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Studies of electron-impact dissociative excitation and ionization using the crossed electron-ion beams technique

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Abstract. Absolute cross sections for heavy ion fragment production due to electron-impact dissociation of $XH_2^+$ ($X = B, C, N, O, F$), $N_2D^+$ and $O_3^+$ have been investigated with the crossed electron-ion beams technique in the energy range 3 – 100 eV. This energy regime covers the dissociative excitation and ionization processes. Two and three-body dissociation channels are observed in these systems and marked resonant-like structure is also observed in the dissociative excitation channels of some systems. It is unclear if direct excitation or resonant capture processes lead to these enhanced dissociative excitation cross sections.

1. Introduction

Plasma chemistry is driven by collisions of free electrons with atomic and molecular species. Low-energy electrons can particularly access dissociative channels that govern branching fractions, energy balance, neutral particle transport, and excited state dynamics. Such low-energy electron collisions take place in the low-temperature regions of fusion plasmas [1, 2] and planetary atmospheres [3]. The physics and chemistry of industrial interests, such as flames, lighting and gas lasers, are likewise areas where the knowledge of these collision processes are needed.

The production of heavy ion fragments from molecular cations due to electron scattering can proceed through various channels. The Direct Dissociative Excitation process proceeds via a vertical transition to either a dissociative excited state or a bound excited state that couples to a dissociative pathway. Both of these pathways result in a charged ion fragment and neutral fragments. The Resonant Dissociative Excitation process proceeds through the resonant capture of an electron to a neutral Rydberg state. This state then decays via autoionization and subsequent dissociation producing a charged ion fragment and neutral fragments. We will refer to both of these process jointly as Dissociative Excitation (DE).

The Dissociative Ionization (DI) process is similar to the dissociative excitation process with the exception that an electron is removed from the system resulting in at least two charged ion fragments. Given that two positively charged fragments are initially in close proximity at the time of dissociation, some amount of Coulomb force is experienced by the mutual repulsion of the charged fragments. This augments the kinetic energy release due to bond breaking in the dissociation process.
Two additional processes are not considered here: Resonant Ion-Pair Formation (RIP) and non-dissociative ionization. While the RIP process can lead to heavy ion fragments, the cross sections for this process are typically small \[4\] and aren’t expected to contribute significantly to our investigation. Non-dissociative ionization of the molecular cation species likewise have small cross sections and do not contribute to singly charged ion fragment measurements.

2. Experiment

2.1. Ion Beams

The molecular ion beams were produced in the ORNL electron cyclotron resonance (ECR) ion source \([5]\) using total working gas pressures of approximately \(10^{-5}\) Torr and injected RF powers of a few Watts at 10 GHz. All of the \(XH_2^+\) molecular ion beams, except \(^{12}\text{CH}_2^+\), were produced by first establishing a plasma on deuterium gas fed into the source. Given that specific charge-to-mass ratios can be contaminated by various molecular species, the pure deuterium plasma allowed for a mass analysis to gauge possible contamination from ion chemistry with the source vacuum residual gas. Once the desired charge-to-mass was determined to be free of contamination, a second working gas was added to the source and the desired species produced via ion chemistry in the source plasma. \(^{11}\text{BD}_2^+\) and \(^{19}\text{FD}_2^+\) were produced by adding \(\text{BF}_3\) to the already established deuterium plasma, \(^{14}\text{ND}_2^+\) was produced by adding \(\text{N}_2\) and \(^{16}\text{OD}_2^+\) was produced by adding \(\text{O}_2\). As discussed in reference \([6]\), \(^{12}\text{CH}_2^+\) was produced from methane gas alone. The \(N_2D^+\) ion beam was also formed by first establishing a deuterium plasma to gauge m/q contamination and then \(N_2\) was added to chemically produce \(N_2D^+\). The \(O_3^+\) ion beam was formed using only \(O_2\) working gas. Deuterated species were used solely for the purpose of separating the ion fragments produced during dissociation from the parent ion beam.

Ions produced by the ECR source were extracted to form beams with energies of \(7 – 10\) keV and were subsequently momentum analyzed by a dipole magnet before being transported, via magnetic and electrostatic elements, to the crossed electron ion beams apparatus. Typical ion beam currents delivered to the crossed-beams apparatus range from 5-100 nA.

