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Electron-impact dissociation and ionization of NH^+ : formation of N^+ and N^{2+}

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Abstract

Absolute cross sections for electron-impact dissociation and ionization of NH^+ leading to the formation of N^+ and N^{2+} products have been measured by applying the animated electron-ion beam method, in the energy range from the respective thresholds up to 2.5 keV. The maximum total cross sections are observed to be $(15.7 \pm 0.7) \times 10^{-17} \text{cm}^2$ and $(11.1 \pm 0.2) \times 10^{-18} \text{cm}^2$ for N^+ and N^{2+} , respectively. Absolute cross sections are determined separately for dissociative excitation and for dissociative ionization processes. The measurements for slow N^+ ions show a noticeable contribution in the low incident electron energy range; these data are attributed to excitation processes. Dissociative excitation is assumed to play a significant role in the collision energy region close to the vertical excitation energies for the lowest electronic transitions in the Franck-Condon region. The yields of fast N^+ ions have also been measured; these energetic dissociations are generally ascribed to ionization processes. Kinetic energy release distributions are seen to extend from 0eV to 15eV for the N^+ fragments and up to 20eV for the N^{2+} ones. Present energy thresholds and kinetic energy release results are compared with available published data, allowing in some cases identification of fragmentation patterns and of molecular states contributing to observed processes. The possibility of dissociative excitation of the molecular ion which could occur via a mechanism involving autoionizing resonances is discussed.

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Key words: ammonia, imidogen, nitrogen, diatomic hydride, molecular ion, electron-ion collision, excitation, ionization, dissociation, electron-impact, absolute cross sections, kinetic energy release.

1. Introduction

The imidogen radical NH is an extremely important species in nitrogen chemical reaction patterns in atmospheric or interstellar media. Its astrophysical observations have a long history and, from the spectroscopic point of view, intense studies were started from as early as 1935 by Lunt *et al.* The NH radical has been observed in the sun (Babcock 1945), in many comets (Meier *et al* 1998) and in stellar atmospheres (Lambert and Beer 1972). Furthermore, the NH^+ cation is considered to be the first step in the formation of ammonia in interstellar molecular clouds (Galloway and Herbst 1989) and it is very plausible that NH^+ is also present in the gas tail of comets. Accordingly, interstellar and protostellar chemistry models contain up to a hundred nitrogen-containing species (Woodall *et al* 2007). An additional interest to determine the properties of NH and NH^+ has been stimulated by studies concerning the combustion of nitramine propellants that are widely used as fuel in astronautic and in aeronautic applications (Adams and Shaw 1992). The NH^+ ion has so far been much less studied than the neutrals NH or CH. Given that NH^+ and CH are isoelectronic molecules, one can get information from parallel studies of their analogous states (Kalemos *et al* 1999). It should be noted however that the order of the two first excited doublet states in CH and NH^+ are reversed, i.e. the sequence $X^2\Pi$ (ground state), $A^2\Delta$, $B^2\Sigma^-$ and $C^2\Sigma^+$ in CH corresponds to the sequence $X^2\Pi$, $A^2\Sigma^-$, $B^2\Delta$, and $C^2\Sigma^+$ in NH^+ (Table 1).

There are numerous possible precursors of NH^+ containing N and H atoms and various chemical reactions can be mentioned for the formation of NH^+ . The exothermic reaction $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$ (rate constant $1.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) is likely to take place in environments where most hydrogen exists as H_2 and where N^+ would result from the ionization of atomic nitrogen (Mitchell *et al* 1978). In a similar way, the charge transfer reaction $\text{N} + \text{H}_2^+ \rightarrow \text{NH}^+ + \text{H}$ (rate constant $1.9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) is also a possible source of NH^+ (Barsuhn 1977).

Although a lot of work has already been done in understanding molecular dynamics, a recurrent difficulty in the study of the dissociation of even simple diatomic molecules is the measurement process by itself. To extract clear information on the dissociation of a typical molecular ion, one needs to be able to discern between the dissociation paths but this can prove challenging. The detection of the charged fragment is not always enough to clearly separate the channels, especially in the case of ionization. With this idea in mind, the dissociation branching ratio of ND^+ has recently been studied by using intense femtosecond laser pulses (McKenna *et al* 2008). To enable a clean measurement of the branching ratio of the two possible dissociation channels, $\text{N}^+ + \text{D}$ and $\text{N} + \text{D}^+$, a 3D imaging technique has been

used. The kinetic energy release and angular distributions of each channel have also been mapped. The ratio of the two dissociation channels was found to be very sensitive to [the laser intensity](#). The result indicates that it is more difficult to dissociate to $N+D^+$ than N^++D , thus requiring higher [laser intensity](#).

[Table 1 and Figure 1](#)

NH^+ is a seven-electron system which arrangements give rise to a multiplicity of states. The electronic configuration of the lowest-lying electronic state ($X^2\Pi$) is described by $1\sigma^2 2\sigma^2 3\sigma^2 1\pi$. The electron excitation requiring the smallest amount of energy involves a transition from the doubly excited 3σ molecular orbital into the nearest partly unoccupied 1π , therefore the configuration $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($\sigma\pi^2$ configuration) leads to the first excited states ($a^4\Sigma^-$, $A^2\Sigma^-$, $B^2\Delta$ and $C^2\Sigma^+$). The next excitation involves the two-electron excitation $3\sigma^2 \rightarrow 1\pi^2$ yielding to the configuration $1\sigma^2 2\sigma^2 1\pi^3$ that produces a single electronic state $2^2\Pi$ (π^3 configuration). In the present article, the energies are determined with respect to the minimum energy of the NH^+ ground electronic state ($X^2\Pi$) at the equilibrium distance ($r_e = 2.02 \text{ a.u.}$), [the energy of which is taken as zero](#). The first excited electronic state $a^4\Sigma^-$ is metastable and it lies only 0.04 eV above the ground electronic state (Colin and Douglas 1968). These two states, $X^2\Pi$ and $a^4\Sigma^-$, are overlapped and they display a strong mutual perturbation (Farnell and Ogilvie 1983). Perturbations were explored in details by Colin (1989) and more recently, Huberts *et al* (2009) reported the analysis of the rotational spectrum of NH^+ in the $v=0$ levels of its $X^2\Pi$ and $a^4\Sigma^-$ states.

The first five excited electronic states of NH^+ (namely $a^4\Sigma^-$, $A^2\Sigma^-$, $B^2\Delta$, $C^2\Sigma^+$ and $2^2\Pi$) resulting from the first two excited configurations ($1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ and $1\sigma^2 2\sigma^2 1\pi^3$) are predicted to be the lowest excited states lying above the ground state. They order in the following way in the Franck-Condon region: $X^2\Pi < a^4\Sigma^- < A^2\Sigma^- < B^2\Delta < C^2\Sigma^+ < 2^2\Pi$ (Figure 1). Five electronic states have been observed so far, the ground state $X^2\Pi$ and the first four excited states ($a^4\Sigma^-$, $A^2\Sigma^-$, $B^2\Delta$ and $C^2\Sigma^+$), all five are bound. The ground state $X^2\Pi$ dissociates to the second limit $N^+(^3P)+H(^2S)$ and not to the lowest dissociation limit $N(^4S)+H(^1S)$. The calculated dissociation energy into $N^+(^3P)+H(^2S)$ is $D_e(X^2\Pi) \geq 4.54 \text{ eV}$ (Amero and Vázquez 2005), which agrees with the measured value of 4.66 eV (Tarroni *et al* 1997). The first excited electronic state $a^4\Sigma^-$ dissociates to the first dissociation limit $N(^4S)+H(^1S)$ and the corresponding calculated dissociation energy is $D_e(a^4\Sigma^-) \geq 3.72 \text{ eV}$ (Amero and Vázquez 2005), matching well the measured value $D_e = 3.66 \text{ eV}$ (Tarroni *et al* 1997). The second

