Elastic differential cross sections for the CF_x (x=1,2,3) radicals

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Abstract. Theoretical rotationally-summed elastic differential cross sections for scattering of electrons by CF_x radicals (x = 1-3) in the low-energy range (below 10 eV) are reported. The calculations used close-coupled expansion with target wavefunctions modelled using complete active space configuration interaction. The body-fixed K-matrices, used to calculate differential cross sections, were generated using the UK R-matrix codes. Comparison of the present results with existing theoretical data for electron collisions with CF and CF_3 radicals is made.

1. Introduction

Electron – molecule collisions occur in many natural environments, such as planetary atmospheres, the interstellar medium and stellar plasmas. Such collision processes lead to both chemical and physical changes of matter in environments associated with lasers, plasma-enhanced chemical vapour deposition (CVD), the lighting industry and plasma processing of materials for microelectronics. To understand any of the above processes the scientific community requires an understanding of the fundamental electron molecule interaction processes that underlie them.

Electron interactions with highly reactive radicals such as CF_x (x=1,2,3) are of particular interest in view of their importance in plasma modelling and developing plasma processing equipment. CF_x radicals are produced under electron bombardment of CF_3I and C_2F_4 plasma reactants (Mason *et al* 2003). CF_3I and C_2F_4 were proposed as replacements for CF_4, C_2F_6, C_3F_8 and c-C_4F_8 feedstock gases (Samukawa *et al* 1999), since the molecules in the second group are strong greenhouse gases. Recent studies have shown that the concentration of CF_x radicals has a significant effect on the behaviour of fluorocarbon plasmas (Chabert *et al* 2003) and that these radicals also occur in significant concentrations in other plasmas (Chabert *et al* 2001). Despite their importance there appears to be only little information about how these radicals interact with low energy electrons. CF_x radicals are highly reactive and experimental studies on highly reactive radicals are extremely difficult. *Ab initio* calculations can, therefore, play an important role in providing data upon which models can be based (Winstead and McKoy 2000).

Low energy electron–molecule collision cross sections (total, elastic, momentum transfer, rotational and vibrational excitation) from threshold up to a few electron volts play a crucial role in determining electron transport properties and electron energy distribution, and have significant importance for modelling low temperature plasmas. Differential cross section give angular information which is necessary for deriving the momentum transfer cross sections, which are important for plasma models; they are also important for comparison between calculated total cross sections and experiments.

Low energy integral elastic and electron impact excitation cross sections for CF, CF_2 and CF_3 radicals have already been published (Rozum *et al* 2002, Rozum *et al* 2003a and Rozum *et al* 2003b). In this paper we extend our work on the database for the plasma modelling and report low energy rotationally-summed elastic differential cross sections for electron collisions with CF_x.

2. Theoretical approach and calculations

2.1. General considerations

Since the details of the R-matrix approach have already been presented elsewhere (Burke and Berrington 1993, Morgan, Tennyson and Gillan 1998, Tennyson and Morgan 1999), only a brief outline of the theory will be given here. The inner region total wavefunction describing scattering of an electron by N-electron molecule is (Burke and Berrington 1993)

$$\Psi_k^{N+1} = A \sum_I \psi_I^N(x_1, ..., x_N) \sum_j \xi_j(x_{N+1}) a_{Ijk} + \sum_m \chi_m(x_1, ..., x_N, x_{N+1}) b_{mk} \quad (1)$$

where A is the anti-symmetrisation operator, x_n is the spatial and spin coordinate of the n^{th} electron, ξ_j is a continuum orbital spin-coupled with the scattering electron and a_{Ijk} and b_{mk} are variational coefficients determined by diagonalizing inner region Hamiltonian.

The R-matrix on the boundary is determined from the Hamiltonian matrix. The R-matrix contains a complete description of the collision problem in the inner region and provides the boundary conditions necessary to solve the problem in the outer region. In the outer region the scattering is described by the coupled single-centre equations. The K-matrix are found by integrating these equations out to infinity.

The T-matrix is obtained trivially from the K matrix

$$\mathbf{T} = 1 - (1 - i\mathbf{K})(1 + i\mathbf{K})^{-1}, \quad (2)$$

and can be used to derive physical observables such as integral and differential cross sections.

