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Ionization of NF_3 by electron impact

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Abstract

The ionization and dissociative ionization of NF_3 by electron impact has been measured by Fourier transform mass spectrometry (FTMS). The total ionization cross-section rises to a maximum value of $2.4 \pm 0.4 \times 10^{-16}$ cm^2 at 140 eV. Estimates of the total single ionization cross-section using ab initio energies with the binary encounter Bethe (BEB) [Y.K. Kim, M.E. Rudd, Phys. Rev. A 50 (1994) 3594] or Deutsch–Märk [Int. J. Mass Spec. 197 (2000) 37] models are roughly twice the measured values. The partial cross-sections creating NF_x^+ ($x = 0, 1, 2, 3$), F^+, and NF_x^{2+} ($x = 1, 2, 3$) are reported. Differences between the FTMS results and quadrupole data and fast atom beam results of Tarnovsky et al. [Int. J. Mass Spectrom. Ion Processes 133 (1994) 175] are discussed. © 2001 Published by Elsevier Science B.V.

1. Introduction

Nitrogen trifluoride (NF_3) provides efficient in situ plasma etching and thermal cleaning of semiconductors and liquid crystal display panels. Its advantages over fluorocarbon based compositions include higher etch rates for equivalent plasma power densities, better etch selectivity, minimal residual contamination, and negligible global warming potential [4]. This etch precursor is produced in large quantities; demand for NF_3 in Japan increased to 150 tons in 1999 and was expected to double in 2000 [5]; BOC Edwards has launched construction of a facility to produce 250 000 kg/year in Pelindaba, South Africa [6]. NF_3 is also used as an oxidizer in high power HF and DF chemical lasers, [7] and as a reagent for chemically reactive interface mass spectrometry [8]. Naturally occuring NF_3 has recently been identified in fluorites and metamorphic rocks [9].

The dissociative ionization of this small molecule is also interesting as support for tests of quantum mechanical constraints on the partitioning among fragments in ionization processes [10]. Electron impact ionization of NF_3 has been studied with magnetic sector, quadrupole, and fast atomic beam techniques by Tarnovsky et al. [3]. The cross-section for production of the parent NF_3^+ ion was quantified, as were values for generation of NF^+, and NF_2^+. Upper bounds were placed on the yields of N^+, and F^+.

In this Letter, we extend the dynamic range of prior work on partial ionization of NF_3 to quantify the partitioning among fragments and to identify dication formation processes. Another strong motivation for the present experimental study is the apparent overestimation of the single ionization cross-sections based on ab initio electronic structure calculations and the binary

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encounter Bethe (BEB) model of Kim and Rudd [1].

2. Experiment

Nitrogen trifluoride NF_3 (Scott Specialty Gases, 99%) was mixed with argon (99.999%, Matheson Research Grade) and admitted through a precision leak valve into a modified Fourier transform mass spectrometry (FTMS) system that has been described in detail elsewhere [11,12]. No impurities other than very small traces of water vapor were identified in the mass spectrum. Ions are formed by electron impact in a cubic ion cyclotron resonance (ICR) trap cell at pressures in the 10^{-7} Torr range. An electron gun (Kimball Physics ELG-2, Wilton, NH) located 2 m from the trap irradiates the gas with a short (2–6 ms) pulse having a few hundred picocoulombs of low-energy electrons. The motions of ions produced by electron impact are constrained radially by a superconducting solenoidal magnetic field ($\approx$2 T) and axially by a nominal electrostatic trapping potential (1–2 V) applied to the trap faces that are perpendicular to the magnetic field. Ions of all mass to charge ratios are simultaneously and coherently excited into cyclotron orbits using a stored voltage waveform [13]. The image currents induced on the two remaining trap faces are then digitized and Fourier analyzed to yield a mass spectrum.

Calculation of the cross-section from the mass spectral intensities requires knowledge of the gas pressure, the electron beam current, and the number of ions produced. It is particularly important that the measurements are made during a time that is short enough to preclude perturbation of the species' distribution by charge transfer reactions. These calibration issues have been discussed elsewhere. [11,12] In the measurements reported here we calibrate the cross-sections using ratios of the ion signals to those of Argon, whose cross-section is known to $\pm$12% from the crossed-beam measurements of Wetzel et al. [14].