excited state $A^2\Sigma^-$ is the lowest excited doublet of NH^+ and its calculated dissociation energy is $D_e(A^2\Sigma^-) \geq 1.70\text{eV}$. The third excited electronic state $B^2\Delta$ dissociates to the third dissociation limit, $N(^2D)+H^+(^1S)$, and the calculated dissociation energy for this state is $D_e(B^2\Delta) \geq 3.25\text{eV}$. The vertical energies for $A^2\Sigma^-$ and $B^2\Delta$ are degenerated and the potential curves corresponding to these two states cross at $\sim 2.1\text{a.u.}$. $C^2\Sigma^+$ is the last of the lowest excited state of NH^+ that exhibits a noticeable dip in its potential curve. The calculated dissociation energy of $C^2\Sigma^+$ is $D_e(C^2\Sigma^+) \geq 2.17\text{eV}$ and the $C^2\Sigma^+$ state correlates to the dissociation limit $N^+(^1D)+H(^2S)$. The $2^2\Pi$ state, which presents only a shallow dip, appears to be predissociative and it also dissociates to the third dissociation limit $N(^2D)+H^+(^1S)$. The $2^2\Pi$ state in NH^+ corresponds to the $D^2\Pi$ state of the isoelectronic CH radical. The $D^2\Pi$ state of the CH radical is clearly bound whereas the $2^2\Pi$ state is repulsive or perhaps metastable. All the remaining states appear to be repulsive, except for some highly excited states (e.g. $2^4\Pi$, $3^2\Delta$ and $3^6\Pi$) (Figure 1, Amero and Vázquez 2004). Table 2 lists the vertical excitation energies of many other higher electronic states of NH^+ , [the dissociation limits of which have not been specified although they can be of importance in the present study](#). Electronic states with the same symmetry and multiplicity may give rise to avoided crossings that make difficult the unequivocal assignment of dissociation limits.

Table 2

The dication $NH^{2+}(X^1\Sigma^+)$ ground state belongs to the $1\sigma^2 2\sigma^2 3\sigma^2$ configuration and it results from the single ionization process, ejection of the electron from the 1π molecular orbital of the monocation $NH^+(X^2\Pi)$. The $NH^{2+}(X^1\Sigma^+)$ potential energy curve is predissociative. It shows a shallow minimum, which depth is 0.11eV , separated by a barrier from the steeply Coulombic repulsive portion of the curve leading to the dissociation limit located 6eV below the minimum. The $X^1\Sigma^+$ state is quasi-bound, nevertheless, given the shallowness of the dip, it is difficult to assess on whether this state is totally repulsive or whether it can contain a vibrational level conferring a metastability. It is worth noting that the dissociation limit of this state corresponds to fragmentation into the second dissociation limit $N^+(^1D)+H^+(^1S)$. As for the first dissociation asymptote $N^+(^3P)+H^+(^1S)$, it lies 1.90eV below the $N^+(^1D)+H^+(^1S)$ one. The vertical ionization potential of the monocation is calculated to be 26.64eV (Amero and Vázquez 2004). This theoretical value is higher than the experimental one ($25 \pm 1\text{eV}$, Proctor *et al* 1981) and slightly lower than the other theoretically predicted one (26.9eV , Pope *et al* 1983 and Koch and Schwarz 1986). The first dissociation limit leading to products without charge separation, $N^{2+}(^2P_{1/2})+H(^2S)$, lies 14.11eV above the $N^+(^1D)+H^+(^1S)$

limit. Hamdan *et al* (1988) performed computations on NH^{2+} indicating that the first excited singlet state ($^1\Pi$ symmetry) would lie 8eV above the ground state while several triplet states would lie in the energy region of 2–4eV above the ground state. Among these states, the metastability of the dication is governed by the $X^1\Sigma^+$ ground state. All the other states appear to be purely repulsive and they should thus play a role in the dissociation processes. The stability of the dication is a subject of conflict between experimentalists: Hamdan *et al* (1988) reported long-lived states of NH^{2+} whereas Proctor *et al* (1981) indicated that NH^{2+} seemed to be unstable and rapidly fragment before reaching the detector.

Characterization of electron-impact cross sections for important atmospheric species is updated thanks to the experimental set-up built up in Louvain-la-Neuve. For instance, experiments of electron interaction with N_2^+ (Bahati *et al* 2001), O_2^+ (Cherkani-Hassani *et al* 2006) and CO^+ (Lecointre *et al* 2006) have already been carried out. High-quality experimental results are thus provided in a form which is convenient to complete databases needed for astrophysical studies.

In the present article, results for electron-impact dissociation and ionization of NH^+ are reported for the formation of N^+ and N^{2+} from their respective appearance thresholds up to 2.5 keV. After the collision, NH^+ dissociates into two different ionic channels resulting in the formation of singly charged atomic products, N^+ and H^+ , which are described by the following reactions:

Dissociative excitation (DE) processes are represented by reactions (1) and (2) whereas the dissociative ionization (DI) process is represented by reaction (3). Reaction 2 has not been studied as the light fragment H^+ could not have been detected because of non-favorable experimental conditions (technical hitches in collecting the ions). The N^+ ion production cross sections σ_{N^+} corresponds to the sum of the dissociative excitation and the ionization processes such that a specific procedure (briefly presented hereafter) was developed to estimate σ_{DE} and σ_{DI} separately. In addition, doubly-charged ions can be produced by asymmetric dissociative ionization (ADI, N^{2+} formation) and by single ionization (SI, NH^{2+} formation), as follows:

The total absolute cross sections for the doubly charged products (N^{2+} σ_{ADI}) are

discussed without attempting to detail contributing processes (reaction 4). Present experimental observations are not conclusive with regards to the stability of the NH^{2+} ion toward dissociation (reaction 5). The $^{14}\text{NH}^+$ primary ion beam (mass-to-charge ratio 15) is contaminated with a small fraction of $^{15}\text{N}^+$ (below 2%). As a consequence, the possible $^{14}\text{NH}^{2+}$ ion is likely to be contaminated with the $^{15}\text{N}^{2+}$ ion (of identical mass-to-charge ratio 7.5), as a results of electron-impact on $^{15}\text{N}^+$.

The experimental set-up, the procedure and the data analysis method are briefly reviewed hereafter allowing the estimation (i) of the absolute cross sections and (ii) of the kinetic energy release distributions (KERDs). The third section is devoted to the presentation and the discussion of the results obtained for the production of the nitrogen ions N^+ and N^{2+} .

