Ionization of low Rydberg He atoms by rotational deexcitation of NH₃

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(Received 28 July 1986)

Ionization of excited helium atoms in $n\,^1P$ ($14 \le n \le 16$) states due to collisions with the polar molecules NH_3 has been studied in a thermal energy crossed-beam experiment. A large ionization signal from these low Rydberg states is observed even though there is insufficient energy available from rotational $\Delta J = -1$, $\Delta K = 0$ relaxation transitions of the molecule. In order to explain our observations, large $|\Delta J|$ transitions must be postulated.

Among the quenching mechanisms that take place in collisions between excited atoms $A^*(nl)$ and neutral targets M, Penning ionization (PI) resulting in the ionization of M is the dominating process when n is small ($n < 3$ or 4). When n reaches 5 or 6, momentum transfer, also called l mixing (lM), becomes of the same order of magnitude as PI. For higher n, lM is dominant in helium, especially for the singlet states where the energy difference $E_{nP} - E_{nD}$ is much smaller than in the triplet states. Also for higher n, collisions with n changing (nC) become important when the target is a molecule M with internal structure, which introduces additional degrees of freedom that are energetically accessible. Both processes can be represented by

$$A^*(nl) + M(J,K) \xrightarrow{\sigma_t} A^*(n'l') + M(J',K'), \quad l\text{M} + n\text{C} .$$

$$(1)$$
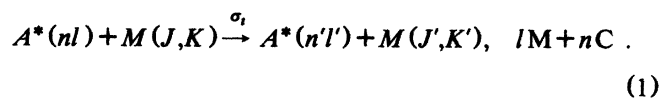
Collisional ionization (CI) of A^* can also take place at high n,

$$A^*(nl) + M(J,K) \xrightarrow{\sigma_i} A^+ + M(J',K'), \quad \text{CI} , \qquad (2)$$
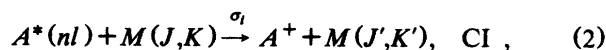
but is expected to be at least one order of magnitude smaller than reaction (1).[1]

Collisions between high Rydberg states $A^*(nl)$ ($25 < n < 50$) and molecules at thermal energies have been widely studied experimentally and theoretically.[1] The experimental measurements generally give the total quenching cross section of the Rydberg atom which includes lM, nC, and CI. Most deal with relatively high levels ($n > 30$) where the binding energy of the excited electron is only some tens of meV. For such low binding energies, the collision can be described correctly within the framework of the impulse approximation which separates explicitly the scattering of the Rydberg electron from that of the ionic core A^+. Often, only the scattering of the electron has been considered in a long-range interaction with the multipoles of the molecule which results in a change in its rotational energy.

Flannery,[2] Matsuzawa,[3] Nakamura, Shirai, and Nakai,[4] Smirnov,[5] Latimer,[6] Petitjean and Gounand,[7] and recently Preston and Lane[8] have calculated expressions for the cross sections σ_t and σ_i defined by reactions (1) and (2). Convenient analytical formulas have been derived by

Petitjean and Gounand:[7] σ_i and σ_t are proportional to the square of the dipole moment for dipolar molecules and to the square of the quadrupole moment for quadrupolar molecules, the latter leading generally to much smaller cross sections. In the case of lM, the resonant character of the reaction is of primary importance to the absolute value of σ_t, and the most populated final states are energy selected by $E_{nl} + E_{J,K} \simeq E_{n'l'} + E_{J',K'}$. In the case of CI, ionization is possible only if the energy ΔE_{rot} released in the rotational transition $J,K \rightarrow J',K'$ is greater than the binding energy of the Rydberg electron, $|E_{nl}| = R/n^{*2}$. The selection rules $\Delta J = -1$, $\Delta K = 0$ in the framework of the dipole Born approximation which is commonly used, lead to $\Delta E_{rot}(-1,0) = 2BJ$ [$E_{J,K} = BJ(J+1) + (B-C) \times K^2$ for a symmetric top molecule such as NH_3; B and C are the rotational constants of the molecule]. In this case, the rotational levels of the molecule participating in ionization and selected by the requirement $\Delta E_{rot}(-1,0) \ge |E_{nl}|$ are

$$J \ge |E_{nl}|/2B . \qquad (3)$$

$Xe(nf) + NH_3$ ionizing collisions were studied for $25 \le n \le 40$ in the work of Kellert *et al.*[9] Rotational relaxation of NH_3 with $\Delta J = -1$ and $\Delta K = 0$ leads to ionization of $Xe(nf)$, $n = 25(31)$ for instance, only for J levels located in the high-energy tail of the distribution $J > 10(7)$. These authors observed an ionization cross section which increases with increasing n as expected; however, it was about five times larger than the theoretical cross section calculated in the dipole Born approximation. In this context, σ_i should vanish when the rotational energy available in a $\Delta J = -1$, $\Delta K = 0$ relaxation of the molecule becomes insufficient to remove the electron from A^*: the smaller the n value, the greater the electron binding energy E_{nl} and the higher the rotational level J from which the transition originates, must be.

