Electron-impact ionization of NH_3 and ND_3

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Absolute partial and total cross sections for electron-impact ionization of NH_3 and ND_3 are reported for electron energies from threshold to 1000 eV. The product ions are mass analyzed using a time-of-flight mass spectrometer and detected with a position-sensitive detector whose output demonstrates that all product ion species are collected with equal efficiency irrespective of their initial kinetic energies. Data are presented for the production of $(NH_3^+ + NH_2^+ + NH^+ + N^+)$, H^+, H_2^+, and NH_3^{2+} from NH_3 and for production of ND_3^+, ND_2^+, ND^+, N^+, D^+, D_2^+, and ND_3^{2+} from ND_3 and for the total cross sections which are obtained as the sum of these partial cross sections. Data are also presented for formation of (ND^+,D^+) and (N^+,D^+) ion pairs. The overall uncertainty in the absolute cross sections for most of the singly charged ions is $\pm 6-8\%$ while that for doubly charged ions is $\pm 20\%$. It is observed that the isotopic composition of the ammonia target has no discernible effect upon the cross sections and that the partial cross sections for many of the lighter ions are much larger than had been previously reported. [DOI: 10.1063/1.1394748]

I. INTRODUCTION

Accurate electron-impact ionization data for molecular targets are necessary for understanding the physics of a vast range of environments, and for the development of quantitative theoretical descriptions of these fundamental processes. In this paper, which is one in a series from this laboratory, cross sections for electron-impact ionization of NH_3 and ND_3 are presented. Ammonia has already been investigated fairly extensively although there is little consensus as to the actual values of most of the cross sections. The reliability of the earliest measurements[1] is questionable, some of the more recent data have been normalized to theoretical calculations,[2] and it is not possible to adequately assign uncertainties to yet other studies.[3,4] Furthermore, there are large discrepancies between the partial cross sections from even the most recent experimental work.[5–8] Quite a few calculations of the NH_3 total cross section have also been reported,[9–14] together with one calculation of the partial cross sections.[12]

This study was undertaken in an effort to resolve these discrepancies and absolute partial cross sections are reported here for production of $(NH_3^+ + NH_2^+ + NH^+ + N^+)$, H^+, H_2^+, and NH_3^{2+} from NH_3 and for production of ND_3^+, ND_2^+, ND^+, N^+, D^+, D_2^+, and ND_3^{2+} from ND_3 for electron energies from threshold to 1000 eV. Only the sum of the NH_3^+, NH_2^+, NH^+, and N^+ cross sections is given since these ions could not be fully resolved by the mass spectrometer. The total ionization cross sections are obtained as the sum of the measured partial cross sections. During the course of this work it was determined that electron-impact ionization of ND_3 may result in production of positive ion pairs and the cross sections for ionization via two of these channels are also reported.

II. APPARATUS AND EXPERIMENTAL METHOD

The apparatus, which is shown in Fig. 1, consists of an electron gun, a time-of-flight mass spectrometer with a position-sensitive detector (PSD), and an absolute capacitance diaphragm pressure gauge (not shown). It has been described in detail previously.[15] Briefly, during a cross-

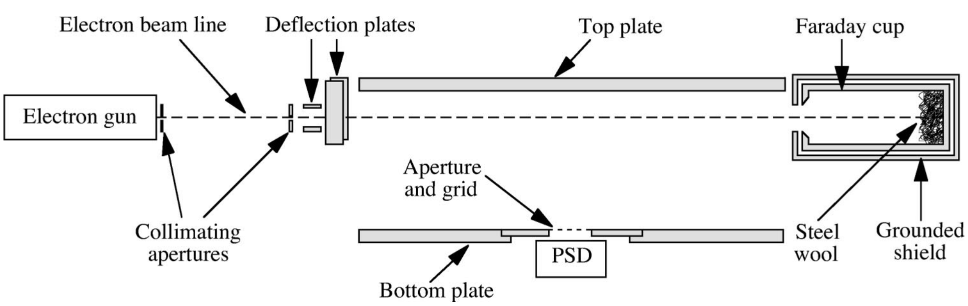

FIG. 1. Schematic diagram of the apparatus.

