PHYSICAL REVIEW A VOLUME 38, NUMBER 9 NOVEMBER 1, 1988

Ionization of low-Rydberg-state He atoms by polar molecules. II. Large rotational-energy transfers and absolute values of the cross sections

A. Pesnelle, C. Ronge, M. Perdrix, and G. Watel
Service de Physique des Atomes et des Surfaces, Centre d'Etudes Nucléaires de Saclay,
91191 Gif-sur-Yvette Cédex, France

(Received 22 December 1987; revised manuscript received 4 April 1988)

The absolute values of cross sections for the collisional ionization of low-Rydberg-state He atoms in the $n\,^1P$ state ($n=14$) by the polar molecules NH_3, SO_2, and acetone (C_3H_6O) are measured in a crossed-beam experiment at thermal kinetic energies, for a well-defined relative velocity. Simultaneous Penning ionization of NH_3 by metastable $He(2\,^3S)$ atoms is carried out *in situ* for calibration. Experimental collisional-ionization cross sections $\sigma_i^{\text{expt}}(v_r)$, for $v_r=2400$ m/s, as large as 9×10^{-15} cm^2 for NH_3, 5×10^{-15} cm^2 for SO_2, and 10^{-14} cm^2 for C_3H_6O at 300 K, are obtained. These large cross sections cannot be explained by the "free-electron model" usually used in Rydberg-atom–molecule collisions: This model predicts no ionization of Rydberg levels as low as $n=14$, since the amount of energy available from rotational $\Delta J=-1$ $\Delta K=0$ relaxation transitions of the molecule is insufficient. Our hypothesis of large $|\Delta J|$ rotational transitions is strengthened by comparison of the results for the three studied molecules.

I. INTRODUCTION

Absolute values for the ionization cross sections in low-Rydberg-state atom-molecule collisions

$$He(n\,^1P)+M(J)\rightarrow He^+ + M(J')+e\ , \qquad (1)$$

with $M=NH_3$, SO_2, and acetone (C_3H_6O) and $n=14$, are needed to clarify the conditions of applicability of the impulse approximation in such collisions,[1] which is the starting point of the free-electron model. This approximation, to be acceptable, requires several conditions to be satisfied, in particular on the characteristic interaction distances between the molecular target M and either the excited electron e in $A^*(r_{e\text{-}M})$ or the core $A^+(r_{A^+\text{-}M})$

$$r_{e\text{-}M} \ll t_n v_n,\quad r_{A^+\text{-}M} \ll t_n v_r\ ,$$

where t_n is the characteristic time of the $e\text{-}A^+$ interaction, i.e., the period of the Rydberg electron, v_n is the electron velocity on its orbit, and v_r is the relative velocity of A^* and M (here $A=He$).

In our first experiment[2] on collisional ionization of $He(n\,^1P)$ excited in low Rydberg states ($14\le n\le 16$) by NH_3,

$$He^*(nl)+NH_3(J,K)\rightarrow He^+ + NH_3(J',K')+e\ , \qquad (2)$$

we could only explain our large ionization signal by assuming that the molecules undergo large rotational relaxation transitions ΔE_{rot} with

$$\Delta E_{\text{rot}}=E_{J,K}-E_{J',K'}\ge |E_{nl}| \qquad (3)$$

in order to ionize the helium atom [for $He(14\,^1P)$, $|E_{nl}|=558.8$ cm^{-1}]. The amounts of rotational energy involved are larger than those delivered in the $|\Delta J|=1$, $\Delta K=0$ rotational transitions which are usually considered in such Rydberg-atom–polar-molecule collisions (for NH_3 at 300 K, typically 100 cm^{-1} at the maximum of the rotational distribution). In order to test our hypothesis, we first improved our measurement method in order to avoid the constraints of certain experimental parameters, and secondly extended these measurements to molecules having different sets of dipole moments and rotational constants such as NH_3, SO_2, and acetone (C_3H_6O).

II. EXPERIMENT

Measurement of the absolute values of the cross sections σ_i was achieved by measuring the He^+ ion signal produced in collisions [termed collisional ionization (CI)]

$$He(n\,^1P)+NH_3(J,K)\rightarrow He^+ + NH_3(J',K')+e \qquad (4)$$

or

$$He(n\,^1P)+SO_2(J,K)\rightarrow He^+ + SO_2(J',K')+e$$

or

$$He(n\,^1P)+C_3H_6O(J,K)\rightarrow He^+ + C_3H_6O(J',K')+e$$

by comparison with ions produced in Penning ionization (PI) of NH_3 by metastable atoms,

$$He(2\,^3S)+NH_3\rightarrow He+NH_3{}^+ + NH_2{}^+ + NH^+ + e\ , \qquad (5)$$

the cross section of which is well known. The measurements were made for a target gas density sufficiently low to be sure of avoiding multicollisions while the ion signal was still strong.[1] The pressures, measured upstream from the multicapillary array, are $P=0.03$ Torr for NH_3 and C_3H_6O and $P=0.04$ Torr for SO_2. Inside the interaction zone, the pressure is several orders of magnitude smaller.

The experimental setup is similar to that used in Ref. 1. However, this time, the time-of-flight (TOF) technique is not used, but a mechanical velocity selector has been added for the reason described hereunder. It is observed on the TOF spectrum of Penning ions that a small $NH_3{}^+$ photoion signal exists. These photoions are produced by ionization of NH_3 by the uv light issued from the metastable source. This photoion peak is located right at the beginning of the time-of-flight spectrum, delayed only by the transit time of such ions in the quadrupole mass spectrometer. The movable mechanical velocity selector, with a 10% velocity resolution, is therefore set up on the metastable He beam for all the measurements made in the present work; it is used to prevent a photoion contribution to the $NH_3{}^+$ signal. The velocity v in this experiment is chosen close to the most probable velocity in the He* beam, such that $v_r = 2400$ m/s.

