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Ionizing collisions of He(n ^1P) atoms in a low-Rydberg state with SF_6 and NO_2 electron-attaching molecules

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The ionization of He atoms, prepared in a well-defined $(n=14)\,^1P$ Rydberg state, in collisions with electron-attaching molecules like SF_6 and NO_2, is studied in a crossed-beam experiment at thermal energies. The ionization cross section is observed to be large for SF_6, reaching 4.2×10^{-13} cm^2, and to be smaller for NO_2, close to 10^{-15} cm^2. The dependence of these two cross sections on the relative velocity of the reactants exhibits a characteristic behavior with a saturation at low velocities, a dependence that is completely different from that obtained with polar molecules. The observation of such a dependence for NO_2 indicates that, for this molecule, the reaction product is an ion pair, as for SF_6, and that ionization is not due to rotational energy transfer even though NO_2 has a dipole moment. This dependence cannot be explained by the "free-electron model" usually used in Rydberg-atom–molecule collisions; it clearly shows that the interaction of the molecule with the ion core cannot be neglected.

I. INTRODUCTION

In addition to collisional ionization, previously studied[1,2] in collisions of He Rydberg atoms with polar molecules such as NH_3, SO_2, and acetone (C_3H_6O) and described by

$$\mathrm{He}^*(nl)+M(J,K)\rightarrow \mathrm{He}^+ + M(J',K')+e\ , \tag{1}$$

where J and K are the rotational quantum numbers, there was a strong interest to extend our work to Rydberg-atom collisions with electron-attaching molecules to confirm our conclusions. As a matter of fact, as early as 1986, we had obtained experimental evidence[3,4] that the colliding system containing Rydberg states as low as the present ones ($n=14$, 15, or 16) could not be treated in the well-known "free-electron model."[5] In this model, usually used up to now for the interpretation of Rydberg-atom–molecule collisions, the molecule interacts only with the Rydberg electron, the core-molecule interaction being disregarded. Our curiosity, therefore, led us to extend our investigation to the interaction between such Rydberg atoms and electron-attaching molecules by the same experimental method, as used for the case of polar molecules, which yields the velocity dependence of the collisional ionization.

Our first observation[6] on SF_6 in 1987 showed that the cross section, in arbitrary units, did not vary as expected from the "free-electron model": the ion core was certainly also playing a role in the collisions with this kind of molecule.

Electron-attaching molecules react with an A^* Rydberg atom by an electron transfer, and the reaction products are

$$A^*(nl)+M\rightarrow A^+ + M^-\ , \tag{2}$$

with the possibility of a dissociation of the molecule. Since 1976, a large number of experimental studies have been performed,[7–10] mainly at Rice University by Dunning and co-workers. In the period 1976–1985, collisions of highly excited Rydberg atoms with SF_6, CCl_4, and other electron-attaching dissociative targets have been studied[7] for Xe(nf) $(25\le n\le 40)$ and Rb (ns,nd) $(38\le n\le 106)$. After comparison of the experimental rate constants due to attachment of Rydberg electrons with that due to free electrons, and taking into account the differences in momentum distributions for these two kinds of electrons, the authors concluded that their data lent support to the free-electron model. Recently, intermediate Rydberg-atom collisions with this kind of molecule have been investigated[8–10] for $K(nd)$ $(9\le n\le 40)+SF_6$ or CCl_4, Ne(ns) $(8\le n\le 72)+SF_6$, and Ne(nd) $(6\le n\le 72)+SF_6$. In these experiments, interesting results have been obtained when taking into account postattachment interactions between the product positive and negative ions in order to explain the low values of the rate constants deviating from the free-electron model for $n\le 20$–25 for SF_6 and $n\le 30$ for CCl_4.

Previously, as early as 1967, several observations of collisional ionization were made with SF_6,[11–14] mostly with a mixture of Rydberg states. Up to now, reaction rates (equal to cross section multiplied by velocity and integrated over the velocity distribution of the reacting particles) were measured as a function of n. Only in one experiment[14] was the velocity dependence of the process searched for; it concerns Ar(nl)$+SF_6$ collisions,[14(a)] where n is not defined by expected to be in the range of $n\approx 15$–60. For this collision the electron-attachment cross section has been measured as a function of the Ar(nl) velocity in the range of 500–2000 m/s: a decrease inversely proportional to the collision velocity has been observed, in agreement with the free-electron model. For the dissociative targets CCl_4 and CCl_3F, leading to reactions Ar(nl)$+CCl_4$(or CCl_3F)$\rightarrow Ar^+ + Cl^- + CCl_3$(or CCl_2F), the dissociative electron-attachment cross section

TABLE I. Data on the molecules discussed in the present paper.

Molecule	Dipole moment (D)	Rotational constants (cm^{-1})	Electron affinity (eV) (Refs. from 1974)	
			adiabatic	vertical
			experimental	
SF$_6$	0^{a}		0.32 ± 0.15^{b}	
			0.46^{c}	
			1.0 ± 0.2^{d}	
			1.05 ± 0.1^{e}	
			theoretical	
			0.7^{f}	
			0.9 to 1.0^{g}	-1.57^{g}
			1.19^{h}	-0.04^{h}
			0.30^{i}	-0.34^{i}
			experimental	
NO$_2$	0.39^{a}	$A=8.0012^{j}$	2.36 ± 0.10^{k}	
		$B=0.43364^{j}$	2.275 ± 0.025^{l}	
		$C=0.41040^{j}$		
			theoretical	
			2.25^{m}	1.43^{m}
			1.51 to 2.05^{n}	
			experimental	
SO$_2$	1.59^{o}	$A=2.02736^{j}$	1.097 ± 0.036^{p}	
		$B=0.34417^{j}$	1.14 ± 0.15^{q}	
		$C=0.293535^{j}$	1.05^{r}	
			2.2 ± 0.1^{s}	
			1.107 ± 0.008^{t}	
			theoretical	
			1.08^{u}	0.84^{u}
			1.03^{v}	0.62^{v}

