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Total electron ionization cross-sections for molecules of astrochemical interest

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ABSTRACT
We describe a newly upgraded instrument for measuring absolute total electron ionization cross-sections over the energy range from 0 to 300 eV, and present cross-sections for nine previously unstudied molecules, as well as several small molecules for which comparison data is available. The measured cross-sections are compared with the predictions of the BEB model, and show reasonable agreement with the model, albeit peaking at higher electron energies than predicted by the model. We show that the maxima in the cross-sections follow an additivity model, such that the molecular cross-sections can be expressed as a sum over contributions from the constituent atoms. These contributions have been determined from a global fit to the data for all molecules studied, and allow maximum cross-sections to be predicted for molecules that have not been studied to date. We demonstrate the expected correlation between the maximum ionization cross-section and the molecular polarisability, and show that the atomic contributions to the cross-section show a similar dependence on the atomic polarisability. The observed correlation can be used as an alternative method for predicting unknown maximum cross-sections.

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1. Introduction
The interstellar medium (ISM) accounts for around 5% of the total mass of our galaxy, and has a rich chemical history. While 98% of the ISM is comprised of hydrogen and helium, well over 200 different molecular species have been positively identified in these regions [1–3]. The very low temperatures (10–100 K) and number densities (ranging from 1 to 10⁶ particles per cubic centimetre) have the consequence that only reactions with diffusion-controlled kinetics are competitive, and the chemistry...
is dominated by gas-phase ion-molecule and radical-radical reactions, and surface catalysed reactions occurring on interstellar dust grains. The very low temperatures and collision rates mean that terrestrial principles of chemical stability simply do not apply, and many species that would be highly unstable on Earth can build up to significant concentrations in the rarefied conditions of interstellar space. However, alongside the many ‘alien’ molecules reported in interstellar gas clouds, there are also many ‘familiar friends’, including simple diatomic and triatomic molecules, as well as more complex organic molecules such as alcohols, aldehydes, nitriles, thiols, and aromatic and polyaromatic compounds. Even molecules as large as fullerenes have recently been positively identified in the ISM [4].

Photoionization is of limited importance in initiating ion-molecule chemistry within interstellar gas clouds: visible and ultraviolet light with sufficient energy to ionise atoms and molecules only penetrates into the outer regions of a cloud, with optical absorption and scattering preventing penetration of such light into the core. Infrared light can penetrate much further, but has insufficient energy to cause ionization. Instead, the most common ionization mechanism is collision with cosmic rays – extremely high-energy particles emitted from stars. Protons form the major constituent of cosmic rays (∼89%), with the remainder made up of alpha particles (9%), and electrons, heavier nuclei, and other more exotic particles (2%) [5].

In addition to high-energy cosmic ray electrons, there is also an abundance of lower-energy electrons within the ISM. These originate from solar winds and from photoionization and Auger processes, and tend to have approximately Maxwellian energy distributions spanning an energy range of a few tens of electron volts [6]. Processes involving scattering of low-energy electrons are therefore likely to be significant in the ISM. The recent Rosetta mission confirmed the presence of copious quantities of electrons in cometary comas, as well as finding compelling spectroscopic evidence for dissociative electron ionization of H₂O and CO₂ [7, 8]. With an increasing number of probes being sent out to study various different regions of space, accurate electron ionization cross-sections are also required in order to allow quantitative analysis of mass spectrometric data from such missions. On-board (and terrestrial) mass spectrometers utilising an electron-impact ion source most commonly employ an electron energy of 70 eV, close to the maximum in the ionization cross-section for most molecules.

In the present work, we report absolute total electron ionization cross-sections over the range from 0 to 300 eV for nine molecules whose presence has been confirmed in the ISM and for which cross-sections have not previously been extensively reported. These include a series of nitriles, together with acrolein, ethanethiol, methyloxirane, and benzene.

2. Experimental methods

2.1. Measurement principle

The absolute total electron ionization cross-section may be determined by measuring the incident and transmitted electron currents when an electron beam passes through a known path length l of a sample at a known temperature T and pressure p.

The cross-section σ measured in a beam-gas scattering experiment can be related to the incident and transmitted electron currents I₀ and I, the path length l through the collision cell, and the number density n of the gas via an expression analogous to the Beer-Lambert law:

\[ \frac{I}{I_0} = e^{-\sigma n l} \]  

(1)

where \( n = \frac{p}{k_B T} \), assuming the gas behaves ideally. If the gas pressure is sufficiently low that the attenuation of the electron beam is very small, Equation (1) may be simplified to give

\[ \frac{I_+}{I_-} = n \sigma l = \frac{p \sigma l}{k_B T} \]  

(2)

where \( I_+ \) and \( I_- \) are the (absolute values of) the ion and electron currents, respectively.

