

Ionization of ammonia and deuterated ammonia by electron impact from threshold up to 180 eV

T. D. Märk, F. Egger, and M. Cheret^{a)}

Institut für Atomphysik der Universität Innsbruck, A 6020 Innsbruck, Austria
(Received 23 June 1977)

Electron impact ionization has been studied in NH_3 and in a mixture of NH_3 and ND_3 as a function of electron energy up to 180 eV with a double focusing mass spectrometer. Absolute partial ionization cross section functions have been obtained in NH_3 for the production of NH_3^+ , NH_2^+ , NH^+ , N^+ , H_2^+ , H^+ , and NH_3^{2+} by normalization against the Ar ionization cross section. The ions NH_2^+ and N^{2+} , produced by the process $\text{NH}_3 + e$, have been found for the first time, and an estimate of the ionization cross section is given. From the measured partial ionization cross section functions the total ionization cross section function of NH_3 has been deduced. In addition, it has been possible to measure the ratio of the partial cross section for double and single ionization of the parent ions ND_2H and ND_3 as a function of electron energy. The ionization cross section results obtained are compared with previous determinations where available and with a recent semiempirical total ionization cross section calculation by Jain and Khare. Using n th root extrapolation the following ionization and appearance potentials have been derived from the low energy cross section function: I.P. ($\text{NH}_3^+/\text{NH}_3$) = 10.4 ± 0.1 eV; A.P. ($\text{NH}_2^+/\text{NH}_3$) = 16.5 ± 0.2 eV; A.P. (NH^+/NH_3) = 22.9 ± 0.5 and 27.2 ± 0.5 eV; A.P. (N^+/NH_3) = 29.5 ± 0.5 eV; A.P. (H_2^+/NH_3) = 14.8 ± 0.2 eV; A.P. (H^+/NH_3) = 23.0 ± 0.2 , 27.7 ± 0.5 , and 30.6 ± 0.5 eV; I.P. ($\text{ND}_2\text{H}^+/\text{ND}_2\text{H}$) = 10.5 ± 0.1 eV; I.P. ($\text{ND}_3^+/\text{ND}_3$) = 10.7 ± 0.1 eV; I.P. ($\text{NH}_3^{2+}/\text{NH}_3$) = 34.4 ± 0.2 eV; I.P. ($\text{NDH}_2^+/\text{NDH}_2$) = 34.6 ± 1.0 eV; I.P. ($\text{ND}_2\text{H}^{2+}/\text{ND}_2\text{H}$) = 34.6 ± 0.5 eV; and I.P. ($\text{ND}_3^{2+}/\text{ND}_3$) = 34.6 ± 0.5 eV. For the doubly ionized parent molecules a square law has been found from threshold up to some 20 eV above onset. The ionization and appearance potentials obtained are also compared with such earlier results as are available.

I. INTRODUCTION

Electron impact ionization of NH_3 near threshold yielding ionization and appearance potentials for the ions NH_3^+ , NH_2^+ , NH^+ , and N^+ has been extensively studied by several authors.¹⁻¹⁰ However, the study of the doubly ionized molecule NH_3^{2+} has been restricted to a mass spectrometric appearance study by Mann *et al.*,¹ the measurement of the first differential ionization efficiency by Dorman and Morrison,¹¹ and a double charge transfer spectroscopy study by Appell *et al.*¹² Furthermore, the authors are aware of only two previous studies concerned with the measurement of the total ionization cross section function in NH_3 ,^{13, 14} and three measurements of the total cross section at a fixed electron energy.¹⁵⁻¹⁷ There are also two studies of the relative ion intensities in NH_3 at a fixed electron energy,^{1, 17} and rather recently of some single partial ionization cross sections of NH_3 .¹⁸ Only one study exists of the ionization potential of the heavy ammonia ion ND_3^+ .² In addition, Jain and Khare¹⁹ have just published data of the total ionization cross section in NH_3 using a semiempirical calculation.

The lack of investigations can probably be attributed to the difficulties encountered when studying ionization cross sections of condensable and reactive gases. The present paper is one in a series from this laboratory and gives results of a thorough and systematic study of the electron impact ionization of the parent ions and of all fragment ions in NH_3 and also in a mixture of NH_3 and ND_3 from threshold up to 180 eV electron energy E . Results reported in the present paper include absolute

partial ionization cross section functions $q(E)$ for the processes $\text{NH}_3 + e \rightarrow \text{NH}_3^+$, $\text{NH}_3 + e \rightarrow \text{NH}_2^+$, $\text{NH}_3 + e \rightarrow \text{NH}^+$, $\text{NH}_3 + e \rightarrow \text{N}^+$, $\text{NH}_3 + e \rightarrow \text{H}_2^+$, $\text{NH}_3 + e \rightarrow \text{H}^+$, and for the first time $\text{NH}_3 + e \rightarrow \text{NH}_3^{2+}$, and also the total ionization cross section function in NH_3 , and the ratios of cross section functions $q(\text{ND}_3^{2+}/\text{ND}_3)/q(\text{ND}_3^+/\text{ND}_3)$ and $q(\text{ND}_2\text{H}^{2+}/\text{ND}_2\text{H})/q(\text{ND}_2\text{H}^+/\text{ND}_2\text{H})$.²⁰ Values of the ionization and appearance potentials of the various parent and fragment ions are also presented and compared with previous data.

II. APPARATUS AND TECHNIQUE

The experimental setup used in the present study is identical with that previously described in detail.^{22, 23} In short, it consists of a molecular type of electron impact source, Varian MAT Intensitron M, and a high resolution double focussing mass spectrometer, Varian MAT CH 5, with a total dynamic range of 1×10^8 . In the course of earlier work the extracting conditions in the ion source have been improved²⁴ in order to reduce disturbing instrumental effects. It thus became possible to obtain quite accurate relative partial ionization cross section functions $q(E)$ of the various ions in NH_3 and ND_3 . The improvement has been achieved by studying the extraction conditions for singly and multiply ionized rare gases²⁴ and adjusting the various extraction potentials to such a value that reproducible and reliable relative partial cross section functions were obtained. Other consistency checks necessary in electron impact studies and the energy scale calibration have been reported and discussed previously.²³

Normalization of the measured relative cross section functions $q(E)$ to yield absolute values has been made by a method described previously,^{22, 23} in which the relative cross section is compared at a particular electron energy with that of the measured value for Ar^+/Ar for

^{a)}Visiting research fellow from Service de Physique Atomique, Centre d'Etudes Nucleaires de Saclay, Gif-sur-Yvette, France.

which absolute cross sections are known. The comparison was usually made near the maximum of $q(\text{Ar}^+/\text{Ar})$, i. e., at 90.5 eV electron energy, setting the presently measured values of $q(\text{Ar}^+/\text{Ar}) + 2q(\text{Ar}^{2+}/\text{Ar})$ equal to the total ionization cross section reported by Rapp *et al.*,²⁵ yielding $q(\text{Ar}^+/\text{Ar}) = 2.43 \times 10^{-16} \text{ cm}^2$.