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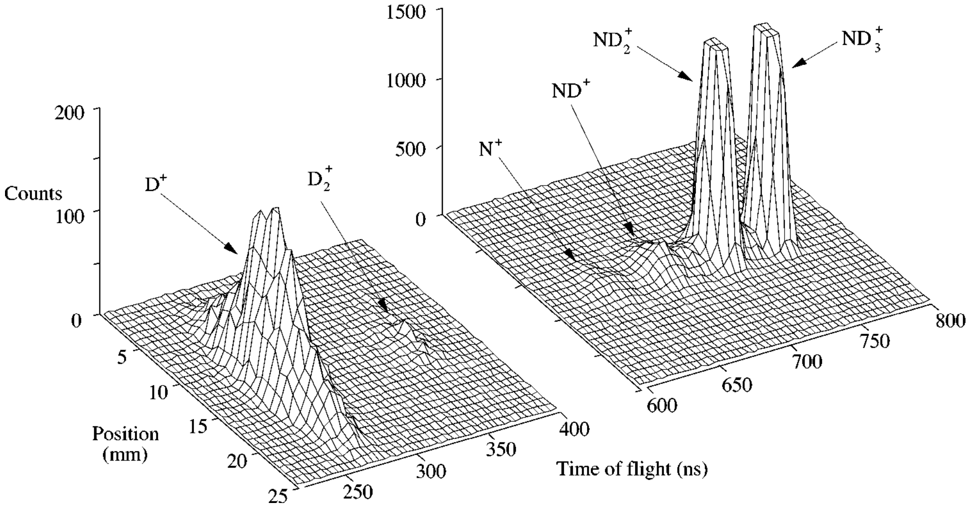

FIG. 2. Position and time-of-flight distribution of ions produced by 100 eV electron impact on ND_3. The position axis indicates the displacement of the ions perpendicular to the axis of the electron beam.

section measurement the entire vacuum chamber is filled with NH_3 or ND_3 at a pressure of 4×10^{-6} Torr. The electron gun produces 20-ns-long pulses at a repetition rate of approximately 10 kHz. These pulses are directed through an interaction region, located between two plates maintained at ground potential, and are collected in a Faraday cup. Approximately 250 ns after each electron pulse, a 3 kV pulse is applied to the top plate to drive any positive ions formed by electron impact toward the bottom plate. Some ions pass through a grid-covered aperture in the bottom plate. These ions are then accelerated and subsequently impact a PSD,[16] which records their arrival times and positions. The ion arrival times are used to identify their mass-to-charge ratios and the ion arrival positions are used to determine the effectiveness of product ion collection. Under conditions in which very few of the incident electrons produce an ion, the partial cross section $\sigma(X)$ for production of ion species X is given by

$$\sigma(X)=\frac{N_i(X)}{N_e n l}, \tag{1}$$

where $N_i(X)$ is the number of X ions produced by a number N_e of electrons passing a distance l through a uniform gas target of number density n.[17] $\sigma(X)$ is then determined by measuring the four quantities on the right-hand side of Eq. (1).[15] Technical details concerning the PSD detection efficiency calibration and use of the capacitance diaphragm gauge may be found in Straub *et al.*[18] and Straub *et al.*,[19] respectively. Note that determination of the absolute gas pressure is more difficult for ammonia than for most other gases used in previous work with this apparatus (due to the relatively long time required for the ammonia pressure reading to reach equilibrium[20]). Consequently, the uncertainties in the present cross sections are very slightly larger than those for our other recent measurements.[21,22]

During the course of this work it was determined that electron-impact ionization of ND_3 may result in production of positive ion pairs via

$$e+ND_3\rightarrow ND^+ + D^+ + \cdots \tag{2}$$

$$e+ND_3\rightarrow N^+ + D^+ + \cdots . \tag{3}$$

Cross sections for production of (ND^+,D^+) and (N^+,D^+) ion pairs were obtained by utilizing a gating procedure which has been described fully by Sieglaff *et al.*[21] It was not feasible to accurately measure the corresponding NH_3 pair production cross sections using this technique because of the limited resolution of the mass spectrometer.

