Measured Lifetime of SF_6^-

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The lifetime of the SF_6 anion was measured at the electrostatic ion storage ring ELISA, where decays in the time span from 100 μs to a few seconds were recorded. We find a nonexponential decay with an approximate $t^{-1.5}$ power-law dependence. The observed decay rate is accounted for by a model for thermionic emission that takes into account the initial energy spread of the SF_6 molecule prior to electron capture as well as some kinetic energy of the captured electron in the applied plasma-ion source. The energy dependent decay rate is described by an Arrhenius decay constant with a preexponential factor and the electron affinity.

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Sulfur hexafluoride (SF_6) is a polyatomic molecule which is widely used as a gaseous dielectric and in plasma etching. In plasmas containing SF_6, low-energy electrons are easily attached and SF_6 anions formed [1]. The first reports on the SF_6^- lifetime appeared already in the 1960s [2,3], but the issue is still of great interest [4–6]. The lifetime of SF_6^- has thus been a topic of debate for several decades mostly because vastly different lifetimes have been reported, depending on the method used for the formation of the ions and the technique used for measuring the lifetime. The lifetimes observed for the metastable SF_6^- hence range from several μs [7,8] to several ms [9,10], and a comprehensive understanding of the problem remains to be established. Usually the sampling time in time-of-flight measurements determines a time window accessible to the specific apparatus and hence limits the measurements carried out. Also, the conditions at the time of formation of the anions appear to influence the lifetime.

Here we present experimental data for the decay of SF_6^-, which cover a wide time span of 4 orders of magnitude. Our measurement shows that the decay is not exponential with a specific lifetime in the μs to ms time range, in agreement with some previous experimental findings [4,10]. We present model calculations of the decay by electron emission that explain the observed decay and enable us to identify the essential parameters that govern the physics responsible for the formation and decay of SF_6^-. The vibrational population of the SF_6 anion is of crucial importance, and a single value for the anion lifetime is expected only when a narrow band of levels is populated with essentially the same decay constant. When a broad energy band is populated and when the decay rate depends strongly on the energy, a nonexponential decay is anticipated [11].

The experiment was performed at the electrostatic ion storage ring ELISA in Aarhus [12,13], equipped with a cold-cathode plasma-ion source for production of SF_6^-. A mixture of 99.5% He and 0.5% SF_6 was introduced in a plasma on atmospheric air to form SF_6^- anions, which were then extracted from the source. Just after the ion source, the ions were accelerated to a kinetic energy of 22 keV. The anions ($m = 146$ amu) were charge and mass selected by a magnet and injected into the storage ring where they circulated with a revolution time of 48 μs. The flight time from the ion source to ELISA is about 30 μs, and thus decays on a time scale shorter than this are not addressed in our experiment.

After each injection the ions were stored in the ring for up to 2 s and data were collected for many thousands of injections. A microchannel plate detector at the end of one of the straight sections of the storage ring (see Fig. 1) was used to detect the neutral particles generated from the decay of the stored ions. The counts of the detector were recorded as a function of time using a multichannel scaler and were used for determining the lifetime of the stored ions.

Once the SF_6 anions have left the ion source, they move in an almost perfect vacuum in ELISA (average pressure is a few times 10^{-11} mbar). Collisional destruction gives a total storage lifetime of about 1 s. Radiative cooling of the vibrations takes place on the millisecond time scale [10], whereas neutralization of hot SF_6^- by electron emission may happen on the microsecond to millisecond time scale as discussed below. In the following we present the data as well as a model calculation that account for the observed decay of SF_6^- by electron emission:

$$SF_6^- \rightarrow SF_6 + e^-. \tag{1}$$

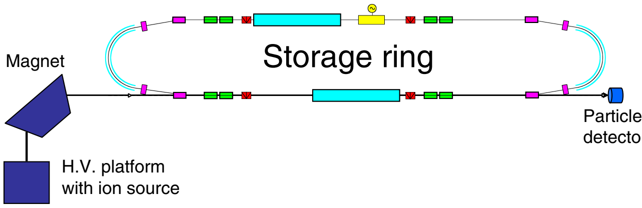

FIG. 1 (color online). The electrostatic ion storage ring ELISA, with a high-voltge (H.V.) platform for the ion source.

