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MEASUREMENTS OF ELECTRON-IMPACT IONIZATION AND DISSOCIATION CROSS SECTIONS IN A CROSSED ELECTRON-SUPERSONIC MOLECULAR BEAM ☆

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A new approach is described for obtaining absolute electron-impact cross sections for ionization, including the partial cross sections for multiple charge excitation and ion dissociation. The method benefits from the use of a supersonic molecular beam, pulsed ion source, and multichannel mass detection. The determination of the partial cross sections for the production of Ne^+, Ne^{2+}, Ar^+, Kr^+, and Kr^{2+} from the neutral atoms, as well as for the production of NH_3^+, NH_2^+, and NH^+ from rovibrationally cold NH_3, are reported and compared with results from other recent work.

1. Introduction

Electron–molecule collisions are ubiquitous in nature and hence of great interest to diverse fields such as astrophysics (aurora borealis, planetary atmospheres, supernova activity), radiation physics (secondary electron effects, condensed-phase spur formations), and plasma physics (discharges and breakdowns, fusion, bremsstrahlung processes). Reliable cross section measurements for ionization and dissociation as a function of the electron-impact (EI) energy are highly desirable, but unfortunately are rather lacking as a result of complexities and difficulties associated with standard experimental techniques [1]. Theoretical calculations have helped to fill the void; however, the results vary widely and are strongly model dependent [1,2]. Accurate experimental data would therefore be of great assistance in evaluating existing theoretical models and would in turn improve the understanding of electron–molecule scattering processes.

Methods for determining absolute EI ionization cross sections σ_{M^+} as a function of electron excitation energy E may be represented by the expression

$$\sigma_M{+}(E)=I_M{+}(E)/I_e(E)n_M l\kappa_M{+}(E)\,, \qquad (1)$$

where I_{M^+} is the detector current for ion mass M^+ and I_e is the electron current through the interaction region of length l and gas density n_M. An instrumental factor κ_{M^+} is included to consider the product of discrimination effects (e.g., ion extraction and transmission efficiency, detector linearity), which are expected to vary with mass and energy. Since the terms in eq. (1) are rarely measured to high accuracy, it is common to measure instead the *relative* cross section as a function of E and to normalize the cross section curve to a single reference value for the *same* atom or molecule. One avoids the need to measure $I_e(E)n_M l$, but still must confront the instrumental factor κ_{M^+} which can have profound influence on the shape of the cross section energy curve. Furthermore, one is limited to species that have some available cross section data.

Discrimination effects encompassed by κ_{M^+} are the major source of problems in measuring cross sections. This is exemplified by the common and representative method involving the use of the three-electrode, Nier-type ion source [3–5]. This device, like many others, is inherently a continuous excitation and extraction source; hence the design of an efficient extraction field that does not adversely affect the properties of the electron beam (in terms of collimation and energy spread) is often a formidable

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challenge. The optimum extraction and focusing conditions are complicated by their tendency to vary with electron energy, ion energy, and mass-to-charge (m/z) ratio. Upon excitation, a series of beam centering and deflection plates must then direct the ions through a number of apertures and slits and into a sector-type mass spectrometer [5]. Finally, discrimination effects due to the thermal energy of the ions and kinetic energy of dissociated fragments can also produce misleading results [1,3].

Large discrepancies in reported EI cross section measurements are rather common. It is now generally conceded [3,6] that many of the early data are unreliable in light of recent improvements in the understanding of instrumental effects. Over the past 20 years, refinement of the experimental techniques and use of correction methods have led to data that show more uniform agreement (which is taken as a measure of the quality of the data). However, in spite of these advances, the measurements are still exceedingly difficult, time-consuming, and fraught with pitfalls. As a result, high quality data are limited to just the inert gases and a few small molecules.