2. Experimental method and apparatus

The animated crossed electron-ion beam method is applied in [the present experiment](#) (Defrance *et al* 1981). The apparatus and the experimental method have been previously [described in detail](#) (Lecointre *et al* 2006). NH^+ ions are extracted from an ECR ion source in which they are obtained by mixing nitrogen N_2 and hydrogen H_2 . Vibrationally excited states of $\text{NH}^+(\nu)$ are likely to be present in the primary ion beam. [The population of excited states can lead to a reduction of the threshold energies for the reactions which occur in the plasma because it is likely to reduce the energy gap between initial and final energy curves.](#) The vibrational population is on the one hand due to interaction with the plasma but may on the other hand also depend on the material and the temperature of the ion source wall. The NH^+ molecular ion beam of well-defined energy (4 keV for the study of N^+ , **8 keV for N^{2+}**) interacts at right angles with an electron beam, [the energy of which](#) is tuned from a few electron volts up to 2.5 keV. Product ions are separated from the primary ion beam by using a double focusing 90° magnetic analyzer. Product ions are further deflected by a 90° electrostatic spherical deflector and directed onto the channeltron detector.

In the animated beam method, the electron beam is swept across the ion beam in a linear motion at a constant speed u . The total number of events K produced during one complete electron beam movement is related to the measured cross section σ_m by

$$\sigma_m = \frac{uK}{I_e I_i \gamma} \frac{v_e v_i q_i e^2}{(v_e^2 + v_i^2)^{1/2}} \quad (6)$$

In this expression, γ is the detector efficiency, I_e and I_i , e and $q_i e$, v_e and v_i , are the electron and ion beam current intensities, the charges and velocities of electrons and ions, respectively.

Assuming $m_i \gg m_e$, the interaction energy E (eV) is given by:

$$E = V_e + \frac{m_e}{m_i} (q_i V_i - V_e) \quad (7)$$

where V_e and V_i , m_e and m_i are the acceleration voltages and masses of electrons and target ions, respectively.

Due to the transfer of internal potential energy, dissociation fragments exhibit both a broad velocity and a broad angular distribution in the laboratory frame. The angular acceptance of the magnet analyzer allows the total transmission of the angular distribution of product fragments emitted at a given velocity v in the laboratory frame. Due to the KER, the velocity distribution usually exceeds the corresponding magnetic analyzer acceptance, which is essentially defined by the size of the analyzing slits. In order to put the cross section on absolute scale, the apparent cross section $\sigma_m(B)$ is first measured at a given electron energy as a function of the analyzer magnetic field B . Next, the velocity distribution is computed from this apparent cross section and the total cross section σ is obtained by integrating this distribution over the entire velocity range. Finally, the total kinetic energy release distribution (KERD), for the investigated fragment, is expressed in terms of the velocity distribution by

$$\frac{d\sigma(E_{KER})}{dE_{KER}} = \frac{-2\mu v_c}{m^2 (1 - \varepsilon/2)} \frac{d}{dv} \left(\frac{1}{v} \frac{d\sigma(v)}{dv} \right) \quad (8)$$

where m is the fragment ion mass, μ is the reduced mass of the fragments, v_c represents the center-of-mass velocity and ε expresses the anisotropy factor. The molecular axis of the target is randomly orientated with respect to the direction of the electron beam. The angular distributions of the fragments, in the centre of mass frame, are closely related to the symmetry of the molecule and to the dynamics of the involved dissociating process. The anisotropy factor ε characterizes the angular distribution of the dissociation products with respect to the velocity of the incident electron, due to the initial orientation of the molecular axis of the target molecule. For the N^+ products, anisotropy factors ε have been estimated to be positive and to range from 2% to 7%, depending on the incident electron energy. The dissociation probability is not isotropic in space in the centre-of-mass frame as anisotropy factors are not negligible. E_{KER} represents the sum of the kinetic energy released to the dissociation fragments. By assuming the fragmentation of the target to be binary only and by applying the momentum conservation, this sum is given by

$$E_{KER} = \frac{m^2 w^2}{2\mu} \quad (9)$$

where w represents the fragment speed in the centre of mass frame.

The shapes of the velocity distributions for singly charged products depend on the electron energy, i.e. on the various E_{KER} involved. The dissociative contributions are deduced from a fitting procedure of the related part of the distribution (Lecointre *et al* 2006). At low energies, i.e. below the ionization threshold, only DE is observed. The width of the spectrum increases significantly with respect to the increasing electron energy, due to the larger kinetic energy released to the fragments which is attributed to the opening of successive new possible channels. The spectrum becomes broader above the ionization threshold because of the Coulomb repulsion experienced by DI fragments. In the experiment, magnetic field scans were recorded at several specific incident electron energies. The spectra exhibit therefore two contributions which indicate the presence of both distinct dissociative contributions: the upper (narrower) part of the distribution corresponds to DE while the lower (wider) part corresponds to DI. Consequently, the pure DI contribution is obtained by fitting the outer part of the spectrum and the associated transmission factor is calculated to put the apparent cross section on absolute scale (σ_{DI}). Absolute cross sections for DE (σ_{DE}) are obtained by subtracting the above-determined DI contribution (σ_{DI}) from the total absolute cross section for the N^+ production (σ_N).

Transmission factors range from 59% at low electron energies down to 38% at high electron energies for N^+ and the transmission factor is about 58% for N^{2+} . For non-dissociating products, total collection is provided because such ions exhibit unaffected velocity distributions. The total uncertainty is estimated to be of the order of $\pm 10\%$ for the total absolute cross sections and to be about $\pm 15\%$ for the dissociative contributions, at maximum (90% confidence limit). The uncertainty associated to the electron energy is estimated to be $\pm 0.5\text{eV}$. The pressure is kept below $1 \times 10^{-9}\text{mbar}$ in the collision chamber during the measurement, in order to reduce the background. For N^+ , the energy of the primary ion beam (4 keV) leads to 95% detection efficiency of the channeltron detector whereas for N^{2+} , the energy of the ion beam (8 keV) is high enough to insure 100% detection efficiency.

3. Results and discussion

The following paragraphs are devoted to the description and the discussion of the results (threshold energies, absolute cross sections and kinetic energy release distributions) which are obtained for the production of N^+ (σ_N , σ_{DE} and σ_{DI}) and N^{2+} (σ_{ADI}). Results are obtained in the incident electron energy range from 2eV to 2500eV.

For singly charged fragments, absolute cross sections are listed in table 3 (σ_N , σ_{DE} and σ_{DI}) and presented in figure 2 and 3, together with the associated total uncertainties. Cross sections (σ_{ADI}) for reaction (4) are listed in table 4 and presented in figure 4, together with their associated total uncertainties. The maximum total cross sections are observed to be $(15.7 \pm 0.7) \times 10^{-17} \text{cm}^2$ and $(11.1 \pm 0.2) \times 10^{-18} \text{cm}^2$ for the N^+ and N^{2+} products, respectively.

Figure 2 and Table 3

3.1 Dissociative excitation

Figure 2 shows present total absolute cross sections for the N^+ formation σ_N together with the absolute cross sections for the two dissociative contributions, σ_{DE} and σ_{DI} . Figure 3 presents the absolute DE cross sections σ_{DE} together with the excited electronic states that correlate to the lowest dissociation limits yielding to the N^+ production. This helps to identify the role of the electronic states involved in the present experiment.

Below the dissociative ionization threshold, total cross sections σ_N are equal to dissociative excitation cross sections σ_{DE} , as only dissociative excitation contributes to the signal. Above the dissociative ionization threshold, DE cross sections are obtained after subtraction of the DI contribution ($\sigma_{DE} = \sigma_N - \sigma_{DI}$) which is estimated independently (see section 2). The N^+ appearance energy is measured to be $(2.5 \pm 0.5) \text{eV}$ and, around the maximum, σ_{DE} is found to be $(8.1 \pm 0.8) \times 10^{-17} \text{cm}^2$ at $E = 21.1 \text{eV}$. A broad peak is displayed between 2eV and 8eV, centered on 5eV, with a maximum value of $3.6 \times 10^{-17} \text{cm}^2$. This peak is attributed to indirect dissociative excitation (IDE) as it is observed below the threshold of direct dissociative excitation (DDE) that is located at $(8.0 \pm 1.0) \text{eV}$ by the change of slope of the cross section curve.