The differential cross section (DCS) for a general polyatomic molecule can be written as (Jain and Thompson 1983a, Jain and Thompson 1984, Gianturco and Jain 1986)

$$\frac{d\sigma}{d\Omega} = \sum_L A_L P_L(\cos\theta), \quad (3)$$

where the $P_L(cos\theta)$ are Legendre polynomials and the A_L are expansion coefficients constructed using the T-matrices (Jain and Thompson 1984, Gianturco and Jain 1986). L runs over the partial waves included in the calculations.

When the scattering involves polar molecules, the interaction potential includes long-range multipole potentials, such as the dipole potential, and a large number of partial waves contribute significantly to the cross section. This leads to the divergent DCS, especially in the the forward direction. This divergence can be removed by the introduction of the rotational motion in the problem. The final elastic DCS are calculated by summing the individual rotational excitation cross sections.

In the fixed nuclei approximation the cross sections are independent of the initial rotational state (Gianturco and Jain 1986). Then the partial differential cross section in a space-fixed frame of reference can be expressed by (3) where coefficients depend on the rotational quantum numbers of the particular rotor state. The presence of a long-range potential implies that a very large number of A_L coefficients needs to be evaluated and a very large set of (l, l') indexes of the T matrix needs to be included. This leads to a very slow convergence of the sum in (3).

To eliminate the above behaviour the DCS (3) can be rewritten as (Sanna and Gianturco 1998)

$$\frac{d\sigma}{d\Omega}(\nu j \to \nu' j') = \frac{d\sigma}{d\Omega}(\nu j \to \nu' j')^{FBA} + \Delta\frac{d\sigma}{d\Omega}(\nu j \to \nu' j'), \tag{4}$$

with

$$\Delta\frac{d\sigma}{d\Omega}(\nu j \to \nu' j') = \frac{1}{4k_{\nu j}^2}\sum_L [A_L(\nu j \to \nu' j') - A_L^{FBA}(\nu j \to \nu' j')] P_L(cos\theta), \tag{5}$$

where superscript FBA means that the relevant quantity is calculated using the First Born approximation. The summation over L in (5) converges rapidly and can be truncated at a given L_{max} with a preselected accuracy.

After being averaged over the vibrational motion, to a good approximation many molecules may be regarded as rigid rotators with fixed moments of inertia. Molecules are divided in four groups depending on the values of these moments of inertia I_a, I_b and I_c:

$I_a = I_b = I_c$ – spherical tops,
$I_a < I_b = I_c$ or $I_a = I_b < I_c$ – symmetric tops,
$I_a \neq I_b \neq I_c$ – asymmetric tops,
$I_a = 0$ and $I_b = I_c$ – linear molecules.

In this work we consider CF which is linear, CF_3 which is an oblate symmetric top and CF_2 which is an asymmetric top. Each of these cases require different formulae for the inclusion of the rotational motion within the rigid rotor approximation.

The DCS (3) for symmetric top molecules, such as CF_3, can be rewritten as

$$\frac{d\sigma}{d\Omega}(JK \to J'K') = \frac{k'}{k}\sum_L A_L(JK \to J'K') P_L(cos\theta), \tag{6}$$

where the final wave vector k' is related to the initial k by the energy balance equation

$$2k'^2 = 2k^2 + E_{JK} - E_{J'K'} \tag{7}$$

and the JK energy level is defined as

$$E_{JK} = AJ(J+1) - (B-A)K^2, \tag{8}$$

where A and B are the two rotational constants of a symmetric top, J is the rotational quantum number and K is the projection of J along a unique I_a or I_c axis. The dominant rotational transitions for C_{3v} or D_{3h} symmetric top molecules are those for which $\Delta K = 0, \pm 3, \pm 6, ...$ (Faure and Tennyson 2002).