We report on a new approach for measuring EI excitation cross sections that obviates many of the instrumental effects that plague other techniques. The present method derives from the combined advantages of (i) supersonic expansion, (ii) pulsed EI ion source, and (iii) multichannel mass detection. These features account for high ion transmission, a large detector field of view, and a relative insensitivity to the usual m/z ratio and kinetic energy discrimination effects. A pulsed electron beam is crossed with the molecular beam in a field-free region, and the ions are subsequently extracted by a pulsed electric field. A calibrated sample containing the target and reference atoms and/or molecules is excited by variable energy electrons, and the resulting ion mass signals are detected simultaneously by a time-of-flight mass spectrometer. In this way, relative cross sections of the target molecule with respect to several reference species serving as internal standards are obtained. The references are chosen on the basis of the quality of known absolute cross sections and nearness in mass to the target molecules. Alternatively, one may derive an effective instrumental excitation curve $I_e(E) n_M l \kappa_{M^+}(E)$ as a function of electron energy E from the measured ion signal intensities $I_{M^+}(E)$ and known cross sections $\sigma_{M^+}(E)$ for a reference species (eq. (1)), thereby allowing direct absolute cross section measurements.

The purpose of this work is to evaluate the utility of this approach with a preliminary demonstration. The energy-dependent cross sections measured here are only as good as the reference data used. Hence, the method is intended to supplement the refined work that provides the necessary data base. However, the present method extends the range of compounds that can be studied, since the supersonic nozzle allows the expansion of condensable and thermally unstable compounds. Furthermore, dissociative ionization can be studied free of the thermal energy content of the neutral precursor. Finally, the measurements are reliable, straightforward, and require very little running time.

2. Experimental

The supersonic molecular beam time-of-flight (TOF) mass spectrometer (MS) consists of differentially pumped source and ionization chambers [7]. A temperature-controlled magnetic solenoid pulsed nozzle [8] in the source chamber is used for the supersonic expansion which enters the ionization chamber through a 1 mm diameter skimmer. Typical expansion conditions are 50 psi He, 500 μm nozzle diameter, 2 cm nozzle–skimmer distance, and 350 μs pulse width. The ambient base pressure in the ionization chamber is typically 3×10^{-8} Torr, rising to about 2×10^{-7} Torr during operation of the pulsed nozzle at 10 Hz.

The pulsed EI ion source for TOF mass spectrometers is based on the design of Pollard and Cohen [9]. The geometry and configuration are diagrammed in fig. 1. Electrons are generated by thermionic emission from a hot tungsten hairpin filament. The voltage applied to the filament V4 determines the electron energy E that impinges on the molecular beam. (The negative side of the filament is tied to a shield can.) The electrons are prevented from exiting the source by grid V3, which is maintained at a lower potential than the filament V4 (using a 30 V Zener diode). An electron beam pulse is admitted to the field-free excitation region by applying a 40 V gate pulse to V3. The electron beam is collimated to

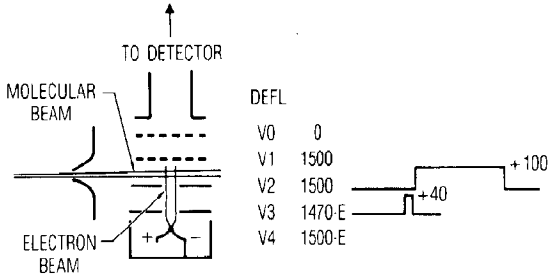

Fig. 1. Geometry and configuration of the crossed electron–supersonic molecular beam, time-of-flight mass spectrometer. The field-free excitation region is defined by the intersection of the molecular and electron beam, which is situated between parallel plate potentials V1 and V2. The electron impact energy E is determined by the difference between the potentials applied to V1 (= V2) and V4. The electron beam is activated by applying a gate pulse to V3; the ions subsequently extracted by applying a pulse to V2. Deflector plates (DEFL) compensate for ion drift resulting from molecular beam velocity.

a diameter of approximately 5 mm by the apertures at V2 and V3. This ensures complete overlap with the molecular beam. The beam divergence is minimized by increasing the ratio of potential differences, (V2−V3)/(V3−V4) (i.e. $E/10$ in the present arrangement).

Electron energies are varied by scanning the voltage applied to plate V3 and filament V4 using a computer-controlled power supply. The excitation region is maintained field free by applying a constant (1500 V) potential to grid V1 and V2. The V2 potential is trimmed to compensate for the V0 ground grid penetrating V1, using a procedure (to be published) that ensures a field gradient across the molecular beam of < 50 mV. The ions formed are then accelerated into the TOFMS by a 100 V repeller pulse applied to V2. The typical timing sequence is 400 ns electron beam pulse, 200 ns delay, and 6 μs repeller pulse.