[a] Reference 41.
[b] Reference 21.
[c] Reference 23.
[d] Reference 24.
[e] Reference 25
[f] Reference 26.
[g] Reference 27.
[h] Reference 28.
[i] Reference 29.
[j] Reference 19.
[k] Reference 30.
[l] Reference 31.
[m] Reference 32.
[n] Reference 33.
[o] Reference 22.
[p] Reference 34.
[q] Reference 35.
[r] Reference 36.
[s] Reference 37.
[t] Reference 38.
[u] Reference 39.
[v] Reference 40.

exhibits a different behavior which levels off at low velocity for $n<26$, leading the authors to suggest that translational energy is used to overcome the reaction endoergicity.[14(b)]

We present here the results of collisional ionization of He atoms in a well-defined low-Rydberg state interacting wit SF$_6$ and NO$_2$,

$$\begin{aligned} &\mathrm{He}^*(14\,{}^1P)+\mathrm{SF}_6\rightarrow \mathrm{He}^+ + \mathrm{SF}_6{}^- \ , \\ &\mathrm{He}^*(14\,{}^1P)+\mathrm{NO}_2\rightarrow \mathrm{He}^+ + \mathrm{NO}_2{}^- \ , \end{aligned} \tag{3}$$

studied in a crossed-beam experiment using a time-of-flight technique. This method allows us to obtain the dependence of the aboslute value of the ionization cross section on the relative velocity between the Rydberg atom and the target molecule. These targets have been chosen for their interesting set of molecular constants, electric dipole moment, and electron affinity. On the one hand, the polar characters of the two molecules are different since SF$_6$ has no dipole moment while NO$_2$ has one; for the collisional ionization with NO$_2$, the channel of ionization of He* via the rotational energy deexcitation of the molecule, as observed on NH$_3$, SO$_2$, and C$_3$H$_6$O,[1,2] can be predominant. On the other hand, the electron affinity (EA) of NO$_2$ is large (and at least a factor of 2 larger than that of SF$_6$, the dispersion of the EA values available for SF$_6$ being large) and represents a reservoir of energy available for ionization of He* in competition with the rotational energy (see Table I).

II. EXPERIMENT

The same experimental setup and time-of-flight (TOF) technique has been employed as in our work on polar molecules. All details can be found in Refs. 1 and 2. This TOF method has proved to be very efficient to derive the velocity dependence of the cross section in many experiments such as Penning and Hornbeck-Molnar ionization measurements.[15]

The principle of the experiment is based on simultaneous measurements of the following.

(i) The He^+ ions produced in the He(14 ^1P)+SF_6 or NO_2 collisions, detected after mass selection through a quadrupole mass spectrometer.

(ii) The fluorescence photons at 506 nm emitted by the He(14 ^1P) atoms decaying to the ground state 1 ^1S, which gives the velocity distribution of the colliding excited projectiles. This measurement is necessary since the velocity distribution of the He(14 ^1P) projectiles is different[1] from that of the He(2 ^1S) metastable atoms from which they originate.

The dependence of the He^+ ion signal as a function of the target gas pressure is measured, as in the case of polar molecules, in order to determine the range of target density where the TOF measurement corresponds to a single-collision process.[1] In a first step, we verified that the target gas density ρ in the interaction zone was proportional to the target gas pressure P, this latter being measured upstream from the multicapillary array. To this end, we measured the Penning ions produced by metastable He(2 ^1S + 2 ^3S) collisions with the target gas as a function of P; we observed a linear dependence of the signal proving that ρ is indeed proportional to P. In a second step, using the mechanical velocity selector (with a 10% resolution) on the He beam to select $v_r = 2400$ m/s, we investigated the dependence of the He^+ signal produced in He(14 ^1P)+SF_6 or NO_2 collisions on P (see Sec. II B 2 in Ref. 1). This signal is plotted as a function of P in Fig. 1, where a linear dependence (slope equal to 1 in log-log coordinates) is observed as proof of a single-collision mechanism for the ionization. The range of pressure where this linear variation exists is larger than that observed in He(14 ^1P) plus polar molecule collisions where rotational energy transfer takes place. A double-collision mechanism of ionization (slope equal to 2 in log-log coordinates) is not observed up to pressures as high as 0.2 Torr for SF_6 and 0.4 Torr for NO_2, while the experiment with polar molecules showed a deviation from the slope equal to 1 already at $P \approx 0.05$ Torr. The TOF experiments have therefore been performed at target pressures ensuring a single-collision ionization process: (i) as low as $P = 0.03$ Torr of SF_6 for which the He^+ signal was sufficiently strong, (ii) slighty higher, $P = 0.11$ Torr, for NO_2 since the He^+ signal produced on this target molecule was much smaller than that on SF_6.

