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THE DISSOCIATIVE ELECTROIONIZATION OF AMMONIA AND AMMONIA-d_3. II. THE H^+ AND H_2^+ DISSOCIATION CHANNELS

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Abstract

The dissociative electroionization of NH_3 (ND_3), in the H^+ (D^+) and H_2^+ (D_2^+) dissociation channels, is investigated in the 18-50 eV electron energy range. The H^+ (D^+) translational energy distribution spectrum shows several components and that of H_2^+ (D_2^+) is continuous. The thermal energy component of the latter distribution is entirely ascribed to H_2^+ /H_2. For both ions the kinetic energy versus appearance energy diagram is obtained and discussed. The H^+ ion at the lowest onset is probably formed at the expense of NH_3^+ ($\tilde{A}^2E$) state. In the 22.5 eV electron energy range both H^+ and H_2^+ are formed by dissociative autoionization. Evidence is also brought for H^+ and H_2^+ formation at 22.5 and 26.5 eV through spontaneous decomposition of NH_2^+. Above 35 eV dissociation of doubly ionized states by Coulomb repulsion is mainly involved.

1. Introduction

Recently, the results on the dissociative ionization of NH_3 in the NH_2^+ and NH^+ dissociation channels have been reported [1]. Translational energy distribution measurements, together with appearance energy determinations allowed us to discuss in detail most of the dissociation processes.

The dissociation of NH_3 into H^+ and H_2^+ has been investigated by a few groups. Appearance energies were measured but very briefly discussed without kinetic energy measurements. The earliest work of Mann et al. [2] and the most recent publication of Mark et al. [3] included both ions. Only the former discussed dissociation processes, while the latter only mentioned onset energies.

Using energy-loss electron spectroscopy and electron-ion coincidence technique, Wight et al. [4] and Brion et al. [5] determined the fragmentation pattern of NH_3, including the H^+ dissociation channels.

More recently Carnahan et al. [6] and Kurawaki and Ogawa [7] published their results on high Rydberg H atoms and excited H (n=2, 3, 4) atoms produced by electron impact on NH_3. Time-of-flight distribution and Doppler profile analysis of Balmer emission lines were used to derive kinetic energy distributions. Dissociative excitation processes, discussed in detail by the authors, can be linked to dissociative ionization work through the "core-ion" model [8,9].

This paper deals with the dissociative electroionization of NH_3 in the H^+ and H_2^+ dissociation channels, including detailed ion translational energy analysis. The results on D^+ and D_2^+ from ND_3 have been added. The 15-50 eV electron energy range is covered in order to include the NH_3 double ionization energy range. Preliminary results on this particular aspect have already been published earlier [1,10].

2. Experimental

The experimental technique, as well as its most recent modifications used in the present work, have extensively been described elsewhere [11,12]. Briefly, the ions produced in a Nier-type ion source by the impact of energy-controlled electrons are allowed to drift out of the ion chamber, are focused on the ion source exit hole, energy analyzed by a retarding lens and mass selected in a quadrupole filter. The detected ion current is continuously scanned as a function of either the electron energy at fixed retarding potential V_R or the retarding potental at fixed electron energy E_e. Both signals are electronically differentiated. The experiment is almost computer controlled.

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The experimental conditions are identical with those described previously [1]. Ammonia (Air Liquide, 99.95%) and ammonia-d_3 (Merk, Sharp & Dome 99.7%) samples, distilled under vacuum, are introduced at 10^{-7} Torr as measured in the vacuum chamber.

The maximum of the NH_3^+ (ND_3^+) ion energy distribution is used as zero-energy calibration point of the translational energy scale. The appearance energy of NH_2^+ (ND_2^+), i.e 15.72 ± 0.1 eV is used to calibrate the electron energy scale.

For each fragment ion, at each retarding potential or electron energy setting, the first derivative of the ionization efficiency curve or of the retarding potential curve is scanned 100-800 times. This procedure is repeated at least five times. The energies quoted in the next sections are average values of these five independent measurements. The quoted errors and drawn error bars are given by the standard deviation. In the diagrams, linear regressions are fitted to the experimental data.

3. Experimental results

As an introductory remark, it has to be pointed out that beside NH_3, two different proton sources could be suspected, (i) Notwithstanding its low intensity after prolongated back out, H_2O is present in the background mass spectrum and produces H^+ with a large cross section. (ii) As will be shown below H_2^+ is probably formed through ionization of H_2 produced by pyrolysis of NH_3 on the electron emitting filament. Furthermore H_2^+ is observed in the H_2O mass spectrum, though with very low intensity.

The simultaneous analysis of D^+/ND_3 and H^+/ NH_3 would remove, at least to a large extent, the former proton source. On the other hand, the kinetic energy distribution and the appearance energies of H^+/ H_2 are available [13] and have to be kept in mind for the interpretation of the experimental results.

The same comments hold for H_2^+ /NH_3. However, most confusing will be the thermal or nearly thermal H_2^+ (D_2^+) ions.

3.1. The H^+ (D^+) dissociation channel

Typical first differential retarding potential curves ofH^+/NH_3 and D^+/ND_3, as observed at 61 eV electron energy, are displayed in fig. 1. The identical shape of these curves indicates the absence of any contaminant, at least at low energy. Beside, a dominant low-energy peak, a shoulder at about 0.25 eV, slope changes around 0.6 eV and 1.5 eV, and finally a maximum near 4.0 eV are observed for H^+. These values slightly shift toward lower energies for D^+. The translational energy spectrum spreads up to 9 eV. Figs. 2 and 3 show the same distribution for D^+ from 76-31 eV and 26.5-20.1 eV respectively. The maximum of the ND_3^+ thermal ion energy distribution (see fig. 3) and the D^+ low-energy peak only coincide for electron energies close to the lowest onset up to 23 eV. In the electron energy range 23-60 eV the same maximum regularly shifts upward to 45 meV. The same phenomenon is observed for H^+ and is represented by the diagram in fig. 4. This means that the thermal H^+ ions are only formed near the lowest onset. Above 23 eV only energetic protons are produced and dominate the translational energy spectrum.

At this point a comparison has to be made between the present results and those obtained for high Rydberg H(Rydb.) atoms and excited H*(n) atoms [6,7]. Concerning the position of the abovementioned features, the present H^+ and D^+ translational energy spectra agree fairly well with the H* (n=2) [6] H* (n=3,4) [7] kinetic energy spectra. However, the relative intensities are quite different, e.g. the distribution peaking at 4.0 eV dominates the H* kinetic energy spectrum at 70 eV electron energy. Surprisingly even less agreement is found with the translational energy spectrum of H(Rydb.) atoms [6], where a maximum at about 5.5 eV is the most intense feature. This could mean that at least for a number of processes leading to H(Rydb.), the "core-ion" model no longer holds.

The first differentiated ionization efficiency curves of H^+/NH_3, as observed for different retarding potential settings V_R, are shown in fig. 5. Vertical bars locate the average position of the successive appearance energies. The same measurements have been performed on D^+/ND_3. For comparison fig. 6 clearly shows both ions having almost the same first differentiated ionization efficiency curve. Six appearance energies have been measured, i.e. 19.5 ± 0.2, 22.6 ± 0.3, 26.2 ± 0.1, 34.9 ± 0.4, 36.2±0.3 and 39.2 ± 0.2 eV. A critical energy is also measured at 45.7 ± 0.3 eV and could only be observed for $0.0 < V_R < 0.9$ V.

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The kinetic energy versus appearance energy plot resulting from these measurements is displayed in fig. 7. The same plot for D^+/ND_3, restricted to the low energy range, is reproduced in fig. 8 together with the results on H^+/NH_3 for comparison. Though both diagrams almost coincide within experimental error, systematic differences are observed which probably should be ascribed to isotope effects.

