aldrich, with a purity of 99+%. No further purification
was under taken except for freeze-thaw-pump cycles.

The typical pressures used to obtain the acrylonitrile spectrum are presented in
Table 7.8 and range from 0.015 torr - 0.750 torr, with attenuation of 10%. Higher
pressures have been used below 5.6 eV in order to guarantee no weak absorption
features were missed.

<table>
<thead>
<tr>
<th>Energy range (eV)</th>
<th>Wavelength (nm)</th>
<th>Pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.88 – 5.64</td>
<td>220 – 320</td>
<td>0.750</td>
</tr>
<tr>
<td>5.54 – 9.32</td>
<td>133 – 224</td>
<td>0.075</td>
</tr>
<tr>
<td>9.25 – 10.08</td>
<td>123 – 134</td>
<td>0.015</td>
</tr>
<tr>
<td>10.00 – 10.97</td>
<td>113 – 124</td>
<td>0.030</td>
</tr>
</tbody>
</table>

Table 7.8 – Photon energy (eV), wavelength (nm) and pressure (torr) ranges
for acrylonitrile photo-absorption measurements.

Results are also compared to electron energy loss (EEL) spectra taken at the
Université de Liège by Motte-Tollet et al. [7.53]. The overall energy resolution quoted
in their experiments is around 30 meV.

7.4.2 Results

Figure 7.6 shows the high resolution photo-absorption cross section spectrum for
incident photon energies between 5.5 eV and 11.0 eV, corresponding to the excitation of
electrons belonging to the outer-most valence shell orbitals. The dashed feature is only
partially recorded due to the cut-off in the transmission of the CaF$_2$ window. No
absorption is observed below 5.8 eV. The energy positions of the major features are in
good agreement with the photo-absorption spectrum reported by Mullen and Orloff [7.54] from 5.3 eV to 9.7 eV. The spectrum for acrylonitrile is also compared to a previously unpublished photo-absorption result taken at the Daresbury Laboratory Synchrotron Radiation Source, where the experimental set up is described in detail by Mason et al. [7.55]. The maximum resolution is estimated to be 0.1 nm.

The structure of acrylonitrile is derived from microwave spectroscopy [7.54, 7.56]. The molecule is planar in the electronic ground state and belongs to the C\textsubscript{s} symmetry group. The single C – H and C – C bonds are of \( \sigma \) character, while C = C comprises one \( \sigma \) and one \( \pi \) bond. The nitrogen atom is bound to a carbon atom by one \( \sigma \) and two \( \pi \) interactions (C – C \( \equiv \) N). The two nitrogen electrons which do not take part in any bonds form a lone pair directed away from the molecule.
Figure 7.6 – VUV photo-absorption spectrum of acrylonitrile in the energy region 5.5 eV to 11.0 eV.
Chapter Seven

The outermost valence molecular orbitals in the ground state of C$_2$H$_3$CN may be represented in the independent particle model as $(1a'')^2$ $(11a'')^2$ $(12a'')^2$ $(2a'')^2$: $\bar{X}^1A'$ [7.57]. The π electrons are delocalised along the C = C - C = N chain by a conjugative interaction between the C = C bond and the C = N bond in the plane perpendicular to the plane of the molecule [7.57]. This conjugation gives rise to two bonding π orbitals $1a''$ and $2a''$ labelled as $\pi_1(C = C - C = N)$ and $\pi_2(C = C - C = N)$ and to two π* orbitals $3a''$ and $4a''$ of anti-bonding character labelled as $\pi_1^*(C = C - C = N)$ and $\pi_2^*(C = C - C = N)$. The π electrons of the C = N group which lie in the molecular plane stay localised in this group for symmetry reasons and lead to only one bonding π orbital $12a'$ labelled as $\pi(C = N)$ and one anti-bonding π* orbital $13a'$ labelled as $\pi^*(C = N)$. The nature and ordering of the LUMOs have been adopted to be $(3a'')^0$, $(13a')^0$, $(4a'')^0$ [7.57].

The next higher LUMOs are σ* in character and their assignment is difficult due to the overlap between the excitation bands of each core levels to the different orbitals of σ* character, and the multielectronic excitation features. Acrylonitrile has 15 normal vibrational modes, presented in Table 7.9 [7.57], eleven of which are symmetric (a') with respect to the molecular plane of symmetry and four anti-symmetric (a'') [7.58]. The vibrational modes considered to be excited in the present spectrum are mainly $\nu_4$, $\nu_5$, $\nu_8$, $\nu_9$, $\nu_{10}$ and $\nu_{12}$.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Vibrational mode</th>
<th>Description</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a'</td>
<td>$\nu_1$</td>
<td>C - H stretching</td>
<td>0.387</td>
</tr>
<tr>
<td></td>
<td>$\nu_2$</td>
<td>C - H stretching</td>
<td>0.382</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$</td>
<td>C - H stretching</td>
<td>0.377</td>
</tr>
<tr>
<td></td>
<td>$\nu_4$</td>
<td>C = N stretching</td>
<td>0.278</td>
</tr>
<tr>
<td></td>
<td>$\nu_5$</td>
<td>C = C stretching</td>
<td>0.200</td>
</tr>
<tr>
<td></td>
<td>$\nu_6$</td>
<td>CH$_2$ deformation</td>
<td>0.176</td>
</tr>
<tr>
<td></td>
<td>$\nu_7$</td>
<td>CH rocking</td>
<td>0.159</td>
</tr>
<tr>
<td></td>
<td>$\nu_8$</td>
<td>CH$_2$ rocking</td>
<td>0.136</td>
</tr>
<tr>
<td></td>
<td>$\nu_{11}$</td>
<td>C - H stretching</td>
<td>0.108</td>
</tr>
<tr>
<td></td>
<td>$\nu_{13}$</td>
<td>C = C - C bending</td>
<td>0.071</td>
</tr>
<tr>
<td></td>
<td>$\nu_{15}$</td>
<td>C - C = C bending</td>
<td>0.030</td>
</tr>
<tr>
<td>a''</td>
<td>$\nu_9$</td>
<td>CHR = C wagging</td>
<td>0.120</td>
</tr>
<tr>
<td></td>
<td>$\nu_{10}$</td>
<td>CH$_2$ = C wagging</td>
<td>0.118</td>
</tr>
<tr>
<td></td>
<td>$\nu_{12}$</td>
<td>C = C torsion</td>
<td>0.085</td>
</tr>
<tr>
<td></td>
<td>$\nu_{14}$</td>
<td>C - C = C bending</td>
<td>0.045</td>
</tr>
</tbody>
</table>

Table 7.9 – Acrylonitrile ground state vibrational energies (eV).
The shape of the cross section and a number of the peaks observed are also consistent with the EELS results taken by Motte-Tollet et al. [12] using incident electrons of 50 eV and analysed at a scattering angle of 10° over an energy loss range of 5.5 eV to 11.5 eV. Under these conditions, electron scattering can be considered to simulate photon interactions [7.59].

The present photo-absorption spectrum shows a broad feature with maximum absorption at 6.526 eV attributed to promotion to the first excited electronic state, \( \tilde{A}^1A' \), corresponding to the \( \pi_2(C = C - C \equiv N) \rightarrow \pi_1^*(C = C - C \equiv N) \) transition [7.57]. The first peak for the second singlet excited electronic state \( \tilde{B}^1A'' \), transition \( \pi_2(C = C - C \equiv N) \rightarrow \pi^*(C \equiv N) \), appears at 7.183 eV and the maximum for the third excited electronic state \( \tilde{C}^1A' \), \( \pi_2(C = C - C \equiv N) \rightarrow \pi_2^*(C = C - C \equiv N) \), at 8.580 eV. The broad structure observed is attributed to pre-dissociation combined with mutual overlap of the valence bands. The peaks above 8.6 eV are associated with Rydberg transitions. However, some mixing of valence and Rydberg transitions is observed, complicating the assignment of features.

### 7.4.2.1 Valence excitation in the 5.5 eV – 8.0 eV energy region

The photo-absorption spectrum in the energy region 5.5 eV to 8.0 eV is shown in Figure 7.7.

![Figure 7.7 - Photo-absorption spectrum in the 5.5 eV – 8.0 eV band of C_2H_3CN.](image)
This region is dominated by an intense broad band extending with a local maximum cross section of 33.31 Mb at 6.526 eV. Superimposed onto the extended structure is an overlapping series of smaller peaks and shoulders. The energy values found for the associated vibrational structure are listed in Table 7.10 and compared with corresponding features observed by Mullen and Orloff [7.54] and Motte-Tollet et al. [7.57]. The energy precision to which some assignments can be given is limited by the diffuse nature of the features.

The lowest energy feature is located at 5.882 eV and has been assigned in accordance with Motte-Tollet et al. [7.57] to the electronic excitation occurring from the highest occupied molecular orbital, \( \pi_2 (C = C - C = N) \), to the lowest singlet excited state, \( \pi_1^* (C = C - C = N) \). The excited state is recognised as being of A' symmetry. Mullen and Orloff [7.54] observe a feature close to this energy but leave it unassigned, preferring to offer the peak at 6.110 eV as corresponding to the valence excitation and attributing the following structure to a \( v_4 \) series, C \( \equiv N \) stretching.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>This work</th>
<th>Mullen &amp; Orloff [7.54]</th>
<th>Motte-Tollet et al. [7.57]</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.882</td>
<td>5.880</td>
<td>5.875</td>
<td>( v_0 )</td>
<td></td>
</tr>
<tr>
<td>6.102</td>
<td>6.110</td>
<td>6.100</td>
<td>( v_4 )</td>
<td></td>
</tr>
<tr>
<td>6.147</td>
<td>6.150</td>
<td>-</td>
<td>( v_4 + v_{12} )</td>
<td></td>
</tr>
<tr>
<td>6.310</td>
<td>6.310</td>
<td>6.310</td>
<td>( 2v_4 )</td>
<td></td>
</tr>
<tr>
<td>6.378</td>
<td>6.380</td>
<td>-</td>
<td>( 2v_4 + v_{12} )</td>
<td></td>
</tr>
<tr>
<td>6.427</td>
<td>6.430</td>
<td>-</td>
<td>( 2v_4 + 2v_{12} )</td>
<td></td>
</tr>
<tr>
<td>6.526</td>
<td>6.530</td>
<td>6.520</td>
<td>( 3v_4 )</td>
<td></td>
</tr>
<tr>
<td>6.641</td>
<td>6.650</td>
<td>6.640</td>
<td>( 3v_4 + v_9 ) or ( 3v_4 + 2v_{10} )</td>
<td></td>
</tr>
<tr>
<td>6.738</td>
<td>6.740</td>
<td>6.750</td>
<td>( 4v_4 )</td>
<td></td>
</tr>
<tr>
<td>6.869</td>
<td>6.860</td>
<td>6.870</td>
<td>( 4v_4 + v_9 ) or ( 4v_4 + 2v_{10} )</td>
<td></td>
</tr>
<tr>
<td>6.977</td>
<td>6.970</td>
<td>7.000</td>
<td>( 5v_4 )</td>
<td></td>
</tr>
<tr>
<td>7.101 (?)</td>
<td>7.080</td>
<td>-</td>
<td>( 5v_4 + v_9 ) or ( 5v_4 + 2v_{10} )</td>
<td></td>
</tr>
<tr>
<td>7.183</td>
<td>-</td>
<td>7.180</td>
<td>( 6v_4 )</td>
<td></td>
</tr>
<tr>
<td>7.319</td>
<td>-</td>
<td>7.320</td>
<td>( 6v_4 + v_9 ) or ( 6v_4 + 2v_{10} )</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.10 – Vibrational assignments in the 5.5 eV – 7.1 eV absorption band of \( C_2H_2CN \) for the lowest energy excited electronic state \( \tilde{A}^1 A' \), corresponding to the \( \pi_2 (C=C-C=N) \rightarrow \pi_1^* (C=C-C=N) \) transition.

