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Study of the SF_6^- Ion Lifetime in a rf Quadrupole Trap

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Abstract. We use an experimental apparatus to study SF_6^- ions lifetimes. These ions are created inside a quadrupole rf trap by charge exchange between highly excited argon atoms and SF_6 molecules. Ions are observed from 200 µs up to 15 ms after their creation time. In order to explain experimental results, collisions with SF_6 molecules and the influence of ionized core of argon are taken into account. A part of SF_6^- ions are stabilized by the last influence. These results evidence a radiative stabilization phenomenon, the lifetime of which is estimated at about 5 ms.

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Since the first determination of Edelson et al. [1], the SF_6^- molecular ion lifetime has been measured by means of several different techniques [2] which lead to a wide range of experimental values, from 10 µs up to a few milliseconds. As shown by statistical unimolecular theories [3, 4] of the autodetachment process:

$$SF_6^-(E(v')) \xrightarrow{\tau_a(E(v'))} SF_6(E(v)) + e(\varepsilon). \qquad (1)$$

The lifetime of an SF_6^- ion strongly depends upon its internal energy which is the sum of the SF_6 electron affinity, the attached electron kinetic energy and its parent molecule internal energy. Thus, the observed distributions of auto-detachment lifetimes reflect the experimental distributions of attaching electron energies and vibrational populations of the SF_6 molecular gas. This has been shown by varying the electron energy at room temperature [2] or varying the SF_6 temperature for a known distribution of electron energies [5]. The most recent estimates of this intrinsic autodetachment lifetime confirm the first measurement made in 1962 and correspond to a range in between 10 and 40 µs. As suggested by Odom et al. [6], the millisecond range measurements do not correspond to the intrinsic lifetime but to collisional or radiative processes.

Time-of-flight measurements of ion lifetimes necessarily possess limited observation windows and the radiofrequency quadrupole traps with their ability to confine ions up to several seconds are thus a very suitable instrument for this type of measurements. However, several problems are connected with this technique: free electrons cannot be used to create negative ions in the subthermal energy range, due to the presence of several volts/cm trapping electric fields. An alternative mean of creation of the SF_6^- ion was used in the present work by charge exchange, inside the trap, between a beam of atoms in highly excited (Rydberg) states and a beam of SF_6 molecules [7]. This ensures a well-defined low-energy (10–40 meV) electron distribution. The creation of the Rydberg

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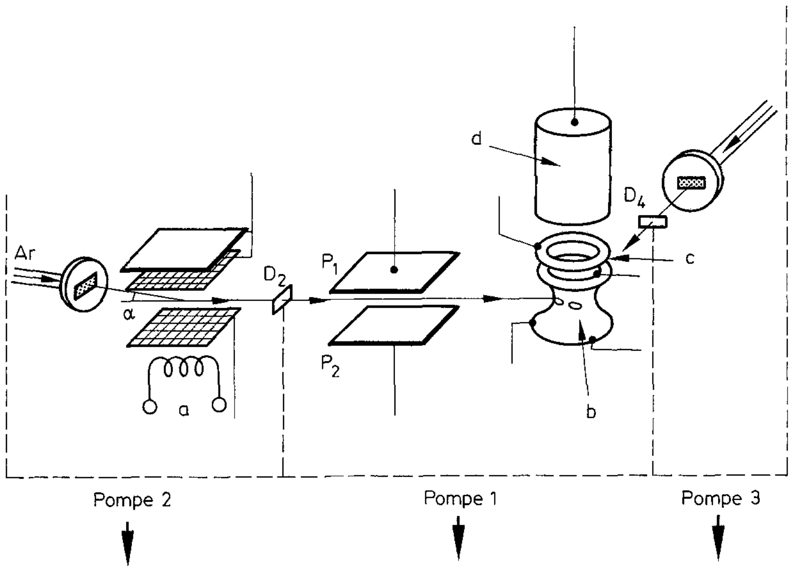

Fig. 1. Schematic representation of the apparatus (a: electron gun, b: ion trap, c: focalization ring, d: electron multiplier)

atoms can be made inside or outside the trap by laser excitation, or by electron bombardment [8]. The solution which was choosen in the present work was electron excitation of an argon beam outside the quadrupole.