Based on the above discussion, ionization in $He(14\,^1P) + NH_3$ collisions should be possible only in transitions from $J \ge 30$: Such levels are unpopulated in our thermal NH_3 distribution at 300 K (see Fig. 1). In our experiment, the observed ionizing collisions between relatively low excited Rydberg states of helium $He(n\,^1P)$ ($14 \le n \le 16$) and NH_3 can best be explained by invoking collisions where $|\Delta J| > 1$. To our knowledge, this is the first evidence that large $|\Delta J|$ transitions can occur with an ef-
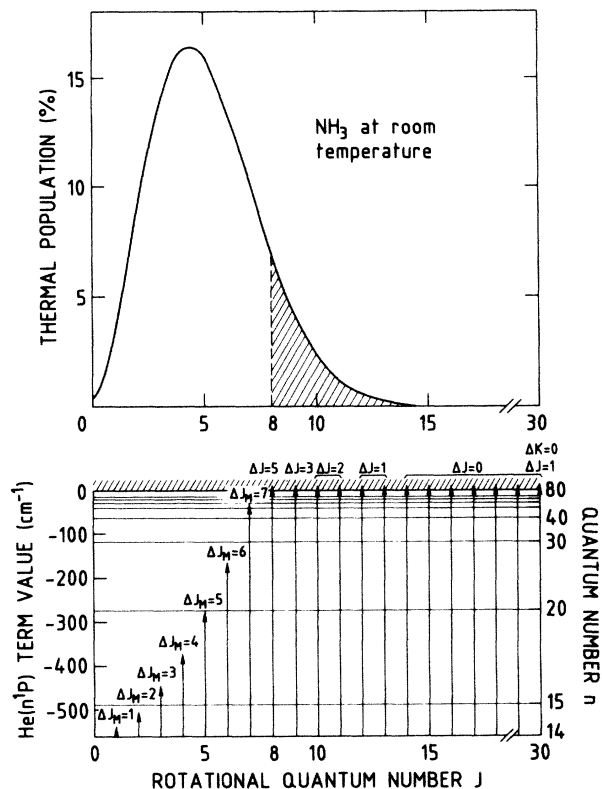
FIG. 1. Rotational population of NH_3 at room temperature [the partial population $J \geq 8$ (shaded area) represents 17% of the total population] and abbreviated term diagram for helium showing the effect of $He(14^1P) + NH_3$ collisions (see text).

FIG. 2. (a) He^+ ion spectra and (b) $He(n\ ^1P) \rightarrow He(1\ ^1S)$ fluorescence light at 50-nm spectra as a function of the laser frequency (one step ≈ 15 MHz at 316–317 nm).

fective probability in ionizing collisions with Rydberg atoms.

The measurements are performed with the three-crossed-beam apparatus described previously in Penning and Hornbeck-Molnar ionization experiments.[10] A metastable $He(2^1S, 2^3S)$ beam, a target beam, and a beam of cw coherent uv light for excitation from the metastable to the radiative level intersect perpendicularly in the extracting chamber of a mass spectrometer. The wavelengths necessary for the $2^1S \rightarrow n\ ^1P$ transitions are close to 316 nm and are generated by intracavity frequency doubling in a single-mode ring dye cavity.[11] In the present experiment, a 4-cm-long rubidium dihydrogen phosphate crystal is used together with the Kiton red dye, leading to a single-mode uv power of 15 to 20 mW. Scans of the laser frequency by 15-MHz steps in the uv are performed by a minicomputer connected to a driven voltage which is sent into the laser instead of the internal voltage. The He^+ ion counts are stored in a block memory and the time duration of the accumulation at each step is adjusted to obtain a satisfactory signal-to-noise ratio. Figure 2(a) shows the normalized He^+ ion spectra obtained for $n = 14$, 15, and 16, as a function of uv frequency. At the same time, the optical resonances are detected by measurement of the photons emitted in the fluorescence to the ground state $n\ ^1P \rightarrow 1\ ^1S$ at 50.5 nm and detected on a channeltron [see Fig. 2(b)].
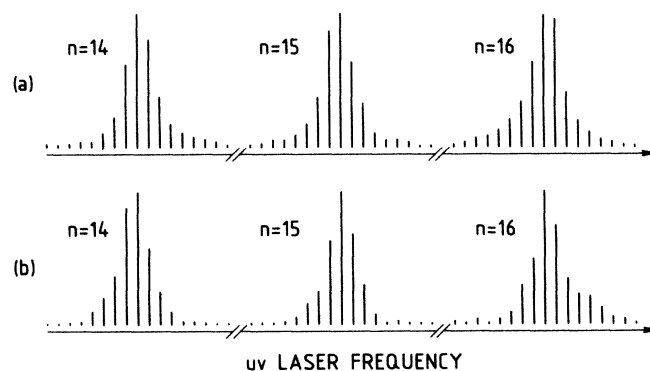
The surprising fact is that we observe a strong He^+ sig-

