

Electron attachment to SF₆ and lifetimes of SF₆⁻ negative ions

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We study the process of low-energy electron capture by the SF₆ molecule. Our approach is based on the model of Gauyacq and Herzenberg [J. P. Gauyacq and A. Herzenberg, *J. Phys. B* **17**, 1155 (1984)] in which the electron motion is coupled to the fully symmetric vibrational mode through a weakly bound or virtual *s* state. By tuning the two free parameters of the model, we achieve an accurate description of the measured electron attachment cross section and good agreement with vibrational excitation cross sections of the fully symmetric mode. An extension of the model provides a limit on the characteristic time of intramolecular vibrational relaxation in highly excited SF₆⁻. By evaluating the total vibrational spectrum density of SF₆⁻, we estimate the widths of the vibrational Feshbach resonances of the long-lived negative ion. We also analyze the possible distribution of the widths and its effect on the lifetime measurements, and investigate nonexponential decay features in metastable SF₆⁻.

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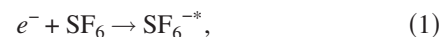
I. INTRODUCTION

Electron attachment to SF₆ is a fascinating problem. In spite of a lot of attention and a wealth of experimental data [1], some basic questions, e.g., that of lifetimes of metastable SF₆⁻, lack definitive answers. In this paper we show that the electron capture process is described well by a zero-range-type model [2]. We determine the parameters of the model by comparing the theory with experimental data on the attachment, total and vibrational excitation cross sections. We then study the autodetachment widths of SF₆⁻, and analyze its lifetimes and nonexponential decay. Here the experimental situation is less clear. Our calculation yields characteristic lifetimes of about a millisecond, using possibly the most accurate set of SF₆⁻ vibrational frequencies [3]. We investigate the nature of nonexponential decay of metastable anions due to level-to-level fluctuations of the widths and a distribution of the incident electron and target energies.

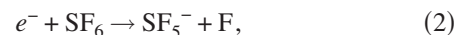
Sulfur hexafluoride (SF₆) has long been known as an electron scavenger because of its large low-energy electron attachment cross section. This feature of SF₆ is important for its applications as a gaseous dielectric and makes for the rich physics of low-energy electron collisions with it. The energy dependence of the electron capture cross section is well established experimentally [1,4–9]. Below 10 meV it shows 1/*v* behavior characteristic of *s*-wave inelastic processes. At higher energies toward 100 meV it approaches 60% of the unitary limit π/k^2 for the reaction cross sections, where *k* is the incident electron momentum (atomic units are used throughout). In addition, SF₆ also has a large elastic scattering cross section reaching $\sim 10^3$ a.u. at electron energies of a few meV, which can be inferred from the measured total cross section [10,11]. Note though that experimental data on low-energy elastic collisions, including differential

cross sections [12], and inelastic scattering cross sections, e.g., those of vibrational excitations [9,13,14], are relatively scarce.

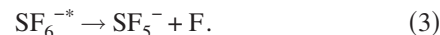
Low-energy electron attachment leads primarily to the formation of long-lived parent negative ions,



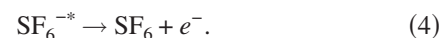
At electron energies $\varepsilon > 0.2$ eV (and below 3 eV) dissociative attachment,



becomes dominant. Although this process is usually regarded as a channel separate from Eq. (1), some recent evidence suggests that SF₅⁻ can be formed in the decay of metastable SF₆⁻ [15,16],



However, at low energies the lifetimes of SF₆^{-*} in the absence of collisions are limited by electron autodetachment,



Numerous SF₆^{-*} lifetime measurements [17–26] show considerable variation, depending on the technique used. Time-of-flight experiments [17–22] typically yield values of several tens of microseconds, while ion-cyclotron-resonance methods [23–26] give values of about a millisecond or larger.