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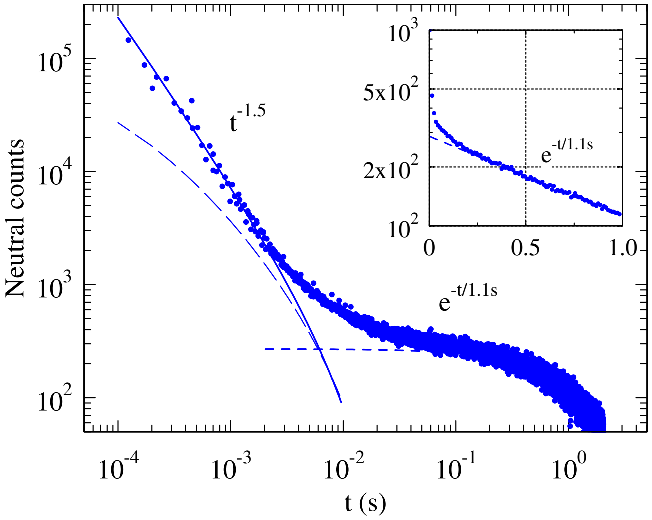

FIG. 2 (color online). Yield of neutrals as a function of time after the injection of SF_6^- into ELISA. The revolution time is 48 μs. The fast decay is accounted for by thermionic emission modeled by the full curve. The long-dashed curve is the model calculation when the electron-energy contribution is ignored. The exponentially decaying long-time component is determined by collisional destruction of stable SF_6^-—see inset (short-dashed curve).

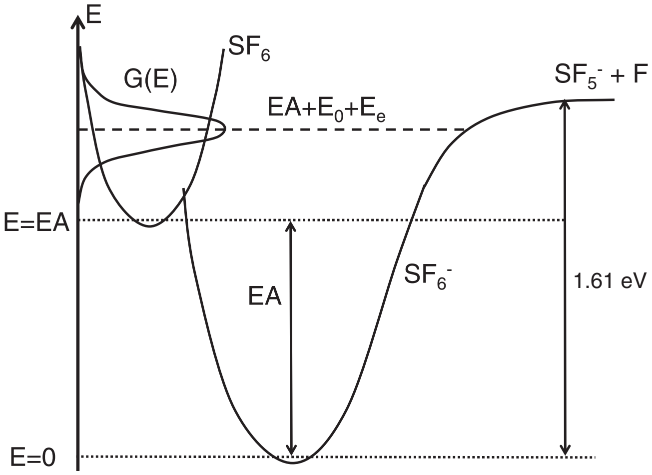

FIG. 3. Schematic potential-energy curves of SF_6 and SF_6^-. Emphasized are the relevant energies as well as the Gaussian energy distribution. The abscissa is the SF stretch coordinate.

In Fig. 2 we show the counts of the neutral products as a function of time after injection into ELISA on a log-log scale. The data show two major features: At times earlier than a few ms, an approximate power-law time dependence is apparent, and after a few hundred ms an exponential decay with a lifetime of about 1.1 s is seen. The latter is associated with collisional destruction in ELISA, and the former is assigned to unimolecular decays [Eq. (1)].

To model the fast decay of SF_6^- we take into account (i) the internal energy distribution of the neutral SF_6 molecules before electron capture, (ii) the kinetic energy of the captured electron, and (iii) the decay rate for thermionic emission $k(E)$ of hot SF_6^-, which is a strong function of the energy.

We choose to take a statistical approach and consider neutralization by thermionic emission [14]. The rate of delayed electron emission is modeled by an Arrhenius rate constant

$$k(E) = \mathcal{A} \times \exp\left(\frac{-\mathrm{EA}}{k_B T_e}\right), \qquad (2)$$

k_B being Boltzmann's constant, T_e the emission temperature, EA the adiabatic electron affinity, $\mathcal{A}$ the preexponential factor, and E the total energy of the anion. The energy dependence appears because T_e depends on the energy, as will be discussed below.

We assume that electrons are captured into vibrationally excited states of the anion in collisions between free electrons and SF_6 (see Fig. 3). This excites primarily the Raman active symmetric stretch "breathing" mode of SF_6^- [4]. Fast intramolecular vibrational redistribution quickly redistributes the energy to other modes, and this leads to vibrationally hot anions in the electronic ground state. As shown below, the emission temperature is of the order of 1000 K, enough to cause thermionic emission. For the adiabatic electron affinity we consider the most recent value of 1.20(±0.05) eV [6] as well as the previously used value of 1.0 eV. The first threshold for dissociation (into $SF_6^- + F$) is at 1.61 eV [5]. For reasons that we discuss later, it is neglected in the following.