Ion signals are collected by measuring current versus ion TOF, using a microchannel plate detector. (High repetition-rate ion counting is also possible by using a continuous molecular beam nozzle.) Mass spectra are recorded with a 200 MHz transient digitizer. Relative cross sections are measured by integrating the relevant ion mass signals, using boxcar averages and digitizing the resulting signals via an analog-to-digital computer interface. A data acquisition program allows repetitive scans as well as adjustable dwell times between electron energy increments.

The reference gases that are seeded in the molecular beam are provided from a calibrated gas cylinder (Matheson) containing the five rare gases. (The mole fractions were chosen to give similar ion signals with 70 eV EI excitation.) The molecular beam sample used for this work was prepared by introducing the rare gas reference sample and an ammonia sample into a sample cylinder and back filling to 95% He. The ratio of rare gas to ammonia was carefully measured and was chosen to give comparable ion signals by EI excitation.

3. Results

The ionization cross sections σ for the atom or molecule of interest were obtained by measuring the relative cross section with respect to a well established reference species. From eq. (1), one obtains the relation

$$\sigma_{M^+}(E)=\frac{I_{M^+}n_r}{I_{R^+}n_M}\,\sigma_{R^+}(E), \qquad (2)$$

where the subscript R denotes the reference. Eq. (2) assumes that the instrumental factor κ_{M^+} in eq. (1) does not differ for the target and reference species, a condition we examine in section 4. Since multiple processes can occur by electron excitation (e.g., multiple charge excitation or dissociative ionization), we use partial cross section to denote each individual process and total cross section to denote the sum of these processes [1,3]. It is important to realize that the measured relative cross sections are *not* normalized to previous measurements of the same species (as is commonly done), but to reference species that are different from the molecule of interest. Hence, absolute cross sections for *previously unmeasured* molecules can be obtained.

To demonstrate the ability to measure reliable absolute cross sections, we report on a series of experiments in which the target molecule cross sections are well known. We have likewise measured cross sections with respect to more than one reference species in order to assess the consistency of the results (as well as the consistency of the reference data). For our test case, we have chosen to study singly and doubly charged ionization of rare gas atoms and dissociative ionization of ammonia. We have used as a

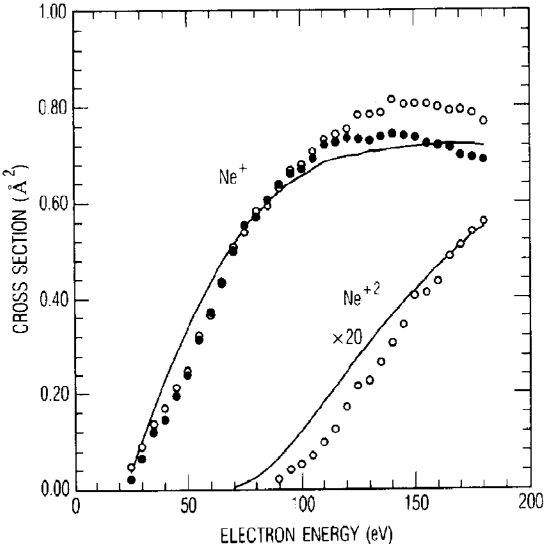

Fig. 2. Electron-excitation cross sections for the processes Ne+e→Ne$^+$+2e and Ne+e→Ne^{2+}+3e, as a function of electron collision energy. Measurements were made relative to reference cross sections for (o) Ar$^+$ and (●) NH$_3^+$. Results of Stephan et al. [10] are represented by (–).