The distribution of electron energies in the ion trap, based on the solution of Laplace's equation for the experimental geometry, is roughly Gaussian with a full-width-at-half-maximum of 0.5 eV due to the electrostatic trapping bias. The mean energy is accurate to $\pm$0.2 eV based on comparison of noble gas ionization thresholds with spectroscopic data.

It is important to note that the ions are not actually collected in the FTMS experiment; only their electromagnetic influence on the antenna is recorded. As a result, the spectrometer sensitivity *is neither mass nor species dependent* for the results described here. We estimate the accuracy in the partitioning among ionic channels relative to argon to be $\pm$4%. Combined with the precision of the crossed-beam measurements on argon, $\pm$12% [14], we estimate the magnitude of the of the cross-sections presented here to be accurate within $\pm$16%.

3. Results and discussion

Five singly charged ions, N^+, F^+, NF_x^+ ($x = 1, 2, 3$) as well as three dications, NF_x^{2+}, ($x = 1, 2, 3$) were observed to form with cross-sections exceeding 10^{-20} cm^2 below 200 eV. The high mass resolution of FTMS was particularly useful in distinguishing the contributions of F^+ and H_3O^+ at a nominal mass of 19 amu, as illustrated in

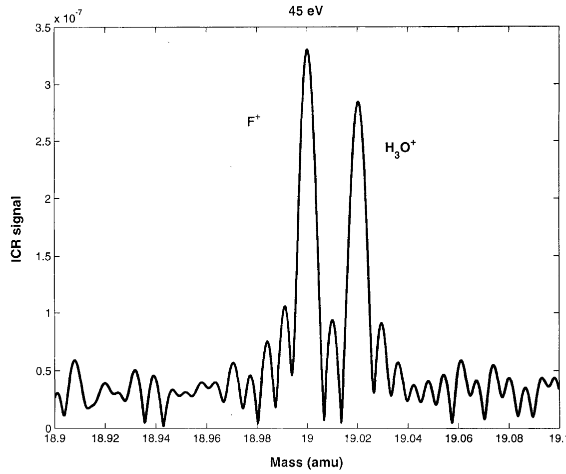

Fig. 1. Fourier transform mass spectrum of NF_3 at 45 eV allows discernment of ion signals between dissociative ionization product F^+ and H_3O^+ that is produced from the very fast protonation of background water vapor.

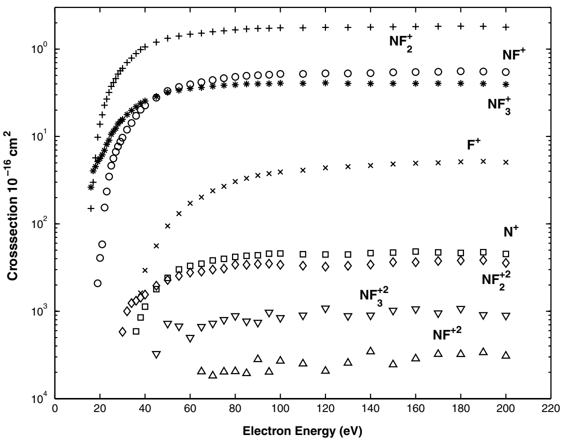

Fig. 2. Partial ionization cross-sections for electron impact on NF_3 from threshold to 200 eV. (+) NF_2^+; (○) NF^+; (∗) NF_3^+; (×) F^+; (□) N^+; (◇) NF_2^{2+}; (▽) NF_3^{2+}; (△) NF^{2+}.