Figure 2 shows a plot for ND_3 in which the product ions' transverse arrival positions at the PSD (i.e., the displacement

TABLE I. Absolute partial ionization cross sections for electron-impact ionization of NH_3. The uncertainties in the $(NH_3^+ + NH_3^+ + NH^+ + N^+)$, H^+, H_2^+, and NH_3^{2+} cross sections are ±6%, ±6%, ±8%, and ±20%, respectively, unless otherwise indicated.

Energy (eV)	$\sigma(NH_n^+)$ (10^{-16} cm^2)	$\sigma(H^+)$ (10^{-17} cm^2)	$\sigma(H_2^+)$ (10^{-18} cm^2)	$\sigma(NH_3^{2+})$ (10^{-19} cm^2)
11.5	0.080±0.010			
12.5	0.162±0.016			
13.5	0.216±0.019			
15	0.331±0.026			
17.5	0.628±0.044			
20	0.946			
22.5	1.20			
25	1.42			
27.5	1.66	0.065±0.007		
30	1.80	0.189	0.20±0.07	
35	2.10	0.573	0.438	
40	2.37	1.09	0.636	
50	2.61	1.93	0.839	0.42±0.21
60	2.75	2.65	0.997	0.79±0.20
70	2.79	3.17	1.06	0.95
80	2.81	3.56	1.07	1.08
90	2.81	3.75	1.08	1.02
100	2.79	3.85	1.08	1.25
120	2.67	3.83	1.01	1.25
140	2.55	3.74	0.969	1.44
160	2.44	3.55	0.844	1.35
200	2.26	3.17	0.756	1.15
250	2.06	2.83	0.668	0.75
300	1.86	2.37	0.560	0.67
400	1.56	1.84	0.405	0.67
500	1.39	1.49	0.363	0.53
600	1.21	1.28	0.293	0.48
800	0.990	0.964	0.240	0.46
1000	0.864	0.810	0.217	0.36

TABLE II. Absolute partial ionization cross sections for electron-impact ionization of ND_3. The uncertainties in the ND_3^+, ND_2^+, ND^+, N^+, D^+, D_2^+, and ND_3^{2+} cross sections are ±6%, ±6%, ±12%, ±8%, ±6%, ±8%, and ±20%, respectively, unless otherwise indicated.

Energy (eV)	$\sigma(ND_3^+)$ (10^{-16} cm^2)	$\sigma(ND_2^+)$ (10^{-16} cm^2)	$\sigma(ND^+)$ (10^{-17} cm^2)	$\sigma(N^+)$ (10^{-18} cm^2)	$\sigma(D^+)$ (10^{-17} cm^2)	$\sigma(D_2^+)$ (10^{-18} cm^2)	$\sigma(ND_3^{2+})$ (10^{-19} cm^2)
11.5	0.065±0.007						
12.5	0.159±0.013						
13.5	0.202±0.014						
15	0.344	0.0012±0.0006					
17.5	0.579	0.0253±0.0021					
20	0.725	0.185					
22.5	0.832	0.325					
25	0.965	0.486	0.0492				
27.5	1.03	0.604	0.102		0.063±0.012		
30	1.06	0.735	0.322	0.41±0.07	0.190	0.14±0.05	
35	1.16	0.891	0.635	0.88±0.08	0.574	0.378	
40	1.23	0.996	0.886	1.68	1.10	0.687	
50	1.30	1.12	1.28	2.97	1.94	0.891	0.43±0.22
60	1.31	1.21	1.48	3.87	2.61	1.02	0.68±0.17
70	1.33	1.23	1.57	4.73	3.15	1.07	0.94
80	1.32	1.24	1.62	5.42	3.56	1.13	0.94
90	1.30	1.25	1.65	5.70	3.71	1.10	1.06
100	1.28	1.24	1.66	5.90	3.83	1.10	1.24
120	1.23	1.22	1.63	6.07	3.86	1.04	1.24
140	1.16	1.18	1.56	6.07	3.78	0.962	1.33
160	1.10	1.12	1.47	5.94	3.60	0.820	1.18
200	1.01	1.05	1.28	5.26	3.21	0.704	1.03
250	0.922	0.961	1.11	4.43	2.77	0.604	0.93
300	0.838	0.887	0.971	3.84	2.40	0.505	0.79
400	0.722	0.751	0.752	2.76	1.89	0.413	0.63
500	0.614	0.657	0.645	2.33	1.52	0.349	0.61
600	0.550	0.586	0.557	1.85	1.30	0.296	0.58
800	0.438	0.475	0.431	1.38	0.996	0.238	0.37
1000	0.390	0.401	0.371	1.15	0.806	0.206	0.30

