Calculated electron impact ionisation fragmentation patterns

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Calculated electron impact ionisation fragmentation patterns

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Abstract

There are many measurements and calculations of total electron impact ionisation cross sections. However, many applications, particularly in plasma physics, also require fragmentation patterns. Approximate methods of deducing partial cross sections are tested based on the use of total cross section computed within the well-used binary encounter Bethe approximation. Partial ionisation cross sections for three series of molecules including CH\textsubscript{4}, CF\textsubscript{4} and CCl\textsubscript{4}; SiH\textsubscript{4} and SiCl\textsubscript{4}; NH\textsubscript{3} and PH\textsubscript{3}, were estimated using two methods. Method one is semi-empirical and uses mass spectroscopy data to fix the partial cross sections at a single electron energy. The second is a fully computational method proposed by Huber et al (2019 J. Chem. Phys. 150 024306). Comparisons with experimental results suggest that the mass spectroscopy method is more accurate. However, as Huber’s method requires no experimental input, this method could be used as a first approximation when no experimental data is available. As mass spectroscopy sometimes provides incomplete datasets, a hybrid method based on the use of both methods is also explored.

Keywords: electron impact ionisation, branching ratios, binary encounter born

(Some figures may appear in colour only in the online journal)

1. Introduction

Electron impact ionisation cross sections have importance in many areas of science including astrophysics and astrochemistry [1], plasma sciences [2–5] and environmental sciences [6, 7]. The wide scope of applications has led to electron impact ionisation cross sections being extensively studied, both experimentally and computationally. Theoretically, a number of empirically motivated models are available for predicting total ionisation cross sections such as the Binary Encounter Bethe (BEB) method proposed by Kim and Rudd [8], the Deutsch–Märk [9] (DM) method and the spherical complex optical potential [10] method. These have been extensively used to calculate the total ionisation cross sections of atoms, molecules, ions, radicals and clusters with generally successful outcomes [11, 12]. In a previous paper by the authors [13] improvements to the computational total cross section using the BEB method were investigated by using effective core potential (ECP) basis sets as well as using a semi-empirical polarizability scaling factor, $\alpha$BEB. An ECP basis set differs from a non-ECP basis set through the use of an effective potential which replaces the core electrons. ECPs can improve the description of relativistic effects in heavy atoms, which in turn improve the representation of the valence orbitals. However, use of an ECP means the ionisation of the inner electrons is no longer modelled, resulting in an underestimation of ionisation cross sections at high energy.
While total electron impact ionisation cross sections are useful, often, it is desirable to know the cross sections of the dissociation products due to ionisation. These can be represented as the total cross section multiplied by a branching ratio for the production of a given species. Such branching ratios are measured, usually at a single electron collision energy, by mass spectroscopy experiments or in specialist experiments designed specifically to study fragmentation patterns [14–20]. These experiments often provide only relative cross sections but they can then be made absolute using BEB or similar procedures [21]. However, there are many cases where measured branching ratios do not exist as a function of electron collision energy; for these it would be desirable to have a reliable theoretical procedure for predicting them. This is particularly true for studies of radicals and energetically unstable species which are of importance in many plasmas but are difficult to study experimentally.

Computational techniques do exist for predicting fragmentation patterns, but these can be very resource demanding and take considerable time to compute. One such technique is the Rice–Ramsperger–Kassel–Marcus (RRKM) theory which uses the potential energy surface of the molecule to compute rate constants and branching ratios [22]. Here, two simplified methods for producing partial ionisation cross sections are considered. These are designed to provide estimated, energy-dependent fragmentation patterns when no direct experimental data is available. The molecules studied are relatively simple but many are used in important industrial applications [1, 3, 4, 23–27], they include: CH₄, CF₄ and CCl₄; SiH₄ and H₂; NaCl and SiCl₄; NH₃ and PH₃.

One method, referred to as the mass spectrum derived method, throughout this work, uses relative data from mass spectra obtained at a single electron impact energy to provide energy-dependent branching ratios [28]. The National Institute of Standards and Technology (NIST) provides an open, easily accessible and extensive database of experimental mass spectra which we use here [29]. These mass spectra were determined using electron ionisation gas chromatography–tandem mass spectrometry. The database contains a series of small molecules and peptides. This method was originally proposed by Hamilton et al [28] and used a correction introduced via the BEB method, shown in section 2.2, to compensate for the different dissociation thresholds of the fragments and to produce fragment cross sections that are energy dependent.

Mass spectra were also used by Irikura [30] for the determination of fragmentation ratios of organic compounds potentially found on the surface of Mars, as sampled by the curiosity rover. The curiosity rover used a known internal calibrant, CO₂, and produced partial ionisation cross sections using in situ mass spectrum data. However, in this case no attempt was made to predict the energy dependence of the fragmentation patterns.

The second method requires no experimental input and was first proposed by Huber et al [31]. This method, referred to as Huber’s method below, uses a calculated dissociation threshold to get a branching ratio approximation which is corrected for energy dependence. Finally, we test a hybrid method which uses Huber’s method to produce branching ratios for any desired fragments not observed in the experimental mass spectrum.

The following section 2 expands on the methods used for the computation of the partial and total ionisation cross sections, with section 3 containing the computational details. Finally, section 4 contains computed cross sections of the seven molecules studied with comparisons to experimental details.