Fig. 1. *The kinetic energy distribution curves of H^+/NH_3 and D^+/ND_3 observed at 61 eV electron energy.*

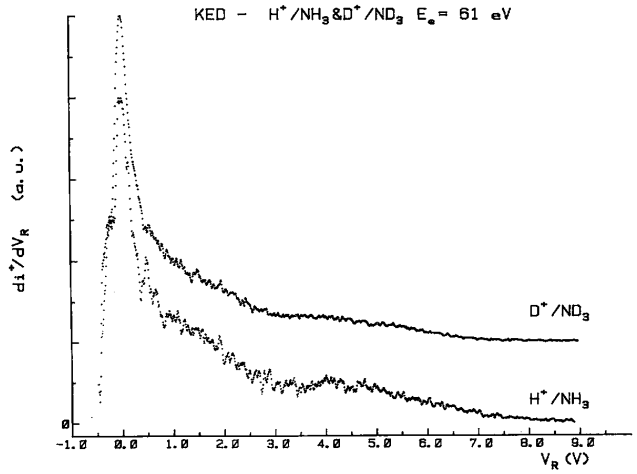

Fig. 2. *Kinetic energy distribution spectra of D^+/ND_3 recorded between 76 and 31 eV electron energy.*

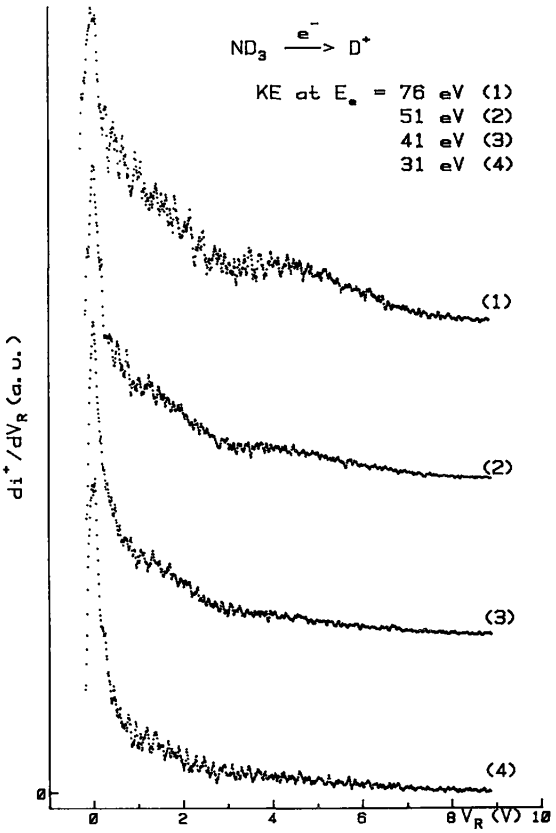

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Fig. 3. *Kinetic energy distribution spectra of D^+/ND_3 recorded between 26.5 and 20.1 eV electron energy. The ND_3^+ distribution is included for comparison.*

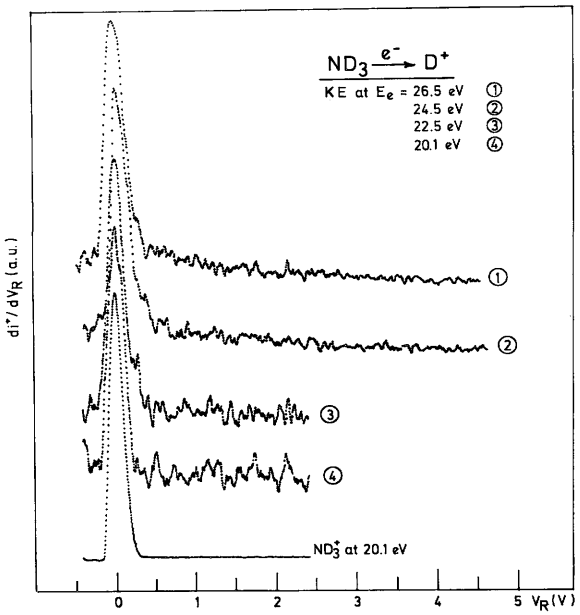
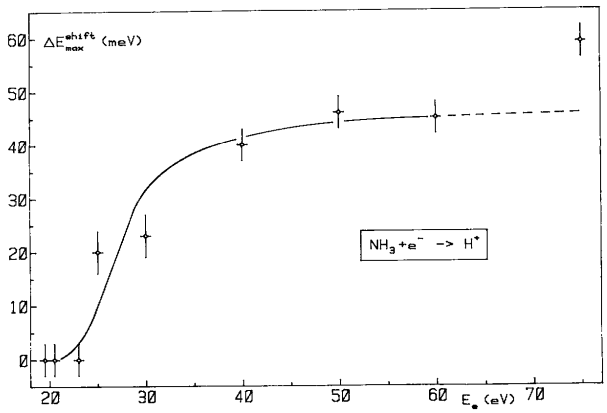


Fig. 4. *Electron energy dependence of the position of the maximum of the H^+ low-energy peak.*



3.2. The H_2^+ (D_2^+) dissociation channel

Despite its low intensity (about 0.05% of total ionization), the H_2^+ ion has been investigated because of its potential importance for the interpretation of NH^+ and N^+ formation at high energies.

The D_2^+/ND_3 translational energy distribution spectrum, as obtained by the first derivative of the retarding potential curve, is shown in fig. 9 for different impact energies of the electrons. The H_2^+/NH_3 ion energy distribution is strictly identical. Both distributions exhibit an intense thermal energy peak and a long and structureless tail, extending to about 5 eV, which disappears below 26 eV electron energy.

The first differentiated ionization efficiency curves ofD_2^+/ND_3, as observed for different values of the retarding potential, are displayed in fig. 10. In fig. 11 the same curve for H_2^+/NH_3 is shown for comparison. For both ions, different appearance energies, marked by a vertical bar, are measured respectively at 15.5 ± 0.2, 22.3 ± 0.2, 26.6 ± 0.3 and 35.7 ± 0.4 eV. The kinetic energy versus appearance energy diagram for both H_2^+/NH_3 and D_2^+/ND_3 is represented in fig. 12.

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Fig. 5. *First differentiated ionization efficiency curves of H^+/NH_3 as observed for indicated retarding potential (V_R) settings. Vertical bars locate the average appearance energies.*