Although the ion lifetimes measurements are made under very low pressure conditions, the trapping times are comparable with the mean collision time and, thus, stabilization or excitation processes leading to neutralization of the negative ions have to be considered. By modifying the residual gas pressure, it is possible to obtain an estimation of these collision cross sections and deduce a first estimate of another stabilization process: radiative de-excitation of the metastable SF_6^- ion.

1. Experimental

1.1. General

The crossed-beam apparatus is shown in Fig. 1: a beam of argon and a beam of SF_6 intersect at the center of a hyperbolic quadrupole radiofrequency trap. Differential pumping is used to ensure a low residual pressure ($\sim 10^{-7}$ Torr) in the scattering region. The Rydberg argon atoms are created by electron impact [8–10] with a rather large n distribution peaking for $n \simeq 20$ as measured either by field ionization or time of flight, corresponding to an external quasi-free electron binding energy ca. 30 meV. The effusive SF_6 beam is at room temperature.

The quadrupole radiofrequency trap which confines the ions created in the collision region is hyperbolic and has the following characteristic dimensions: $z_0 = 1$ cm, $r_0 = 1.4$ cm. The electric field frequency is 140 kHz with ca. 30 V rms voltage. Under these normal conditions, confinement is possible only for ionic species with a mass above 80 a.m.u.; the trapping well is a few eV deep. The upper quadrupole cap is made out of a grid through which can be ejected the trapped ions towards an electron multiplier. In order to respect the electrical symmetry of the trap, the extraction electronic device simultaneously commutes the two end caps with equal dc potentials of opposite signs. For reproducibility, a constant phase relationship is applied between the extracting potentials and the radiofrequency voltage. The electron multiplier is followed by a counting chain connected to an on-line PDP 11-03 minicomputer.

1.2. Timing Procedure

The electron gun used for the argon-beam bombardment, is turned on for 10 µs with a repetition rate of 10^2 to 10^3 Hz. An extremely small proportion (10^{-9}–10^{-10}) of the argon beam is in highly excited states and reaches the collision region within 200 µs. During this time of flight of neutral particles, a negative voltage is applied to the trap in order to eliminate any SF_6^- ion produced by electrons. At the arrival of the Rydberg atoms, a fraction of the molecular SF_6^- ions is confined and their lifetimes are determined by counting the number of these ions remaining in the trap after variable time delays elapsed since the 10 µs pulse creating the excited atoms. For each shot, an extremely small number of ions is counted (typically 10^{-2} per shot) and a special single-channel analyser was constructed for this purpose, driven by the minicomputer.

2. Results

In order to be able to measure lifetimes of unstable ions, it was found necessary to determine the

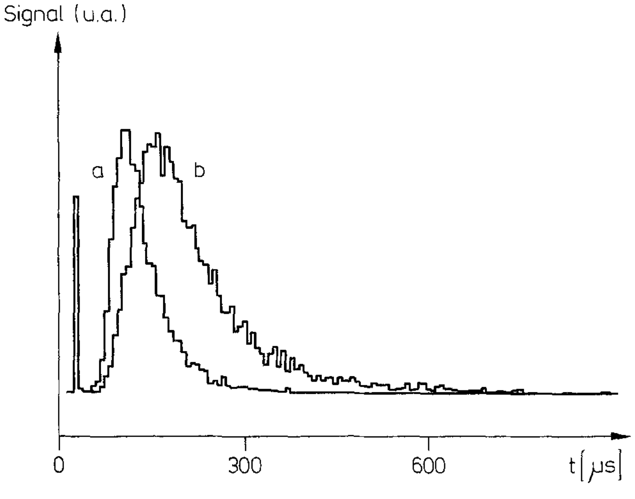

Fig. 2a and b. Arrival time dispersion of atoms in the reaction zone. Rydberg atoms (a) are statistically faster than metastable atoms (b) amplitudes are normalized

confinement characteristic of the trap with stable ions. The trapping conditions depend upon the charge and mass of the ions, the electrical conditions and the machining precision. The calibration was made with Xe^+ ions, with a mass comparable to the SF_6^- ion mass. These ions were produced by electron bombardment inside the trap of a xenon partial pressure of a few 10^{-7} Torr.