The measurement of the ratio of the gas density of argon to the gas under study in the collision chamber necessary for this absolute calibration has been made by means of the method of effusive flow.^{23,25,26} The gas pressure in a gas reservoir is measured with an absolute capacitance manometer. According to Rapp *et al.*,²⁵ and Märk *et al.*,²³ the results thus obtained are believed to be more accurate than those based on absolute McLeod-gage measurements in each gas. In all normalization procedures the ion currents have been measured either with a Faraday collector cup or with a 16 dynode multiplier. In the latter case corrections for the different secondary emission coefficients γ for the different ions have been made by calibration with the Faraday cup.²⁷ A correction to the absolute cross section curves of ions containing N has been made for the isotopic abundance²⁶ of nitrogen ($^{14}\text{N} = 99.6\%$), and a correction for the isotopic abundance²⁶ of argon ($^{40}\text{Ar} = 99.6\%$) to $q(\text{Ar}^+/\text{Ar})$.

The accuracy of the measured ion currents was in general better than $\pm 1\%$. For very low ion currents, e. g., as in the case of NH_3^+ or H_2^+ , however, the statistical error could be as large as $\pm 5\%$. The accuracy of the density ratio necessary for the absolute calibration of the cross section values depends on the accuracy of measurement of the pressure (capacitance manometer Barocel $\pm 0.05\%$) and on the adequacy of the assumption of effusive flow. In accordance with Rapp *et al.*,²⁵ and Märk *et al.*,²³ the accuracy for repeated measurements at different effusive flow conditions was found to be about $\pm 4\%$. These error bars have been recently confirmed by an electron impact study of the rare gases in this laboratory.²⁴ Thus, the estimated maximum possible error, excluding that of the absolute value for $q(\text{Ar}^+/\text{Ar})$, is about 10%.

The ammonia samples used were obtained from Professor E. Mayer, Institut für Anorganische Chemie, University of Innsbruck and distilled *in vacuo* through a -10°C cold trap and purified from N_2 and O_2 contaminants *in vacuo* with help of a -180°C cold trap. Impurities still present were determined mass spectrometrically ($\text{H}_2\text{O} < 1\%$, $\text{N}_2 < 0.5\%$) and allowed for in the calibration calculations (see below).

III. RESULTS AND DISCUSSION

A. Ionization cross section functions

The absolute ionization cross sections obtained for the processes $\text{NH}_3 + e \rightarrow \text{NH}_3^+$, $\text{NH}_3 + e \rightarrow \text{NH}_2^+$, $\text{NH}_3 + e \rightarrow \text{N}^+$, $\text{NH}_3 + e \rightarrow \text{H}_2^+$, $\text{NH}_3 + e \rightarrow \text{H}^+$, and $\text{NH}_3 + e \rightarrow \text{NH}_3^{2+}$ are shown semilogarithmically as a function of electron energy in Figs. 1–3. A representative set of values of all absolute cross section functions measured in NH_3 is given numerically in Table I.

In Fig. 4 is plotted as $q' = q(\text{NH}_3^+) + q(\text{NH}_2^+) + q(\text{N}^+)$

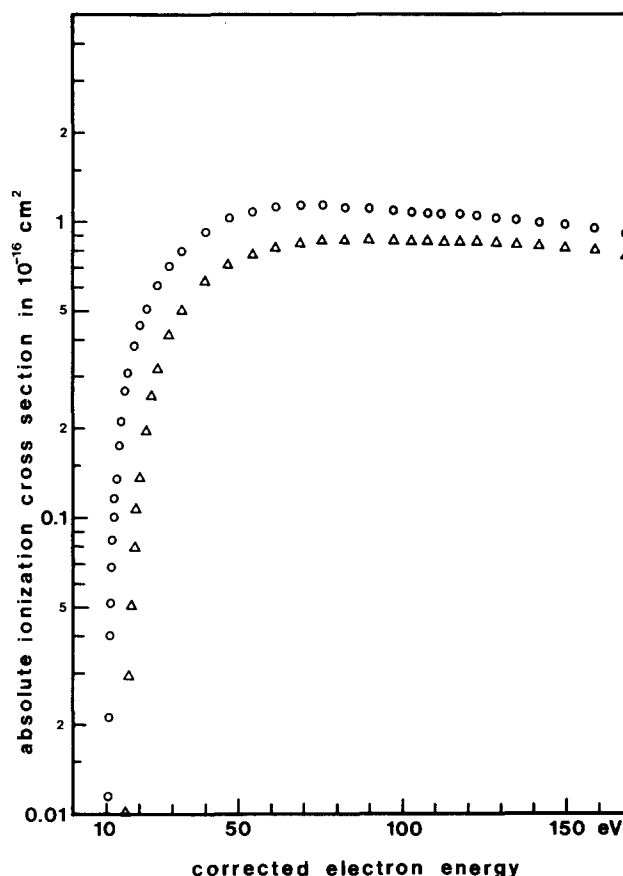


FIG. 1. Absolute partial ionization cross sections $q(\text{NH}_3^+/\text{NH}_3)$, designated o, and $q(\text{NH}_2^+/\text{NH}_3)$, designated Δ , as a function of corrected electron energy. The energy scale of the present data was calibrated by means of the linear extrapolation method, taking the ionization potential of Ar^+ as 15.76 eV (spectroscopic value).