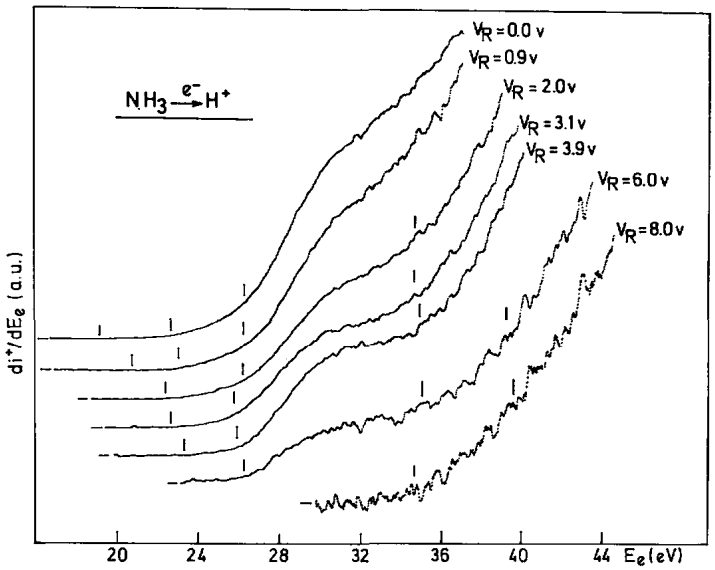
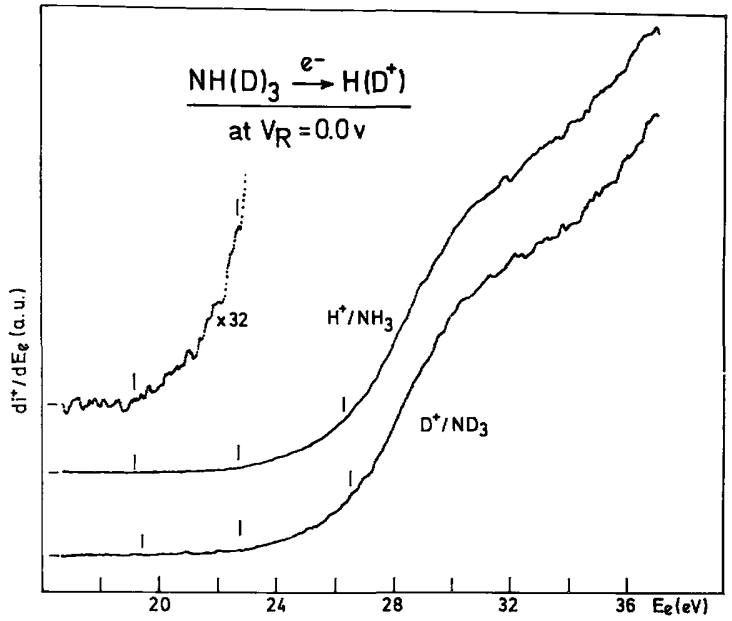


Fig. 6. *Comparison of the first differentiated ionization efficiency curves of H^+/NH_3 and D^+/ND_3, both recorded at V_R=0.0 V. Vertical bars locate the average appearance energies at low electron energies.*



4. Discussion

For clarity in the following discussion, the results obtained in the present work are summarized in table 1. All the thermodynamical and spectroscopic data used to calculate critical energies are gathered in table 2.

4.1. The H^+ (D^+) dissociation channel

The lowest onset determined for the H^+ production from NH_3^+ is 19.5 ±0.2 eV. This result disagrees

drastically with previously published electron impact results, i.e. 23.3±0.5 eV [2] and 23.0±0.2 eV [3]. The discrepancy is at least of 3.5 eV. However, the present result is consistent with the measurements for D^+/ND_3 for which an appearance energy of 19.4 ± 0.2 is obtained (see fig. 8).

Fig. 7. *The kinetic energy versus appearance energy plot for H^+/NH_3.*

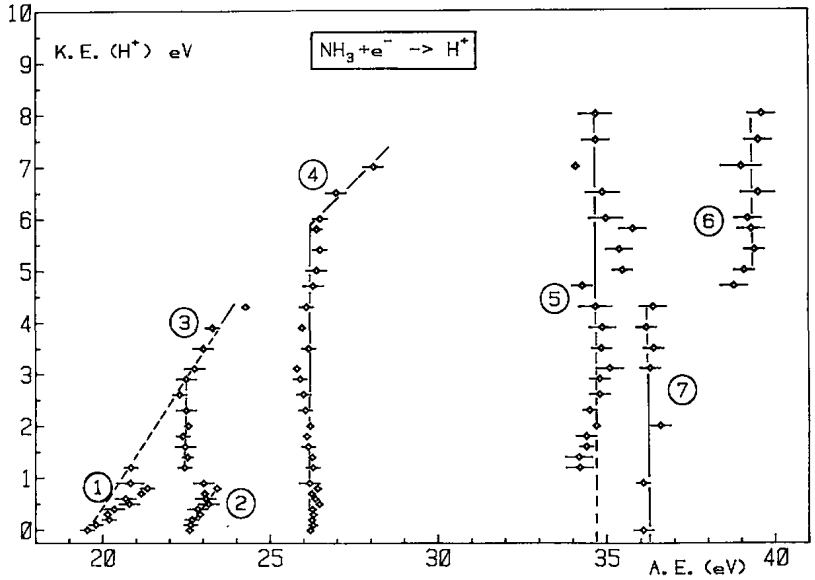
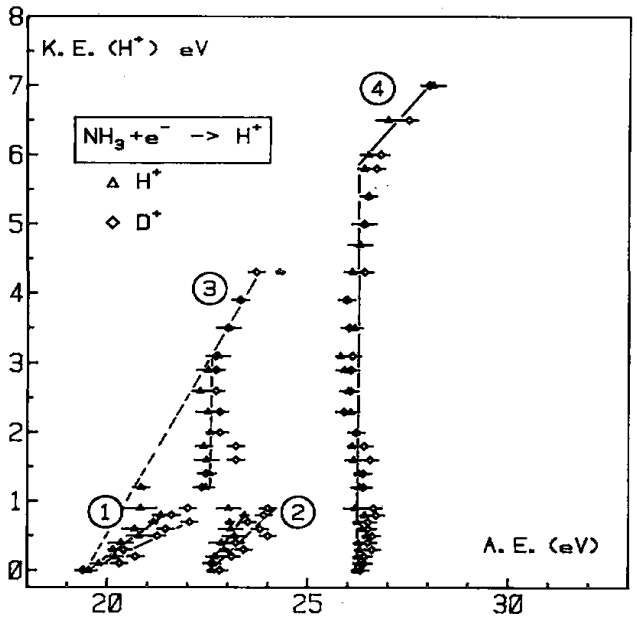


Fig. 8. *The kinetic energy versus appearance energy plot for H^+/NH_3 (-Δ-) and D^+/ND_3 (-◊-) between 18 and 33 eV electron energy.*



The kinetic energy versus appearance energy diagram related to this threshold is the straight line (1) in fig. 7. In spite of the scattering of the onset measurements for 0-0.9 V retarding potential, a least-squares fit gives a correlation coefficient of 0.96 for a straight line extrapolating to 19.67 eV with a slope of 0.49. For the same measurements in D^+/ND_3, the straight line extrapolates to 19.62 eV with a slope of 0.29 and a correlation coefficient of 0.95.

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Fig. 9. *Kinetic energy distribution spectra of D_2^+/ND_3 as observed at indicated electron energies.*

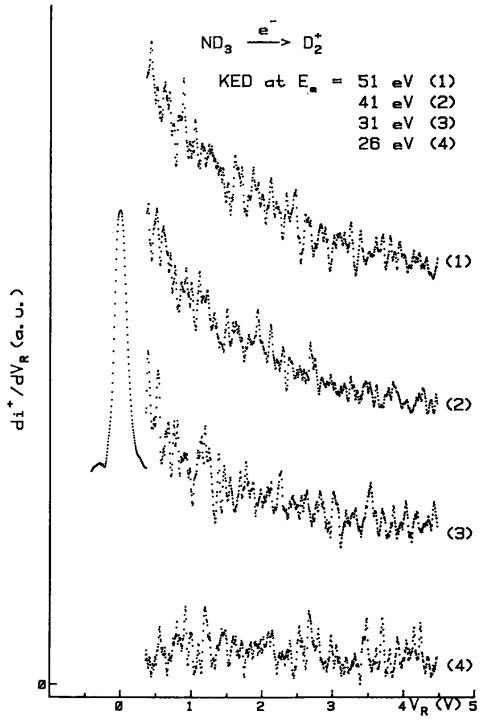

Fig. 10. *First differentiated ionization efficiency curves of D_2^+/ND_3 recorded at indicated retarding potential settings V_R. Vertical bars locate the average appearance energies.*