of the ions perpendicular to the electron beam axis) have been combined with their flight times. The widths in both position and time of the various ion peaks are due to the ions' initial velocities perpendicular to the electron beam in addition to the transverse spatial extent of the electron beam itself. The width of the ND_3^+ peak is due primarily to the spatial extent of the electron beam, but the widths of the lightest ion peaks are determined largely by the energies with which these ions are formed. Figure 2 clearly shows that even the most energetic ions are collected.

The absolute uncertainties in the ($NH_3^+ + NH_2^+ + NH^+ + N^+$), H^+, H_2^+, and NH_3^{2+} partial cross sections are ±6%, ±6%, ±8%, and ±20%, respectively. The uncertainties in the ND_3^+, ND_2^+, ND^+, N^+, D^+, D_2^+, and ND_3^{2+} cross sections are ±6%, ±6%, ±12%, ±8%, ±6%, ±8%, and ±20%, respectively. Although the statistical accuracy of the ND^+ and N^+ measurements is high, the accuracy of these cross sections is compromised by slight overlaps between adjacent peaks in the time-of-flight spectra. The uncertainties in the (ND^+,D^+) and (N^+,D^+) ion pair production cross sections are due primarily to counting statistics and are ±15% and ±20%, respectively. Near the threshold for formation of each species the uncertainties in the cross sections are of course greater and are given in the tables. The mean energy of the electron beam was established to within ±0.5 eV by observing the threshold for He^+ formation in the presence of the NH_3 target gas.

III. RESULTS AND DISCUSSION

The measured partial cross sections for NH_3 and ND_3 are listed in Tables I and II. All of the measured NH_3 cross sections were found to be essentially identical to those for ND_3. The level of agreement observed here is demonstrated in Fig. 3, which shows a comparison of the cross sections for production of ($NH_3^+ + NH_2^+ + NH^+ + N^+$) and H^+ from NH_3 to the cross sections for production of ($ND_3^+ + ND_2^+ + ND^+ + N^+$) and D^+ from ND_3. Clearly the

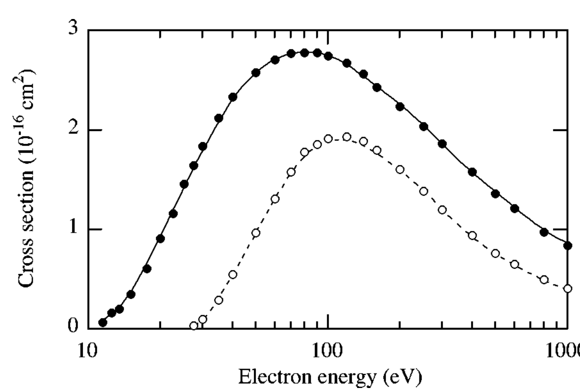

FIG. 3. Comparison of the present ND_3 and NH_3 partial cross sections: ($ND_3^+ + ND_2^+ + ND^+ + N^+$) from ND_3 (●); ($NH_3^+ + NH_2^+ + NH^+ + N^+$) from NH_3 (—); D^+ from ND_3 (○); H^+ from NH_3 (---). Note that the D^+ and H^+ data have been multiplied by 5.

