C-I and C-F bond-breaking dynamics in the dissociative electron ionization of CF₃I

Hansjochen Köckert, David Heathcote, Jason W. L. Lee, Weiwei Zhou,
Vincent Richardson, and Claire Vallance*
*Department of Chemistry, University of Oxford, Chemistry Research
Laboratory, 12 Mansfield Rd, Oxford OX1 3TA, UK*
e-mail: claire.vallance@chem.ox.ac.uk

Abstract

We present a comprehensive experimental study into the dissociative electron ionization dynamics of CF₃I at energies ranging from 20 to 100 eV. A beam-gas instrument has been used to measure the absolute total ionization cross-section for the molecule over the energy range from 0 to 300 eV. Coupled with data from an electron-molecule crossed beam velocity-map imaging instrument, this allows absolute partial ionization cross-sections to be determined for formation of each ionic fragment. These reveal a number of fragmentation channels involving both C-I and C-F bond cleavage, in some cases followed by further fragmentation of the resulting molecular ion. Velocity-map images have been recorded for the I⁺ and CF₃⁺ products of C-I bond cleavage and the CF₂I⁺ products of C-F bond cleavage. Analysis of fragment kinetic energy distributions extracted from the images reveals that CF₃⁺ product of C-I bond cleavage appears to be formed via a statistical mechanism occurring over long timescales, while the CF₂I⁺ products of C-F cleavage are formed via a much faster, more direct dissociation mechanism involving one or more repulsive states of the parent molecular ion. The I⁺ fragments arising from C-I bond cleavage display behaviour intermediate between the two extremes. For all fragments, the images show little or no dependence on the energy of the incident electron, implying that the initially excited ion state or states undergo rapid relaxation to the dissociative state(s) in all cases. Only a very small fraction of the incident electron's kinetic energy is released into kinetic energy of the recoiling atomic and molecular fragments, implying that most of the available energy remains with the two departing electrons. The kinetic energy distributions obtained for the various fragments of dissociative electron ionization are compared with the corresponding distributions reported from photoionization studies in order to gain insight into the electronic states involved.

1 Introduction

Trifluoroiodomethane, CF₃I, is widely used as a relatively environmentally friendly plasma etching gas [1]. Partly as a result of this, but also from a more fundamental perspective, CF₃I has become something of a benchmark system for studying photoionization dynamics. Valence shell ionization is known to lead to the formation of a number of different fragment ions, depending on which

electronic state or states of the ion are accessed [2]. The photoionization dynamics of CF₃I have been studied using a variety of experimental techniques, including time-of-flight mass spectrometry [3], electron-ion coincidence methods [4, 5, 6, 2, 7], and velocity-map imaging [8, 9]. Investigations at a range of different wavelengths spanning excitations to the first few excited states of the ion have allowed the state-specific dynamics to be elucidated in some detail. These will be discussed more fully in Section 3.4

In contrast to photoionization, electron ionization is a collisional process which does not obey optical selection rules, and in which the precise amount of energy transferred to the molecule during the electron-molecule collision is not easy to infer. There is therefore considerable uncertainty about which electronic state or states the ion is formed in, and whether these are the same states accessed during photoionization. Recent experimental advances [10, 11, 12, 13] have made it possible to study the dynamics of electron ionization by multi-mass velocity-map imaging, which allows speed and angular distributions to be recorded for the ionic products of an electron molecule collision as a function of the incident electron kinetic energy. The data from such experiments provides considerable insight into the nature of the electronic state or states leading to production of each fragment. In the present work, we investigate the electron ionization dynamics of CF₃I at a range of energies from 20 to 100 eV, and interpret our results in light of knowledge of low-lying electronic states of the ion gleaned through photoionization studies.

