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Ionization of ammonia molecules by collision with metastable neon atoms

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Abstract

The ionization of ammonia molecules in collision with metastable neon atoms has been studied by measuring the energy spectrum of emitted electrons and the mass spectrum of product ions. The results show that nascent NH_3^+ ions are formed in the ground, $X^2A'_1$, and in the first excited, A^2E , states. The latter then gives rise to dissociation leading to NH_2^+ ion fragments. The $\text{NH}_2^+/\text{NH}_3^+$ ratio is much lower than in case of NeI photoionization, indicating that the particle interaction strongly influences the ionization dynamics. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The collision of an excited atom A^* with a target molecule BC characterized by an ionization potential lower than the atom excitation energy, can lead to the autoionization of the collision complex:



The ionic complex $[A \cdots BC^+]$ then continues the collision leading to the formation of different ions. In addition to the formation of BC^+ ions in different vibronic states (Penning ionization) and associate ions ABC^+ (associative ionization), an ion–molecule reaction between ground state A and BC^+ can occur (rearrangement ionization), as well as the dis-

sociation of excited BC^+ molecular ions (dissociative ionization).

These collisional autoionization processes have been the subject of several experimental and theoretical studies and two review articles have summarized the most important conclusions which have been drawn [1,2].

Experimental studies on the dynamics of autoionization of collisional complexes can be worked out by measuring different observables such as, for example, the kinetic energy spectra of the emitted electrons or the collision energy dependence of total and partial (for the formation of a specific ionic product) ionization cross-sections. Actually, these three measurements provide different and complementary information. The electron energy spectra provide information about the vibronic internal state distribution of the nascent ion within the collisional complex. The energy dependence of the total ioniza-

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tion cross-section provides information about the optical potential, which describes the collision up to the ionization event. The energy dependence of partial ionization cross-section provides information on the ionic complex evolution towards the final products.

In the present work, a study of the ionization of ammonia molecules by metastable neon atoms has been carried out by measuring the experimental observables mentioned above. A joint study has been performed by two laboratories, one for the electron kinetic energy measurements (University of Brest) and one for the ionization cross-section measurements as a function of collisional energy (University of Perugia).

The low-resolution energy spectrum of emitted electrons in the Ne^*-NH_3 collisional autoionization was measured by Cermak [3]. It was determined that the ionization leads to the formation of nascent X^2A_1 and A^2E states of NH_3^+ . No other studies, to the best of our knowledge, have been reported in the literature about the Ne^*-NH_3 collisional autoionization. However, the analogous He^*-NH_3 system has been studied by Ohno et al. [4], who reported the spectrum of emitted electrons in $\text{He}^*(2^3S)$ Penning ionization compared with the electron spectrum in He I photoionization. It was found that, in both cases, the nascent NH_3^+ ions are produced in the ground and the first excited electronic states, with a remarkably lower A^2E/X^2A_1 population ratio, in the case of Penning ionization [4].

The present study shows that the ionization of NH_3 by metastable neon atom collision produces nascent NH_3^+ ions in the two lower electronic states, as in the case of helium metastable atoms and in agreement with the previous observation of Cermak [3]. The mass spectrometric measurements indicate that NH_3^+ and NH_2^+ ions are produced. The $\text{NH}_2^+/\text{NH}_3^+$ ratio is strongly lower in collisional autoionization compared to Ne I photoionization. This ratio shows a significant energy dependence which is related to the population of the two electronic states of the nascent NH_3^+ ions.

2. Experimental

The experimental results presented here have been obtained in two different laboratories, by using ex-

perimental apparatus described in detail in Refs. [5,6]. A general description of such apparatus is given in this section.

2.1. The Brest apparatus: the energy analysis of product electrons

The Brest apparatus consists of two effusive beams on the horizontal plane with an electron energy analyzer, which can be also rotated, when required, in order also to analyze the angular dependence of emitted electrons.

The two beams are produced by microcapillary array sources and the rare gas atoms are excited to their metastable states by electron impact. The rare gas source temperature can be heated and therefore the most probable metastable atom velocity, v^* , is given by $v^* = (2kT/m)^{1/2}$, where T and m are the temperature and atomic mass, respectively. The relative collision velocity can also be adjusted by varying the angle between the two beams, from 45° to 90° .