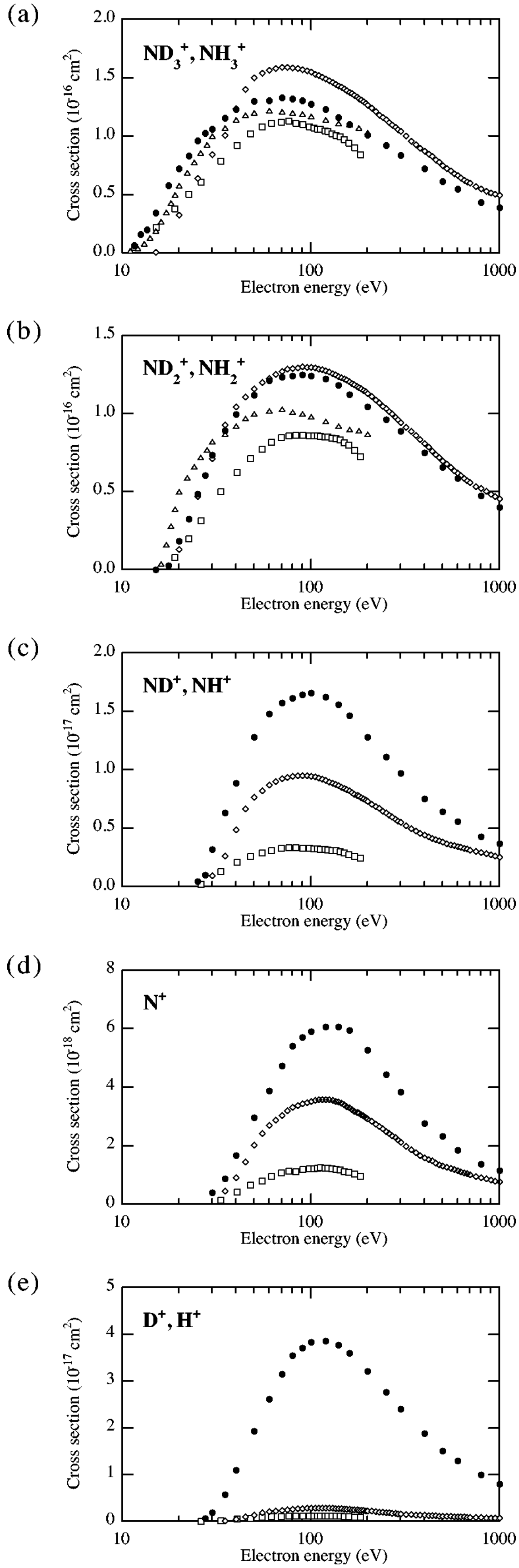

FIG. 4. Present ND_3^+, ND_2^+, ND^+, N^+, and D^+ cross sections (●) together with the NH_3 data of Mark *et al.* (□); the NH_3 data of Rao and Srivastava (◇); and the ND_3 data of Tarnovsky *et al.* (△).

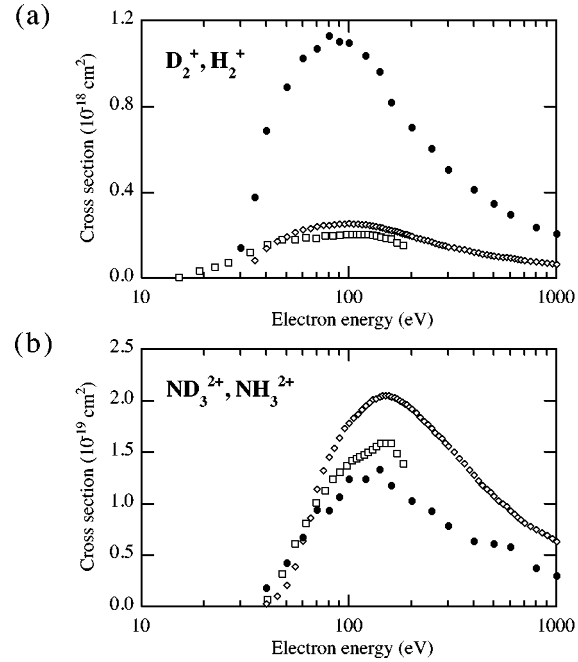

FIG. 5. Present D_2^+ and ND_3^{2+} cross sections (●) together with the NH_3 data of Mark *et al.* (□); and the NH_3 data of Rao and Srivastava (◇).

