

THE DOUBLE IONIZATION OF AMMONIA. ITS DISSOCIATION INTO THE DOUBLY IONIZED FRAGMENT N^{2+}

R. LOCHT and J. MOMIGNY

Institut de Chimie, Département de Chimie Générale et de Chimie Physique, Université de Liège, Bâtiment B6, Sart-Tilman, 4000 Liège 1, Belgium

The double ionization and dissociation of NH_3 into the doubly ionized fragment N^{2+} is investigated by electron impact. Two double ionization energies of NH_3 are directly measured at 34.8 ± 0.2 and 39.4 ± 0.5 eV. A third critical energy observed at 66 eV is assigned to a NH_3^{2+} state whose ionization energy is at 61 eV. Two appearance energies are observed for the N^{2+} ion at 65.9 ± 1.7 and 74.3 ± 2.6 eV. The translational energy distribution of N^{2+} is shown to be essentially thermal. The former onset is ascribed to the dissociation of the 61 eV state of NH_3^{2+} , the latter originates from a doubly ionized NH_3^{2+} state at 70 eV.

Compared to the literature dedicated to ionization and dissociation of molecular cations, the abundance of work devoted to double ionization is very small. This statement has to be ascribed to the generally low abundance of double ionized species. Until recently, only electron impact and high-energy ion impact allowed us to observe these species. The improvement of high-energy light sources, e.g. He (II) resonance lamps, and even more the increasing number of electron synchrotron radiation facilities, allowed us to reach photon energies far above the 21.22 eV energy limit. These developments were the starting point of an increasing number of publications in the field of double and even multiple ionization.

During the last few years, the double ionization of NH_3 has been studied by several techniques including double charge transfer spectroscopy (DCTS) [1], charge stripping reaction technique (CSR) [2] and double photoionization (PI) [3]. The latest conventional electroionization work (EI), measuring onset energies, has been published by Dorman and Morrison [4].

Very few investigations of the dissociation of doubly ionized states into singly and/or doubly charged fragment ions have been carried out. Boyd et al. [5] studied the metastable decomposition of NH_3^{2+} into singly as well as doubly ionized fragment ions. The dissociation of doubly charged NH_3 into pairs of singly charged ions has recently been studied by photoionization using the photoion-photoion coincidence (PIPICO) technique [3]. Several theoretical calculations have been devoted to the NH_3 dication, using a variety of techniques [1, 6-8].

The aim of this work was to investigate the double ionization of NH_3 , as well as its dissociation, as a complementary source of information for the detailed study of the dissociative ionization of NH_3 and ND_3 in the 15-45 eV energy range. This work is still in progress [9]. The doubly ionized species, observed in the mass spectrum of NH_3 , are included in this work.

The experimental apparatus and the experimental conditions used in the course of this work have been described in detail elsewhere [10]. At the present time the instrument is fully computer controlled [11]. The ammonia and ammonia- d_3 , purchased from Air Liquide and Merck, Sharp & Dohme respectively, are distilled under high vacuum to reduce the traces of water in the samples. Special care is taken to reduce the background signal of N^+ and O^+ by prolonged bake-out at 250° C. Owing to the low intensity of the signals, each first differentiated ionization efficiency curve was scanned 600-700 times, requiring 20-30 h. This operation was repeated at least 10-15 times. The onset energies reported in this work are averaged values from these 10-15 independent measurements. The error limits mentioned are the standard deviation.

In table 1 are listed the relative intensities of all the fragment ions detected in the mass spectrum of NH_3 and ND_3 as observed by the impact of 100 eV electrons. For comparison, previous 70 eV electron impact data [12] and the most recent 40.8 eV photoionization data [13] are included in this table. No significant

discrepancies are observed between electron impact data, especially when it is noticed that in the present work no extraction field is applied to the ion beam. This particular experimental condition could explain the lower intensity observed for the lighter ions in the present work. However, compared to photoionization at equal ionizing particles energy, e.g. 40 eV electron energy (see fig. 1), the NH_3^{2+} ion intensity drops to 5% of its intensity at 100 eV. As a result, double ionization by photoionization has a larger cross section than by electroionization, as it has been pointed out by Tsai and Eland [13].