In the case of asymmetric tops, such as CF_2, the K is no longer a good quantum number and is replaced by τ. The DCS is described by the equation

$$\frac{d\sigma}{d\Omega}(J\tau \rightarrow J'\tau') = \frac{k'}{k}\sum_L A_L(J\tau \rightarrow J'\tau')P_L(cos\theta). \tag{9}$$

Selection rules for the transitions $J\tau \rightarrow J'\tau'$ were discussed by Jain and Thompson (1983b) and by Faure *et al* (2003). They found that only those between symmetric (even τ) states or antisymmetric (odd τ) states are allowed. This leads to $\Delta\tau = 0, \pm 2, \pm 4, ...$ The energy balance equation is

$$2k'^2 = 2k^2 + E_{J\tau} - E_{J'\tau'}. \tag{10}$$

The energy levels of asymmetric tops do not follow a simple formulae even within the rigid rotor approximation, but are easy to generate numerically.

Formulae for the A_L coefficients, which are different for symmetric and asymmetric tops, are given in Gianturco and Jain (1986) and will not be repeated here.

For linear and diatomic molecules, such as CF, the differential cross section can be represented in more convenient form (Sanna and Gianturco 1998)

$$\frac{d\sigma}{d\Omega}(\nu j \rightarrow \nu' j') = \frac{k_{\nu' j'}}{k_{\nu j}}\sum_{l_t}\frac{1}{4k_\nu k_{\nu'}}C(jl_tj', 000)^2\sum_L B_L(\nu \rightarrow \nu', l_t)P_L(cos\theta), \tag{11}$$

where $B_L(\nu \rightarrow \nu', l_t)$ are expansion coefficients which for collisions with $^1\Sigma$ state can be written as

$$B_L(\nu \rightarrow \nu', l_t) = (-1)^{l_t+L}\sum_{ll'\bar{l}\bar{l}'m_lm_{l'}} i^{l-l'}(-i)^{\bar{l}-\bar{l}'}\left[(2l+1)(2l'+1)(2\bar{l}+1)(2\bar{l}'+1)\right]^{1/2}$$
$$\times\, C(\bar{l}lL;000)C(l'\bar{l}'L;000)(-1)^{m_l+m_{\bar{l}}}W(ll'\bar{l}\bar{l}';jL)M^{m_l}_{\nu l,\nu' l'}M^{m_{\bar{l}}}_{\nu\bar{l},\nu'\bar{l}'}, \tag{12}$$

with

$$M^{m_l}_{\nu l,\nu' l'} = \sum_{m_l}(-1)^{m_l}C(ll'l_t;m_l-m_l0)T_{\nu l,\nu' l'}. \tag{13}$$

where $T_{\nu l,\nu' l'}$ are the familiar T-matrices.

The *POLYDCS* program utilizing the above equations for the differential cross sections was written be Sanna and Gianturco (1998). The space-fixed K-matrices and quantities, which characterize the target molecule and are required by the *POLYDCS*, were obtained from R-matrix calculations.

Table 1. Equilibrium bond lengths r_{C-F} (in a_0) and FCF angle were applicable (in degrees) for CF, CF_2 and CF_3 radicals. The ground state dipole moments μ (in Debye) and quadrupole moments Q (in atomic units) for CF, CF_2 and CF_3 radicals calculated using the UK R-matrix codes at equilibrium geometries. Also given are experimental and theoretical data for the ground state dipole moments available from the literature.

			μ			Q
Radical	r_{C-F}	angle	This work	Observed	Theory	This work
CF	$2.44^{a,b}$		0.64	0.645 ± 0.014^{e}		1.10493
CF_2	2.46^{c}	104.8^{c}	0.448	0.469 ± 0.026^{f}	0.44^{g}	0.12714
CF_3	2.53^{d}	110.7^{d}	0.51	0.43 ± 0.07^{i}		0.10438

[a]From Porter *et al* (1965)
[b]From Carroll and Grennan (1970)
[c]From Kirchhoff *et al* (1973)
[d]From Jamada and Hirota (1983)
[e]From Saito *et al* (1982)
[f]From Kirchhoff *et al* (1973)
[g]From Russo, Sicilia and Toscano (1992)
[i]From Butkovskaya *et al* (1979).

3. Generation of K-matrices

The UK R-matrix codes (Morgan *et al* 1998, Tennyson and Morgan 1999) were employed to compute the body-fixed K-matrices within the fixed-nuclei approximation.