It has been proposed that a \( v_4 \) series begins at 5.882 eV with further features assigned to combinations of \( v_4 \) with \( v_{12} \) excitations and of \( v_4 \) with either \( v_9 \) or \( v_{10} \) [7.15]. The modes \( v_9 \), \( v_{10} \), and \( v_{12} \), corresponding to CHR = C wagging, \( CH_2 = C \) wagging, and
C\_\text{C torsion}, respectively, are anti-symmetric and thus would be expected to show very weak cross section as single excitations [7.25]. However, double excitation or combination with another mode can increase the cross section. As the neutral ground state excitation energies for \( \nu_9 \) and \( \nu_{10} \) are very similar in energy, it is not possible to distinguish between them [7.15]. Assignment to transitions involving the modes \( \nu_{13}, \nu_{14}, \) and \( \nu_{15} \) is also not straightforward since they are reported only by Raman spectroscopy in the liquid phase [7.20, 7.58].

At the high end of the energy range of Figure 7.7, further vibrational structure is observed overlapping with the previous structure. The peaks are attributed to the transition from the outermost occupied orbital \( \pi_2(C = C - C = N) \rightarrow \pi^*(C = N) \), assigned in accordance with Motte-Tollet \textit{et al.} [7.57] as the second excited state \( \tilde{B}^1A'' \). The vibrational analysis associated with this transition leads to a short series of \( \nu_4 \) and \( \nu_4 + \nu_8 \), CH\_2 rocking, presented in Table 7.11. The \( \nu_{00} \) transition for this electronic band has been assigned at 7.183 eV.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>This work</th>
<th>Mullen &amp; Orloff [7.54]</th>
<th>Motte-Tollet \textit{et al.} [7.57]</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.183</td>
<td>7.190</td>
<td>7.185</td>
<td>( \nu_{00} )</td>
<td></td>
</tr>
<tr>
<td>7.319</td>
<td>7.320</td>
<td>7.325</td>
<td>( 1\nu_8 )</td>
<td></td>
</tr>
<tr>
<td>7.451</td>
<td>7.460</td>
<td>7.455</td>
<td>( 1\nu_4 )</td>
<td></td>
</tr>
<tr>
<td>7.593</td>
<td>7.590</td>
<td>7.595</td>
<td>( 1\nu_4 + 1\nu_8 )</td>
<td></td>
</tr>
<tr>
<td>7.739 (?)</td>
<td>7.740</td>
<td>7.740</td>
<td>( 2\nu_4 )</td>
<td></td>
</tr>
<tr>
<td>7.907</td>
<td>-</td>
<td>-</td>
<td>( 2\nu_4 + 1\nu_8 )</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.11 – Vibrational assignments in the 7.1 eV – 7.8 eV absorption band of C\_2H\_3CN for the second excited electronic state \( \tilde{B}^1A'' \), corresponding to the \( \pi_2(C=C-C\equiv N) \rightarrow \pi^*(C\equiv N) \) transition.

\textbf{7.4.2.2 Valence excitation in the 7.8 eV – 9.0 eV energy region}

In this range, shown in detail in Figure 7.8, the spectrum consists of a fairly sharp peak with cross section 25.96 Mb at 8.580 eV and a diffuse vibrational structure characterised by the modes \( \nu_5 \) and \( \nu_9 \) or \( \nu_{10} \).

It has been suggested [7.15] that the series of peaks is related to the population of the third valence excited state formed by the excitation of an electron from the outermost occupied orbital \( \pi_2(C = C - C = N) \rightarrow \pi_2^*(C = C - C = N) \), of A' symmetry, in accordance with Motte-Tollet \textit{et al.} [7.57].

The assignments for the third excited electronic state, \( \tilde{C}^1A' \), are given in Table 7.12. Previously [7.57], the associated structure could not be analysed fully due to
nitrogen contamination. However, the peaks observed at 7.907 eV and 8.580 eV are assigned by Motte-Tollet et al. [7.57] to the Rydberg transitions 3s\sigma and 3p\lambda. It is suggested here that these asymmetrical peaks represent superpositions of valence and Rydberg interactions.

Figure 7.8 – Photo-absorption spectrum in the 7.8 eV – 9.0 eV band of C\textsubscript{2}H\textsubscript{3}CN.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>This work</th>
<th>Mullen &amp; Orloff [7.54]</th>
<th>Motte-Tollet et al. [7.57]</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.907</td>
<td>7.90</td>
<td>7.895</td>
<td>\nu_{00}</td>
<td></td>
</tr>
<tr>
<td>8.077 (?)</td>
<td>8.07</td>
<td>-</td>
<td>\nu_{13}</td>
<td></td>
</tr>
<tr>
<td>8.206 (?)</td>
<td>8.24</td>
<td>-</td>
<td>2\nu_{5}</td>
<td></td>
</tr>
<tr>
<td>8.389 (?)</td>
<td>8.41</td>
<td>-</td>
<td>3\nu_{5}</td>
<td></td>
</tr>
<tr>
<td>8.580</td>
<td>-</td>
<td>8.595</td>
<td>4\nu_{5}</td>
<td></td>
</tr>
<tr>
<td>8.652 (?)</td>
<td>8.67</td>
<td>-</td>
<td>4\nu_{5} + \nu_{10} or \nu_{10}</td>
<td></td>
</tr>
<tr>
<td>8.738 (?)</td>
<td>8.74</td>
<td>-</td>
<td>5\nu_{5}</td>
<td></td>
</tr>
<tr>
<td>8.837</td>
<td>-</td>
<td>8.840</td>
<td>5\nu_{5} + \nu_{10} or \nu_{10}</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.12 – Vibrational assignments in the 7.9 eV – 9.0 eV absorption band of C\textsubscript{2}H\textsubscript{3}CN for the third excited electronic state C\textsuperscript{1}A\textsuperscript{′}, corresponding to the \pi_{2}(C=C−C≡N) → \pi^{*}(C=C−C≡N) transition.
Chapter Seven

7.4.2.3 Rydberg series converging to 10.924 eV, 12.353 eV and 13.017 eV IPs

The peak energies and Rydberg assignments converging to 10.924 eV, the ionic ground state \( X^2A'' \), are shown in Figure 7.9 and Table 7.13. Due to the diffuseness and uncertainty in their peak positions some structures have been represented by dashed lines. Also shown in the table are the relevant quantum defects and suggested combinations of Rydberg and vibrational excitations to account for previously unassigned features. In agreement with previous work [7.57], the lowest energy peak attributed to a Rydberg transition, at 7.907 eV, is assigned as 3\( 3\sigma \) in a series converging to an ionisation potential of 10.924 eV, the associated quantum defect being 0.88. The peak at 8.580 eV is assigned to an \( np\lambda \) progression including \( n = 3, 4, \) and 5, converging to the first ionisation limit. The peak at 9.205 eV is considered to match that observed by Motte-Tollet et al. [7.57] at 9.215 eV, assigned to the \( n = 3 \) term of an \( nd\pi \) series with \( \delta \) equal to 0.19. Recognition of this feature has suggested two further assignments corresponding to the combination of vibrational excitation and the Rydberg transition \( 3d\pi \) [7.15]. The photoelectron work of Delwiche et al. [7.21] reports vibrational progressions of \( \nu_4 \) and \( \nu_5 \) for the 10.924 eV band with energies 0.248 and 0.180 eV, respectively, closely matching the energy differences observed between the \( 3d\pi \) transition and the assigned vibrational structure in the present spectrum.

The assignments to \( 3d\delta \) and \( 4d\delta \) transitions and to \( 4d\delta + 1\nu_5 \) excitation are made in agreement with Motte-Tollet et al. [7.57]. The peak at 10.379 eV and the shoulder at 10.547 eV are tentatively added to the \( nd\delta \) series, converging to 10.924 eV.

The features at 10.247 eV, 0.126 eV from 10.121 eV (5\( 3\sigma \)), 10.064 eV, 0.097 eV from 9.967 eV (4\( d\pi \)), and 10.147 eV, 0.180 eV from 9.967 eV (4\( d\pi \)), are in close agreement to the PES modes \( \nu_8, \nu_{11} \) and \( \nu_6 \), respectively [7.21] at 0.115 eV, 0.104 eV and 0.178 eV.

Elden’s plots (section 3.2.5.2) were obtained in Figure 7.10 giving the variation of the quantum defect (\( \delta_0 \)) with the reduced term energies (\( n^* \))\(^2 \) for the Rydberg series converging to the ionic electronic ground state. For each Rydberg series the variation of \( \delta_0 \) with the reduced term energy is linear confirming the previous assignments. For the \( n\sigma \) and \( nd\pi \) series, the slight deviation for the lowest (\( n^* \))\(^2 \) terms is consistent with the uncertainty in the assignment.
Figure 7.9 – Assignment of the C$_2$H$_3$CN Rydberg series converging to the ionisation potentials 10.924 eV, 12.353 eV and 13.017 eV.
Table 7.13 – Energy values, quantum defect and assignment of the Rydberg series converging to 10.924 eV, the ionization limit corresponding to the ionic electronic ground state $\tilde{X}^2A''$ of C$_2$H$_3$CN.