In order to tentatively apprehend the complex structure exhibited by the DE cross section, the corresponding data presented in figures 2 and 3 have been fitted. The cross section for indirect processes (IDE), which is characterized by the above-mentioned peak, is described by the fitting function:

$$\sigma_{IDE} = a \left(1 - \frac{E_{th}}{E} \right)^b \frac{1}{E^c} \times (10^{-17} \text{cm}^2) \quad (10)$$

The analytic fit functions for direct processes (DDE) are taken in Born-Bethe form appropriately modified to describe the cross section behavior in the near-threshold region (Lecointre *et al* 2008):

$$\sigma_{DDE} = a \left(1 - \frac{E_{th}}{E} \right)^b \frac{1}{E} \ln(e + cE) \times (10^{-17} \text{ cm}^2) \quad (11)$$

The electron energy E and the threshold energy E_{th} are expressed in electron-Volts. e is the Euler's number and a , b , c are the fitting parameters. Although these functions contain only three fitting parameters, they nonetheless reproduce the measured data well within their experimental uncertainties. Three main contributions have thus been isolated from the present DE cross sections for the N^+ production σ_{DE} , the sum of which satisfactorily reproduce the experimental data.

Excitation might be influenced by excited vibrational levels populated within the $X^2\Pi$ ground state or within the $a^4\Sigma^-$ excited state if vibrationally excited states of $NH^+(v)$ are present in the ion beam. This would contribute to enlarge the Franck-Condon region and subsequently lower the observed thresholds. The spacing between vibrational energy levels has been estimated by using the vibrational energy expression of Dunham (1932) with the harmonic vibrational frequencies w_e and the anharmonic constants $w_e x_e$ obtained by Palmieri *et al* (1998) for the ground and excited states of NH^+ ($X^2\Pi$, $a^4\Sigma^-$, $A^2\Sigma^-$, $B^2\Delta$ and $C^2\Sigma^+$). More than 20 vibrational levels are present in the $X^2\Pi$ state and around 15 in the other excited states. An explanation for a possible shift observed between experimental and expected reaction thresholds would be that almost all vibrationally excited states of $NH^+(v)$ are populated in the ion beam. Considering that NH^+ is formed via the endothermic charge exchange reaction $H_2^+(v') + N \rightarrow NH^+(v) + H$, this mechanism would necessitate the presence of highly excited $H_2^+(v')$ vibrational levels. Such a high vibrational population has already been observed in experiments involving hydrogen as primary ions (Abdellahi El Ghazaly *et al* 2004). The exothermic reaction $N^+ + H_2(v'') \rightarrow NH^+(v) + H$ is less likely to be put forward in the present case. Indeed, the vibrational populations of $H_2(v'')$ were investigated in plasma conditions and, depending on plasma parameters, a large increase of the lower vibrationally excited levels is observed up to $v''=4$ only whereas higher levels undergo no more than a weak enhancement (Heger *et al* 2001).

Figure 3

One might wonder whether the lowest threshold (IDE, 2.5eV) could be associated with the three lowest doublet states, [the dissociation limit of which](#) correlates with N^+ formation or with resonant processes due to capture of the incident electron.

The three lowest doublet states are $X^2\Pi$ ($N^+(^3P) + H(^2S)$), $A^2\Sigma^-$ ($N^+(^3P) + H(^2S)$) and $C^2\Sigma^+$ ($N^+(^1D) + H(^2S)$) (Table 1 and Figure 1). These states are nevertheless bound and non-

dissociative, which means that they should not contribute to the N^+ formation if there is no vibrational population involved. For the ground state $X^2\Pi$, the dissociation limit may be reached considering that all the vibrational levels located within the potential depth are populated ($\geq 4.5\text{eV}$). The first accessible excited state $A^2\Sigma^-$ (disregarding the $a^4\Sigma^-$ metastable state as it overlaps the ground state) is located 3.11eV above the ground state and the potential well is 1.70eV deep. This implies that, once more, at least 4.5eV are required to reach the $N^+(^3P)+H(^2S)$ dissociation limit. Last, the $C^2\Sigma^+$ excited state lies 4.54eV above the ground state, the corresponding potential well is 2.17eV deep such that almost 7eV are needed to get to the $N^+(^1D)+H(^2S)$ limit. The present N^+ appearance threshold (2.5eV) is, in any case, much lower than these expected energies.

Therefore, such a low experimental threshold can be attributed more likely to the initial capture of the incoming electron into a doubly excited state of NH:

In the energy range starting above a few eV, the Rydberg series that converge to excited electronic states of the ion become accessible. In this case, the incoming electron falls into a valence orbital of the ion and excites one of the target electrons into the Rydberg state. Whatever happens, the ion core is excited and the neutral state lies within the electronic continuum of the neutral molecule (also called Feshbach resonance). Finally, the system autoionizes and dissociates.

Owono *et al* (2007 and 2008) carried out calculations of potential energy curves for Rydberg states of NH, with a particular emphasis on the Rydberg states which arise from the $1s^2 2s^2 2p^2 3s$ configuration of nitrogen and from the $2s$ and $2p$ configurations of hydrogen. A range of about 11eV above the electronic ground state $X^3\Sigma^-$ has been covered by the calculations which corresponds to the first eight dissociation limits. The states of $^1\Sigma^-$, $^1\Pi$, $^1\Delta$, $^3\Sigma^-$, $^3\Pi$, $^3\Delta$, $^5\Sigma^-$ and $^5\Pi$ symmetries have thus been investigated. It appears that the highest computed Rydberg states ($2^1\Sigma^+$, $6^3\Pi$ and $3^5\Pi$) exhibit vertical excitation energies in the $11\text{--}14\text{eV}$ range from the $X^3\Sigma^-$ potential minimum. Keeping in mind that the ionization energy of NH is 13.34eV , these Rydberg states are found to be in the vicinity of the NH^+ ground state $X^2\Pi$ at the equilibrium distance. Higher-lying Rydberg states (not computed yet to the author's knowledge) that are located above the ground state $X^2\Sigma^+$ would thus play an

undeniable role in the low electron energy range. To conclude, we can say that the IDE channel is the consequence of the NH^{**} Rydberg states. The corresponding first contribution shown in figure 3 is peaked on 5eV and it exhibits a cross section of $3.6 \times 10^{-17} \text{cm}^2$ at maximum.

DDE occurs by electron-impact causing a transition to a repulsive excited electronic state with enough internal energy to induce fragmentation. The threshold for this process is well-defined by the vertical excitation energy (VEE) to the dissociating state in the Franck-Condon region. The first dissociative state that correlates with N^+ formation ($\text{N}^+(^3\text{P})+\text{H}(^2\text{S})$) is the $2^4\Sigma^-$ state and its corresponding threshold is 10.48eV (Table 1). The second dissociative state which could be of interest is the $1^4\Pi$ state ($\text{N}^+(^3\text{P})+\text{H}(^2\text{S})$), the threshold of which is at 12.43eV. Taking into consideration the effect of the NH^+ vibrational population, the second experimental DE threshold (DDE, 8.0eV) can be related to the $2^4\Sigma^-$ state and the $1^4\Pi$ state may also be directly evoked. Higher-lying repulsive states (e.g. $3^2\Pi$ and $2^2\Delta$, 14.36eV and 14.81eV, respectively) surely contribute to the N^+ formation but their individual contribution can not be clearly distinguished from the present experimental data (Figure 3a). The second channel presented in figure 3 is attributed to these DDE processes. It is the dominant channel which is centered on 21eV and which exhibits a maximum cross section of $7.6 \times 10^{-17} \text{cm}^2$.