Fig. 1 displays the direct as well as the first differentiated double ionization efficiency curves of the NH_3^{2+} dication. The latter shows a quasi-linear rise-up to about 42 eV and a fairly continuous decrease is observed between 50 and 100 eV. A change of the negative slope has to be noticed at about 66 eV. Fig. 2 shows the ionization efficiency curves on an expanded energy scale. Two ionization energies are measured, i.e. at 34.8 ± 0.2 and at 39.4 ± 0.5 eV.

Table 2 allows us to compare the present data to the most recent experimental and theoretical results on the double ionization energies of NH_3 . For the first ionization energy good agreement is found, within the error limits, between the present results, double charge transfer [1], photoionization [3] and theoretical predictions [1,6-8]. All quantum-mechanical calculations agree to describe the NH_3^{2+} ground state by the \tilde{X}^1A_1 symmetry obtained by removal of two $3a_1$ electrons. Although stable toward dissociation, this state is found to be dissociative over a long time scale by both PIPICO [3] as well as by electroionization [5,9]. When the former experiment measured coincidences between NH_2^+ and H^+ ions [3], in the latter an appearance energy at about 35 eV is measured for both the NH_2^+ and the H^+ ions [9]. Furthermore, H_2^+ ions are produced at the same energy [9].

Concerning the second double ionization energy, measured at 39.4 ± 0.5 eV, satisfactory agreement is only found between the present work and double charge transfer spectroscopy [1]. Dorman and Morrison [4] measured an onset at 36.8 eV (given without error limit). Mann et al. [15], in their earliest measurement on the NH_3^{2+} dication, measured an ionisation energy of 42 ± 3 eV. Configuration interaction calculations determined a double ionization energy at 38.96 eV corresponding to $\text{NH}_3^{2+}(\tilde{A}^1E)$ state obtained by the simultaneous ionization of the ($3a_1$) and ($1e$) orbitals of NH_3 , rather than to a $\text{NH}_3^{2+}(\tilde{X}^1E)$ produced by the removal of two electrons from the same ($1e$) orbital which would have an ionization energy of about 45 eV [1,8]. $\text{NH}_3^{2+}(\tilde{A}^1E)$ and (3A_2) states were calculated, at about 37.1 and 42.9 eV respectively [8].

Surprisingly no ionization energy was measured in the energy range of 39 eV by photoionization [3]. No PIPICO signal has been measured [3]. However, in the H^+ dissociation channel, onsets are measured at both energies of 34.9 ± 0.4 and at 39.2 ± 0.2 eV [9] proving that the Franck-Condon region simultaneously crosses the attractive well and the repulsive part of both the potential energy surface of the \tilde{X}^1A_1 and of the \tilde{A}^1E states of NH_3^{2+} .

By double charge transfer spectroscopy [1] and by photoionisation [3], an ionization energy is determined at 44.6 ± 0.7 and 44.5 ± 0.6 eV respectively. PIPICO signals, observed at this energy, "may be due to coincidences between NH^+ and H^+ or N^+ and H^+ " [3].