The peaks considered to be related to Rydberg series converging on the ionic electronic first excited state, $\tilde{A}^2A'$ are listed in Table 7.14. The ionisation potential associated with this state is 12.353 eV and the series are located above 9 eV.

Within the present spectral range only the lowest energy, $n = 3$ terms amongst the previously assigned $n\sigma$, $n\pi$, $n\delta$, $n\pi$, and $n\delta$ series [7.57] are observed. Delwiche et al. [7.21] report a $v_4$ series with excitation energy 0.248 eV for this state and a further vibrational series with energy difference 0.148 eV, suggested to be consistent either with the $v_7$ or $v_8$ vibrational modes, CH rocking and CH$_2$ rocking, respectively. Also reported is a $v_{13}$ mode with an energy of 0.061 eV and in agreement with the $3\pi + v_{13}$ 10.684 eV feature. Remarkably, the feature at 9.967 eV has been previously assigned to $4\pi$ (IP, 10.294 eV) for the Rydberg series which could explain
the broadness of that structure in Figure 7.9 due to the overlapping of the two involved transitions.

Figure 7.10 — Elden’s diagrams for the variation of the quantum defect ($\delta_0$) with the reduced term energies ($n^*$)² for the first terms of the Rydberg series converging to the ionic electronic ground state.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Motte-Tollet et al. [7.57]</th>
<th>Quantum defect ($\delta$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.017</td>
<td>9.055</td>
<td>0.98</td>
<td>3σσ</td>
</tr>
<tr>
<td>9.967</td>
<td>9.963</td>
<td>0.61</td>
<td>3πκ</td>
</tr>
<tr>
<td>10.039</td>
<td>-</td>
<td>-</td>
<td>3πκ + 1ν₁₃</td>
</tr>
<tr>
<td>10.217</td>
<td>-</td>
<td>-</td>
<td>3πκ + 1ν₄</td>
</tr>
<tr>
<td>10.516</td>
<td>10.527</td>
<td>0.28</td>
<td>3σσ</td>
</tr>
<tr>
<td>10.647</td>
<td>-</td>
<td>-</td>
<td>3σσ + ν₇ or 3σσ + ν₈</td>
</tr>
<tr>
<td>10.624</td>
<td>10.643</td>
<td>0.20</td>
<td>3ππ</td>
</tr>
<tr>
<td>10.684</td>
<td>-</td>
<td>-</td>
<td>3ππ + ν₁₃</td>
</tr>
<tr>
<td>10.744</td>
<td>-</td>
<td>-</td>
<td>3ππ + ν₇ or 3ππ + ν₈</td>
</tr>
<tr>
<td>10.772</td>
<td>10.783</td>
<td>0.07</td>
<td>3δδ</td>
</tr>
</tbody>
</table>

Table 7.14 — Energy values, quantum defect and assignment of the Rydberg series converging to 12.353 eV, the ionization limit corresponding to the ionic electronic first excited state $\tilde{A}^2A'$ of $\text{C}_2\text{H}_3\text{CN}$.

Three series in the energy range of this spectrum are suggested to converge on the ionisation potential 13.017 eV, associated with the ionic electronic second excited
state, $\tilde{B}^2 A'$. The recommended assignments are given in Table 7.15. Peaks at 9.530 eV, 10.354 eV and 10.675 eV are assigned in accordance with Motte-Tollet et al. [7.57] to transitions $3s\sigma$, $3p\lambda$ and $3p\lambda$. The peak at 9.679 eV, 0.149 eV from 9.530 eV has been assigned in agreement to the vibrational mode reported by Delwiche et al. [7.21] (0.141 eV) in the second excited ionic state. The feature at 9.679 eV has been previously assigned to $3p\lambda$ (IP, 10.294 eV) explaining the broadness of that structure in Figure 7.9. A shoulder at 9.232 eV remains unassigned.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Motte-Tollet et al. [7.57]</th>
<th>Quantum defect ($\delta$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.530</td>
<td>9.547</td>
<td>1.03</td>
<td>$3s\sigma$</td>
</tr>
<tr>
<td>9.679</td>
<td>-</td>
<td>-</td>
<td>$3s\sigma + 1\nu_8$</td>
</tr>
<tr>
<td>10.354</td>
<td>10.379</td>
<td>0.74</td>
<td>$3p\lambda$</td>
</tr>
<tr>
<td>10.675</td>
<td>10.695</td>
<td>0.59</td>
<td>$3p\lambda$</td>
</tr>
</tbody>
</table>

Table 7.15 – Energy values, quantum defect and assignment of the Rydberg series converging to 13.017 eV, the ionization limit corresponding to the ionic electronic second excited state $\tilde{B}^2 A'$ of C$_2$H$_3$CN.

### 7.4.2.4 Absolute cross sections

The cross sectional values of acrylonitrile corresponding to energies between 6 eV and 9.5 eV are compared to the data of Mullen and Orloff [7.54] recorded in steps of 0.5 eV. The present measured cross section is around 400% higher than that of Mullen and Orloff. To our knowledge, no other acrylonitrile photo-absorption data has been reported over the range of the present spectrum. In addition, as shown in Figure 7.6, the present result is in good agreement with the lower resolution result recorded at the Synchrotron Radiation Facility, Daresbury, UK. The cross sections measured at the two facilities match to within 10%, with the exception of a difference of 35% observed at 9.429 eV for the sharp Rydberg peak positioned in the high energy extreme of the spectral range available at Daresbury. Erroneous low cross section values may result from a fall in optical transmission close to the experimental cut off frequency. The estimated error in absolute photo-absorption cross section for a previous result taken using the Daresbury apparatus is given as ± 20% [7.60].

### 7.4.3 Environmental evaluation for acrylonitrile

The atmospheric photolysis lifetime of acrylonitrile has been modelled using a program referred in Chapter 3, section 3.2.5.3. The program considers a simplified
system and evaluates the photolysis rate as a product of the solar actinic flux and the molecular photo-absorption cross section at different wavelengths and altitudes. The residence time is calculated for a molecule at a fixed altitude in a sunlit, clear atmosphere. The rate of photolysis of acrylonitrile is found this way to be of the order $10^{-5}$ s$^{-1}$ in the stratosphere and $10^{-6}$ s$^{-1}$ at lower altitudes (Figure 7.11).

![Figure 7.11](image_url)  

**Figure 7.11** – The photolysis rates (s$^{-1}$ nm$^{-1}$) vs. wavelength (nm) and photon energy (eV) for acrylonitrile as a function of altitude (0 – 50 km) in Earth’s atmosphere.

These rates give stratospheric residence times by photolysis in the order of hours. In the troposphere, the calculated residence time rises from around 10 days at higher altitudes to over one year below 15 km. Thus, at altitudes below around 20 km, the present result is consistent with previous understanding that degradation occurs dominantly by reactions with photochemically produced hydroxyl radicals [7.14]. The half life of acrylonitrile by these processes is estimated to be between 1.0 and 3.5 sunlit days.

### 7.5 Comparison of acetonitrile with acrylonitrile

The photo-absorption spectra of both CH$_3$CN and C$_2$H$_3$CN are dominated by transitions from $\pi \rightarrow \pi^*$ (C = N) orbitals. For both molecules, these transitions feature (C = N) bonds. In the case of acrylonitrile, the valence excitations observed are assigned
to $\pi_2(C = C - C \equiv N) \rightarrow \pi_1^*(C = C - C \equiv N)$, $\pi_2(C = C - C \equiv N) \rightarrow \pi^*(C \equiv N)$, and $\pi_2(C = C - C \equiv N) \rightarrow \pi_2^*(C = C - C \equiv N)$. For acetonitrile, the lowest observed valence band is assigned to $\pi(C - C \equiv N) \rightarrow \pi^*(C - C \equiv N)$. For both molecules, $C - H$ excitation is limited because of the very stiff nature of the bonds. This is evident in the observed vibrational excitations. For acrylonitrile, by far the most commonly assigned modes are $\nu_4$ and $\nu_5$, corresponding to $C \equiv N$ and $C = C$ stretching, respectively. Similarly, the dominant symmetric modes for vibrational excitation of acetonitrile are considered to be $C \equiv N$ and $C - C$ stretching, $\nu_2$ and $\nu_4$. The $C - C \equiv N$ bending mode for acetonitrile, $\nu_8$, also seems to be very readily excited.

A significant difference, however, is observed when nitrogen lone pair excitations for each molecule are compared. Excitation from the nitrogen lone pair electrons of acrylonitrile is not visible in the present range. However, the transition $n_N \rightarrow \pi^*(C - C \equiv N)$ makes a significant contribution to the spectrum of acetonitrile. The lone pair for acrylonitrile lies in an orbital separated from the lowest unoccupied orbital by the $(12a')^2$ and $(2a'')^2$ orbitals, whereas that for acetonitrile is only separated by the occupied $(2e)^4$ orbital. Therefore, it is expected excitation from the lone orbital of CH$_3$CN to require markedly lower energy than that of C$_2$H$_3$CN and thus to appear in the VUV photo-absorption spectrum.

Comparison of Figures 7.1 and 7.6, shows that the photo-absorption cross section of acrylonitrile is greater at low energies than that for acetonitrile. Thus, in the lower atmosphere, the photolysis rate of acrylonitrile is significant whereas one would not expect it to make a noticeable contribution to the destruction of acetonitrile. Both molecules absorb strongly at short wavelengths, however, no significant similarity in the Rydberg structures of acrylonitrile and acetonitrile is apparent within the energy range of this work.

7.6 Summary

Photo-absorption spectra of acetonitrile and acrylonitrile have been recorded in the wavelength range 115 nm to 320 nm (10.8 eV to 3.9 eV). The high resolution available in our apparatus has allowed several features to be observed for the first time and new assignments have been suggested. The present results are found to be in close agreement to previous photo-absorption measurements and electron energy loss spectra. More significant variations are evident when comparing the absolute cross sections of
bands. In the case of acrylonitrile, a significantly higher absorption cross section is reported in the present work than previously reported. This suggests the molecule has a shorter residence time in the stratosphere than expected. It would be instructive to incorporate the present results into a detailed atmospheric model to reevaluate quantitatively the residence times and the environmental effects of acetonitrile and acrylonitrile.