The third and last channel starts from about 35eV, it is observed to be broad as its maximum is found to be $2.3 \times 10^{-17} \text{cm}^2$ around 250eV (Figure 3b). Many electronic states, the vertical excitation energies of which are included in the 20–40eV range, can contribute to the DE signal (Table 2). They can explain for the intricacy of the shape of the DE cross section, although the dissociation limits of these high-lying states have not been clearly identified.

3.2 Ionization

The present threshold energy for dissociative ionization is found to be $(20.0 \pm 1.0) \text{ eV}$. The maximum absolute cross section for DI is found to be $(12.1 \pm 0.4) \times 10^{-17} \text{cm}^2$ at 95.1eV (Figure 2), which is 50% higher than the DE cross section at maximum. The present experimental threshold is found to be lower than the calculated vertical ionization potential of NH^+ as the direct transition $\text{X}^1\Sigma^+$ state in the Franck-Condon region should occur in the 25–27eV range (see Amero and Vázquez 2004, Pope *et al* 1983, Koch and Schwarz 1986 and Proctor *et al* 1981). Such an observation may indicate that DE processes possibly contaminate the signal that is attributed to DI. Potential energy curves show that high-lying sextet states of NH^+ (e.g. $1^6\Pi$, $2^6\Pi$, $2^6\Sigma^+$ and $3^6\Sigma^+$) cross the $\text{X}^1\Sigma^+$ state of NH^{2+} (Figure 1) such that autoionization

could occur for reasonably large internuclear distances. Indirect processes could thus have an effect on the ion pair production and on the expected threshold for dissociative ionization.

Table 4 and Figure 4

For the N^{2+} channel, two distinct energy thresholds are observed at (31.5 ± 0.5) eV and at (36.1 ± 0.5) eV (Figure 4). The first dissociation limit leading to products with asymmetric charge distribution (i.e. asymmetric dissociative ionization, ADI) $N^{2+}(^2P) + H(^2S)$ lies around 34 eV, which is included between the two present experimental thresholds. The present energy threshold can be related to a transition to the first excited state of $^1\Pi$ symmetry of NH^{2+} (Hamdan *et al* 1988). The maximum cross section for the N^{2+} production is measured to be $(11.1 \pm 0.2) \times 10^{-18} \text{ cm}^2$ at 115.1 eV, one order of magnitude lower than the maximum DI cross section. As above-mentioned in the case of excitation, the vibrational population of the NH^+ ions is also expected to lower the measured DI and ADI thresholds.

Attempts to observe single ionization products NH^{2+} are challenging. To date, it is not yet possible to illustrate the stability of the NH^{2+} dication. At the matching mass-to-charge ratio ($m/z = 7.5$), cross sections have been measured from 27.1 eV up to 2.5 keV, with a maximum of $(7.0 \pm 0.2) \times 10^{-19} \text{ cm}^2$ observed at 115.1 eV (two orders of magnitude lower than the maximum DI cross section). Nevertheless one can not exclude the single ionization of the nitrogen isotope $^{15}N^+$ to contaminate the $^{14}NH^+$ signal. Although the present reaction threshold (27.1 eV) has been measured to be close to both the estimated and the measured values for NH^{2+} formation (ranging from 25 eV to 26.9 eV, Hamdan *et al* 1988, Amero and Vázquez 2004, Pope *et al* 1983, Koch and Schwarz 1986 and Proctor *et al* 1981); this threshold energy can also be compared to the $^{15}N^+$ single ionization threshold (29.6 eV, Yamada *et al* 1989). Such contribution of $^{15}N^+$ makes us unable to confirm whether or not the NH^{2+} ($X^1\Sigma^+$) ground state is bound.

Figure 5 and Table 5

The Bethe-plot of present ionization cross sections shows that experimental data are adjusted along straight lines from above 40 eV (Figure 5). It illustrates the fact that the energy dependence of the electron-impact ionization cross sections σ_i (where σ_i stands for σ_{DI} or σ_{ADI}) can be satisfactorily represented by the Bethe-form:

$$\sigma_i = \frac{a}{EI_i} \left[\ln \left(\frac{E}{I_i} \right) + b \right] \quad (13)$$

The fitting parameters, a ($\text{cm}^2 \text{ eV}^2$) and b , are listed in table 5. I_i (eV) represents the ionization threshold energy for DI and ADI depending on which channel is under investigation.

Expected single-step processes describe well both the DI (σ_{DI}) and the ADI (σ_{ADI}) channels. A similar linear behavior has already been pointed out when studying the CO^+ target (Lecointre *et al* 2006). The core excitation of NH^+ $1\sigma \rightarrow 1\pi$ occurs at 410eV (Amero and Vázquez 2004) but no break in linearity can be observed from the present Bethe-plots which may have been a sign of such a process.

The total ionization cross section σ_I for NH^+ is calculated by summing the dissociative ionization cross sections ($\sigma_I = \sigma_{DI} + \sigma_{ADI}$), which maximum is estimated to be $(13.2 \pm 0.4) \times 10^{-17} \text{cm}^2$ at 85.1eV. It is interesting to compare the total ionization cross section for the two isoelectronic systems. Total ionization cross sections have been calculated only for CH by the binary-encounter Bethe (BEB) model (Kim *et al* 1997) and by the Deutsch–Märk (DM) formalism (Deutsch *et al* 2000). Both calculations agree very well with one another over the entire range of electron energies and with the experimental data of Tarnovsky *et al* (1997) below 30eV. At maximum, both the models estimated the CH ionization cross section to be about $25 \times 10^{-17} \text{cm}^2$ whereas Tarnovsky *et al* (1997) measured this cross section to be about $20 \times 10^{-17} \text{cm}^2$. The comparison of total ionization cross sections along an isoelectronic sequence relies on the Thomson’s classical scaling law (Thomson 1912), which predicts that the total cross sections scale according to the inverse of the square of the corresponding ionization threshold energy $I_i(\text{eV})$. The energy threshold is 10.6eV (Liu and Verhaegen 1970) for CH that is about two times lower than the present 20eV for NH^+ . Consequently, the total ionization cross section for CH should be about four times larger than the one of NH^+ and not only two times. It can be concluded from the present study that the comparison of the two isoelectronic molecular species is not successful and that the classical formula is inappropriate for molecular ions. Differences among the potential energy diagrams for CH and for NH^+ which have been pointed out by Liu and Verhaegen (1970) may explain such a discrepancy. In the case of atomic species, Ancarani and Hervieux (2005) discussed a similar phenomenon that is that the validity of a scaling law is not obvious for nonhydrogenic targets such as alkali-metal-like ions.