The two kinds of ions, He^+ and $(NH_3{}^+ + NH_2{}^+ + NH^+)$, produced in CI and PI, respectively [reactions (4) and (5)], are measured *in situ* using the laser on [CI with $He(14\,{}^1P)$] and off [PI with $He(2\,{}^3S)$]. Simultaneously with the He^+ ion measurement, the fluorescence signal $14\,{}^1P \rightarrow 1\,{}^1S$ is measured in order to remove the constraints related to the excitation efficiency parameter used in Ref. 2 to deduce the cross-section absolute values. The following two signals are recorded.

(i) The collisional-ionization signal produced in $He(14\,{}^1P) + NH_3$, related to a one-fluorescence-photon emission, given by the ratio of the ion signal to the fluorescence signal [see formula (8) in Ref. 1], is equal to

$$\frac{1}{\rho}\left[\left[\frac{N^+(v)}{N^*(v)-I^*_{\rm BG}(v)}\right]_\rho - \left[\frac{N^+(v)}{N^*(v)}\right]_{\rho=0}\right] = \frac{4\pi k T_{14P}}{\Omega R}\, v\,\sigma_{\rm eff}^{\rm expt}(v) , \qquad (6)$$

where $I^*_{\rm BG}$ is the background signal, k is the collection efficiency of our experimental system, including the collection coefficient and the mass analyzer transmission, Ω is the solid angle of fluorescence detection, R is the 50.6-nm photon detection efficiency, T_{14P} is the lifetime of the He* atoms[3] (0.163 29 μs), ρ the total density of target molecules in the interaction region, v the He* velocity, and $\sigma_{\rm eff}^{\rm expt}(v)$ the effective experimental ionization cross section.

(ii) The PI ion signal per second is given by

$$N_{\rm PI} = k'\rho\sigma_{\rm PI}\phi^m(2\,{}^3S)V_2 , \qquad (7)$$

since, in this case, the metastable atoms, due to their long lifetime, cross the whole target volume with the result that the flux ϕ^m is constant over this volume. The constant k' represents the same collection efficiency as defined above but this time for Penning ions (masses 17, 16, and 15 for $NH_3{}^+$, $NH_2{}^+$, and NH^+), V_2 is the metastable He-NH_3 interaction volume, and $\sigma_{\rm PI}$ is the Penning ionization cross section; PI is performed only on triplet metastable states $He(2^3S)$ by using a $2\,{}^1S$ quenching lamp with a 99% efficiency.

From the ratio of formulas (6) and (7), we deduce the ratio of the absolute values of $\sigma_{\rm eff}^{\rm expt}$ and $\sigma_{\rm PI}$:

$$\frac{\sigma_{\rm eff}^{\rm expt}}{\sigma_{\rm PI}} = \frac{k'R\Omega V_2 n^m(2\,{}^3S)}{k4\pi T_{14P}N_{\rm PI}} \times\left[\left[\frac{N^+}{N^*-I_{\rm BG}}\right]_\rho - \left[\frac{N^+}{N^*-I_{\rm BG}}\right]_{\rho=0}\right] . \qquad (8)$$

All the terms are replaced by their numerical values. The ratio k'/k is reduced to the ratio of the mass-spectrometer transmissions which are inversely proportional to the square root of the ion mass; then $k'/k = (\frac{4}{16})^{1/2}$, $\Omega/4\pi = 0.021$, $R = 0.13$, and $V_2 = 0.028$ cm^3. The density of metastable $He(2\,{}^3S)$ atoms n^m was measured on this setup[4] and reached 300±100 cm^{-3} taking the velocity selector transmission into account.

III. RESULTS

The effective ionization cross section $\sigma_{\rm eff}^{\rm expt}(v)$ is related to the experimental ionization cross section $\sigma_i^{\rm expt}(v_r)$ as previously;[1] for $v_r = 2400$ m/s, the difference between the two cross sections, calculated as in our previous work,[5] is observed to be negligible because of the greater weight of the three studied molecules as compared with that of He, except for the lightest molecule NH_3 and only at low velocity $v < 2500$ m/s; even in this case, the difference remains slight. The experimental $\sigma_i^{\rm expt}(v_r)$ cross section is relevant to the total density ρ of the target NH_3, SO_2, or C_3H_6O molecules.

We postulated[2] large relaxation transitions of several quanta of rotational energy $|\Delta J| > 1$ for the NH_3 molecule in order to explain our experimental observations. It is a fact that the rotational transition $\Delta E_{\rm rot}$ must be larger than the ionization energy of our Rydberg atoms $He^*(14\,{}^1P)$ [for $He(14\,{}^1P)$, $|E_{nl}| = 558.8$ cm^{-1}] and must therefore satisfy the condition (3); we concluded that only that fraction of NH_3 molecules, for which the condition $J \geq 8$ is satisfied, is effective. Therefore the measured cross section $\sigma_i^{\rm expt}(v_r)$ is related to the ionization cross section $\sigma_i(v_r;J)$ by

$$\sigma_i^{\rm expt}(v_r) = \sum_{J=J_{\rm min}}^{\infty} \sigma_i(v_r;J)p(J) , \qquad (9)$$

where $J_{\rm min}$ is the minimum J value for which the ionization of $He(n\,{}^1P)$ is possible, $\sigma_i(v_r,J)$ is the ionization cross section for the elementary process

$$He(14\,{}^1P) + NH_3(J) \rightarrow He^+ + NH_3(J \rightarrow J') + e$$

resulting from relaxation of molecules of given rotational quantum number J, and $p(J)$ is the population of molecules having a rotational quantum number J. Formula (9) can be written

$$\sigma_i^{\rm expt}(v_r) = \sum_{J=0}^{\infty} \sigma_i(v_r;J)p(J) , \qquad (10)$$

since $\sigma_i(v_r;J)$ is taken as equal to zero for $0 \leq J < J_{\rm min}$ when the energy balance given by inequality (3) is not satisfied. We define an average ionization cross section $\sigma_i(v_r)$ by

$$\sigma_i(v_r)=\sigma_i^{\text{expt}}(v_r)/p \;, \tag{11}$$

where p is the fraction of target molecules available for the reaction

$$p=\sum_{J=J_{\min}}^{\infty} p(J) \;. \tag{12}$$

This average cross section $\sigma_i(v_r)$ is a good estimation of $\sigma_i(v_r;J)$ if the latter varies slowly with J in the $J_{\min}\leq J<\infty$ region. The cross section $\sigma_i(v_r)$ will always be larger than $\sigma_i^{\text{expt}}(v_r)$ since $p<1$ (for NH_3 for instance, $J_{\min}=8$ and $p=0.17$; see below).