Table 1 Comparison of the photoionization (PI) and electroionization (EI) mass spectra of NH_3 and ND_3 at the indicated ionizing particle energies (base peak NH_3^+ or $\text{ND}_3^+ = 100$)

| | NH_2^+ | NH^+ | N^+ | H_2^+ | H^+ | NH_3^{2+} | N^{2+} |
|----------------------|-----------------|---------------|--------------|----------------|--------------|--------------------|-----------------|
| EI, 100 eV this work | 73 | 2.5 | 0.7 | 0.09 | 0.16 | 0.15 | 0.005 |
| EI, 70 eV [12] | 70 | 2.5 | 0.6 | - | 0.5 | 0.09 | - |
| PI, 41eV[13] | 85 | 8.0 | 1.2 | - | - | 0.1 | - |
| | ND_2^+ | ND^+ | N^+ | D_2^+ | D^+ | ND_3^{2+} | N^{2+} |
| EI, 100 eV this work | 85 | 5.8 | 3.3 | 0.05 | 1.0 | 0.1 | 0.011 |
| PI, 41eV[13] | 95.6 | 9.6 | 2.8 | - | 5.8 | 0.12 | - |

Fig. 1. The direct electroionization efficiency curve of the NH_3^{2+} dication and its first derivative in the energy range 30-100 eV. For the explanation of the dashed curve, see the text.

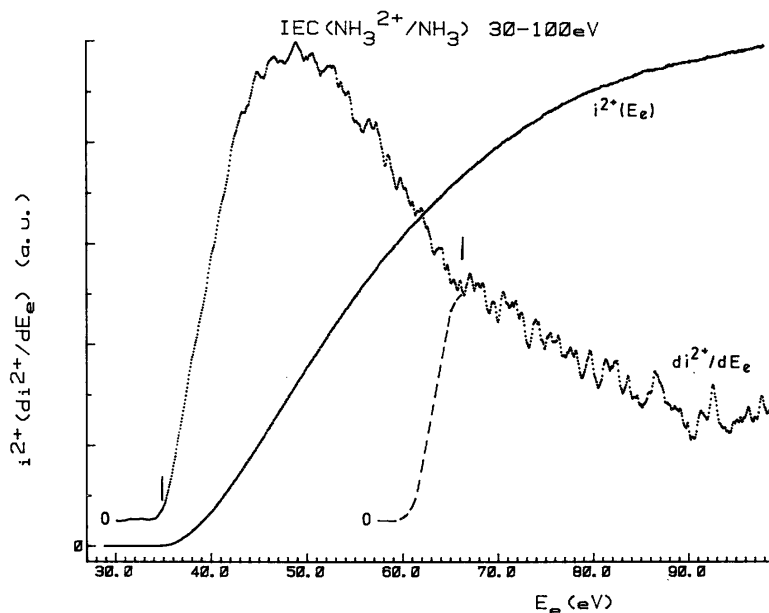
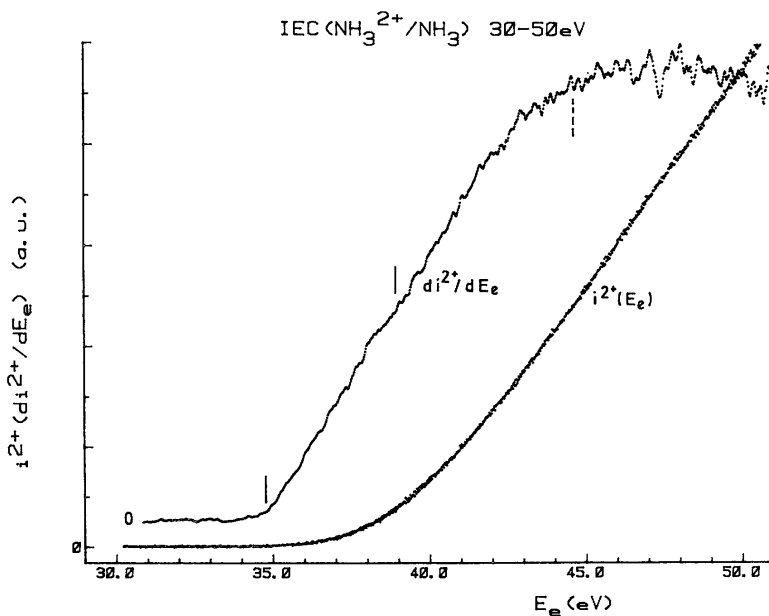


Fig. 2. The direct electroionization efficiency curve of the NH_3^{2+} dication and its first derivative in the energy range 30-50 eV. Vertical bars indicate ionization energies. The ionization energy at 44.5 eV, measured by DCTS [1] and PI [3], is indicated by a dashed vertical bar.