2.2. Beam-gas instrument

The beam-gas instrument used to perform the absolute total electron ionization cross-section measurements reported in this manuscript is based on an original design by Harland and coworkers [9], and is shown schematically in Figure 1. The experimental assembly is mounted within a vacuum chamber maintained at a base pressure of \( 10^{-8} \) mbar by a turbomolecular pump. Electrons are generated by thermionic emission at a resistively heated tungsten-rhenium filament, and focused into a beam by the combined electric field generated by a ‘top-hat’-shaped shield located behind the filament and an Einzel lens (lens elements L₁ to L₃ in Figure 1). A homogeneous ∼ 200 G magnetic field generated by a pair of N42 Neodymium-iron-boron permanent magnets connected by an iron yoke helps to constrain the electron beam to the instrument axis. The beam enters a cylindrical collision cell filled with the sample gas of interest to a pressure of ∼ \( 10^{-4} \) mbar, where a small fraction of the electrons collide with and ionize the gas. The resulting positive ions are collected as an ion current at the negatively biased
internal walls of the collision cell, while the electrons transmitted through the cell are re-collimated by a pair of lens elements (labelled L4 and L5 in Figure 1) and detected as an electron current at the positively-biased Faraday cup. The electron and ion currents are recorded using Keithley Model 486 and Model 6487 picoameters, respectively. All internal metal surfaces are coated in colloidal graphite in order to reduce surface scattering of electrons and ions.

The temperature of the sample gas is recorded by a chromel-alumel thermocouple embedded in the wall of the collision cell, with the assumption that the sample gas reaches thermal equilibrium with the walls of the cell. The sample gas enters through a port on one side of the collision cell, and an MKS Type 690A Baratron capacitance manometer mounted on the opposite side of the cell records the sample pressure.

2.3. Instrument optimisation

Due to the advanced age of the previous incarnation of our beam-gas instrument, all internal components were redesigned, refabricated, and reoptimised as part of the present work. Extensive SIMION electron and ion trajectory simulations were performed in order to optimise the geometry of the electrostatic lens elements, collision cell, and detector in order to ensure complete detection of the electrons transmitted through the collision cell and the ions formed in the electron-molecule collisions. Simulated electron and ion trajectories for a nominal electron energy of 100 eV are superimposed on the diagram of the instrument shown in Figure 1.

After fabrication and assembly of the new instrument, the electrostatic lens potentials and other experimental parameters were optimised experimentally in order to ensure complete detection of both transmitted electrons and ions formed within the collision cell, and also to ensure that the experiment was operating under conditions such that Equation (2) is valid. The optimised experimental parameters are listed in Table 1.

2.4. Experimental protocol

When turning on the electronics after a period of shutdown, a relatively long warm-up period of a few hours is needed in order to ensure that the picoameters and capacitance manometer are operating stably. A further warm-up period of 30 minutes is allowed after turning on the filament current in order to allow the system to reach thermal equilibrium prior to beginning measurements. The electron energy is controlled by varying the filament potential relative to the potential at the centre of the collision cell. To record an ionization cross-section, the electron energy is scanned from 0 to 290 eV in steps of between 0.25 and 5 eV. At each electron energy, 30 measurements of the ion and electron currents, temperature, and pressure are made and averaged in order to determine the ionization cross-section via Equation (2).

Ideally, the potential along the axis of the collision cell would be exactly equal to zero. In practice, the SIMION simulations indicated that under the optimised conditions of our experiment, there was a small variation of the potential along the axis where electron-molecule collisions occur. This requires a correction to the nominal electron energy set at the filament in order to reflect the actual electron energy in the interaction region. To perform the correction, a normalised instrument function

| Parameter                      | Value                  |
|--------------------------------|------------------------|
| Filament potential            | 0 to −300 V            |
| Shield potential              | −2.5 V with respect to filament potential |
| L1                             | −2 V                   |
| L2                             | −2 V                   |
| L3                             | Ground                 |
| Cell potential                | −10 V                  |
| L4                             | Ground                 |
| L5                             | −2 V                   |
| Faraday cup potential         | +150 V                 |
| Filament current              | ≤ 2.5 A                |
| Sample pressure               | ~ 2 × 10⁻⁴ mbar        |
| Background pressure           | < 1 × 10⁻⁷ mbar        |
| Electron beam current         | ≤ 50 nA                |
| Ion current                   | ≤ 2 nA                 |
Table 2. Molecules for which absolute total electron ionization cross-sections were measured in the present study.