+ $q(\text{N}^+) + q(\text{H}_2^+) + q(\text{H}^+) + 2q(\text{NH}_3^{2+})$ as a function of electron energy. If the dissociatively produced fragment ions have very little initial kinetic energy the above sum of all cross sections q' will be equal to the total ionization cross section q_t , because no discrimination due to initial kinetic energy will occur in the source of the mass spectrometer. Saalfeld *et al.*,²⁸ have studied carefully the positive ion fragmentation pattern for several group VB hydrides and have found that if the fragment ions contained excess kinetic energy it was negligible. Thus, the partial ionization cross sections of the fragment ions obtained in the present study will be equal to the true cross sections and the above sum of all partial cross sections q' will be equal to the total cross section $q_t(\text{NH}_3)$.

Figure 4 also shows total ionization cross section values for NH_3 reported by other authors. Points designated o in Fig. 4 represent the total ionization cross section function as measured by Gomet.^{13,18} In order to obtain absolute cross section values Gomet has measured the gas pressure in the collision chamber with help of a Balzers ionization gage calibrated by the company for air. In order to correct for the different ionization probability of NH_3 this gage has been calibrated for NH_3 with a Knudsen comparator gage. This method has been confirmed with a McLeod gage. Triangular

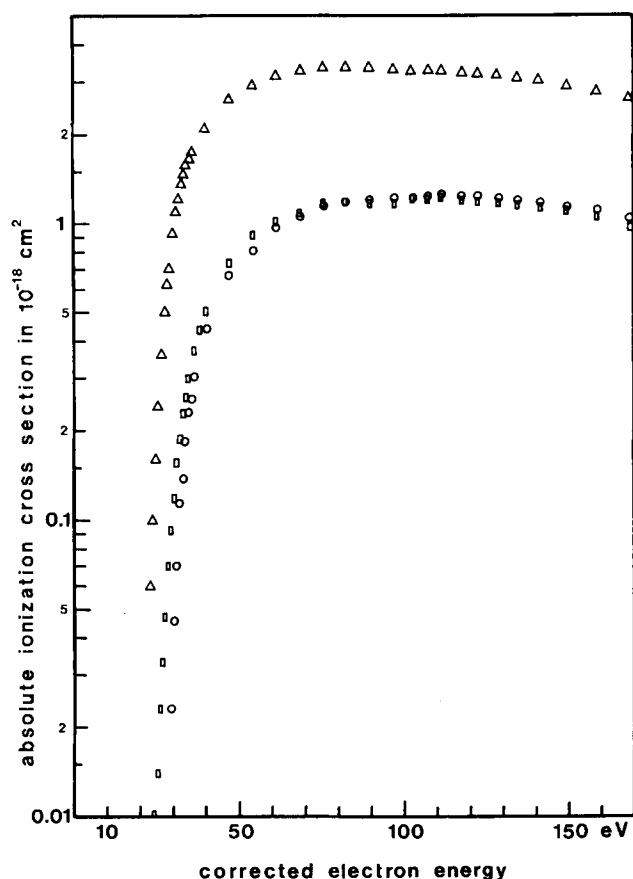


FIG. 2. Absolute partial ionization cross sections $q(\text{NH}^+/\text{NH}_3)$, designated Δ , $q(\text{N}^+/\text{NH}_3)$, designated o , and $q(\text{H}^+/\text{NH}_3)$ designated \square , as a function of corrected electron energy.

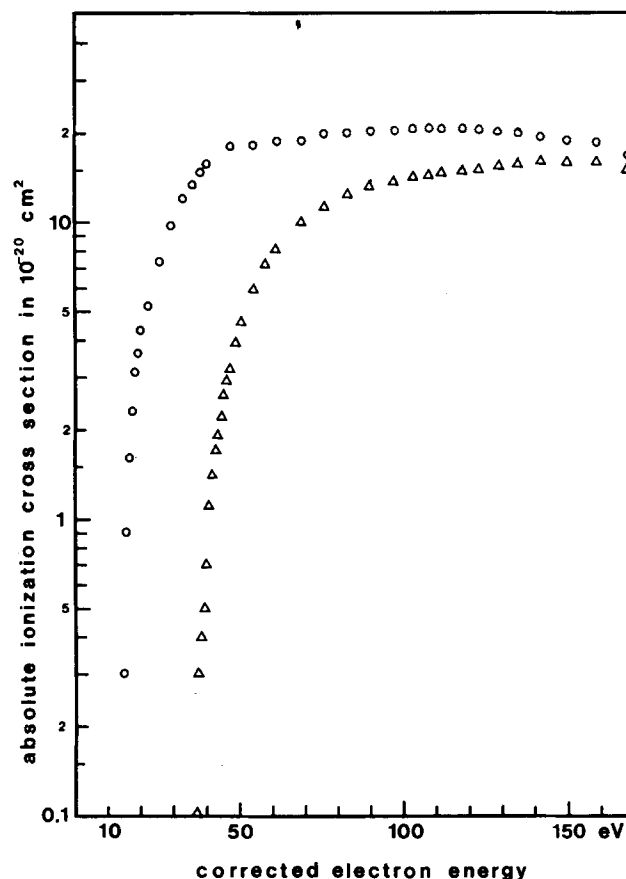


FIG. 3. Absolute partial ionization cross sections $q(\text{H}_2^+/\text{NH}_3)$, designated o , and $q(\text{NH}_3^{+*}/\text{NH}_3)$, designated Δ , as a function of corrected electron energy.

TABLE I. Absolute partial ionization cross sections $q(\text{NH}_3^+/\text{NH}_3)$, $q(\text{NH}_2^+/\text{NH}_3)$, $q(\text{NH}^+/\text{NH}_3)$, $q(\text{N}^+/\text{NH}_3)$, $q(\text{H}_2^+/\text{NH}_3)$, $q(\text{H}^+/\text{NH}_3)$, and $q(\text{NH}_3^{+*}/\text{NH}_3)$ for different corrected electron energies.