Low energy electron attachment to acetonitrile (CH$_3$CN) is also reported in the energy range from about zero up to 10 eV with an energy resolution of 140 meV. Electron attachment is shown to be a purely dissociative process with the production of the five anionic fragments: CH$_2$CN$, CHCN$, CCN$, CN$ and CH$_3$. Previous work has shown that such fragments are formed with low kinetic energy allowing the present instrument to detect all fragment ions and thus determine an absolute cross section for the production of each anion. Those fragment ions are observed in two energy regions, the first between 1 eV and 4 eV, the second in excess of 6 eV, suggesting that there are two energy regions where electron scattering resonances are formed. Quantum chemical and trajectory calculations have been carried out to complement the experimental results.
7.7 References

[7.1] www.epa.gov/opptintr/chemfact/acenit.txt
[7.19] www.staff.ncl.ac.uk/j.g.smith/chy002/chy002.html
Chapter 8

Conclusions and future work

One never notices what has been done; one can only see what remains to be done.  
Marie-Curie (1867 – 1934)

In this chapter a summary of the main results will be given and suggestions for future investigations will be made.

8.1 VUV spectroscopy

A comprehensive set of absolute high resolution photo-absorption cross sections has been made for dimethylsulphide, (CH₃)₂S, acetaldehyde, CH₃CHO, trifluoromethyl sulphur pentafluoride, SF₅CF₃, dichlorodifluoromethane, CCl₂F₂, acetonitrile, CH₃CN and acrylonitrile, C₂H₃CN.

8.1.1 Dimethylsulphide, (CH₃)₂S

The photo-absorption spectrum has been recorded in the energy range 5.0 eV to 11 eV and the first absolute cross sections for λ > 210 nm (< 5.9 eV) have been obtained. The spectrum reveals low intensity features below 6.0 eV attributed mainly to excitations from sulphur lone pair electrons (ns) to σ* orbitals. Above 6.0 eV the spectrum is mainly characterised by transitions from the HOMO into Rydberg orbitals of nsσ, npλ, ndσ and ndπ character with associated vibrational excitation. Assignments of the Rydberg series quantum defects are supported by the Elden’s plots obtained.

It has been proposed for the first time, according to the observed patterns, that non-adiabatic transitions between 1'A'' ← 2'A'' states involve significant geometrical changes inducing rich vibrational activity.

Photolysis rates and local lifetimes were obtained and it has been concluded that in the marine atmosphere (DMS) can be transformed into condensable acidic sulphur
products and through gas-to-particle conversion can become an important natural source of atmospheric sulphate aerosols.

8.1.2 Acetaldehyde, CH$_3$CHO

The photo-absorption spectrum has been obtained in the energy region 3.5 eV to 11 eV, with clear evidence in the low energy region for optically forbidden states. The absorption bands have been classified as an overlapping between valence transitions of $(n \rightarrow \pi^*)$, $(\pi \rightarrow \pi^*)$ and $(\sigma \rightarrow \pi^*)$ and members of Rydberg series converging to the lowest ionisation potential. $(\sigma \rightarrow \pi^*)$ transitions have been detected for the first time and were tentatively assigned to be at 10.436 eV.

Particular attention was devoted to the assignments of the structure in the 3.6 eV - 5.2 eV energy region due to singlet to triplet transitions. Those transitions are optically forbidden and therefore should not be observed in photo-absorption spectra. However, in reality no transition is totally forbidden, and they are observed in the photo-absorption spectra as having less than 1% magnitude than the allowed transitions. A $^3\text{n}s$ Rydberg series has been experimentally identified for the first time.

From the environmental point of view it seems that the atmospheric sinks for CH$_3$CHO are mainly reactions with OH radicals rather than photolysis. Acetaldehyde can easily act as a chlorine removal in the atmosphere, decreasing ozone depletion by halogens.

8.1.3 Trifluoromethyl sulphur pentafluoride, SF$_5$CF$_3$

SF$_5$CF$_3$ photo-absorption cross sections shows only one absorption feature in the 4.0 eV to 11 eV energy region, where the lowest-lying excited state lies ~ 8 eV above the ground state. The EELS data obtained was normalised to a known cross section at a particular wavelength measured in the optical experiment (9.336 eV) in order to obtain absolute cross sections at shorter wavelengths. From a PES measurement, ionisation potentials were obtained with higher resolution than in earlier measurements. Rydberg series converging to the different ionisation energies have been proposed for the first time, and Elden’s plots were obtained confirming some overlapping nature between valence and Rydberg transitions.

The ~ 1 eV energy gap between the photo-absorption cross section and the solar actinic fluxes for altitudes lower than 50 km leads to an overall lifetime of the order of a thousand years.
High-resolution temperature dependent infrared spectra were obtained and a new limit has been established for SF₅CF₃ radiative forcing at ~ 0.6 Wm⁻² ppb⁻¹, allowing to compute the global warming potential in a 100 years time to be around 18500 (22000 for SF₆).

8.1.4 Dichlorodifluoromethane, CCl₂F₂

The photo-absorption cross section for CCl₂F₂ was obtained for the energy region 5.5 eV to 11 eV and shows low absorption features below 8.5 eV that have been assigned to excitations that lead to prompt dissociation along the C – Cl bond due to the strong repulsive nature of the σ* excited state. The structures above 8.5 eV have been assigned to Rydberg series converging to the four lowest ionisation potentials of the \( \tilde{X}^2 B_3 \), \( \tilde{A}^2 B_1 \), \( \tilde{B}^2 A_2 \) and \( \tilde{C}^2 A_1 \) ionic states and a long vibrational progression involving CCI stretching mode with 16 quantum numbers has been clearly assigned.

The photolysis rates and local lifetimes were evaluated and the implications for ozone depletion and related mechanisms in the Earth’s atmosphere have been discussed in both gas phase and condensed phase.

The present high resolution photo-absorption cross sectional data have been recommended by the newly NASA edition *Chemical Kinetics and Photochemical Data for use in Atmospheric Studies* from February, 1 2003.

8.1.5 Acetonitrile, CH₃CN

The 4.0 eV – 11 eV photo-absorption spectrum shows low absorption structure below 9.0 eV assigned to \((\pi \rightarrow \pi^*)\) valence transitions with associated vibrational excitation involving CH₃ stretching, CH₃ deformation, C ≡ N stretching and C – C ≡ N bending modes. Above 9.0 eV there is overlapping between the \((n_N \rightarrow \pi^*)\) valence transition and the \(n\sigma\) Rydberg series converging to the two lowest ionisation potentials. Vibrational excitation is also observed with mainly C – C(N) stretching and C – C ≡ N bending modes. Other Rydberg series have also been assigned as \(n\pi\sigma\), \(n\pi\pi\) and \(n\sigma\).

Environmental evaluations estimate a very low role for photolysis process in the troposphere and therefore destruction of acetonitrile is dominated by reactions with atmospheric species, in particular with OH radicals.
8.1.6 Acrylonitrile, $\text{C}_2\text{H}_3\text{CN}$

Comparison of acetonitrile with acrylonitrile has been made on the basis of the photo-absorption spectra where excitations in the valence bands are dominated by transitions from $\pi \rightarrow \pi^*$ ($\text{C} = \text{N}$) orbitals for both molecules. A significant difference, however, is observed when nitrogen lone pair excitations for each molecule are compared. The photo-absorption spectrum obtained in the energy region 5.5 eV to 11 eV shows transitions to singlet excited states. Valence transitions in the 5.5 eV - 9.0 eV energy region have been assigned from the HOMO, $\pi_2(\text{C} = \text{C} - \text{C} = \text{N})$, resulting in vibrational excitation with several modes being affected. New vibrational excitation patterns were proposed for the first time and the optical data has been compared to previous EELS. Rydberg series of $n\sigma$, $np\lambda$, $n\delta\pi$ and $nd\delta$ character were identified converging to the three lowest ionisation potentials. Elden's plots obtained on the quantum defect and reduced term energies bases confirmed the proposed assignments of those series.

The environmental impact of this molecule in the Earth's atmosphere was evaluated and due to the fast photolysis rates observed, the residence times in the upper stratosphere were estimated to be of the order of hours. However, at lower altitudes (below 20 km) the main sink process is reactions with OH reactions.

8.2 Electron attachment studies

Electron attachment experiments have been performed in the gas phase for acetonitrile, $\text{CH}_3\text{CN}$, and in the condensed phase for trifluoromethyl sulphur pentafluoride, $\text{SF}_5\text{CF}_3$.

8.2.1 Acetonitrile, $\text{CH}_3\text{CN}$

Low energy electron attachment has been reported in the energy range from about zero up to 10 eV with an energy resolution of 140 meV. Electron attachment is shown to be a purely dissociative process with the production of the five anionic fragments: $\text{CH}_2\text{CN}^-$, $\text{CHCN}^-$, $\text{CCN}^-$, $\text{CN}^-$ and $\text{CH}_3^-$. Previous work has shown that such fragments are formed with low kinetic energy allowing the present instrument to detect all fragment ions and thus determine an absolute cross section for the production of each anion. Those fragment ions are observed in two energy regions, the first between 1 eV and 4 eV, the second in excess of 6 eV, suggesting that there are two energy regions
where electron scattering resonances are formed. Quantum chemical and trajectory calculations have been carried out to complement the experimental results.

8.2.2 Trifluoromethyl sulphur pentafluoride, SF$_5$CF$_3$

Electron stimulated desorption measurements of condensed phase SF$_5$CF$_3$ have been carried out on a Au (111) surface yielding a remarkably strong F$^-$ desorption signal from a resonance located at 11 eV, in contrast to the gas phase effective dissociative electron attachment (DEA) into into SF$_5^-$ + CF$_3$ at energies below 2 eV. Desorption from sub-monolayers of SF$_5$CF$_3$ on amorphous H$_2$O ice is more effective compared to desorption from a Xe surface. Implications for the heterogeneous photochemistry of SF$_5$CF$_3$ adsorbed on ice or dust particles in the Earth’s atmosphere are considered to be important if photo-induced decomposition of adsorbed molecules (involving weakly bound excess electrons) may readily occur at wavelengths where the gas phase molecule is photo-chemically inactive.

SF$_5$CF$_3$ clusters produced by adiabatic expansion on a seeded argon gas were obtained and negative ions formed by the interaction of a TEM low energy electron gun, revealed the formation of a stable parent ion in contrast to the experiments in the gas phase. Apart from the SF$_5^-$ and SF$_5$CF$_3^-$ detected in the 300 amu of the quadrupole mass range, solvated fragment ions Ar$_n$ SF$_5^-$ (n = 1, 2) and complexes of the form Ar$_n$ SF$_5$CF$_3^-$ (n = 0 – 3) containing the un-dissociated parent anion, have been observed.

