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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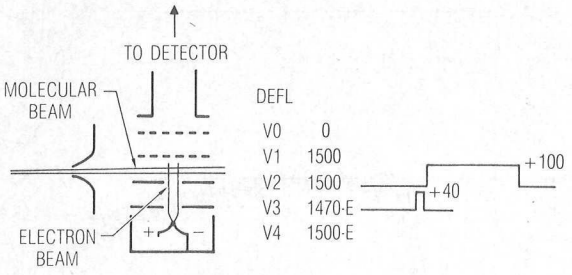

Fig. 1. Geometry and configuration of the crossed electron–supersonic molecular beam, time-of-flight mass spectrometer. The field-free excitation region is defined by the intersection of the molecular and electron beam, which is situated between parallel plate potentials V1 and V2. The electron impact 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

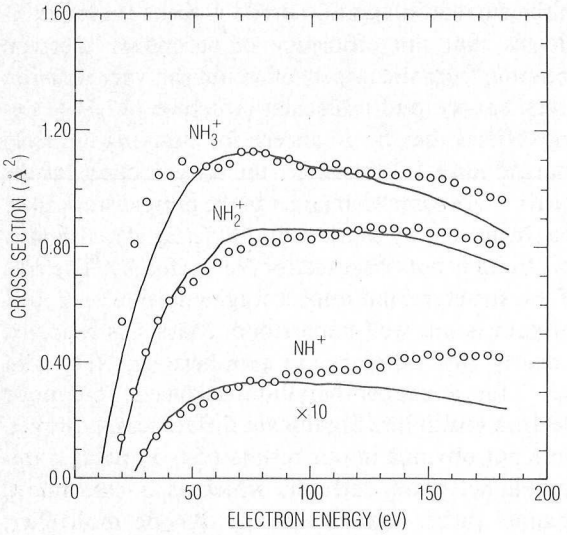

Fig. 5. Electron-excitation cross sections for the processes $NH_3+e\rightarrow NH_3^+ +2e$, $NH_3+e\rightarrow NH_2^+ +H+2e$, and $NH_3+e\rightarrow NH^+ +2H+2e$, as a function of electron collision energy. Measurements were made relative to reference cross sections Ar^+. Results of Mark et al. [11]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

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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References

[1] T.D. Märk and G.H. Dunn, eds., Electron impact ionization (Springer, Berlin, 1985).
[2] E. Weingold and I.E. McCarthy, in: Advances in atomic and molecular physics, Vol. 14, eds. D.R. Bates and B. Benderson (Academic Press, New York, 1978);
M. Inokuti, Y. Itikawa and J.E. Turner, Rev. Mod. Phys. 50 (1978) 23.
[3] T.D. Märk, in: Electron–molecule interactions and their applications, ed. L.G. Christophorou (Academic Press, New York, 1984) ch. 3.
[4] A.O. Nier, Rev. Sci. Instr. 11 (1940) 212; 18 (1947) 398.
[5] T.D. Märk, Intern. J. Mass Spectrom. Ion Phys. 45 (1982) 125.
[6] L.J. Kieffer and G.H. Dunn, Rev. Mod. Phys. 38 (1966) 1.
[7] J.A. Syage, J.E. Pollard and R.B. Cohen, Appl. Opt. 26 (1987), to be published.
[8] J.A. Syage, P.M. Felker and A.H. Zewail, J. Chem. Phys. 81 (1984) 2233;
B.W. Keelan, J.A. Syage, J.F. Shepanski and A.H. Zewail, International Conference Proceedings of Laser 83 (STS Press, McLean, 1985) p. 718.
[9] J.E. Pollard and R.B. Cohen, Rev. Sci. Instr. 58 (1987) 32.
[10] K. Stephan, H. Helm and T.D. Märk, J. Chem. Phys. 73 (1980) 3763.
[11] T.D. Märk, F. Egger and M. Cheret, J. Chem. Phys. 67 (1977) 3795.
[12] A. Crowe, J.A. Preston and J.W. McConkey, J. Chem. Phys. 57 (1972) 1620.
[13] D. Rapp and P. Englander-Golden, J. Chem. Phys. 43 (1965) 1464.
[14] R.C. Wetzel, F.A. Baiocchi, T.R. Hayes and R.S. Freund, Phys. Rev. A 35 (1987) 559.
[15] D. Mathur and C. Badrinathan, Intern. J. Mass Spectrom. Ion Processes 57 (1984) 167;
P. Nagy, A. Skutlartz and V. Schmidt, J. Phys. B13 (1980) 1249.
[16] A. Crowe and J.W. McConkey, Intern. J. Mass Spectrom. Ion Phys. 24 (1977) 181.
[17] C. LaLau, in: Advances in analytical chemistry and instrumentation, Vol. 8, ed. A.L. Burlingame (Wiley, New York, 1970) p. 93;
C.N. Burrous, A.J. Lieber and V.T. Zaviantseff, Rev. Sci. Instr. 38 (1967) 1477.
[18] T.D. Märk, Z. Naturforsch. 32a (1977) 1559.
[19] S. Sass and T.L. Fisher, Org. Mass. Spectrom. 14 (1979) 257.