E (eV)	$q(\text{NH}_3^+)$ (10^{-16} cm^2)	$q(\text{NH}_2^+)$ (10^{-16} cm^2)	$q(\text{NH}^+)$ (10^{-18} cm^2)	$q(\text{N}^+)$ (10^{-18} cm^2)	$q(\text{H}_2^+)$ (10^{-18} cm^2)	$q(\text{H}^+)$ (10^{-18} cm^2)	$q(\text{NH}_3^{+*})$ (10^{-18} cm^2)
183.0	0.844	0.724	2.45	0.96	0.154	0.893	0.139
170.5	0.901	0.765	2.61	1.03	0.166	0.975	0.149
159.5	0.944	0.797	2.77	1.10	0.184	1.05	0.159
150.5	0.974	0.815	2.89	1.12	0.187	1.10	0.159
142.5	0.996	0.831	3.01	1.17	0.192	1.13	0.159
135.5	1.01	0.840	3.09	1.19	0.198	1.15	0.156
129.5	1.02	0.843	3.13	1.21	0.201	1.17	0.153
123.5	1.04	0.849	3.17	1.23	0.203	1.18	0.150
118.5	1.05	0.852	3.19	1.23	0.205	1.19	0.148
112.5	1.06	0.854	3.23	1.26	0.205	1.20	0.146
108.5	1.06	0.858	3.25	1.23	0.206	1.20	0.144
103.5	1.07	0.856	3.25	1.21	0.205	1.20	0.142
98.0	1.08	0.860	3.29	1.21	0.203	1.17	0.137
90.5	1.10	0.863	3.31	1.19	0.201	1.16	0.131
83.5	1.11	0.863	3.33	1.12	0.199	1.14	0.124
76.5	1.13	0.860	3.33	1.14	0.198	1.12	0.113
69.5	1.12	0.845	3.29	1.07	0.187	1.08	0.101
62.0	1.11	0.817	3.13	0.96	0.189	1.02	0.081
55.0	1.08	0.774	2.91	0.80	0.182	0.906	0.061
47.7	1.02	0.711	2.59	0.66	0.180	0.731	0.032
40.5	0.922	0.622	2.11	0.43	0.156	0.505	0.007
33.3	0.789	0.499	1.34	0.14	0.120	0.228	...
26.1	0.609	0.315	0.24	...	0.073	0.023	...
22.5	0.505	0.197	0.052
19.0	0.379	0.079	0.033
15.1	0.220	0.003
11.6	0.052

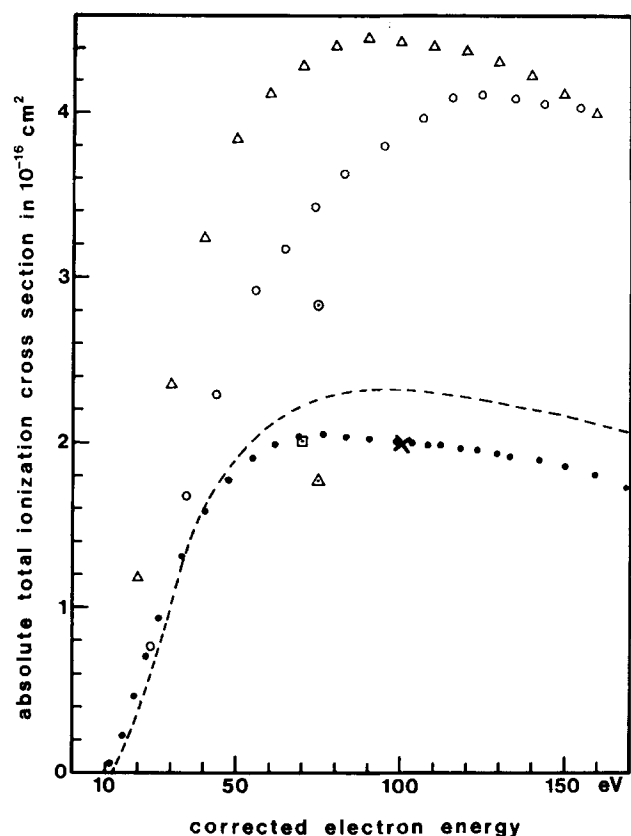


FIG. 4. Absolute total ionization cross section of NH_3 : ● present data; ○ Gomet^{13,18}; Δ Djuric-Preger *et al.*¹⁴; □ De Maria *et al.*¹⁶; ○ Lampe *et al.*¹⁵ experimental results; Δ Lampe *et al.*¹⁵ theoretical calculation according to Otvos *et al.*²⁹; and × Melton.¹⁷ The relative results of De Maria *et al.* and Lampe *et al.* have been converted to the same absolute units as used in the present paper (see text). Also shown are the results of a recent semiempirical calculation of the total ionization cross section reported by Jain and Khare,¹⁹ designated ---.

points in Fig. 4 represent the total ionization cross section function as measured by Djuric-Preger *et al.*¹⁴ The pressure of the target gas has been determined by an absolute gas flow method through a porous plug.

Also shown in Fig. 4 are values of the total ionization cross section at 75 eV electron energy reported by Lampe *et al.*¹⁵ The upper point corresponds to a measurement of the saturation ion current on the ion repeller of a cycloidal focussing mass spectrometer, where the ion current has been calibrated versus the known absolute total ionization cross section for argon by the effusive flow method. The lower point designates the result of a calculation based on the additivity rule of Otvos *et al.*²⁹ Further, in Fig. 4 a value of the total ionization cross section at 70 eV electron energy is shown, measured by De Maria *et al.*¹⁶ They have measured the ion currents due to the fragmentation of molecules, including NH_3 , with a Nier-type mass spectrometer at 70 eV electron energy and taken the sum of these currents to be a measure of the total ionization cross section.³⁰ With help of a modified flow method they have calibrated these cross section values using argon as reference gas. Also shown in

Fig. 4 is a value of the total ionization cross section at 100 eV electron energy obtained in a study by mass spectrometry of the decomposition of NH_3 in a wide range radiolysis source by Melton.¹⁷ The pressure in each collision compartment of the radiolysis source has been determined using Ar as a standard and by two other methods (ionization gage and ion molecule reactions). To test the accuracy of the method the cross section of each positive ion in NH_3 has been determined by Melton separately and then the sum has been compared to the total cross section obtained without mass analysis, i.e., collecting all ions on the ion repeller.