2. Method

2.1. Total ionisation cross section

In this work, partial ionisation cross sections are produced by imposing branching ratios onto total ionisation cross sections determined through the use of the BEB method [8], shown in equation (1)

\[
\sigma_{\text{BEB}} = \frac{S}{t + u + 1} \left[ \frac{\ln t}{2} \left( 1 - \frac{1}{t^2} \right) + 1 - \frac{1}{t} - \ln t \right].
\]  

Here, \( S = 4\pi a_0^2 N (R/B)^2 \), with \( a_0 \) the Bohr radius, \( R \) the Rydberg energy, \( N \) the orbital occupation, \( B \) the binding energy, \( t = T/B \) where \( T \) is the energy of the incoming electron, and \( u = U/B \) where \( U \) is the orbital kinetic energy. The total cross section is found by summing the BEB cross sections for each of the occupied orbitals in an atom or molecule. A key feature of this method is that it does not require fitting parameters and can be used when the dipole oscillator strengths are not known. This makes the method extremely flexible for estimating ionisation cross sections as the only parameters required are the occupation numbers, binding energy and kinetic energies of each of the orbitals, all of which can be obtained through a Hartree–Fock calculation.

The BEB approach inherently treats single ionisation. However, in a similar approach to Nishimura et al [32], we assume that Auger processes are likely to double the ionisation cross section for ionisation from molecular orbitals that have a binding energy greater than the double ionisation threshold.

2.2. Branching ratios

We compare two methods for producing the branching ratios used in the determination of the partial cross sections. The first method, discussed in section 2.3, relies on the use of experimental mass spectrum data. The second method, discussed in section 2.4, uses Huber’s method and thus is solely computational and predictive. If the MSD method does not provide all of the fragmentation patterns desired then Huber’s method can be used to provide information on the missing fragments giving a hybrid method which contains all of the fragmentation information desired.

A crucial requirement of the definition of the calculated branching ratios is that they should sum to unity and should be zero when the energy of the colliding electron \( (T) \) is below the threshold of the dissociation pathway

\[
\Gamma_i (T) = \begin{cases} 
\frac{b_i}{\sum_j b_j} & T \geq D_i \\
0 & T < D_i
\end{cases}
\]  

(2)
where, $D_i$ is the appearance threshold of species $i$ due to break- up (dissociation) of the parent ion, $\Gamma_i$ is the branching ratio of species $i$ and $b_i$ is some intensity value of species $i$ and $n$ is the number of possible pathways.

In this work we estimate partial ionisation cross sections by multiplying the BEB total ionisation cross section with the respective branching ratio as

$$\sigma_i(T) = \Gamma_i(T)\sigma_{\text{BEB}}(T). \quad (3)$$

The threshold for the formation of each fragment must be aligned with the ionisation threshold plus the appropriate dissociation energy in case of fragmentation of the parent ion. Hamilton et al. [28] proposed modifying the BEB method to include the dissociation thresholds directly within the BEB model by adjusting the value of $T$ to give $t_i$ for each fragmentation process considered

$$t_i = \left(\frac{T}{B - D_i}\right). \quad (4)$$

However, this is not used here. Instead, branching ratios were used to obtain the energy dependency of the partial cross sections. Only the BEB of the parent molecule was used.

### 2.3. Mass spectrum method

Experimental mass spectra can be used to determine the branching ratios at a given energy using equation (2). In this case $b_i$ represents the intensity of the species $i$ at the energy at which the measurement was taken. The intensities for each fragment was taken using the most abundant isotopologue and not corrected for isotopic abundances, although this could be done.

Usually the mass spectrum only defines the branching ratio at a single electron impact energy ($T_{\text{ref}}$). In the MSD method the ratio can be made energy dependent using

$$\Gamma_i(T) = \begin{cases} 0 & T < D_i \\ \Gamma_i(T_{\text{ref}}) \left[1 - \left(\frac{D_i}{T}\right)^n\right] & T \geq D_i. \end{cases} \quad (5)$$

This equation is only strictly valid if we assume that the known branching ratios are the asymptotic branching ratios, that is as $T$ goes to infinity, the branching ratio goes to the known branching ratio which equivalent to assuming $T_{\text{ref}} = \infty$. This means that when we take the known branching ratios at a finite reference energy, we do not reproduce the known branching ratios at that reference energy. However, the error is often less than 15% for the main fragments. The error will increase the lower the reference energy is, and also the closer the highest threshold is to the reference energy. That is we are making the assumption when we are using these equations that the reference energy is sufficiently high that all channels are open, and that the branching ratios are all stable.

The value of $\gamma$ in equation (5) is used to control how quickly the asymptotic value of $\Gamma_i$ is reached. It was determined to be $1.5 \pm 0.2$ by Janev and Reiter [33]. The value of 1.5 was adopted in this work. There are many ways that the energy dependency could have been included. A result of using this method is that the energy-dependence for each fragment is a smooth monotonic function, which, when combined with the smooth BEB cross sections, results in partial cross sections that are all smooth curves. We note the recent study by Amorim et al. [34] found some variation of the shape of the fragmentation curves as function of energy but at present we have no means of predicting this behaviour.

The mass spectra used were taken from the openly accessible NIST Mass Spectral Library [29]. However these datasets do not give an energy at which the spectra were taken. An older version of the manual [35] gives a value of 70 eV so we assumed this value is true for all spectra. Due to the experimental method used for the measurement of some molecules, not all fragments are present in the spectra and there may be other issues with the detection of certain (particularly light) fragments. The branching ratios of missing fragments can be estimated using Huber’s method outlined below.