8.3 Future work

One of the major challenges of atmospheric modelling is to prove a more accurate and precise way to characterise the lifetimes and photolysis rates of molecular systems by including various parameters associated with transport phenomena, cloud effects, winds and diffusion. Access to the synchrotron radiation facilities, and the study of electron-molecule interaction experiments (in both gas and condensed phases) will allow a better understanding of the chemical dynamics of the removal processes and allow development of better field instrumentation in order to monitor gaseous emissions into the Earth’s atmosphere.

8.3.1 VUV photo-absorption investigations

Investigations into the electronic spectroscopy of several molecules of atmospheric interest using the photo-absorption apparatus at the Institute of Storage
Ring Facilities at the University of Aarhus, Denmark are ongoing. In the near future the effect of temperature on the excitation cross sections should be evaluated and measured, since it determines the initial population of the rotational, vibrational and electronic states.

VUV photo-absorption on ice surfaces (e.g., water and ammonia) from temperature dependent sub-monolayers of CFCs, halocarbons, HCFCs, SF$_5$CF$_3$, ..., should be performed and implications for the heterogeneous photochemistry of those molecular species adsorbed on ice or dust particles in the Earth’s atmosphere could be simulated and evaluated, and the results compared and complemented with electron stimulated desorption experiments already started. Desorption fragmentation should then be mass spectrometrically analysed which would allow better information on the chemical dynamics of the dissociation processes involved (preferably by analysing the kinetic energy release distributions). In situ infrared assisted spectroscopy is an extremely important tool for condensed ices in order to obtain information on the energies of the vibrational modes of the molecular species at the surface, especially when unimolecular decomposition is not effective in transferring enough translational energy to the fragment to leave the polarisation force that keeps it trapped at the surface. Photo-electrons and mass spectrometric fragments emitted should be analysed and information on the bond and binding energies obtained, as well as the kinetic energy profiles.

Taking advantage of the linear and circular polarised synchrotron radiation beam, experiments involving circular dichroism could be performed in order to extract information on the symmetry of the electronic transitions. It would be possible to investigate also the Rydberg absorption bands with respect to the polarisation of the transitions, the dipole moment, and mean polarisability changes that occur upon excitation between the ground and excited states.

8.3.2 EELS and PES

Electron energy loss and photo-electron spectroscopies are two powerful tools which used together with photo-absorption will allow characterising the electronic excitations into valence and Rydberg states and ionic states.

Due to the optically forbidden singlet-triplet transitions of several molecules studied, in particular CH$_3$CHO, CF$_3$I, C$_2$F$_4$, ..., near-threshold electron energy-loss spectroscopy studies should be included in the future because it allows better
characterisation of these states by access to the related negative ion resonances as a function of the residual electron energy.

### 8.3.3 Theoretical calculations

Theoretical calculations are clearly needed if we are to have a better understanding of the molecular states. Electron scattering resonances calculations are especially needed for the present case of SF$_5$CF$_3$, where neither the electronic configuration of this molecule is known nor is there any agreement onto its symmetry.

Calculations are also required to understand the effect of charge transfer at surfaces and to fully characterise the condensed-phase negative molecular ion states at low energies where electron capture is very active but the desorption signal is suppressed.

### 8.3.4 EA and ESD experiments

Electron attachment and detachment processes, known as electron transfer reactions, play an important role in many fields of pure and applied science, in the gas phase (e.g., discharges, gaseous dielectrics, atmospheric processes) as well as in the condensed phase (e.g., electrochemistry and biochemical systems).

Low energy electron attachment experiments in both the gas and condensed phase are extremely important for the characterisation of the negative ion resonances/states, playing an important role in the molecular physics of the atmosphere and plasmas, due to the involvement of kinetically energetic electrons and the formation of highly reactive short-lived excited species. Therefore, studies on atmospheric interest molecules should continue.

Further condensed-phase experiments using sub-monolayers of CFCs (mainly CCl$_2$F$_2$, and SF$_5$CF$_3$ on ammonia) are needed in order to understand the implications and mechanisms of the heterogeneous photochemistry in the Polar Stratospheric Clouds and how this may affect ozone depletion by halogen release. Studies on the kinetic energy release distributions are needed in order to understand the dissociation mechanisms and obtain information on the lifetimes of the temporary negative ions. These experiments will provide valuable information on how the energy is (re)distributed inside the molecule prior to the dissociation processes; electronic state and kinetic energy of the dissociative states forming a particular fragment are determined by energy analysis. Therefore information on the excitation energy that
remains in the internal modes of fragments and/or adsorbed partners can be evaluated, providing valuable data for theoretical modelling of the dissociation processes and energy distribution on molecular dissociation.

Within these different fields the general idea of non-covalent Van der Waals interactions between molecules and their behaviour when they are subjected to excitation or ionisation plays a central role in many fields of present-day natural science. The link between gas and condensed phases should always be accompanied by cluster experiments because these represent a link between matter in its gaseous and condensed form (bulk liquids or solids).
Appendix I

Headlight effect

I don’t see the logic of rejecting data just because they seem incredible.

Sir Fred Hoyle (1915 – 2001)

When electrons move with relativistic velocities the exhibited emitted radiation is described as the headlight effect, which is an important process that collimates synchrotron output.

Briefly, an unstable particle with velocity \( v \) is emitting particles. In a moving frame \( \chi' \), of velocity \( v \) the unstable particle is at rest and emits isotropically. Therefore is required the distribution in a stationary \( \chi \) frame. The frames are related between themselves as illustrated:

![Reference frames in headlight effect](image)

where the velocity of an emitted particle \( \mu' \) can be expressed as:

\[
\mu' = \mu'_x \cos\theta' x' + \mu'_y \sin\theta' y'
\]  \hspace{1cm} \text{(AI.1)}

and the angle given by the tangent:

\[
\tan\theta' = \frac{\mu'_y}{\mu'_x}
\]  \hspace{1cm} \text{(AI.2)}

similarly, the direction as observed in frame \( \chi \) is \( \theta \) with the tangent given by:

\[
\tan\theta = \frac{\mu_y}{\mu_x}
\]  \hspace{1cm} \text{(AI.3)}

the velocity components are related by:
Appendix I: Head Light Effect

\[ \mu_x = \frac{\mu_x' + v}{1 + \mu_x' v/c^2} \quad \text{and} \quad \mu_y = \frac{\mu_y'}{\gamma(1 + \mu_x' v/c^2)} \]  \hspace{1cm} (AI.4)

and:

\[ \gamma = \frac{1}{\sqrt{1 - v^2/c^2}} \]  \hspace{1cm} (AI.5)

Substituting equation AI.4 into AI.3 gives:

\[ \tan \theta = \frac{\mu_y'}{\gamma(\mu_x' + v)} = \frac{\tan \theta'}{\gamma(1 + v/\mu_x')} \]  \hspace{1cm} (AI.6)

hence as v → c, γ → ∞ and tanθ → 0 irrespective of θ'. Thus emission in χ' in any direction will be confined to the direction of the velocity vector v in frame χ, where the radiation is being collimated. The next figure shows the effect of a certain velocity input and calculated angle θ for 5 degrees increment of θ'. The plotted blue lines were obtained using:

\[ x = a \cos \theta \quad \text{and} \quad y = a \sin \theta \]  \hspace{1cm} (AI.7)

with a the magnitude and a constant.

![Figure AI.2 - The headlight effect for several electron energies.](image)
Appendix II

List of publications

The one duty we owe to history is to rewrite it.

Oscar Wilde (1854 – 1900)

Published papers (17):

1. An experimental study of SF₅CF₃ by electron energy loss spectroscopy, VUV photo-absorption, and photoelectron spectroscopy

2. Electron excitation of tetrafluoroethylene, C₂F₄

3. The electronic states of isoxazole studied by VUV absorption, electron energy-loss spectroscopies and ab initio multi-reference configuration interaction calculations

4. Low energy electron attachment to CH₃CN
   W Sailer, A Pelc, P Limão-Vieira, N J Mason, J Limtrakul, P Scheier, M Probst and T D Márk

5. Low energy electron interaction with free and bound SF₅CF₃: negative ion formation from single molecules, clusters and nanofilms
   R Balog, M Stano, P Limão-Vieira, C König, I Bald, N J Mason and Eugen Illenberger

6. High resolution photo-absorption studies of acrylonitrile, C₂H₃CN, and acetonitrile, CH₃CN
   S Eden, P Limão-Vieira, P A Kendall, N J Mason, S V Hoffmann, S M Spyrou

7. The electronic states of 2-furanmethanol (furfuryl alcohol) studied by photon absorption and electron impact spectroscopies

8. VUV photoabsorption by hexafluoropropene
   S Eden, P Limão-Vieira, N J Mason and S V Hoffmann

9. 2-methylfuran: An experimental study of the excited electronic levels by electron energy loss spectroscopy, UV-VUV photo-absorption spectroscopy
   A Giuliani, J Delwiche, S V Hoffmann, P Limão-Vieira, N J Mason, M-J Hubin-Franskin
Appendix II: List of publications

10. High resolution VUV photo-absorption of acetaldehyde, CH$_3$CHO
    P Limão-Vieira, S Eden, N J Mason and S V Hoffmann

11. Absolute photo-absorption cross sections and electronic state spectroscopy of selected
    fluorinated hydrocarbons relevant to the plasma processing industry
    P Limão-Vieira, S Eden, N J Mason

12. Electron and photon induced processes in SF$_6$CF$_3$

    S Eden, N J Mason, P Limão-Vieira, M Kitajima, M Okamoto, H Tanaka, D Newnham and S Hoffmann

14. Temperature dependent high-resolution infrared photo-absorption cross sections of
    trifluoromethyl sulphur pentfluoride
    P A Kendall, N J Mason, G A Buchanan, G Marston, P Tegeder, A Dawes, S Eden, P Limão-
    Vieira, D A Newnham

    N J Mason, P Limão-Vieira, S Eden, P Kendall, S Pathak, A Dawes, J Tennyson, P Tegeder, M
    Kitajima, M Okamoto, K Sunohara, H Tanaka, H Cho, S Samukawa, S V Hoffmann, D
    Newnham and S M Spyrou