Using the ion-cyclotron-resonance method, Odom *et al.* [24] found that the apparent lifetime of SF₆^{-*} varied as a function of the observation time, and surmised that SF₆⁻ were formed in a distribution of states with different lifetimes. The most recent study that used a Penning ion trap [26] also points to the formation of ions with a range of 1–10 ms lifetimes. A similar conclusion was derived from the time-of-flight measurements by Delmore and Appelhans [20,21] at microsecond time scales. Their analysis of the SF₆^{-*} decay indicated multiple lifetimes or groups of lifetimes in the interval between 2 and 30 μs , and showed that the population of states with different lifetimes depended on

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the temperature of SF_6 molecules. On the other hand, Ref. [22] where a free jet expansion was used to cool down the SF_6 molecules, reported a single lifetime of $19.1 \pm 2.7 \mu\text{s}$. All these differences are usually attributed to the differences in the experimental conditions under which SF_6^{--*} are formed, i.e., the incident electron energy and the internal energy of the target molecule [1]. However, detailed understanding is still lacking.

In contrast to the problem of lifetimes, the process of low-energy electron attachment to SF_6 is described well by a simple zero-range-type model of Gauyacq and Herzenberg [2]. According to this model, the incoming s -wave electron undergoes strong resonant scattering on a virtual or weakly bound level of the SF_6 molecule, with a near-zero energy. Electron trapping occurs via population of this fully symmetric state which is strongly coupled to the symmetric stretch (“breathing”) vibrational mode ν_1 . Electron capture initiates the motion of the fluorine nuclei toward the equilibrium configuration of the negative ion. This process is accompanied by rapid intramolecular vibrational redistribution (IVR) of the breathing mode energy among other vibrational degrees of freedom. As a result, the probability for the nuclei to return to the equilibrium configuration of the neutral SF_6 becomes small, and long-lived metastable anions are formed.

In this paper we perform a comprehensive study of electron attachment using the zero-range model. The attachment cross section is sensitive to the behavior of the SF_6 and SF_6^- potential energy curves, as a function of the S-F bond length, near their merging point. Details of this behavior are incorporated in the model via two parameters, namely, the energy of the virtual (or weakly bound) level and its coupling to the breathing mode. We develop a new effective matching procedure that connects the region of electron capture near the merging point, where the zero-range model can be applied, with the outer region of adiabatic semiclassical nuclear motion. We also generalize the model to include the possibility of the nuclear framework to oscillate back to its initial configuration, in order to study the influence of the rate of IVR on $e^- + \text{SF}_6$ collisions. Our aim here is to test the model by comparison with experimental data on the attachment, total and vibrational excitation cross sections, and thus determine its parameters. Another goal is to compare these parameters with the results of potential curve calculations. The SF_6 and SF_6^- potential curves have been established quite well by now [3,27], overcoming earlier uncertainties [28–32].

A somewhat different theoretical approach was taken recently by Fabrikant *et al.* [9]. It starts from the R -matrix formalism, and goes beyond the model of Gauyacq and Herzenberg by including the long-range polarization potential $-\alpha/2r^4$ and dipole coupling between the s and p waves. Contributions of higher electron partial waves are also included, to describe the elastic and vibrational excitation cross sections more accurately. In this theory the two parameters of the s -wave coupling to the ν_1 mode are allowed to be complex. Their values are found by fitting the experimental attachment and total cross sections. However, the use of complex parameters makes them phenomenological, and the physical connection with the molecular potential curves is lost.

The second part of our paper concerns the evaluation of lifetimes of SF_6^{--*} due to electron autodetachment. The first

estimates of the metastable anion lifetimes and their relation to the attachment cross section, vibrational spectrum density of SF_6^- and electron affinity of SF_6 were made in Ref. [18]. The rate constants of the processes (3) and (4), were later studied [33–36] using the quasiequilibrium (or RRKM) theory [37]. The approach of Refs. [18,33,34] is based on the principle of detailed balance, and requires the knowledge of the attachment cross section and the anion vibrational spectrum density. The standard RRKM approach is similar, assuming in addition that the transition probability is unity, i.e., that the attachment cross section is equal to its unitary limit. On the other hand, the RRKM requires the knowledge of the density of so-called transition states. The autodetachment lifetime depends strongly on such parameters as the electron affinity E_a and vibrational spectrum density of SF_6^- , which were not known well. Using different sets of data, lifetimes from microseconds to milliseconds were obtained in a wide range of incident electron energies. It should be noted that these methods yield the detachment rates (inverse lifetimes) averaged over the ensemble of metastable anion states. The distribution of lifetimes within such ensemble that may cause a variation in the observed lifetimes, has not been studied.