CF, CF_2 and CF_3 wavefunctions were taken from the earlier calculations of Rozum *et al* (2002), Rozum *et al* (2003a) and Rozum *et al* (2003b) respectively, where full details can be found. These studies considered various geometries, but here all the calculations are carried out at the equilibrium geometries presented in table 1. In our inner region R-matrix calculations on CF_2 and CF_3 we used the 6-311G* (11s5p1d / 4s3p1d) Gaussian basis set. The basis set for CF consisted of the Slater Type Orbitals of Cooper and Kirby (1987) for carbon and McLean and Yoshimine (1967) for fluorine atom with added two diffuse basis functions on each atom. Our target calculations employed different strategies and models for the three radicals. Target parameters obtained during these calculations are in good agreement with the available experimental and theoretical data. The scattering processes involving polar molecules are dominated by dipole interactions. It is, therefore, important to use a correct dipole moment in scattering calculations. The ground state dipole moments for CF_x (x = 1,2,3) radicals calculated using the UK R-matrix codes and used for calculations of DCS are shown in table 1.

In our scattering calculations the continuum orbitals were represented by Gaussian Type Orbitals of Faure *et al* (2001) up to g ($l \leq 4$) partial waves for CF_2 and CF_3. For CF we used numerical functions up to g ($l \leq 6$) partial waves. The rotational constants calculated using the UK R-matrix codes and used by *POLYDCS* are given

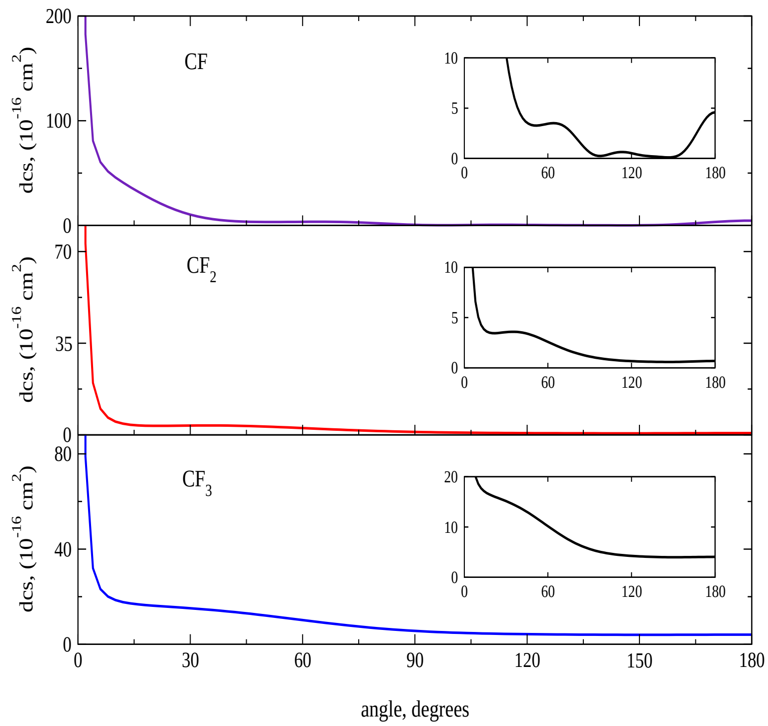

Figure 1. Elastic differential cross sections for CF (top figure), CF_2 (middle figure) and CF_3 (bottom figure) radicals at the incident electron energy of 2 eV. The insets show the structure in the DCS for non-forward scattering.

in table 2. Our tests showed that inclusion of the quadrupole moment (table 1) gives

Table 2. Rotational constants A, B and C (in μeV) at the equilibrium geometry of CF, CF_2 and CF_3. These values are used to calculate differential cross sections.

Radical	A	B	C
CF		170.4618	170.4618
CF_2	43.7127	350.8105	49.9348
CF_3	22.6745	43.7042	43.7042

a negligible contribution to the rotationally-summed elastic differential cross sections. Thus, differential cross sections for CF_2 calculated with and without the quadrupole moment are indistinguishable.

As the UK polyatomic R-matrix code work with symmetries lower than D_{2h}, all calculations on CF_3 were performed in C_s point group. In order to compute differential cross sections, the K-matrices for CF_3 were converted to its natural symmetry by mapping C_s channels to the C_{3v} ones (Faure and Tennyson 2002).