| Molecular structure | Names |
|---------------------|-------|
| CH₃CHO | acrolein (propanal) |
| CH₃CHN | acrylonitrile (2-propenenitrile/cyanoethene) |
| CH₃CN | methylcyanide (acetonitrile/cyanomethane/ethanenitrile) |
| CH₃CH₂CN | ethylcyanide (propionitrile) |
| CH₃CH₂CH₂CN | propylcyanide (butyronitrile) |
| CH₃CH₂CH₃ | isopropylcyanide (2-methylpropanenitrile) |
| CH₃CH₂SH | ethanethiol (ethylmercaptan) |
| H₂C₃ = C -CH₃ | methyloxirane (propyleneoxide) |
| c-C₆H₆ | benzene |

describing the distribution of electron energies along the collision cell axis, as determined from the SIMION simulations, was deconvoluted from the data. This brought the measured ionization thresholds into good agreement with reported literature values, providing independent validation of the correction process.

Preliminary measurements were made on a series of small molecules, namely CO₂, C₂H₄, C₃H₆, N₂O, and SF₆, in order to compare the performance of our instrument with data from previously published measurements from other research groups. The molecules for which we present new measurements are listed in Table 2. Many of these molecules are known by various different names; we have included the most common of these in the table for clarity.

2.5. Binary-encounter Bethe (BEB) model calculations

The Binary-encounter Bethe (BEB) model has been shown by a number of authors to reproduce the total electron ionization cross-section reasonably well for a wide range of molecules [10–14]. The model is a simplified form of the binary-encounter-dipole (BED) model, which employs a weighted combination of two different limiting theories describing the electron ionization process. Small-impact-parameter, or ‘hard’ collisions are described by modified Mott theory [15, 16], and large-impact-parameter or ‘soft’ collisions are described by Bethe cross-section theory [17–19]. A switching function is employed to control the relative weighting of the Mott and Bethe cross-sections as a function of electron energy.

A key parameter appearing in the BED model is the differential dipole oscillator strength, which is a challenging quantity to calculate accurately. The BEB model employs a simplified approach to the calculation of this parameter. The full derivation of the BED model, and its subsequent simplification to the BEB model, can be found in reference [18]. Here we simply present the final expression for the BEB cross-section, \( \sigma_{\text{BEB}} \):

\[
\sigma_{\text{BEB}} = \sum_{\text{orbitals},i} \left\{ \left( \frac{S_i}{t_i + (u_i + 1)} \right) \left[ \ln \frac{t_i}{2} \left( 1 - \frac{1}{t_i^2} \right) + \left( 1 - \frac{1}{t_i} - \frac{\ln t_i}{t_i + 1} \right) \right] \right\}
\]

with

\[
t_i = \frac{T}{B_i}, \quad u_i = \frac{U_i}{B_i}, \quad S_i = 4\pi a_0^2 N_i \left( \frac{R_\infty}{B_i} \right)^2
\]

The sum in Equation (3) is over the atomic or molecular orbitals of the atom or molecule. \( T \) is the kinetic energy of the incident electron, \( B_i \) and \( U_i \) are the orbital binding energy and average kinetic energy of the ejected electron, respectively, and \( N_i \) is the orbital occupation number. The parameters \( a_0 \) and \( R_\infty \) are the Bohr radius and the Rydberg constant, respectively. It should be noted that within the calculation, \( T \) must be greater than \( B_i \) for a given molecular orbital in order to generate a non-zero cross-section, i.e. the incident electron must have sufficient energy to overcome the binding energy of the bound electron.

As input to the BEB model, one simply requires calculated binding energies and kinetic energies for each molecular orbital. The quality of these calculated properties is important in determining the performance of the BEB model, with the parameters of the highest-lying orbitals having the largest effect on the cross-section. We have previously carried out an extensive benchmarking study to determine the optimum electronic structure methods for calculating orbital binding and kinetic energies for input to the BEB model [12]. These methods are described below, and offer a good balance between computational accuracy and calculation run time. The Gaussian 09 electronic structure package [20] was used for all calculations.