In the present paper we analyze the dependence of the autodetachment rate on the incident electron energy in the interval from zero to 300 meV for different target temperatures. Our calculations are based on the accurate values of the attachment cross section, and take into account the distribution of the target SF_6 molecules over the rotational and vibrational states, as well as the rotational and vibrational degrees of freedom of the SF_6^- anion. We also analyze fluctuations of the decay rate over the ensemble of metastable SF_6^- , to see if they can explain observations of nonexponential decay.

II. ELECTRON SCATTERING AND CAPTURE

A. Attachment model

Following the approach of Gauyacq and Herzenberg [2] we employ the zero-range potential (ZRP) model to describe the electron interaction with SF_6 . ZRP theory is a well-known tool suitable for problems of low-energy electron scattering and negative ions [38,39], especially in those cases when the cross section is enhanced by the existence of a shallow bound state or low-lying virtual level with zero angular momentum (i.e., in the s wave). Application of the ZRP method to the $e^- + \text{SF}_6$ system provides the wave function for the continuous spectrum electron and SF_6 in the vicinity of its equilibrium configuration. On the other hand, the wave function of SF_6^- formed as a result of electron attachment can be described in the Born-Oppenheimer approximation, treating the nuclear motion semiclassically. Matching of these wave functions yields the electron attachment cross section together with those of elastic scattering and vibrational excitation.

The electronic state responsible for the capture process is a fully symmetric weakly bound state of $e^- + \text{SF}_6$. Outside the molecule the electron wave function ψ_0 is spherically symmetric, and is given by

$$\psi_0 = \sqrt{\frac{\kappa}{2\pi}} \frac{e^{-\kappa r}}{r}, \quad (5)$$

where r is the electron coordinate and κ is related to the bound state energy $\varepsilon_0 = -\kappa^2/2$. The energy ε_0 depends on all nuclear coordinates. However, due to its symmetry, this electron state is most strongly coupled to the breathing (symmetric stretch) vibrational mode of SF₆. This allows one to consider ε_0 and κ as functions of the normal coordinate q of the breathing mode, $q = R - R_0$, where R is the S-F bond length, and R_0 is its value at the equilibrium of SF₆. Near the equilibrium, $\kappa(q)$ can be expanded in a power series. Keeping the first two terms [2],

$$\kappa(q) = \kappa_0 + \kappa_1 q, \quad (6)$$

where $\kappa_1 > 0$, since the binding increases with the increase in R ($R = 3.25$ a.u. at the equilibrium of SF₆⁻, while $R_0 = 2.96$ a.u. [3]).

The negative ion bound state (5) exists when $\kappa > 0$, i.e., for $q > q_0 \equiv -\kappa_0/\kappa_1$, while $\kappa < 0$ corresponds to a virtual state [40]. The absolute value of κ_0 is expected to be small, $|\kappa_0| \ll 1$ a.u., because for the electron capture to be effective, the scattering length κ^{-1} should be large in the Frank-Condon region. The sign of κ_0 indicates whether the negative ion state is real or virtual at the equilibrium of the neutral. The two cases are illustrated in Fig. 1, which shows the potential curves of SF₆ and SF₆⁻ for the symmetric stretch coordinate.