To account for the decay (i.e., creation of neutral SF_6 in ELISA), we start from the basic equation

$$N(t) = N_0 e^{-kt}, \qquad (3)$$

where N is the number of stored ions at time t. We assume the distribution of the total initial energy ($SF_6 + e^-$) to be Gaussian, centered at $E_0 + E_e$, where E_0 is the average SF_6 vibrational energy and E_e is some effective kinetic energy of the captured plasma electron. The capture cross section favors capture of low-energy electrons, but some contribution is expected nevertheless. After electron capture the system further gains an energy corresponding to the electron affinity, and the total vibrational energy becomes $E = E_0 + E_e + \mathrm{EA}$. Assuming little collisional quenching of the vibrational population of the SF_6^- ions, the energy distribution of SF_6^- may by described by the same Gaussian $G(E)$ but centered at $E = \mathrm{EA} + E_0 + E_e$ (see Fig. 3). We then arrive at the following expression for the production rate ($R = -dN/dt$) of neutrals in the reaction given in Eq. (1):

$$R(t) = N_0 \int G(E)k(E)\exp(-k(E)t)dE. \qquad (4)$$

The integration in Eq. (4), which is from EA to infinity, accounts for a spread in the internal energy originating from the distribution of energies in *neutral* SF_6 and of the captured electron.

It is essential to use the right emission temperature in Eq. (2). In the following we work with canonical temperatures (T) and heat capacities (C) for the neutral molecules in thermal equilibrium in the ion source and microcanonical temperatures (T_m) and heat capacities (C_m) for the anions stored under vacuum conditions in ELISA. For the stored SF_6^- in ELISA the energy is conserved as long as the coupling to the radiation field is neglected, but variations in the internal vibrational energy in the ion ensemble lead to a corresponding variation in the emission temperature T_e.

The emission temperature may conveniently be expressed as [14]

$$T_e(E) = T_m(E) - \frac{\mathrm{EA}}{2C_m} - \frac{\mathrm{EA}^2}{12C_m^2 T_m(E)}, \tag{5}$$

where we emphasize the energy dependence of the microcanonical temperature. The last two terms are the first and second order finite heat bath corrections [15]. They are significant corrections due to the energy loss associated with the electron emission. Specific values are given in Table I.

The internal energy and heat capacity are calculated in the harmonic approximation from

$$E = \sum_i \{h\nu_i/[\exp(h\nu_i/k_B T) - 1]\}, \tag{6}$$

where the sum is over all normal mode frequencies (ν_i) [16,17]. The microcanonical heat capacity of the isolated anions [used in Eq. (5)] is given by $C_m = C - k_B$ [14].

We do not know the exact effective electron temperature and use E_e and σ_0 as variable parameters. Good agreement with the experiment is obtained for $E_0 + E_e \simeq 0.35$ eV and a total width of the Gaussian $\sigma_0 = 0.17$ eV. The internal energy (E_0) of neutral SF_6 before electron capture amounts to about 0.07 eV at room temperature ($T_0 = 300$ K), and the contribution to the width is almost 0.1 eV.

We calculate the microcanonical temperature from the normal modes of the SF_6 anion. That is, we use the Beyer-Swinehart algorithm [18] to obtain the density of states $\rho(E)$ in SF_6^-. T_m is given according to the definition:

$$k_B T_m(E) = \frac{1}{\frac{d}{dE}\ln(\rho(E))}. \tag{7}$$

To a good approximation $T_m[\mathrm{K}] = 840E[\mathrm{eV}] + 270$. The density of states, and hence the microcanonical temperature at the energy of formation ($\mathrm{EA} + E_0 + E_e$), depends on the chosen value of EA—see Table I.

Figure 4 shows $k(E)$ and $G(E)$ for our model values. The chosen preexponential factor $\mathcal{A}$ gives a decay rate for electron detachment which is in good agreement with that calculated recently by Troe, Miller, and Viggiano [5] It is evident from Fig. 4 that the high energy tail of the distribution $G(E)$ is associated with lifetimes shorter than the times considered in our experiment. Dissociation into $SF_5^- + F$ sets in with a decay rate which exceeds that of electron emission for E greater than about 1.7 eV [5], but this decay is only observable prior to injection into ELISA due to the high decay rate and hence not observable at the time scale of the present experiment.