### 2.4. Huber’s method

Huber et al. [31] outlined a method for the determination of branching ratios for diatomic molecules. At threshold, Huber et al. proposed a relationship between the dissociation threshold for the formation of a fragment from the parent ion and the branching ratio:

$$b_i = \left(\frac{1}{D_i}\right)^\beta, \quad (6)$$

where $\beta$ was determined to be 3 by Huber et al. [31, 36] through comparison with experimental branching ratios. $\beta$ is not energy dependent. The value $b_i$ can then be used in equation (2) to determine the branching ratio. The energy dependence of these branching ratios is then determined using equation (5); this allows for an estimation of the branching ratio at energies above the various dissociation thresholds. Finally, the branching ratios are normalised to satisfy equation (2).

Huber et al. [31] also proposed the addition of a so called structural factor, $\zeta$, which allows for other processes not included within the threshold approximation:

$$\Gamma_i' = \Gamma_i(T)\zeta, \quad (7)$$

where $\Gamma'$ is the real branching ratio. The value $\zeta$ can most easily be determined from the experimental branching ratio using

$$\zeta = \frac{\Gamma_{\exp}}{\Gamma_i(T)}, \quad (8)$$

where the superscript ‘exp’ represents experimental data. It has been observed that for the dissociation of single C–H bonds, $\zeta \leq 1$ and for more complex dissociation, $\zeta > 1$ [31]. Here we assume $\zeta = 1$ but note that other values could be explored in a future implementation of our methodology.

### 2.5. Fragment selection process

The selection of the possible fragments from the target molecule is an important step in Huber’s method. The model,
as proposed by Huber et al., included the fragmentation pathways:

\[ \text{AB} + e^- \rightarrow \text{AB}^+ + 2e^- \]
\[ \text{AB}^+ + 2e^- \rightarrow \text{A}^+ + \text{B} + 2e^- \]

or,

\[ \text{AB}^+ + 2e^- \rightarrow \text{A} + \text{B}^+ + 2e^- , \]

where AB is an arbitrary molecule. The dissociation pathways presented are assumed to be barrierless as they depend only on the dissociation energy (see equation (6)) of the particular pathway.

For polyatomic species, there are often multiple fragmentation pathways [37], resulting in the same ionic fragments. This is particularly true for light fragments, for example in the break up of methane, \( \text{CH}_4 \), the fragment \( \text{H}^+ \) could form as a result of breaking one to four bonds:

\[ \text{CH}_4 + e^- \rightarrow \text{H}^+ + \text{CH}_3 + 2e^- \]
\[ \text{CH}_4 + e^- \rightarrow \text{H}^+ + \text{H} + \text{CH}_2 + 2e^- \]
\[ \text{CH}_4 + e^- \rightarrow \text{H}^+ + 2\text{H} + \text{CH} + 2e^- \]
\[ \text{CH}_4 + e^- \rightarrow \text{H}^+ + 3\text{H} + \text{C} + 2e^- . \]

In the Huber model only the lowest energy pathway is included, for example the dissociation energy resulting \( \text{H}^+ + \text{CH}_3 \) is used for the \( \text{H}^+ \) threshold. This is usually the pathway with the fewest number of bond breaks. All of the molecules studied here contain several atoms of the same element, which means that the formation of ions of that element can occur through one or multiple bond breaks, such as the case above.

The threshold approximation cannot accurately model the formation of molecular ions that are not the result of simple bond breaking in the parent ion. For example, the formation of \( \text{H}_2^+ \) or \( \text{H}_3^+ \) from \( \text{CH}_4 \) requires the formation of new bond(s) which do not appear in the target. As the formation of these fragments relies on processes such as post-ionisation collisions and/or complicated transition states, these pathways are not considered in the model used here, as the branching ratio will not depend on the energetics of the resulting fragments alone.

Pathways arising from double ionisation of the parent ion are not included in the model. In double ionisation process, the fragmentation would be influenced by the Coulombic repulsion of the two positive charges making fragmentation more likely. However, as the value for \( \beta \) above was not found to be energy dependent by Huber et al., this suggests that the formation of, for example, \( \text{A}^+ \), through double ionisation is insignificant.

### 3. Computational details

#### 3.1. Total ionisation cross sections

Total ionisation cross sections were determined using the BEB method as implemented in quanemol electron collisions (QEC) version 1.2 [38]. QEC is a graphical user interface that uses MOLPRO [39] to perform the necessary target calculations. It is worth noting that although the BEB method is used in this work, the branching ratio equations can be applied to any total ionisation cross section, observed or calculated. All calculations below used Gaussian type orbital cc-pVDZ [40] basis sets which were previously found adequate to give converged BEB results [13]. For \( \text{CCl}_4 \) and \( \text{SiCl}_4 \) an ECP basis set was used: ECP10MWB [41] on the Si and Cl and ECP2MWB on the C. These core potential basis sets were chosen after an extensive investigation into the effect of ECPs on the total ionisation cross section [13]. Initial geometries were obtained from the Computational Chemistry Comparison and Benchmark Database (CCCBDB) [42]. Geometries were re-optimised within QEC. QEC provides the option to specify an experimental ionisation threshold which is then used in the calculation, however, the default is to use Koopmans’ theorem [43] which allows for the ionisation potential (IP) to be replaced with the binding energy of the highest occupied molecular orbital. Use of Koopmans’ theorem has been shown to provide a reliable estimate of the effective ionisation threshold and it was adopted here. In our model, the formation of the parent ion was assumed to determine the IP.