To the right of the merging point q_0 , indicated in Fig. 1 by vertical arrows, the negative ion energy $U_0(q)$ is given by the sum of that of the neutral SF₆ and the bound state energy $\varepsilon_0(q) = -\kappa^2(q)/2$. The SF₆ potential curve shown was calculated in Ref. [27]. Near the equilibrium it can be approximated by $\frac{1}{2}M\omega^2q^2$, where ω and M are the frequency and mass of the breathing mode. Using Eq. (6) one obtains a quadratic approximation for the SF₆⁻ potential curve near the merging point,

$$U_0(q) \approx \frac{M\omega^2q^2}{2} - \frac{(\kappa_0 + \kappa_1q)^2}{2}. \quad (7)$$

For q to the far right of the merging point, $U_0(q)$ should approach the anion potential energy curve, e.g., that calculated in Ref. [27].

In this model the electron scattering length κ^{-1} depends on the breathing vibrational coordinate q . This means that the electron interacts only with this particular mode, and no other vibrations are excited in the process of electron scattering or capture. Hence, all nuclear coordinates except q can be omitted, and the total wave function of the system can be written as

$$\Psi(\mathbf{r}, q) = e^{i\mathbf{k}\cdot\mathbf{r}} \chi_{n_0}(q) + \sum_n \frac{f_n}{r} e^{ik_n r} \chi_n(q). \quad (8)$$

The wave function (8) is an expansion over the SF₆ breathing mode vibrational states $\chi_n(q)$, taken in the harmonic approximation, with energies $E_n = \omega(n + \frac{1}{2})$. The first term in Eq. (8) describes the electron with momentum $\mathbf{k} \equiv \mathbf{k}_{n_0}$ incident on the target in the initial state n_0 . The sum over n accounts for

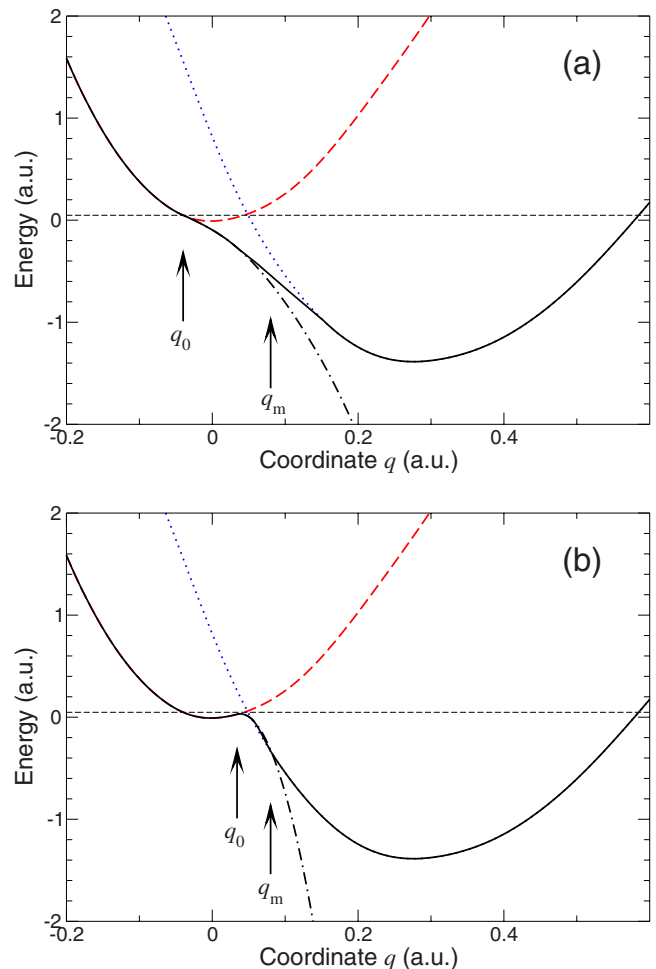


FIG. 1. (Color online) SF₆ and SF₆⁻ potential curves for the symmetric stretch coordinate. Dashed and dotted curves are the SF₆ and SF₆⁻ energies, respectively, calculated using the second-order Møller-Plesset perturbation theory [27]. Dot-dashed curves show the SF₆⁻ energy in the quadratic approximation for $q_0 = -0.04$, $\kappa_1 = 2.0$ (a) and $q_0 = 0.034$, $\kappa_1 = 4.1$ (b). Solid curves interpolate between the quadratic and numerical SF₆⁻ potential curves and represent the lowest adiabatic energy of the $e^- + \text{SF}_6$ system. Horizontal dashed lines show the lowest total energy of $e^- + \text{SF}_6$ collision, $\omega/2$.

