PHYSICAL REVIEW A VOLUME 40, NUMBER 12 DECEMBER 15, 1989

Ionization of low-Rydberg-state He atoms by dipole-forbidden rotational deexcitation of NH_3

Toshizo Shirai
Department of Physics, Japan Atomic Energy Research Institute, Tokai-mura 319-11, Japan

Hiroki Nakamura
Division of Theoretical Studies, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

(Received 23 June 1989)

A theoretical study of the ionization of $He(n=14\,^1P)$ atoms in thermal collisions with NH_3 was carried out within the semiquantal approximation. The charge-dipole Glauber differential cross section was employed for the electron-molecule rotational deexcitation process. Calculated thermally averaged cross sections show quite a strong n dependence, especially for $n \le 17$. A comparison is made between the present results and recent experiments.

Experimental studies of the ionization in thermal collisions of low-Rydberg-state He atoms with ammonia,

$$\mathrm{He}(n\,^1P)+\mathrm{NH}_3(J,K)\rightarrow \mathrm{He}^+ +\mathrm{NH}_3(J',K')+e\ , \tag{1}$$

were carried out by Ronge *et al.*[1] and Pesnelle *et al.*[2] for the principal quantum number $n=14$. The ionization cross section σ_i^{expt} they have obtained varies as V^{-2} in the relative velocity range $1100 \le V \le 2500$ m/s and its absolute value at $V=2400$ m/s is $(9\pm4)\times10^{-15}$ cm^2. Since the energy transfer from relative translational motion to atomic excitation is much less effective in the thermal collisions, the ionization occurs mainly owing to the energy transfer from molecular rotation to atomic excitation. This fact was experimentally verified in Ref. 1. Rotational energy of a symmetric top molecule is given by

$$E_{JK}=BJ(J+1)+(C-B)K^2\ , \tag{2}$$

where J and K are the rotational quantum numbers. The rotational constants B and C are $B=9.44$ cm^{-1} and $C=6.20$ cm^{-1} in the case of NH_3. In dipole-allowed deexcitation ($J'=J-1$, $K'=K$), the released energy $2BJ$ exceeds the binding energy of $He(14\,^1P)$ ($\varepsilon_{nl}=558.8$ cm^{-1}) only when $J \ge 30$. The Boltzmann average of J in the thermal distribution of NH_3 at 300 K is only 5.25, and the fraction of highly excited levels with $J \ge 30$ is very small (see Table I). Therefore, the ionization induced by dipole-forbidden rotational deexcitation of NH_3 is considered to be a major mechanism of the process in Eq. (1).

TABLE I. Fraction of NH_3 molecules that can ionize $He(n=14)$ at 300 K.

ΔJ	$\max(\Delta J,J^*)$	$p(\Delta J)$ (%)
1	30	2.55×10^{-11}
2	16	0.0136
3	11	1.19
4	9	3.81
5	8	5.10
6	8	3.74
7	8	2.52
8	8	1.39
9	9	0.584

In a previous paper[3] (referred to as I hereafter), the ionization collisions of $Xe(n)+CO$, HCl, HF, and LiF in the range $20 \le n \le 100$ were investigated theoretically by using a version[3] of the semiquantal approximation.[4] We employed the dipole-Glauber approximation which takes into account not only the dipole-allowed ($\Delta J \equiv J-J'=1$) but also the dipole-forbidden ($\Delta J>1$) deexcitations of molecules. It was found that the ionization caused by the dipole-forbidden ($\Delta J>1$) transitions becomes dominant in the case of low-Rydberg atoms.

Here we investigate the ionization process (1) by using essentially the same method used before. The thermally averaged ionization cross section is estimated. Equation (2.5) of I should, however, be slightly modified as given below in order to deal with a symmetric top molecule,

$$\begin{aligned}\bar{\sigma}_{nl}(V)&=\sum_{J=J_{\min}}^{\infty}\ \sum_{K=-J}^{J}\ \sum_{J'=0}^{J'_{\max}}\ \sum_{K'=-J'}^{J'} f_{JK}\sigma_{nl,JK;J'K'}(V)\\ &=\sum_{\Delta J=1}^{\infty}\ \sum_{J=\max(\Delta J,J^*)}^{\infty}\ \sum_{K=-(J-\Delta J)}^{J-\Delta J} f_{JK}\sigma_{nl,JK;J-\Delta JK}(V),\end{aligned} \tag{3}$$

where

$$f_{JK}=\frac{(2J+1)\exp(-E_{JK}/kT)}{\displaystyle\sum_{J=0}^{\infty}\sum_{K=-J}^{J}(2J+1)\exp(-E_{JK}/kT)}\ ,$$

$$\begin{aligned}&J_{\min}=\min\{J:E_{J0}\ge\varepsilon_{nl}\}\ ,\\ &J'_{\max}=\max\{J:E_{JK}-E_{J'K}\ge\varepsilon_{nl}\ \text{ at given } J \text{ and } K\}\ ,\\ &J^*=\min\{J:E_{JK}-E_{J-\Delta JK}\ge\varepsilon_{nl}\ \text{ at given } \Delta J \text{ and } K\}\ .\end{aligned} \tag{4}$$

k is the Boltzmann's constant and T is temperature. $\sigma_{nl,JK;J'K'}(V)$ in Eq. (3) is the cross section of the process (1) for the specified initial and final states [see Eq. (2.1) of