#### 3.2. Dissociation thresholds

The balance between computer time and the accurate calculation of the dissociation thresholds of the relevant ions was investigated. Using MOLPRO it was found that satisfactory results could be generated relatively quickly using the couple-cluster method at the CCSD(T) level using Dunning’s basis set cc-pVQZ [40], where possible or reducing to cc-pVTZ, or cc-pVDZ when necessary. The formation threshold, \( D_i \), for each fragment, i.e. where the onset of dissociation occurs, was determined using the pathway and equation as shown below for an arbitrary molecule AB to form \( \text{A}^+ \),

\[ \text{AB} + e^- \rightarrow \text{A}^+ + \text{B} + 2e^- \]

\[ D_{\text{A}^+} = E(\text{A}^+) + E(\text{B}) - E(\text{AB}^+) + \text{IP}, \]

where \( E(X) \) is the energy of species \( X \). These thresholds were corrected for basis set superposition error using a counterpoise correction.

To ensure the fragment thresholds determined here were in line with the total ionisation cross section threshold, they were...
shifted so that all fragmentation energies were relative to the Koopmans’ theorem IP. The formation of the parent ion was equal to Koopmans’ theorem IP.

4. Results and discussion

Three series of molecules were studied, including CH$_4$, CF$_4$ and CCl$_4$ making the CX$_4$ series, SiH$_4$ and SiCl$_4$ making the SiX$_4$ series and finally NH$_3$ and PH$_3$ making the XH$_3$ series. Cross sections are presented up to the highest experimental energy measured. In cases where the data points are larger than the experimental error, no error bars are shown.

4.1. Methane cross sections

A more in-depth study is presented for the first molecule, CH$_4$. Calculated dissociation thresholds are shown in table 1 and compared to the appearance energies (AE) from experimental data [44].

All calculated thresholds are within the experimental range except for CH$_2^+$ and H$^+$. There are multiple pathways that could be used for the formation of these two fragments, and thus the preferred pathway may be different from the lowest energy bond breaking pathway considered here.

The total ionisation cross section of CH$_4$ is shown in figure 1, as well as partial cross sections calculated using the MSD method, Huber’s method and a hybrid method consisting of calculated thresholds where the MSD was not available for a particular fragment ion. The calculated BEB total ionisation cross section is in as good agreement as expected; a similar peak position but a slight underestimation in comparison to the experimental cross section [44]. This underestimation is expected as the BEB method does not fully account for double ionisation channels.

A comparison between the known branching ratios and computed branching ratios assumed to be at a reference energy of 70 eV can be seen in table 2. The percentage errors have the expected trend where those fragments with the highest energy dissociation thresholds have the largest errors.

The partial cross sections of the MSD method for CH$_4$ show a closer match to experimental values than Huber’s method. This is evident in the most abundant fragments, CH$_4^+$ and CH$_3^+$, lying within the experimental error range; whereas Huber’s method significantly underestimates these partial cross sections. The difference between the hybrid model in comparison to the MSD is minimal, as the only change to the model is the inclusion of the fragment H$^+$ which has a relatively small partial cross section.

In order to be able to compare the models for calculating partial cross sections in more detail, we provide the percentage ion abundances in table 3. These abundances were determined at 30 eV as this energy is high enough that most singly charged fragments will have formed, but below the double ionisation threshold of CH$_4$. From this table, we can see that the MSD method has the correct ordering of the abundances of the different ion fragments in comparison to the experimental data, with the exception of the very light fragments H$^+$ and H$_2^+$. For Huber’s method, which uses the dissociation energies to calculate branching ratios, we find an overestimation of the H$^+$ ion, as well as CH$^+$ and CH$_2^+$ ions, and an underestimation of the parent CH$_4^+$. The overestimation of the fragment H$^+$ is carried through from Huber’s model into the hybrid model. As discussed above, the fragment H$^+$, as determined from Huber’s method, would have many possible pathways of formation, of which only the

<table>
<thead>
<tr>
<th>Energy</th>
<th>CH$_4^+$</th>
<th>CH$_3^+$</th>
<th>CH$_2^+$</th>
<th>CH$^+$</th>
<th>C$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 eV</td>
<td>1.34</td>
<td>1.45</td>
<td>3.88</td>
<td>10.7</td>
<td>18.4</td>
</tr>
</tbody>
</table>

Figure 1. Total and partial ionisation cross sections of CH$_4$. The circle data points are absolute experimental values by Song et al [44]. The solid and dash curves are from this work. The left figure uses the MSD method, the centre figure uses Huber’s method and the right figure uses the hybrid method.
Table 3. Percentage abundances for the ion fragments of CH₄ that were determined from the three methods outlined in this work. Abundances were taken at 30 eV and are presented in percentages. Experimental values for CH₄ were taken from the recommendations of Song et al [44].