elastic scattering ($n = n_0$) and vibrationally inelastic processes ($n \neq n_0$). Energy conservation, $\frac{1}{2}k^2 + E_{n_0} = \frac{1}{2}k_n^2 + E_n$, determines the corresponding electron momenta, $k_n = \sqrt{k^2 - 2\omega(n - n_0)}$.

Note that the sum in Eq. (8) includes both open (real k_n) and closed ($k_n = i|k_n|$) channels. In the former, the electron escapes but the nuclear motion is finite. Closed channels involve the electron localized near the origin, with the vibrational motion in progressively higher n states. Its contribution describes electron attachment, with the nuclei sliding down the negative ion potential curve toward greater q . It takes the form of the SF₆⁻ anion adiabatic wave function $\Psi_{\text{att}}(\mathbf{r}, q)$ (see below). Of course, the true anion potential curve (Fig. 1) does not allow for the infinite nuclear motion, as the nuclear framework swings back to the neutral equilibrium after one vibrational period. However, in a molecule with many vibrational degrees of freedom the energy may dissipate into other modes, providing for electron capture on much longer time scales.

The electronic parts of the wave function (8) are plane or spherical waves, which ensures its correct asymptotic form. They are solutions of the free-particle Schrödinger equation. This is in accordance with the ZRP method, in which the potential affects the wave function through the boundary condition at the origin,

$$\left. \frac{1}{r\Psi} \frac{\partial(r\Psi)}{\partial r} \right|_{r=0} = -\kappa(q). \quad (9)$$

Because of the $r \rightarrow 0$ limit, the ZRP affects only the electron s wave.

Applying Eq. (9) with $\kappa(q)$ from Eq. (6) to the wave function (8) and projecting the resulting equation onto each of the nuclear vibrational states χ_n , one obtains a set of linear equations for the amplitudes f_n ($n=0, 1, \dots$) [2] as follows:

$$(ik_n + \kappa_0)f_n + \frac{\kappa_1}{\sqrt{2M\omega}}(\sqrt{n}f_{n-1} + \sqrt{n+1}f_{n+1}) = -\delta_{n0}. \quad (10)$$

The general solution of this second-order recurrence relation is a linear combination of two independent solutions with arbitrary coefficients. One ‘‘boundary condition’’ is provided by Eq. (10) with $n=0$. The other boundary condition is set at large n . It is related to the asymptotic behavior of $\Psi_{\text{att}}(\mathbf{r}, q)$ at large q . The analysis presented in Appendix A shows that there is a simple relation between the nuclear coordinate q and the quantum number n of the terms in the expansion, Eq. (8), which contribute significantly to the wave function at this q ,

$$n \approx n_0 + [k^2/2 - \varepsilon_0(q)]/\omega. \quad (11)$$

Hence, the wave function $\Psi(\mathbf{r}, q)$ from Eq. (8) must be extended to the region where the incident electron is bound, and matched at some point $q=q_m$ with the negative ion wave function $\Psi_{\text{att}}(\mathbf{r}, q)$. The choice of q_m should not affect the capture cross section. Physically, it is restricted to the range of validity of expansion (6), so q_m should not be too large, but sufficient to neglect nonadiabatic effects.