A. Data with NH_3

1. *Experimental ionization cross section* σ_i^{expt}

Inserting the experimental data into formula (8), we obtain for NH_3

$$\sigma_i^{\text{expt}}=(1.5\pm0.6)\sigma_{\text{PI}} \;. \tag{13}$$

Several experimental values of the quenching rate constants of He($2\,^3S$) by NH_3 are given in the literature; we find 74, 84, 94, and 50×10^{-11} cm^{3}s^{-1} in Refs. 6, 7, 8, and 9, respectively, from which can be extracted the cross sections equal to 53, 60, 67, and 36×10^{-16} cm^2, respectively. Keeping that of Schmeltekopf and Fehsenfeld[7] as in our previous paper,[2] we obtain

$$\sigma_i^{\text{expt}}=9\pm4\times10^{-15}\ \text{cm}^2 \tag{14}$$

at $v_r=2400$ m/s. Any error $\Delta\sigma_{\text{PI}}$ in σ_{PI} would be reflected in the σ_i^{expt} value, presented here for NH_3, by the additional term $\pm1.5\Delta\sigma_{\text{PI}}$ in (14).

2. *Ionization cross section* σ_i

The NH_3 molecule in a symmetric-top molecule; in this case, two of the three principal moments of inertia are exactly equal, $I_A=I_B$; I_C is larger than I_B (then $C<B$), and this leads to an oblate shape. The rotational-energy levels are defined by[10]

$$E_{J,K}=BJ(J+1)+(C-B)K^2 \;. \tag{15}$$

The values of the rotational constants A, B, and C are given in Table I.

The rotational distribution at a given temperature T is calculated by[10]

$$f_J=g_{J,K}\exp(-E_{J,K}/kT)\Big/\sum_{J=0}^{\infty}\sum_{K=-J}^{J}(2J+1)\exp(-E_{J,K}/kT) \;, \tag{16}$$

where $g_{J,K}=2(2J+1)$ for $K\neq0$ and $2J+1$ for $K=0$, as shown on Fig. 1. Using formula (15), it is possible to deduce the lowest rotational level J_m from which the largest possible transition (i.e., to the ground state $J=0$ $K=0$) satisfies condition (3); this gives the fraction of the rotational level distribution allowing ionization of He*. We find $J_{\min}=8$, from which a $|\Delta J|=5$ to 8 transition satisfies (3); rotational transitions with smaller $|\Delta J|$ become efficient from higher levels; they are noted on Table II. To obtain the right amount of energy with a $\Delta J=-1$, $\Delta K=0$ transition, the latter should originate in $J\geq30$; the population of such levels is 10^{-13} at 300 K, that is to say, no ionization signal can be seen. Under these conditions, p given by formula (12) indicates that only 17% of the target molecules are efficient for ionization of the present Rydberg atom. Inserting $p=0.17$ in formula (11), we obtain

$$\sigma_i=(5\pm2)\times10^{-14}\ \text{cm}^2 \;. \tag{17}$$

It is worth noting that the reference cross section σ_{PI} is not exactly the PI cross section of NH_3 by He($2\,^3S$) but the quenching cross section of He($2\,^3S$) by NH_3 which is just the upper limit for the PI cross section, and that it is averaged over the velocity distribution of the reactants since it is deduced from a rate constant. Any error $\Delta\sigma_{\text{PI}}$ in σ_{PI} would be reflected in the σ_i value by the additional term $\pm9\Delta\sigma_{\text{PI}}$ in (17).

TABLE I. Dipole moment D and rotational constants of the molecules studied in the present experiment.

	D (debye)	A (cm^{-1})	B (cm^{-1})	C (cm^{-1})
NH_3	1.47[a]	9.4443[b]	9.4443[b]	6.196[b]
SO_2	1.59[a]	2.027 36[b]	0.344 17[b]	0.293 535[b]
C_3H_6O	2.89[a]	0.339 07[b]	0.284 04[b]	0.163 78[b]
CO	0.112[a]			
NO	0.07–0.16[c]			
O_2	0.0[c]			
C_4H_6	0.0[c]			

[a] Reference 23.

[b] Reference 22.

[c] Reference 24.

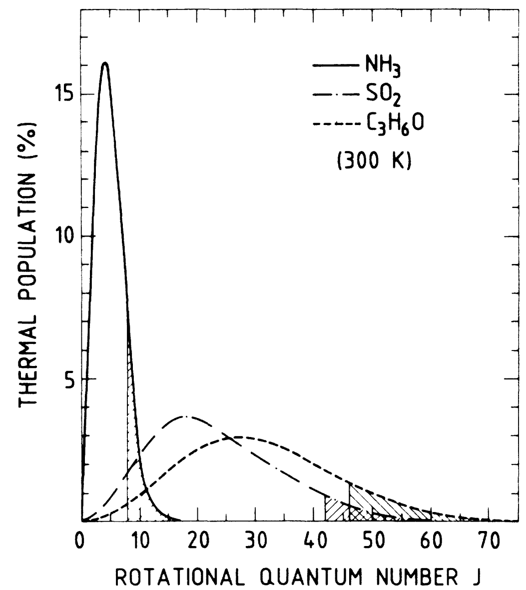

FIG. 1. Rotational distribution of the molecules studied in the present experiment. The shaded area represents the part p of this distribution where the molecules have a rotational number $J > J_{\min}$ and thus sufficient rotational energy for ionization of He($14\,^1P$) in large $|\Delta J|$ transitions: $J_{\min} = 8$, 42, and 46, and $p = 0.17$, 0.07, and 0.15 for NH_3 SO_2, and C_3H_6O, respectively.