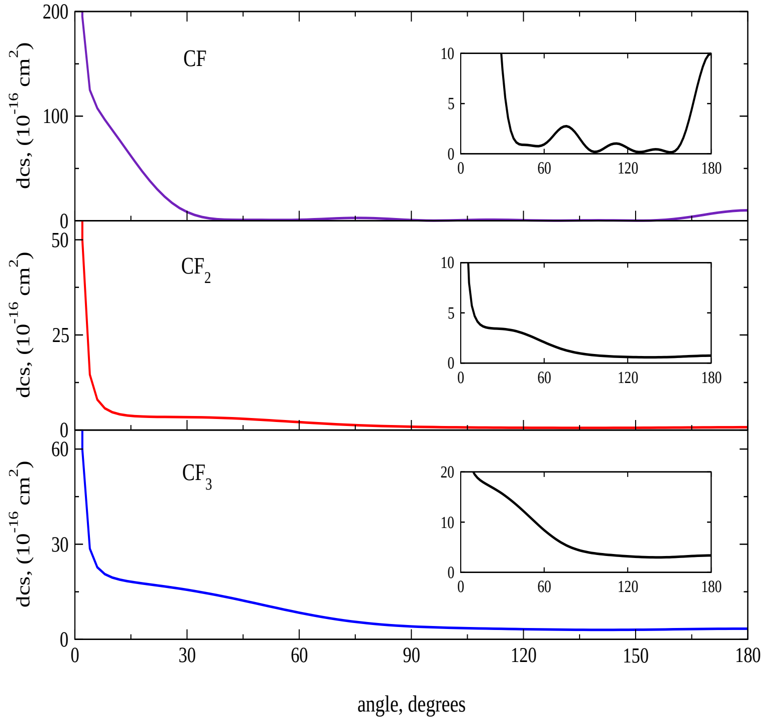

Figure 2. Elastic differential cross sections for CF (top figure), CF_2 (middle figure) and CF_3 (bottom figure) radicals at the incident electron energy of 3 eV.

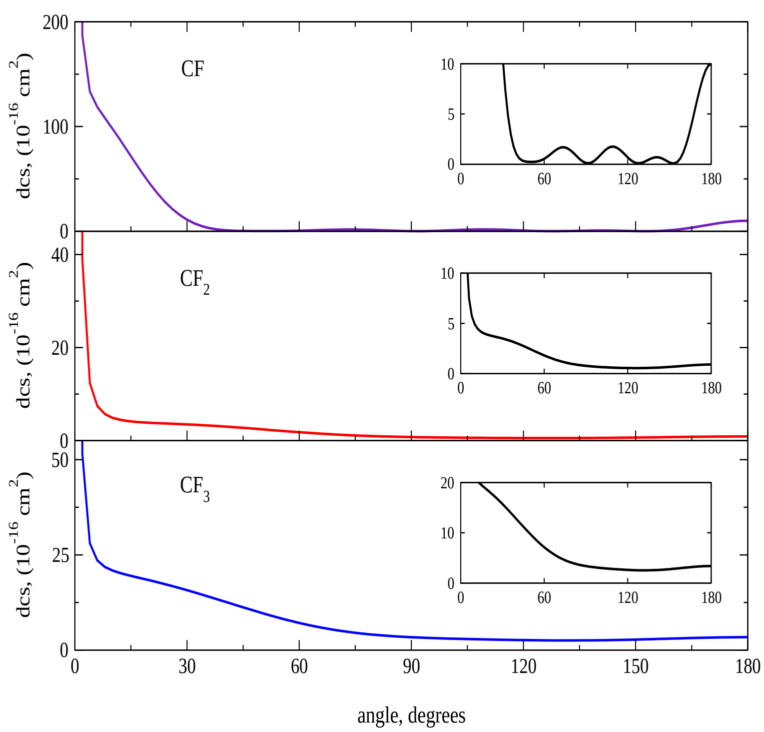

Figure 3. Elastic differential cross sections for CF (top figure), CF_2 (middle figure) and CF_3 (bottom figure) radicals at the incident electron energy of 4 eV.