2 Experimental methods

2.1 Total electron ionization cross-section measurement

The total electron ionization cross-section for CF₃I was measured using a beam-gas instrument that has been described in detail previously [14] and is shown schematically in Figure 1(a). Briefly, electrons from a tungsten-rhenium filament are focused into a beam and passed through a collision cell containing the sample gas at a pressure of $\sim 2 \times 10^{-4}$ Torr. The transmitted electron beam is refocused and detected as an electron current at a Faraday cup, while ions formed in electron-molecule collisions within the collision cell are collected as a positive ion current on the walls of the cell. The electron and ion currents are measured using Keithley Model 486 and Model 6487 picoammeters, respectively. The temperature T and pressure p of the gas within the collision cell are measured with a Type K Chromel-Alumel thermocouple, and an MKS Type 690A capacitance manometer. The total electron ionization cross-section σ measured in a beam-gas scattering experiment can be related to the incident and transmitted electron currents I_0 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:

$$\frac{I}{I_0} = e^{-n\sigma l} \quad (1)$$

where $n = p/k_{\text{B}}T$, 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 (see Appendix) to give

$$\frac{I_+}{I_-} = n\sigma l \quad (2)$$

where I_+ and I_- are the (absolute values of) the ion and electron currents, respectively, and n , σ , and l are defined as before.

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).

2.2 Crossed-beam velocity-map imaging measurements

The Oxford electron-molecule crossed-beam apparatus has been described in detail previously[12], and is shown schematically in Figure 1(b). The assembly is housed within a high-vacuum chamber with a background pressure of $\sim 10^{-8}$ Torr, and the electrostatic optics and flight tube are enclosed within a pair of μ -metal cylinders in order to screen the low energy electrons employed in the experiment from any external electric or magnetic fields.

During an experimental cycle, the CF_3I sample gas undergoes a pulsed supersonic expansion through a Parker-Hannifin Series 9 solenoid valve, is collimated by a 1 mm skimmer (Beam Dynamics), and enters a three-element velocity-map imaging electrostatic lens assembly [15] comprising repeller, extractor, and ground plates through a 3 mm aperture in the centre of the repeller plate. All lens elements are grounded when the molecular beam enters. Midway between the repeller and extractor lens elements, the molecular beam is intersected by a pulsed electron beam from an ELS100 electron gun (PSP Vacuum Technology). The electron beam is approximately 1 mm in diameter at the crossing point, with a pulse length of ~ 200 ns and an energy spread of 250 meV FWHM. The kinetic energy of the electrons can be varied between 10 and 100 eV, though in the present experiments there was insufficient signal to record images below 40 eV. The beam is pulsed by applying a pulsed retarding potential to one of the grounded elements within the electron gun's focusing optics.

Once the electron beam has cleared the interaction region, the velocity-mapping lens is pulsed up to the appropriate velocity-mapping potentials in order to extract ions formed in the electron-molecule collisions. In the present experiments, the repeller potential was set to 2000 V and the extractor to 1510 V. The ions traverse a field-free flight tube and are velocity mapped onto a position sensitive detector comprising a pair of microchannel plates and a P47 phosphor screen (Photonis). The ions separate according to their mass-to-charge ratio as they fly along the flight tube, and the resulting time-of-flight spectrum allows the various fragment ions to be identified and quantified. Time-of-flight spectra

Figure 1: (a) Beam-gas instrument used to measure the absolute total electron ionization cross-section of CF_3I ; (b) electron-molecule crossed-beam velocity-map imaging instrument used to measure partial cross-sections and product kinetic energy and angular distributions.

are recorded by acquiring the total optical signal from the phosphor screen using a photomultiplier (Hamamatsu H10721-01). Velocity-map images of a selected fragment are recorded by using a gated intensified CCD camera (Photonic Science Mini FDI) to capture optical images from the phosphor for ions arriving during the time gate of interest.

Time-of-flight spectra were accumulated over 6000 acquisition cycles at a repetition rate of 10 Hz, and were recorded at 21 electron energies over the range from 0 to 100 V in 5 eV steps. Images for the I^+ , CF_3^+ and CF_2I^+ fragments were recorded at electron energies of 40, 60, 80, and 100 eV, and accumulated over 100,000 to 600,000 acquisition cycles, depending on the signal intensity. Background images were also recorded, for which the electron pulse was timed to arrive at the interaction reaction before the molecular beam pulse. These were subtracted from each signal image to obtain the data presented in Section 3.3.