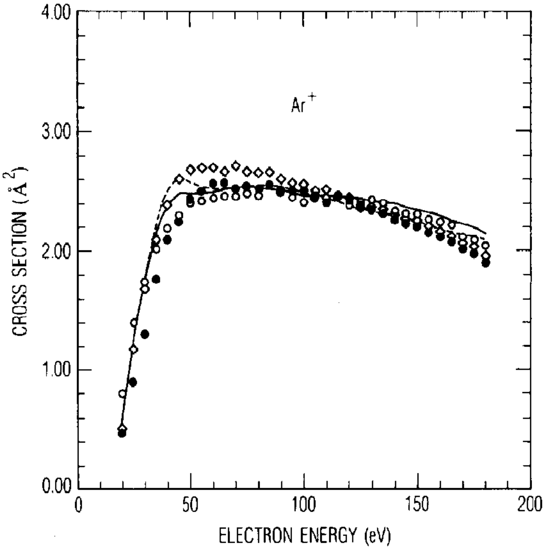

Fig. 3. Electron-excitation cross sections for the process Ar+e→Ar$^+$+2e, as a function of electron collision energy. Measurements were made relative to reference cross sections for (o) Kr$^+$, (●) NH$_3^+$, and (◇) NH$_2^+$. Results of Stephan et al. [10] are represented by (–) and those of Crowe et al. [12] by (– – –).

reference data base, the recent results of Stephan et al. [10] for the rare gases and of Märk et al. [11] for NH$_3$, since these measurements are among the best to date. This is not to exclude other recent measurements which might be equally suitable as reference data [12–16]. Perhaps an average of these results would be more appropriate in the future. The electron energy range reported here is limited by the reference data used (i.e. 180 eV). Otherwise, the energy range by the present method is limited only by the potentials applied to the ion source grids (fig. 1).

The measured absolute partial cross sections for rare gas EI ionization are presented in figs. 2–4 for Ne, Ar, and Kr, respectively. The symbols represent data measured in this work. For comparison, we have included curves representating the data of Stephan et al. [10] and Crowe et al. [12]. It should be understood that the quality of the measured cross sections here can be no better than the reference data used. Since the measured cross sections in this work use the data of Stephan et al. [10] and Märk et al. [11] for the reference as well as for comparison, the discrepancies obtained are a function of the systematic errors of both the current method and that of these workers. The agreement is reasonably good, judging by the discrepancies usually obtained between different studies. These results indicate internal consistency for different gases by both the present

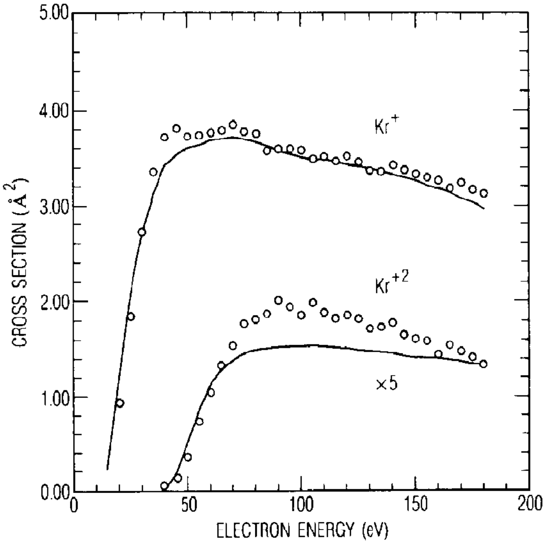

Fig. 4. Electron-excitation cross sections for the processes Kr+e→Kr$^+$+2e and Kr+e→Kr^{2+}+3e, as a function of electron collision energy. Measurements were made relative to reference cross sections for Ar$^+$. Results of Stephan et al. [10] are represented by (–).

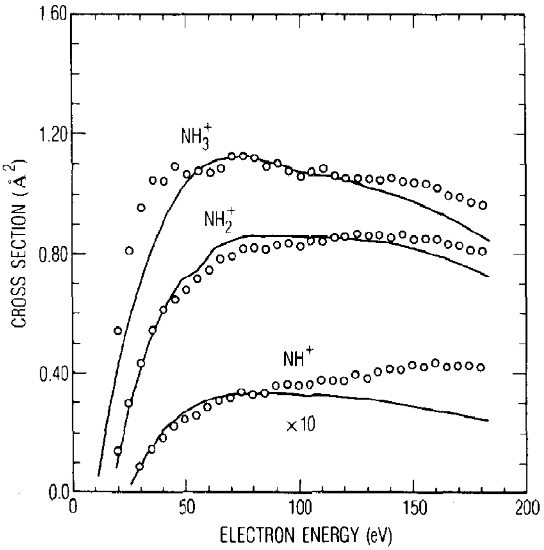

Fig. 5. Electron-excitation cross sections for the processes $NH_3+e\rightarrow NH_3^+ +2e$, $NH_3+e\rightarrow NH_2^+ +H+2e$, and $NH_3+e\rightarrow NH^+ +2H+2e$, as a function of electron collision energy. Measurements were made relative to reference cross sections Ar^+. Results of Mark et al. [11] are represented by (–).

method and that of Stephan et al.