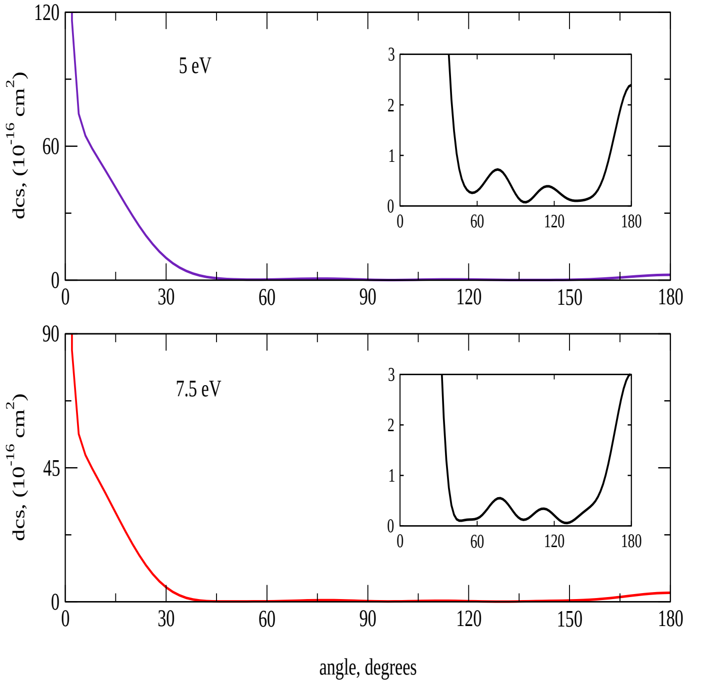

Figure 4. Elastic differential cross sections for CF at the incident electron energy of 5 eV (top figure) and 7.5 eV (bottom figure).

4. Results and discussion

In figures 1, 2 and 3 we present our calculated differential cross sections for CF_x radicals at incident electron energies of 2 eV, 3 eV and 4 eV. There is no experimental data for the differential cross sections for CF_x (x = 1,2,3) radicals at these electron scattering energies.

Figures 4 and 5 show cross sections similar to those presented above, but with incident electron energies 5 and 7.5 eV for CF, and 6.5, 7, 8 and 9 eV for CF_3. We chose these particular energies of the incident electron in order to compare our DCS with the results of Lee *et al* (2002) and Diniz *et al* (1999) for CF and CF_3 respectively. These calculations used a similar treatment of nuclear motion to us, but treated the electronic problem using a single SCF target state and the static exchange approximation. Our experience is that the static exchange approximation is often not adequate for low energy scattering.

Our DCS were computed on a regular grid of 91 angles. The DCS for all three systems can be analysed by considering three distinct angular regimes. First the strongly forward regime ($\theta < 5$) were all our calculations show a very sharp peak. Second the forward regime ($5 \leq \theta < 30$) where our cross sections show a steady decrease and third the sideways and backwards scattering regions ($\theta \geq 30$), where our cross sections show considerable structure.

Before discussing individual results in detail it is worth making some general observations. Neither of the previous studies (Lee et al 1999, Diniz et al 1999) give a very sharp peak near $\theta = 0$. As we find this behaviour even in our static exchange calculations, the most likely explanation is that the previous studies did not consider a fine enough grid of angles at small values of θ. The size of the cross section in the forward regime depends, in general, on the square of the dipole moment and differences with previous studies can be understood in these terms. Conversely the structure in the DCS at larger angles depends on the details of calculations with significant differences appearing between our static exchange and more complete calculations in this region.

Our differential cross sections for CF (figure 4) are much higher than that calculated by Lee *et al* (1999). The magnitude of our DCS at the scattering angle 10^o is 54.0×10^{-16} cm^2 at the incident electron energy 5 eV and 40.6×10^{-16} cm^2 at 7.5 eV. The magnitude of Lee *et al's* DCS at the same scattering energies and angles is about 2×10^{-16} and 3×10^{-16} cm^2 respectively. These differences can be explained by the smallness of the ground state dipole moment for CF, 0.12 Debye, in Lee *et al's* calculations. Our CAS-CI model gives the CF dipole moment value of 0.64 Debye, which is in agreement with the experimental value of 0.645 Debye (Saito *et al* 1983). Our differential cross sections are significantly more structured then DCS of Lee *et al* (1999). We attribute this difference to the more sophisticated treatment of the scattering. A similar level treatment has been demonstrated to give excellent results for the strongly dipolar water molecule (Faure *et al* 2004a, 2004b). Our test SCF calculations give the CF dipole moment 0.30 Debye. Using this wavefunction in a static-exchange calculation showed that the structure for scattering in the non-forward direction depends on the target model used and a level of treatment.

