COLLISION OF SF_6 MOLECULES WITH Xe(nf) RYDBERG ATOMS IN A QUADRUPOLE TRAP. DEPENDENCE OF THE SF_6^- ION LIFETIME ON n

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Collisions between Xe(nf) Rydberg atoms with SF_6 molecules produce unstable excited SF_6^-* molecular ions. We experimentally show that the lifetime of these ions is related to the principal quantum number n of the incident Rydberg atom. The smaller the value of n the longer is the lifetime of the ions.

1. Introduction

SF_6 has been the subject of increasing attention due to its ability to attach an electron at thermal energy (a few meV) with a large cross section, to form the corresponding excited SF_6^-* ion [1–3].

Rydberg atoms (RA) obtained by electron beam excitation have played an important role in collisions with SF_6 [4–9], since the average kinetic energy of the Rydberg electron, which may be identified with its binding energy for high values of the principal quantum number n, is in the thermal range.

Using dye lasers, one can obtain RAs with a well defined value of n and collisions of such RAs with SF_6 molecules provide details of the nature of the electron attachment mechanism and on the corresponding temporal and energetic properties of SF_6^- ions [10–15].

In our case the reaction is

$$SF_6 + Xe(nf) \xrightarrow{k_f} SF_6^-{}^* + Xe^+, \qquad (1)$$

where k_f is the formation rate constant. This reaction which leads to unstable SF_6^-* ions may be followed by different channels with their corresponding times:

$$SF_6^-{}^* \xrightarrow{\tau_a} SF_6 + e^-,$$

(kinetic energy) autodetachment, (2)

$$\xrightarrow{\tau_d} SF_5^- + F,$$

dissociative attachment, (3)

$$\xrightarrow{\tau_r} SF_6^- + h\nu,$$

radiative stabilization, (4)

$$\xrightarrow{\tau_c} SF_6^- + \text{energy},$$

collisional stabilization, (5)

$$\xrightarrow{\tau_n} SF_6 + e^-,$$

(kinetic energy) collisional detachment. (6)

k_f and some of these characteristic times like τ_a and τ_d are functions of the kinetic energy of the attached electron [16,17] while others like τ_c and τ_n may depend on the pressure of the gas over a certain range. In addition, τ_a and τ_d are dependent on the internal energy of the SF_6^- ion [6]. And since the lifetime of an SF_6^-* ion depends upon its internal energy which is the sum of the SF_6 electron affinity, the kinetic energy of the attached electron and the internal energy

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of its parent molecule, a wide range of lifetimes has been measured experimentally. And because the techniques employed possess different observation temporal windows, times from 10 μs up to a few milliseconds have been found [18].

The radiofrequency quadrupole trap is a suitable instrument for lifetime measurements due to its ability to confine ions for up to several seconds. The method used in this work for the creation of the SF_6^- ions was charge exchange, inside such a trap, between SF_6 molecules and xenon RAs in crossed beams.

2. Experimental procedure

A thermal beam of Xe atoms formed by a multichannel diffuser was excited by a pulsed electron beam outside the trap. A small fraction of the emerging atoms were in the metastable $6s'[1/2]_0$ and $6s[3/2]_2$ states in the notation $nl\{K\}_J$, the prime on l indicating $j=1/2$ [19]. Only the $J=0$ state has been used in our experiment. In addition a small fraction of excited atoms were in Rydberg states. The atomic beam passed through parallel plates in a dc electric field of the order of 3400 V/cm, and was further intersected at right angles by both an unfocused N_2-pumped dye laser and a beam of SF_6 molecules at room temperature. The interaction region was located at the center of the trap. Due to the distance between the electron excitation region of Xe atoms and the trap, and also to the dc electric field, no RAs were present in the trap without the laser. By varying the wavelength of the dye laser, selective excitation of levels of the $nf[3/2]_1$ series was achieved from the $6s'[1/2]_0$ metastable states. The characteristics of the trap and the associated electronic devices and timing procedure are roughly the same as those described in ref. [9]. With gas beams, the pressure was of the order of 8×10^{-7} Torr outside the trap, while the density was about 2×10^{11} particles cm^{-3} inside the trap with the same crossed beams intensities of xenon and SF_6. The N_2-pumped dye laser (coumarin 460 and 480) had a linewidth of the order of 1.5 cm^{-1} at 460 nm as measured with a SOPRA 1150 mm spectrometer associated with a Reticon scanner. The overall resolution and precision were respectively 0.15 cm^{-1} and ±2 cm^{-1}. The repetition rate was 39 pulses/s with a pulse peak power of 10 kW as determined with an ED100 Gentec joulemeter associated with the temporal lineshape of the laser pulse (fwhm of 7 ns).