The electron energy analyzer is a 127° cylindrical selector with a resolution of ~ 50 meV at a transmission energy of 3 eV. Such a characteristic has been verified by measuring the spectrum of photoelectrons, which are emitted by argon atoms under He I radiation. The geomagnetic field is reduced to ≤ 20 mG by Helmholtz coils surrounding the electron spectrometer.

2.2. The Perugia apparatus: measurement of the total and partial cross-sections

The Perugia apparatus basically consists of an effusive metastable neon atom beam, which crosses at right angles an effusive secondary beam, produced by a microcapillary array. The ions produced in the collision zone are extracted, focused, mass analyzed by a quadrupole filter and then detected by a channel electron multiplier.

The neon beam can be produced by two sources, which can be used alternately. The first one is a standard effusive source at room temperature coupled with an electron bombardment device, while the second is a microwave discharge beam source operating with pure neon at a pressure of ~ 1 Torr.

Together with metastable atoms, the discharge source produces a large number of NeI photons. This allows comparative studies of Penning ionization and photoionization.

The metastable atom velocity can be analyzed by a time-of-flight (TOF) technique: the beam is pulsed by a rotating slotted disk and the metastable atoms are counted, using a multiscaler, as a function of the delay time from the beam opening. By using this technique, the velocity dependence of the cross-section is obtained. Time delay spectra of the metastable atom arrival at the collision zone are recorded, as well as the time spectra of the product ion intensity, then the relative cross-sections, $\sigma(E)$, are obtained for a given delay time τ according to the equation

$$\sigma(E) = \frac{N^+(\tau)}{N^*(\tau)} \frac{v^*}{v_r},$$

where N^+ and N^* are the intensities of the product ions and metastable atoms, respectively; v^* is the laboratory velocity of the metastable atoms; and v_r is the relative collision velocity. By the TOF technique, the separation of photo-ions and Penning-ions is very easy, the former being detected at practically zero delay time.

Absolute values of total ionization cross-sections for different species can be obtained by the measurement of relative ion intensities in the same conditions of metastable atom and target gas density in the crossing region. This allows the various systems to be put on a relative scale which can be normalized by reference to a known cross-section such as, in the present case, the Ne^*-Ar absolute total ionization cross-section by West et al. [7].

3. Results and discussion

The energy spectrum of the electrons emitted in the ionization of ammonia molecule by metastable neon atoms, at average collision energy of 45 meV, is reported in Fig. 1. Two bands appear: one peaked around 5.6 eV and another one, at lower energy, interrupted around 0.5 eV as this represents the minimum energy that can be significantly analyzed in the present arrangement. The absolute cross-section for total ionization as a function of collision energy is reported in Fig. 2. The value of the cross-section is high ($\sim 60 \text{ \AA}^2$ at 45 meV) and shows a strongly decreasing trend with increasing

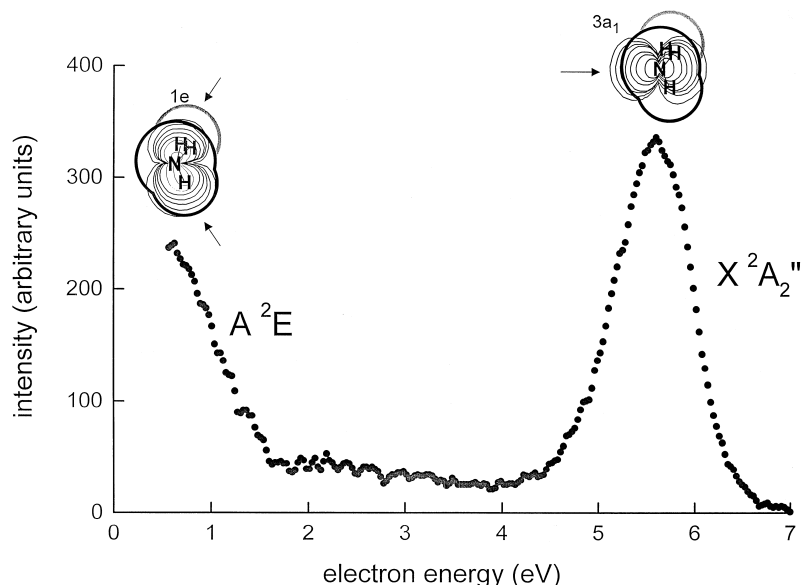


Fig. 1. The energy spectrum of emitted electrons in the ionization of NH_3 molecules by metastable neon atoms, at an average collision energy of 45 meV. The two bands correspond to two different orientations of the ammonia molecule with respect the approaching metastable neon atom, at the instant of the ionization event.