Differential cross sections for CF_3, obtained in this work and presented in figure 5, agree reasonably with the results of Diniz *et al* (1999), although our differential cross sections are higher (by about 40% in the forward direction). CF_3 is a polar molecule and the Hartree-Fock Self-Consistent Field method, used by Diniz *et al* to represent the CF_3 target wavefunctions, does not always give accurate ground state dipole moments. This will affect the magnitude of cross sections. Diniz *et al* do not quote the CF_3 dipole moment value used in their calculations and do not give an adequate description for the basis set used. This makes comparisons with Diniz *et al's* value for the ground state dipole moment of CF_3 impossible. Our SCF test calculations, performed using the 6-311G* Gaussian basis sets, give the CF_3 SCF ground state dipole moment 0.74 Debye, that differ significantly from the experimental value of 0.43 ± 0.07 Debye (Butkovskaya *et al* 1979).

It is notable that all our differential cross sections are dominated by dipole interactions, especially in the forward direction. This suggests that any experimental measurement of the total (elastic) cross section will be very difficult, as with water (Faure *et al* 2004b). For this reason comparison between theory and experiment for elastic scattering by strongly dipolar systems are best done using differential rather than integral cross sections.

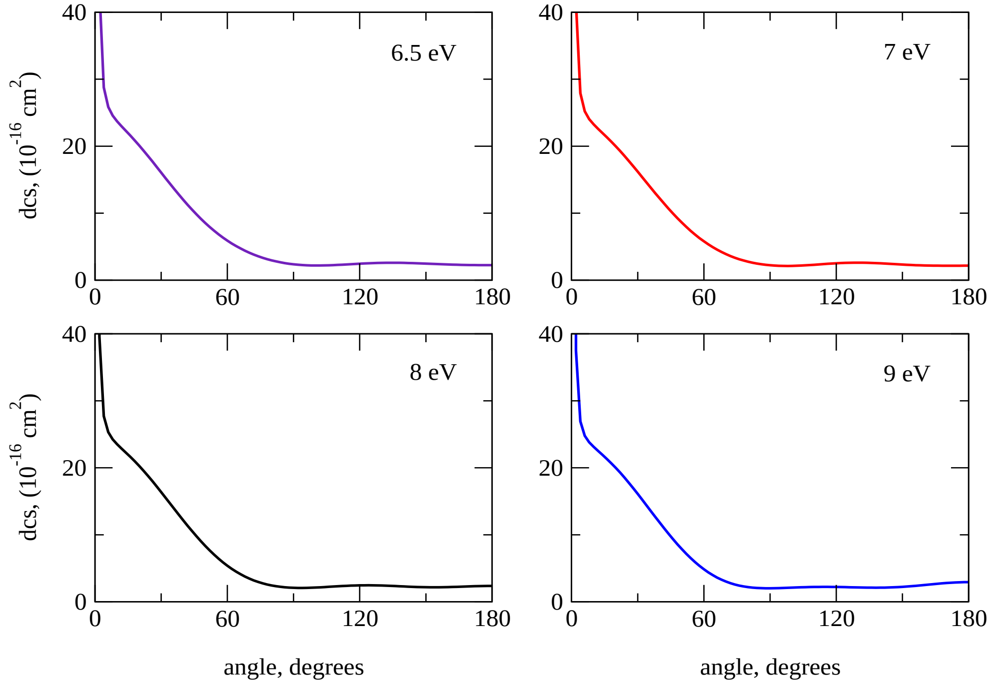

Figure 5. Elastic differential cross sections for CF_3 at the incident electron energy of 6.5 eV (top left figure), 7.5 eV (top right figure), 8 eV (bottom left figure) and 9 eV(bottom right figure).

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