Because Lampe *et al.* and De Maria *et al.* have expressed their values in relative units of different total argon cross sections a conversion of their values to the units used in the present paper was required, i.e., using the total cross section of Argon reported by Rapp *et al.*²⁵ It can be seen that our experimental values lie between the two values of Lampe *et al.*¹⁵ and are in excellent agreement with the value of De Maria *et al.*¹⁶ and of Melton,¹⁷ whereas the values of Gomet¹³ and of Djuric-Preger *et al.*¹⁴ differ from the present result by a factor of about 2. The difference in magnitude may be due to uncertainties in the absolute normalization of the cross sections, e.g., McLeod calibration used by Gomet, a method which according to Rapp *et al.*²⁵ is subject to considerable doubt for heavy gases. This seems to be further confirmed by the fact that the values of the absolute total cross section of H_2O reported by Gomet in the same paper are also a factor of about 2 higher than the values reported by Schutzen *et al.*³¹ The latter have determined the pressure of the water vapor with a temperature bath technique. It may further be seen from Fig. 4 that the present curve peaks near 75 eV, whereas the curve of Gomet has its peak near 125 eV electron energy. It is interesting to note that the same difference in shape is observed between the total cross section function of H_2O , where the curve of Schutzen *et al.* peaks near 90 eV, but the curve of Gomet near 130 eV. This different shape appears to be a feature of the study of Gomet. Because of lack of experimental detail given by Djuric-Preger *et al.*¹⁴ it is difficult to evaluate their pressure calibration. Hence, it is of interest to compare the measured total ionization cross section functions of NH_3 with the results of the recent semiempirical calculations reported by Jain and Khare.¹⁸ It can be seen from Fig. 4 that the calculated cross section values of Jain and Khare are in much better agreement with the present total cross section function than that of Gomet¹³ and that of Djuric-Preger, Belic, and Kurepa.¹⁴ In assessing the reliability of the calculations of Jain and Khare a comparison of their values of such systems is useful where there are well known experimental cross section values. It follows that the calculations of Jain and Khare are at electron energies of 100 eV and above in agreement with experiment²⁵ to better than 25%. This suggests that the present measurements are superior to those of Gomet and of Djuric-Preger *et al.*

The partial ionization cross section functions obtained in the present study can be compared only with the pre-

TABLE II. Partial ionization cross sections of the fragment ions in NH_3 divided by that of the parent ion NH_3^+ in % at three different electron energies as measured by Mann *et al.*,¹ Melton,¹⁷ Gomet,¹⁸ in the present study, and listed in the Catalog of Mass Spectral Data of NBS.³³ Whereas all results reported in the present study have been obtained with an electron current in the ion source of 50 μA , values designated in parentheses have been obtained with a 150 μA electron current. At 70 eV Lifschitz and Long⁹ report a $\text{NH}_2^+/\text{NH}_3^+$ ratio at 77%, which is in good agreement with the present value of 75.5%.

Electron energy	47.7 eV		100 eV					150.5 eV	
	Gomet	Present study	Mann <i>et al.</i>	Catalog	Melton	Gomet	Present study	Gomet	Present study
$q(\text{NH}_2^+/\text{NH}_3)/q(\text{NH}_3^+/\text{NH}_3)$	38	70	78	80	80	44	80(83.4)	38	84
$q(\text{NH}^+/\text{NH}_3)/q(\text{NH}_3^+/\text{NH}_3)$	4.9	2.5	4.5	7.5	9	8.6	3.0(5.5)	3.0	3.0
$q(\text{N}^+/\text{NH}_3)/q(\text{NH}_3^+/\text{NH}_3)$	0.6	0.6	1.7	2.2	3	1.6	1.1(1.9)	0.9	1.2
$q(\text{H}_2^+/\text{NH}_3)/q(\text{NH}_3^+/\text{NH}_3)$	0.9	0.2	0.02	0.02	2.6	0.2	0.2	0.12	0.2
$q(\text{H}^+/\text{NH}_3)/q(\text{NH}_3^+/\text{NH}_3)$	8.6	0.7	0.5	0.5	2.6	8.5	1.1	2.3	1.1
$q(\text{NH}_3^{2+}/\text{NH}_3)/q(\text{NH}_3^+/\text{NH}_3)$...	0.03	0.01	0.13(0.10)	...	0.16

vious results of Mann *et al.*,¹ Melton,¹⁷ and Gomet.¹⁸ Mann *et al.*, however, have reported only the relative ion intensities as a result of a mass spectrometric study of the products of ionization and dissociation of ammonia at 100 eV electron energy. Gomet, on the other hand, has determined the partial single ionization cross section functions by measuring the relative amounts of the produced singly ionized ions in a linear rf mass spectrometer³² and by normalizing their sum on the total ionization cross section.¹³ The latter has been measured by the same author and, as already discussed above, differs by a factor of 2 from various other results. Because of this difference in absolute normalization it is not meaningful to compare the absolute values of the present results of the partial cross section functions (Fig. 1–3), but rather their shape and their relative values, i. e., the fragmentation pattern.

It can be seen from Fig. 1–3 that the NH_3^+ curve peaks near 70 eV (150 eV), NH_2^+ near 90 eV (125 eV), NH^+ near 80 eV (100 eV), N^+ near 110 eV (115 eV), H_2^+ near 110 eV (55 eV), H^+ near 110 eV (80 eV), and NH_3^{2+} near 150 eV, as compared with the value of the peak of Gomet¹⁸ in parentheses, respectively. Table II gives the partial ionization cross section of the fragment ions relative to that of the parent ion NH_3^+ at three different electron energies 47.7, 100, and 150.5 eV. The agreement between the results of the different authors is generally poor. From Table II it may be seen that the present values agree with those of Mann *et al.*, Melton, and the values listed in the catalog of mass spectral data of NBS³³ only for NH_2^+ . The agreement between the present values and the experimental results of Gomet is rather poor. Especially striking is the low value for NH_2^+ (factor of 2) and the high value of NH^+ and H^+ (factors of 2 and 10, respectively) when comparing the values of Gomet with that of Mann *et al.* and the present study. A possible explanation would be a contamination of the mass spectrometer system of Gomet by his preceding H_2O measurements, which would tend for instance to increase the H^+ signal through H^+ ions from H_2O (H^+ being the most abundant fragment ion in H_2O).³¹ Also,

a possible N_2 impurity, as confirmed by Gomet in reporting a N_2^+ signal, will result in a too high N^+ signal. Both impurities N_2 and H_2O have been monitored in the present study, and the affected NH_3 -fragment ion signal has been corrected, e. g., the N^+ signal by about 2% and the H^+ signal by about 3% at an electron energy of 90.5 eV. Values given in Table II in parentheses designate present results obtained at a higher electron current in the ion source, i. e., 150 instead of 50 μA as usual. At this high electron current secondary processes can be important and falsify the electron impact fragmentation pattern of NH_3 . It is interesting, however, that these values are in better agreement with the previous results of other authors, e. g., for NH^+ and N^+ .