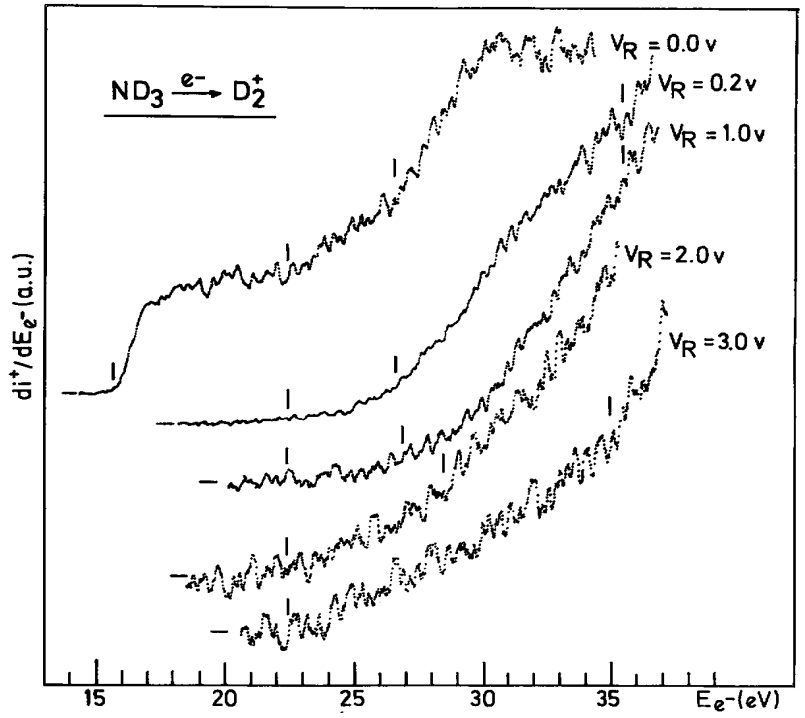

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***Fig. 11**. First differentiated ionization efficiency curves of H_2^+/NH_3 recorded at V_R=0.0 V and 0.2 V shown for comparison with D_2^+/ND_3.*

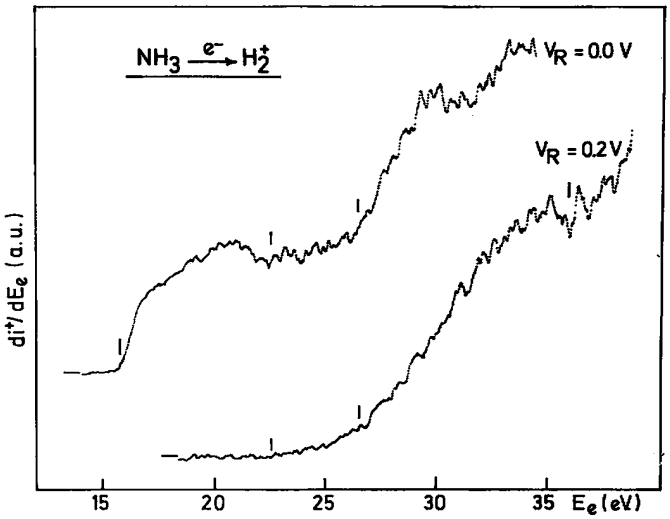

***Table 1.** The kinetic energy distributions (KED) and appearance energies (AE) (eV) for H^+ (D^+) and H_2^+ (D_2^+) from NH_3 and ND_3 as obtained in this work*

	KED	AE
H^+ (D^+)	0.0-45 meV	19.5 ± 0.2
	shift	22.6 ± 0.3
	≈0.25	26.2 ± 0.1
	≈0.6	34.9 ± 0.4
	≈1.5	36.2 ± 0.3
	≈4.0	39.2 ± 0.2
		45.7 ± 0.4
H_2^+ (D_2^+)	(0.0) [a]	(15.5±0.2)[a]
		22.3 ±0.2
		26.6 ±0.3
		35.7 ±0.4

[a] In parentheses data ascribed to H_2^+ (D_2^+) from H_2 (D_2).

***Table 2.** Disocation energies (D), ionization energies (IE) and excitation energies (EE) (eV) used in this work [a]*

$D(NH_2\text{-}H)$=4.51 ± 0.09[b]	$EE(NH_2^+(\tilde{X}\ ^3B_1))$ = 0.0[d]
$D(NH\text{-}H)$ = 3.90 ± 0.09 [b]	$EE(NH_2^+(\tilde{a}\ ^1A_1))$ = 0.99[d]
$D(N\text{-}H)$ = 3.69[c]	$EE(NH_2^+(\tilde{b}\ ^1B_1))$ = 2.23[d]
$D(H\text{-}H)$ =4.476[c]	$EE(NH_2(\tilde{X}\ ^2B_1))$=0.0[f]
	$EE(NH_2(\tilde{A}\ ^2A_1))$ = 1.27[f]
$IE(NH_2)$ = 11.46 ± 0.01[d]	$EE(NH(X\ ^3\Sigma^-))$=0.0[g]
$IE(NH)$ = 13.49 ± 0.01 [d]	$EE(NH(a^1\Delta))$ = 1.558 [g]
$IE(H_2)$ = 15.496[c]	$EE(NH(b\ ^1\Sigma^+))$=2.629 [g]
$IE(H)$ = 13.595 [e]	$EE(NH(A\ ^3\Pi))$ = 3.69[g]
$IE(N)$ = 14.549[e]	$EE(NH(c\ ^1\Pi))$ = 5.423 [g]
	$EE(NH^+(X\ ^2\Pi))$=0.0[h]
$EE(N(^4S))$=0.0[e]	$EE(NH^+(a\ ^4\Sigma^-))$ =0.044 [h]
$EE(N(^2D))$=2.38[e]	$EE(NH^+(A\ ^2\Sigma^-))$ = 2.674 [h]
	$EE(NH^+(B\ ^2\Delta))$=2.847 [h]
	$EE(NH^+(C\ ^2\Sigma^+))$ =4.409 [h]

[a] 1 eV=23.060 kcal mol^{-1} = 8065.73 cm^{-1}. [b] Ref. [14]. [c] Ref. [15]. [d] Ref. [16]. [e] Ref. [17]. [f] Ref. [18]. [g] Ref. [19]. [h] Ref. [20].

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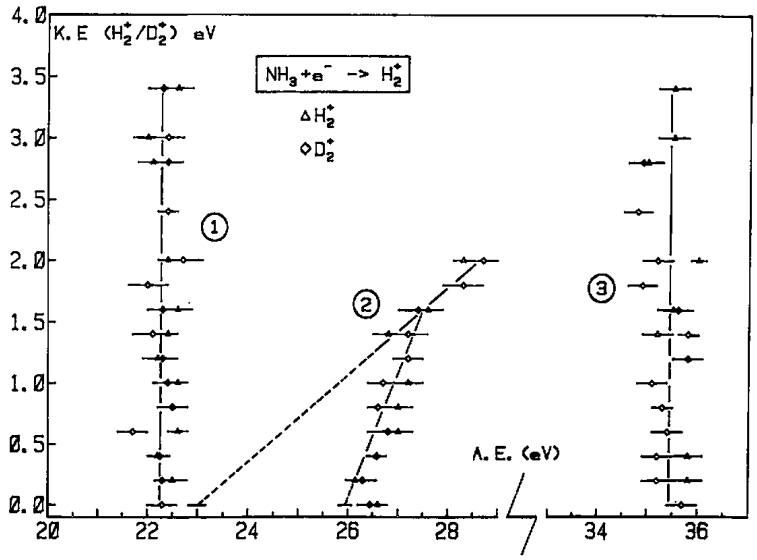
Fig. 12. *The kinetic energy versus appearance energy plot for H_2^+/NH_3 (-Δ-) and D_2^+/ND_3 (-◊-) between 20 and 36 eV electron energy.*



The slope of 0.49 could suggest that the observed H^+ would be produced by dissociative ionization of H_2. As will be mentioned below, H_2 is in fact produced very likely by thermolysis of NH_3 on the electron emitting filament. In this case the linear dependence of the kinetic energy upon the electron energy would indeed be a straight line with a slope of 0.5. However, the same phenomenon being observed for ND_3, the same slope of 0.5 has to be expected. Experimentally a slope of 0.29 is observed. Furthermore, the appearance energy of H^+/H_2 is well below 19.5eV, i.e. 18.1 eV [13].