2.2.1 Analysis of time-of-flight spectra

Because the time-of-flight spectra are recorded using the optical signal from the phosphor screen of the ion imaging detector, each time-of-flight peak has a ~ 100 ns long ‘tail’ arising from the decay lifetime of the P47 phosphor. This was deconvoluted from the signal by fitting each peak in the time-of-flight spectrum to the convolution of a Gaussian and an exponential and then plotting only the Gaussian component of each peak. An example of a measured and a deconvoluted time-of-flight spectrum is shown in Figure 2

2.2.2 Analysis of velocity-map images

After centering, the velocity-map images were processed using the pBASEX algorithm [16] and the pyAbel software package [17] to extract the speed and angular distributions of the various dissociative ionization products. Initially the speed distributions are obtained in pixel units. The conversion factors required to convert from pixel number to fragment velocity, and hence kinetic energy, were determined from ion trajectory simulations performed using the SIMION8.0 software package (Scientific Instrument Services Inc).

The angular distributions for all fragments were found to be isotropic within experimental uncertainty, and will not be considered further in the present work.

3 Results and discussion

3.1 Total ionization cross-section

The total electron ionization cross-section for CF_3I over the energy range from 0 to 290 eV is shown in Figure 3. The ionization threshold is measured to be 10.24 eV, which agrees well with the recommended value [18] of 10.28 eV. The cross-section reaches a maximum of $(9.4 \pm 0.4) \times 10^{-20} \text{ m}^2$ at an electron energy of 129 eV. This is somewhat higher than the energy of the maximum

Figure 2: Example of (a) a time-of-flight spectrum recorded for the dissociative electron ionization fragments of CF_3I ; (b) the same spectrum deconvoluted to remove the effect of the phosphor decay lifetime of the imaging detector.

reported in previous measurements [19, 1, 20]. There is quite wide variation in total ionization cross-section measurements reported by different authors for many molecules, and it is difficult to attribute these to any well-established single cause. It is challenging to measure absolute cross-sections, and the very small signals involved, coupled with the many different designs of low-energy electrostatic optics employed in different instruments, make it unsurprising that there is some variation between measurements reported by different research groups. Many of the differences between instruments are likely to arise either from energy-dependent changes in the detection efficiency of the electron or ion current or from stray fields affecting the true electron energy in the interaction region. While we cannot discount these completely, these are two effects that we have made great efforts to minimise within our instrument.

3.2 Partial ionization cross-sections and fragmentation channels

The total ionization cross-section shown in Figure 3 reflects the total probability of forming an ion in an electron-molecule collision at a given energy. However, it reveals nothing about the identity of the resulting ion, which may be a parent ion or any one of a number of possible fragment ions. The probability of forming a particular ion is quantified by the partial ionization cross-section for formation of that ion. Partial cross-sections for each fragment ion may be determined from the time-of-flight spectra recorded in the electron-molecule crossed-beam

Figure 3: Absolute total electron ionization cross-section for CF_3I recorded over the electron energy range from 0 to 290 eV. The data are compared with previous measurements [19, 1, 20] and with the predictions of the Deutsch-Märk model [21]

experiments. A selection of time-of-flight spectra, recorded at electron energies of 20 eV, 60 eV, and 100 eV, are shown in Figure 4(a). These spectra have been deconvoluted according to the procedure described in Section 2.2.1.

Partial ionization cross-sections, shown in Figure 4(b) were determined by normalising the sum of the time-of-flight peak intensities recorded at a given energy to the measured total ionization cross-section at that energy. Plotting the resulting normalised peak intensities for each fragment as a function of electron energy then yields the partial cross-sections.

Both the time-of-flight spectra and the partial cross-sections reveal that a number of different fragments are formed in collisions of electrons with CF_3I . These are listed, together with their mass-to-charge ratios, appearance potentials (where available), and relative abundance at an energy of 100 eV, in Table 1.

In decreasing order of abundance at 100 eV, the observed product ions are I^+ , CF_3I^+ , CF_3^+ , CF^+ , CF_2I^+ , CF_2^+ , C^+ , F^+ , and I^{2+} . These abundances are in reasonable agreement with previous partial ionization cross-sections measured at 70 eV by Fourier-transform ion cyclotron resonance mass spectrometry [25], with differences most probably originating from the different temperatures of the sample gas in the two experiments.