B. Data with SO_2

1. *Experimental ionization cross section* σ_i^{expt}

The absolute value of σ_i^{expt} in the case of SO_2 is derived by comparison with σ_i^{expt} for NH_3, for the same velocity $v_r = 2400$ m/s. Since the only difference in the two measurements concerns the density ρ of the target, it suffices to make the ratio of the left-hand terms of formula (6) for NH_3 and SO_2 to obtain the cross section

$$\sigma_i^{\text{expt}}(SO_2) = 0.52\sigma_i^{\text{expt}}(NH_3) \ , \tag{18}$$

then, using (14),

$$\sigma_i^{\text{expt}} = (5 \pm 2) \times 10^{-15}\ \text{cm}^2 \tag{19}$$

at $v_r = 2400$ m/s. As for NH_3, any error $\Delta\sigma_{\text{PI}}$ would be reflected in the σ_i^{expt} value by the additional term $\pm 1\Delta\sigma_{\text{PI}}$ in (19).

2. *Ionization cross section* σ_i

While the NH_3 molecule is an exact symmetric-top molecule, SO_2 is an asymmetric-top molecule with three different principal moments of inertia. However, two of them, I_B and I_C, are nearly equal and much larger than the third one I_A. The rotational constants A, B, and C, inversely proportional to I_A, I_B, and I_C, are shown in Table I: we see that the difference $B - C$ is very small (≈ 0.05 cm^{-1}) and $A \gg B$ and C by one order of magnitude. When we calculate the parameter b given by[10]

$$b = (B - C)/[A - \tfrac{1}{2}(B + C)] \ , \tag{20}$$

which is an estimation of how much the molecule deviates from a symmetric-top shape, we obtain $b = 0.015$, which is very small. Therefore SO_2 can be considered here as a very-slightly-asymmetric-top molecule near the limiting case of the prolate symmetric top, the rotational levels of which are given by

$$E_{J,K} = \tfrac{1}{2}(B + C)J(J + 1) + [A - \tfrac{1}{2}(B + C)]K^2 \ . \tag{21}$$

The series of rotational levels can then be calculated for SO_2 as simply as for NH_3; owing to the fact that the rotational constants are smaller, the rotational levels of SO_2 are seen to be much closer together than those of NH_3. Consequently, both $J_{\min}$ and $|\Delta J|$ values are larger than those obtained for NH_3. This time, for SO_2, $J_{\min} = 42$ and extremely large $|\Delta J|$ transitions originating from $J_{\min}$, such that $|\Delta J| = 36$ to 42, are necessary to satisfy condition (3) (see Table III). In this case, the fraction p of the SO_2 molecules efficient for ionization of the present Rydberg atom does not exceed 7%; therefore,

$$\sigma_i = (7 \pm 3) \times 10^{-14}\ \text{cm}^2 \ . \tag{22}$$

Again in this case, any error $\Delta\sigma_{\text{PI}}$ would be reflected in the σ_i value by the additional term $\pm 11\Delta\sigma_{\text{PI}}$ in (22).

TABLE II. Rotational deexcitation transitions of NH_3 allowing ionization of He($14\,^1P$): $J,K \rightarrow J',K'$ ($K'_{\min}$ is a value which varies with K).

J	K	$p(J)$ (%)	J'	K' for $J' < J'_0$	K' for $J' \geq J'_0$	J'_0	$\lvert\Delta J\rvert$
0–7			No ionizing transitions				
8	0–6	7.44	0–3	0-J'	$K'_{\min}$-J'	3	5–8
9	0–9	4.67	0–6	0-J'	$K'_{\min}$-J'	4	3–9
10	0–10	2.68	0–8	0-J'	$K'_{\min}$-J'	6	2–10
11	0–11	1.42	0–9	0-J'	$K'_{\min}$-J'	6	2–11
12	0–12	0.69	0–11	0-J'	$K'_{\min}$-J'	7	1–12
13	0–13	0.32	0–12	0-J'	$K'_{\min}$-J'	9	1–13
14	0–14	0.13	0–14	0-J'	$K'_{\min}$-J'	10	0–14
15	0–15	0.05	0–15	0-J'	$K'_{\min}$-J'	11	0–15
. . .							

TABLE III. Rotational deexcitation transitions of SO_2 allowing ionization of He($14\,^1P$): $J \rightarrow J'$.

J	$p(J)$ (%)	J'	$\lvert \Delta J \rvert$
0–41	No ionizing transition		
42	0.89	0–6	36–42
43	0.80	0–11	32–43
44	0.71	0–14	30–44
45	0.64	0–17	28–45
. . .			
50	0.34	0–27	23–50
. . .			
55	0.17	0–35	20–55
. . .			
60	0.07	0–43	17–60
. . .			

TABLE IV. Rotational deexcitation transitions of acetone (C_3H_6O) (in the approximation of a spherical-top molecule) allowing ionization of He($14\,^1P$): $J \rightarrow J'$.

J	$p(J)$ (%)	J'	$\lvert \Delta J \rvert$
0–45	No ionizing transition		
46	1.43	0–5	41–46
47	1.33	0–10	37–47
48	1.23	0–14	34–48
49	1.13	0–17	32–49
50	1.04	0–19	31–50
. . .			
55	0.64	0–30	25–55
. . .			
60	0.37	0–38	22–60
. . .			

C. Data with acetone (C_3H_6O)

1. *Experimental ionization cross section* σ_i^{expt}

The absolute value of σ_i^{expt} in the case of C_3H_6O is also derived by comparison with σ_i^{expt} for NH_3, for the same velocity $v_r = 2400$ m/s. We obtain

$$\sigma_i^{\text{expt}} = (1 \pm 0.4) \times 10^{-14}\ \text{cm}^2\ . \tag{23}$$

As previously, any error $\Delta\sigma_{\text{PI}}$ would be reflected in the σ_i^{expt} value by the additional term $\pm 1.5\Delta\sigma_{\text{PI}}$ in (23).