I]. Here we have used the selection rule $K = K'$ in the dipole approximation. The cross section $\bar{\sigma}_{nl}(V)$ is the quantity to be compared with the experimental one σ_l^{expt}.

The Glauber differential cross section $\sigma_{J,K;J'K'}(p,v)$ for the transition $NH_3(J,K) \rightarrow NH_3(J',K')$ induced by a simple charge-dipole interaction corresponds to $\sigma_{J,J'}(p,v)$ in the right-hand side of Eq. (2.1) of I and can be readily derived in the same way as that of Ashihara *et al.*[5] In terms of the auxiliary function $I_{l,m}(\xi)$ defined in the Appendix of Ref. 5, a final expression is given by

$$\sigma_{J,K;J'K'}(p,v) = k^2(2J+1)\sum_{l,m}(2l+1)\frac{(l-m-1)!!(l+m-1)!!}{(l+m)!!(l-m)!!}\left[\begin{pmatrix} J & J' & l \\ K & K' & 0 \end{pmatrix}\right]^2\left[\frac{2eD}{\hbar v}\right]^4\frac{1}{\xi^4}[I_{l,m}(\xi)]^2, \quad l-m\text{:even} \qquad (5)$$

where ξ is the reduced momentum transfer $(2D/ea_0)p/mv$. Here D is the molecular dipole moment (D=0.578 a.u. in the case of NH_3); e and m, the charge and mass of the electron; a_0, the Bohr radius; p, the momentum transfer; v, the relative velocity; and k, the wave number of the electron. The 3-j symbol appearing in Eq. (5) indicates that only the rotational transitions with $K = K'$ are allowed in the dipole approximation. Itikawa[6] calculated the rotational excitation cross sections of NH_3 by electron impact using the Born approximation for charge-multipole interaction and showed that the transition with $\Delta K \neq 0$ is about six orders of magnitude less probable compared to the dipole transition with $\Delta K = 0$. Therefore, in the present calculation, we have taken into account only the charge-dipole interaction.

Figure 1 shows the calculated results of $\sigma_{\Delta J=2}(J,K)$ $[\sigma_{\Delta J}(J,K) \equiv \sigma_{14\,^1P,JK;J-\Delta JK}(V)]$ at V=2480 m/s and its thermal average $[\langle\sigma_2(J,K)\rangle_{\mathrm{th}} = f_{J,K}\sigma_2(J,K)]$ against K for $16 \le J \le 23$. While $\sigma_2(J,K)$ are as large as $2 \sim 3\times10^{-14}$ cm^2 for $K \le 6$, they monotonically decrease to $1\times10^{-15} \sim 5\times10^{-16}$ cm^2 with increasing $K > 6$, and the thermally averaged cross sections become smaller than 5×10^{-20} cm^2. This is owing to the small population of $NH_3(J,K)$ with $J \ge 16$. The fraction $p(\Delta J)$ of the rotational state distribution at T=300 K which can ionize He(14 ^1P),

$$p(\Delta J) = \sum_{J=\max(\Delta J, J^*)}^{\infty} \; \sum_{K=-(J-\Delta J)}^{J-\Delta J} f_{J,K} \qquad (6)$$

is given in Table I as a function of ΔJ. As is seen from this table, $p(2)$ is two orders of magnitude smaller than $p(\Delta J)$ with $\Delta J \ge 3$. This is the reason why the thermally averaged cross section $\langle\sigma_2(J,K)\rangle_{\mathrm{th}}$ becomes so small.