The observed abundances suggest that following the ionization step, the two most likely fragmentation pathways involve cleavage of the carbon-iodine bond, with the charge residing on one or other of the resulting CF_3 and I fragments:

Figure 4: (a) Time-of-flight spectra for the fragments arising from dissociative electron ionization of CF_3I at incident electron energies of 20, 60, and 100 eV; (b) partial ionization cross-sections for the observed fragment ions.

Table 1: Observed ionic fragments, together with their mass-to-charge ratio m/z , appearance potentials [18, 22, 23, 6, 4, 24], and relative abundance at 100 eV, for the dissociative electron ionization products of CF_3I .

fragment	m/z	Appearance potential / eV	Relative abundance at 100 eV
C^+	12	33.0 ± 1.0	0.065
F^+	19	33.0 ± 1.0	0.055
CF^+	31	19.9 ± 0.3	0.120
CF_2^+	50	-	0.064
I^{2+}	63.5	-	0.014
CF_3^+	69	11.26 ± 0.5	0.161
I^+	127	13.4 ± 0.1	0.284
CF_2I^+	177	13.40 ± 0.05	0.070
CF_3I^+	196	10.28 ± 0.07	0.167

and

The corresponding fluorine-loss channels are also observed:

and

Thermodynamic data used to calculate the above reaction endoergicities were taken from references [18, 26, 27, 28, 29]. The smaller molecular fragments, CF^+ , CF_2^+ , and C^+ , are likely to be formed via secondary fragmentation of the molecular ions formed in processes described by Equations 3 to 6 above, and will not be considered further in the present work.

3.3 Velocity-map images and fragment speed and angular distributions

Three of the primary fragments from Equations 3 to 6, namely the I^+ , CF_3^+ , and CF_2I^+ ions, yielded large enough signals for velocity-map images to be recorded. Figures 5, 6, and 7 show the velocity-map images for each of these fragments at electron energies of 40, 60, 80, and 100 eV, together with the corresponding Abel-inverted images and kinetic energy distributions for each fragment. Unfortunately, the signal levels were not high enough to record reliable images at electron energies below 40 eV. For visualisation purposes, the images have been symmetrised about the propagation direction of the electron beam (vertical axis of the images). The kinetic energy distributions have been smoothed using a three-point running average. Note that since the product channel involves four particles - the atomic and molecular fragments and the ejected and scattered electron - it is not generally possible to convert the kinetic energy for a particular fragment into a total kinetic energy release for the corresponding channel.

Based on the data shown in Figures 5 to 7, a number of observations may be made:

1. The kinetic energies of the fragments are very small relative to the incident electron energy, implying that the incident electron transfers only a small fraction of its energy to the molecule.
2. For all fragments, the images and speed distributions show little or no dependence on the electron energy.
3. The kinetic energy distributions for the CF_2I^+ fragments resulting from C-F bond cleavage have a markedly different structure from those recorded for the CF_3^+ and I^+ products of C-I bond cleavage. While the C-I cleavage channels yield fragment kinetic energy distributions that peak at or close to zero and decay out to higher energies, the kinetic energy distribution

Figure 5: Velocity-map images, Abel-inverted images, and kinetic energy distributions for the I^+ dissociative electron ionization product of CF_3I at electron energies of 20, 40, 60, and 80 eV. The direction of travel of the electron beam provides the axis of symmetry for the Abel inversion, and is shown in the top left image for each fragment.

Figure 6: Velocity-map images, Abel-inverted images, and kinetic energy distributions for the CF_3^+ dissociative electron ionization product of CF_3I at electron energies of 20, 40, 60, and 80 eV. The direction of travel of the electron beam provides the axis of symmetry for the Abel inversion, and is shown in the top left image for each fragment. The dotted line shows a fit to the kinetic energy distribution for the 100 eV data using a statistical model by Klots *et al* [30] (see text for details).