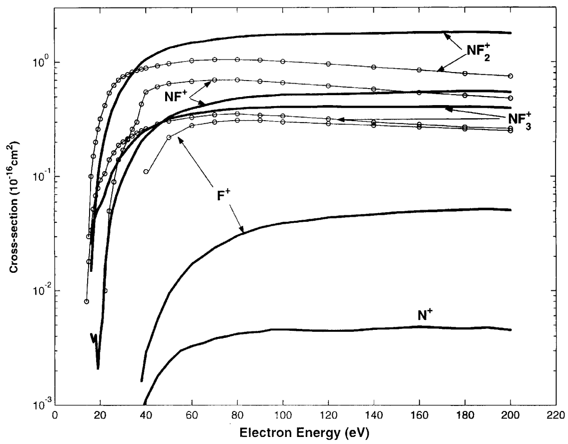

Fig. 3. Comparison of partial ionization cross-sections for production of singly charged fragments from the fast atom beam method of [3] (○) and FTMS (solid lines).

Fig. 1. Experimental results for each of the eight ionized products are shown in Fig. 2.

Ionization of NF_3 has been reported using fast atom beam, magnetic sector, and quadrupole instruments by Tarnovsky et al. [3]. These measurements were calibrated, as were the present results, with reference to the crossed-beam determinations of argon ionization by Wetzel et al. [14]. The cross-sections for production of the parent NF_3^+ ion and the total ionization cross-section are in excellent agreement among the various methods. There are differences, however, in the partitioning among dissociatively ionized fragment channels as can be seen in Table 1 for 70 eV electron impact and more generally in Fig. 3. One way to rationalize these differences is to consider the internal energy of molecules that comprise the fast atom beam. NF_3 is ionized in a Colutron ion source and the NF_3^+ ions are accelerated to several keV, then neutralized by charge transfer from Xe. Internal vibrational [15] or electronic [16] excitation in the collisionally neutralized molecule may play a role in the enhanced fragmentation observed in the beam experiments.

The dynamic range of the FTMS experiments reveal cross-sections for N^+ and F^+ shown in Fig. 2, and are consistent with the upper bounds of 0.1 and 0.3×10^{-16} cm^2 reported by Tarnovsky et al. The yield for the doubly charged ions is small, with the ordering among NF_x^{2+} yields different than that for the corresponding monocations.

The total single ionization cross-section can be calculated using the BEB model [1]. Briefly, this model sums contributions to the cross-section σ using ab initio estimates of the molecular orbital occupation numbers N, binding energies B, orbital U, and incident T kinetic energies according to the formula:

Table 1
Comparison of partial ionization cross-sections from FTMS, fast atom beam, quadrupole, and magnetic sector techniques ([3]) following 70 eV electron impact

Species	FTMS	Error	Beam	Error	Quadrupole	Error	Sector
NF_3^+	0.38	±0.06	0.347	±0.03	0.35	±0.03	0.348
NF_2^+	1.58	±0.25	1.05	±0.20	1.03	±0.05	
NF^+	0.44	±0.07	0.70	±0.15	0.49	±0.04	
N^+	0.024	±0.004	<0.3		0.33	±0.05	
F^+	0.004	±0.0006	<0.1		0.09	±0.01	

$$\sigma_{\mathrm{BEB}} = \frac{S}{t+u+1}\left[\frac{Q\ln t}{2}\left(1-\frac{1}{t^2}\right) + (2-Q)\left(1-\frac{1}{t}-\frac{\ln t}{t+1}\right)\right],$$

where

$$t = \frac{T}{B}, \quad u = \frac{U}{B}, \quad S = 4\pi a_0^2 NR^2/B^2,$$

a_0 is the Bohr radius, R is the Rydberg constant, and Q is a weighted integral of the target's continuum dipole oscillator strength that is routinely set equal to unity in the BEB method.

Fig. 4 shows the results of BEB cross-section estimates using orbital binding and kinetic energies computed by Winstead from ab initio theory at the RHF/6-311 + G(2d) level of theory [17]. This overestimation is retained when the experimental ionization potential is used with uncorrelated wavefunctions at a similar level of theory [18]. The Deutsch–Märk formalism also overestimates the magnitude of the total single ionization cross-section by a factor of ≈ 2; similar discrepancies between theoretical and experimental values were reported for NF_x and CF_x ionization [2]. Huo has recently reported cross-sections based on the binary encounter dipole method [1] using a shielded dipole potential and correlated wavefunctions for the first four ionization potentials [19]. The results of these calculations are in much better agreement with the present experimental results than those of either the BEB or DM approach; one hopes that this new theoretical approach will reconcile the gap between other computed and measured ionization cross-sections.