The lowest energy required for the production of H^+ from NH_3 through

$$NH_3+e^-\rightarrow NH_2(\tilde{X}\,^2B_1)+H^+(^1S_g)+2e^-,$$

is calculated at 18.105 eV, based on the data listed in table 2. As shown in fig. 6, in the first differentiated ionization efficiency curve of H^+ and D^+ no signal could be detected below 19.5 eV. Therefore the energy difference between measured and calculated onset has to be ascribed to the excitation of NH_2 only, i.e. 19.5 — 18.1 = 1.4 eV. This energy difference is close to the excitation energy of NH_2 in its $^2A_1$ state found at 1.27 eV by optical spectroscopy (see table 2). The most probable mechanism to be invoked for the threshold at 19.5 eV is

$$NH_3+e^-\rightarrow NH_3^+(\tilde{A}\,^2E)\rightarrow NH_2(\tilde{A}\,^2A_1)+H^+ + 2e^-,$$

and lies in the energy range of the NH_3^+ ($\tilde{A}\,^2E$) state. From previous work, this state is known to be split by Jahn-Teller interaction into $^2A' + ^2A''$ states [21] and to give rise to NH^+ and NH_2^+ by predissociation [21, 1]. The photoelectron band related to the $\tilde{A}\,^2E$ state has a shape suggesting that this state is populated well above 16.9 eV [22], the lowest appearance energy of NH^+ [1]. It seems to be likely that at 19.5 eV dissociative ionization is observed through the direct population of the $\tilde{A}\,^2E$ ($^2A' + ^2A''$) dissociation continuum. However, at the present time the fact that the lowest dissociation process calculated at 18.105 eV is not observed, remains unexplained.

The expected slope for the dissociation process involving H^+ and NH_2 is m_{NH2}/m_{NH3} = 16/17=0.94, while the observed slope is s=0.49. This indicates that the excess energy with respect to the dissociation limit at 19.5 eV is shared to a large extent (about 50%) between translational and internal (essentially vibrational) energy of NH_2. This analysis is confirmed by the measurements on D^+/ND_3. A slope s_i=0.29 is observed instead of the expected value of m_{ND2}/m_{ND3} = 18/20=0.9.

Both processes involving vibrational energy content of NH_2 and ND_2, the ratio of the two experimental slopes s_i/s has to be related to the isotope effect on the vibrational frequencies of both species. This isotope effect is usually measured by $\rho = (\nu^i/\nu)^2$. For a triatomic molecule of the type XY_2, the relationships between ρ and the

molecular masses are given by Herzberg [23]. When the antisymmetric frequency is chosen, $\rho_3 = (v_3^i/v_3)^2=0.56$, whereas for the symmetric vibrations $\rho_{1,2}(v_{1,2}^i I/v_{1,2})^2=0.28$. A fairly good agreement is found between ρ_3 and $s_i/s= 0.59$, in spite of the poor correlaton coefficient of the least-squares fit. This might be an indication that essentially v_3 is active in this process.

As mentioned above, two investigations of dissociative excitation were performed on H atom formation from NH_3. Both studies include the kinetic energy distributions and threshold energy measurements. These results can be "extrapolated" to dissociative ionization work. Furthermore, Böse and Sroka [24] examined various H (Lyman) emissions produced by electron impact on NH_3 without kinetic energy measurements.

Carnahan et al. [6] measured the first onset at 17.8± 0.8 and 23.2 ± 0.7 eV for H(n=2) and H (Rydb.) atoms respectively. For both processes the minimum translational energy carried by the H atom is about 0.1 eV. Kurawaki and Ogawa [7] observed the first onset at 21.0 ± 0.8 and 22.5 ± 0.8 eV for H(n=3) and H(n=4) atoms carrying respectively 1.0 eV and 1.0 eV kinetic energy. None of these energies correlate with a dissociative ionization appearance energy of 19.5 ± 2 eV. However, Böse and Sroka [24] measured an onset at 16.1 ± 0.4 eV for H (Lym.-α). When the energy difference of IE(H) — EE(H, n=2) = 3.4 eV is added to this value, a threshold of 19.5 ± 0.4 eV is obtained for H^+/NH_3.

In fig. 7 two onsets are observed around 22.6 eV, i.e. 22.6 ±0.3 eV, in the kinetic energy range 0-0.8 eV (see straight line (2)), and 22.4 ± 0.1 eV (see vertical line (3)). This latter process is observed over the 2.8-4.3 eV kinetic energy range. Fig. 8 shows the result of the same measurements for D^+/ND_3.

At 22.6 ± 0.3 eV enough energy is available to produce the proton through

$$\begin{aligned} &NH_3 + e^- \\ &\longrightarrow NH_3^{**}(\text{autoionization}) + e^- \\ &\qquad \hookrightarrow NH(X\,^3\Sigma^-) + H(^2S_g) + H^+ \\ &\qquad\qquad + KE(0\,eV) + e^- , \end{aligned}$$

for which the lowest onset is calculated at 22.01 ± 0.2 eV from the data listed in table 2. The higher excitation of NH_2 although possible cannot be considered because of lack of data. If the energy difference of 0.5 ± 0.3 eV in excess between experimental and calculated threshold is significant, it would be ascribed to internal energy of the NH radical, since no translational energy is available at the onset (see diagram (2) in fig. 7). From the following discussion, most likely, the excess energy above the onset is partitioned between vibrational and translational energy.

The straight line (2) starting at 22.6 ± 0.3 eV is the result of a least-squares fit, has a slope of 0.89 and extrapolates to 22.51 eV. The correlation coefficient is rather poor, i.e. 0.93. The expected slope of H^+, produced through the abovementioned process, is roughly given by $m_{NH}/2m_{NH3}$ = 0.44. Notwithstanding the poor correlation, the discrepancy between experimental and expected slope is large. Furthermore, when the same fit is applied to the corresponding data of D^+/ND_3 (see fig. 8, line (2)), a straight line with a slope of 0.54 and extrapolating to 22.47 is obtained. The correlation is also 0.93. The slopes are significantly different: the eight onsets measured for D^+ are systematically higher than the corresponding data for H^+. Moreover, as evidenced earlier in this discussion, for a diatomic radical $\rho=(v^i/v)^2= \mu/\mu^i=0.94/1.75=0.54$, whereas $s_i/s\approx 0.5/0.9\approx$ 0.55. These arguments tend to support a partition of the total excess energy between vibrational and translational energy.