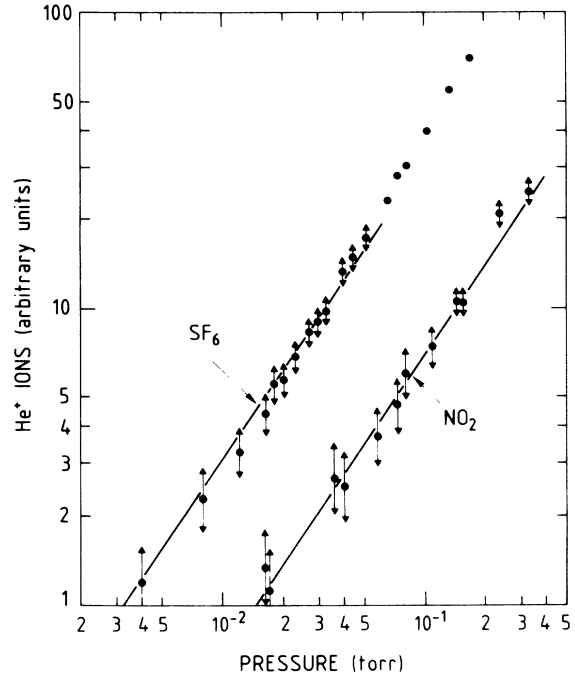

FIG. 1. Dependence of the He^+ ion signal on the target gas pressure for ionizing collisions [reaction (3)] normalized to equal fluorescence signal intensities. Closed circles, measurements; solid line, calculated linear variation (slope 1 in log-log coordinates). The pressure value is that measured upstream from the multicapillary array. The arbitrary units of the He^+ ions for the two curves SF_6 and NO_2 are not correlated.

III. TOF SPECTRA AND EXPERIMENTAL CROSS SECTIONS $\sigma_i^{\text{expt}}(v_r)$

The formulas describing the TOF spectra have been given in detail in Ref. 1 (see Sec. II C) and will only be summarized here. They are expressed as a function of the He velocity v, which is related to the He* time of flight τ by the relation $v = L/\tau$ (L is the flight path between the chopper and the interaction region).

The He^+ TOF spectrum $N^+(\tau)$ (expressed as a function of v) is given by

$$N^+(v) = k\rho\sigma_{\text{eff}}^{\text{expt}}(v)\delta\tau \int\int\int_{V_1} \Phi^*(v;x,y,z)dx\,dy\,dz \tag{4}$$

and the TOF spectrum $N^*(\tau)$ of fluorescence photons (expressed as a function of v) by

$$N^*(v) = \frac{R\Omega}{4\pi T_{14P}}\delta\tau\frac{1}{v} \int\int\int_{V_1} \Phi^*(v;x,y,z)dx\,dy\,dz\ , \tag{5}$$

where k is the collection efficiency of our experimental system including collecting coefficient and mass-analyzer transmission, ρ is the total density of target molecules in the interaction region, $\sigma_{\text{eff}}^{\text{expt}}(v)$ is the so-called experimental effective ionization cross section, $\delta\tau$ is the channel width of the multichannel TOF analyzer, Ω is the solid angle of fluorescence light detection, R is the detection efficiency of the fluorescence photons at 50.6 nm, and V_1 is the volume of the three-beam intersection (He*, target gas, and laser).

The TOF spectra are reported in Figs. 2 and 3 for both gases. For the fluorescence photons, it is the $N^* - N^*_{BG}$ signal which is shown, where N^*_{BG} is the background signal on the photon detector without laser. The ion signal is much smaller for NO_2 than for SF_6; therefore it has been necessary to extend the counting time for NO_2 to about six times the one for SF_6 in order to obtain a satisfactory signal-to-noise ratio.

Since for both SF_6 and NO_2 the target molecules are much heavier (mass 146 and 46, respectively) than He, the difference between $\sigma_{\rm eff}^{\rm expt}(v)$ and $\sigma_i^{\rm expt}(v_r)$ [where v is the He* velocity and v_r the relative velocity of the reactants He* and SF_6(or NO_2)] is negligible. The experimental ionization cross section $\sigma_i^{\rm expt}(v_r)$ can therefore simply be set equal to the measured $\sigma_{\rm eff}^{\rm expt}(v)$. The experimental ionization cross section is thus given by (considering the background signals to exist on both ion and photon detectors)

$$\sigma_i^{\rm expt}(v_r)=\frac{\Omega R}{4\pi k p T_{14P} v_r}\left[\left[\frac{N^+(v)}{N^*(v)-N^*_{\rm BG}(v)}\right]_p - \left[\frac{N^+(v)}{N^*(v)}\right]_{p=0}\right] . \qquad (6)$$

The cross sections $\sigma_i^{\rm expt}(v_r)$ are shown on Figs. 4 and 5 for SF_6 and NO_2, respectively. Both exhibit the same type of variation as a function of v_r, with a well-marked maximum. This behavior versus v_r is completely different from that expected in the free-electron model: in the case of electron-attaching targets, this model even reduces to equating the rate constants for the interaction of a free electron with a molecule and for the interaction of a Rydberg atom with a molecule, providing a monotonic v_r^{-1} variation.

