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Ion-pair formation in the collision of high Rydberg argon atoms with SF_6 and C_6F_6 and negative ion lifetimes

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The ion-pair formation in collision between argon atoms in high Rydberg states (HR) with SF_6 and C_6F_6 has been investigated. The absolute cross sections are inversely proportional to the Ar(HR) velocity and increase monotonically with increasing principal quantum number n. Measurements of the negative ion lifetimes against autodetachment are reported and are $>20\,\mu$sec for SF_6^- and $\sim 1\,\mu$sec and $>20\,\mu$sec for $C_6F_6^-$. The present data are reviewed in light of the theoretical predictions of "free electron" models and the results of free electron experiments.

I. INTRODUCTION

Collisions of highly excited rare gas atoms with various molecules have been experimentally studied by several authors.[1–19] Depending on the nature of the molecule, different ionization processes have been observed. For molecules which possess large thermal electron attachment cross sections, formation of an ion pair via dissociative or nondissociative attachment of the highly excited Rydberg electron may occur.[11–19]

Matsuzawa[20–22] has investigated theoretically the latter collision. His model is based on the assumption that because of the large separation between the Rydberg electron and its ionic core, the interaction of the target molecule with the core can be neglected. The excited electron thus behaves as if it were free with an energy corresponding to its orbital motion. Following this essentially "free electron" model the rate constant for transfer of the excited electron to the target molecule should be equal to the rate constant for attachment of a free electron having the same kinetic energy as the Rydberg electron.

Negative ion formation is generally viewed as proceeding via the capture of an electron in the field of the ground or excited electronic state of the molecule.[23] The time the electron is retained by the molecule is referred to as the negative ion lifetime τ_a. Depending on the magnitude of τ_a three classes of negative ions have been identified[23]: (i) extremely short-lived (10^{-15} sec $<\tau_a<10^{-12}$ sec) which can be observed as resonances in electron scattering studies, (ii) moderately short-lived (10^{-12} sec $<\tau_a<10^{-6}$ sec)—these can be stabilized and observed in high pressure swarm experiments, and (iii) long-lived ($\tau_a>10^{-6}$ sec) which can be observed with a conventional mass spectrometer.

In the present experiment the negative and positive ions formed in the collision of highly excited (HR) argon atoms with SF_6 and C_6F_6 have been analyzed using a coincidence TOF mass spectrometer. This technique of mass analysis has been applied for the first time to negative ion lifetime measurements. A comparison of the present results with calculated[24] and measured values[25–32] for the autodetachment lifetime τ_a of free electrons enables one to determine the role of the ionic core in the outcome of the experiments.

In the present paper, relative cross sections for the nondissociative electron attachment of the Rydberg electron for different ranges of the principal quantum number n and different Ar-beam velocities are reported.

II. EXPERIMENTAL APPROACH

The apparatus which is shown in Fig. 1 has been described in detail elsewhere[33] and only the essential features and the procedure for lifetime measurements will be described here.

A supersonic beam of ground state argon atoms is excited by a magnetically confined electron beam. After removal of the unwanted charged particles, and because of the deviation of the excited beam with respect to the neutral one, only long-lived excited species (metastable and HR) are allowed to pass between two parallel plates (n analyzer) and enter the interaction region where they cross an effusive jet of neutral molecules (XY). A field ionization technique is used to select different n ranges of HR atoms. The acceleration of the argon atoms is obtained by using an H_2 seeded beam (velocity range 5 to 20×10^4 cm/sec).

The mass analysis of the charged products of the reaction was obtained with a negative ion or electron-positive ion coincidence time-of-flight mass spectrometer (CTOF). Depending on the polarity of the constant electric field applied on the grids which limit the interaction zone the positive or negative collision products are mass analyzed. The negative or positive species formed in coincidence with them are drawn in the opposite direction and detected by a detector. The signal of this detector starts a time-to-amplitude converter (TAC) and thus indicates the moment of formation of the charged pair. Electrons will have a flight time of a few nsec between the point of formation and the detector, while negative ions will reach the detector within $\sim 1\,\mu$sec. Therefore the TOF of a positive ion (Ar^+, for example) produced in an ion pair process ($Ar^+ + XY^-$) will be apparently shorter than the TOF of the same ion formed in coincidence with an e^-.