2. *Ionization cross section* σ_i

The molecule acetone is also an asymmetric-top molecule with three different rotational constants A, B, and C, two of them, A, and B, being nearly equal (see Table I). We see that the difference $A - B$ is very small (≈ 0.05 cm^{-1}) but this time, contrary to the SO_2 molecule, A and B are not small compared with C; A and $B \approx 2C$. When we calculate the parameter b given by[10]

$$b = (A - B)/[C - \tfrac{1}{2}(A + B)]\ , \tag{24}$$

which estimates how much the molecule deviates from an oblate symmetric-top shape, we obtain $b = 0.7$, which is not small. The consequence of this is that the approximation of the rotational-energy levels by

$$E_{J,K} = \tfrac{1}{2}(A + B)J(J + 1) + [C - \tfrac{1}{2}(A + B)]K^2 \tag{25}$$

is not very good. Another possibility consists in approximating this molecule by a spherical top in which the three moments of inertia are exactly equal; the rotational-energy levels are then given by

$$E_{J,K} = (A + B + C)J(J + 1)/3\ . \tag{26}$$

This approximation multiplies the energy values obtained by formula (25) by a factor 0.846; the two sets of conclusions which will be drawn are therefore not basically different from each other, as we can see here: the lower rotational level from which a transition satisfies condition (3) is (i) in approximation (25), $J_{\min} = 42$ and $\lvert \Delta J \rvert = 41$ to 42 necessary from $J_{\min}$; in this case, the fraction p of the C_3H_6O molecules efficient for ionization of the present Rydberg atom is $p = 25\%$; (ii) in approximation (26), $J_{\min} = 46$ and $\lvert \Delta J \rvert = 41$ to 46 necessary from $J_{\min}$ (see Table IV); therefore, $p = 15\%$.

Considering the approximation of C_3H_6O by a spherical top is more satisfying, although not perfect; we keep $p = 0.15$ and

$$\sigma_i = (7 \pm 3) \times 10^{-14}\ \text{cm}^2\ . \tag{27}$$

As previously, any error $\Delta\sigma_{\text{PI}}$ would be reflected in the σ_i value by the additional term $\pm 11\Delta\sigma_{\text{PI}}$ in (27). The results for the three molecules are summarized in Table V.

IV. CONTRIBUTION OF THE IONIZATION BY BLACKBODY RADIATION

The choice of a target pressure P located in the linear part of the He signal versus P guarantees that a one-collision mechanism is responsible for ionization.[1] However, the two-step process including l mixing or n changing during one collision with NH_3,

$$\text{He}(14\,^1P) + NH_3(J) \rightarrow \text{He}(nl) + NH_3(J')\ , \tag{28}$$

followed by ionization by blackbody radiation,

$$\text{He}(nl) + h\nu_b \rightarrow \text{He}^+ + e\ , \tag{29}$$

are not excluded by our experimental procedure. It is therefore necessary to estimate the fraction of He^+ ions which could be possibly produced by this two-step mechanism.

A. Ionization of He($14\,^1P$) by blackbody radiation

In the background signal on the ion detector (laser on, target pressure off), there is a contribution of blackbody radiation photoionization to the He^+ signal,

TABLE V. Experimental cross sections for the collisional ionization of He($14\,^1P$) atoms (it is necessary to add to the error bars noted here a contribution due to the PI cross-section uncertainty: see text, Sec. III).

	σ_i^{expt} (10^{-14} cm^2)	$p=\sum_{J=J_{\min}}^{\infty} p(J)$	$J_{\min}$	σ_i (10^{-14} cm^2)
NH_3	0.9±0.4	17%	8	5±2
SO_2	0.5±0.2	7%	42	7±3
C_3H_6O	1.0±0.4	15%	46	7±3

$$\mathrm{He}(14\,^1P)+h\nu_b \rightarrow \mathrm{He}^+ + e\ . \tag{30}$$

The number of He^+ ions, produced per second, by photoionization of He($14\,^1P$) is given by

$$N_b^+(v)=kW\int\int\int_{V_1} n^*(x,y,z;v)dx\,dy\,dz\ , \tag{31}$$

where $W=\int_0^\infty c n_p(\nu)\sigma_{\mathrm{ph}}(\nu)d\nu/4$ is the photoionization rate by blackbody radiation,[11]

$$n_p(\nu)=8\pi\nu^2/c^3[\exp(h\nu/kT)-1]$$

is the blackbody radiation density at temperature T, σ_{ph} is the photoionization cross section of He($14\,^1P$), k is the He^+ detection efficiency of our experimental system, V_1 is the interaction volume, and $n^*(x,y,z;v)$ is the He($14\,^1P$) density. The fluorescence signal per second is given by[1]

$$N^*(v)=\frac{R\Omega A_{14P\rightarrow 1S}}{4\pi}\int\int\int_{V_1} n^*(x,y,z;v)dx\,dy\,dz\ . \tag{32}$$

The ratio of (31) and (32) provides

$$\frac{N_b^+(v)}{N^*(v)}=\frac{4\pi k W}{R\Omega A_{14P\rightarrow 1S}}\ , \tag{33}$$

from which we can estimate N_b^+. For this purpose, we use the hydrogen photoionization cross sections calculated by Burgess[12] for $n=14$ to estimate W ($W\approx 200$ s^{-1}) and a coefficient $k\approx 0.04$ deduced from comparison of Penning ionization experimental signals with calculated ones. The total fluorescence signal (integrated over the whole velocity distribution in the beam) is $N^*\approx 8\times 10^4$ counts/s; this leads to

$$N_b^+(14\,^1P)\approx 40 \text{ counts/s}\ ,$$

which is only 10% of the background signal, and thus negligible.

The blackbody radiation could also induce transitions from $14\,^1P$ towards nl levels; the calculations of Theodosiou[13] show that the decrease of the He($14\,^1P$) lifetime due to such an interaction with blackbody radiation does not exceed 0.4% at 300 K and is thus negligible.