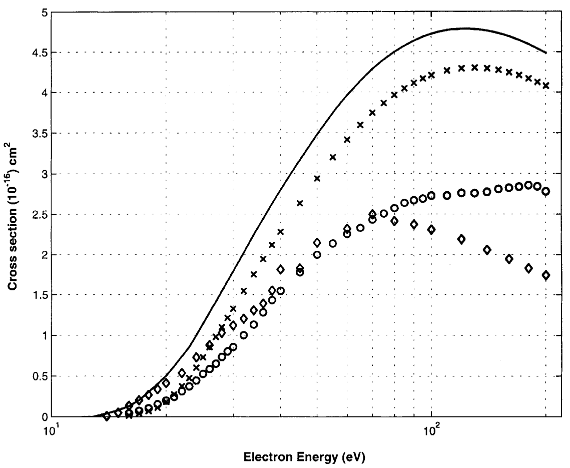

Fig. 4. BEB estimates of single ionization cross-sections using RHF/6-311 + G(2d) wavefunctions (×) [17], correlated wavefunctions and the BED model according to Huo [18] (solid line), FTMS data including contributions from dications (○), and experimental results of Tarnovsky et al. (◇).

The FTMS results in Fig. 4 shows little variation of the total single ionization cross-section between 100 and 200 eV. By comparison, the results of Tarnovsky et al. [3] reach a maximum at 70 eV and then decline by 30% as the energy increases to 200 eV. Confidence in the present results is enhanced by independent calibration of the measured signal against the known argon ionization cross-section at each electron energy, under which condition the negligible $d\sigma/d\epsilon$ above 100 eV is confirmed.

NF_3 displays the intriguing characteristic that, with the exception of F_2^+, all possible ion fragments are observed. Similar results have been reported for isovalent NH_3 [20]. The parent NH_3^+ ion is formed with a low threshold, but yields of more extensively dissociated NH^+ and NH_2^+ are higher above 80 eV. The proportion of atomic H^+ and N^+ are lower than that of the parent ion, and one doubly charged ion is reported. Quantitative comparison of the thresholds and cross-sections for ammonia and nitrogen trifluoride displays different ordering, but the only qualitative differences in the spectra are the formation of diatomic H_2^+ and the absence of NH_x^{2+} ($x = 1, 2$) from the ammonia spectra. The electronic structures of NF_x and NF_x^+ have been extensively studied, primarily with a view to establishing the thermodynamic properties of various ion and neutral species [21–23]. The ground electronic state is orbitally nondegenerate, so that no Jahn–Teller distortion from C_{3v} symmetry is predicted, although the lowest energy conformation is predicted to have a larger dihedral angle than that of neutral NF_3 [17]. Closer examination of the potential energy of the NF_3^+ ion potential energy surfaces may, on comparison with those for NH_3^+, provide insight into quantum constraints on the fragmentation patterns of these small molecular ions.

4. Conclusions

The cross-sections for ionization of nitrogen trifluoride by electron impact have been measured from threshold to 200 eV by FTMS. The cross-section for production of NF_3^+ ($0.38 \pm 0.06 \times 10^{-16}$ cm^2) and the total cross-section ($2.4 \pm 0.4 \times 10^{-16}$ cm^2) are in excellent agreement with earlier measurements. The yield of less extensively dissociated NF_2^+ is found to be higher than previously reported, and full cross-sections for N^+ and F^+ are reported. Three dications, NF_x^{2+} ($x = 1$, 2, 3), are also observed to form with cross-sections of (2.7, 34, and 8.4×10^{-20} cm^2), respectively, at 100 eV. The BEB and Deutsch–Märk models overestimate the total single ionization cross-section by a factor of about 2. It is suggested that comparison of the fragmentation patterns for ammonia and nitrogen trifluoride may provide insight into quantum constraints on dissociative ionization.

Acknowledgements

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