isotopic composition of the ammonia target has no measurable effect upon the electron-impact ionization cross sections and therefore the cross sections for production of NH_3^+, NH_2^+, NH^+, and N^+ from NH_3, which could not be individually determined because of the inadequate resolution of the mass spectrometer, should be equivalent to the cross sections for production of ND_3^+, ND_2^+, ND^+, and N^+ from ND_3. Therefore, although both NH_3 and ND_3 data are tabulated, for clarity, only the ND_3 data are plotted in the following figures.

The partial cross sections of Mark *et al.*[5] Rao and Srivastava,[7] and Tarnovsky *et al.*[8] whose uncertainties are typically ±11–15%, and which were all normalized to other absolute measurements, are shown for comparison with the present ND_3 measurements in Figs. 4 and 5. The most obvious trend observed from these plots is that the discrepancy between the various measurements becomes progressively greater as the mass of the fragment ion decreases (Fig. 4).

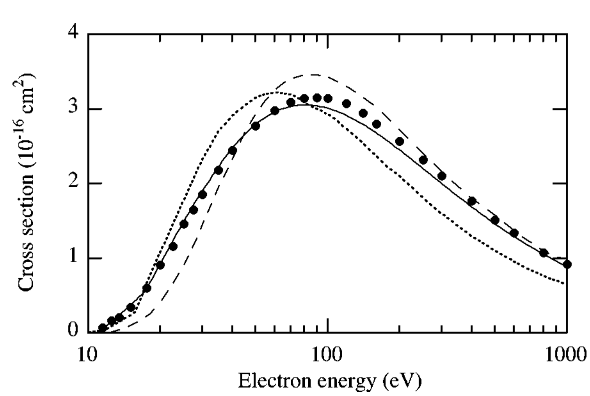

FIG. 6. Total cross section: present ND_3 results (●); BEB theory of Kim *et al.* (1996) (—); calculations of Saksena *et al.* (1997) (---); DM theory of Deutsch *et al.* (2000) (···).

TABLE III. Absolute cross sections for production of (ND^+,D^+) and (N^+,D^+) ion pairs by electron-impact ionization of ND_3. The uncertainties in these cross sections are ±15% and ±20%, respectively, unless otherwise indicated.

Energy (eV)	$\sigma(ND^+,D^+)$ $(10^{-18}\ cm^2)$	$\sigma(N^+,D^+)$ $(10^{-19}\ cm^2)$
60	0.81±0.22	2.8±1.0
70	1.18±0.24	3.6±1.2
80	1.39	5.3±1.3
90	1.64	5.9
100	1.67	7.7
120	1.73	7.1
140	1.70	6.7
160	1.58	8.2
200	1.49	6.3
250	1.37	6.3
300	1.13	5.3
400	0.82	3.8
500	0.75	3.5
600	0.63	3.0
800	0.48	1.4±0.3
1000	0.32	1.0±0.3

This is consistent with the incomplete collection of the lighter more energetic fragment ions in the earlier studies. Such effects are not uncommon, but the magnitude of the discrepancy between the present D^+ cross section and the earlier data is particularly striking. The reason for such a large discrepancy is, however, apparent from Fig. 2, which shows that D^+ product ions are formed with considerable kinetic energy and may therefore easily escape collection. The data in Fig. 5 exhibit similar behavior. The present cross section for production of ND_3^{2+}, which is formed with relatively little kinetic energy, is not too dissimilar from those reported previously, but the present cross section for production of light D_2^+ fragment ions is much larger than the other measurements.