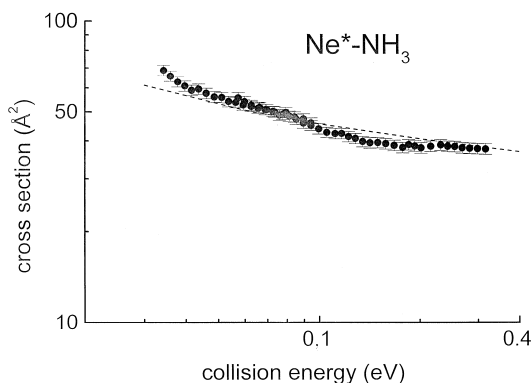


Fig. 2. Absolute total ionization cross-section for $\text{Ne}^*(^3\text{P}_{2,0})\text{-NH}_3$ as a function of the collision energy. The dashed line is a theoretical calculation performed with an optical potential, whose real part is a pure van der Waals interaction and the imaginary part is a parametric function with best-fit parameters (see text).

collision energy. In Fig. 3, the collision energy dependence of the $\text{NH}_2^+/\text{NH}_3^+$ branching ratio is shown. The ratio shows a relative increase in the fragment ion when the collision energy increases.

The two bands in the electron spectrum of Fig. 1 correspond to the formation of nascent NH_3^+ ions in two electronic states: the ground, $\text{X}^2\text{A}'$, and the first excited, A^2E , states. The ground state is produced by the removal of one electron from the $3a_1$ orbital of the neutral molecule, which corresponds to the non-bonding lone-pair orbital of the N atom. The excited state comes from ionization from the $1e$ orbital, which corresponds to the N–H bonding orbital. These two orbitals, whose electron density distributions are schematized in Fig. 1, have adiabatic ionization potentials of 10.15 and 14.98 eV, respectively [8,9].

The formation of the two NH_3^+ electronic states corresponds to different orientations of the molecule, at the instant of the ionization, with respect to the incoming metastable atom. In fact, according to the electron exchange model [10], Penning ionization occurs through an electron transfer from the orbital of the ammonia molecule to be ionized into the inner-shell vacancy of the metastable Ne^* atom, followed by the ejection of its 3s electron. Since the ionization occurs mainly at the turning point of the collision, the geometry of the intermediate complex at such a distance is crucial for determining the

orbital that is preferentially ionized. Due to a higher overlap with the ionic core of the metastable atom, when at the turning point the ammonia molecule is oriented with the lone-pair orbitals directed toward the Ne^* atom (collision toward the N atom, along the C_{3v} axis), then one electron is removed from the $3a_1$ orbital, leading to the production of the ground state $\text{NH}_3^+(\text{X}^2\text{A}')$ ion. When at the turning point the ammonia molecule is oriented with the H atoms directed toward the Ne^* atom (collision toward the H atoms), then one electron is removed from the N–H $1e$ bonding orbital leading to the formation of the excited $\text{NH}_3^+(\text{A}^2\text{E})$ ion. It can be noted that ground state $\text{NH}_3^+(\text{X}^2\text{A}')$ ions could be also produced by collision complexes where the metastable atom is approaching NH_3 along the C_{3v} axis on the side of the three hydrogen atoms (see Fig. 1). It has to be noted that the steric hindrance of the three hydrogen atoms makes the ionization probability in this case much lower than for the approach on the side of the nitrogen atom.