A typical coincidence TOF mass spectrum of the positive ions obtained in the collision of HR argon atoms with SF_6 is shown in Fig. 2(a). The two peaks are assigned to the following processes:

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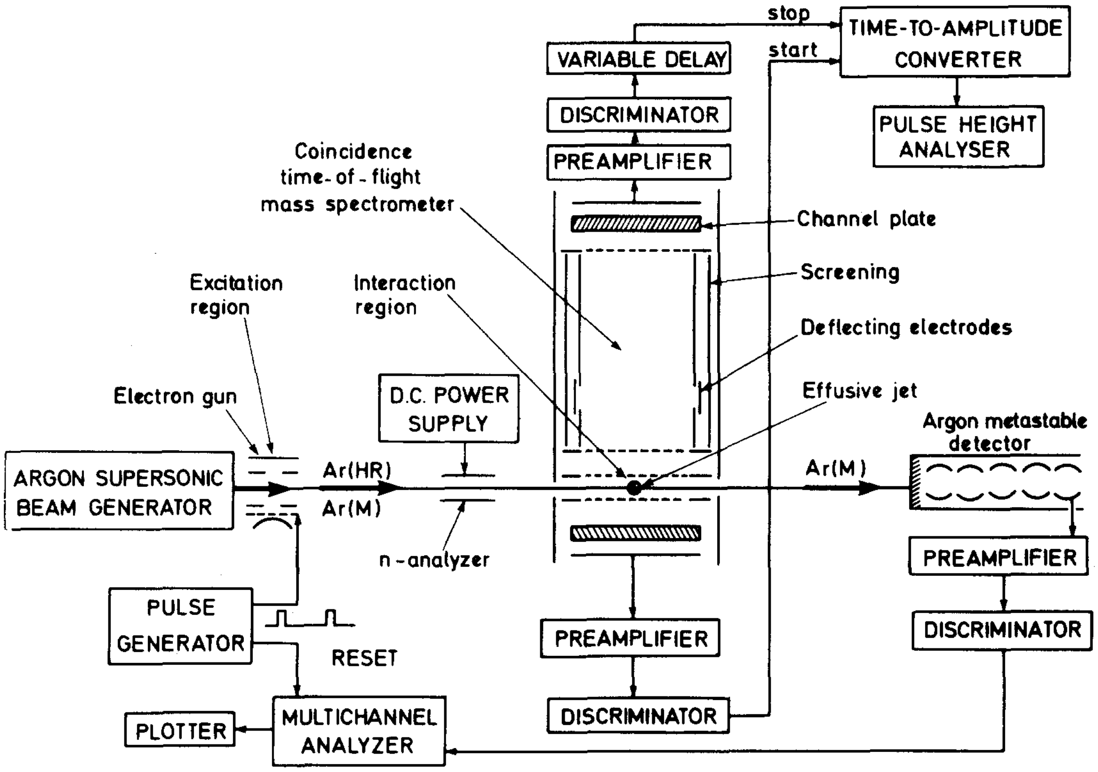

FIG. 1. Schematic diagram of the apparatus.

(i) The nondissociative electron attachment in the collision

$$\mathrm{Ar(HR)} + \mathrm{SF_6} \xrightarrow[k_{\mathrm{AA}}]{\sigma_{\mathrm{AA}}} \mathrm{Ar^+} + \mathrm{SF_6^-} \tag{1}$$

gives rise to the peak at 3.2 μsec. The start is given by the negative ion SF_6^-.

(ii) The ionization of HR argon atoms in the electric field present in the interaction region (~100 V/cm) and by blackbody radiation or in collision with residual gas molecules like H_2O gives the couple $Ar^+ + e^-$. The corresponding peak appears at 5 μsec and remains without measurable change after the target gas is removed from the system.