B. Collisional l mixing or n changing followed by photoionization by blackbody radiation

Looking carefully to the resonances which are necessary to undergo efficient collisional n changing and l mixing for NH_3, [see reaction (28)], with a large cross section induced by electron-dipole interaction, we find only one channel where the energy excess $|\Delta E|$ is reasonably small: $14\,^1P\rightarrow 16\,^1D,F,G,\ldots$ with $|\Delta E|\approx 2.0$ cm^{-1}. For that purpose, the He energy-level quantum defects given in Ref. 14 are used. Using the analytical formulas of Petitjean and Gounand[15] to estimate the relevant cross section, we find that $\sigma^d\approx 4\times 10^{-12}$ cm^2. Another channel, $14\,^1P\rightarrow 18\,^1D,F,G,\ldots$ with $|\Delta E|\approx 6.4$ cm^{-1}, leads to $\sigma^d\approx 4\times 10^{-13}$ cm^2, i.e., one order of magnitude smaller.

The number of He(nl) atoms produced per second in such a process is given by

$$N^{**}(v)=\rho p(J)\sigma^d(v)v\int\int\int_{V_1} n^*(x,y,z;v)dx\,dy\,dz\ , \tag{34}$$

where $p(J)$ is the fraction of NH_3 molecules having the suitable rotational quantum number J. The number of He* ions produced per second in the photoionization process (29) is thus

$$N_b^+(v)=kW_{nl}\int\int\int_{V_3} n^{**}(x,y,z;v)dx\,dy\,dz\ , \tag{35}$$

where W_{nl} is the He(nl) photoionization rate which can be taken[12] such that $W_{nl}<W$ (with $W\approx 200$ s^{-1}). The integral over V_3, the volume in which the He(nl) atoms survive, represents the number of He(nl) atoms inside this volume: it can be estimated by considering that, in our experimental conditions of cw excitation, a stationary state is established and the numbers of He(nl) atoms produced and quenched per second are thus equal. An overestimation of this integral is therefore given thanks to the fluorescence signal from He(nl) (number of fluorescence photons emitted per second),

$$N_f^{**}(v)=\frac{1}{\tau_{nl}}\int\int\int_{V_3} n^{**}(x,y,z;v)dx\,dy\,dz\ , \tag{36}$$

which is one of their quenching processes: $N^{**}(v)\geq N_f^{**}(v)$. Consequently, and using formulas (32) and (34), we find

$$\frac{N_b^+(v)}{N^*(v)}\leq\frac{4\pi k W\rho p(J)\sigma^d(v)v\tau_{nl}}{R\Omega A_{14P\rightarrow 1S}}\ . \tag{37}$$

Inserting the largest n-changing cross section ($\sigma^d\approx 4\times 10^{-12}$ cm^2 for the n-changing process $14\,^1P\rightarrow 16\,^1D,F,G,\ldots$) and the experimental data inside

(37), we obtain (with an averaged value $\tau_{16} \approx 15$ μs for τ_{nl}, $nl = 16\,^1D,F,G,\ldots$)

$$N_b^+(16\,^1D,F,G,\ldots) \leq 160 \text{ counts/s} .$$

This signal is less than 5% of our He^+ signal, and consequently is negligible. It is, in fact, even smaller as the analytical n-changing cross sections σ^d, based on the impulse approximation, are expected to overestimate the process by one-half or one order of magnitude.[15]

In the case of SO_2, the expected contribution of blackbody radiation is still smaller; this is due to the fact that the rotational constant B is very small (see Table I) and the rotational levels which would be involved in quasiresonant dipole-allowed n changing leading to large cross sections are not populated at 300 K.

In the case of NH_3, inversion of the molecule could provide an energy of 0.7 cm^{-1}, and thus induce l mixing on the $n = 14$ level. We have verified that this process is negligible by doing the same measurement on ND_3 for which the inversion energy is too small (0.05 cm^{-1}) to induce such l mixing: we have observed for ND_3 a signal of the same order of magnitude as for NH_3. Let us note that Kellert *et al.*[16] have not observed the NH_3 inversion either.

In conclusion, the He^+ signal measured in the present experiment is mainly due to direct collisional ionization of He($14\,^1P$) atoms.

V. DISCUSSION AND CONCLUSION

The experimental ionization cross sections σ_i^{expt} (relevant to the total target gas density) obtained presently are in the $0.5-1\times10^{-14}$ cm^2 range (see Table V). We observe that, even though C_3H_6O has a stronger dipole than NH_3 and SO_2 (about a factor of 2), its cross section is not larger than the NH_3 one. The surprising fact comes from the SO_2 and C_3H_6O molecules where extremely large rotational transitions (several tenths) are necessary to explain the signal.

The σ_i^{expt} value given by Kellert *et al.*[16] for the lowest level ($n = 25$) studied in Xe(nf)+NH_3 collisions is close to 3×10^{-13} cm^2, i.e., a factor of 30 larger than the present one. The difference can be explained by the fact that only 176 cm^{-1} are necessary to ionize $n = 25$; in the dipole-allowed $|\Delta J| = 1$, $\Delta K = 0$ rotational deexcitation of NH_3, which leads to a large cross section, such an amount of energy is provided by the $J \geq 10$ fraction of the rotational distribution f_J of NH_3 at 300 K [see formula (16)]: this represents 5.4% of the total density of the target gas. In our case, a negligible fraction ($<10^{-13}$) of f_J could participate in ionization of He($14\,^1P$). In the hypothesis of large $|\Delta J|$ transitions, in Ref. 16 the $J \geq 4$ fraction would be efficient for ionization of Xe($25f$): this represents 74% of the total density instead of 17% in our case; furthermore, for Xe($25f$), the necessary transitions would not exceed $|\Delta J| = 4$.