Figure 7: Velocity-map images, Abel-inverted images, and kinetic energy distributions for the CF_2I^+ dissociative electron ionization product of CF_3I at electron energies of 20, 40, 60, and 80 eV. The direction of travel of the electron beam provides the axis of symmetry for the Abel inversion, and is shown in the top left image for each fragment.

of the C-F fragmentation products peaks away from zero, leading to a relatively well-defined ring in the CF_2I^+ velocity-map images.

4. The CF_3^+ and I^+ products of C-I bond cleavage have kinetic energy distributions that are similar in form, but the CF_3^+ products have much lower kinetic energies than the I^+ products.

The first of these observations implies that the electron ionization process can be viewed to some extent primarily as a collision between the incident and target electron. In all cases, less than 1% of the incident electron energy appears as kinetic energy of the detected ionic fragment, implying that most of the incident electron energy goes into overcoming the binding energy of the target electron and into kinetic energy of the two departing electrons, with only a small amount of energy transferred into the rest of the molecular framework. This is consistent with a simple model in which the electron kinetic energy is used to estimate the time taken for the electron to traverse a molecular diameter. For electrons ranging in energy from 20 eV to 100 eV, this is on the order of 10^{-17} to 10^{-16} s. This is on the timescale of electronic motion within a molecule, but several orders of magnitude faster than nuclear motion, and it is therefore not surprising that transfer of energy from the electron into vibrational modes of the motion in the initial collision is inefficient.

Electron-molecule collisions are known to generate nascent parent ions in a variety of different electronic states[12, 13]. In the present work, the lack of dependence on electron energy implies rapid relaxation from the initially excited ionic state(s) to the dissociative state(s) in all cases, with the excess energy being released into internal degrees of freedom of the molecular fragment through a combination of internal conversion, intersystem crossing, and intramolecular vibrational energy transfer. The resulting fragment kinetic energy is then determined by the topology of the dissociative state rather than by the initial energy of the ion, and shows little variation as a function of electron energy. In the case of C-F bond cleavage, the CF_2I^+ fragment has an approximately Gaussian kinetic energy distribution peaking at around 0.13 eV. This is consistent with rapid impulsive dissociation along one or more repulsive potential energy surfaces. In contrast, the CF_3^+ products of C-I bond cleavage show a Boltzmann-like kinetic energy distribution peaking near zero kinetic energy. This implies a dissociation occurring over much longer timescales, over which the available energy becomes statistically distributed over the available internal states of the ion prior to dissociation. Dissociation in these cases usually occurs from high-lying vibrational levels of a bound electronic state, often the electronic ground state or a higher-lying metastable state. The CF_3^+ kinetic energy distributions can be fitted reasonably well using the statistical ‘model free’ approach developed by Klots [30], which predicts a distribution of the form

$$P(E_T) = E_T^l \exp(-E_T/k_B T^\ddagger) \quad (7)$$

where E_T is the total translational kinetic energy release, l is a parameter that ranges from 0 to 1, and $T^\ddagger$ is a lower limit to the temperature of the transition

state of the dissociating parent ion. Figure 6 shows a fit to the 100 eV data, which yields a transition state temperature of 725 K.

The I^+ fragments arising from C-I bond cleavage display behaviour intermediate between the two extremes described above for CF_2I^+ and CF_3^+ , peaking at low kinetic energies, but with a high energy tail extending out to around 1.0 eV or so.

3.4 Comparison with photoionization studies

We are not aware of any previous studies in which the kinetic energy release of fragments arising from electron ionization of CF_3I has been measured with high resolution. However, there are a number of studies [5, 6, 2, 31] into the photoionization of CF_3I and photodissociation of CF_3I^+ that can help to shed some light on the possible identities of the electronic states involved in the various observed fragmentation pathways. We note that any comparisons with photoionization data must be treated with caution, since the optical selection rules that apply in the case of a photoinitiated process do not apply in the case of a collisionally-induced process such as electron ionization. However, previous work by Thorne and Beauchamp [32] has indicated that a large fraction (up to 60%) of CF_3I^+ ions formed via electron ionization at 70 eV are either born in or rapidly relax to vibrationally excited levels of the electronic ground state. It therefore seems likely that the dynamics of dissociative electron ionization are dominated by the ground and first few electronically excited states of the ion, and hence that comparison with the corresponding photoionization processes, which also populate these states, has the potential to provide considerable insight into the fragmentation dynamics. A partial correlation diagram for these states is shown in Figure 8.