A. Lifetime measurements

Until now no assumptions on the negative ion lifetime have been made. In the mass analysis performed above the negative ion lifetime τ_a must be larger than the flight time to the detector (1.8 μsec). On the other hand, it is possible to determine lifetimes of temporary negative ions using the present arrangement of the CTOF mass spectrometer. If during its flight to the detector a negative ion undergoes autodetachment (i.e., an electron is ejected), the start on the TAC will be given by the ejected electron at a time equal to the flight time of the negative ion before the autodetachment took place (and smaller than the flight time of the negative ion to the detector). Therefore a number of ion counts will be distributed throughout the region between the two peaks corresponding to processes (i) and (ii).

If an exponential decay law is assumed for the autodetachment of electrons the number of negative ions which undergo autodetachment is given by the equation

$$N(t) = \alpha e^{-t/\tau_a} , \tag{2}$$

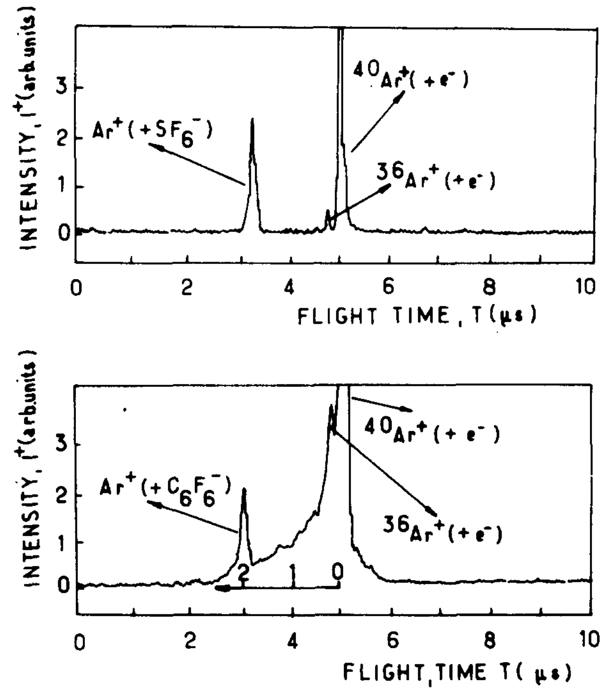

FIG. 2. Coincidence time-of-flight mass spectra of the positive reaction products in the collision of HR argon atoms with (a) SF_6 and (b) C_6F_6. The opposite abcissa scale is used for the negative ion lifetime measurements.

TABLE I. Absolute reaction cross sections σ (10^{-12} cm^2) and rate constants k (10^{-8} cm^3 sec^{-1}) for the collision of Ar(HR) with SF_6 and C_6F_6 at two argon velocities for different n ranges. Comparison with values reported in the literature at thermal energy.

	SF_6				C_6F_6	
	6.07		17.03		6.0	
v_r (10^4 cm/sec)	σ_{AA}	k_{AA}	σ_{AA}	k_{AA}	σ_{AA}	k_{AA}
Ar (40–50)	2.3 ± 0.5	14 ± 2.8	0.54 ± 0.1	0.92 ± 0.2	1.27 ± 0.2	7.6 ± 1.5
Ar (35–40)	2.1 ± 0.4	12.7 ± 2.5	0.51 ± 0.1	0.87 ± 0.2	1.28 ± 0.2	7.7 ± 1.5
Ar (33–35)	1.9 ± 0.4	11.5 ± 2.3	0.46 ± 0.1	0.78 ± 0.2	0.98 ± 0.2	5.9 ± 1.2
Ar (30–33)	1.8 ± 0.3	10.9 ± 2.2	0.51 ± 0.1	0.87 ± 0.2	0.83 ± 0.2	5.0 ± 1.0
Ar (28–30)	1.6 ± 0.3	9.7 ± 1.9	0.56 ± 0.1	0.96 ± 0.2	0.76 ± 0.2	4.6 ± 0.9
Ar (26–28)	1.4 ± 0.3	8.5 ± 1.7	0.5 ± 0.1	0.85 ± 0.2	0.62 ± 0.1	3.7 ± 0.7
Ar (25–26)	1.4 ± 0.3	8.5 ± 1.7	0.47 ± 0.1	0.8 ± 0.2	0.65 ± 0.1	3.9 ± 0.8
Ar (24–25)	1.3 ± 0.2	7.9 ± 1.6	0.49 ± 0.1	0.83 ± 0.2	0.72 ± 0.1	4.3 ± 0.9
Ar (22–24)	1.0 ± 0.2	6.1 ± 1.2	0.53 ± 0.1	0.9 ± 0.2	0.64 ± 0.1	3.8 ± 0.8
Ar (21–22)	1.2 ± 0.2	7.3 ± 1.4	0.49 ± 0.1	0.83 ± 0.2	0.68 ± 0.1	4.1 ± 0.8
Xe (nf)	12.0 ± 2[a]	38 ± 8[a]				3 ± 0.8[b]
Ar (HR)	1.5 ± 0.1[c] 1.7 ± 0.1[d]					