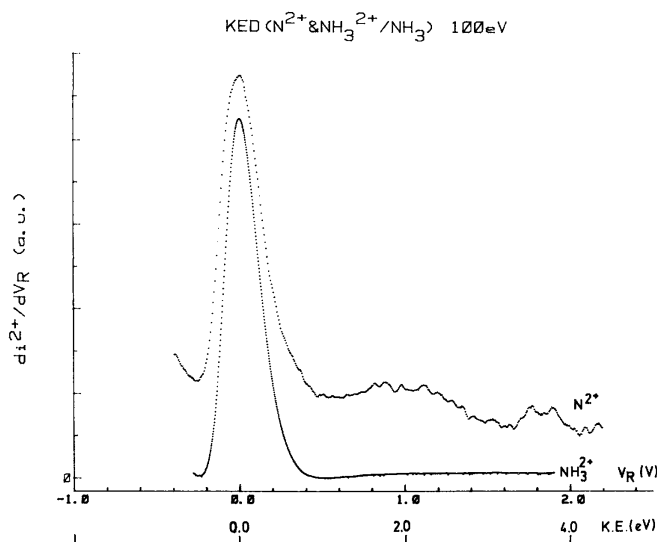
By electroionization, in this work, this ionization energy would be located in the plateau of the first differentiated ionization efficiency curve of NH_3^{2+} as shown in figs. 1 and 2. No distinguishable structure could be observed at about 45 eV. As the overall shape of these curves would suggest, the third double ionization energy of NH_3 could be masked by autoionization. However, the dissociative ionization of NH_3 leading to NH^+ and H^+ and/or H_2^+ shows thresholds respectively at 46.8, 46.1, and 47.2 eV in the corresponding ionization efficiency curves [9]. On the contrary, no critical energy is measured around 46 eV for N^+ [9]. These results remove the uncertainty mentioned in the PIPICO work [3].

Table 2 Experimental and theoretical double ionization energies (eV) of NH_3 with respect to the neutral NH_3 ground state

| | | | |
|--------------------|---------------------------|----------------|----------------|
| DCT spectr. [1] | 35.3 ± 0.7 | 38.9 ± 0.7 | 44.6 ± 0.7 |
| CSR [2] | $32.4 \pm 0.3^{\text{a}}$ | - | - |
| PI [3] | 35.4 ± 0.5 | - | 44.5 ± 0.5 |
| EI [4] | 33.7 ± 0.2 | 36.8 | - |
| [12] | 34.4 ± 0.2 | - | - |
| [14] | - | 42.0 ± 3.0 | - |
| this work | 34.8 ± 0.2 | 39.4 ± 0.5 | - |
| theory [1] SCF | 33.68 | 37.04 | 43.99 |
| CI | 34.51 | 38.96 | 45.41 |
| [6] | 34.6 | - | - |
| [7] | 34.6 | - | - |
| [8] | 34.8^{b} | 38.7 | 45.5 |
| Auger spectr. [15] | 35.4 ± 0.1 | 40.1 ± 0.1 | 46.1 |
| [16] | 34.0 | 39.0 | 45.3 |
| [17] | 33.4 ± 0.5 | 37.6 ± 0.5 | 44.1 ± 0.5 |

^a) Using IP (NH_3) = 10.175 eV [14]. ^b) Using IP (NH_3^+) = 34.8 eV as determined in this work.

Fig. 3. The kinetic energy distribution spectrum of $\text{N}^{2+}/\text{NH}_3$ and $\text{NH}_3^{2+}/\text{NH}_3$ as recorded with 100 eV electrons.