3. Results and discussion

The study of the SF_6^- ion lifetime requires previous spectroscopic identification of the Xe Rydberg states involved. Pulsed field ionization techniques and the signal of Xe^+ ions formed by collision of Xe RAs and SF_6 molecules according to relation (1) were used. We obtained sharp peaks of the $nf[3/2]_1$ series with much weaker peaks of the $np[1/2]_1$ series as observed by several authors [19–22]. The peak identification is unambiguous since previous investigators [19,21,22] have calculated and/or measured the position of the levels of these series. Fig. 1 shows a partial spectrum of Xe^+ ion peaks corresponding to the nf series. No np peaks are visible while we have obtained very weak np peaks by field ionization. This may be attributed to a lower value of the cross section for SF_6^- ion formation from np states than from nf states.

Before the study of the temporal behaviour of the SF_6^- ions, the stability diagram of SF_6^- was constructed to define the best confinement conditions of the trap. Moreover, measures of unstable ion lifetimes requires the determination of the confinement characteristics of the trap with stable ions. The calibration was made with Xe^+ ions which have a mass (131 amu) comparable to the SF_6^- ion (146 amu). The Xe^+ ions were produced by collision of SF_6 molecules with Xe RAs produced by electron beam excitation. As for SF_6^- ions the best confinement conditions have been determined for Xe^+ ions, as well as their temporal evolution in the trap. In the confinement temporal "window" used for SF_6^- ions after their formation (2–7 ms) this evolution is well approximated by an exponential as shown in fig. 2. The corresponding time constant τ_s for stable ions was then measured from statistical calculations involving about 15 experiments. We have found $\tau_s^{-1}\approx30$ s^{-1} with a statistical standard deviation $\sigma=15$ s^{-1}. SF_6^- ions were then produced and confined under the same gas pressure conditions as above. Counting started about 2 ms after the laser shot because of the

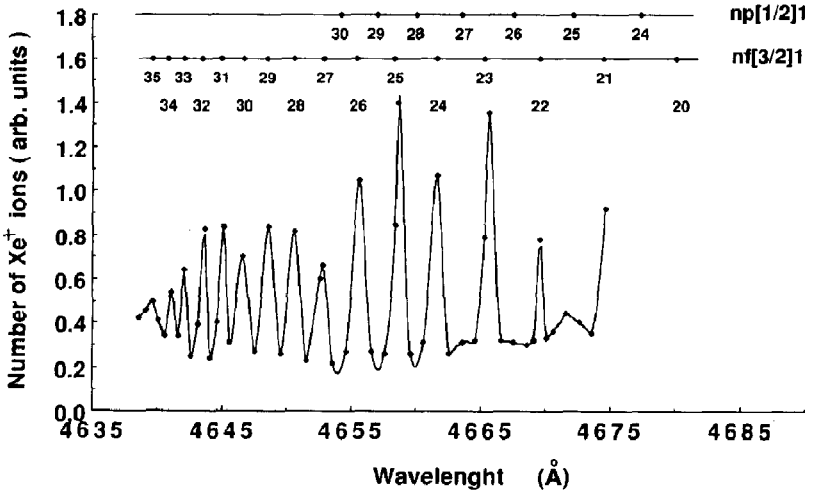

Fig. 1. Partial spectrum of Xe^+ ions produced by charge exchange between Xe(nf) Rydberg atoms and SF_6 molecules, as a function of the laser wavelength.

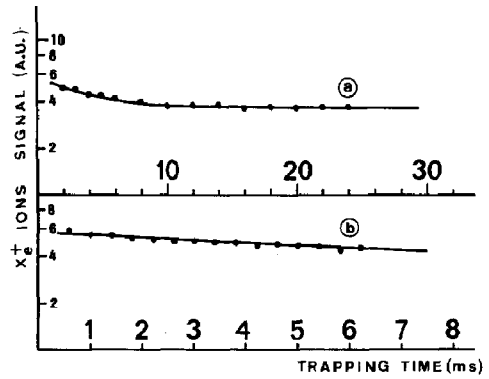

Fig. 2. The temporal signal of trapped Xe^+ ions: (a) with a large confinement temporal range; (b) in our confinement temporal "window".

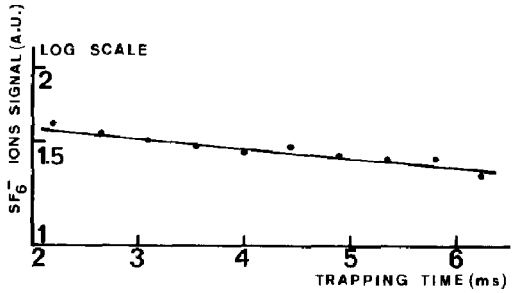

Fig. 3. The temporal signal of trapped SF_6^- ions in our confinement temporal window for $n=13$.

presence of an electron signal before that time due to metastable Xe atoms impinging upon the trap walls. However these electrons, whose energy is of the order of several eV, cannot generate SF_6^- ions. This was verified in our experiments where no ion confinement signal was observed in the absence of Xe Rydberg atoms. This is due to a very small cross section for such electron kinetic energies [2,23]. Fig. 3 gives an example of the temporal evolution of the number of SF_6^- ions in the trap for $n=13$. We have found a mean statistical value of 0.3 SF_6^- ion per laser pulse. Thus, in spite of their short lifetimes ($\approx 10^{-6}$ s for $n=13$, the lifetime increasing as n^3), some RAs give rise to SF_6^- ions before their removal by spontaneous radiation emission. This is connected with probability considerations and with very large cross sections in RA–target collisions and in thermal electron attachment to SF_6 processes. Repetitive operations of creation, confinement and counting, with addition of the counts, gave significant SF_6^- signals.