One of the most comprehensive reported studies is a photoelectron-photoion coincidence study by Low *et al.* [5]. The authors were able to correlate the photoelectron signals arising from each electronic state of the CF_3I^+ ion with the fragment ions arising from each state and the kinetic energy release associated with each fragmentation pathway. The $\tilde{\text{X}}^2\text{E}_{1/2}$ ground state of the ion was found to correlate with $\text{CF}_3^+(\tilde{\text{X}}^1\text{A}_1) + \text{I}^2\text{P}_{3/2}$ fragments. This channel is associated with low kinetic energy release, which can be modelled well by a statistical phase space calculation. These results have been reproduced by a number of authors [3, 5, 6, 7, 8]. While it is difficult to compare our CF_3^+ kinetic energy distributions resulting from dissociative electron ionization directly with those obtained directly following photoexcitation at specific energies, the low kinetic energy release seen in our data would certainly be consistent with statistical dissociation on the ground state of the ion.

Interpreting previous data relating to the first excited $\tilde{\text{A}}^2\text{A}_1$ state of the CF_3I^+ ion is less straightforward. A number of authors [2, 5, 6, 8] have shown that excitation to this state leads to the formation of both I^+ and CF_3^+ products. The state can be produced by ionization of a C-I bonding electron from neutral CF_3I [33], is strongly repulsive along the C-I bond direction, and correlates with $\text{CF}_3 + \text{I}^+$ products. Several studies [5, 2, 9] have confirmed that the I^+

Figure 8: Partial correlation diagram for the $\tilde{X}$ to $\tilde{E}$ states of CF_3I^+ , based on data from photoelectron spectroscopy studies [5, 2, 8, 9, 7]. State symmetries, where known, are shown in both the C_{3V} (A_1 , A_2 , E) and extended ($E_{1/2}$, $E_{3/2}$) point groups.

from this state is formed with relatively high kinetic energy, consistent with rapid dissociation along a repulsive potential energy curve, and that the kinetic energy distribution shows little or no dependence on the photon energy. This contrasts with the kinetic energy distribution observed for I^+ in the present work. Though the distribution shows no dependence on electron energy, the I^+ kinetic energy peaks very close to zero, which is inconsistent with direct dissociation on a strongly repulsive surface. We therefore believe that the $\tilde{\text{A}}$ state of the ion does not make a dominant contribution to the I^+ signal. CF_3^+ products arising from the $\tilde{\text{A}}$ state are thought to be formed on the ground-state following radiationless population transfer from the $\tilde{\text{A}}$ state. The CF_3^+ products have been shown [5, 2, 9] to have a kinetic energy distribution peaking close to zero, with the peak shifting to higher kinetic energy at shorter excitation wavelengths.

Photoexcitation of the ion to the $\tilde{\text{B}}^2\text{A}_3$, $\tilde{\text{C}}^2\text{E}$, and $\tilde{\text{D}}$ states leads to cleavage of a C-F bond and formation of CF_2I^+ fragments as the primary ion products [5]. The kinetic energy distributions for dissociation from these states reveal substantial kinetic energy release, with total kinetic energy releases for the process ranging from around 0.9 to 1.2 eV, indicating direct dissociation along a repulsive potential in each case. This behaviour is qualitatively consistent with the kinetic energy distributions of the CF_2I^+ fragments observed in the present study. The kinetic energy distribution measured for the CF_2I^+ products of dissociative electron ionization peaks at around 0.13 eV. If we think of dissociative electron ionization as a two-step process involving collisional removal of an electron followed by two-body dissociation, then based on the kinetic energy of the CF_2I^+ fragments and conservation of momentum, the total kinetic energy release associated with the dissociation step must be around 1.34 eV, close to the values observed for dissociative photoionization from the $\tilde{\text{B}}$, $\tilde{\text{C}}$, and $\tilde{\text{D}}$ states.