<table>
<thead>
<tr>
<th>Fragment</th>
<th>CH⁺</th>
<th>CH₂⁺</th>
<th>CH₃⁺</th>
<th>CH₄⁺</th>
<th>H⁺</th>
<th>C⁺</th>
<th>H₂⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>52.51</td>
<td>40.54</td>
<td>5.058</td>
<td>1.127</td>
<td>1.108</td>
<td>0.1197</td>
<td>0.0579</td>
</tr>
<tr>
<td>MSD</td>
<td>47.83</td>
<td>42.70</td>
<td>7.281</td>
<td>2.115</td>
<td>0.000</td>
<td>0.0690</td>
<td>0.000</td>
</tr>
<tr>
<td>Huber’s</td>
<td>35.56</td>
<td>36.49</td>
<td>12.18</td>
<td>3.352</td>
<td>12.26</td>
<td>0.1728</td>
<td>0.000</td>
</tr>
<tr>
<td>Hybrid</td>
<td>42.61</td>
<td>38.04</td>
<td>6.486</td>
<td>1.884</td>
<td>10.92</td>
<td>0.0615</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Figure 2. Total and partial ionisation cross sections of CF₄. The circle data points are absolute experimental values by Bonham [45]. The solid and dash curves are from this work. The left figure uses the MSD method, the centre figure uses Huber’s method and the right figure uses the hybrid method.

The lowest energy route is included in the model. This results in an overestimation. The dissociation threshold was approximately 6 eV lower than the experimental appearance energy, resulting in the fragment abundance being larger than the experiment.

4.2. CX₄ series

Comparative ionisation cross sections for CF₄ and CCl₄ can be seen in figures 2 and 3 respectively. Similarly to the methane cross sections, for these two molecules the BEB total ionisation cross section agrees well, particularly at low energy in comparison to experimental data for both CF₄ and CCl₄. The position of the peak in the BEB ionisation cross section of CCl₄ is in close agreement with the experiment, and overall the cross sections are again slightly underestimated.

The experimental partial cross sections for the different ion fragments resulting from ionisation of CF₄ were dominated by the CF₃⁺ fragment. Figure 2 shows that this is fragment is also the most abundant when partial ionisation cross sections are determined using the MSD method. For partial cross sections calculated using Huber’s method this fragment is still the most abundant species, however the height of the cross section is significantly reduced. In contrast, for CCl₄, both Huber and the MSD method give partial cross sections for CCl₃⁺ that are similar to the experimental data, with the MSD method slightly overestimating at the peak, and Huber’s model slightly underestimating.

Table 4 shows percentage abundances of the fragments resulting from the ionisation of CF₄ and CCl₄ at 30 eV for quantitative comparison of the models for predicting partial ionisation cross sections. In the case of CF₄, most of the dissociation channels are closed, due to the thresholds being higher than 30 eV. The experimental data shows that most of the ionisation products are CF₃⁺ at 93.37% and small amounts of CF₂⁺ and CF⁺. When producing partial cross sections using the MSD method, this result is preserved, as the CF₃⁺ fragment is again the most significant contributor to the cross section. With Huber’s model, however, because of the similarities in the dissociation thresholds for CF₃⁺ and CF₂⁺, the partial cross sections for these species are very similar and thus CF₃⁺ is significantly underestimated whilst CF₂⁺ is significantly overestimated. Furthermore, the fragments CF⁺ and F⁺ are also overestimated. The experimental appearance energy of F⁺ is at 35 eV. This means that F⁺ fragment forms between 30 and 35 eV. Due to its relatively light mass, the measurement of F⁺
Figure 3. Total and partial ionisation cross sections of CCl₄. The circle data points are absolute experimental values by Lindsay et al. [46]. The solid and dash curves are from this work. The left figure uses the MSD method, the centre figure uses Huber’s method and the right figure uses the hybrid method.

Table 4. Percentage abundances for the fragments of series CX₄ that were determined from the three methods outlined in this work. Abundances were taken at 30 eV and are presented in percentages. Experimental values for CF₄ are by Bonham [45] and values for CCl₄ are by Lindsay et al [46].

<table>
<thead>
<tr>
<th>Fragment</th>
<th>CF₄⁺</th>
<th>CF₂⁺</th>
<th>CF⁺</th>
<th>F⁺</th>
<th>C⁺</th>
<th>CF₃⁺</th>
<th>CF₂⁺</th>
</tr>
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<tbody>
<tr>
<td>Experimental</td>
<td>93.37</td>
<td>6.434</td>
<td>0.1935</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
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</tr>
<tr>
<td>MSD</td>
<td>84.87</td>
<td>9.622</td>
<td>2.921</td>
<td>2.583</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Huber’s</td>
<td>40.49</td>
<td>35.71</td>
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<td>7.263</td>
<td>0.2569</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Hybrid</td>
<td>84.66</td>
<td>9.598</td>
<td>2.913</td>
<td>2.577</td>
<td>0.2563</td>
<td>0.000</td>
<td>0.000</td>
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</table>

<table>
<thead>
<tr>
<th>Fragment</th>
<th>CCl₂⁺</th>
<th>CCl₂⁺</th>
<th>CCl⁺</th>
<th>Cl⁺</th>
<th>C⁺</th>
<th>Cl₃⁺</th>
<th>CCl₃⁺</th>
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<tbody>
<tr>
<td>Experimental</td>
<td>60.72</td>
<td>17.50</td>
<td>17.01</td>
<td>4.104</td>
<td>0.3758</td>
<td>0.2868</td>
<td>0.000</td>
</tr>
<tr>
<td>MSD</td>
<td>72.92</td>
<td>14.27</td>
<td>8.603</td>
<td>4.189</td>
<td>0.02194</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Huber’s</td>
<td>61.06</td>
<td>22.09</td>
<td>9.151</td>
<td>7.280</td>
<td>0.4136</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

should be taken as a lower limit as the ion collection could be incomplete [45]. This could explain why F⁺ is included in the models but not the experiment. However, using just dissociation energies to obtain thresholds for appearances of ions has also allows a significant amount of the F⁺ and C⁺ ions. This leads to two fragments having cross section values that were not detected at 30 eV experimentally. The hybrid method produces abundances which are a reflection of the constituent methods accuracies.