It was observed during the course of this investigation that special care is needed to accurately determine the H_2^+ cross section because even small amounts of background D^+ ions resulting from prior introduction of deuterated ammonia could easily cause an apparent increase in this cross section. In an earlier study on H_2O and D_2O we found the H_2^+ cross section to be a factor of 2 greater than that for D_2^+.[20] Because the cross section for formation of H_2^+ from H_2O is much smaller than that for formation of H_2^+ from NH_3, and therefore much more susceptible to contamination by D^+, it now seems highly probable that the H_2^+ cross section reported in that study was too high and that the correct cross section for production of H_2^+ from H_2O is similar to that for D_2^+ from D_2O.

The NH_3^+ and NH_2^+ partial cross sections have been calculated by Saksena *et al.*[12] by extending the Mayol and Salvat[23] semiphenomenological approach to molecules. Although their calculations are in fair agreement with the present ND_2^+ data at higher energies, the agreement for ND_3^+ is poor. The threshold behavior of both calculated cross sections also differs considerably from these measurements.

The present ND_3 total electron-impact ionization cross section is shown in Fig. 6 together with a number of theoretical calculations. Prior experimental total cross sections[5,7] are not included in this plot because, as discussed previously, it appears that all ions were not collected in these studies. The calculation of Kim *et al.*,[13] obtained using the binary-encounter-Bethe model, and that of Saksena *et al.*[12] predict the energy at which the cross section peaks more accurately than the semiclassical Deutsch–Märk formalism.[14] Although the calculation of Kim *et al.*[13] is in excellent agreement with the present data, it should be noted that because this theoretical approach assumes the target molecule will ionize when energetically possible the calculated cross section is, strictly speaking, an upper limit to the total ionization cross section[24] and the agreement may therefore not be quite as good as it appears. At energies in excess of ~40 eV the calculation of Saksena *et al.*[12] is in reasonable agreement with experiment. The measurements of Djuric *et al.*[3] (not shown), although of unstated accuracy, are in very good agreement with present total cross section in both form and magnitude.

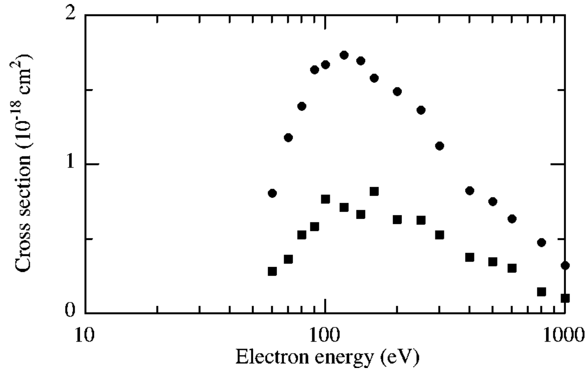

FIG. 7. Cross sections for production of (ND^+,D^+) ion pairs (●); and (N^+,D^+) ion pairs (■).

Cross sections for formation of (ND^+,D^+) and (N^+,D^+) ion pairs are given in Table III and plotted in Fig. 7. Presently no other experimental or theoretical data exist with which to compare these cross sections, however, their magnitude is similar to those observed for pair production in CF_4[21,25] and SF_6.[22]

IV. CONCLUSION

Absolute partial cross sections are reported for the production of $(NH_3^+ + NH_2^+ + NH^+ + N^+)$, H^+, H_2^+, and NH_3^{2+} from NH_3 and for production of ND_3^+, ND_2^+, ND^+, N^+, D^+, D_2^+, and ND_3^{2+} from ND_3 for electron energies from threshold to 1000 eV. Data are also presented for formation of (ND^+,D^+) and (N^+,D^+) ion pairs. The apparatus geometry is of simple design embodying a short-path-length time-of-flight mass spectrometer and position-sensitive detection of the product ions, which unequivocally demonstrates that all fragment ion species are collected with equal efficiency irrespective of their initial kinetic energy. The NH_3 and ND_3 cross sections are found to be essentially identical, and the partial cross sections for lighter fragment ions are found to be considerably greater than had been previously reported. Agreement with recent theoretical calculations is generally satisfactory.