2.1. *Metastable vs. Rydberg Atoms Signals*

Inside the electron gun which creates the Rydberg argon atoms, a large proportion of argon metastable atoms are also produced. When these metastable atoms encounter the trap walls, they give birth to electrons which, in turn, may produce spurious SF_6^- ions. In order to discriminate against this undesirable SF_6^- ion signal as compared to the SF_6^- ion signal corresponding to the low-energy quasi-free Rydberg electrons, one takes advantage from the following fact: inside the Maxwellian velocity distribution, due to their shorter lifetimes and higher creation efficiency (varying as n^{-3}), the most numerous Rydberg atoms correspond to $n \sim 20$ and must possess higher velocities (Fig. 2) than the metastable atoms, in order to reach the collision region before their radiative quenching [8].

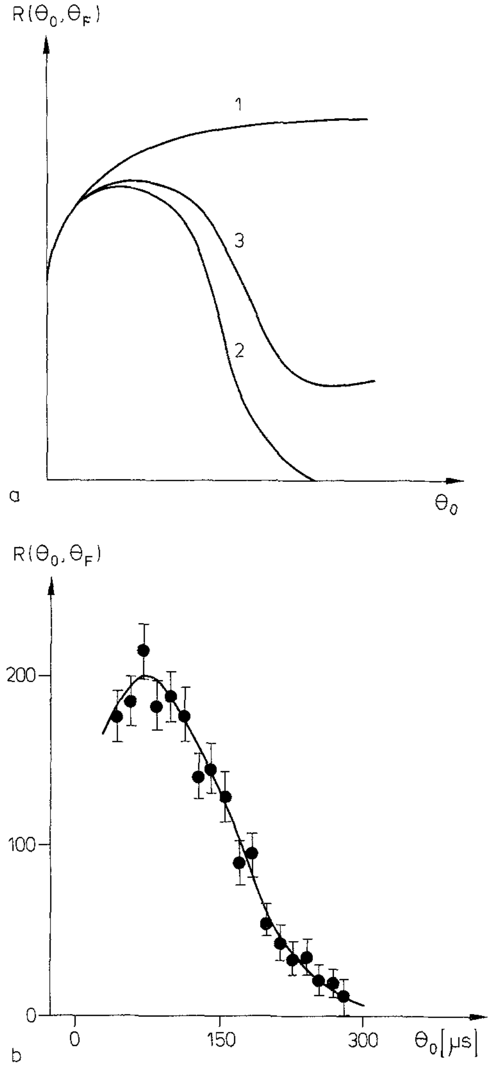

Fig. 3a and b. Representation of $R(\theta_0, \theta_f)$ vs. θ_0. (a) Schematic shape of $R(\theta_0, \theta_f)$ for three cases. (Curve *1*: ions creation is governed by the metastable atoms, Curve *2*: ions creation is governed by the Rydberg atoms, and Curve *3*: ions creation is governed by a mixture of metastable and Rydberg atoms). (b) Experimental curve

In the experiment, the SF_6^- ions are confined from time θ_0 and their number is measured at time θ_f. This extraction time is chosen such as the number of Rydberg atoms is then very small as compared to the number of metastable atoms. We define $R(\theta_0, \theta_f)$ the ratio between the number of SF_6^- ion still present at time θ_f and the number of metastable atoms entering the trap during the time interval (θ_0, θ_f).

$$R(\theta_0, \theta_f) = \frac{\int_{\theta_0}^{\theta_f} f_s(t)\phi(\theta_f - t)dt}{\int_{\theta_0}^{\theta_f} f_m(t)dt}, \qquad (2)$$

where $f_s(t)$ is the creation time density of the SF_6^- ions, $\phi(t)$ a decreasing function which takes into account the finite lifetime of these ions and $f_m(t)$ the arrival time density of the metastable atoms.

Three different cases can be considered (Fig. 3a):

a) the SF_6^- ions are produced by electrons issued from the metastable atoms. Then $f_s(t)$ is proportional to $f_m(t)$ and the function $R(\theta_0, \theta_f)$ is an increasing function (Curve *1*).