3.3 Kinetic energy release

The kinetic energy of the fragments resulting from electron-impact on NH^+ is provided by the internal energy of $(NH^+)^*$ before dissociation (equation 12). Kinetic energy release distributions (KERDs) have been obtained for N^+ at the electron energies for which the magnetic scans have been performed (Figure 6). The lowest incident electron energy for

which a KERD has been determined is $E = 15.1\text{eV}$ whereas the highest one is $E = 295.1\text{eV}$. At low incident electron energies, present KERDs are mainly due to dissociative excitation whereas ionization is the dominant contribution for the KERDs measured at the highest incident energies. This statement is illustrated in figure 6 when looking at the two extreme distributions measured for 15.1eV (Figure 6(a)) and for 295.1eV (Figure 6(d)). For 15.1eV , the first peak is the dominant one as its amplitude is two times bigger than the one of the second peak. For 295.1eV , the situation is then reversed as in this case, the second peak has double the amplitude of the first one.

Figure 6 and Table 6

The distributions determined for N^+ ions are broad as they extend up to $E_{\text{KER}} = 11\text{--}14\text{eV}$. Each distribution is separated into two individual contributions which are adequately reproduced by Gaussian functions. The first one exhibits its centre below 6eV and it is commonly attributed to dissociative excitation mainly. Due to Coulomb explosion, dissociative ionization usually makes the KERDs becoming broader. Consequently, the second contribution that is found above 6eV is generally attributed to dissociative ionization. Nevertheless, it appears that excitation processes still play a role in this KER range. Both the two peaks describing the KERD measured at 15.1eV are due to excitation processes only as this electron energy is below the ionization threshold. It shows that there is a DE contribution in the second peak of the distributions. For the KERDs obtained for the two highest electron energies, the DI contribution should extend down to 3eV , if not even to near zero, meaning that the first Gaussian contribution includes a proportion of DI.

Table 6 lists the expected kinetic energies related to the electronic states that correlate to the N^+ formation, estimated in the Franck-Condon region for the ground state NH^+ (Amero and Vázquez 2004 and 2005). For each concerned excited molecular state, the expected KER is calculated as the difference between the VEE and the energy associated to the corresponding dissociation limit. In the present experiment, it is unfortunately impossible to distinguish the individual contribution of each electronic state and only the mean kinetic energy release ($\overline{E_{\text{KER}}}$) can thus be estimated. Present $\overline{E_{\text{KERs}}}$ are deduced from the analysis of the Gaussian functions which describe the two contributions composing each KERD. The mean kinetic energies range from 1.4eV up to 5.5eV for the first contribution, and they range from 6.7eV up to 9.7eV for the second one. Full width at half maximum FWHM corresponding to every contribution is also reported in table 7 in order to estimate each individual Gaussian distribution width.

From table 6, it appears than the expected kinetic energies for excitation ($N^+ + H$) are included in the 5.7–9.2eV range. For $E = 95.1\text{eV}$, the first contribution of the KERD can be attributed to DE as it is centered on 5.5eV which is in good agreement with the expected KER range and especially to the $2^4\Sigma^-$ state input. Generally speaking, the theoretical E_{KERs} are compatible with the present mean kinetic energies that are deduced from the second contribution of each KERD. This result is unexpected as these contributions in the high E_{KER} region are more likely to be attributed to ionization processes. It points out that [dissociative excitation contributes partly to the second component](#) deduced from each KERD whatever the electron energy can be.

The experimental mean kinetic energies which are found to be below 5eV cannot be related to [any electronic state](#) listed in table 6. The above-mentioned indirect processes, such as the resonant capture, should be responsible for the low KER range which is observed in the experimental distributions although it has not been theoretically predicted so far.

For N^{2+} , the distribution that has been determined at 95.1eV extends from 0eV up to 20eV. This KERD can be decomposed into two Gaussian contributions, [the corresponding \$\overline{E_{\text{KERs}}}\$ of which are found to be at 5.7eV and at 12.2eV \(Figure 7\)](#). The ground state of NH^{3+} , yielding $N^{2+} + H^+$, may be represented by a coulombic repulsive potential energy curve, although no numerical curve is presently available in the literature. These triply-charged species are precursors that drive N^{2+} with high kinetic energy, the energy corresponding to the $N^{2+} + H^+$ dissociation limit is expected to be about 48eV. The KER is estimated as the energy difference between this value and the pure Coulomb potential in the Franck-Condon region. Dissociation via the NH^{3+} precursor hence leads to E_{KER} values around 11eV to 15eV, which is comparable with the measured values.

[Table 7 and Figure 7](#)

4. Conclusion

[Absolute cross sections for electron-impact dissociation and ionization of \$NH^+\$ into \$N^+\$ and \$N^{2+}\$ products have been measured in the energy region from their respective thresholds to 2.5 keV in a crossed electron-ion beam experiment. Potential energy curves are presented for the dissociation channels; they are of importance for the detailed discussion of \[the present experimental results\]\(#\). Indirect dissociation \(IDE\) is expected for incident energies below the direct excitation threshold \(DDE\). Consequently, for the \$N^+\$ fragment, the signal which occurs below the threshold for direct excitation is associated with resonance enhanced excitation.](#)

The cross sections contain significant contributions from several resonant states which autoionize into electronically excited states. The doubly excited states (Feshbach resonances) which lie below the direct dissociation threshold are formed when the incoming electron excites the target ion and is captured into a bound orbital. The first excited states of the ion NH^+ can be parents to one or more Rydberg series in the neutral molecule NH^{**} . The excited neutral molecule evolves in time, thereby the system autoionizes and the ion returns to its original electronic state or to an excited state. This produces efficient dissociation of NH^+ at collision energies well below the direct excitation threshold. From the calculations of Owono *et al* (2007), it appears that superexcited states of NH may exist and present energies which are around the ones of NH^+ excited states, at the equilibrium distance. Further calculations should enlighten such a situation, as well as the role of vibrational excitation of the parent ion and of the subsequent broadening of the Franck-Condon region. The analysis of the fragment velocity distributions allows the determination of the kinetic energy release for dissociation products, at selected electron energies. It emerges from the analysis of these KERDs that excitation and ionization contributions are mixed up such that one contribution can not be easily isolated from the other.

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References

- Abdellahi El Ghazaly M O, Jureta J J, Urbain X and Defrance P 2004 *J. Phys. B: At. Mol. Opt. Phys.* **37** 2467
- Adams G F and Shaw R W Jr 1992 *Annu. Rev. Phys. Chem.* **43** 311
- Amero J M and Vázquez G J 2004 *Int. J. Quant. Chem.* **99** 353
- Amero J M and Vázquez G J 2005 *Int. J. Quant. Chem.* **101** 396
- Ancarani L U and Hervieux P -A 2005 *Phys. Rev. A* **72** 034701
- Babcock H D 1945 *Astrophys J.* **102** 154

Bahati E M, Jureta J J, Belic D S, Cherkani-Hassani H, Abdellahi M O and Defrance P 2001 *J. Phys. B: At. Mol. Opt. Phys.* **34** 2693

Barsuhn J 1977 *Astron. Astrophys. Suppl.* **28** 453

Cherkani-Hassani H, Belic D S, Jureta J J and Defrance P 2006 *J. Phys. B: At. Mol. Opt. Phys.* **39** 5105

Colin R 1989 *J. Mol. Spectrosc.* **136** 387

Colin R and Douglas A E 1968 *Can. J. Phys.* **46** 61

Defrance P, Brouillard F, Claeys W and Van Wassenhove G 1981 *J. Phys. B: At. Mol. Phys.* **14** 103

Deutsch H, Becker K, Matt S and Märk T D 2000 *Int. J. Mass Spectrom.* **197** 37