Our model calculation is compared to the data in Fig. 2. It reproduces well the fast decay for times earlier than a few ms where the approximate $t^{-1.5}$ power law is observed. We emphasize that the particular power-law time dependence is a consequence of the integration over the energy and the particular decay rate. It is essential that the energy contribution of the plasma electrons is taken into account for the model to match the experimental data satisfactorily (see Fig. 3). Asymptotically, at late times, anions of the highest internal energy have decayed and only a vanishing fraction of them are left at $E = \mathrm{EA}$. The calculated decay rate thus eventually turns exponential with a decay time of $k(E = \mathrm{EA})^{-1}$. The agreement between the experiment and

TABLE I. Values applied in the model calculations.

Parameter	Value	Value
T_0	300 K	300 K
E_0	0.07 eV	0.07 eV
C (300 K)	6.62×10^{-4} eV/K	6.62×10^{-4} eV/K
σ_0	0.17 eV	0.17 eV
$E_e + E_0$	0.35 eV	0.35 eV
EA	1.20 eV	1.0 eV
$\mathcal{A}$	7×10^{10} s^{-1}	1.5×10^{10} s^{-1}
C_m	1.18×10^{-3} eV/K	1.18×10^{-3} eV/K
$T_m(\mathrm{EA} + E_0 + E_e)$	1572 K	1404 K
$T_e(\mathrm{EA} + E_0 + E_e)$	1009 K	938 K

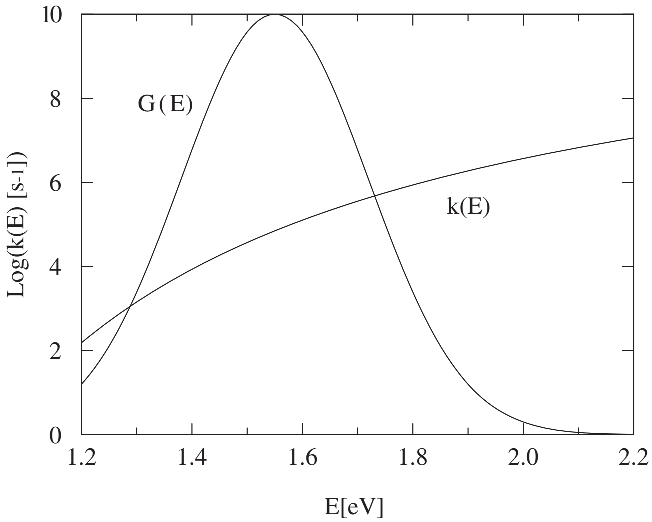

FIG. 4. The energy distribution $G(E)$ (arbitrary linear scale) and the decay rate $k(E)$ (log scale) for the applied model (here $\mathrm{EA} = 1.2$ eV).

the model calculation is not restricted to the specific choice of EA being 1.2 eV. The data are equally well reproduced with the "standard" value of EA ~ 1 eV with the preexponential factor and the temperatures adjusted accordingly (see Table I).

At times greater than 200 ms the data display a decay which is exponential and due to collisional destruction of some *stable* SF_6^- with the background gas in ELISA. In the intermediate time regime we believe that radiative cooling [10] and/or collisional deexcitation might play a role, meaning that states initially above $E = \mathrm{EA}$ eV may decay into highly excited vibrational states below the threshold which are stable towards electron emission. These states presumably have a larger collisional cross section, and hence a shorter storage lifetime than the SF_6^- ground state anions.

In conclusion, we measured the lifetime of the SF_6^- anion in the 100 μs to 2 s time window. The decay exhibits an approximate $t^{-1.5}$ time dependence at early times owing to unimolecular electron emission, and an exponential decay at late times for electronically stable SF_6^- anions. We presented a model based on thermionic emission that accounts for the observed nonexponential decay. The characteristic power-law dependence appears as a result of the energy dependent decay rate for electron emission and the integration over the energy distribution of excited SF_6 anions. We emphasize that the energy contribution of the captured plasma electron as well as the internal energy of the neutral molecule prior to anion formation are essential in the model.

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