Two other experiments concern collisional ionization of Rydberg states which are not well defined because they are produced by electron bombardment, and a complete distribution from $n = 10$ or 20 to about 80 exists in the projectile beam. The first one is that of Hotop and Niehaus,[17] who studied $He^* + NH_3$ and SO_2; they obtained (1.5 ± 0.4) and (1.1 ± 0.5)$\times10^{-13}$ cm^2, respectively, which are larger than ours by a factor of 17 and 22, respectively. The second one is that of Shepard and Kocher,[18] who give for $Li^* + NH_3$ collisions an ionization cross section equal to (1 ± 0.3)$\times10^{-12}$ cm^2, two orders of magnitude larger than ours. In both experiments, the cross sections are quite large, which is not surprising due to the large-n distribution; so many high-n values can contribute to the signal thanks to rotational-energy transfers due to the simplest $|\Delta J| = 1$, $\Delta K = 0$ dipole-allowed transitions which are sufficiently energetic; in this case, the free-electron model is verified for certain.

We also carried out this experiment on molecules which present different characteristic values, such as very small or absence of dipole moment: CO, NO, O_2, and (1,3) butadiene (C_4H_6) (see Table I). No measurable He^+ ion signal could be observed, which shows the preponderant role of the molecular dipole in this ionization process.

An experiment of collisional ionization of a mixture of Rydberg Ne^* atoms ($17 \leq n \leq 40$) by several nonpolar molecules, including (1,3) butadiene (C_4H_6), was carried out by Uematsu *et al.*[19] They measured cross sections close to $10^{-15}-10^{-14}$ cm^2, and attributed the ionization process to vibrational energy transfer from the molecule to the Rydberg electron provided the molecule had at least one low-frequency ir-active vibrational mode. In the present experiment, no signal was observed. The main difference between these two experimental setups is that in Ref. 19, no selective excitation of Ne^* Rydberg states was performed. A complete distribution of n ($17 \leq n \leq 40$) with a maximum around $n = 28$ exists in the beam, which leads to the following range for the ionization energy $|E_{nl}|$: $70 \leq |E_{nl}| \leq 380$ cm^{-1} with a maximum at 140 cm^{-1}, i.e., exactly in the thermal energy range (300 K ≈ 200 cm^{-1}). Unlike the rotational level population, which exhibits a maximum, the vibrational level population shows a purely exponential decrease,

$$f_V = \exp(-w_e V/kT) \Bigg/ \left[1 + \sum_{v=1}^{\infty} \exp(-w_e V/kT) \right] . \tag{38}$$

The molecule (1,3) butadiene, in fact, features many such modes, the populations of which are quite large as shown on Table VI. It is therefore possible that vibrational relaxation of the molecule is an efficient process for ionization of the highest-n range of the Rydberg distribution in the experiment described in Ref. 19. In our experiment, $|E_{nl}|$ reaches 558.8 cm^{-1} and the lowest modes populated at 300 K do not produce sufficient energy. We did, in fact, calculate the populations of the lowest vibrational levels for NH_3, SO_2, C_3H_6O, and C_4H_6 by formula (38). Postulating vibrational transitions of any quanta (without considering any selection rule such as $|\Delta V| = 1$), we see on Table VI that no vibrational level of NH_3 and SO_2 is sufficiently populated to ionize He($14\,^1P$); in the case of acetone (C_3H_6O), a two-quanta relaxation in the 391

TABLE VI. Vibrational modes (Ref. 22) (only the lowest ones are noted) and population of the vibrational levels 1–4. The asterisk indicates that a $V \rightarrow V=0$ vibrational transition could ionize the He($14\,{}^1P$) level (in the hypothesis of $|\Delta V| \geq 1$).

	Mode w_e (cm^{-1})	$p(V=1)$ (%)	$p(V=2)$ (%)	$p(V=3)$ (%)	$p(V=4)$ (%)
NH_3	932.5	1*			
	968.3	1*			
SO_2	517.6	7.1	0.5*		
	1151.3	0.3*			
C_3H_6O	391	12.3	1.8*		
	530	6.7	0.5*		
	787	2*			
C_4H_6	163	24.7	11	4.9	2.2*
	301	17.3	3.9*	0.9*	
	513	7.2	0.6*		
	520	7.2	0.6*		
	686	3.2*			
	890	1.1*			
	907.8	1.1*			
	911	1.1*			
	967	0.8*			
	987	0.8*			

cm^{-1} mode ($V=2$ has a 1.8% population) and a one-quanta relaxation in the 787 cm^{-1} mode ($V=1$ has a 2% population) are possible, but concern only 4% of the molecule density. By comparison with (1,3) butadiene (C_4H_6), where 14.7% of the molecule density could be involved in ionizing transitions of any quanta, we can see that the contribution of such transitions is still less probable for acetone. The fact that no signal due to vibrational relaxation could be detected with (1,3) butadiene leads us to conclude that this process cannot be efficient *a fortiori* for acetone.

A comparison can also be made with the very recent calculations of Shirai and Nakamura[20] for the $\mathrm{Xe}^* + \mathrm{HCl}$ system in the $20 \leq n \leq 100$ range. These authors used the Glauber approximation instead of the dipole-Born for the e-M interaction in the frame of the free-electron model and have thus shown that large-$|\Delta J|$ rotational transitions ($|\Delta J| = 1$ to 4) contribute to ionization in a non-negligible manner for the lowest levels, this contribution increasing when n decreases. Since HCl, although diatomic, has a dipole moment and a rotational constant of the same order of magnitude as those of NH_3 (for HCl, $D = 1.1$ D and $B = 10.4\ \mathrm{cm}^{-1}$) it is instructive to compare these two molecules; these authors have made a summation with respect to $|\Delta J|$ and an average over the rotational distribution f_J for these molecules at 300 K of the $\sigma_i(J, J - |\Delta J|)$ cross sections; the comparison must therefore be made with the experimental ionization cross section σ_i^{expt}. For $n = 20$, they obtain 5.7×10^{-15} cm^2, which is very close to the present result. It would be very interesting to make the same calculation for NH_3 and for levels still lower than 20.