Dunham J L 1932 *Phys. Rev.* **41** 721

Farnell L and Ogilvie J F 1983 *J. Mol. Spectrosc.* **101** 104

Galloway E T and Herbst E 1989 *Astron. Astrophys.* **211** 413

Hamdan M, Mazumdar S, Marathe V R, Badrinathan C, Brenton A G and Mathur D 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** 2571

Heger B, Fantz U, Behringer K 2001 *J. Nucl. Mater.* **290** 413

Hübers H- W, Evenson K M, Hill C and Brown J M 2009 *J. Chem. Phys.* **131** 034311

Kalemos A, Mavridis A and Metropoulos A 1999 *J. Chem. Phys.* **111** 9536

Kim Y-K, Ali M A and Rudd M E 1997 *J. Res. Natl. Inst. Stand. Technol.* **102** 693

Koch W and Schwarz H 1986 *Int. J. Mass Spectrosc. Ion. Processes* **68** 49

Lambert D L and Beer R 1972 *Astrophys. J.* **177** 541

Lecointre J, Belic D S, Cherkani-Hassani H, Jureta J J and Defrance P 2006 *J. Phys. B: At. Mol. Opt. Phys.* **39** 3275

Lecointre J, Belic D S, Jureta J J, Janev R and Defrance P (2008) *Eur. Phys. J. D* **50** 265

Liu H P D and Verhaegen G 1970 *J. Chem. Phys.* **53** 735

Lunt R W, Pearse R W B and Smith E C W 1935 *Nature* **136** 32

McKenna J, Sayler A M, Gaire B, Johnson N G, Parke E, Carnes K D, Esry B D and Ben-Itzhak I 2008 *Phys. Rev. A* **77** 063422

Meier R, Wellnitz D, Kim S J and A'Hearn M F 1998 *Icarus* **136** 268

Mitchell G F, Ginsburg J L and Kuntz P J 1978 *Astrophys. J. Suppl.* **38** 39

Owono Owono L C, Jaidane N, Kwato Njock M G and Ben Lakhdar Z 2007 *J. Chem. Phys.* **126** 244302

Owono Owono L C, Ben Abdallah D, Jaidane N and Ben Lakhdar Z 2008 *J. Chem. Phys.* **128** 084309

Palmieri P, Tarroni R, Mitrushenkov A O and Rettrup S 1998 *J. Chem. Phys.* **109** 7085

Pope S A, Hillier I H, Guest M F and Kendrick J 1983 *Chem. Phys. Lett.* **95** 247

Proctor C J, Porter C J, Ast T, Bolton P D and Beynon J 1981 *Org. Mass Spectrom.* **16** 454

Tarroni R, Palmieri P, Mitrushenkov A, Tosi P and Bassi D 1997 *J. Chem. Phys.* **106** 10265

Tarnovsky V, Levin A, Deutsch H and Becker K 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** 139

Thomson J J 1912 *Philos. Mag.* **23** 449

Woodall J, Agúndez M, Markwick-Kemper A J and Millar T J 2007 *Astron. Astrophys.* **466** 1197

Yamada I, Danjo A, Hirayama T, Matsumoto A, Ohtani S, Suzuki H, Takayanagi T, Tawara H, Wakiya K and Yoshino M 1989 *J. Phys. Soc. Jpn.* **58** 1585

Table 1. Vertical excitation energies (VEE) of the doublet, [quartet](#) and sextet electronic states that correlate to the lowest dissociation limits of NH^+ at $r_e(\text{X}^2\Pi)$.

State	VEE (eV)	Dissociation limit
$\text{X}^2\Pi$	0.00	$\text{N}^+(^3\text{P})+\text{H}(^2\text{S})$
$\text{a}^4\Sigma^-$	0.00	$\text{N}(^4\text{S})+\text{H}^+(^1\text{S})$
$\text{A}^2\Sigma^-$	3.11	$\text{N}^+(^3\text{P})+\text{H}(^2\text{S})$
$\text{B}^2\Delta$	3.11	$\text{N}(^2\text{D})+\text{H}^+(^1\text{S})$
$\text{C}^2\Sigma^+$	4.54	$\text{N}^+(^1\text{D})+\text{H}(^2\text{S})$
$2^2\Pi$	7.83	$\text{N}(^2\text{D})+\text{H}^+(^1\text{S})$
$2^4\Sigma^-$	10.48	$\text{N}^+(^3\text{P})+\text{H}(^2\text{S})$
$1^4\Pi$	12.43	$\text{N}^+(^3\text{P})+\text{H}(^2\text{S})$
$2^2\Sigma^+$	12.81	$\text{N}(^2\text{P})+\text{H}^+(^1\text{S})$
$3^2\Pi$	14.36	$\text{N}^+(^1\text{D})+\text{H}(^2\text{S})$
$2^4\Pi$	14.54	$\text{N}(^4\text{P})+\text{H}^+(^1\text{S})$
$2^2\Delta$	14.81	$\text{N}^+(^1\text{D})+\text{H}(^2\text{S})$
$4^2\Pi$	15.76	$\text{N}(^2\text{P})+\text{H}^+(^1\text{S})$
$3^2\Sigma^+$	16.45	$\text{N}^+(^1\text{S})+\text{H}(^2\text{S})$
$3^4\Sigma^-$	16.52	$\text{N}^+(^5\text{S})+\text{H}(^2\text{S})$
$2^2\Sigma^-$	16.83	$\text{N}(^2\text{D})+\text{H}^+(^1\text{S})$
$1^6\Sigma^-$	19.40	$\text{N}^+(^5\text{S})+\text{H}(^2\text{S})$
$2^6\Sigma^-$	25.73	$\text{N}(^4\text{S})+\text{H}^+(^1\text{S})$

Table 2. Vertical excitation energies (VEE) of the highest doublet, [quartet](#) and sextet electronic states of NH^+ at $r_e(X^2\Pi)$.

State	VEE (eV)
$3^4\Pi$	17.57
$4^2\Sigma^+$	17.64
$5^2\Pi$	18.44
$3^2\Delta$	18.93
$6^2\Pi$	18.95
$1^4\Delta$	19.09
$1^4\Sigma^+$	19.24
$7^2\Pi$	19.39
$4^4\Sigma^-$	19.52
$3^2\Sigma^-$	19.70
$4^4\Pi$	19.92
$5^4\Sigma^-$	21.15
$5^4\Pi$	22.26
$6^4\Pi$	22.68
$7^4\Pi$	23.80
$1^6\Pi$	27.13
$3^6\Sigma^-$	27.98
$2^6\Pi$	29.64
$4^6\Sigma^-$	30.19
$3^6\Pi$	31.37
$4^6\Pi$	33.77
$5^6\Pi$	40.84

Table 3. Absolute cross sections for the total production of N^+ and for the related dissociative contributions (90% confidence limit).