I^+ is formed as a minor product from the $\tilde{\text{B}}$ and $\tilde{\text{C}}$ states, together with CF_3^+ , and is a significant product from both the $\tilde{\text{D}}$ and $\tilde{\text{E}}$ states of the ion [5]. Low *et al* report average kinetic energy releases for I^+ associated with the $\tilde{\text{D}}$ and $\tilde{\text{E}}$ states of 0.4 eV and 0.6 eV, respectively. In the present study we see significantly higher kinetic energy release in the I^+ formation channel than in the CF_3^+ channel, with kinetic energy distributions that peak at around 0.2 eV and extend out to 1 eV or so, which may be consistent with the involvement of these higher-lying states. We note that while in our study I^+ is the dominant channel observed following electron ionization at all energies, a number of photoionization studies have shown the branching ratios into the energetically accessible fragments to be strongly dependent on photon energy [2, 8]. This could perhaps suggest that there is a reasonable probability of forming these higher lying states in a collision with a high energy electron.

3.5 Conclusions

We have presented a comprehensive experimental study into the dissociative electron ionization dynamics of CF_3I at a series of electron energies in the range from 20 to 100 eV. We report absolute total and partial ionization cross-sections

for the various fragmentation products, which reveal a number of fragmentation channels involving both C-I and C-F bond cleavage, in some cases followed by further fragmentation of the resulting molecular ion. Velocity-map images of the CF_3^+ products of C-I bond cleavage imply that these products are formed via a statistical dissociation mechanism over relatively long timescales, while images recorded for the CF_2I^+ products of C-F bond cleavage suggest a much faster, more direct dissociation involving one or more repulsive states of the parent molecular ion. I^+ displays intermediate behaviour between these two extremes. All measured fragment ion kinetic energy distributions show little or no dependence on the energy of the incident electron, implying that the initially excited ion state or states undergo rapid relaxation to the dissociative states in all cases.

Based on comparison with data from photoionization studies, and in particular due to the strong similarities between the CF_3^+ kinetic energy distributions recorded in the two types of study, we tentatively propose that CF_3^+ is most probably formed via statistical dissociation of CF_3I^+ in its electronic ground state. Most photoionization studies have concluded that I^+ is formed primarily via rapid impulsive dissociation from the $\tilde{\text{A}}$ state of the ion. However, this is inconsistent with the low kinetic energy release observed for the I^+ ion in the present study. Instead, it seems likely that I^+ is formed via higher lying states, potentially the $\tilde{\text{D}}$ and $\tilde{\text{E}}$ states of CF_3I^+ . Cleavage of the C-F bond to form CF_2I^+ is proposed to occur on the $\tilde{\text{B}}$, $\tilde{\text{C}}$, and $\tilde{\text{D}}$ states, and yields fragment kinetic energy distributions that are qualitatively similar to those observed in photodissociation studies on the CF_3I^+ ion via these states.

Conflicts of Interest

There are no conflicts of interest to declare.

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Appendix: derivation of the expression used to determine total electron ionization cross-sections from experimental data

Assuming that ionization is the dominant outcome of an electron-molecule collision in a beam-gas experiment at the electron energies of interest in the present study, the incident and transmitted electron beam currents, denoted I_0^- and I^- , respectively, are related by an expression analogous to the Beer-Lambert law:

$$\frac{I^-}{I_0^-} = e^{-n\sigma l} \quad (8)$$

where n is the number density of the gas, σ is the electron ionization cross-section, and l is the path length through the gas. Since each scattered electron yields one scattered ion, we have $I^- = I_0^- - I^+$, with I^+ the ion current, and therefore

$$\frac{I_0^- - I^+}{I_0^-} = e^{-n\sigma l} \quad (9)$$

If the experiment is carried out under conditions of sufficiently low pressure, only a very small fraction of electrons are lost from the beam, and we can make the

approximations that $I_0^- \approx I^-$ and $e^{-n\sigma l} \approx 1 - n\sigma l$. Making these substitutions yields

$$\frac{I^- - I^+}{I^-} = 1 - n\sigma l \quad (10)$$

which can be rearranged to give Equation 2.

$$\frac{I^+}{I^-} = n\sigma l \quad (11)$$