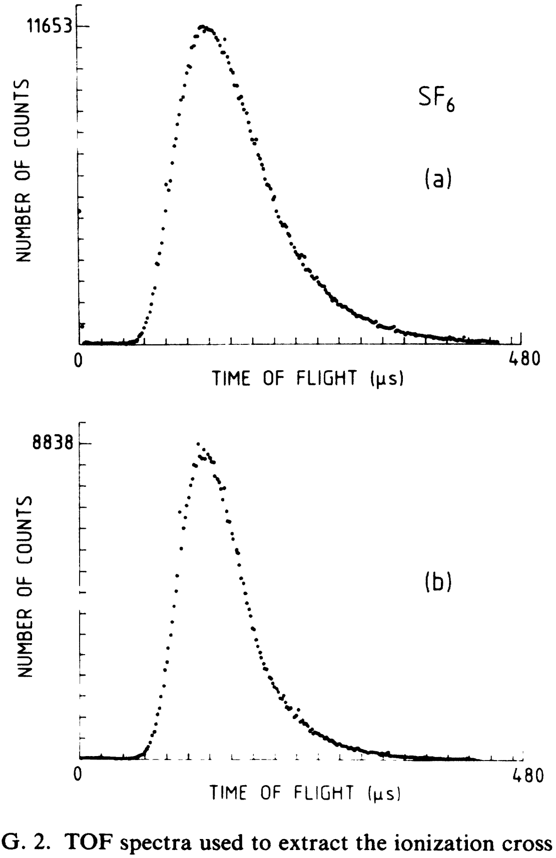

FIG. 2. TOF spectra used to extract the ionization cross section $\sigma_i^{\rm expt}(v_r)$ for He($14\,^1P$)+SF_6 collisions. (Channel width is 2 µs.) (a) Fluorescence photons; (b) He^+ ions produced in the collision.

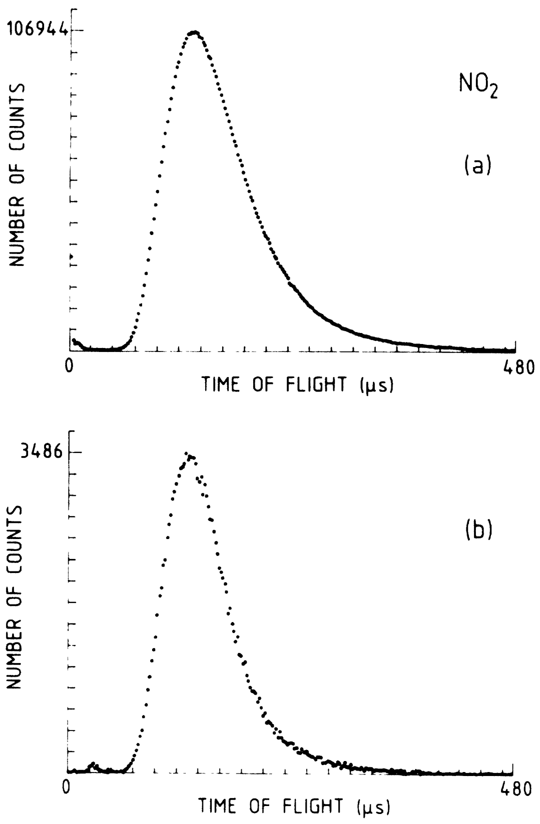

FIG. 3. TOF spectra used to extract the ionization cross section $\sigma_i^{\rm expt}(v_r)$ for He($14\,^1P$)+NO_2 collisions (as in Fig. 2).

IV. ABSOLUTE VALUES OF $\sigma_i^{\rm expt}(v_r)$

The absolute values of $\sigma_i^{\rm expt}$ for SF_6 and NO_2 are determined by comparison to the $\sigma_i^{\rm expt}$ for NH_3 following the method described in Ref. 2 for the polar molecules SO_2 and C_3H_6O. A mechanical velocity selector is introduced into the He* beam with the rotation frequency set to select the velocity $v_r \approx v = (2400 \pm 120)$ m/s, which corre-

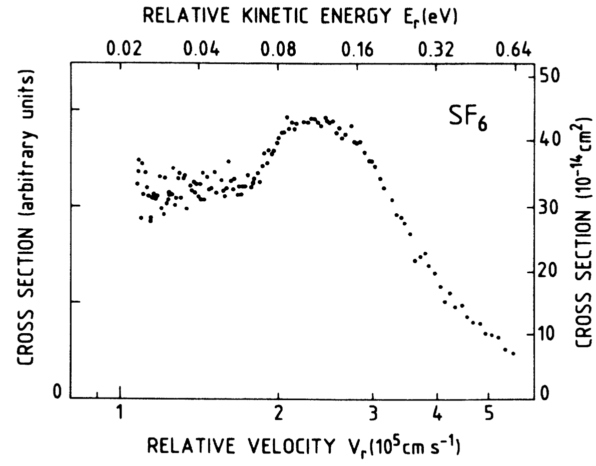

FIG. 4. Ionization cross section $\sigma_i^{\rm expt}(v_r)$ for He($14\,^1P$)+SF_6 collisions [reaction (3)] as a function of the relative velocity and kinetic energy of the reactants.

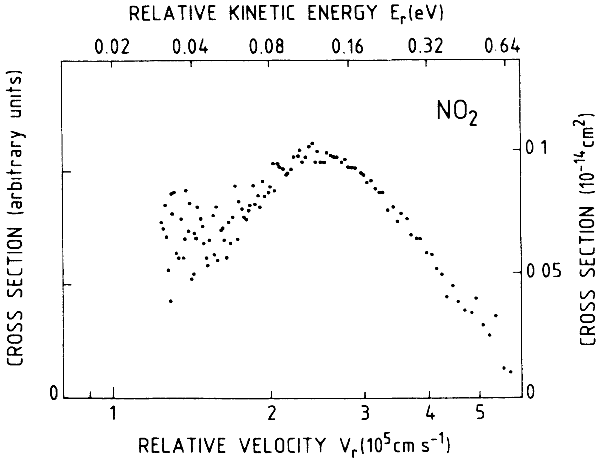

FIG. 5. Ionization cross section $\sigma_i^{\text{expt}}(v_r)$ for He(14 ^1P)+NO$_2$ collisions (as in Fig. 4).