The production of NH_3^+ and NH_2^+ ions is readily explained by the different behavior of the populated electronic states. In fact, photoionization studies have shown that the ground state $\text{X}^2\text{A}'$ is stable [11–13], while the excited A^2E state is associated to a Jahn–Teller distortion that leads to an almost complete (80%) dissociation into NH_2^+ and NH^+ ion fragments with threshold energies of 15.8 and 16.9 eV, respectively [14–16]. Due to the electronic energy of

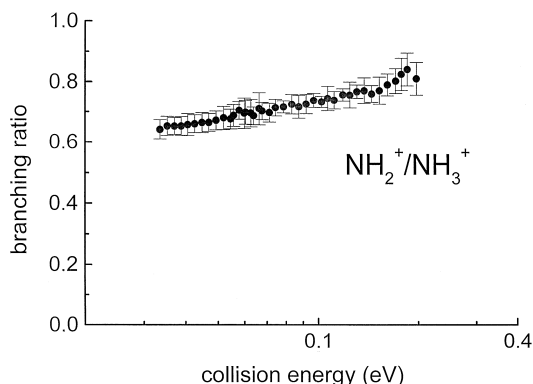


Fig. 3. The $\text{NH}_2^+/\text{NH}_3^+$ branching ratio as a function of the collision energy in the collisional autoionization of NH_3 molecule by metastable neon atom.

metastable neon atoms (16.6 eV for $^3\text{P}_2$ and 16.7 eV for $^3\text{P}_0$) only NH_3^+ and NH_2^+ ions can be produced in thermal energy collisions, as is actually observed.

At a collision energy of 45 meV, the $\text{NH}_2^+/\text{NH}_3^+$ ratio reported in Fig. 3 shows a value of 0.65. This ratio corresponds to the ratio of the areas of the two bands of the spectrum of Fig. 1, which amounts to $\sim 0.7 \pm 0.1$, when the proper extrapolation to zero kinetic energy is done on the A^2E band. This observation is consistent with the above considerations, indicating that the dissociation of excited A^2E primary ions is almost complete.

Taking advantage of the fact that the microwave discharge source provides metastable neon atoms and also NeI photons, the ratio of $\text{NH}_2^+/\text{NH}_3^+$ ions produced by NeI photo- and Ne^* collisional autoionization has been measured under the same experimental conditions. It has been found that in NeI photoionization the ratio is 1.1, in excellent agreement with the value measured by Samson et al. [17], while in metastable neon atom collisions, the ratio is sensibly lower being between 0.65 and 0.75 over the whole collision energy range presently investigated. This remarkable difference indicates that the Ne^*-NH_3 interaction strongly influences the ionization dynamics. An analogous effect has been observed in the HeI photo- and $\text{He}^*(^3\text{S})$ -Penning ionization of ammonia [4]. One possible explanation lies in the fact that ammonia is a molecule with a large permanent dipole moment ($\mu = 1.49$ D) and this can have a significant effect on the interaction potential energy surface of the colliding particles. The negative pole and the presence of the lone pair of electrons can cause an extensive s-p hybridization of metastable neon (and helium) [2], which leaves the ionic core of the metastable atom unshielded and leads to a strong electrostatic interaction. This attraction has the effect of shortening the range of repulsion, producing an accessibility to the $3a_1$ orbital larger than in photoionization [2,4].

No specific information is present in the literature on the interaction potential of metastable neon atoms with ammonia molecules. However, the possible s-p hybridization of the excited neon atom for an approach toward the end of the nitrogen atom and the expected much less attractive interaction for an approach along the end of the hydrogen atoms should characterize this interaction as strongly anisotropic.

To discuss this argument, a comparison can be made with the analogous $\text{Ne}^*-\text{H}_2\text{O}$ system. Water is a molecule with a larger dipole moment ($\mu = 1.85$ D) than ammonia and is characterized by two lone-pair orbitals on its negative end. Therefore, one might expect that the attraction introduced by s-p hybridization here would be present to an even larger extent. Bentley [18] calculated by an ab initio method the potential energy surface for $\text{Ne}^*-\text{H}_2\text{O}$ interaction which shows a deep potential well for the approach of metastable neon to the oxygen end of the molecule (~ 0.25 eV at 2.5 Å) and a much weaker attraction for an approach to the H ends. This interaction shows a much larger attractive energy than inferred from a simple van der Waals potential. Analogous strongly anisotropic characteristics were also found for the $\text{He}^*-\text{H}_2\text{O}$ potential energy surface [19–21].