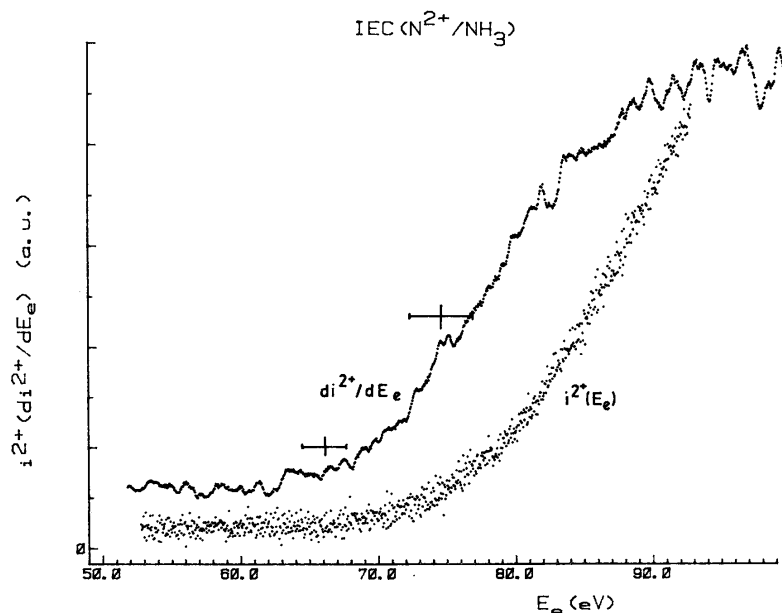
As mentioned earlier in this work, a noticeable change in slope is observed in the first differentiated ionization efficiency curve of NH_3^{2+} at about 66 eV. As discussed below, the first appearance energy measured for the N^{2+} ion is at 65.9 ± 1.7 eV. In this energy range the doubly charged fragment is produced with neutral H atoms and/or an H_2 molecule almost without translational energy. The doubly ionized NH_3^{2+} state, which dissociates at this energy, is expected to have a deep potential well. By Auger electron spectroscopy [16-18] doubly ionized states were detected at about 61.3 and 70 eV. These two states were described by $(2a^{-1}, 1e^{-1})^1E$ and $(2a^{-2})^1A_1$ configurations respectively. It is very likely to correlate the critical energy observed at 66 eV with the existence of the 1E state at about 61.3 eV ionization energy. This is shown by the dashed curve, drawn in fig. 1 and starting at about 61 eV.

The kinetic energy distribution of N^{2+} as observed for 100 eV electrons, is shown in fig. 3 together with that of NH_3^{2+} used for the translational energy scale calibration. The doubly ionized fragment N^{2+} exhibits an important thermal distribution as well as a weak high-energy contribution at about 1.8 eV kinetic energy. The low intensity of the signal does not allow us to measure an appearance energy of this distribution. However, the comparison of the distribution shown in fig. 3 and that of N^{2+} from N_2 , published earlier [19], unambiguously shows that the signal at $m/e = 7$ is only produced by NH_3 .

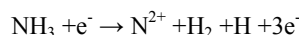
This statement is confirmed by the ionization efficiency curve and its first derivative shown in fig. 4.

Two onsets are measured, i.e. 65.9 ± 1.7 and 74.3 ± 2.6 eV. For N^{2+} from N_2 the lowest onset was measured at 61.1 ± 0.5 eV [19].

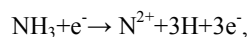
Fig. 4. The direct electroionization efficiency curve of the N^{2+}/NH_3 dication and its first derivative over the energy range 50-100 eV. Vertical bars locate the average onsets while the horizontal bars refer to the error limit on the threshold energies.



The dissociation mechanisms expected at this energy, and producing N^{2+} ions, are only



or



for which the lowest thermodynamic onsets would be 51.7 and 56.2 eV respectively [20,21]. The energy difference between the lowest observed threshold, i.e. 65.9 eV, and the calculated onsets, is about 14.2 ± 1.7 and 9.7 ± 1.7 eV respectively. On the other hand, at least a part of the N^{2+} ions are known to carry only thermal energy (see fig. 3). The excess energy has essentially to be electronic energy.