To account for the experimental results a two-step proton production mechanism has to be invoked, i.e.

$$\begin{aligned} &NH(D)_3 + e^- \rightarrow NH(D)_3^{**} \\ &\quad \rightarrow NH(D)_2^+ + H(D) + 2e^- , \\ &NH(D)_2^+ \rightarrow NH(D)(X\,^3\Sigma^-) + H(D)^+ , \end{aligned}$$

where the proton carries 15/16=0.94 of the total translational energy, close to the observed slope. This agreement would suggest total energy conversion into translational energy. Expecting the same reaction sequence in ND_3, the theoretical slope for D^+ would be 0.88 while the observed one is 0.54. This discrepancy can only be ascribed

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to the excess energy partitioning between translational and vibrational energy. This latter would account for the abovementioned isotope effect.

At about the same energy, i.e. 22.4 ± 0.1 eV, a vertical line followed by a straight line is observed. The least-squares fit of the data points (3) in the diagram of fig. 7 gives a straight line with a slope of 0.93 and extrapolates to 19.31 eV. The correlation coefficient is 0.97. The corresponding data for D^+/ND_3 (see fig. 8) are in very good agreement. Compared to the expected slope of 0.94, straight line (3) is related to a dissociative ionization process where the excess energy is entirely converted into translational energy of the fragments. The slope of 0.93 and the extrapolated appearance energy $AE_{KE=0}$= 19.3 eV clearly indicate that H^+ is produced by the process

$$\begin{aligned} &NH_3 + e^- \\ &\longrightarrow NH_3^*(\text{autoionization}) + e^- \\ &\qquad \hookrightarrow NH_2(\tilde{A}\,^2A_1) + H^+ + e^- \\ &\qquad\qquad + KE(2.9\text{–}4.3\ \text{eV})\ . \end{aligned}$$

The excess energy with respect to the dissociation limit is entirely converted into translational energy carried away by the fragments.

As already mentioned elsewhere [1], at the energy of 22.6 eV several dissociation processes have been observed, leading to NH_2^+ and NH^+. However, the photoelectron spectrum of NH_3 clearly shows no cross section for ionization of NH_3 at this energy [25]. As suggested earlier, the intermediate state of NH_3 producing NH_2^+, NH^+ and H^+ has to be a neutral super-excited state which could have a Rydberg character. In this case this state could be a member of a series converging to the NH_3^+ ($\tilde{B}^2A_1$) state whose adiabatic ionization energy is 24.0 eV [25]. The photoelectron band at this energy is structureless, the $\tilde{B}^2A_1$ state could be considered as unstable at least in the Franck-Condon region. The NH_3^* state giving rise to the abovementioned processes would have the same property.

The comparison with previous electron impact work is more feasible in the energy range of 22.5 eV. Mann et al. [2] measured the first onset of H^+ at 22.5 ±0.5 eV and interpreted this threshold by the formation of NH and H. Mark et al. [3] observed the first appearance energy of the proton at 23.0 ± 0.2 eV, without interpretation.

Considering the dissociative excitation experiments involving H*(*n*) and H(Rydb.) atoms, most experiments agree fairly well by measuring an onset near 22.5 eV, i.e. 22.5±0.8 eV for H(*n*=4) carrying 1-3 eV kinetic energy [7] and 23.7±0.7 eV for H (Rydb.) carrying 0.4-4 eV kinetic energy [6]. Böse and Sroka [24] determined a second onset for H(Lym.-α) at 21.8 ± 0.8 eV. The authors agree to assign to these energies the same process

$$NH_3 + e^- \rightarrow H^* + H + NH + e^-\ ,$$

but only Kurawaki and Ogawa [7] were able to distinguish two H(*n*=4) contributions at 22.5 ± 0.8 eV, i.e. that with 1 eV kinetic energy is ascribed to the abovementioned process, whereas a 3 eV kinetic energy component is assigned to

$$NH_3 + e^- \rightarrow NH_2 + H(n=4) + e^-\ ,$$

in agreement with the present work. Carnahan et al. [6] ascribed the H(2s) and H(Rydb.), at 21.8 and 23.2 eV respectively, to the same process involving, however, 0.4-10 eV kinetic energy.

A vertical line spread over 6 eV translational energy carried by H^+ is observed at 26.2 ± 0.1 eV. A straight line (4) in fig. 7, defined by only three data points, extends to about 7 eV with a slope of 0.55. This value has to be compared with either (i) 0.94 if the proton is produced through the dissociation of the NH_2^+ into NH and H^+ or (ii) 0.44 when H^+ is directly produced by dissociative ionization of NH_3 together with NH and H. When the former process takes place, the discrepancy between observed and calculated slopes could be ascribed to the excess energy partition between translational and internal energy of the polyatomic fragment. In this case an isotope effect ought to be observed. The results on D^+/ND_3 at the same energy (see fig. 8) do, however, not differ significantly. When the latter process is involved, both slope values are in fairly good agreement and no

drastic isotope effect on the slope, i.e. 0.4 instead of 0.44, is expected.

However, taking into account the minimum translational energy of 6 eV, i.e. 13.6 eV in terms of total kinetic energy, and the onset at 26.2 eV, a minimum appearance energy $AE_{KE=0}$=12.6 eV is calculated. This energy does not fit any dissociative ionization limit of NH_3^+.

Altogether these arguments strongly suggest that the proton is produced at 26.2 eV by dissociative ionization of H_2. It will be shown in section 4.2 that free H_2 is produced by thermolysis of NH_3 on the electron emitting filament.

A further reason to suspect the H^+/H_2 production is that Köllman [13] measured an onset at 26.1 ±0.5 eV, in very good agreement with the present value. However, the translational energy range covered by these protons is 4.5-8.0 eV; for 6 eV kinetic energy the onset is about 29 eV.

Despite these evidences, there still remain arguments for the direct H^+ production from NH_3 at 26.2 eV. (i) The isotope effect is not observed because of the restricted number of data points in diagram (4) in fig. 8. (ii) Starting from 6 eV kinetic energy, an appearance energy $AE_{KE=0}(H^+)$ = 19.7 eV, very close to 19.5 eV (the first onset ascribed to H^+/NH_3), is obtained, (iii) The energy of 26.2 eV corresponds to the vertical ionization energy of the $NH_3^+(\tilde{B}^2A_1)$ state [25] which is known to give rise to fragments with large amounts of kinetic energy [1].

In the high electron energy range, i.e. above 34 eV, four appearance energies are measured: 34.9 ± 0.4, 36.2 ± 0.3, 39.2 ± 0.2 and 45.7 ± 0.4 eV. The same results are obtained for D^+/ND_3. The kinetic energy versus appearance energy diagrams related to these critical energies are shown in fig. 7 by vertical lines (5), (7) and (6) respectively. The last onset being observed for $0.0 < V_R < 0.9$ V has not been included in this figure.

As mentioned earlier [1], dissociation processes of doubly ionized NH_3 states are mainly involved in this energy range. Ionization energies corresponding to NH_3^{2+} formation were measured at 34.9 ± 0.2 and 39.4 ± 0.5 eV [10]. By PIPICO a doubly ionized state is observed at 44.5 ± 0.5 eV [26]. When doubly ionized states dissociate into singly ionized fragments, the appearance energy for both species must be equal. Some of these processes have already been discussed in the frame of the NH_2^+ (ND_2^+) and NH^+ formation from NH_3 [1].