In this region one can write $\Psi_{\text{att}}(\mathbf{r}, q)$ in the Born-Oppenheimer approximation,

$$\Psi_{\text{att}}(\mathbf{r}, q) = \psi_0(\mathbf{r}, q)\chi(q), \quad (12)$$

where $\psi_0(\mathbf{r}, q)$ is the bound electron wave function (5), which depends on the nuclear coordinate via $\kappa=\kappa(q)$, Eq. (6), and $\chi(q)$ is the wave function of the nuclear motion of the anion. It is, in general, a superposition of the outgoing and incoming (reflected) waves,

$$\chi(q) = A\chi^{(+)}(q) + B\chi^{(-)}(q), \quad (13)$$

where $\chi^{(\pm)}$ can be written explicitly in the semiclassical (WKB) approximation [40], as $\chi^{(\pm)} = v^{-1/2}e^{\pm i\int p dq}$, p and v being the classical nuclear motion momentum and velocity.

The amplitude of reflection, $R=B/A$, depends on the behavior of the negative ion term $U_0(q)$ far from the merging point and also on the coupling of the anion breathing mode to the other vibrational modes (i.e., on the effectiveness of IVR). In the absence of such coupling one has $|R|=1$ and no capture takes place. In treating electron attachment to SF₆,

the usual assumption is that this coupling is strong, i.e., $|R| \ll 1$, so that only the outgoing wave is retained in Eq. (13) [2].

In order to find the solutions of Eq. (10) corresponding to $\chi^{(\pm)}(q)$, note that for a sufficiently large n one has $ik_n + \kappa_0 \approx -\sqrt{2\omega n}$, and Eq. (10) turns into a recurrence relation with constant coefficients. Hence, asymptotically, the two independent solutions of Eq. (10) behave as $f_n \propto \xi^n$, where ξ is either of the two complex-conjugate roots of the corresponding characteristic equation. It turns out (see Appendix A) that one of these solutions corresponds to $\chi^{(+)}$, while the other corresponds to $\chi^{(-)}$.

In practice, Eq. (10) approaches the constant-coefficient limit slowly, as the coefficients vary slowly with n [41]. However, this slowness does allow us to truncate the set (10) at some large $n=N$ by using $f_{N+1} = \xi f_N$, where ξ satisfies the quadratic equation,

$$\kappa_1 \sqrt{\frac{N+1}{2M\omega}} \xi^2 - (|k_N| - \kappa_0)\xi + \kappa_1 \sqrt{\frac{N}{2M\omega}} = 0, \quad (14)$$

and where $k_N = i\sqrt{2\omega(N-n_0) - k^2} = i|k_N|$ is imaginary. The two roots of Eq. (14) are

$$\xi_{\pm} = \frac{\sqrt{M\omega}(|k_N| - \kappa_0)}{\sqrt{2(N+1)\kappa_1}} \pm i \left[\sqrt{\frac{N}{N+1}} - \frac{M\omega(|k_N| - \kappa_0)^2}{2(N+1)\kappa_1^2} \right]^{1/2}. \quad (15)$$

The choice of N is related to the matching point q_m by means of Eq. (11). The expression in square brackets is real because the anion potential (7) must decrease at large q , which requires $\kappa_1^2 > M\omega^2$. Note also that $|\xi_{\pm}|^2 = \sqrt{N/(N+1)} \approx 1$ for large N , which means that $\xi_{\pm} = e^{\pm i\beta}$ is just a phase factor.

As follows from Appendix A, solving the set of $N+1$ equations (10) ($n=0, 1, \dots, N$) with the additional condition $f_{N+1} = \xi_+ f_N$, generates a set of amplitudes (we denote them $f_n^{(+)}$) that corresponds to the $A\chi^{(+)}$ part of the nuclear wave function (13). On the other hand, using $f_{N+1} = \xi_- f_N$, one obtains a set of amplitudes $f_n^{(-)}$, which corresponds to $B\chi^{(-)}$. There is a simple linear relation between the amplitudes $f_n^{(+)}$ and $f_n^{(-)}$, and R at large n : $f_n^{(-)}/f_n^{(+)} \equiv R_f = e^{-i\delta_n} R$, where δ_n is a phase [see Eq. (A20)].