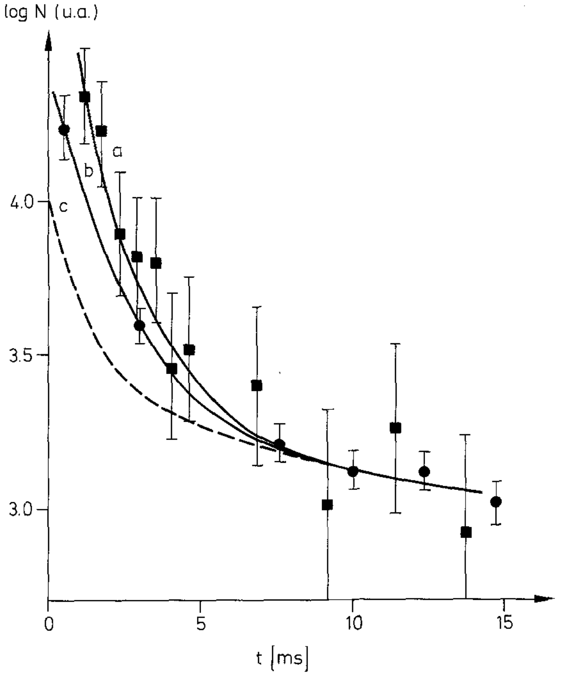

Fig. 4. Experimental curves showing the decay of SF_6^- ions in the rf trap. Curve *a* corresponds to a density of about 5×10^{10} mol cm^{-3} for the parent SF_6 neutral gas. Curve *b* corresponds to a density of about 10×10^{10} mol cm^{-3}. Curve *c* is the apparatus function: G_W. Error bars length represents twice the standard deviation

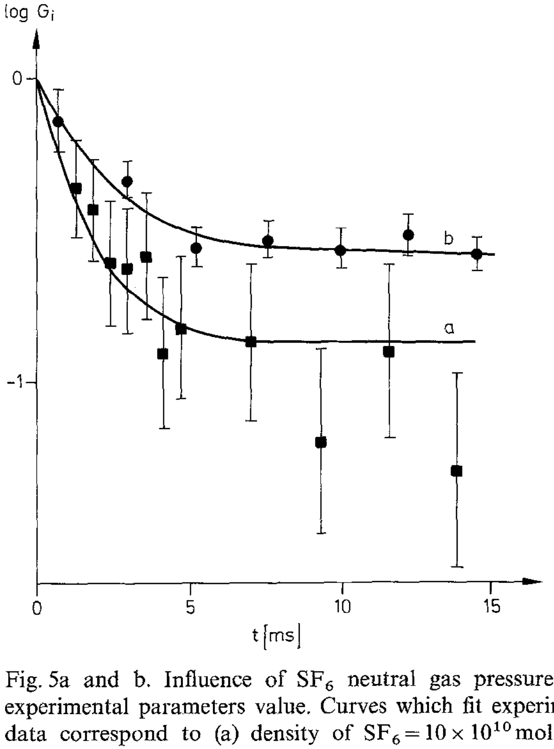

Fig. 5a and b. Influence of SF_6 neutral gas pressure upon experimental parameters value. Curves which fit experimental data correspond to (a) density of $SF_6 = 10 \times 10^{10}$ mol cm^{-3}; $\tau_a = \infty$; $\tau_R = 5$ ms; $\tau_S = 10$ ms; $\tau_n = 3$ ms; and (b) density of $SF_6 = 5 \times 10^{10}$ mol cm^{-3}; $\tau_a = \infty$; $\tau_R = 5$ ms; $\tau_s = 20$ ms; $\tau_n = 6$ ms

b) The SF_6^- ions are produced by collisions of the Rydberg atoms. Then, the $f_s(t)$ function decreases rapidly with θ_0 since the Rydberg atoms have short lifetimes ($\sim 70\,\mu$s) and the $R(\theta_0, \theta_f)$ function is rapidly decreasing (Curve *2*).

c) The ions are produced by the simultaneous contribution of both preceeding phenomena. Whatever may be their respective weighting, the $R(\theta_0, \theta_f)$ curve, which is first decreasing, must become again increasing since for the largest time intervals, the metastable atoms influence overpass that of the Rydberg atoms (Curve *3*).

The experimental determination of the $R(\theta_0, \theta_f)$ curve (Fig. 3b) confirms that, within the measurement errors, the electrons produced by the metastable atoms do not contribute to the SF_6^- signals which we use further.