The H^+ (D^+) ions appearing at 34.9 ± 0.4 eV, spread over 8 eV translational energy, are probably related to the NH_2^+ (ND_2^+) ions observed at 35.4 ± 0.3 eV. This onset was ascribed to

$$\begin{aligned} ND_3 + e^- &\longrightarrow ND_3^{2+}(^1A_1, (3a_1^{-2})) + 3e^- \\ &\hookrightarrow ND_2^+(^1A_1) + D^+ , \end{aligned}$$

for which an onset energy is calculated at 30.5 eV (see data listed in table 2). The energy difference of about 35.4 - 30.5 = 5 eV between observed and calculated onsets is ascribed to translational energy carried by both ND_2^+ and D^+, i.e. 0.5 and 4.5 eV respectively. As for ND_2^+ a translational energy of 0.7 eV is measured [1], D^+ is observed up to 8 eV. Above 5 eV kinetic energy, protons could be produced with other fragments, i.e. H^+, NH^+ and N^+. For NH^+ no threshold is observed in the vicinity of 35 eV [1]. Moreover, these protons being of low intensity, H^+ ions produced by the dissociation of H_2^+ ($^2\sum_u^+$) could become important [13]. As mentioned earlier, free H_2/NH_3 is known to be formed. The large scattering of the data above 5 eV does not allow a least-squares fit.

No comparison can be made with previous electron impact data. Only Mark et al. [3] mention an onset at 30.6 ±0.5 eV. No critical energy is found in the energy range 26-34 eV in the present work. However, H(*n*=4) and H(Rydb.) atoms have been observed with excitation thresholds at 33.3 ± 1.2 eV [7] and 33.8 ± 1.0 eV [6], respectively. The former fragments carry 4-5 eV kinetic energy whereas the latter are produced with 3.5-8.2 eV kinetic energy. These processes could be related to the protons observed at 34.9 ± 0.4 eV with kinetic energies higher than 5 eV.

By photoionization [26], H^+ and NH_2^+ coincidences are measured at 35.4 ±0.5 eV in good agreement with both D^+ and ND_2^+ onsets observed by electron impact in this work.

The appearance energy at 39.21 0.2 eV is observed for $5.0 < V_R < 8.0$ V retarding potential. The simultaneous observation of a double-ionization energy of NH_3 at 39.4 ± 0.5 eV would suggest that this state dissociates [10]. Though 8 eV protons could be formed through

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$$\begin{aligned} &NH_3 + e^- \\ &\longrightarrow NH_3^{2+}[{}^1E, (2e^{-1})(3a^{-1})] + 3e^- \\ &\qquad \hookrightarrow NH_2^+ + H^+ + KE(8.5\,eV)\,, \end{aligned}$$

no onset is observed at this energy for NH_2^+ nor NH^+ [1]. An alternative explanation of this critical energy would be the dissociation of a highly excited, singly ionized NH_3^+ state. In this case the NH_3^{2+} ionic state would be formed through autoionization which would compete with dissociation. Kurawaki and Ogawa [7] determined an excitation onset for H(n=4) atoms at 38.4 ± 1.5 eV carrying 8-12 eV kinetic energy. Through the "core-ion" model, the corresponding dissociative ionization process would lie at about 39.3± 1.5 eV accounting for IE(H)-EE(H,n= 4) = 0.85 eV. However, no H(Rydb.) atoms have been detected in this energy range by Carnahan et al. [6].

Between 34.9 and 39.2 eV an onset at 36.2 ± 0.3 eV is less clearly observed in the first differentiated ionization efficiency curve of H^+, but could be observed up to 4.3 eV kinetic energy. As it has already been pointed out [1], appearance energies were measured at 36.6 ± 0.3 and 36.2 ± 0.4 eV for ND_2^+/ND_3 and NH^+/NH_3, respectively. It has been shown that the NH^+ formation occurs through

$$\begin{aligned} &NH_3 + e^- \rightarrow NH_3^{2+}({}^3E/{}^1A_1) \\ &\rightarrow NH^+(X\,{}^2\Pi) + H_2^+(X\,{}^2\Sigma_g^+) + 3e^-\,. \end{aligned}$$

The corresponding threshold for ND_2^+ has been interpreted by

$$\begin{aligned} &ND_3 + e^- \rightarrow ND_3^{2+}({}^3E) \\ &ND_2^+(\tilde{X}\,{}^3B_1) + D^+ + 3e^-\,. \end{aligned}$$

The onset for this process is calculated at 29.5 eV, using the data listed in table 2. The amount of total translational energy carried away by the fragments in this process would be 6.7 eV, i.e. 6 eV by D^+ and 0.7 eV by ND_2^+. Experimentally ND_2^+ is observed up to 0.9 eV whereas the D^+ ion could be measured up to 4.3 eV kinetic energy.

As mentioned in section 3, the appearance energy at 45.7 ± 0.4 e V could only be measured with a reasonable accuracy up to 1.0 eV kinetic energy. At this energy the H^+ contribution very rapidly decreases with increasing retarding potential and the signal/noise ratio becomes worse.

For ND_2^+ as well as NH^+ a threshold energy is measured at 46.5 ± 0.4 and 46.4 ± 0.5 eV; the ions carrying at least 0.7 and 0.9 eV translational energy respectively [1]. Probably these critical energies are related to one another. In addition PIPICO measurements were performed in this energy range and a component, unresolved with respect to m/e= 14 and m/e= 15, has an onset at 44.5±0.5 eV. On the other hand, H(n=4) [7] H(Rydb.) atoms [6] were observed up to 41.7±1.7 eV with translational energies of 8-12 eV.

At this energy, the proton is very likely produced through both

$$\begin{aligned} &NH_3 + e^- \longrightarrow NH_3^{2+} \\ &\qquad \longrightarrow NH^+(A\,{}^2\Sigma^-) + H({}^2S_g) + H^+ + 3e^-, \\ &\qquad \hookrightarrow NH_2^+(?) + H^+ + 3e^-\,, \end{aligned}$$

even when for experimental reasons H^+ (D^+) could not be observed at V_R > 1.0 V. On the basis of the data listed in table 2 and the observed 7.6 eV total translational energy carried by NH^+ [1], the energy required for the abovementioned NH^+-producing process is 45.8 eV.

In the NH_2^+ dissociation channel, the measurements were performed on ND_3. On ND_2^+ only 0.7 eV kinetic energy is measured, i.e. 7 eV total translational energy. The D^+ ion is observed up to 1 eV kinetic energy. The highest dissociation limit for ND_2^+ formation, which could be calculated from the data listed in table 2, lies at 32.7 eV. By adding 7 eV total translational energy of the fragments, an energy of 39.7 eV is obtained. The energy difference of about 7 eV between the observed onset and the foregoing energy balance could only be

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ascribed to the excitation of ND_2^+.

4.2. The H_2^+ (D_2^+) dissociation channel

The lowest appearance energy measured for both H_2^+ and D_2^+ (see figs. 10 and 11) lies at 15.5 ± 0.2 eV. This value is in very good agreement with that published by Mann et al. [2], who observed only one onset at 15.5 ± 0.5 eV. Mark et al. [3] mentioned a threshold at 14.8 ± 0.2 eV.

At this energy the first differentiated ionization efficiency curve rises very steeply and this part of the curve is suppressed by applying 0.2 V retarding potential. The H_2^+ (D_2^+) ions produced at 15.5 eV are thermal and are the only contribution to the thermal peak observed in the kinetic energy distribution displayed in fig. 9. Moreover, the ionization energy of molecular H_2 is 15.496 eV (see table 2), in very good agreement with the onset energy for H_2^+ (D_2^+) in this work. Together these arguments strongly suggest that free H_2 is produced from NH_3 in the ion source (likely by thermolysis on the electron emitting filament). The same phenomenon is observed for ND_3.

The first onset ascribed to H_2^+ (D_2^+) formation through dissociative ionization of NH_3 (ND_3) lies at 22.3 ± 0.2 eV. Its dependence upon the retarding potential is given by a vertical line (1) in fig. 12. Within experimental error, the data related to H_2^+" and D_2^+ behave in the same way.