As already mentioned there exist no other measurements of the absolute cross section function of process $\text{NH}_3 + e \rightarrow \text{NH}_3^{2+} + 3e$, except this one and that of Mann *et al.*¹ (see Table II), which is lower by a factor of about 10. It is possible, however, to prove the reliability of the present determination by comparing it with the results of deuterated ammonia. In Table III is listed the ratio of measured partial cross sections for double and single ionization of the parent ions of NH_3 , ND_3 , and ND_2H , i. e., $q(\text{NH}_3^{2+}/\text{NH}_3)/q(\text{NH}_3^+/\text{NH}_3)$, $q(\text{ND}_3^{2+}/\text{ND}_3)/q(\text{ND}_3^+/\text{ND}_3)$, and $q(\text{ND}_2\text{H}^{2+}/\text{ND}_2\text{H})/q(\text{ND}_2\text{H}^+/\text{ND}_2\text{H})$, for different electron energies. By comparing the three columns of Table III it may be seen that the sets of experimental values are identical within the experimental error. This is to be expected, in agreement with theoretical considerations based on the Born approximation.²³ Moreover, as there is the same agreement between $q(\text{D}_2^+/\text{D}_2)$ and $q(\text{H}_2^+/\text{H}_2)$,²⁵ and $q(\text{D}_2\text{O}^+/\text{D}_2\text{O})$ and $q(\text{H}_2\text{O}^+/\text{H}_2\text{O})$,²² the above result is to be expected from the concept of a qualitative additivity rule.^{29,15} It is further interesting to note that $q(\text{NH}_3^{2+}/\text{NH}_3)/q(\text{NH}_3^+/\text{NH}_3)$ is within the experimental error equal to $q(\text{PH}_3^{2+}/\text{PH}_3)/q(\text{PH}_3^+/\text{PH}_3)$, as measured by Märk *et al.*,³⁴ both gases being group VB monohydrides.

In addition to the study of the doubly ionized parent ion NH_3^{2+} a search was made for doubly ionized fragment ions which have not been reported hitherto. With help

TABLE III. Ratio of partial double and single ionization cross section of the parent ions of NH_3 , ND_3 , and ND_2H as a function of corrected electron energy.

Corrected electron energy in eV	$q(\text{NH}_3^{**})/q(\text{NH}_3^*)$ in %	$q(\text{ND}_3^{**})/q(\text{NH}_3^*)$ in %	$q(\text{ND}_2\text{H}^{**})/q(\text{ND}_2\text{H}^*)$ in %
183.0	0.165	0.160	0.157
170.5	0.165	0.157	0.155
159.5	0.168	0.158	0.148
150.5	0.163	0.157	0.151
142.5	0.159	0.152	0.146
135.5	0.156	0.151	0.141
129.5	0.149	0.146	0.140
123.5	0.145	0.141	0.135
118.5	0.141	0.138	0.134
112.5	0.138	0.135	0.129
108.5	0.135	0.133	0.128
103.5	0.133	0.130	0.126
98.0	0.126	0.125	0.122
90.5	0.119	0.119	0.118
83.5	0.111	0.115	0.110
76.5	0.100	0.102	0.098
69.5	0.089	0.091	0.085
62.0	0.073	0.076	0.070
55.0	0.055	0.056	0.051
48.0	0.031	0.031	0.029
40.5	0.007	0.008	0.007
36.0	0.000	0.000	0.000

of the total available dynamic range of the mass spectrometer it was possible to detect at mass number 8 the ion NH_2^{**} and at mass number 7 the ion N^{**} , produced via processes $\text{NH}_3 + e \rightarrow \text{NH}_2^{**}$ and $\text{NH}_3 + e \rightarrow \text{N}^{**}$, respectively. Correcting for the impurity ion O^{**} from O_2 at mass number 8 and N^{**} from N_2 at mass number 7³⁵ a partial ionization cross section at 135 eV electron energy could be deduced from the measured ratios $q(\text{NH}_2^{**}/\text{NH}_3)/q(\text{NH}_3^{**}/\text{NH}_3) \cong 0.002$ and $q(\text{N}^{**}/\text{NH}_3)/q(\text{NH}_3^{**}/\text{NH}_3) \cong 0.066$ of the order of $q(\text{NH}_2^{**}/\text{NH}_3) \cong 3 \times 10^{-22}$ and $q(\text{N}^{**}/\text{NH}_3) \cong 1 \times 10^{-20} \text{ cm}^2$. No evidence could be detected for the existence of NH^{**} , although it would have been observed in the mass spectrometer if the cross section for its production had been $\geq 10^{-23} \text{ cm}^2$.

The present study has been extended also to deuterated ammonia. Because the available sample was not pure ammonia- d_3 , but rather a mixture of NH_3 and ND_3 [e. g., $p(\text{ND}_3) : p(\text{ND}_2\text{H}) : p(\text{NDH}_2) : p(\text{NH}_3) = 12 : 11 : ? : ?$, the latter two $< 1\%$], and the content of water and heavy water was not known, it was not possible to analyze the ion current data in a way to obtain accurate absolute cross section values of deuterated ions. It was only possible to measure accurately the ion current ratios $\text{ND}_3^{**}/\text{ND}_3^*$ and $\text{ND}_2\text{H}^{**}/\text{ND}_2\text{H}^*$ as listed in Table III and already discussed above. It is interesting to note, however, that the fragmentation pattern measured in the present study in deuterated ammonia is, within the experimental error, the same as that in normal ammonia. This result is in accordance with observations in phosphine and deuterated phosphine by Märk *et al.*³⁴

B. Ionization and appearance potentials

From the low-energy cross section behavior ionization and appearance potentials have been derived by

means of the linear extrapolation method. Moreover, due to excited states of the produced ions and due to different dissociation processes, both with a relatively high transition probability, the ionization cross section function exhibits in certain cases distinct breaks corresponding to higher ionization potentials. The obtained results are listed in Table IV. The values of I. P. ($\text{NH}_3^*/\text{NH}_3$), A. P. ($\text{NH}_2^*/\text{NH}_3$), and A. P. (H_2^*/NH_3) are in excellent agreement with results obtained for the minimum potentials by previous electron impact studies.^{1, 3-5, 7, 8, 10}

The two measured appearance potentials of NH^+ are 4.3 eV apart. This energy difference corresponds about to the dissociation energy of molecular hydrogen, and suggests that NH^+ is produced by the two reaction processes $\text{NH}_3 + e \rightarrow \text{NH}^+ + \text{H}_2 + 2e$ and $\text{NH}_3 + e \rightarrow \text{NH}^+ + 2\text{H} + 2e$. Reed *et al.*,⁶ using the extrapolated voltage difference technique, found an A. P. (NH^+) of 17.1 and 21.6 eV. Such a low A. P. (NH^+) value was not observed by Morrison *et al.*,¹⁰ using the first differential plot method. In accordance with the present results Morrison *et al.* found an increase at 23.0 eV and a vertical ionization potential of 27 eV for the steepest part of the NH^+ curve.