We have calculated the cross sections $\langle\sigma(\Delta J,J)\rangle_{\mathrm{th}}$ $[\equiv \sum_K \langle\sigma_{\Delta J}(J,K)\rangle_{\mathrm{th}}]$ for ΔJ=2 to 9, which are plotted in Fig. 2 against J at a fixed value of ΔJ. In Fig. 3 the

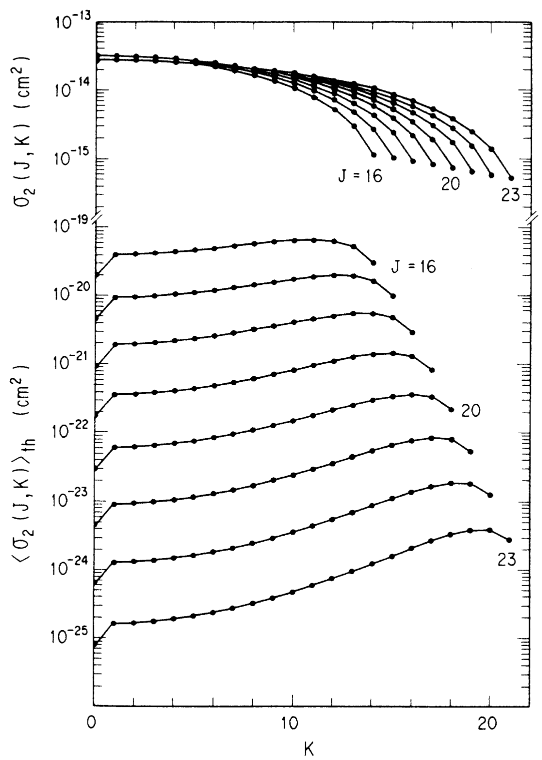

FIG. 1. Rotational quantum number (K) dependence of cross sections $\sigma_{\Delta J=2}(J,K)$ and its thermal average $\langle\sigma_2(J,K)\rangle_{\mathrm{th}}$ for He(n = 14 ^1P) + $NH_3(J,K) \rightarrow He^+ + e + NH_3(J',K')$ at relative velocity V=2480 m/s. Here $J'(=J-\Delta J)=J-2$ and $K = K'$.

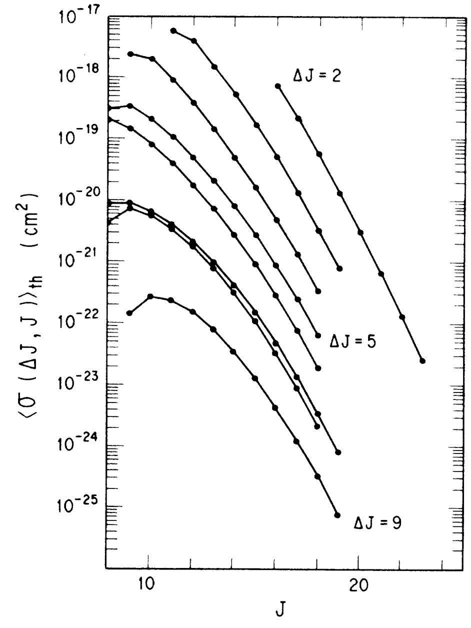

FIG. 2. Rotational quantum number (J) dependence of thermally averaged cross sections $\langle\sigma(\Delta J,J)\rangle_{\mathrm{th}}$ for He(n = 14 ^1P) + $NH_3(J) \rightarrow He^+ + e + NH_3(J')$ at relative velocity V=2480 m/s. $\Delta J = J' - J$.

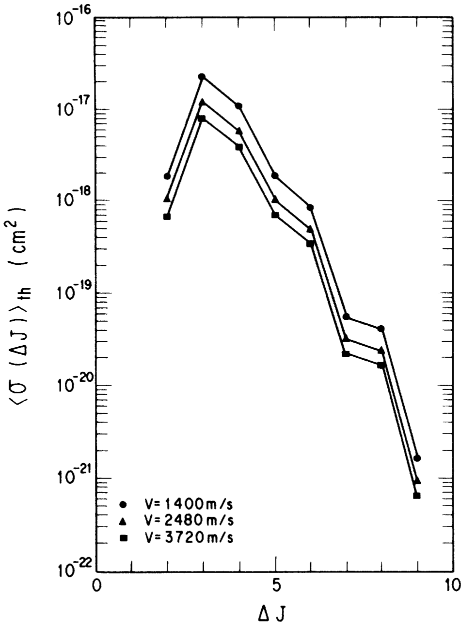

FIG. 3. $\Delta J(=J'-J)$ dependence of thermally averaged cross sections $\langle\sigma(\Delta J)\rangle_{\text{th}}$ for $\text{He}(n=14\,{}^1P)+\text{NH}_3(J)\rightarrow\text{He}^++e+\text{NH}_3(J')$ at relative velocities $V=1400$, 2480, and 3720 m/s.