Molecular geometries were optimised at HF/aug-cc-pVTZ level [21–23]. Orbital binding energies for the optimised geometry were then calculated using partial third-order (P3) electron propagator theory [24]. This approach was shown in our earlier benchmarking study [12] to account sufficiently well for electron correlation that accurate ionization potentials and binding energies are obtained. A plot of the P3 binding energies vs the HF energies yields a linear scaling factor that accounts for the effect of electron correlation on the binding energies. The orbital kinetic energies were also scaled by the same factor in order to ensure that the virial theorem is satisfied. The final scaled binding and kinetic energies were then substituted into Equation (3) to obtain the BEB cross-sections.
3. Results and discussion

3.1. Testing and comparison with previous work

Having recently upgraded and reoptimised the beam-gas scattering instrument, as described in Section 2, our first set of measurements aimed to establish the extent to which we could reproduce previously measured ionization cross-sections for a series of small molecules. The total absolute electron ionization cross-sections measured for CO2, C2H4, C3H6, N2O, and SF6 are shown in Figure 2, together with previous experimental data from Rapp and Englander-Golden [25], Orient and Srivastava [26], and Nishimura and Tawara [27], and BEB model [10, 18] calculations from Kim and coworkers [10, 11, 19, 28]. Though there is significant variability between different experimental data sets, and between the experimental data and the predictions of the BEB model, our measurements appear to be in good agreement with published data within these limits. The experimentally measured cross-sections systematically peak at higher electron energies than predicted by the BEB model, but the model performs reasonably well in predicting the absolute magnitude of the cross-section across the entire energy range studied.

3.2. Molecules of astrochemical interest

Figures 3 and 4 show the measured absolute total electron ionization cross-sections for the nine molecules of astrochemical interest listed in Table 2, together with data from our BEB model simulations. As observed in Section 3.1 for the reference molecules studied, the BEB model tends to underestimate the electron energy at which the peak in the ionization cross-section appears, but gives a reasonable prediction of the magnitude of the cross-section. The exception is ethanethiol, for which the BEB model as presented in Section 2.5 underestimates the maximum cross-section by around 15%. This is a known problem when applying the BEB model to molecules containing atoms from the third row of the periodic table and beyond [10]. The origin of the discrepancy lies in the treatment of the orbital kinetic energy. The electron kinetic energy within a given molecular orbital is much greater in regions near the core than in the outer regions of the orbital; however, ionization is much more likely to occur in the outer regions. In the context of electron ionization, the ‘effective’ kinetic energy is therefore lower than the orbital kinetic energy returned from the electronic structure calculations, which is averaged over the entire orbital. A number of corrections to the kinetic energy have been proposed in order to improve the agreement between the BEB model and experimental data for molecules containing heavy atoms [10, 29, 30]. These involve identifying any molecular orbitals with contributions from heavy-atom atomic orbitals above some predefined threshold, and dividing the orbital kinetic energies $U$ for these molecular orbitals by the principal quantum number for the relevant atomic orbital. One of the most problematic aspects of this approach lies in identifying the appropriate threshold for the contribution of ‘heavy atom’ atomic orbitals to each molecular orbital at which to trigger the kinetic energy correction. In Figure 4 we show the results of the BEB model for ethanethiol with no correction, and with the kinetic energy correction triggered at thresholds of 50% and 75% involvement of ‘heavy atom’ atomic orbitals in a molecular orbital. The cross-section calculated using the lower threshold agrees better in magnitude with the experimentally measured cross-section. However, the peak in the cross-section moves to lower electron energy, and further away from that measured experimentally, as the correction threshold is reduced.

As expected, the experimentally measured cross-sections scale with molecular size. Electron ionization cross-sections are often described in terms of various ‘additivity rules’, in which the total cross-section can be considered to be the sum of contributions from individual atoms, functional groups, or molecular orbitals. The latter description, in terms of a sum over molecular orbitals, forms the basis for the BEB model discussed above. When analysing experimental data, it becomes rather more difficult to consider a sum over molecular orbitals. However, it is straightforward to establish whether an additivity rule based on atomic contributions can be applied to the data. To investigate the contribution of H, C, N, O, S, and F atoms to the total cross-section, we have performed a global fit of the maximum cross-sections recorded for each of the 14 molecules studied (including the set of small molecules described in Section 3.1) to the following expression:

$$\sigma_{\text{max}} = n_{\text{CC}} + n_{\text{CN}} + n_{\text{CO}} + n_{\text{CF}} + n_{\text{SCS}}$$

where $n_i$ is the number of atoms of type $i$ in the molecule, and $c_i$ is the contribution to the total cross-section of a single atom of type $i$. The optimum values for the atomic contributions $c_i$ to the molecular cross-section were determined by minimising a $\chi^2$ fitting function, defined as

$$\chi^2 = \sum_k (\sigma_{\text{max,fit}} - \sigma_{\text{max,expt}})^2$$

where $\sigma_{\text{max,fit}}$ and $\sigma_{\text{max,expt}}$ are the fitted and experimentally measured maximum cross-sections, respectively, and the summation is over the set of molecules studied.