sponds to the maximum in the Maxwell-Boltzmann distribution. The He$^+$ signals to be compared are normalized to the fluorescence-photon signals in order to correct for the effect of slight uv laser-power fluctuations, which may have existed. With these precautions it is sufficient to compare the terms

$$\frac{1}{p}\left[\left[\frac{N^+(v)}{N^*(v)-N^*_{BG}(v)}\right]_p-\left[\frac{N^+(v)}{N^*(v)}\right]_{p=0}\right] \qquad (7)$$

for SF$_6$ (or NO$_2$) to that for NH$_3$ to yield

$$\sigma_i^{\text{expt}}(\text{SF}_6)\approx 46\sigma_i^{\text{expt}}(\text{NH}_3) \qquad (8)$$

and

$$\sigma_i^{\text{expt}}(\text{NO}_2)\approx 0.11\sigma_i^{\text{expt}}(\text{NH}_3)\ . \qquad (9)$$

Since in our previous work on polar molecules[2] the experimental ionization cross secton $\sigma_i^{\text{expt}}(v_r=2400$ m/s) for He(14 ^1P)+NH$_3$ had been found to be equal to $(9\pm4)\times10^{-15}$ cm^2, the following absolute values can be deduced: for SF$_6$,

$$\sigma_i^{\text{expt}}(v_r=2400\ \text{m/s})=(4.2\pm2)\times10^{-13} \qquad (10)$$

and for NO$_2$,

$$\sigma_i^{\text{expt}}(v_r=2400\ \text{m/s})=(1\pm0.5)\times10^{-15} \qquad (11)$$

both in cm^2. The error bars in Eqs. (10) and (11) do not include any possible error of the Penning-ionization cross section σ_{PI} of NH$_3$ by metastable He(2 ^3S) atoms. This cross section enters into the determination of σ_i^{expt} (NH$_3$), as shown in Ref. 2 (see Sec. II and III A 1), where we have chosen among the four available values of σ_{PI} the one of Schmeltekopf and Fehsenfeld[16] ($\sigma_{\text{PI}}=60\times10^{-16}$ cm^2) to calibrate our experimental setup. Consequently, we suggest introducing into our final results an additional uncertainty of $\pm70\Delta\sigma_{\text{PI}}$ for SF$_6$ and of $\pm0.2\Delta\sigma_{\text{PI}}$ for NO$_2$.

V. DISCUSSION AND CONCLUSION

A. Identification of the ionization process for NO$_2$

For the NO$_2$ molecule, the measurement of the same type of velocity dependence of the cross section $\sigma_i^{\text{expt}}(v_r)$ as for SF$_6$ is an unambiguous signature for an ionizing process to be identical to the one of SF$_6$, i.e., ionization due to the molecular electron affinity, leading to He$^+$+NO$_2$$^-$ ion-pair formation.

However, since the NO$_2$ molecule possesses a nonnegligible dipole moment (see Table I) an alternative ionization process has to be discussed: it is the ionization by rotational energy transfer as observed for NH$_3$, SO$_2$, and C$_3$H$_6$O.[1,2] The molecule NO$_2$ is a very slightly asymmetric-top molecule near the limiting case of a prolate top since $B\approx C$ and $A>B$ and C (see Table I). A calculation of the coefficient b [see formula (20) in Ref. 2], which is an estimation of how much the molecule deviates from a pure symmetric-top shape, yields $b=0.003$, which is extremely small. Therefore the series of rotational levels can be simply obtained like those of a symmetric-top molecule [see formula (21) in Ref. 2]. As in Ref. 2, we can deduce the rotational deexcitation transitions of NO$_2$ which could be able to ionize He(14 ^1P): ionization of He(14 ^1P) would be possible with NO$_2$(J,K) in rotational levels $J\geq J_{\min}=36$, with large $|\Delta J|$ transitions, $|\Delta J|=34$–36 from $J_{\min}$, $|\Delta J|=29$–37 from $J_{\min}+1$, $|\Delta J|=26$–38 from $J_{\min}+2$, and so on (see Table II). The fraction of NO$_2$ molecules, for which the condition $J\geq36$ is satisfied, is 7.4% at 300 K. These ionizing transitions are very close to those encountered in He(14 ^1P)+SO$_2$.

However, a strong difference exists between the two cross sections $\sigma_i^{\text{expt}}(v_r)$ for NO$_2$ and SO$_2$. The presence of a maximum in $\sigma_i^{\text{expt}}(v_r)$ for NO$_2$ around 0.10 eV is the consequence of the Coulomb attraction between the positive and the negative product ions as is shown in the following section (see Sec. V B). Such a maximum, characteristic of a lack of energy in the colliding system, does not exist in the case of ionization by rotational energy transfer (see Figs. 5–7 in Ref. 1) because the molecule remains neutral in the final channel and energy is only required for the escape of the Rydberg electron which has a

TABLE II. Rotational deexcitation transitions of NO$_2$ which would allow ionization of He (14 ^1P): $J\rightarrow J'=J-|\Delta J|$.

J	$p(J)$ (%)	J'	$\|\Delta J\|$
0–35		No ionizing transitions	
36	1.02	0 to 2	34 to 36
37	0.90	0 to 8	29 to 37
38	0.80	0 to 12	26 to 38
39	0.70	0 to 14	25 to 39
40	0.61	0 to 17	23 to 40
50	0.12	0 to 34	16 to 50
60	0.015	0 to 47	13 to 60

well-defined binding energy. The reasons why rotational energy transfer is predominant for SO_2 and inefficient for NO_2 cannot be given precisely so far, but some indication appears in the comparison of the molecular data: (i) SO_2 has a large dipole moment (1.59 D), a factor of 4 larger than the one of $NO_2(0.39D)$; (ii) the electronic affinity of SO_2 (1.1 eV is the value presently accepted) is half the one of NO_2(2.3 eV for the average value).