[a] Reference 16, $n = 31$.
[b] Reference 19, $n = 26$.
[c] Reference 12, value obtained from observation of Ar^+ production.
[d] Reference 12, value obtained from observation of SF_6^- production.

where α is a constant and τ_a the lifetime of the negative ion against autodetachment. The value of τ_a is determined from the slope of a plot of $\ln N(t)$ versus the time of flight of the negative ion before autoionization. This time is measured on the same time scale as in Fig. 2(a) but in an opposite direction taking as origin the peak at 5 μsec ($Ar^+ + e^-$).

A coincidence TOF mass spectrum of the positive ions obtained in the collision of HR argon atoms with C_6F_6 is shown in Fig. 2(b). The peak at 3 μsec corresponds to the nondissociative electron attachment to C_6F_6. Its integral must be equal to the number of temporary $C_6F_6^-$ ions which have not undergone autodetachment 2 μsec after the moment of formation. It is evident that the values of lifetime accessible by the technique described above are limited by the flight time of the negative ion to the detector. An increase of this flight time can be achieved by TOF mass analysis of the negative ions. In this case the TAC is started by the positive ions. The stop signal can be externally delayed so that e^- as well as negative ions can be detected. Because of the loss of e^- in the field free region, measurements with this mode of the CTOF mass spectrometer will be possible only after modifications of the apparatus and a wider range of lifetime values will be accessible for the experiment ($\tau_{max} \sim 20$ μsec).

B. Reaction cross-section measurements

The reaction cross section σ_R has been related to the experimentally measured quantities by the following equation:

$$\sigma_R(\bar{v}_{rel}) = \frac{1}{N_{XY}} \ln \frac{I_0}{I_0 - I^{+\,or\,-}} , \qquad (3)$$

where N_{XY} is the number density of the target molecule XY in (part/cm^3), I_0 the initial intensity of HR atoms, $I^{+\,or\,-}$ the intensity of positive or negative ions formed in the reaction, and $\bar{v}_{rel}$ the average velocity of the HR argon beam relative to the target molecule.

Using a field ionization technique the intensity of well-defined groups of n states (I_0^n) and of the ions produced by them ($I_n^{+\,or\,-}$) in the reaction can be separately detected and the n dependence of the cross section σ_R obtained.

The absolute cross sections have been estimated by a normalization based on the absolute cross section for the reaction Ar(HR) + CCl_4 measured by the present authors[33] in a collision chamber experiment.

III. RESULTS AND DISCUSSION

Values of the absolute cross section for nondissociative electron attachment σ_{AA} and the rate constants k_{AA} obtained following the procedure described in Sec. II B are given in Table I for the collision

$$\mathrm{Ar(HR)} + \mathrm{XY} \rightarrow \mathrm{Ar}^+ + \mathrm{XY}^- , \qquad (4)$$

where $XY = SF_6$ and C_6F_6 for different ranges of n and two Ar-beam velocities.

A total uncertainty of ~20% is present in the cross-section measurements although the uncertainty in relative values is somewhat less (~10%). The rate constants are calculated from the approximate relation $k_{AA} = \sigma_{AA} \bar{v}_{rel}$.