For the final molecule, CCl₄, the MSD method did not include the two smallest fragments, Cl₂⁺ and CCl₃⁺, of which, the latter has a dissociation threshold higher than 30 eV and so is not observed experimentally at this energy. The abundances of the different fragments compared to the experiment are in reasonable agreement with the largest percentage difference being 12.2% and the relative abundances are preserved. Huber’s method gave similar abundances to the MSD method however, this method was also missing the Cl₃⁺ fragment due to the fragment selection process. The value at 30 eV for the most abundant species CCl₃⁺ lie closer to the experimental value than the MSD method. The hybrid method, despite being used, is not presented in table 4 as the fragment percentages were the same as the MSD method at this energy.

4.3. SiX₄ series

The total and partial cross sections for the SiX₄ series can be seen in figures 4 and 5. The shape and magnitude of the BEB total cross sections are similar to the experimental curves. For SiH₄ the total cross section is slightly smaller in magnitude than the experimental error around the peak. However for SiCl₄, the total cross section is just within the experimental error at the peak of the cross section.
Figure 4. Total and partial ionisation cross sections of SiH₄. The circle data points are absolute experimental values by Basner et al [26]. The solid and dash curves are from this work. The left figure uses the MSD method, the centre figure uses Huber’s method and the right figure uses the hybrid method.

Figure 5. Total and partial ionisation cross sections of SiCl₄. The circle data points are absolute experimental values by Basner et al [47]. The solid and dash curves are from this work. The left figure uses the MSD method and the right figure uses Huber’s method.

It can be seen in figure 4, that the partial cross sections for SiH₄ look the most similar to experimental values when using the MSD (or hybrid) method. The fragment H⁺ is missing in the MSD method but not in the hybrid method which is, therefore, the most complete. However, the hybrid method clearly underestimates the three most common fragments: SiH₃⁺, SiH₂⁺ and SiH⁺. The experimental data shows that the most abundant fragment at most energies is SiH₂⁺. The MSD method only predicts this fragment as most abundant above 25 eV. In Huber’s model the abundance of SiH₂⁺ is significantly underestimated, to the extent that SiH₃⁺ is predicted to be the most abundant ion for all energies.

For the partial cross sections of SiCl₄, it is less clear from figure 5 which method replicates the experimental values the best. Both the MSD method and Huber’s model predict near identical abundances of SiCl₂⁺ and SiCl⁺, however the experimental data shows that SiCl₂⁺ should be the dominant fragment ion. The values of the partial cross sections at the peak show that Huber’s method is in slightly closer agreement with the experimental data for the most dominant ion.

As with the CX₄ series, a table containing the fragment abundances at 30 eV can be used to evaluate the accuracy of the partial cross sections determined using each method. This table is shown as table 5.

For the molecule SiH₄, the MSD method produces results that are generally closer to the experimental results, in terms of both the order of fragment abundance and of the magnitude than Huber’s model. The significant exception is SiH₂⁺ which is overestimated by the experiment by around 10%. As a result, the other fragments are slightly underestimated.
Huber’s method however, as can be seen in figure 4, overestimates the fragment \( \text{SiH}_2^+ \) and underestimates the fragments \( \text{SiH}_3^+ \), \( \text{SiH}^+ \) and \( \text{Si}^+ \). The fragment \( \text{H}^+ \) does not match the experimental results well. While the experimental measurement should be taken as a lower limit [26], the Huber model consistently overestimates light fragments as only the lowest energy route is considered. The fragment order of Huber’s method is different to the experiment. This poor agreement is reflected in the hybrid method through the inclusion of the \( \text{H}^+ \) fragment from Huber’s method.

The hybrid model was not calculated for \( \text{SiCl}_4 \), as the mass spectrum used in the MSD method contained all fragments detected experimentally. For the ions detected at 30 eV, presented in table 5, the fragment abundance order from both methods is different from the experiment. Both the MSD and Huber’s methods have similar abundances for \( \text{SiCl}_3^+ \) and \( \text{SiCl}_4^+ \), whereas the experimental data shows \( \text{SiCl}_3^+ \) should be 1.7 times more abundant than \( \text{SiCl}_4^+ \). Both methods also have the abundance of \( \text{SiCl}_3^+ \) greater than \( \text{SiCl}_4^+ \) in contrast to the experimental data. Finally, in the MSD method, there is also a significant overestimation of the \( \text{Si}^+ \) ion abundance.

### Table 5. Percentage abundances for the fragments of series \( \text{SiX}_4 \) that were determined from the three methods outlined in this work. Abundances were taken at 30 eV and are presented in percentages. Experimental values for \( \text{SiH}_4 \) are by Basner et al [26] and values for \( \text{SiCl}_4 \) are by Basner et al [47].