Given that the flight time from the ion source to the interaction region was on the order of a few microseconds, it is not expected that any vibrational excitations, with lifetimes ranging in the milliseconds, would relax before reaching the interaction region. The current experiment
Table 1. Absolute experimental uncertainties. These uncertainties are combined with the relative uncertainties at a 90% confidence level to determine the total uncertainty in each data point.

| Source of Uncertainty                  | Uncertainty (%) |
|----------------------------------------|-----------------|
| Product ion detection and pulse processing | ±5              |
| Transmission of product ion to detector  | ±4              |
| Absolute value of form factor           | ±4              |
| Ion current measurement                | ±2              |
| Electron current measurement           | ±2              |
| Ion velocity                           | ±1              |
| Electron velocity                      | ±1              |
| Quadrature Sum                         | ±8.2            |

has no means to determine the initial rovibrational distribution of the parent molecular ions.

2.2. Crossed-beams Method

The ORNL crossed electron ion beams apparatus is shown schematically in Figure 1. Incident molecular ions passed through a 90° electrostatic analyzer to remove any ions that may have undergone charge exchange or dissociative interactions with the residual gas of the vacuum system during beam transport. The analyzed molecular ion beam then passed through the interaction region perpendicular to the magnetically confined electron beam. The center-of-mass interaction energy was tuned by adjusting the extracted electron beam energy.

The details of the custom electron gun have been discussed previously [7, 8]. Electrons are produced by an indirectly heated planar cathode and extracted over a uniform electrostatic field to define the electron beam energy. A 250 G magnetic field, coaxial to the electron gun direction, confines the electrons and together with the extraction apertures form a uniform rectangular beam (approximately 2 mm wide and 10 mm in height) over the 2 mm interaction region. Opposite the interaction region, the electrons are collected by a Faraday cup constructed of stacked, tantalum, razor-edged blades oriented with the sharp edges towards the beam. The collector is biased by a +300 V battery to minimize electron loss that would lead to an inaccurate electron current measurement needed for absolute cross section determinations. Typical electron beam currents are ~10 µA at 10 eV and ~250 µA at 100 eV. The electrons are chopped at 1 kHz in order to separate fragment ion signals due to electron impact as compared to collisions with the residual gas.

Fragment ions produced by dissociation of the parent ion beam are separated from the parent ion beam by a double-focusing dipole magnetic. Depending on the mass ratio of the fragment ion to the parent ion beam molecule, the parent beam is collected in one of three different Faraday cups used to measure the incident ion beam current. The fragment ions of interest are directed towards a vertical 90° electrostatic deflector which steer the fragment ions into a discrete dynode electron multiplier detector. The detector (ETP model 14880) has an acceptance window of 25 × 10 mm with the widest dimension oriented in the dispersion plane of the analyzing magnet so as to collect all of the ion fragments regardless of kinetic energy release during dissociation. This detector is capable of counting particle impacts in excess of a million events per second with little deadtime. This capability was essential given that background signal rates for some of the ion fragment channels investigated were more than could be sustained by a conventional
channel electron multiplier.

The absolute cross sections for heavy fragment ion production were determined from measured quantities by

\[
\sigma(E) = \frac{R}{I_I I_e v_i v_e} \frac{q e^2 \sqrt{v_i^2 + v_e^2}}{\epsilon} F,
\]

where \(\sigma(E)\) is the absolute cross section at the center-of-mass energy \(E\), \(R\) is the fragment ion signal rate, \(q e\) is the charge of the incident ions, \(v_i\) and \(v_e\) are the incident ion and electron velocities, \(\epsilon\) is the detection efficiency (90%), and \(F\) is the form factor.

The overlap of the ion and electron beams in the direction orthogonal to both beams, here labeled the \(z\) direction, was measured at each interaction energy with a rotatable slit probe scanned across both the ion and electron beams in the interaction region. Current profiles of the ion and electron beams, \(I_I(z)\) and \(I_e(z)\) respectively, were measured independently and a form factor, \(F\), was determined by

\[
F = \frac{\int I_e(z) \, dz \int I_I(z) \, dz}{\int I_e(z) I_I(z) \, dz}.
\]

The predominant systematic uncertainties associated with the experiment are listed in Table 1 with the estimated error for each component at a high confidence level (equivalent to a 90% confidence level for statistical uncertainties). These errors are treated as random sign errors, summed in quadrature, and combined with the statistical uncertainty of each data point (at a 90% confidence level) to determine the total uncertainty. Detailed discussions of the experimental uncertainties have been published previously by [9]. All absolute cross section figures in this report indicated uncertainties at a 90% confidence level.