The number of particles involved in the dissociation process(es), as well as the large number of possible excited states, make it speculative to propose any assignment. However, as noticed earlier in this discussion, it seems to be likely to correlate the onset measured at 65.9 eV with the dissociation of a $NH_3^{2+}(^1E)$ state observed at 61 eV by Auger electron spectroscopy [16-18]. Similarly, the second threshold of N^{2+} , measured at 74.2 eV, could be ascribed to the dissociation of the $NH_3^{2+}(^1A_1)$ state observed at about 70 eV [16-18].

It has to be noticed that a translational energy distribution of N^{2+} , recorded with 100 eV electrons and peaking at 1.8 eV, is observed. Due to the low intensity of the signal, it has not been possible to measure appearance energies for these ions.

Acknowledgement

We acknowledge the Fonds de la Recherche Fondamentale Collective (FRFC) and the University of Liège for financial support and the Belgian Government for an Action de Recherche Concertée (ARC) contract.

References

- [1] J. Appel and J.A. Horsley, *J. Chem. Phys.* 60 (1974) 3445.
- [2] C.J. Proctor, C.J. Porter, T. Ast, P.D. Bolton and J.H. Beynon, *Org. Mass Spectrom.* 16 (1981) 454.
- [3] D. Winkoun and G. Dujardin, *Z. Physik D4* (1986) 57.
- [4] F.H. Dorman and J.D. Morrison, *J. Chem. Phys.* 35 (1959) 575.
- [5] R.K. Boyd, S. Singh and J.H. Beynon, *Chem. Phys.* 100 (1985) 297.
- [6] W. Koch and H. Schwarz, *Intern. J. Mass Spectrom. Ion Processes* 68 (1986) 49.
- [7] S.A. Pope, I.H. Hillier, M.F. Guest and J. Kendrick, *Chem. Phys. Letters* 95 (1983) 247.
- [8] F. Tarantelli, A. Tarantelli, A. Sgamellotti, J. Schirmer and L.S. Cederbaum, *Chem. Phys. Letters* 117 (1985) 577.
- [9] R. Loch, Ch. Servais, M. Ligot and J. Momigny, to be published.
- [10] R. Loch and J. Schopman, *Intern. J. Mass Spectrom. Ion Phys.* 15(1974) 361.
- [11] Ch. Servais, R. Loch and J. Momigny, *Intern. J. Mass Spectrom. Ion Processes* 74 (1986) 179.
- [12] T.D. Mark, F. Egger and M. Cheret, *J. Chem. Phys.* 67 (1977) 3795.
- [13] B.P. Tsai and J.H.D. Eland, *Intern. J. Mass Spectrom. Ion Phys.* 36 (1980) 143.
- [14] M.J. Weiss and G.M. Lawrence, *J. Chem. Phys.* 53 (1970) 214.
- [15] M.M. Mann, A. Hustrulid and J.T. Tate, *Phys. Rev.* 58 (1940) 340.
- [16] R.W. Shaw, J.S. Jen and T.D. Thomas, *J. Electron Spectry.* 11 (1977) 91.
- [17] J.M. White, R.R. Rye and J.E. Houston, *Chem. Phys. Letters* 46 (1977) 146.
- [18] R. Camilloni, G. Stefani and A. Giardini-Guidoni, *Chem. Phys. Letters* 50 (1977) 213.
- [19] R. Loch and J. Momigny, *Chem. Phys. Letters* 66 (1979) 574.
- [20] B. deB. Darwent, Bond dissociation energies in simple molecules, NSRDS-NBS 31 (1970).
- [21] CE. Moore, Atomic energy levels, Vol. 1, NBS Circ. 467 (1949).