nal, even though an ionizing $\Delta J = -1$, $\Delta K = 0$ rotational transfer is not possible since the rotational constants of NH_3 are $B = 9.44$ cm^{-1} and $C = 6.20$ cm^{-1}. In Fig. 3, we observe that 428 to 559 cm^{-1} are necessary to ionize the He^* levels considered, yet the available rotational energy $\Delta E_{rot}(-1,0)$ in a $\Delta J = -1$, $\Delta K = 0$ transition does not exceed 94 cm^{-1} at the maximum $J = 5$ of the rotational population (see Fig. 1). For $n = 14(16)$, rotational $\Delta J = -1$, $\Delta K = 0$ relaxation of NH_3 must originate from $J \geq 30(21)$ to satisfy $\Delta E_{rot}(-1,0) \geq |E_{nl}|$. However, the total fractional population in $J \geq 30$ is 6×10^{-13} (6 molecules per cm^3 for a typical total target density of 10^{13} cm^{-3}) only.

The order of magnitude of the He^+ ion counting rate I_{CI} can be deduced from the relationship

$$I_{CI} = kL\alpha I_m \rho \sum_{J=30}^{\infty} \sigma_i(J) p(J) \ , \qquad (4)$$

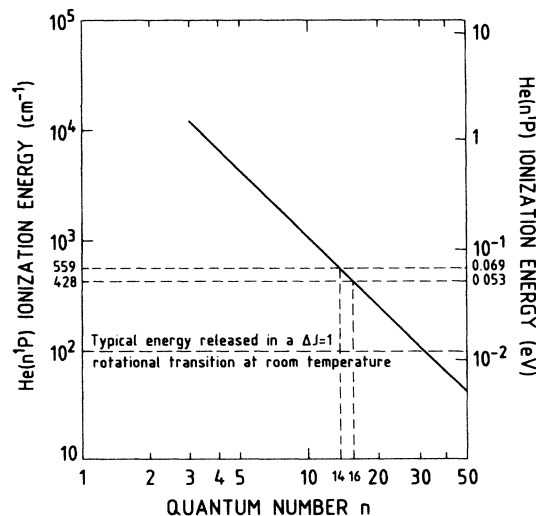where k is the detection efficiency of our experimental sys-

FIG. 3. Ionization energy of $He(n\ ^1P)$ calculated with a quantum defect $\delta = -0.012$ from Ref. 12. The energy released by typical $|\Delta J| = 1$, $\Delta K = 0$ transitions is shown.

tem including the collection coefficient and the mass-analyzer transmission $(k \ll 1)$, and L the average target thickness. Since the excited states $\mathrm{He}(n\,^1P)$ have a short lifetime $(\tau_p \approx 1.5 \times 10^{-7}$ s for $n = 14)$ and definitely cannot contribute to the process after deexcitation to the ground state $1\,^1S$, L can be approximated by $L \approx v\tau_p$, i.e., $L = 0.04$ cm for $v = 2.5 \times 10^5$ cm s^{-1}. I_m is the incident flux of metastable atoms and α the average laser excitation efficiency, ρ is the total density of $\mathrm{NH_3}$ molecules, $p(J)$ is the population of $\mathrm{NH_3}$ molecules having a rotational quantum number J, and $\sigma_i(J)$ is the ionization cross section due to the relaxation of molecules of rotational number J.