Nondissociative electron attachment is the dominant reaction channel for the collision Ar(HR) + SF_6 in agreement with other studies[12–18] involving rare gas high Rydberg atoms. No SF_5^- ions produced in a dissociative electron attachment to SF_6 and no Penning ions SF_6^+ by both high Rydberg and metastable argon atoms have been observed.

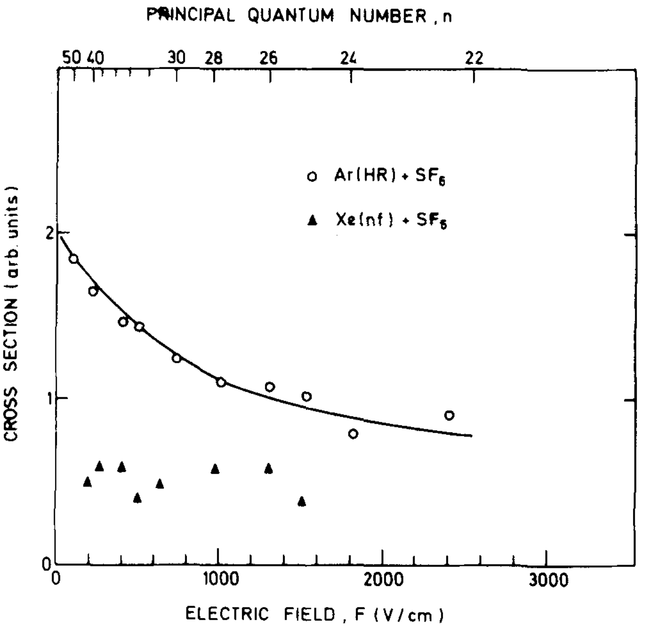

FIG. 3. Relative cross sections for the nondissociative electron attachment in the collision of HR argon and xenon atoms with SF$_6$ as a function of the principal quantum number n. o: Ar(HR) + SF$_6$, $v_r = 6.07 \times 10^4$ cm/sec. Δ: Xe(nf) + SF$_6$, $v_r = 3.27 \times 10^4$ cm/sec (Ref. 16).

In order to test the hypothesis of the theory of Matsuzawa[20–22] the present rate constants for process (4), together with other bound electron data[12,16,17] have been compared to the rate constants for attachment of free electrons[34–41] of energy ϵ

$$e(\epsilon) + \mathrm{XY} \underset{\sigma_e}{\xrightarrow{k_e}} \mathrm{XY}^- , \tag{5}$$

where ϵ is equal to the binding energy of the Rydberg electron.

The comparison of the rate constant values reported in the literature for processes (4) and (5) shows that they are of the same order of magnitude. This fact was predicted by the "free electron" model of Matsuzawa.

The variation of the relative cross section for process (4) measured in the present experiment as a function of n is shown in Fig. 3. The cross section σ_{AA} increases monotonically with the principal quantum number n. A similar dependence on n has been reported by Hiraishi *et al.*[15] but only a weak increase with n has been observed by West *et al.*[17] The dependence of σ_{AA} shown in Fig. 3 may be explained by the combined effect of two features. As n increases the atoms become progressively larger (radius $\sim n^2$) and the outer electron less strongly bound ($E_n \sim n^{-2}$).

To investigate further the role of the Rydberg electron in the nondissociative electron attachment to SF$_6$ the relative cross sections have been measured as a function of the HR argon velocity, and thus as a function of the translational energy of the reaction for different n ranges. It was found that the cross sections for all n values follow a v^{-1} law, typical[42] for reactions which proceed without any apparent energy threshold, and thus its magnitude is proportional to the collision time.

It is important to ensure that the cross section σ_{AA} really describes the electron attachment process and that the loss of negative ions due to autoionization is taken into account. There is considerable disagreement in the literature as to the magnitude of the lifetime τ_a against autodetachment of the SF$_6^-$ ion as measured in free electron experiments. The latter measurements are made mainly using two techniques: time of flight (TOF) and ion–cyclotron resonance (ICR). The reported values include (in units of μsec): 10,[25] 25,[26] 68,[27] (TOF experiments) and 500,[28] between 100–10^4,[29] $\geqslant 3 \times 10^5$[30] (ICR experiments).