16. High resolution VUV photo-absorption cross-section for dimethylsulphide, (CH$_3$)$_2$S
    P Limão-Vieira, S Eden, P A Kendall, N J Mason and S V Hoffmann

17. VUV photo-absorption cross section for CCl$_3$F$_2$
    P Limão Vieira, S Eden, P A Kendall, N J Mason and S V Hoffmann

Papers in preparation (1):

18. VUV spectroscopy of CF$_3$Cl, CF$_3$Br, CH$_3$I and CH$_3$Cl
    S Eden, P Limão-Vieira, N J Mason and S V Hoffmann

Referred abstracts presented at conferences (14):

19. Negative ion formation by low electron energy to condensed SF$_6$CF$_3$ molecules
    P Limão-Vieira, S Eden, N J Mason, R Balog, C König, I Bald and E Illenberger

20. Spectroscopic studies of valence, Rydberg and ionic states of tetrafluoroethylene, C$_2$F$_4$

21. Electronic state spectroscopy of SF$_6$CF$_3$ by gas-phase and condensed phase conditions
    P Limão-Vieira, S Eden, N J Mason, A Giuliani, M-J Hubin-Franskin, J Heinesch, J Delwiche, R Balog and E Illenberger
Appendix II: List of publications

22. Electronic excitation of tetrafluoroethylene, C$_2$F$_4$

23. On the role of CCl$_2$F$_2$, (CH$_3$)$_2$S and SF$_5$CF$_3$ in stratospheric ozone depletion and global warming
P Limão-Vieira, P A Kendall, S Eden and N J Mason
VI Iberian Joint Meeting on Atomic and Molecular Physics, Madrid, Spain, (2003) 185.

24. High resolution VUV photo-absorption and electronic state spectroscopy of tetrafluoroethylene, C$_2$F$_4$
S Eden, P Limão-Vieira and N J Mason
VI Iberian Joint Meeting on Atomic and Molecular Physics, Madrid, Spain, (2003) 183.

25. Electron and photon induced processes in SF$_6$CF$_3$
P Limão Vieira, P A Kendall, S Eden and N J Mason

26. Absolute photo-absorption cross sections and electronic state spectroscopy of fluorinated selected hydrocarbons relevant to the plasma processing industry
S Eden, P Limão Vieira and N J Mason

27. Electron and photon induced processes in plasma etching gases
S Eden, P Limão Vieira and N J Mason

28. Electron scattering from molecular systems relevant to plasma industry: A combined experimental and theoretical study
N J Mason, S Eden, P Kendall, P Tegeder and P Limão Vieira

29. Electron and photon induced processes in plasma etching gases
P Limão Vieira, S Eden, and N J Mason
V Iberian Joint Meeting on Atomic and Molecular Physics, Lisbon, Portugal, (2002) 49.

30. Electron and Photon Impact Studies of CF$_3$I

31. Studies of CF$_3$I: Electron and Photon Impact Spectroscopy
S Eden, P Limão Vieira, N J Mason, M Kitajima, M Okamoto, H Tanaka and S Samukawa

32. Electron induced chemistry in technological plasmas: data for CF$_3$I, C$_2$F$_4$ and associated dissociative fragments
I Rozum, S Eden, P Limão-Vieira, N J Mason and J Tennyson

Oral contributions (3):

33. Electron and photon induced processes in plasma etching gases
V Iberian Joint Meeting on Atomic and Molecular Physics, Lisbon, March 23-26, 2002.

34. Experimental studies to assess the environmental impact of SF$_6$CF$_3$ in the atmosphere

35. Environmental impact of SF$_6$CF$_3$
Appendix III

Proof of publications

It is wise to disclose what cannot be concealed.

Thomas Hardy (1759 – 1805)

Dimethylsulphide, (CH_3)_2S

High resolution VUV photo-absorption cross-section for dimethylsulphide, (CH_3)_2S

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Received 24 September 2002, in final form 9 October 2002

Abstract

The photo-absorption spectrum of (CH_3)_2S has been measured using synchrotron radiation in the range 5.011 eV (250-180 nm). Electronic state assignments have been suggested for each of the observed absorption bands incorporating both valence and Rydberg transitions. Four Rydberg series have been assigned converging to the ionisation potential limit 6.658 eV. Rydberg envelope of each series are classified according to the magnitude of the quantum defect. The measured vacuum-ultraviolet (VUV) cross-sections are used to derive the photolysis rate of (CH_3)_2S in the terrestrial atmosphere.

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1. Introduction

Dimethylsulphide (DMS), (CH_3)_2S, is the most abundant sulphur compound found in seawater and plays an important role in the global sulphur cycle. DMS is a product of biodegradation of organosulphur compounds in marine environments, which upon release into the atmosphere is changed into a different sulphur species, e.g., sulphur dioxide, methane-sulphonic acid, sulphate and sulphonic acid, all of which can contribute to the acidity of rain. Moreover, sulphur gases are known to be precursors of sulphate aerosol particles and cloud condensation nuclei over remote parts of the oceans and could also act as a feedback mechanism in climate regulation which affects the Earth’s radiative balance by direct scattering of solar radiation [1]. It has now become clear that the natural sulphur cycle has been seriously disturbed by anthropogenic gaseous emissions. Studies on DMS and its oxidation products in marine atmosphere, production and release in local estuaries and distribution in surface waters have therefore recently become the subject of intense research [2-4].

In this Letter we report new data on the photo-absorption cross-section and electronic spectroscopy of (CH_3)_2S. The electronic states have been studied previously [5-7] as have its photoelectron spectra, photo-ionisation spectra, electron...
Electronic state spectroscopy of acetaldehyde, CH₃CHO, by high-resolution VUV photo-absorption

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Received 16 May 2003; in final form 26 June 2003

Abstract

The high-resolution photo-absorption cross-section of CH₃CHO has been measured using synchrotron radiation in the range 3.0-11 eV (413 nm > λ > 113 nm). Electronic state assignments have been suggested for each of the observed absorption bands incorporating both valence and Rydberg transitions. Valence transitions to the singlet and triplet states are assigned. Six Rydberg series have been assigned converging to the ionisation energy limit 10.229 eV. Rydberg orbitals of each series are classified according to the magnitude of the quantum defect (δ). The measured VUV cross-sections are used to derive the photolysis rates of acetaldehyde in the terrestrial atmosphere.

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1. Introduction

Acetaldehyde, CH₃CHO, is created and destroyed by photolysis in the terrestrial atmosphere. The most common formation mechanism is considered to be the photochemical degradation of organic compounds followed by oxidation.

CH₃CHO may subsequently be removed from the atmosphere by photolysis and through low-altitude reactions with other trace compounds. The molecule typically reacts with the hydroxyl radical, OH, nitrogen trioxide, NO₃, and peroxyacyl nitrates (RC(O)OONO₂). The H-atom abstracting reaction of acetaldehyde with hydroxyl radicals produces the acetyl radical, CH₂CO. This fragment reacts with molecular oxygen to form peroxyacyl radicals (CH₃C(O)OO) that in turn react with NO and NO₂. The products of the nitrogen dioxide interactions include the peroxyacyl nitrates: CH₃C(O)OONO₂, CH₃CH₂C(O)OONO₂. These gases may contribute to global warming.

Acetaldehyde is the simplest of the aldehydes and is an important spectroscopic intermediate between formaldehyde (H₂CO) and acetone.
Electron and photon induced processes in SF₅CF₃


Abstract

The photo-absorption cross section of trifluoromethyl sulphur pentafluoride, SF₅CF₃, has been measured using synchrotron radiation in the range of 4-11 eV (1310 nm > λ > 110 nm) and comparisons made with electron energy loss spectroscopy (EELS). The measured VUV cross sections are used to derive the photolysis rate of SF₅CF₃ in the terrestrial atmosphere. It is estimated that the lifetime for this molecule is the order of a 1000 years and the calculated global warming potential (GWP) is found to be between 13000 and 18000, making it one of the most potent global warming gases in the terrestrial atmosphere.

Keywords: VUV photo-absorption, Synchrotron radiation; Greenhouse gas; Photolysis rates

1. Introduction

Concern of the effect of climate change arising from global warming has grown over the last 20 years and is now the subject of major political discussions. The recent report of the International Panel for Climate Change (IPPC) forecasts that mean global temperatures may rise by as much as 5.8°C by the end of the century (www.ipcc.ch, 2001). The major contributions to such global warming are strong greenhouse gases compounds such as CO₂, CH₄ and N₂O. However, there are many gases which although present in much smaller quantities have a significant contribution to global warming due to their large infrared absorptions and long lifetimes in the terrestrial atmosphere.

A newly discovered totally anthropogenic origin molecule is trifluoromethyl sulphur pentafluoride (SF₅CF₃). According to a recent report (Sturges et al., 2003), it possesses the largest radiative forcing on a per molecule basis of all gases present in the atmosphere, 0.57 Wm⁻²ppb⁻¹. Moreover, the levels in the atmosphere for this molecule although currently small, > 0.13 parts per trillion by volume, are growing at a 6% per year rate or in mass terms, the total burden is 3600 tonnes increasing at 210 tonnes per year.

Since SF₅CF₃ has no natural source its presence in the terrestrial atmosphere seems to be related to SF₅ radicals (a breakdown product of SF₅) formed by high-voltage discharges in reaction with CF₃ radicals from fluoropolymeric surfaces (Kennedy and Mayhew, 2001). SF₅ is used in high voltage circuit breakers due to its high dielectric strength, transformers, accelerators and other high voltage equipment.

The electron energy loss spectra (EELS) of SF₅CF₃ has recently been measured and revealed that the threshold for the lowest-lying excited electronic state lies ~8 eV above the ground state (Kendall and Mason, 2001, 2003, respectively), confirming the prediction of a high dissociation energy for the SF₅ CF₃ bond (Gutir et al., 2002) of about 4 eV.

In this paper we report a high resolution, absolute photo-absorption spectrum of SF₅CF₃ in the energy
Appendix III: Proof of publications

Trifluoromethyl sulphur pentafluoride, SF₅CF₃ (2)

Temperature dependent high-resolution infrared photoabsorption cross-sections of trifluoromethyl sulphur pentafluoride

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Received 18 June 2002; in final form 4 November 2002

Abstract

Absolute infrared photoabsorption cross-sections have been measured over the range 600 to 1500 cm⁻¹ for the powerful greenhouse gas SF₅CF₃ at high resolution (0.07 cm⁻¹) and at temperatures between 203 and 298 K. Our data indicate that the integrated absorption intensity shows a weak negative dependence on temperature. It is concluded therefore that previous calculations of radiative forcings and global warming potentials based on room-temperature data are reasonable estimates for the atmosphere, but may be low by a few percent.