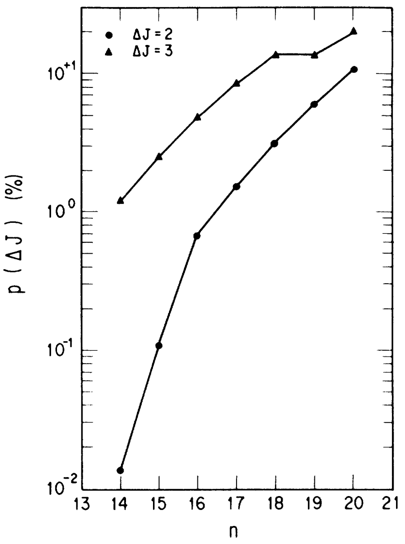

FIG. 4. Fraction of NH_3 molecules which can ionize He(n) at 300 K.

cross sections $\langle\sigma(\Delta J)\rangle_{\text{th}}$ $[\equiv\sum_J\langle\sigma(\Delta J,J)\rangle_{\text{th}}]$ are shown as a function of ΔJ. There appears a maximum at $\Delta J=3$. The decrease at $\Delta J=2$ in Fig. 3 results from the small population of NH_3 with $J\geq 16$ as mentioned above. The decrease at $\Delta J>3$ is due to the fact that dipole-forbidden rotational transition becomes very improbable as ΔJ increases. Summing $\langle\sigma(\Delta J)\rangle_{\text{th}}$ over ΔJ, we obtain $\bar{\sigma}_{14\,{}^1P}$ at $V=2480$ m/s is 2.05×10^{-17} cm^2. For $V=1400$ and 3720 m/s, the $\bar{\sigma}_{14\,{}^1P}$ cross sections have been estimated to be 3.83×10^{-17} cm^2 and 1.36×10^{-17} cm^{-2}, respectively. These values give the V^{-1} dependence of the cross section as in I rather than the V^{-2} dependence found by experiment.[1]

Thus we have two problems in respect to a comparison with the experiment.[2] In our calculations the cross section $\sigma_2(J,K)=2\sim3\times10^{-14}$ cm^2 for $\Delta J=2$ (see Fig. 1) is roughly the same as the experimental cross section $\sigma_i\sim5\times10^{-14}$ cm^2 [see Eq. (17) of Ref. 2], but the thermally averaged cross section $\bar{\sigma}_{14\,{}^1P}=2.05\times10^{-17}$ cm^2 is about two orders of magnitude smaller than $\sigma_i^{\text{expt}}\simeq8\times10^{-15}$ cm^2 at $V=2480$ m/s [9×10^{-15} cm^2 at 2400 m/s, see Eq. (14) of Ref. 2]. The following two reasons may easily be thought of for this discrepancy: (1) The $\Delta K=0$ selection rule in the dipole-Glauber approximation. If the rotational transition $(J=10,K=0)\rightarrow(J=8,K=8)$ could occur with the same order of cross section as that for the transition of $\Delta J=2$ and $\Delta K=0$, as is assumed in Ref. 2, then $\bar{\sigma}_{14\,{}^1P}$ would become the same order as σ_i^{expt}. However, since the $\Delta K\neq0$ transitions are supposed to be induced by the higher multipole (at least octupole) interactions,[6] this does not seem to be very probable. Besides, the present calculations show quite strong J- and K-dependences of the cross section. (2) Effect of ionic core. Although this could not be neglected especially for small n, we cannot give any quantitative estimate about this at this moment. A similar experiment for higher n atoms, say He($n=20$), could provide us with a certain key to this question.

There is another aspect we would like to point out. That is the n dependence of the process (1). As is seen from our previous results on Xe+HCl (see Table III of I), n dependence of the cross section is quite strong. Here we have estimated also the fraction $p(\Delta J)$ of NH_3 which can ionize He(n) as a function of n (see Fig. 4). It is clearly seen that $p(\Delta J=2)$ for He(17) is two orders of magnitude greater than that for He(14). This means that the thermally averaged cross section for He($n=17$) becomes easily two orders of magnitude larger than that for He($n=14$). Experimental study on the n dependence of the process (1) would thus be very intriguing and necessary.

We gratefully thank Dr. A. Pesnelle of Centre d'Etudes Nucléaires de Saclay for useful discussions. One of us (T.S.) would like to express his thanks to Dr. N. Shikazono and Dr. S. Igarasi of Japan Atomic Energy Research Institute for their encouragement during this work.

---

[1] C. Ronge, A. Pesnelle, M. Perdrix, and G. Watel, Phys. Rev. A **38**, 4552 (1988).

[2] A. Pesnelle, C. Ronge, M. Perdrix, and G. Watel, Phys. Rev. A **34**, 5146 (1986); **38**, 4560 (1988).

[3] T. Shirai and H. Nakamura, Phys. Rev. A **36**, 4290 (1987), referred to as I.

[4] M. R. Flannery, in *Rydberg States of Atoms and Molecules*, edited by R. F. Stebbings and F. B. Dunning (Cambridge University, Cambridge, 1983), p. 393.

[5] O. Ashihara, I. Shimamura, and K. Takayanagi, J. Phys. Soc. Jpn. **38**, 1732 (1975).

[6] Y. Itikawa, J. Phys. Soc. Jpn. **30**, 835 (1971).