ACKNOWLEDGMENT

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[1] F. W. Lampe, J. L. Franklin, and F. H. Field, J. Am. Chem. Soc. **79**, 6129 (1957); G. De Maria, L. Malaspina, and V. Piacente, Ricerca Scientifica, Parte 2, Sez. A **3**, 681 (1963); C. E. Melton, J. Chem. Phys. **45**, 4414 (1966); J. C. Gomet, Comptes Rendus. Academie Sciences **281**, 627 (1975).
[2] A. Crowe and J. W. McConkey, Int. J. Mass Spectrom. Ion Phys. **24**, 181 (1977); K. Bederski, L. Wojcik, and B. Adamczyk, *ibid.* **35**, 171 (1980).
[3] N. Djuric, D. Belic, M. Kurepa, J. U. Mack, J. Rothleitner, and T. D. Märk, in Proceedings of the XII International Conference on the Physics of Electronic and Atomic Collisions, Gatlinburg, TN, 1981, p. 384.
[4] J. A. Syage, Chem. Phys. Lett. **143**, 19 (1988).
[5] T. D. Märk, F. Egger, and M. Cheret, J. Chem. Phys. **67**, 3795 (1977).
[6] M. V. V. S. Rao and S. K. Srivastava, J. Geophys. Res., [Atmos.] **96**, 17563 (1991).
[7] M. V. V. S. Rao and S. K. Srivastava, J. Phys. B **25**, 2175 (1992).
[8] V. Tarnovsky, H. Deutsch, and K. Becker, Int. J. Mass Spectrom. Ion Processes **167/168**, 69 (1997).
[9] D. K. Jain and S. P. Khare, J. Phys. B **9**, 1429 (1976).
[10] S. P. Khare and W. J. Meath, J. Phys. B **20**, 2101 (1987).
[11] S. P. Khare, S. Prakash, and W. J. Meath, Int. J. Mass Spectrom. Ion Processes **88**, 299 (1989).
[12] V. Saksena, M. S. Kushwaha, and S. P. Khare, Physica B **233**, 201 (1997).
[13] Y.-K. Kim, W. Hwang, N. M. Weinberger, M. A. Ali, and M. E. Rudd, J. Chem. Phys. **106**, 1026 (1997).
[14] H. Deutsch, K. Becker, S. Matt, and T. D. Märk, Int. J. Mass. Spectrom. **197**, 37 (2000).
[15] H. C. Straub, P. Renault, B. G. Lindsay, K. A. Smith, and R. F. Stebbings, Phys. Rev. A **52**, 1115 (1995); **54**, 2146 (1996).
[16] R. S. Gao, P. S. Gibner, J. H. Newman, K. A. Smith, and R. F. Stebbings, Rev. Sci. Instrum. **55**, 1756 (1984).
[17] The NH_3 and ND_3 used in this work were obtained from Sigma-Aldrich Inc. and have specified purities of 99.99% and 99%, respectively.
[18] H. C. Straub, M. A. Mangan, B. G. Lindsay, K. A. Smith, and R. F. Stebbings, Rev. Sci. Instrum. **70**, 4238 (1999).
[19] H. C. Straub, P. Renault, B. G. Lindsay, K. A. Smith, and R. F. Stebbings, Rev. Sci. Instrum. **65**, 3279 (1994).
[20] H. C. Straub, B. G. Lindsay, K. A. Smith, and R. F. Stebbings, J. Chem. Phys. **108**, 109 (1998).
[21] D. R. Sieglaff, R. Rejoub, B. G. Lindsay, and R. F. Stebbings, J. Phys. B **34**, 799 (2001).
[22] R. Rejoub, D. R. Sieglaff, B. G. Lindsay, and R. F. Stebbings, J. Phys. B **34**, 1289 (2001).
[23] R. Mayol and F. Salvat, J. Phys. B **23**, 2117 (1990).
[24] H. Nishimura, W. M. Huo, M. A. Ali, and Y.-K. Kim, J. Chem. Phys. **110**, 3811 (1999).
[25] M. R. Bruce, C. Ma, and R. A. Bonham, Chem. Phys. Lett. **190**, 285 (1992); M. R. Bruce, L. Mi, C. R. Sporleder, and R. A. Bonham, J. Phys. B **27**, 5773 (1994).