The presence of a strong attractive potential in Ne^*-NH_3 is in agreement with the large absolute value of the total ionization cross-section and its collision energy dependence of Fig. 2 which shows a strongly decreasing trend [22,23]. Moreover, the presence of a deep well along the direction of the lone-pair orbital on the nitrogen atom has been characterized for the $\text{Na}-\text{NH}_3$ interaction (~ 0.26 eV at 2.75 Å) [24]. The well-known analogies of the interactions of sodium and metastable neon atoms with several partners suggest the presence of a similar potential well in Ne^*-NH_3 . A further indication of the anisotropic character of the Ne^*-NH_3 intermolecular potential is found in the electron energy spectrum of Fig. 1. Here, negative shifts of 300 ± 30 meV for the X^2A and 100 ± 30 meV for the A^2E have been observed. These shifts can be interpreted by a different attractive potential in the collision entrance channel for the two orientations of Fig. 1, rather than for differences in the exit channel, which is expected to be represented by a similar long-range ion-induced dipole interaction for both the ionic states.

To test indirectly the necessity of invoking an attractive anisotropic potential for explaining the present results, an attempt has been made to analyze the total cross-section in terms of a simple van der Waals optical isotropic potential. An estimate of a pure van der Waals interaction potential for Ne^*-NH_3 has been performed [25,26] then an adjustable

imaginary part has been added to this potential to fit the experimental cross-sections. A semiclassical ionization cross-section calculation was carried out through the JWKB approximation [1]. The result of the best-fit calculation is reported in Fig. 2 and it is well evident that, even forcing the imaginary part of the optical potential, the slope of the calculated cross-sections it is not satisfactorily reproduced.

The observed increase of the $\text{NH}_2^+/\text{NH}_3^+$ ratio at increasing collision energies (see Fig. 3) can be explained as a consequence of the larger production of dissociative $\text{NH}_3^+(\text{A}^2\text{E})$ ions compared to the ground state $\text{NH}_3^+(\text{X}^2\text{A}')$. An influence of the collision energy on the Jahn–Teller distortion responsible of the fragmentation of the nascent $\text{NH}_3^+(\text{A}^2\text{E})$ can be discarded by analogy with other systems where such an influence has been not observed [27,28]. An attempt to verify directly a larger production of the excited $\text{NH}_3^+(\text{A}^2\text{E})$ state at higher collision energies has been made by measuring the electron energy spectra at different collision energies. However, the large experimental error introduced by electrons close to zero kinetic energy did not allow significant results to be obtained. In the light of these considerations, it appears that, in the present case, the fragmentation pattern of the ions is a better tool for characterizing the relative population of the two electronic states and its energy dependence. The NH_2^+ and NH_3^+ ions are separated by only 1 atomic mass. This makes any error on ion collection efficiency or transmission through the mass filter negligible.

The observed increase of population of the excited $\text{NH}_3^+(\text{A}^2\text{E})$ state as a function of the collision energy can be simply explained by the increase of the total available energy. In terms of the electron energy spectrum of Fig. 1, when the collision energy is increased, both bands shift to higher energies and the area of the lower-energy band consequently increases. However, a second explanation can justify the larger population of the excited state at higher collision energies. This explanation takes into account the anisotropy of interaction combined with the electron density distribution of the $3a_1$ and $1e$ orbitals. It has been observed that the anisotropy of interaction can influence not only the electron band shifts but also the relative formation of the electronic states of the primary ion as a function of collision

energy [29–31]. In the present case, at lower collision energies the stronger attraction in the proximity of the N atom makes the $\text{Ne}^+ \cdots \text{NH}_3$ turning point geometry more favored compared to the $\text{Ne}^+ \cdots \text{H}_3\text{N}$ one. However, when the collision energy increases, the geometry of the complex at the turning point becomes more statistical, leading to a relative increase of the excited state population. In a recent study of $\text{Ne}^+-\text{CH}_3\text{Cl}$ collisions by quasi-classical trajectories, it has been found that this effect is actually present [28]. There are no arguments for deciding which one of the above two possible explanations is dominant, but very likely both energy and dynamical effects are simultaneously operative.

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