Some possible explanations for the differences between the first three time-of-flight results have been discussed by Compton *et al.*[26] and Klots.[43] The autodetachment lifetimes of long-lived negative ions like SF$_6^-$ formed via nuclear excited Feshbach resonances and their dependence on the energy distribution of the incident electron has been calculated by Christophorou *et al.*[24] In spite of the fact that an increase of σ_e with decreasing energy of the electron is predicted by the theory, time-of-flight mass spectrometric measurements[44] of the SF$_6^-$ lifetime have not indicated any such variation, and an overall apparent lifetime of ~ 30 μsec was obtained.

The measurements of τ_a are very sensitive to the total energy of the colliding systems. Klots[43] has pointed out that even negative ions formed by monoenergetic electrons will have a range of energies reflecting the thermal distribution of the original neutral molecule and therefore no unique autodetachment lifetime can be expected.

The formation of SF$_6^-$ ions in a number of autoionizing states has been observed[28,29] in ICR experiments, and Odom *et al.*[29] have demonstrated that the observed lifetimes of this ion are dependent upon the experimental observation time.

Thus, the discrepancy between the TOF and ICR values is explained by these authors[29] as being the difference in the observation times (time window) in the different studies. When a time window of 20–30 μsec is used, as in the case of TOF experiments, only the autodetachment processes taking place during the first tens of μsec will be observed, whereas for a time window of 1 msec, used in the experiment of Henis *et al.*,[28] the processes taking place in a time of the order of the msec will be observed.

Odom *et al.*[29] were unable, however, to elucidate the formation mechanism of these ions. The variation of electron energy distribution, which is supposed to be at the origin of the longer lifetimes observed in ICR experiments, gave contradictory results. It has been found that collisional stabilization accounts partly[29] or negligibly[30,31] for the experimental data obtained. Foster *et al.*[30] proposed a radiative process as the mechanism leading to stable SF$_6^-$ in the low pressure experiment. On a time scale of several msec the radiative stabilization could be important but it does not explain the shorter measured lifetimes.[25–29]

We have estimated that the SF_6^- ions formed in the present collision experiment have lifetimes longer than ~20 μsec. This is demonstrated by the fact that in the CTOF mass spectrum of the positive [Fig. 2(a)] and negative reaction products of the collision $Ar(HR) + SF_6$ no additional ion counts have been measured which would result from autodetachment [ion flight time has been varied between (2–15) μsec] and no significant increase of the peak at 5 μsec ($Ar^+ + e$) resulting from very short-lived negative ions has been observed.

The formation of SF_6^- ion in the processes (4) have been observed by Foltz *et al.*[16] for Xe (nf) + SF_6, Astruc *et al.*[18] for $Ar(HR) + SF_6$, and Klots[14] for $He(HR) + SF_6$. No measurements of the lifetime of SF_6^- have been made in these studies but these ions are supposed[14,16,18] to have longer lifetimes than the free electron results (the ICR values were probably not included in the comparison).

Klots[14] suggests that the SF_6^- ions are formed in a short-lived excited state and are subsequently stabilized by collisions with the ionic core of the Rydberg atom.

The autodetachment and dissociation of the SF_6^- ions formed in high Rydberg argon collisions have been experimentally and theoretically studied by Astruc *et al.*[18] Central to their model is the assumption that the interaction between the target and the ionic core cannot be neglected. The highly vibrationally excited SF_6^- ion loses during the interaction $Ar^+–SF_6^-$ a part of its internal energy which is given up as kinetic energy ΔE to the Ar^+ core. It is thus possible to stabilize a part of the negative ions and to detect them.