Formula (4) leads to the maximum value for I_{CI},

$$I_{\mathrm{CI}} < kL\,\alpha I_m \rho p\,\sigma_i(J = 30)\ ,\qquad(5)$$

where p is the fraction of $\mathrm{NH_3}$ molecules available for the reaction, since $\sigma_i(J)$ decreases as J increases for a given colliding system. Such a calculation leads to

$$I_{\mathrm{CI}} < 8 \times 10^4 k\,\rho p\,\sigma_i(J = 30)\ \text{counts/s}\ .$$

Now, in the usual $\Delta J = -1$, $\Delta K = 0$ hypothesis where only the molecules with $J \geq 30$ participate in ionization, $\rho p \approx 6$ cm^{-3}. The cross section $\sigma_i(J = 30)$ for $\mathrm{He}(n\,^1P)$ $+ \mathrm{NH_3}$ can be calculated by use of the analytical formulas of Petitjean and Gounand[7] based on the dipole Born approximation for the e-$\mathrm{NH_3}$ interaction. For the rotational transition $\Delta J = -1$, $\Delta K = 0$ with $J = 30$, the following value $\sigma_i(J = 30) = 8 \times 10^{-13}$ cm^2 is obtained. This leads to a negligible value $I_{\mathrm{CI}} < 10^{-7}$ counts/s.

Seeking another possible explanation, we consider a multicollision process, with the ionizing collision preceded by several $l\mathrm{M} + n\mathrm{C}$ transitions. For $\mathrm{He}(14\,^1P)$, four transitions, each satisfying $\Delta J = -1$, $\Delta K = 0$ would be necessary. Furthermore, resonances between the rotational energy released in the transition and the energy gap $E_{n''l''} - E_{n'l'}$ for excitation of intermediate levels must exist for the cross section not to be negligible. To examine this possibility, we carefully investigated the dependence of the I_{CI} signal on the $\mathrm{NH_3}$ density measured upstream from the multicapillary array. A linear dependence, indicative of a one-collision ionization mechanism, is observed for values of the pressure $P < 0.08$ Torr (see Fig. 4).

In the light of these measurements, a one-collision ionization with $|\Delta J| > 1$ must be considered. Rotational excitation of molecules with up to several tens ΔJ have been observed in rotational-rainbow scattering with ground-state atoms.[13] In this case, the anisotropy of the interaction potential between the atom and the molecule is at the origin of a strong rotational coupling.[14] A direct extension to the collision presently studied, considering the large value of the mean radius of the He^* atom $(\langle r \rangle = 293a_0$ for $14\,^1P$ in the hydrogenic approximation), could hardly be made.

Transitions with $\Delta J > 1$, constituting a deviation from the dipole Born approximation, have also been observed in rotational excitation of molecules by slow electrons.[15] Other approximations, of Glauber type, which take into account terms of all orders in the interaction potential (i.e., terms of shorter range which were neglected in the dipole Born approximation), have better interpreted $\Delta J = 0$ and $\Delta J > 1$ rotational transitions.
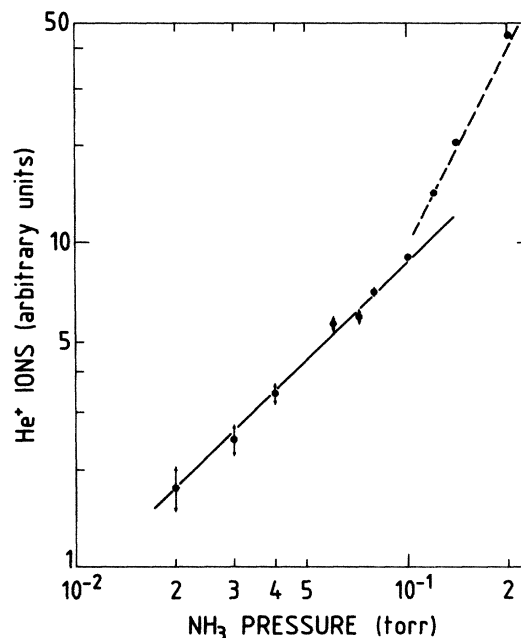

FIG. 4. $\mathrm{NH_3}$ pressure dependence of the experimental He^+ ion signal for $\mathrm{He}(14\,^1P) + \mathrm{NH_3}$ collisions; filled circles with error bars, measurements; full line, calculated linear variation (slope $=1$ in log-log coordinates); dotted line, calculated quadratic variation (slope $=2$ in log-log coordinates). The background signal existing at zero pressure has been subtracted.