Because of the low transition probability of the lower state of the ion the onset of N^+ is not clearly defined.¹⁰ Breaks in the cross section function for N^+ have previously been observed at 22.6, 24.1, 26.7, and 28.6 eV,⁶ the last in good agreement with the present value, corresponding according to Morrison *et al.*¹⁰ to the process $\text{NH}_3 + e \rightarrow \text{N}^*(^1\text{D}) + 3\text{H}(^2\text{S}) + 2e$. The present results of H^+ with 23.0, 27.7, and 30.6 eV can only be compared with the values 23.3 ± 0.5 and 26.9 ± 0.5 eV as measured by Mann *et al.*¹ by the linear extrapolation method. The ionization potentials for the deuterated ions ND_2H and ND_3 with 10.5 ± 0.1 and 10.7 ± 0.1 eV, respectively, are in excellent agreement with relative measurements of Neuert,² i. e., normalizing his relative I. P. values with I. P. (NH_3^*) = 10.4 eV gives

TABLE IV. Ionization and appearance potentials of parent and fragment ions in ammonia and deuterated ammonia.

Ion	Ionization or appearance potential in eV		
I. P. ($\text{NH}_3^*/\text{NH}_3$)	10.4 \pm 0.1		
A. P. ($\text{NH}_2^*/\text{NH}_3$)	16.5 \pm 0.2		
A. P. (NH^*/NH_3)	22.9 \pm 0.5,	27.2 \pm 0.5	
A. P. (N^*/NH_3)	29.5 \pm 0.5		
A. P. (H_2^*/NH_3)	14.8 \pm 0.2		
A. P. (H^*/NH_3)	23.0 \pm 0.2,	27.7 \pm 0.5,	30.6 \pm 0.5
I. P. ($\text{ND}_2\text{H}^*/\text{ND}_2\text{H}$)	10.5 \pm 0.1		
I. P. ($\text{ND}_3^*/\text{ND}_3$)	10.7 \pm 0.1		
I. P. ($\text{NH}_3^{**}/\text{NH}_3$)	34.4 \pm 0.2		
I. P. ($\text{NDH}_2^{**}/\text{NDH}_2$)	34.6 \pm 1.0		
I. P. ($\text{ND}_2\text{H}^{**}/\text{ND}_2\text{H}$)	34.6 \pm 0.5		
I. P. ($\text{ND}_3^{**}/\text{ND}_3$)	34.6 \pm 0.5		

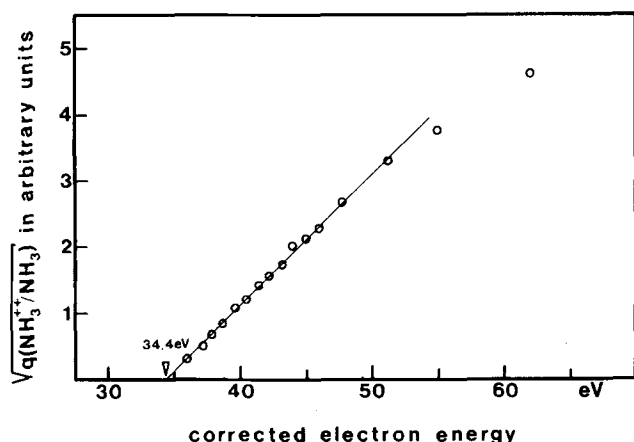


FIG. 5. Square root of the double ionization cross section $q(\text{NH}_3^{2+}/\text{NH}_3)$ versus corrected electron energy.

I. P. $(\text{ND}_2\text{H}^+/\text{ND}_2\text{H}) = 10.57 \pm 0.02$ and I. P. $(\text{ND}_3^+/\text{ND}_3) = 10.62 \pm 0.03$ eV.

Figure 5 shows a plot of the square root of the double ionization cross section function near threshold of the process $\text{NH}_3 + e \rightarrow \text{NH}_3^{2+}$. It can be seen that a square threshold law is followed for some 20 eV above onset. A similar result is found for NDH_2^+ , ND_2H^+ , and ND_3^+ . This result is in support of theoretical arguments,^{36, 37} which say that the probability for the occurrence of a process of direct n -fold ionization induced by electron impact varies above threshold as the n th power of the excess energy.

On the assumption that the n th power rule is correct the minimum double ionization potential was taken in the present study as the point to which the square root of the double ionization cross section function extrapolated to the energy axis. From Table IV it may be seen that these double ionization potentials of the parent ion of ammonia and various deuterated ammonia are within the experimental error the same; a possible difference could only be related to a difference in zero-point energies.

Only NH_3^{2+} has been previously observed and studied mass spectrometrically by other authors.^{1, 11, 12} Mann *et al.*¹ estimated a minimum ionization potential for NH_3^{2+} of 42 ± 3 eV, probably by the linear extrapolation method. Dorman *et al.*¹¹ measured the first differential of the ionization cross section of NH_3^{2+} and found a minimum I. P. $(\text{NH}_3^{2+}) = 33.7 \pm 0.2$ eV. From a break in this curve they further deduced a higher I. P. $(\text{NH}_3^{2+}) = 36.8$ eV. More recently, Appell *et al.*¹² measured the ionization potentials corresponding to the formation of the lowest-lying states of doubly ionized ammonia by double charge transfer spectroscopy, obtaining $\text{NH}_3^{2+}(^1A_1) = 35.3 \pm 0.7$ and $\text{NH}_3^{2+}(^1E) = 38.9 \pm 0.7$ eV. They also carried out a SCF calculation with an STO basis set, yielding $\text{NH}_3^{2+}(^1A_1) = 33.68$ and $\text{NH}_3^{2+}(^1E) = 37.04$ eV, and a CJ calculation with a Gaussian lobe basis set, yielding $\text{NH}_3^{2+}(^1A_1) = 34.51$ and $\text{NH}_3^{2+}(^1E) = 38.96$ eV. Keeping in mind that the CJ calculation yields more accurate values than the SCF calculation¹² the present experimentally obtained result of $\text{NH}_3^{2+}(^1A_1) = 34.4 \pm 0.2$

eV is in excellent agreement with theory, whereas the value of Dorman *et al.* is too low and the value of Appell *et al.* too high. No evidence has been found in the present study of $\text{NH}_3^{2+}(^1E)$, probably due to the very low signal of NH_3^{2+} and a low transition probability to this excited state of the ion.