3. Results and Discussion

3.1. \(e^- + XH_2^+ (X = B, C, N, O, F)\)

Figures 2 and 3 show the combined absolute cross sections for production of \(XH^+\) and \(X^+\) heavy ion fragments, respectively. Table 2 lists the various \(XH_2^+\) DE and DI dissociation channels and corresponding thresholds. These thresholds were determined by using NIST [10] ionization energies and heats of formation. For all systems, except FD\(_2^+\), the infinite dissociation limit of neutral fragments was verified by comparison to the ground state dissociation energies measured for dissociative recombination at storage rings [11, 12, 13, 14, 15]. The CH\(_2^+\) data were measured with the ORNL crossed-beams apparatus previously and are reproduced here from Vane et al. [6].

The absolute cross sections plotted in Figure 2, for the dissociation channel leading to \(XH^+\), show a clear similarity for the underlying DE and DI processes with the DI cross sections all converging around 100 eV. For the BD\(_2^+\) and CH\(_2^+\) species, a large resonant-like structure is seen in the DE region. ND\(_2^+\) and OD\(_2^+\) also exhibit small resonant-like peaks. It is unclear if this is a direct excitation to a dissociative state or if there is a contribution from a resonant capture process that proceeded via autoionization and subsequent dissociation. Lecointre et al. [16] have recently measured this same structure in the DE of CD\(_2^+\), however, their results indicate a peak cross section about a factor of four smaller. Their results also do not exhibit a two-body X\(^+\) DE process. This is likely due to unknown excited ro-vibrational states of the parent molecular ion in each experiment as source conditions are likely different in each case. The differences could also be representative of an isotope effect if indirect processes are governing the dynamics.

Figure 3 shows the absolute cross sections for \(X^+\) fragment production along with the lowest energy DE thresholds that appear to contribute to the cross sections. If the thresholds for DE are used as a guide to determine if a two- or three-body process is contributing to an observed cross section, it appears that the BD\(_2^+\) and CH\(_2^+\) cations exhibit a two-body DE process while
the remaining XH$_2^+$ species all exhibit a three-body break up when X$^+$ fragments are produced. This is mirrored by the observed two- and three-body dissociation dynamics seen in storage ring DR measurements for these species [11, 12, 13]. We also note that the rising slope of the cross sections near threshold vary depending on the threshold value, i.e., lower energy thresholds tend to exhibit a sharper increase while higher energy thresholds tend to show a more gradual increase in cross section as a function of collision energy. The lower energy thresholds that
Table 2. Dissociation channels producing heavy fragment ions and their corresponding thresholds in eV. See text for description of how thresholds were determined.