Figure 5 shows a plot of the fitted maximum cross-sections against the measured maximum cross-sections.
Figure 2. Total absolute electron ionization cross-sections measured for CO$_2$, C$_2$H$_4$, C$_3$H$_6$, N$_2$O, and SF$_6$, together with previous experimental data from Rapp and Englender-Golden [25], Orient and Srivastava [26], and Nishimura and Tawara [27], and BEB model calculations from Kim and coworkers [10, 11, 19, 28].

The plot is a straight line with a slope almost identically equal to one, with $R^2 = 0.9958$, showing that the additivity rule is obeyed very closely for the molecules studied. The optimised atomic contributions $c_i$ to the maximum ionization were found to be: $c_H = 0.574$; $c_C = 1.611$; $c_N = 1.300$; $c_O = 1.055$; $c_F = 0.576$; $c_S = 4.121$. Equation (4) may therefore be used together with these values to estimate maximum total electron ionization cross-sections for any molecule containing only H, C, N, O, F, and S atoms. This offers a straightforward route to determining the maximum cross-section for molecules that are too unstable to investigate experimentally, which...
Figure 3. Total absolute electron ionization cross-sections measured for acrolein, acrylonitrile, methylcyanide, ethylcyanide, propylcyanide, and isopropylcyanide, together with BEB model calculations.

includes many, if not most, of the molecules observed to date in the interstellar region.

We have shown previously that the maximum total electron ionization cross-section correlates strongly with molecular polarisability volume. The molecules investigated in the present study also exhibit this correlation. Figure 6(b) shows the correlation between ionization cross-section and molecular polarisability volume for 63 medium-sized organic and halocarbon species measured in our previous work (black circles), with the values for the nine new molecules investigated in the present work shown as red circles. As shown in Figure 6(b), we find that the atomic contributions $c_i$ to the molecular cross-section determined above also correlate reasonably strongly with
Figure 4. Total absolute electron ionization cross-sections measured for ethanethiol, methyloxirane, and benzene, together with BEB model calculations. For ethanethiol, BEB calculations have been carried out with three different heavy atom correction thresholds – see text for details.

Figure 5. Plot of the best-fit maximum electron ionization cross-sections from Equation (4) against the experimentally measured values. The plot has a slope of 0.998 and $R^2 = 0.9944$.

the corresponding atomic polarisability volumes. This is perhaps unsurprising, given that additivity rules based on atomic parameters have previously also been used to estimate molecular polarisabilities [31]. However, the correlation is not as strong as that observed for the molecular polarisability, presumably reflecting the extent to which the atomic orbitals are distorted when bonding to form molecular orbitals.

Based on a straight line fit to the molecular polarisability plot in Figure 6(a), we obtain an alternative to Equation (4) for determining unknown molecular maximum electron ionization cross-sections when the molecular polarisability is known. These may be estimated from the empirical expression:

$$\sigma_{\text{max}} = 1.4908\alpha - 0.2507$$

where $\alpha$ is the molecular polarisability volume. The molecular polarisability is a straightforward property to calculate for any molecule using any standard electronic structure package.

4. Conclusions

We have described a newly upgraded instrument for measuring absolute total electron ionization cross-sections over the energy range from 0 to 300 eV, and have presented cross-sections for nine molecules which have not previously been extensively studied, as well as for several small molecules for which comparison data is available. The measured cross-sections have been
Figure 6. (a) Correlation between maximum electron ionization cross-section and molecular polarisability for a series of 63 medium sized organic and halocarbon species [12], and for the nine new molecules investigated in the present work; (b) Correlation between the atomic contributions to the molecular ionization cross-sections determined from Equation (4) and the atomic polarisability.

compared with cross-sections calculated using the BEB model, and it has been found that while the model predicts the correct magnitude for the cross-section, the calculated cross-sections tend to peak at lower electron energy than measured experimentally. We have shown that the data follow an additivity model, such that the maximum measured cross-sections for each molecule can be predicted based on a set of atomic contributions determined from a global fit to the data. This model also allows maximum cross-sections to be predicted for molecules that have not been studied to date, or cannot be studied experimentally for reasons of instability or potential safety hazards. The new molecules investigated in the present study have ionization cross-sections that follow the previously observed correlation with molecular polarisability, and we present an alternative expression for calculating unknown maximum ionization cross-sections when the molecular polarisability is known or can be calculated.

Disclosure statement

No potential conflict of interest was reported by the authors.

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