<table>
<thead>
<tr>
<th>( \text{SiH}_4 ) Fragment</th>
<th>( \text{SiH}_3^+ )</th>
<th>( \text{SiH}_4^+ )</th>
<th>( \text{Si}^+ )</th>
<th>( \text{H}^+ )</th>
<th>( \text{H}_2^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>44.74</td>
<td>32.18</td>
<td>12.56</td>
<td>8.596</td>
<td>1.763</td>
</tr>
<tr>
<td>MSD</td>
<td>41.56</td>
<td>41.71</td>
<td>9.837</td>
<td>6.369</td>
<td>0.000</td>
</tr>
<tr>
<td>Huber’s</td>
<td>18.77</td>
<td>54.82</td>
<td>10.34</td>
<td>4.292</td>
<td>11.77</td>
</tr>
<tr>
<td>Hybrid</td>
<td>37.18</td>
<td>37.32</td>
<td>8.801</td>
<td>5.698</td>
<td>10.53</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \text{SiCl}_4 ) Fragment</th>
<th>( \text{SiCl}_3^+ )</th>
<th>( \text{SiCl}_4^+ )</th>
<th>( \text{SiCl}_3^2+ )</th>
<th>( \text{Cl}^+ )</th>
<th>( \text{Si}^+ )</th>
<th>( \text{SiCl}_4^2+ )</th>
<th>( \text{SiCl}_3^2+ )</th>
<th>( \text{SiCl}_2^2+ )</th>
<th>( \text{Si}^2+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>42.58</td>
<td>24.82</td>
<td>22.74</td>
<td>5.613</td>
<td>10.97</td>
<td>9.907</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>MSD</td>
<td>30.23</td>
<td>28.05</td>
<td>7.333</td>
<td>19.79</td>
<td>4.699</td>
<td>9.907</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Huber’s</td>
<td>36.48</td>
<td>36.57</td>
<td>7.915</td>
<td>10.97</td>
<td>5.942</td>
<td>2.118</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

The \( \text{XH}_3 \) series contains two molecules, \( \text{NH}_3 \) and \( \text{PH}_3 \). Placing an ECP on the phosphorus atom in \( \text{PH}_3 \) has been found [13] to worsen the agreement between the total BEB cross section and the experimental results. Hence, the total cross sections of both molecules in this series were calculated using the cc-pVDZ basis set. For both molecules, the total BEB ionisation cross section were in close agreement with experimental results, as shown in figure 6 for \( \text{NH}_3 \) and figure 7 for \( \text{PH}_3 \).

It can be seen in figure 6, that the MSD method for the calculation of partial cross sections for \( \text{NH}_3 \) seems to agree well with the experiment for the fragments included. Particularly, the MSD method correctly predicts the \( \text{NH}_3^+ \) parent ion as being the most abundant especially at low electron impact energy. The partial cross section for \( \text{NH}_3 \), the next most abundant fragment, is also well produced. The MSD method however significantly underestimates the abundance of \( \text{H}^+ \) ions particularly at intermediate energies. Conversely, Huber’s method determined the \( \text{H}^+ \) fragment abundance to have a reasonably close agreement with the experimental results from around 50 eV, but overestimates it at lower energies. However, Huber’s method significantly overestimates the parent ion, and underestimates the contribution of \( \text{NH}_2^+ \) to the ionisation cross section. In this case, the hybrid method produces partial cross sections for all fragments which could be used as a reasonable first approximation, as the hybrid method benefits from taking the \( \text{H}^+ \) results from the Huber method.

The experimental partial cross sections for the ionisation of \( \text{PH}_3 \) shown in figure 7, show similar abundances of \( \text{PH}^+ \) and the parent ion \( \text{PH}_3^+ \) at all energies. Both the MSD and Huber’s method do not reproduce this result. For both methods the abundance of the parent ion is overestimated, and the abundance of \( \text{PH}^+ \) is significantly underestimated. As a consequence, the less abundant fragments are also inaccurate.

Table 6 compares the fragment abundances at 30 eV. For both molecules, the experimental measurement of \( \text{H}^+ \) can be taken as a lower limit as this light fragment would be more energetic and therefore the ion collection could be incomplete [48, 50]. This could explain part of the discrepancies between the experimental and computational results for \( \text{H}^+ \).

The mass spectrum data used in the MSD method for \( \text{NH}_3 \) did not include the fragments \( \text{H}_2^+ \), \( \text{H}^+ \) or \( \text{NH}_2^+ \). Excluding these fragments, the MSD method produces partial cross sections which have the same fragment order as the experiment. Huber’s method also agrees with the experimental data in fragment abundance order. The computed dissociation threshold indicates that the fragment \( \text{N}^+ \) would not have formed at 30 eV, however, this fragment was detected experimentally. Furthermore, Huber’s method does not include the fragment \( \text{H}_2^+ \) due to the fragment selection process.

Of the experimentally detected ions from \( \text{PH}_3 \), the MSD method was missing the fragments \( \text{H}_2^+ \), \( \text{H}^+ \), \( \text{PH}_2^+ \) and \( \text{P}^+ \). The double ions of \( \text{PH}_2^+ \) and \( \text{PH}^+ \) were detected experimentally at 30 eV. The calculated thresholds indicated that these fragment pathways should not be energetically feasible.
Figure 6. Total and partial ionisation cross sections of NH$_3$. The circle data points are absolute experimental values by Rejoub et al [48]. The solid and dash curves are from this work. The left figure uses the MSD method, the centre figure uses Huber’s method and the right figure uses the hybrid method.