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Keywords: Photoabsorption, Spectroscopy, Greenhouse gas, SF₅CF₃; Cross-sections

1. Introduction

Global warming is a topic of great concern to society; the recent International Panel for Climate Change (IPCC) report [1] indicated that the mean global surface temperature may rise by as much as 5.8 °C by the end of the 21st century. The bulk of the contributions to global warming arise from increased atmospheric levels of CO₂, CH₄ and N₂O. However, molecules that are effective infra-red absorbers in the atmospheric "window regions" between 800 and 1200 cm⁻¹ can also make significant contributions, even though they are present at only low levels. One such molecule is SF₅CF₃, which is a particularly effective greenhouse gas that has only recently been detected in the atmosphere [2].

Starges et al. discovered SF₅CF₃ in the mass spectra of stratospheric air samples collected in...
Low energy electron interaction with free and bound SF$_5$CF$_3$:

Negative ion formation from single molecules, clusters and nanofilms

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(Received 25 June 2003; accepted 19 August 2003)

The interaction of free electrons with the potent greenhouse molecule SF$_5$CF$_3$ is studied under different degrees of aggregation: single molecules at collision free conditions, clusters within a supersonic molecular beam and condensed molecules. Electron collisions with single molecules are dominated by SF$_5^-$ formation produced via dissociative electron attachment (DEA) within a resonance located below 2 eV. In clusters, undissociated parent ansoms SF$_5$CF$_3$ (and larger complexes containing undissociated ansoms) are observed in addition to the fragment ions. This indicates that (i) SF$_5$CF$_3$ possesses a positive adiabatic electron affinity and (ii) low energy attachment is partly channeled into nondissociative processes when the molecule is coupled to an environment. Electron impact to condensed phase SF$_5$CF$_3$ exhibits a remarkably strong F desorption signal appearing from a pronounced resonance located at 11 eV while in the gas phase at 11 eV only a weak DEA signal is observed. Electron induced desorption from sub-monolayers of SF$_5$CF$_3$ on an amorphous H$_2$O ice surface is found to be more efficient compared to desorption of SF$_5$CF$_3$ from a Xe surface. The implications of these results for the heterogeneous photochemistry of SF$_5$CF$_3$ adsorbed on ice or dust particles in the Earth's atmosphere are discussed. © 2003 American Institute of Physics. [DOI: 10.1140/1.1617978]

I. INTRODUCTION

Trifluoromethyl sulphur pentafluoride (SF$_5$CF$_3$) has been recently discovered in stratospheric air at concentrations of about 0.12 ppt with the tendency to increase at a rate of about 6% per year. The molecule is of anthropogenic origin, its sources, however, are not yet clearly identified. Since the trends in concentration of SF$_5$F and SF$_5$CF$_2$ have tracked each other very closely it has been suggested that SF$_5$CF$_3$ may be generated from breakdown products of SF$_5$F (Ref. 1) which has widespread applications in many gas induced high power, high voltage devices. SF$_5$CF$_3$ possesses several strong IR bands in the "atmospheric IR window" (600–1300 cm$^{-1}$) with absorption cross sections in the range of 10$^{-19}$–10$^{-17}$ cm$^2$. It is therefore considered the most effective greenhouse gas on a per molecule basis in the Earth's atmosphere. Such a high global warming potential (GWP) of SF$_5$CF$_3$ can be based upon its high IR absorption cross sections and the assumption of an atmospheric lifetime comparable to that of SF$_5$F. However, it has recently been shown that SF$_5$CF$_3$ is very effectively decomposed into SF$_5^-$ + CF$_3$ (Refs. 2, 3) by low energy dissociative electron attachment. This is in striking contrast to its unsubstituted analogue SF$_5^-$ which indeed possesses one of the highest cross sections for thermal electron attachment (exceeding that of SF$_5$F), the process, however, is virtually nondissociative forming a long lived SF$_5^-$ at ambient temperatures. However, the existence of resonances of dissociative character as found in SF$_5$CF$_3$ may be directly related to the heterogeneous photochemical activity of a molecule. Photo-induced decomposition of molecules adsorbed on dust or aerosol particles (involving weakly bound excess electrons) within the Earth's atmosphere could then readily occur at wavelengths where the gas phase molecule is photochemically inactive leading to a reduced atmospheric lifetime.

In this paper we study low energy electron induced reactions in free and bound SF$_5$CF$_3$ induced by low energy electrons in the energy range 0–18 eV. The experiments include negative ion formation from gas phase molecules under single collision conditions, from molecular aggregates as a supersonic beam and electron stimulated desorption (ESD) of negative ions from SF$_5$CF$_3$ nanofilms and from sub-monolayers of SF$_5$CF$_3$ adsorbed on the surface of solid Xe and amorphous water ice. The aim of the present study is to obtain information on how the intrinsic reactivity of the compound towards low energy electrons is affected by its real environment.

II. EXPERIMENT

The experiments were performed (i) in a crossed electron beam-molecular beam arrangement (single SF$_5$CF$_3$ molecules and homogeneous clusters) and (ii) in a UHV surface experiment (condensed phase molecules) as described earlier. Single molecules were obtained by means of gas
VUV photo-absorption cross-section for CCl$_2$F$_2$

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Abstract

The photo-absorption spectrum of CCl$_2$F$_2$ has been measured using synchrotron radiation in the range 5.5–11 eV (225 > λ > 110 nm). Electronic state assignments have been suggested for each of the observed absorption bands incorporating both valence and Rydberg transitions. The high resolution achieved has allowed vibrational series on one of these bands to be assigned for the first time. The measured VUV cross-sections may be used to derive the photolysis rate of CCl$_2$F$_2$ in the terrestrial atmosphere.

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1. Introduction

Dichlorodifluoromethane (CCl$_2$F$_2$ or CFC-12) is a halogenated hydrocarbon extensively used in refrigeration systems, as a foam blowing agent and as an aerosol propellant. It also plays an important role in the plasma etching industry [1,2] for reactive ion etching (RIE) of Ge/Si as it can be readily dissociated to produce Cl and F radicals [3].

Halogenated hydrocarbons or halocarbons such as CCl$_2$F$_2$ are (under photolysis) a source of atmospheric radicals and therefore are widely recognised to contribute significantly to stratospheric ozone depletion [4,5] by Cl or Br atoms released by photolysis. Halogenated hydrocarbons are also strong greenhouse gases, CCl$_2$F$_2$ has a residence time in the atmosphere of about 100 years and an estimated global warming potential of 8500 in a 100-year period [6]. Thus, under the regulations of the Montreal Protocol and its amendments, the use of CCl$_2$F$_2$ in industry must be phased out and alternatives found within the next decade.

In this paper we report new data on the photo-absorption cross-section and electronic spectroscopy of CCl$_2$F$_2$. The electronic structure of this molecule has been studied previously [7–13] as have its photo-absorption, photo-ionisation and photo-fragmentation cross-sections [4,8,10,11,14]. The vacuum-ultraviolet (VUV) absorption spectrum of CCl$_2$F$_2$ in the wavelength range 120–200 nm (10–6 eV) was first measured during the 1950s by Zobel and Duncan [15] and subsequently discussed by Doucet et al. [10] together with a comparison with the photo-electron spectrum. An energy loss spectrum using 500 eV electrons was...
Acetonitrile & acrylonitrile, CH₃CN and C₂H₃CN

High resolution photo-absorption studies of acrylonitrile, CH₃CN, and acetonitrile, CH₃CN

S. Eke et al., P. Limus-Vieira et al., P. Kendall et al., A.J. Mason et al., S.V. Hallinan et al., and S.M. Spenner

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Abstract. High resolution photo-absorption spectra of acrylonitrile and acetonitrile have been recorded in the wavelength range 15 to 120 nm (9.8 to 13.3 eV). Results are compared with previous photo-absorption measurements and electronic energy loss spectra and, in some cases, are found to be in close agreement. The high resolution achieved in the present work has allowed some structures to be observed for the first time and new assignments have been suggested accordingly. The role of the molecules in the terrestrial atmosphere is discussed.

PACS. 32.30.1m Visible and ultraviolet spectra

1 Introduction

Acrylonitrile, also known as vinyl cyanide and 2-propionitrile, does not occur naturally but is produced in great quantities industrially [1]. World production in 2000 was estimated at 16 million metric tons [2]. The compound is used primarily in the manufacture of acrylic fibres and as a raw material in the fabrication of plastics, nitrite esters and other resinous materials. As an electronic material, thin films of the molecule can be deposited onto metallic substrates [3]. Acrylonitrile is released into the environment as gas and in waste water during its production and use. Other sources include combustion of coal and the release from fibres and plastics. Due to the carbon-nitrogen double bond, acrylonitrile is expected to serve as the key reactant towards atmospheric photo-oxidation by hydroxyl radicals and other oxidants.

Acetonitrile, otherwise known as methyl cyanide and methanimine, is an important industrial gas. Though also used to make pesticides, its major application lies in the extraction of insecticidal and cheese chemicals. Most importantly, it is a fluorocarbon, an important industrial gas. Though also used to make pesticides, its major application lies in the extraction of insecticidal and cheese chemicals. Most importantly, it is a fluorocarbon, a greenhouse gas, and a potential substitute for chlorofluorocarbons.

2 Summary of the structure and properties of the molecules

The structure of acrylonitrile is derived from microwave spectroscopy [10,11]. The molecule is planar in the electronic ground state and belongs to the C₂v symmetry group. Following the approximate sequence, the single C–H and C–C bonds are of σ character, while C=C contains one σ and one π bond. The nitrogen atom is bound to a carbon atom (C–C≡N) by one σ and two π interactions. The two nitrogen electrons are
Acetonitrile, CH₃CN

Low energy electron attachment to CH₃CN


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Received 8 June 2003; in final form 15 September 2003

Abstract

Low energy electron attachment cross-sections for acetonitrile (CH₃CN) are reported in the energy range from about 0 up to 10 eV determined with an energy resolution of 140 meV. Electron attachment is shown to be a purely dissociative process with the production of the five anionic fragments CH₃CN⁻, C₂H₅CN⁻, CCN⁻, CN⁻ and CH⁻ observed in two energy regions, the first between 1 and 4 eV, the second in excess of 6 eV. Quantum chemical and trajectory calculations have been carried out to complement the experimental results.