The lowest threshold which could be calculated for H_2^+ production from NH_3 is at 19.45 ± 0.18 eV by using the data listed in table 2. This energy corresponds to the reaction

$$\begin{aligned} &NH_3 + e^- \\ &\longrightarrow NH_3^*(\text{autoionization}) \\ &\quad \longrightarrow H_2^+(X\,^2\Sigma_g^+) + NH(X\,^3\Sigma^-) + 2e^- . \end{aligned}$$

Experimentally both H_2^+ and D_2^+ carry away 3.4 eV kinetic energy. The appearance energy $AE(H_2^+)_{KE=0}$=22.3-3.4Xl7/15 = 18.5 eV. This value is lower than that for the predicted dissociation mechanism mentioned above. The discrepancy between calculated onset and latter value is about 1.0 ±0.4 eV. In the discussion of the results on the NH_2^+ and NH^+ ion formation [1], discrepancies of 0.24 ±0.13 and 0.5 ± 0.3 eV have already been mentioned. They were ascribed to an overestimate of one or both dissociation energies *D* (NH_2-H) and (NH-H).

Considering all the fragment ions studied so far, appearance energies are measured at about 22.6 eV for NH_2^+ [1], NH^+ [1], H^+ (see table 1) and H_2^+. This critical energy lies where no ionization cross section is measured for NH_3 [25]. All abovementioned ions are formed with large amounts of kinetic energy. The neutral NH_3* state is very likely a Rydberg state, member of a series converging to the NH_3^+ ($\tilde{B}^2A_1$) state. This latter being almost dissociative, the NH_3^* state is very probably unstable in all the dissociation channels. Therefore dissociative autoionization will be the most probable mechanism of H_2^+ formation at 22.3 eV.

From 26.6 ±0.3 eV the first derivative of the ionization efficiency curve of H_2^+ (D_2^+) rises more steeply. The kinetic energy versus appearance energy plot is shown in fig. 12 by diagram (2). Owing to the scattering of the measurements, the data related to H_2^+ and D_2^+ are not distinguishable. From 0.2 eV translational energy, the data more or less clearly deviate from a vertical line at about 26.6 eV.

Taking into account all the measurements related to both H_2^+ and D_2^+, the best correlation is found when gathering the data into two groups. Two fits are found by this way: (i) a first straight line between 0.2 and 1.4 eV kinetic energy, with a slope of 0.9 extrapolating to 26 eV with a correlation of 0.8 and (ii) a second straight line spread over 1.4-2.0 eV with a slope of 0.35 extrapolating to 23.0 eV with a correlation coefficient of 0.95.

The slope expected for the kinetic energy versus appearance energy straight line depends on the dissociation mechanism involved,

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$$\begin{aligned} NH_3 + e^- &\longrightarrow NH + H_2^+ + 2e^- , && (a)\\ &\longrightarrow N + H + H_2^+ + 2e^- , && (b)\\ &\longrightarrow NH_2^+ + H \longrightarrow N + H_2^+ + 2e^- , && (c) \end{aligned}$$

i.e. roughly 0.88, 0.27 and 0.87 for reactions (a), (b) and (c) respectively.

The slowest rising straight line has to be related to reaction (b): (i) the experimental slope of 0.35 compares favourably with the expected value of 0.27 and (ii) the extrapolated threshold of 23 eV is close to the calculated onset of 23.1 eV. The steeply rising straight line could be ascribed to either reaction (a) or (c) or both. Using the data of table *2,* the corresponding appearance energies are 19.51 and 23.12 eV. Introducing the excitation energy of NH, the highest dissociation limit calculated for reaction (a) is 24.9 eV. For the two-step reaction (c), when both the parent ion NH_2^+ and the product N contain excitation energy, i.e. are formed in the ã $^1A_1$ and ^2D state respectively (see table 2), an onset of 26.46 eV can be calculated. This value is comparable to the extrapolation at 26 eV.

These processes have to occur through the NH_3^+ ($\tilde{B}^2A_1$) state, whose vertical ionization energy lies at about 26 eV and which very probably is unstable in the Franck-Condon region. The dissociation of NH_3^+ at the expense of the same state has been observed for NH^+ and H^+ but not for NH_2^+. The latter ion would be formed, but spontaneously dissociates through reaction (c).

In the high electron energy range only one onset is measured for H_2^+ (D_2^+) at 35.7 ± 0.4 eV. This threshold is observed up to 3.4 eV translational energy (see vertical line (3) in fig. 12). In this energy range double ionization of NH_3 occurs [10] as well as dissociation of doubly ionized states [1,26]. In this case the two singly ionized species will have the same appearance energy and will share the same total translational energy.

Energetically the lowest dissociation process leading to H_2^+ from a doubly ionized state is

$$\begin{aligned} NH_3 + e^- &\rightarrow NH_3^{2+}\\ &\rightarrow H_2^+(X\,^2\Sigma_g^+) + NH^+(X\,^2\Pi) + 3e^- , \end{aligned}$$

for which an onset is calculated at 32.8 eV by using the data listed in table 2.

For the NH^+ ion, the threshold measured at 36.2 ±0.4 eV [1] agrees within experimental error with the onset measured for H_2^+. Furthermore, on NH^+ a kinetic energy of 0.4 eV is observed, i.e. 0.4x17/2=3.4 eV total translational energy. For H_2^+ a total kinetic energy of 3.4x17/15 = 3.85 eV is estimated. From both measurements the energy level of the dissociation limit is given by the energy difference 35.7(36.2)-3.85(3.4) =31.85(32.8) eV.

Taking into account the accuracy on the data, the fairly good correlation between the measurements on NH^+ and H_2^+ as well as the closeness of calculated and experimentally derived dissociation limits allow us to ascribe the abovementioned dissociation mechanism to the appearance energy of H_2^+ at 35.7 eV. However, no conclusion can be drawn whether the NH_3^{2+} state involved is a $^1A_1$ or a ^3E state.

5. Conclusion

The dissociative ionization of NH_3 in both the H^+ and H_2^+ dissociation channels has been investigated by recording the translational energy distribution of both species at different electron energies and by measuring their appearance energies at increasing retarding potential. The simultaneous examination of D^+ and D_2^+ formation from ND_3 has proved to be helpful in the discussion of the experimental results.

At the lowest onset, only H^+ is directly produced by dissociative ionization of NH_3, very likely through the NH_3^+ ($\tilde{A}^2E$) state. Vibronic energy of NH_2 has to be involved in this process. This is confirmed by an isotope effect due to ND_2 on the slope of the kinetic ' energy versus appearance energy diagram. The H_2^+ ion is produced by direct ionization of H_2 formed by thermolysis of NH_3 on the electron emitting cathode.

In the energy range 20-26 eV, both species are produced by dissociative autoionization at about 22.5 eV and direct dissociative ionization at 26 eV. However, some evidences are brought to show that a part of the H^+

ion current, formed at 22.6 eV, is produced by the spontaneous dissociation of NH_2^+. The same mechanism is invoked for a part of the H_2^+ ion current observed at 26.2 eV. The H^+ ions appearing at this latter energy could be produced by dissociative ionization of H_2.

In the high electron energy range of 35-50 eV, mainly direct dissociation of doubly ionized states of NH_3 is involved. Most of the processes invoked to account for the experimental data have already been discussed for the appearance of NH_2^+ and NH^+ from NH_3 in a previous work [1]. Though a double ionization energy of NH_3 was measured at 39.5 eV and an H^+ formation threshold at about the same energy, very likely a dissociation of a highly excited, singly ionized NH_3 state is involved.

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