E (eV)	Total (10^{-17} cm 2)		DI (10^{-17} cm 2)		DE (10^{-17} cm 2)	
	σ_N	$\Delta\sigma_N$	σ_{DI}	$\Delta\sigma_{DI}$	σ_{DE}	$\Delta\sigma_{DE}$
2.1	0.0	1.0			0.0	1.0
3.1	0.8	0.9			0.8	0.9
4.1	2.6	0.8			2.6	0.8
5.1	3.6	0.4			3.6	0.4
6.1	3.2	0.3			3.2	0.3
7.1	2.2	0.5			2.2	0.5
9.1	3.5	0.5			3.5	0.5
11.1	4.6	0.5			4.6	0.5
15.1	6.3	0.4			6.3	0.4
17.1	7.2	0.5			7.2	0.5
19.1			-0.1	0.4		
21.1	8.5	0.5	0.4	0.6	8.1	0.8
25.1	9.9	0.6	2.6	0.6	7.3	1.0
30.1	11.2	0.7	4.7	0.6	6.5	1.0
35.1	12.4	0.8	6.0	0.4	6.4	0.9
40.1	13.1	0.5	8.4	0.6	4.8	1.0
45.1	13.7	0.2	9.4	0.7	4.3	0.9
55.1	14.2	0.6	10.3	0.7	3.9	0.8
65.1	14.6	0.6	11.2	0.7	3.4	0.8
75.1	15.4	0.7	11.2	0.5	4.2	0.9
85.1	15.7	0.7	12.1	0.4	3.5	0.8
95.1	15.3	0.8	12.1	0.6	3.2	0.9
115.1	15.1	0.6	11.7	0.5	3.3	0.6
135.1	14.0	0.5	11.0	0.7	3.0	0.8
155.1	13.7	0.6	10.5	0.5	3.2	0.7
195.1	12.1	0.6	9.3	0.6	2.9	0.7
245.1	11.4	0.6	8.3	0.6	3.1	0.7
295.1	9.6	0.6	7.4	0.5	2.2	0.7
395.1	8.9	0.6	6.4	0.5	2.5	0.7
495.1	7.4	0.6	5.5	0.3	1.9	0.6
595.1	7.0	0.4	4.9	0.3	2.1	0.5
795.1	6.0	0.4	4.0	0.4	2.1	0.4
995.1	4.9	0.4	3.4	0.3	1.6	0.4
1495.1	3.9	0.3	2.5	0.2	1.4	0.3
1995.1	2.8	0.3	2.0	0.2	0.8	0.3
2495.1	2.3	0.2	1.7	0.2	0.7	0.2

Table 4. Absolute cross sections for the formation of N^{2+} (90% confidence limit).

E (eV)	N^{2+} (10^{-18} cm^2)	
	σ_{ADI}	$\Delta\sigma_{\text{ADI}}$
31.1	-0.01	0.08
33.1	0.04	0.02
35.1	0.10	0.03
37.1	0.31	0.04
38.1	0.50	0.06
40.1	1.06	0.09
42.1	1.71	0.13
45.1	2.58	0.09
47.1	3.34	0.14
50.1	4.17	0.11
55.1	5.50	0.07
65.1	7.18	0.15
75.1	8.90	0.16
85.1	9.81	0.15
95.1	10.65	0.16
115.1	11.13	0.17
135.1	11.12	0.18
155.1	10.74	0.10
195.1	10.02	0.19
245.1	9.08	0.15
295.1	8.28	0.14
395.1	7.20	0.13
495.1	6.20	0.11
595.1	5.49	0.10
795.1	4.49	0.09
995.1	3.92	0.10
1495.1	2.79	0.07
1995.1	2.27	0.08
2495.1	2.04	0.07

Table 5. Parameters, I_i (eV), a ($10^{-14} \text{ cm}^2 \text{ eV}^2$) and b , for the Bethe-plots (equation 13) of the ionization cross sections σ_{DI} and σ_{ADI} ($\pm 5\%$).

Channel	σ_{DI}	σ_{ADI}
I_i	20.0	36.1
a	19.6	4.57
b	-0.42	-0.18

Table 6. Kinetic energy release (KER) corresponding to the dissociative electronic states of NH^+ that correlate to the N^+ formation.

State	Dissociation limit	E_{KER} (eV)
$\text{X}^2\Pi$	$\text{N}^+(^3\text{P})+\text{H}(^2\text{S})$	-
$\text{A}^2\Sigma^-$	$\text{N}^+(^3\text{P})+\text{H}(^2\text{S})$	-
$\text{C}^2\Sigma^+$	$\text{N}^+(^1\text{D})+\text{H}(^2\text{S})$	-
$2^4\Sigma^-$	$\text{N}^+(^3\text{P})+\text{H}(^2\text{S})$	5.7
$1^4\Pi$	$\text{N}^+(^3\text{P})+\text{H}(^2\text{S})$	7.7
$3^2\Pi$	$\text{N}^+(^1\text{D})+\text{H}(^2\text{S})$	7.5
$2^2\Delta$	$\text{N}^+(^1\text{D})+\text{H}(^2\text{S})$	7.9
$3^2\Sigma^+$	$\text{N}^+(^1\text{S})+\text{H}(^2\text{S})$	7.5
$3^4\Sigma^-$	$\text{N}^+(^5\text{S})+\text{H}(^2\text{S})$	6.3
$1^6\Sigma^-$	$\text{N}^+(^5\text{S})+\text{H}(^2\text{S})$	9.2

Table 7. Mean kinetic energy release values $\overline{E_{\text{KER}}}$ and corresponding contributions' full width at half maximum ^(*) (*FWHM*), at indicated electron energies.

E (eV)	15.1	45.1	95.1	295.1
N ⁺	1.4±0.1 (<i>1.9±0.2</i>)	2.2±0.1 (<i>2.5±0.2</i>)	5.5±0.5 (<i>6.1±0.7</i>)	3.7±0.3 (<i>4.2±0.5</i>)
	6.7±0.8 (<i>6.3±1.7</i>)	6.8±0.1 (<i>3.3±0.2</i>)	9.7±0.2 (<i>2.3±0.5</i>)	8.1±0.1 (<i>2.8±0.1</i>)
N ²⁺			5.7±0.5 (<i>8.8±0.6</i>)	
			12.2±0.8(<i>5.7±0.5</i>)	

^(*) The FWHM corresponds to the value in italic inside brackets.

Figure 1. Potential energy curves of NH^+ and NH^{2+} . Potential energy is given with respect to the bottom of the ground $X^2\Pi$ state well. The curves [have been deduced by Amero and Vázquez \(2004 and 2005\)](#).

Figure 2. Absolute cross sections for the N^+ production versus the electron energy: total absolute cross sections ($\blacktriangle$), together with the dissociative excitation contribution ($\times$) and with the dissociative ionization one ($\square$). The solid curve results from a fitting procedure of the present experimental data to help distinguish the dissociative excitation channel.

Figure 3. Absolute cross sections for the dissociative excitation channel ($\text{N}^+ + \text{H}$), versus the electron energy ($\blacktriangle$): (a) together with the excited electronic states that correlate to the lowest dissociation limits yielding to the N^+ production and (b) over the whole energy range. Dashed and solid curves result from fitting procedures of the present experimental data for DE (equations 10 and 11).

Figure 4. Total absolute cross sections for the N^{2+} production versus the electron energy.

Figure 5. Bethe-plot of dissociative ionization cross sections, for ($\blacktriangle$) $\text{N}^+ + \text{H}^+$ and for ($\times$) $\text{N}^{2+} + \text{H}$. Each full line results from the fitting procedure using the Bethe-Born formula (equation 13).

Figure 6. Total kinetic energy release distributions for N^+ fragments for the following electron energies: (a) 15.1eV, (b) 45.1eV, (c) 95.1eV and (d) 295.1eV. Solid curves result from multi-peak fitting procedures and dashed curves correspond to independent contributions (Gaussian functions).

Figure 7. Total kinetic energy release distribution for N^{2+} fragments at $E=95.1\text{eV}$. Solid curve results from multi-peak fitting procedures and dashed curves correspond to independent contributions (Gaussian functions).