As pointed out in ref. [6], the autodetachment consists of several decay processes with different time constants, and the number of SF_6^- ions follows a non-exponential decay except over a short observation temporal range where an approximate exponential decay may be considered. This would explain the

discrepancy in the experimental "lifetime" values for the different techniques employed and mentioned in ref. [6]. Here we can consider such an exponential decay in our observation temporal range as verified by the curve of fig. 3 and by all the other curves obtained. Consequently, the number of SF_6^- ions present in the trap at time t may be expressed as

$$N_i(t)=N_i(0)\,[\eta+(1-\eta)\,\exp(-t\tau_e^{-1})]\times\exp(-t\tau_s^{-1}), \quad (7)$$

where $N_i(t)$ is the sum of stable and excited SF_6^- ions numbers at time t in the trap. η is the stabilization factor, i.e. the proportion of SF_6^- ions which have been stabilized at $t=\infty$. We can set

$$\eta=\eta_0+(1-\eta_0)\tau_c(\tau_r^{-1}+\tau_{sc}^{-1}), \quad (8)$$

where η_0 shows a possible stabilization at $t=0$ by energy transfer from the SF_6 molecule to the ionic core of Xe^+ (ionic core effect hypothesis) [7,24]. τ_c is the mean global "lifetime" of SF_6^{-*} and is given by

$$\tau_c^{-1}=\tau_a^{-1}+\tau_r^{-1}+\tau_c^{-1}(\rho)+\tau_n^{-1}(\rho), \quad (9)$$

where τ_c and τ_n may depend upon the pressure factor ρ. The dissociative attachment indicated by relation (3) can be neglected here since at room temperature the proportion of SF_6^- against SF_5^- ions is less than about 10^{-4} [7,25]. Under our pressure conditions, it is reasonable [26] to consider that τ_c and τ_n have very large values compared to τ_a since it has been shown [27] that one collision is not sufficient for an ion to acquire enough kinetic energy to be neutralized on the trap walls, and that stabilizing collisions are not efficient enough (1 over 4 collisions) [6,9]. So under our experimental conditions we can write

$$\tau_c^{-1}\approx\tau_a^{-1}+\tau_r^{-1}. \quad (10)$$

Fig. 4 shows the dependence of the slope d log N_i/dt (right vertical scale) on both the electron binding energy and n.

To have a rough approximation of τ_e one can consider that as the slope of log $N_i(t)$ is constant over our temporal "window" and as τ_r may be of the order of 100 ms [28] both the radiative stabilization and the ionic core effect can be neglected in a first approximation. This assumption eventually can lead to values of τ_e that are too large but does not modify its dependence on n. Relation (7) then reduces to

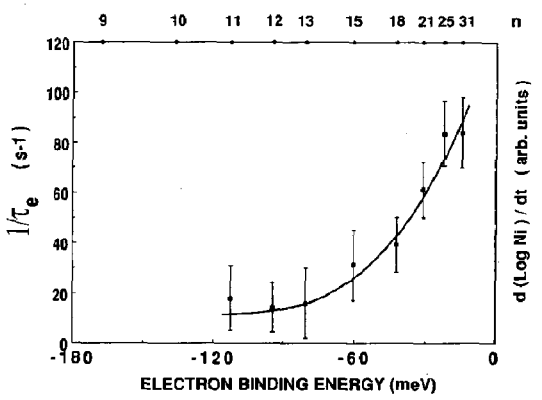

Fig. 4. d log $N_i(SF_6^-)/dt$ (right scale), and τ_e^{-1} (left scale) as a function of both the electron binding energy and n.

$$N_i(t)=N_i(0)\,\exp[-t(\tau_e^{-1}+\tau_s^{-1})] \quad (11)$$

with τ_e corresponding essentially to the autodetachment process. Now, τ_e^{-1} can easily be deduced from experimental results and is reported on the left vertical scale in fig. 4. The curve shows clearly that the "lifetime" increases as n decreases, which is equivalent to an increase of the stabilization of the SF_6^- ions. A first attempt to interpret this result is to consider the energy E of the SF_6^{-*} ion,

$$E=\mathrm{EA}+E_V-\Delta E_e(n)-\Delta E_c(n), \quad (12)$$

where EA and E_V are the electron affinity and the vibrational energy of the SF_6 molecule; $\Delta E_e(n)$ is the energy of the Rydberg electron and $\Delta E_c(n)$ the SF_6^{-*} to Xe^+ ionic core transferred energy in the hypothesis of the existence of this effect. As it is evident that the two last terms of (12) increase as n decreases, this leads to a reduction of the internal energy of the ion and to an enhancement of its stabilization and therefore of τ_e. Experimental investigations are currently underway to determine the nature and the numerical values of τ_e.

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