Figure 7. Total and partial ionisation cross sections of PH$_3$. The circle data points are absolute experimental values by Märk and Egger [49]. The solid and dash curves are from this work. The left figure uses the MSD method, the centre figure uses Huber’s method and the right figure uses the hybrid method.

For the remaining fragments PH$_3^+$ and P$^+$, the MSD method produces fragment abundances that are close to the experimental results. Huber’s method largely underestimates the cross sections due to almost 75% of the partial cross sections being attributed to PH$_3^+$. Huber’s method overestimates the fragments which are missing from the MSD method. This is reflected in the hybrid method. Overall, none of the methods produced fragment magnitudes or fragment abundance orders which were similar to the experimental results. It is possible that, as the models used here do not include all possible electronic processes at all energies, that other processes are particularly prominent in PH$_3$ and therefore the threshold approximation fails. This could lead to both overestimation and underestimation of fragment abundances.
Table 6. Percentage abundances for the fragments of series XH₃ determined from the three methods outlined in this work. Abundances taken at 30 eV and are presented in percentages. Experimental values for NH₃ are by Rejoub et al [48] and values for PH₃ are by Märk and Egger [49].

### NH₃

<table>
<thead>
<tr>
<th>Fragment</th>
<th>NH₃⁺</th>
<th>NH₂⁺</th>
<th>NH⁺</th>
<th>H⁺</th>
<th>N⁺</th>
<th>H₂⁺</th>
<th>NH₂⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>57.24</td>
<td>39.69</td>
<td>1.739</td>
<td>1.026</td>
<td>0.2246</td>
<td>0.07884</td>
<td>0.000</td>
</tr>
<tr>
<td>MSD</td>
<td>65.96</td>
<td>32.09</td>
<td>1.955</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Huber’s</td>
<td>79.47</td>
<td>9.398</td>
<td>3.596</td>
<td>7.536</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Hybrid</td>
<td>61.41</td>
<td>29.87</td>
<td>1.820</td>
<td>6.897</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

### PH₃

<table>
<thead>
<tr>
<th>Fragment</th>
<th>PH⁺</th>
<th>PH₂⁺</th>
<th>PH⁺</th>
<th>H⁺</th>
<th>H₂⁺</th>
<th>PH₂⁺</th>
<th>P⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>41.78</td>
<td>38.25</td>
<td>10.74</td>
<td>8.503</td>
<td>0.5413</td>
<td>0.000</td>
<td>8826</td>
</tr>
<tr>
<td>MSD</td>
<td>5.950</td>
<td>70.91</td>
<td>12.48</td>
<td>10.29</td>
<td>0.000</td>
<td>0.000</td>
<td>0.1249</td>
</tr>
<tr>
<td>Huber’s</td>
<td>8.959</td>
<td>73.80</td>
<td>4.872</td>
<td>3.364</td>
<td>9.006</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Hybrid</td>
<td>5.459</td>
<td>65.06</td>
<td>11.45</td>
<td>9.443</td>
<td>8.262</td>
<td>0.000</td>
<td>0.1146</td>
</tr>
</tbody>
</table>

## 5. Conclusion

Total and partial ionisation cross sections were computed for a range of small, single centred molecules including: CH₄, CF₄ and CCl₄; SiH₄ and SiCl₄; NH₃ and PH₃. Total ionisation cross sections were computed using the BEB method, while the partial ionisation cross sections were computed using one semi-empirical method and one fully computational method: the MSD method and Huber’s method.

Comparison with experimental results indicate that there is good agreement in the total ionisation cross sections produced using the BEB ionisation model. The shape and position of the maxima agree well with experimental data, although the method overall underestimates the total ionisation cross sections in the case of each of the molecules presented here.

For partial cross sections, the MSD method produces results that are more accurate than Huber’s method. However, the MSD method is often missing fragments as they are not included in the mass spectrum, particularly light fragments such as H⁺. Huber’s method requires no experimental input and therefore could be used as a first approximation when no experimental data is available. A limitation to Huber’s method is the formation of fragments outside of the fragment selection process, also resulting in missing fragments. Furthermore, when multiple fragmentation pathways are energetically available, only the lowest energy route is included which results in inaccuracies. It is also clear that dissociation energies alone are insufficient for correctly estimating branching ratios.

A hybrid method can be produced using the MSD method with Huber’s method to fill in fragments not included by the MSD method. This can be used to provide a fuller data set but is still limited by the inaccuracies in the methods used to determine the branching ratios.

While this work was being completed Goswami et al [51] proposed a method similar to those discussed here. In their method, the BEB cross section is computed for each fragment and the ions are characterized by appearance energy instead of the ionisation energy. Goswami et al only considered a single system, methyl alcohol, but their resulting partial cross sections are in good agreement with measurements. Further comparisons between our methods and theirs would be useful.

The plan is to implement fragmentation predictors based on both the MSD and Huber method, or some improved version, in a future version of QEC [38] to allow for the automatic generation of fragmentation patterns alongside the BEB calculation of total electron impact ionisation cross sections which is already available.

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## Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: https://doi.org/10.5281/zenodo.5482796.

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## References