2.2. SF_6^- *Ions Lifetimes Measurements*

The SF_6^- ions created inside the trap by collision between high Rydberg argon atoms and SF_6 molecules can disappear for two independant reasons. The first one corresponds to the previously determined working function of the trap which we will call $G_W(t)$ and the second corresponds to the SF_6^- ion lifetime itself, with a characteristic law $G_l(t)$. If $f_R(t)$ is the arrival time distribution of the Rydberg argon atoms and v_0 the total number of SF_6^- ions created, at some given time t, the number of SF_6^- ions which are still present inside the trap is given by

$$v(t) = v_0 \int_0^t f_R(\theta) G_W(t-\theta) G_l(t-\theta) d\theta\,. \tag{3}$$

Unfortunately, the precision of the experimental results is not sufficient to allow the deconvolution of this expression. For small values of the time θ, it is also difficult to determine the working function $G_W(\theta)$ of the trap and thus, to determine the variations of the lifetimes for values smaller than 200 µs.

On the contrary, it is possible to adjust the two curves corresponding, respectively, to stable ions (Xe^+) and unstable ions (SF_6^-) for time longer than 8 ms (Fig. 4). This indicates that the proportion of the SF_6^- ions which is stabilized depends on the residual gas pressure ϱ. Let $K(\varrho)$ be the stabilization factor ($0 \leqq K(\varrho) \leqq 1$) i.e. the proportion of SF_6^- ions which have been stabilized against autodetachment. The lifetime distribution $G_l(t)$ can be approximated by the expression:

$$G_l(t, \varrho) = K(\varrho) e^{-t/\tau(\varrho)} + [1 - K(\varrho)]\,. \tag{4}$$

By changing the residual pressure ϱ, it is possible to discriminate between intrinsic or radiative stabilization processes and collisional processes.

The measurements provide values of $K(\varrho)$ with an order of magnitude ca. 0.5 which decreases when the SF_6 residual pressure increases (Fig. 5).