IV. ACKNOWLEDGMENTS

The authors are grateful to the Österreichischer Fonds zur Förderung der wissenschaftlichen Forschung for financial assistance under Projects No. 1490, 1727, and 2781. The authors also wish to thank Professor M. Pahl, head of the department, for the opportunity to use the mass spectrometer system Varian MAT CH5. We are grateful for a critical reading of the manuscript by Professor R. N. Varney, Fulbright guest professor at the Institut für Atomphysik, Universität Innsbruck.

- ¹M. M. Mann, A. Hustrulid, and J. T. Tate, *Phys. Rev.* **58**, 340 (1940).
- ²H. Neuert, *Z. Naturforsch. Teil A* **7**, 293 (1952).
- ³S. N. Foner and R. L. Hudson, *J. Chem. Phys.* **29**, 442 (1958).
- ⁴D. C. Frost and C. A. McDowell, *Can. J. Chem.* **36**, 39 (1958).
- ⁵J. Collins, *Can. J. Chem.* **37**, 1053 (1959).
- ⁶R. I. Reed and W. Snedden, *J. Chem. Soc.* **1959**, 4132.
- ⁷C. J. Varsel, F. A. Morrell, F. E. Resnik, and W. A. Powell, *Anal. Chem.* **38**, 182 (1960).
- ⁸R. W. Kiser and E. J. Gallegos, *J. Phys. Chem.* **66**, 947 (1962).
- ⁹C. Lifshitz and F. A. Long, *J. Chem. Phys.* **41**, 2468 (1964).
- ¹⁰J. D. Morrison and J. C. Traeger, *Int. J. Mass. Spectrom. Ion Phys.* **11**, 277 (1973).
- ¹¹F. H. Dorman and J. D. Morrison, *J. Chem. Phys.* **35**, 575 (1961).
- ¹²J. Appell and J. A. Horsley, *J. Chem. Phys.* **60**, 3445 (1974).
- ¹³J. C. Gomet, *Methodes Phys. Anal.* **5**, 269 (1969).
- ¹⁴N. Djuric-Preger, D. Belic, and M. Kurepa, *Proceedings of the VIIIth Symposium on the Physics of Ionized Gases*, Dubrovnik, (1976), p. 54.
- ¹⁵F. W. Lampe, J. C. Franklin, and F. H. Field, *J. Am. Chem. Soc.* **79**, 6129 (1957).
- ¹⁶G. De Maria, L. Malaspina, and V. Piacente, *Ric. Sci. Parte 2 Sez. A* **3**, 681 (1963).
- ¹⁷L. E. Melton, *J. Chem. Phys.* **45**, 4414 (1966).
- ¹⁸J. C. Gomet, *C. R. Acad. Sci. Ser. B* **281**, 627 (1975).
- ¹⁹D. K. Jain and S. P. Khare, *J. Phys. B* **9**, 1429 (1976).
- ²⁰Following Kieffer²¹ a nomenclature is used in the present paper, whereby $q(X^+/X)$ designates the cross section for the production of X^+ from X via the process $X + e \rightarrow X^+ + 2e$.
- ²¹L. J. Kieffer, JILA Information Center Report No. 6, Boulder, CO 1968.
- ²²T. D. Märk, *J. Chem. Phys.* **63**, 3731 (1975).
- ²³T. D. Märk and F. Egger, *Int. J. Mass Spectrom. Ion Phys.* **20**, 89 (1976).
- ²⁴T. D. Märk, F. Egger, E. Hille, M. Cheret, H. Störi, and K. Stephan, *Proceedings of the Xth International Conference on the Physics of Electronics and Atomic Collisions*, Paris (1977), p. 1070.
- ²⁵D. Rapp and P. Englander-Golden, *J. Chem. Phys.* **43**, 1464 (1965).
- ²⁶C. Brunnee and H. Voshage, *Massenspektrometrie* (Thiemig, Munich, 1964), pp. 97–100.
- ²⁷T. D. Märk, *Proceedings of the 3rd International Conference on Solid Surfaces*, Wien (1977), p. 1341.

- ²⁸F. E. Saalfeld and H. J. Svec, *Inorg. Chem.* **2**, 46 (1963).
- ²⁹J. W. Otvos and D. P. Stevenson, *J. Am. Chem. Soc.* **78**, 546 (1956).
- ³⁰The total ionization cross sections obtained with this method are only reliable if the fragment ions of the studied molecule have negligible excess kinetic energy. This is true only for a limited number of molecules, but certainly not for N₂ and O₂, whose total cross sections reported by De Maria are well below the values reported by Rapp *et al.*²⁵ This is very likely due to a discrimination in detection efficiency of the energetic dissociated ions.
- ³¹J. Schutten, F. J. De Heer, H. B. Moustafa, A. J. H. Boerboom, and J. Kistemaker, *J. Chem. Phys.* **44**, 3924 (1966).
- ³²J. C. Gomet and J. J. Le Jeune, *C. R. Acad. Sci. Ser. B* **273**, 612 (1971).
- ³³Catalog of Mass spectral data, Natl. Bur. Stand. (U.S.) Spec. Publ. (1948).
- ³⁴T. D. Märk and F. Egger, *J. Chem. Phys.* **67**, xxxx (1977).
- ³⁵A. Crowe and J. W. Mc Conkey, *J. Phys. B* **6**, 2108 (1973).
- ³⁶G. H. Wannier, *Phys. Rev.* **100**, 1180 (1955).
- ³⁷S. Geltman, *Phys. Rev.* **102**, 171 (1956).