B. Comments on the velocity dependence of $\sigma_i^{\text{expt}}(v_r)$

The interesting feature of the saturation in $\sigma_i^{\text{expt}}(v_r)$ when v_r decreases yields direct information on the interactions responsible for the ionization, in particular, on the interaction of the core He^+ with the molecule which has to be taken into account in addition to the one of the electron with the molecule, as is shown below.

It has been verified in several experiments with high-Rydberg states ($n > 30$) that the rate constant for electron transfer does not vary with n, i.e., with the electron energy, in agreement with the predictions of the free-electron model. For lower values of n, the mean radius of the Rydberg electron is smaller, and therefore the internuclear distance at which the electron transfer takes place is smaller. As a consequence, the Coulomb attraction between the He^+ and the $SF_6{}^-$ (or $NO_2{}^-$) ions increases, and is not any longer negligible.

The saturation of the cross section observed in the present work can be compared to the decrease of the rate constant k observed for n decreasing below 20 in $K(nd)+SF_6$ experiments,[8,10] and in Ne(ns or nd)+SF_6 experiments.[9] These authors have been obliged to take into account the postattachment Coulomb interaction between the product ions to explain this decrease.

Using the same reasoning leads us to consider the Coulomb attraction E_C between the He^+ and the $SF_6{}^-$ (or $NO_2{}^-$) ions and to compare it with the relative kinetic energy E_r^f of the He^+ and the $SF_6{}^-$ (or $NO_2{}^-$) ions at the time of their formation. If the Coulomb attraction $|E_C|$ is larger than the relative kinetic energy E_r^f, the ion pairs stay electrostatically bound and are unable to separate, so that free He^+ ions are not created. This domain is then defined by

$$E_r^f < |E_C| \ . \tag{12}$$

Let us calculate these two quantities.

(a) The Coulomb interaction E_C is given by

$$E_C = Z_1 Z_2 e^2 / R(\text{He}^+\text{-SF}_6{}^-) \ , \tag{13}$$

where $Z_1 e$ and $Z_2 e$ are the charges of the interacting positive and negative ions, respectively, and $R(\text{He}^+\text{-SF}_6{}^-)$ is the distance of the two ions at the time of their formation. This distance is equal to $R(\text{He}^*\text{-}M)$ at the time of the capture of the Rydberg electron by the molecule M, when using the hypothesis that the internuclear distance does not change during the electron capture.

To first approximation, it is reasonable to consider that the capture of the Rydberg electron during the approach of the molecule M toward the He* atom takes place at a distance of the order of magnitude of the mean radius $\langle r_{n,l} \rangle$ of the Rydberg electron, i.e.,

$$R(\text{He}^*\text{-}M) \approx \langle r_{n,l} \rangle \ , \tag{14}$$

leading to the following expression for $Z_1 = Z_2 = 1$:

$$|E_C| = e^2 / \langle r_{n,1} \rangle \ . \tag{15}$$

In the case of $n = 14$, $l = 1$, after laser excitation, we obtain $\langle r_{14p} \rangle = 293 a_0$ and

$$|E_C| \approx 0.093 \text{ eV} \ . \tag{16}$$

(b) The relative kinetic energy E_r^f of the product ions He^+ and $SF_6{}^-$ (or $NO_2{}^-$) at the time of their formation cannot easily be deduced. The removal of the Rydberg electron from the He* atom requires an energy $|E_{nl}| = 558.8$ cm^{-1} (0.07 eV); the adiabatic electron affinity reaches a value $|E_{\text{EA}}| \geq 0.3$ eV for SF_6 (a large spectrum of values is available; $|E_{\text{EA}}| \approx 1$ eV seems now to be accepted) and $|E_{\text{EA}}| \approx 2.3$ eV for NO_2.

It results in an excess of energy in the colliding system, which can be even larger when taking into account the rotational and vibrational energies of the molecule before the electron transfer.

This excess of internal energy could be either transferred to excitation (electronic, rovibrational) energy of the negative ion leading to a $SF_6{}^{-*}$ ($NO_2{}^{-*}$) ion, or to translational He^+-$SF_6{}^-$ ($NO_2{}^-$) energy involving $E_r^f > E_r$. Since no data are available concerning the characteristic of the negative ion produced in the collision, let us simply consider, in a first step, that the transfer of internal energy to the relative motion of the product ions is negligible. In this case, the relative kinetic energy E_r^f can be approximated by the relative kinetic energy of the reacting particles He* + M:

$$E_r^f \approx E_r \ . \tag{17}$$

The domain of energy where no free He^+ and $SF_6{}^-$ ions are created, given by formula (12), is then defined by

$$E_r < 0.093 \text{ eV} \ . \tag{18}$$

In Figs. 4 and 5, we do observe, for both SF_6 and NO_2 molecules, a change of the behavior of the cross section $\sigma_i^{\text{expt}}(v_r)$ when E_r decreases below ≈ 0.1 eV: this value is in agreement with the one defined by formula (18). The cross section $\sigma_i^{\text{expt}}(v_r)$ stops increasing when v_r decreases, exhibits a maximum around $E_r \approx 0.11$ eV (the maximum extends, in fact, from 0.09 to 0.13 eV), and levels off to some finite value for smaller E_r. We can therefore conclude that, with the present experimental conditions $n = 14$, $v_r \approx 2200$ m/s ($E_r \approx 0.1$ eV) the postattachment Coulomb interaction is actually not negligible, and that no significant amount of internal energy is transferred to product-ion translational energy.