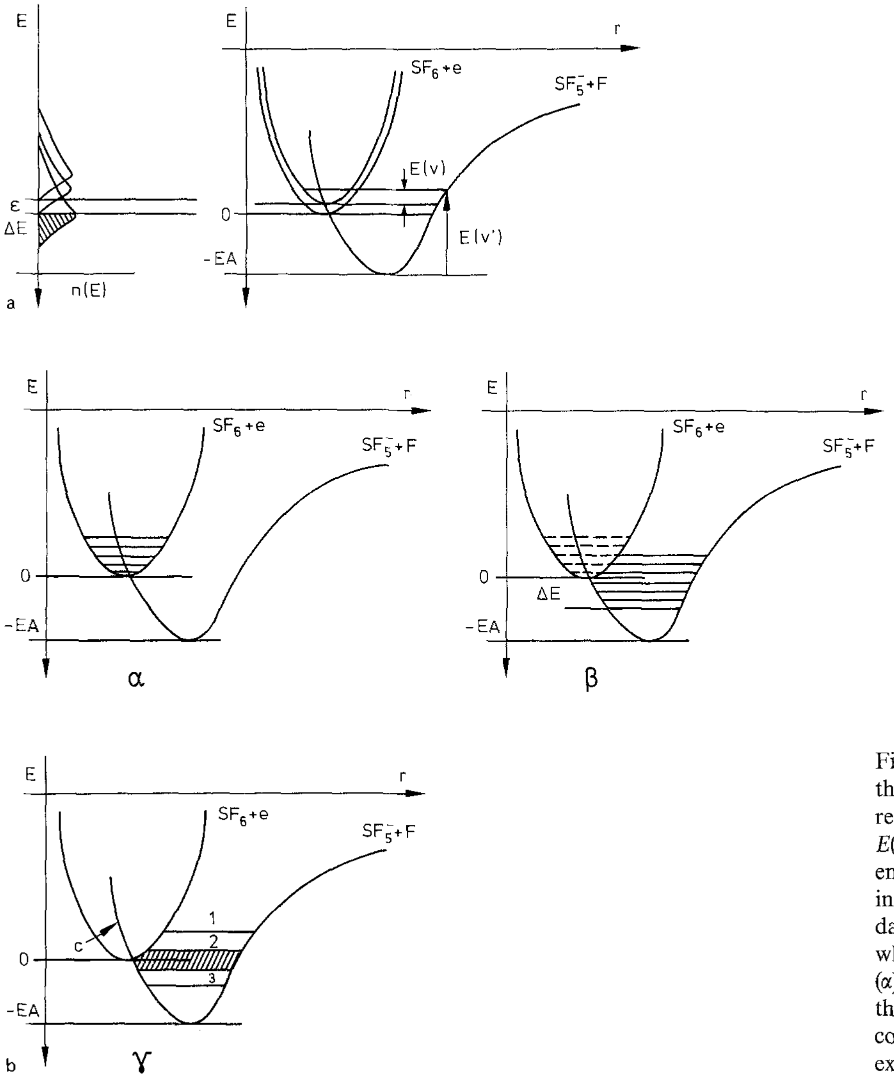

Fig. 6a and b. Schematic representation of the model. (a) Energetic properties of reactants. $E(v)$: SF_6 energy distribution; $E(v')$: SF_6^- energy distribution: ε: electron energy distribution; ΔE: loss of energy by influence of the ionized core of argon. The dashed zone corresponds to the part of ions which are stabilized. (b) Three state model (α): before reaction; (β): after creation; (γ): three state model; c represents the (SF_6+e) continuum, state 2 is enhanced because its exact position has to be estimated

3. Discussion

Although a quadrupole trap provides experimental conditions which are more free from environmental perturbations than a discharge or a flowing-afterglow, for example, the long observation times which are obtained require to take into account collisional effects on a long time scale as compared to the estimated intrinsic lifetime of the SF_6^- ion. Inside the trap, the pressure is the sum of the partial pressures of argon, background vacuum and the SF_6 parent gas. The orders of magnitude are such that the only collisions which must be considered are the SF_6^-–SF_6 collisions. With a collision rate of $7\times10^{-10}\,\mathrm{cm^3\,mol^{-1}\,s^{-1}}$ [11] and a neutral molecular density of $5.2\times10^{11}\,\mathrm{mol\cdot cm^{-3}}$, the mean-free time between collisions is $\tau_c \simeq 4\,\mathrm{ms}$. The SF_6^- ions which are created with a mean kinetic energy of 0.2 eV suffer collisions with the SF_6 thermal bath which tend to cool them. It has been shown [12] that after a first collision, nearly none of the ions can acquire kinetic energy in a collision enough to enable it to be neutralized on the trap walls.

In order to interpret our experimental measurements, we use the following simplified model: the SF_6^- are created by attachment of thermal electrons on SF_6 molecules with a room temperature vibrational energy distribution. The influence of the ionic core of the Rydberg atoms is such that a given amount of internal energy ΔE of the SF_6^- ion is given to the ionic core Ar^+ (as kinetic energy) thus partially stabilizing the negative ions (Fig. 6).

The SF_6^- ions are thus created over a rather wide distribution of internal energies which reflects the contribution of the internal energy distribution of the SF_6 molecule, of the kinetic energy of the attached electrons, and the ionic core stabilization energies. Arbitrarily we divide this distribution into 3 parts: the upper 1) corresponds to SF_6^- ions with short autodetachment lifetimes ($\tau_a \leqq 50\,\mu s$) as compared to our instrumental time resolution ($\sim 200\,\mu s$). The middle one 2) corresponds to the ensemble of SF_6^- ions which are coupled to the $\{SF_6 + e\}$ continuum by different mechanisms (intrinsic autodetachment, collisional detachment or collisional excitation followed by autodetachment...) with characteristic time constants larger than 200 µs. The lower part 3) is made of SF_6^- ions with internal energies such that the preceeding mechanisms are not allowed, and thus, possess infinite lifetimes.

Spontaneous emission couples these states. Although a large variety of radiative lifetimes exits, we will only consider a single one τ_R. By collision, ions in state 2 can be stabilized towards state 3 with a characteristic time constant $\tau_S(\varrho)$ depending upon the SF_6 beam pressure ϱ. These collisions can also couple state 2 to the $\{SF_6 + e\}$ continuum with a time constant $\tau_d(\varrho)$.