In this context, we have determined all the rotational transitions $J,K \to J',K'$ in $\mathrm{NH_3}$ that satisfy $\Delta E_{\mathrm{rot}} = E_{J,K} - E_{J',K'} \geq |E_{nl}|$ [$E_{nl} = 558.8$ cm^{-1} for $\mathrm{He}(14\,^1P)$]. These transitions are shown by arrows in Fig. 1. We observe that no transitions from $J \leq 7$ are ionizing whatever ΔJ and ΔK may be. The energy released in the transition is maximum for $J,K = 0 \to J' = 0, K' = 0$, therefore $|\Delta J| = J$ (noted ΔJ_M in Fig. 1), and is shown by the length of the arrows. However, many transitions from $J \geq 8$, with $|\Delta J| > 1$, are ionizing; they are defined by J, $K = 0 - J \to J'$, $K' = 0 - J'$ with the following values:

$J = 8 \to J' = 0$-5, therefore $|\Delta J| = 5$-8 ;

$J = 9 \to J' = 0$-6, therefore $|\Delta J| = 3$-6 ;

$J = 10 \to J' = 0$-8, therefore $|\Delta J| = 2$-10 ;

$J = 11 \to J' = 0$-11, therefore $|\Delta J| = 2$-11 ;

$J = 12 \to J' = 0$-12, therefore $|\Delta J| = 1$-12 ,

and so on. The minimum value of $|\Delta J|$ is noted ΔJ in Fig. 1, the maximum value is $|\Delta J| = J$. The values of $\delta K = |K| - |K'|$ ($E_{J,K}$ is a function of K^2 only) are generally such that large $|\delta K|$ are associated to small $|\Delta J|$, and vice versa, in order to provide sufficient energy.

From our experimental measurements, we can deduce an estimation of the experimental ionization cross section σ_i^{expt} relevant to the total density of the $\mathrm{NH_3}$ molecules. This cross section is defined by

$$\sigma_i^{\mathrm{expt}} = \sum_{J=0}^{\infty} \sigma_i(J)p(J) = \bar{\sigma}_i p\ ,$$

where $\bar{\sigma}_i$ is the average value over J $(J \geq 8)$ of the cross section for the one-collision ionization defined previously. For this purpose, Penning ionization (PI) by metastable helium atoms,

$$He(2\,^1S) + NH_3 \rightarrow NH_3^+,\ NH_2^+ \cdots + He + e, \quad PI\ ,\quad (6)$$

which occurs with the laser off and whose cross section is known,[16] is carried out *in situ* simultaneously with the measurement devoted to CI; its ion signal I_{PI} is used to eliminate in (4) the unknown detection coefficient k. Then

$$\frac{I_{CI}}{I_{PI}} = \frac{\sigma_i^{\text{expt}}}{\sigma_{PI}} \frac{L}{L'} \alpha\beta\ , \quad (7)$$

where β is the ratio of the quadrupole mass spectrometer transmissions for masses 4 and 16 or 17, L' is the path length of the metastable atoms through the target gas. We then obtain an order of magnitude $\sigma_i^{\text{expt}} \simeq 0.8$ to 2×10^{-14} cm^2. We can estimate the size of the relevant electron-molecule ionization cross section in first approximation[6] by equating the rate constants weighted by the fraction p of the available molecules with $J \geq 8$, $p \simeq 0.17$, $\sigma_i^{\text{expt}} v \simeq \sigma_e v_e p$. We obtain $\sigma_e \simeq 0.8$ to 2×10^{-15} cm^2, a value which is two orders of magnitude smaller than the cross section σ_e deduced by the same calculation from the results on $Xe(31f) + NH_3$ in a $|\Delta J| = 1$, $\Delta K = 0$ ionizing transition.[9]

Experiments on several other molecules, to be reported

elsewhere, have shown that the dipole moment of the molecule plays the primary role in the ionization of low Rydberg states by these $|\Delta J| > 1$ transitions. Molecules, such as NH_3, which have substantial dipole moment (for NH_3, $D = 1.47$ D), all yield ion signals from $He(n\,^1P)$ with $14 \leq n \leq 16$, while those with no or very small dipole moment [for C_4H_6 (1,3-butadiene), $D = 0$ D; for CO, $D = 0.097$ D] give no observable signal.

In conclusion, we report experimental evidence for ionization in excited atom-polar molecule thermal collisions by a mechanism different from the one usually used to explain ionization in previous studies. We propose a process based on $|\Delta J| > 1$ rotational relaxation of the molecule.

The interesting concept of multiple electron-molecule encounters during a single collision, proposed by Preston and Lane,[8] could be used also to explain our observations.

This process can also occur for large n and may explain the difference observed between the cross section measured by Kellert *et al.*[9] and the theoretical predictions based on dipole Born approximation.

Studies are presently underway on various dependences of the signal with different parameters, in particular He*-molecule velocity dependence, and details will be given in a forthcoming paper.

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