The process of stabilization could not be discussed in the absence of exact values of the lifetime of SF_6^- formed in HR collisions. Our experimental device does not permit us to vary the observation time and to verify the hypothesis of Odom *et al.*[29] The energy of the electrons in the HR experiments is very well defined and is not only close to zero but negative. The knowledge of the potential surfaces of the negative ion and the parent neutral molecule and their respective positions would surely advance the understanding of the autodetachment process and the possible stabilization of the negative ion by the ionic core of the Rydberg atom.

In contrast to the data obtained for SF_6 the CTOF mass spectrum of the positive ions formed in the collision of Ar(HR) with C_6F_6 [Fig. 2(b)] shows that in addition to the stable negative ion, autodetachment of the $C_6F_6^-$ is also observed in agreement with the observation of Hildebrandt *et al.*[19] No ions $C_6F_5^-$ and F^- produced in dissociative electron attachment to C_6F_6 have been observed. The complication introduced by autodetachment explains the disagreement between the rate constants obtained in the experiment with HR atoms[19] and free electrons.[45,46]

Following the procedure described in Sec. II A the negative ion lifetime of $C_6F_6^-$ has been determined and an average value of 0.92 μsec has been obtained. As mentioned in Sec. II A the intensity of the peak at 3 μsec [Fig. 2(b)] is expected to be equal to the number of $C_6F_6^-$ ions which have not autoionized ~2 μsec after the moment of formation but a significantly larger intensity has been found. On the other hand, if the lifetime τ_a of $C_6F_6^-$ is 0.92 μsec, almost all negative ions would autoionize in flight to the detector when the CTOF mass spectrum of the negative ions is measured (flight time ~10 μsec). However, a peak corresponding to process (4) has been observed and its intensity mentioned above.

Thus, in the collision between Ar(HR) and C_6F_6 a part of the negative ions have lifetimes longer than 10 μsec and the others undergo autodetachment within ~0.9 μsec.

The observed reaction is then

$$Ar(HR) + C_6F_6 \rightarrow (Ar^+ \cdots C_6F_6^-) \rightarrow \begin{cases} Ar^+ + C_6F_6^- \,, & (6a) \\ Ar^+ + C_6F_6 + e^- \,. & (6b) \end{cases}$$

In the present experiment the binding energy of the Rydberg electrons varies between ~6–36 meV but no significant variation of the measured lifetimes as a function of the principal quantum number and thus of the energy has been observed.

The electron attachment to C_6F_6 below ~5 eV has been investigated in free electron experiments[45–48] and proceeds via three resonant processes, one at thermal energy[45–47] and two others at about 0.4–0.7 eV[46,48] and 4.5 eV,[48] respectively, which correspond to a temporary capture of the incident electron into an unoccupied σ orbital[48,49] and the π-molecular orbitals $\pi_{4,5}$ and π_6[48] of the neutral molecule in its electronic ground state.

In benzene (C_6F_6 is expected[50] to have the same D_{6h} symmetry) where the first three π orbitals are occupied, the 1.4 eV negative ion resonance has been associated with capture into the degenerated orbitals π_4 and π_5[35,51,52] and the negative ion resonance observed[53,54] at 4.85 eV with capture into the π_6 orbital. The energy of the lowest lying negative ion resonance in the fluorinated benzenes[32] decreases (the electron affinity increases) in going from C_6H_6 to C_6F_6. The electron affinity of C_6F_6 has been determined to be $\geq 1.8 + 0.3$ eV.[55] The lifetimes of the $C_6F_6^-$ ion at 0.0 eV have been measured using the TOF[32] and ICR techniques.[31] They are, as in the case of SF_6, in considerable disagreement. The reported values are 12 (Ref. 32) and 800 μsec.[31] No additional explanation for this difference can be given.

Two lifetimes have been observed in the present experiment: one of the order of ~0.9 μsec, which was not observed by Naff *et al.*[32] and Woodin *et al.*,[31] and a second lifetime, longer than some tens of μsec. It must be noted that the present technique is sensible at small observation time (some tenths of μsec). The lifetime of $C_6F_6^-$ being shorter than that of SF_6^-, the measurements have been made in the region of lifetime accessible by our apparatus. Even in this case, however, we are limited to longer observation times and further information is necessary for the full understanding of the electron attachment process.

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