Ions created in state 1 have a short lifetime and will not be experimentally counted. We assume that the observed SF_6^- ions are created either in the metastable state 2 [13] with a probability π_0 or in the stable state 3 with probability $1 - \pi_0$.

From our experimentally determined parameters $K(\varrho)$ and $\tau(\varrho)$, we deduce the preceeding model parameters τ_a, τ_R, $\tau_d(\varrho)$, $\tau_R(\varrho)$, and π_0. For this, we use the following inequalities:

$$0 \leqq \pi_0 \leqq 1; \quad \tau_a, \tau_R, \tau_S(\varrho), \quad \tau_d(\varrho) > 0, \tag{5}$$

and the relations

$$K(\varrho) = \left(\frac{1}{\tau_a} + \frac{1}{\tau_S(\varrho)}\right) \pi_0 \tau(\varrho), \tag{6}$$

$$\tau(\varrho) = \frac{1}{\tau_a} + \frac{1}{\tau_R} + \frac{1}{\tau_R(\varrho)} + \frac{1}{\tau_d(\varrho)}. \tag{7}$$

The solution of these equations is then $\pi_0 \simeq 1$ and $\tau_a \gg 10$ ms, up to infinite. The first result indicates that no ions are created in the state 3 and shows the weakness of the ionic ion stabilization process. On the other hand, the second one suggests that the SF_6^- ions that we observe are those which have been stabilized, during their creation by charge exchange between an SF_6 molecule and a Rydberg argon atom, by the presence of the ionic core Ar^+.

We also find

$$\tau_S \simeq 20\,\text{ms}, \quad \tau_d \simeq 6\,\text{ms}, \quad \text{and} \quad \tau_R \simeq 5\,\text{ms}.$$

If we compare these last values with the mean free time between collisions evaluated to 4 ms, we see that the stabilizing collisions are not very efficient (1 over 4 collisions) [6]. On the contrary, collisions which remove the SF_6^- ions towards the continuum C, either by collisional detachment [14] or collisional dissociation [15] into $SF_5^- + F$, are very efficient (almost every collision).

The stabilization by radiative emission has been examined by Odom et al. [6]. The rate constant for spontaneous emission is proportional to the square value of the dipole matrix elements between vibrational levels of the SF_6^- ion, the upper one belonging to the "metastable" set, the lower level belonging to the stable set of internal states. Our measurement of the radiative lifetime gives a factor of 0.34 for the dipole moment of the SF_6^- ion as compared to that of the neutral SF_6. This assumes that the corresponding frequency of the emitted photon is the same for SF_6^- or SF_6. Although this is most probably invalid for all the vibrational frequencies of SF_6^-, it has been shown recently [16] that, at least, one vibrational frequency, in the region of interest near the ground state of neutral SF_6, coincides for the SF_6^- ion with the ν_3 frequency of the molecule. This modification of the dipole moment is, most probably, due to the change of polarizability of the negative molecular ion as compared to the neutral molecule.

4. Conclusion

The rf quadrupole trap is a very suitable tool for measuring metastable ion lifetimes. For short time scale, the limitation comes from the arrival time dispersion of the excited atoms which give birth to the negative ions. Thus, creation, inside the trap, by short (<100 ns) laser pulses of short lived Rydberg atoms ($\sim 1\,\mu s$) would be more desirable. On the contrary, there is no limitation for the long time scale up to several seconds. Electrons created by autodetachment are immediately expelled and, thus, cannot produce spurious effects.

The experimental measurements of the SF_6^- ion lifetimes may be interpreted with two very different hypothesis:

a) the SF_6^- ion autodetachment times have values which spread from the µs range up to several tenths of milliseconds,

b) the SF_6^- ions have short autodetachment lifetimes ($<50\,\mu s$) and stabilizing processes allow their observation on a long time scale [17]. We ruled out the first explanation because the ion signal decay curves lead to mean lifetime τ_a lying above 20 ms. This is completely contradictory with the measured values in the µs range [2].

On the other hand, the second hypothesis, is compatible with most previous measurements of the intrinsic autodetachment lifetime, with the ionic core stabilization process, as well as the present determination of the radiative lifetime. The creation of SF_6^- ions by means of well defined laser-excited Rydberg atoms should provide further informations on this ionic core effect.

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