To come back to the conditions of applicability of the impulse approximation, the basis of the free-electron model, the absolute values of the ionization cross sections give an estimation of the interaction ranges and help us to conclude on the inequalities

$$r_{e\text{-}M} \ll t_n v_n \ , \tag{39a}$$

$$r_{A^+\text{-}M} \ll t_n v_r \ . \tag{39b}$$

Without preconceiving the interaction mainly responsible for the ionization experimentally observed (among the electron-molecule or core-molecule interactions), an order of magnitude of both interaction distances is given by $(\sigma_i/\pi)^{1/2}$, where σ_i is the cross section measured in the present experiment; let us choose that for NH_3 [see formula (17)]. We then obtain

$$r_{e\text{-}M} \approx r_{A^+\text{-}M} \approx 24 a_0 \ .$$

It becomes

$$r_{e\text{-}M} \approx 0.02 t_n v_n \quad \text{which is} \ll t_n v_n$$

or (40a)

$$t_{e\text{-}M} \approx 0.02 t_n \quad \text{which is} \ll t_n$$

and for the two limits of our thermal velocity range, 5 to 25×10^{-4} a.u.,

$$r_{A^+\text{-}M} \approx 0.6 \text{ to } 2.8 t_n v_r \quad \text{which is not} \ll t_n v_r$$

or (40b)

$$t_{A^+\text{-}M} \approx 0.6 \text{ to } 2.8 t_n \quad \text{which is not} \ll t_n \ .$$

We observe that the inequality (40b) is not satisfied in the present experimental case of low-Rydberg-state atoms and thermal velocity. In the same range of thermal velocities, only Rydberg states such that

$$n \geq 41 \tag{41}$$

lead to $t_{A^+\text{-}M} \leq 0.1 t_n$, with a factor 0.1 inserted in order to correctly satisfy the inequality (39b) [with a factor 0.2 instead of 0.1 inserted in order to satisfy less strictly the inequality (39b), (41) becomes $n \geq 33$].

On the other hand, for such low Rydberg levels ($n = 14$), higher velocities than those presently observed are needed; they are

$$v_r \geq 3 \times 10^6 \text{cm/s} \tag{42}$$

to have $t_{A^+\text{-}M} \leq 0.1 t_n$ [less strictly, with a factor 0.2 instead of 0.1, (42) becomes $v_r \geq 1.5 \times 10^6$ cm/s].

In conclusion, we believe that a satisfying description of the ionizing collision of Rydberg states as low as those presently studied would include, in a first step, a complete consideration of the electron-molecule interaction with possible $|\Delta J| > 1$ rotational transitions of the molecule, since the dipole-Born approximation proves not to be suitable to explain ionization in the present case of molecules with relatively strong dipoles; and in a second step, the core-molecule interaction, since here light Rydberg atoms are involved, which could better explain the velocity dependence of the cross section. However, it must be said to the credit of the free-electron model that this model and the relevant analytical cross-sections formula are extremely easy to use and provide, without a computer, an order of magnitude for processes at thermal energies involving Rydberg states, but only in the range $n > 35$ or 40. These limits are strengthened by our observations on collisional ionization of He($14\,^1P$) by electron attaching molecules, details of which will be given in a forthcoming paper.[21]

ACKNOWLEDGMENTS

We gratefully thank Dr. F. Gounand, Professor H. Nakamura, Professor M. Matsuzawa, and Professor F. B. Dunning for fruitful discussions and comments on this experiment and results. It is a pleasure to acknowledge J. P. Felix, D. Sevin, and F. Thoyer for improving our data-acquisition system.

---

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

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

[3] C. E. Theodosiou, Phys. Rev. A **30**, 2910 (1984).

[4] L. A. Lompré, G. Mainfray, B. Mathieu, G. Watel, M. Aymar, and M. Crance, J. Phys. B **13**, 1799 (1980).

[5] A. Pesnelle, G. Watel, and C. Manus, J. Chem. Phys. **62**, 3590 (1975); J. Fort, J. J. Laucagne, A. Pesnelle, and G. Watel, Phys. Rev. A **14**, 658 (1976).

[6] R. C. Bolden, R. S. Hemsworth, M. J. Shaw, and N. D. Twiddy, J. Phys. B **3**, 61 (1970).

[7] A. L. Schmeltekopf and A. C. Fehsenfeld, J. Chem. Phys. **53**, 3173 (1970).

[8] W. Lindinger, A. L. Schmeltekopf, and F. C. Fehsenfeld, J. Chem. Phys. **61**, 2890 (1974).

[9] T. Ueno, A. Yokoyama, S. Takao, and Y. Hatano, Chem. Phys. **45**, 261 (1980).

[10] G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules,* (Van Nostrand, New York, 1966), Chap. 1.

[11] I. I. Sobelman, *An Introduction to the Theory of Atomic Spectra* (Pergamon, New York, 1972).

[12] A. Burgess, Mem. R. Astron. Soc. **69**, 1 (1964).

[13] C. E. Theodosiou, At. Data Nucl. Data Tables **36**, 97 (1987).

[14] J. W. Farley and W. H. Wing, Phys. Rev. A **23**, 2397 (1981).

[15] L. Petitjean and F. Gounand, Phys. Rev. A **30**, 2946 (1984).

[16] F. G. Kellert, K. A. Smith, R. D. Rundel, F. B. Dunning, and R. F. Stebbings, J. Chem. Phys. **72**, 3179 (1980).

[17] H. Hotop and A. Niehaus, J. Chem. Phys. **47**, 2506 (1967).

[18] C. K. Shepard and C. A. Kocher, J. Chem. Phys. **78**, 6620 (1983).

[19] M. Uematsu, K. Yamanouchi, T. Kondow, and K. Kuchitsu, Chem. Phys. **85**, 413 (1984).

[20] T. Shirai and H. Nakamura, Phys. Rev. A **36**, 4290 (1987).

[21] C. Ronge, A. Pesnelle, M. Perdrix, and G. Watel (unpublished).

[22] G. Herzberg, *Molecular Spectra and Molecular Structure III. Electronic Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1966).

[23] D. E. Strogryn and A. P. Strogryn, Mol. Phys. **11**, 371 (1966).

[24] *Handbook of Chemistry and Physics,* edited by R. C. Weast (Chemical Rubber Company, Cleveland, 1964), Chap. E, p. 37.