Cross sections for dissociative ionization of NH_3 are presented in fig. 5. Although the absolute cross section scales are in relatively good agreement with the previous results of Märk et al. [11], the energy dependence differs; NH_3^+ exhibiting a low energy enhancement, and the fragments NH_2^+ and NH^+ showing a high energy enhancement. These discrepancies are discussed below.

Perhaps the most important attribute of the present method for measuring absolute EI cross sections is the simplicity and speed at which data can be obtained. By using a pulsed extraction field and then accelerating the ions to high energy (1500 V in this case), unit collection efficiency becomes approachable. The total time required to record each cross section curves (20–180 eV) reported here varied from 10 to 20 min. It was found that adjusting the dwell time between electron energy steps versus total number of scans (to maintain constant total run time) had negligible effect on the results. Likewise, measurements that were repeated, showed excellent reproducibility.

4. Discussion

We classify the major instrumental discrimination factors as those associated with (i) the extraction of ions from the excitation region, (ii) the focusing of the ions into the mass spectrometer, (iii) uniformity and accuracy of the gas density, electron density, and interaction length, and (iv) mass- and energy-dependent detector gain effects. The most common ion sources (e.g. the Nier type) rely on a continuous extraction field to draw the ions out during electron excitation. This arrangement imposes the conflicting requirements for a large field gradient to extract ions completely and a small field gradient to minimize the energy dispersion of the electron beam. A compromise condition is reached by monitoring the ion signals as a function of extraction (or repeller) potential in order to identify the saturation point. The saturation curves, however, vary with the electron energy, ion energy, *m/z* ratio, and the potentials of the focusing electrodes. These many factors conspire to make absolute calibration very difficult.

Recently, Märk et al. [10,11] refined the Nier-type ion source by creating an extraction field via the penetration of an external field through a slit in the upper ion source electrode. They identified conditions for high ion extraction efficiency and showed that the electron energy spread due to the penetrating extraction field is a small fraction of the field gradient itself. Even so, the measurements are very difficult and require extreme care to avoid instrumental discrimination effects. Because absolute calibration of cross sections is still rather difficult, these authors normalized their results by equating the cross section maxima to the absolute measurements of Rapp and Englander-Golden [13].

Our approach toward overcoming the problems associated with the overall transmission efficiency of ions from source to detector is to use a pulsed ion source and large ion acceleration fields. The pulsed ion source allows true field-free excitation, followed by a relatively large extraction field (100 V/cm) to completely remove the ions formed. A subsequent acceleration field (1500 V/cm) minimizes the transit time to the detector, thereby avoiding losses due to initial ion kinetic energy. This is particularly important for dissociative ionization where highly energetic fragment ions can escape the detector field of view in other experimental systems. In the present configuration, the large directed kinetic energy imparted equally to all ion masses by the extraction and acceleration fields makes the energy spread due to dissociation or other sources negligible by comparison (i.e. kinematic compression by maximizing E in the energy distribution $\Delta E/E$). Crowe et al. [12] used a field-free excitation volume, but relied on the ions to drift through two apertures before being accelerated into a quadrupole mass spectrometer. Their results for the process $Ar+e \rightarrow Ar^+ + 2e$ are in excellent agreement with the present work (fig. 3). Other studies have fared less well in uniformity of agreement.

Our measured ion signals were subject to some m/z-dependent effects arising from the use of a deflection field to compensate for the forward velocity of the molecular beam (fig. 1). Although the optimum voltage varies with mass, the deflection field operates over a wide range of masses and is far less constrained than systems that must account for precise focusing through slits and apertures. Hence, the intensity dependence is not severe and is easily correctable by measuring the attenuation of an ion/mass signal versus deflection voltage. The effect of the deflection field also becomes less important as the masses of the target and reference species are more closely matched.