For both molecules we observe that both $\sigma_i^{\text{expt}}(v_r)$ decrease but not to zero in the low-energy range experimentally accessible, 0.03–0.1 eV. The approximation adopted, i.e., $R(\text{He}^+\text{-}M^-) \approx \langle r_{n,1} \rangle$, would lead to an ionization cross section $\sigma_i^{\text{expt}}(v_r)$ equal to zero in the domain defined by formula (18), i.e., $E_r < 0.09$ eV. To explain this behavior, two points of view can be developed.

(i) The approximation $R(\mathrm{He}^*\text{-}M) \approx \langle r_{n,l} \rangle$ [see formula (14)] gives only an order of magnitude for $R(\mathrm{He}^*\text{-}M)$. The finite values of $\sigma_i^{\mathrm{expt}}(v_r)$ below 0.09 eV can be attributed to the spatial extension of the electron wave function beyond $\langle r_{n,l} \rangle$. Interactions at distances larger than $\langle r_{n,l} \rangle$ can still produce free ions; for instance, at $E_r = 0.07$ eV, all the captures of the Rydberg electron taking place at $R(\mathrm{He}^*\text{-}M) > 388a_0 = e^2/E_r$ produce still free He^+ ions since they correspond to $E_C < E_r$. Such a distance is consistent with the extension of the $n = 14$, $l = 1$ wave function.

(ii) The relative velocity of the colliding partners becoming smaller, the conditions of the collision become more favorable for a transfer of internal energy to product-ion translational energy; therefore

$$E_r^f > E_r \ , \tag{19}$$

allowing He^+ ions to separate from the negative ion even if the incoming channel kinetic energy E_r is small. Internal-translational energy transfers have been observed in several experiments: for instance, in rotational excitation or deexcitation of molecules,[17] several quanta of rotational energy (ΔJ up to several tens) can be transferred.

For the present molecules, we can roughly estimate the amount of internal energy available at 300 K. For SF_6, the lack of data concerning rotational quantum numbers prevents us from estimating the population of the rotational levels. For the vibrational energy, the populations $p(V)$ of the lowest vibrational levels V, calculated in the approximation of the harmonic oscillator [using formula (38) in Ref. 2], are the following: for the vibrational modes $\omega_e = 346$, 523, 615, 642, 773, and 948 cm^{-1} (0.043, 0.065, 0.076, 0.080, 0.096, and 0.117 eV),[18] $p(V=1) = 15.4$, 7.5, 5.0, 4.4, 2.4, and 1%, respectively, and $p(V=2) = 2.9\%$ for the first mode, the others being smaller than 1%.

For NO_2, we have calculated the population of the rotational levels J with the constants given in Table I. The population exceeds 1% over the range $4 \leq J \leq 36$; it reaches 4% for the level $J = 15$ which contains a rotational energy of 101 cm^{-1} (0.012 eV). Using the same approximation as for SF_6, only the vibrational mode $\omega_e = 749.8$ cm^{-1} (0.09 eV) (Ref. 19) has a population larger than 1%: $p(V=1) = 2.7\%$. We observe therefore that $J \rightarrow J - \Delta J$ rotational and $V \rightarrow V - \Delta V$ vibrational transitions could provide an energy of several tens of meV, which is actually the order of magnitude of E_r in the low-energy range considered; such an internal-translational energy transfer increases by a factor of 2 the value of E_r^f which becomes large enough to overcome E_C. The finite values of the ionization cross section $\sigma_i^{\mathrm{expt}}(v_r)$ around 0.04 eV would therefore be explained.

However, the fraction of internal energy of the neutral molecule which is kept as internal energy of the negative molecular ion is not known; neither the values of cross sections for internal-translational energy transfers for our experimental situation, nor their dependence on collision velocity to indicate if these transfers are favored at low v_r, is available in the literature. Furthermore, the behavior of $\sigma_i^{\mathrm{expt}}(v_r)$ in the very low-energy range 0.03–0.06 eV is not as clearly established as in the 0.06–0.11-eV range, due to the dispersion of the experimental points. In conclusion, the arguments concerning the energy transfers are yet speculative and additional experimental investigations would be necessary to conclude on these specific internal-translational energy transfers.

In conclusion to this subsection, the postattachment Coulomb interaction cannot be neglected at low collision velocity for Rydberg states as low as the one studied here ($n = 14$); the present measurement of velocity dependence of the cross section allows us to observe this phenomenon directly in the experimental data.

On the other hand, the velocity dependence of $\sigma_i^{\mathrm{expt}}(v_r)$ at larger velocity, $v_r > 3000$ m/s ($E_r > 0.17$ eV), is steeper than the v_r^{-1} behavior expected on the basis of the free-electron model in its simpler version, and certainly the core-molecule interaction, so far disregarded in the free-electron model, should be taken into account also in this kinetic energy range, as concluded in our work on polar molecules.[1,2]

C. Comments on the absolute values of $\sigma_i^{\mathrm{expt}}(v_r)$

No other experimental data are available for NO_2. For SF_6, a comparison with some previous measurements is possible. Since they have been carried out with experimental conditions different from the present ones, these experimental conditions have to be specified each time.

Our present result on SF_6 is $\sigma_i^{\mathrm{expt}}(v_r = 2400\ \mathrm{m/s}) = (4.2 \pm 2) \times 10^{-13}$ cm^2 (see Table III). It is smaller (and this was expected) than the first results published on $\mathrm{Xe}(nf) + \mathrm{SF}_6$ by Dunning and co-workers[7] in 1976 and 1977 on high-n levels, $25 < n < 38$ and $25 < n < 40$, respectively. Since quasiconstant values for the rate constant k and the cross section σ over the n range were given in Ref. 7, we have deduced average values over the seven and eight values measured, $\langle k \rangle_{\mathrm{high}\ n} = (4.0 \pm 0.8) \times 10^{-7}$ cm^3/s, and $\langle \sigma \rangle_{\mathrm{high}\ n} = (1.2 \pm 0.2) \times 10^{-11}$ cm^2. The present $\sigma_i^{\mathrm{expt}}(v_r = 2400\ \mathrm{m/s})$ is 30 times smaller than $\langle \sigma \rangle_{\mathrm{high}\ n}$. This is not surprising when considering the argument of the post attachment Coulomb interaction between the product ions, made later on for intermediate-n values (see Sec. V B).