1. Introduction

Acetonitrile CH₃CN (also known as cyanomethane or methyl cyanide) is an important atmospheric and astrophysical molecule. In the terrestrial atmosphere, acetonitrile has recently been shown to be a useful gaseous tracer of biomass burning since simultaneous CO and acetonitrile measurements may be used to characterize the ratio of biomass burning to fossil fuel combustion – a key issue for current global warming studies. Acetonitrile is also an important molecular species observed in gas clouds of the interstellar medium where it is believed to be synthesized by heterogeneous chemistry on interstellar dust grains. Acetonitrile is therefore recognized as a fundamental building block of the amino acids and thus an important precursor molecule in the study of the origins of life. Hence it is important to study these mechanisms by which acetonitrile may be dissociated through the interactions with photons, electrons and surfaces.
Appendix III: Proof of publications

Trifluoromethyl iodide, CF₃I

VUV and low energy electron impact study of electronic state spectroscopy of CF₃I


Abstract

The electronic states of CF₃I have been investigated using photon and electron energy loss spectroscopy from 4 to 20 eV (310 nm – 60 nm). Assignments have been suggested for each of the observed absorption bands incorporating both valence and Rydberg transitions. Vibrational structure in each of these bands is observed for the first time. Absorption cross-sections have also been measured and are compared with earlier measurements. Int. J. Mass Spectrom. 223, 224 (2003) 647-666.

Keywords: VUV, absorption, Electron energy loss, Spectroscopy, Synchrotron radiation.

1. Introduction

In the manufacture of ultra-large-scale-integrated circuits, it is necessary to fabricate predetermined patterns on a scale of less than 0.1 mm and fine structures with an aspect ratio of more than 10 on a silicon wafers with diameters of greater than 30 cm. This process requires a well-collimated, spatially uniform, high-density plasma source operating under low-pressure conditions [1]. The main feed gases used by the plasma etching industry are perfluorocarbons (CF₃, C₂F₆, C₃F₈, CHF₃), and C₂F₆) however, these are also strong greenhouse gases and therefore, under the terms of the Kyoto Protocol, must be replaced by alternative compounds that have low "global warming potentials" [2]. One possible replacement is CF₃I since, due to the weak C-I bond, it should be possible
Trifluoromethyl iodide, CF$_3$I and dichlorodifluoromethane, CCl$_2$F$_2$

Absolute photo-absorption cross sections and electronic state spectroscopy of selected fluorinated hydrocarbons relevant to the plasma processing industry

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Abstract

Photo-absorption cross sections have been measured for methyl iodide, CF$_3$I ($110$ nm $>$ $i$ $>$ $110$ nm) and dichlorodifluoromethane, CCl$_2$F$_2$ ($125$ nm $>$ $i$ $>$ $100$ nm) using synchrotron radiation. Electron energy loss spectroscopy was also used to probe the electronic and vibronic excitation of CF$_3$I. Electronic states have been assigned to each of the observed absorption bands incorporating both valence and Rydberg transitions. The measured VUV cross sections are used to derive the photolysis rates in the terrestrial atmosphere and hence determine the potential importance of each gas in global warming and ozone depletion.

Keywords: Plasma etching; VUV photo-absorption; Electron energy loss spectroscopy (EELS); Synchrotron radiation; Photolysis rates

1. Introduction

The development of low-temperature plasmas has led to a multi-billion commercial industry employing many hundreds of thousands of people across the globe. Examples are fluorocarbon laser etching and chemical vapour deposition, plasma-enhanced chemical vapor deposition, plasma-enhanced atomic layer deposition, plasma etching of semiconductor wafers, and plasma-assisted chemical vapor deposition. In industry, the stability of the discharge frequently impacts the design and utility of the process, and the heterogeneous wall chemistry often impacts its reproducibility and reliability. However, there is still yet a lack of quantitative and experimental understanding of a wide range of phenomena that occur in low-temperature collision-dominated plasmas.

Typically, they are high-pressure collision-dominated plasmas that have energies of few tenths of eV. The gas purity is often important, and the physics and chemistry of the excited atomic states dominate the discharge characteristics. In industrial applications, the stability of the discharge frequently impacts the design and utility of the process, and the heterogeneous wall chemistry often impacts its reproducibility and reliability. However, there is still yet a lack of quantitative and experimental understanding of a wide range of phenomena that occur in low-temperature collision-dominated plasmas.

Appendix III: Proof of publications

Trifluoromethyl iodide, CF$_3$I and dichlorodifluoromethane, CCl$_2$F$_2$
2-methyl furan, C₅H₆O

2-methyl furan: An experimental study of the excited electronic levels by electron energy loss spectroscopy, vacuum ultraviolet photoabsorption, and photoelectron spectroscopy

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The vacuum ultraviolet absorption spectrum of 2-methyl furan has been recorded between 5 eV (248 nm) and 9.91 eV (125 nm) and absolute photoabsorption cross sections measured. The electronic excited states of the molecule have also been probed using high resolution electron energy loss spectroscopy. Recorded under electric dipole conditions, it has confirmed the magnitude of the photoabsorption cross section values and extended the optical oscillator strength values up to 12 eV.

Measurements at several scattering angles have allowed the angular behavior of differential cross section ratios for some features in the 5–7.1 eV region to be measured, which in turn have helped in the assignments of electronic states to observed absorption bands. A high-resolution photoelectron spectrum was measured and allowed the two lowest ionization energies to be determined, these have been used in the identification of the related Rydberg states. Vibrational fine structure in the photoelectron spectrum has also been analyzed. The spectrum is dominated by intense π–π* transitions. Rydberg series associated with the first and second ionization energies have been identified. The effects of symmetry reduction induced on the furan ring by the methyl substitution are also discussed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1569060]

I. INTRODUCTION

An introduction to the paper, the results of a spectroscopic study of furan derivatives. The substitution effect of an H atom by a methyl group on the singlet excited electronic energy levels of the furan ring is investigated.

This work is motivated by the basic importance held by the furan moiety in many fields of chemistry. It is a building block and a structural unit in organic chemistry, polymer science, and biochemistry. Moreover, furan and some of its derivatives are considered as volatile organic compounds, pollutants, and toxic compounds. Recently, the formation of furan has been reported in the atmosphere due to oxidation of tropospheric 1,3-butadiene. Although the furan molecule has been extensively studied theoretically and experimentally, little data exists on the spectroscopy and no absolute cross sections are available for 2-methyl furan in the ultraviolet (UV) range.

We report here new data on the electronic spectroscopy of 2-methyl furan in the 5–12 eV energy region. High resolution vacuum UV (VUV) photoabsorption using synchrotron radiation has provided absolute cross sections and electron energy loss spectroscopy (HREELS) in electric dipole (e–e) conditions gave access to excitation cross sections at higher energy. HREELS in the fixed impact energy and variable scattering angle mode has allowed us to derive the angular dependence of the differential cross sections (DCSs) for some features. HeI photoelectron spectroscopy of the two highest occupied molecular orbitals (HOMOs) is reported at higher resolution than previously and allowed us to determine the ionization energies and the vibrionic envelope of the corresponding ionic states. These data have been used to help in the assignment of the vibrational fine structure accompanying some transitions to the first Rydberg states.
Hexafluoropropene, $\text{C}_3\text{F}_6$

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VUV photoabsorption by hexafluoropropene

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Abstract

The high-resolution photoabsorption spectrum of hexafluoropropene is reported in the wavelength range 115–320 nm (10.8–3.9 eV). Assignments are proposed for the features observed. The photolysis rate and lifetime of the molecule in the atmosphere are modelled as a function of altitude and compared with previous calculations made considering hexafluoropropene reactions with OH radicals.

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1. Introduction

Hexafluoropropene, also known as hexafluoropropylene, perfluoro-1-propene, perfluoropropane and perfluoropropylene is a colourless and odourless gas produced commercially by temperature-controlled pyrolysis of chlorodifluoroethylene [1]. The gas is used in the production of copolymers and has attracted interest as a simulant for engine nacelle certification tests [2]. Significantly, as a source of CF$_3$ and CF$_4$ radicals, hexafluoropropene has been the subject of investigation as a potential feed gas for the plasma etching of silicon dioxide [3]. Conventional SiO$_2$ etching is carried out using CF$_4$, CHF$_3$ and c-C$_2$F$_5$. All of these species have high global warming potentials (GWP) as they absorb strongly in the infrared and have very long residence times in the Earth’s atmosphere [4,5]. As the current generation of plasma reactors release a high proportion of feed gas into the atmosphere, the use of these high-GWP reactants must be reduced under the terms of the Kyoto protocol [6]. Hexafluoropropene emissions are considered to have a negligible global warming effect due to the short atmospheric lifetime of the molecule due to its high reactivity with OH radicals [2,7,11]. Acerboni et al. [7] have used FT-IR spectroscopy to study the reactions of OH and ozone with hexafluoropropene and determine the rate coefficients to be ($2.67 \pm 0.7 \times 10^{-12}$) and ($6.2 \pm 1.5 \times 10^{-12}$) cm$^3$ molecules$^{-1}$ s$^{-1}$, respectively. Accordingly, Womeldorf et al. [2] give the ozone depletion potential (ODP) of the molecule as zero.

Hexafluoropropene has symmetry $C_s$ and 21 identified vibrational modes of excitation in the
I. INTRODUCTION

The furan molecule plays a central role in many fields of chemistry. Like pyrrole and thiophene it is pseudo-aromatic, but it retains properties related to those of the conjugated dienes and this contributes to its versatility in organic synthesis. Compounds incorporating the furan ring are of major importance in pharmaceutical, polymer, and materials science. Recently, furan compounds have also been implicated in environmental and atmospheric chemistry. Given this, it is of interest to explore how the electronic structure of furan is affected on substitution of the ring hydrogen atoms by functional groups. We have already reported on the valence-shell electronic spectroscopy of 2-methylfuran.1 We now present a comprehensive spectroscopic study on 2-furanmethanol (commonly known as furfuryl alcohol) the derivative obtained by substitution of an H atom of furan by a CH₂OH group (Fig. 1).

As well as being of interest because of its relationship to furan, furfuryl alcohol is important in its own right as a synthetic reagent. Currently, it is widely employed in the production of different kinds of resins and polymers used in coating technology, and potential technological applications make it one of the most important furanic derivatives on the market. The geometric structure of furfuryl alcohol (Fig. 11) has been established from microwave spectroscopy and ab initio