| Dissociation Channel | X = B | C | N | O | F |
|----------------------|-------|---|---|---|---|
| $e^{-} + \text{XH}_2^+$ | 4.8   | 4.8 | 6.1 | 5.5 | 7.5 |
| $\rightarrow \text{X}^+ + \text{H} + \text{e}^-$ | 6.7   | 9.0 | 10.8 | 10.5 | 14.7 |
| $\rightarrow \text{X}^+ + \text{H}_2 + \text{e}^-$ | 2.2   | 4.5 | 6.3 | 6.0 | 10.2 |
| $\rightarrow \text{XH}^+ + \text{H}^+ + 2\text{e}^-$ | 18.4  | 18.4 | 19.7 | 19.1 | 21.1 |
| $\rightarrow \text{X}^+ + \text{H}^+ + \text{H} + 2\text{e}^-$ | 20.3  | 22.6 | 24.4 | 24.1 | 28.3 |
| $\rightarrow \text{X}^+ + \text{H}_2^+ + 2\text{e}^-$ | 17.6  | 19.9 | | | |
| $e^{-} + \text{N}_2D^+$ | 11.2 | | | | |
| $\rightarrow \text{ND}^+ + \text{N} + \text{e}^-$ | 12.3 | | | | |
| $\rightarrow \text{ND} + \text{N}^+ + \text{e}^-$ | 7.1 | | | | |
| $\rightarrow \text{N}^+_2 + \text{D} + \text{e}^-$ | 25.8 | | | | |
| $\rightarrow \text{N}^+_2 + \text{D}^+ + 2\text{e}^-$ | 20.7 | | | | |
| $\rightarrow \text{N}^+ + \text{N} + \text{D}^+ + 2\text{e}^-$ | 29.0 | | | | |
| $e^{-} + \text{O}_3^+$ | 0.6 | | | | |
| $\rightarrow \text{O}_2^+ + \text{O} + \text{e}^-$ | 2.2 | | | | |
| $\rightarrow \text{O}_2 + \text{O}^+ + \text{e}^-$ | 7.4 | | | | |
| $\rightarrow \text{O}^+_2 + \text{O}^+ + 2\text{e}^-$ | 14.3 | | | | |
| $\rightarrow \text{O}^+_2 + \text{O}^+ + \text{O} + 2\text{e}^-$ | 21.0 | | | | |

initially contribute to DE also seem to produce larger relative cross sections.

3.2. $e^{-} + \text{N}_2D^+$

Figure 4 shows the absolute cross sections for heavy fragment ion production from N₂D⁺ along with the thresholds for the various DE and DI dissociation channels. The corresponding threshold values are given in Table 2. The thresholds are determined in the same manner as discussed in the previous section. As can be seen in Figure 4, the DE region is dominated by N⁺ production. This channel also shows a slight resonant-type feature as seen for the BD₂⁺ and CH₃⁺ species discussed in the previous section. The DE channels leading to ND⁺ and N⁺ can also be seen in Figure 4. These channels are a result of N–N bond breaking that was previously a surprising result of DR measurements of N₂D⁺ [14]. These two channels have similar DE thresholds and the relative cross sections appear to remain similar until the DI threshold is reached. These two channels share a common DI channel, i.e., ND⁺ + N⁺ and, assuming a two-body breakup model, should exhibit identical DI cross sections. However, The N⁺ product channel shows a larger cross section. This suggests that a three-body breakup dynamic is contributing, namely the N⁺ + N + D⁺ channel at 29 eV. This three-body channel would increase the apparent N⁺ cross section given that multiple dissociation channels could contribute. This increase is observed in Figure 4, as compared to the ND⁺ DI cross section. A similar three-body effect has also been observed by Lecointre et al. [17] for C₂D⁺.

3.3. $e^{-} + \text{O}_3^+$

Figure 5 shows the absolute cross sections for heavy fragment ion production from O₃⁺ producing O₂⁺ and O⁺ fragments along with the various DE and DI thresholds. The corresponding thresholds are given in Table 2 and have been determined in the same manner as described
previously. As can be seen in figure 5, the DE region is dominated by a large cross section for the production of $O^+_2$. The crossed-beam apparatus could not measure sufficiently low in electron energy, due to reduce electron currents at low energy, to establish the threshold behavior for this channel. This relatively large cross section could also indicate a resonant-like feature as observed for $BD^+_2$, $CH^+_2$ and $N_2D^+$.

The $O^+$ fragment channel threshold, however, could be reached and a sharp onset in cross section is observed. The presence of a contribution to the $O^+$ channel below the $O^+ + O + O$ threshold indicates that the two-body process contributes dominantly to the dissociation. The DI cross sections are observed to converge at around 100 eV. It is worth noting that the DR measurements for $O^+_3$ show a propensity for three-body breakup [15] while the DE process seems to follow a two-body dissociation dynamic.

4. Conclusion
The absolute cross section for the production of heavy fragment ions from the triatomic species $XH^+_2$, $N_2D^+$ and $O^+_3$ due to electron impact have been investigated in the energy range of 3 – 100 eV using the crossed electron-ion beams apparatus at Oak Ridge National Laboratory. Two- and three-body dissociation channels are observed as well and resonant-like contribution to DE. It is unclear if these resonant-like features are due to direct excitation or to resonant capture processes. More theoretical effort is needed to help clarify these effects.

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