The high extraction and detection efficiency ensures that variations as a function of mass will be minimal, thus supporting the assumption leading to eq. (2) that κ_{M^+} is constant with mass. Mass- and energy-dependent effects are to a large extent eliminated by working with constant energy ions and choosing reference species whose masses are similar to the target species. A potential concern in supersonic expansions is a bias toward heavier masses along the center of the expansion, thereby altering the ratio of target and reference density in the collimated molecular beam from the premixed value. Again, the concern is minimized by choosing constituents of similar mass. Reasonable differences in mass can be tolerated, as evidenced by the similarity of cross section results derived using different reference gases (figs. 2–5).

A greater concern exists in the use of a microchannel plate electron multiplier detector operated in the current integration mode. Recent evidence indicates that the efficiency of secondary electron emission from the impact of an ion can vary with ion mass, energy, and molecular structure [17,18]. Energy effects may be a concern for studying multiply charged ions. For instance, the cross section results for Kr^{2+} are somewhat larger in the present work than that measured by Märk et al. [11] (fig. 4), although this trend is not observed for Ne^{2+} (fig. 2). The role of ion structure and impact fragmentation on detector gain is not well understood. Märk has reported a nearly 20% difference in gain between NH_3^+ and NH^+ for a copper–beryllium-surfaced 16-dynode electron multiplier. Significant differences, however, were not obvious in our results (fig. 5) using a microchannel plate detector, which is a continuous channel rather than a discrete dynode multiplier. Further examination of the detector gain discrimination effects is warranted. Likewise, ion counting rather than current integration will be considered as a means for compensating for detector gain discrimination effects.

Although we have obtained very good agreement with previous results for the rare gases, the present method should find its greatest utility in studies involving dissociative ionization. Previous methods that use weak extraction fields are susceptible to losses due to highly energetic fragment ions. This may partly explain the discrepancy between the present versus previous measurements [11] of the partial cross section measurements for NH_2^+ and NH^+ fragment ions at increasing electron energies (cf. fig. 5). It is also possible, however, that the time scales for mass detection are sufficiently different that metastable decay may change the cross section energy dependence with time. We are exploring this possibility by recording fragment ion signals as a function of extraction field delay time (to be published). Finally, it is intriguing to consider whether rovibrationally cold ammonia prepared in the supersonic expansion could exhibit different behavior than a room temperature sample. For instance, the thermal energy that is maintained in the ionization process could promote dissociation, thereby giving smaller fragment cross sections. As an example, significant parent ion signals were observed for organophosphonate molecules prepared in a supersonic molecular beam (unpublished), that were reported to be absent in thermal samples under similar 70 eV ionization conditions [19].

5. Conclusion

We have presented a method for obtaining reliable electron excitation cross sections for singly and multiply charged ionization and dissociative ionization using an approach that benefits from (i) supersonic expansion, (ii) pulsed ion source, and (iii) multichannel mass detection. In view of the extreme difficulties and many shortcomings in obtaining absolute cross sections by other methods, the present approach provides a simple, straightforward, and rapid means for obtaining absolute partial cross sections that are relatively free of m/z ratio and kinetic energy discrimination effects.

The present work represents the initial attempt at applying supersonic molecular beam techniques to the study of electron excitation processes. A number of simple modifications are being considered to further improve the accuracy of cross section measurements. For instance, an einzel focusing ion lens will be examined as a better solution than the present deflector plate arrangement for obtaining a uniform detector field of view that is insensitive to m/z ratio. Likewise, ion counting detection will be examined by operating the pulsed ion source at high repetition rates ($\geqslant$20 kHz; limited by the TOF of the largest ion mass [9]) in a continuous molecular beam.

As larger molecules become the focus of electron excitation studies, the supersonic molecular beam technique will ultimately prove essential. The internal energy content of thermal molecules increases with molecular size, eventually becoming the limiting factor for energy resolution. This energy is effectively removed in a supersonic expansion. A supersonic molecular beam nozzle can also accommodate a wider range of compounds, enabling the study of condensable materials, thermally unstable compounds, and molecular clusters.

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