In their recent results on $\mathrm{K}(nd) + \mathrm{SF}_6$, Zollars *et al.*[8] ($9 < n < 40$) and Zheng, Smith, and Dunning[10] ($12 < n < 25$) given only values of the rate constant k. For $n = 14$, $k_{14} = (7.5 \pm 3) \times 10^{-8}$ cm^3/s, which was six times smaller than their remeasured $k_{\mathrm{high}\ n} = (4.5 \pm 1) \times 10^{-7}$

TABLE III. Experimental cross sections for the collisional ionization of He(14 ^1P) atoms with attaching molecules for $v_r = 2400$ m/s (it is necessary to add to the error bars noted here a contribution due to the PI cross section uncertainty; see text, Sec. IV).

target molecule	σ_i^{expt} (10^{-14} cm^2)
SF_6	42 ± 20
NO_2	0.10 ± 0.05

cm^3/s. Unfortunately, these authors do not mention the average collision velocity in their beam-gas experiment. We can make, however, the hypothesis that $\langle v_r \rangle$ in Ref. 10 is close to that in Ref. 7 since $k_{\text{high } n}$ in Ref. 10 is close to $\langle k \rangle_{\text{high } n}$ in Ref. 7. With such a hypothesis, the cross section σ_{14} deduced from k_{14} appears to be about $(2.3\pm1)\times10^{-12}$ cm^{-2}, i.e., 5.5 times larger than the present σ_i^{expt}.

Harth *et al.*,[9] observing a strong decrease of the cross section in the collision Ne($14d$)+SF$_6$ below $n=20$, give the value $\sigma_{14}=(7\pm2)\times10^{-13}$ cm^2, which is only 1.7 times larger than ours.

Beterov *et al.*[20] also observe a fast decrease of the collisional rate constant k_n when n decreases in Na(np)+SF$_6$ collisions and give the value $k_{14}=5\times10^{-8}$ cm^3/s, i.e., 1.5 times smaller than that in Ref. 10.

In 1981, Dimicoli and Botter[14(a)] have studied the Ar*+SF$_6$ system, (i) first in a mixture of n states ($15<n<60$) which yielded $\sigma_{15\text{-}60}=(17\pm4)\times10^{-13}$ cm^2 at $v_r=570$ m/s, and $\sigma_{15\text{-}60}=(8\pm2)\times10^{-13}$ cm^2 at $v_r=2100$ m/s, which are, respectively, 7 and 15 times smaller than $\langle \sigma \rangle_{\text{high } n}$ obtained in Xe(nf)+SF$_6$ collisions of Refs. 7 and 8; (ii) secondly, for ten different n values in the $21<n<50$ range. While at $v_r=600$ m/s they observed a regular decrease of σ_n when n decreases, $\sigma_{40\text{-}50}=\sigma_{\text{high } n}=(2.3\pm0.5)\times10^{-12}$ cm^2, and $\sigma_{21\text{-}22}=(1.2\pm0.2)\times10^{-12}$ cm^2, at $v_r=1700$ m/s they obtained quasiconstant σ_n values over the range of n values, the average value of which is $\langle \sigma \rangle_{\text{all } n}=(5.1\pm0.4)\times10^{-13}$ cm^2. We observe that these experimental results are generally smaller than those in Ref. 10, a factor 6–8 for the closest velocities (which are the lowest ones), and a factor 17–26 for the highest velocities.

The dispersion of all these values proves that such measurements of absolute values are difficult. Therefore we can consider as satisfactory the difference between the cross section $\sigma_i^{\text{expt}}(n=14)$ presently measured at $v_r=2400$ m/s and (i) σ_{14} deduced from Ref. 10 by only a factor of 5.5, and (ii) σ_{14} deduced from Ref. 9 by only a factor of 1.7, noting that our result is smaller than that in Ref. 10 like all the other experimental results.

D. Conclusion

The results presented here clearly demonstrate that the ionization in collisions of low (n) Rydberg state atoms ($n=14$) with electron-attaching molecules is not explained by the free-electron model in its simpler version. This model predicts an ionization rate constant equal to that for thermal electron attachment, leading to a cross section inversely proportional to the collision velocity. The ionization cross sections obtained for both SF$_6$ and NO$_2$ molecules present a maximum unexpected in the free-electron model, and then decrease more steeply with increasing collision velocity than the v_r^{-1} law expected in this model.

We have observed already, in our work on the same Rydberg atoms colliding with polar molecules,[1,2] that the velocity dependence of the ionization cross section does not follow the behavior expected from the free-electron model, and suggested already that taking into account only the interaction between the Rydberg electron and the molecule is not sufficient for a proper description of such collision processes.

We show that a qualitative and satisfactory description of the ionizing process for such low-Rydberg states has to include the core-molecule interaction, of which the posttattachment Coulomb interaction between the product ions is the most simplified version. The present data give direct evidence of this interaction; the good agreement of this simplified model with the experiment, in particular, concerning the location of the maximum in $\sigma_i^{\text{expt}}(v_r)$, clearly indicates that the charged core plays an important role in the interaction.

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