In the general case $R \neq 0$, the solution f_n of the recurrence relations (10) that matches $\Psi_{\text{att}}(\mathbf{r}, q)$, Eqs. (12) and (13), has the form

$$f_n = C(f_n^{(+)} + f_n^{(-)}), \quad (16)$$

where C is a normalization constant. Therefore, we can set $f_{N+1} = C(1+R_f)$ and $f_N = C(\xi_+^{-1} + R_f \xi_-^{-1})$. The amplitudes f_n for $n=N-1, \dots, n_0$ are then found successively from Eq. (10). The same is done for f_n with $n=0, \dots, n_0$, starting from an arbitrary f_0 , e.g., $f_0=1$. The two solutions are then matched at $n=n_0$, and the overall normalization is determined by substitution in the inhomogeneous equation (10) with $n=n_0$.

In practice, Eq. (10) can be truncated at relatively low $n=N$, e.g., $N \sim 10$ can be used for electron energies below 350 meV without significant error. By means of Eq. (11), this allows us to keep a physically meaningful value of the matching coordinate, $q_m=0.08$ (see Fig. 1).

The elastic ($n=n_0$) and vibrationally inelastic ($n \neq n_0$) cross sections are given by

$$\sigma_n = \frac{4\pi}{k} k_n |f_n|^2, \quad (17)$$

where k_n is real for the open channels. The total cross section is given by the optical theorem [40], as

$$\sigma_t = \frac{4\pi}{k} \text{Im} f_{n_0}, \quad (18)$$

and the attachment cross section is obtained as

$$\sigma_{\text{att}} = \frac{4\pi}{k} \left(\text{Im} f_{n_0} - \sum_n |f_n|^2 \text{Re} k_n \right). \quad (19)$$

It can also be found directly from the asymptotic behavior of f_n for closed channels, Eq. (A15).

Note that in comparison with Ref. [2], our method allows one to account for nonzero reflection, i.e., for incomplete vibrational relaxation, and provides the cross sections of all processes (not just attachment).

B. Numerical results

The model described in Sec. II A contains five parameters. The frequency of the SF₆ breathing mode is well established experimentally, $\omega=96$ meV= 3.5×10^{-3} a.u. [1], and the corresponding mass is $M=6m_F=2.1 \times 10^5$ a.u. The other parameters of the model, namely, κ_0 and κ_1 , which characterize the anion potential curve, and the reflection amplitude R , are not known *a priori*.

To determine their values and to verify the model itself, we have performed numerical calculations of the cross sections in a wide range of parameters, and compared the results with the experimental data on attachment [1,5,8], total scattering [11], and vibrational excitations [9]. Our calculations have been done for the target molecules in the ground vibrational state of the breathing mode (i.e., $n_0=0$), since at room temperature the fraction of excited states of this mode is small.

The ZRP model is expected to work best at low electron energies. Here the attachment data is the most accurate of all the measured SF₆ cross sections, and we use it as our main guide in the search for the optimal parameters. To characterize the discrepancy between the theory and experiment we calculate the “mean-squared relative error,” $\eta = \frac{1}{36} \sum_{i=1}^{36} [\Delta\sigma_{\text{att}}(\varepsilon_i) / \sigma_{\text{att}}(\varepsilon_i)]^2$, where $\Delta\sigma_{\text{att}}$ is the difference between the theoretical and experimental cross sections, using 36 energies ε_i between 0.1 and 160 meV, as given in the tables of recommended cross sections in Ref. [1]. Let us first examine the results obtained for $R=0$ (rapid IVR), and then look at the effect of the reflected wave $R \neq 0$ (incomplete IVR).

1. Rapid IVR ($R=0$)

The values of η for $R=0$ are shown on a density plot in Fig. 2(a), as a function of κ_1 and $q_0 = -\kappa_0 / \kappa_1$. The range of parameters is limited by $\kappa_1 > \sqrt{M}\omega = 1.6$ a.u., and the use of

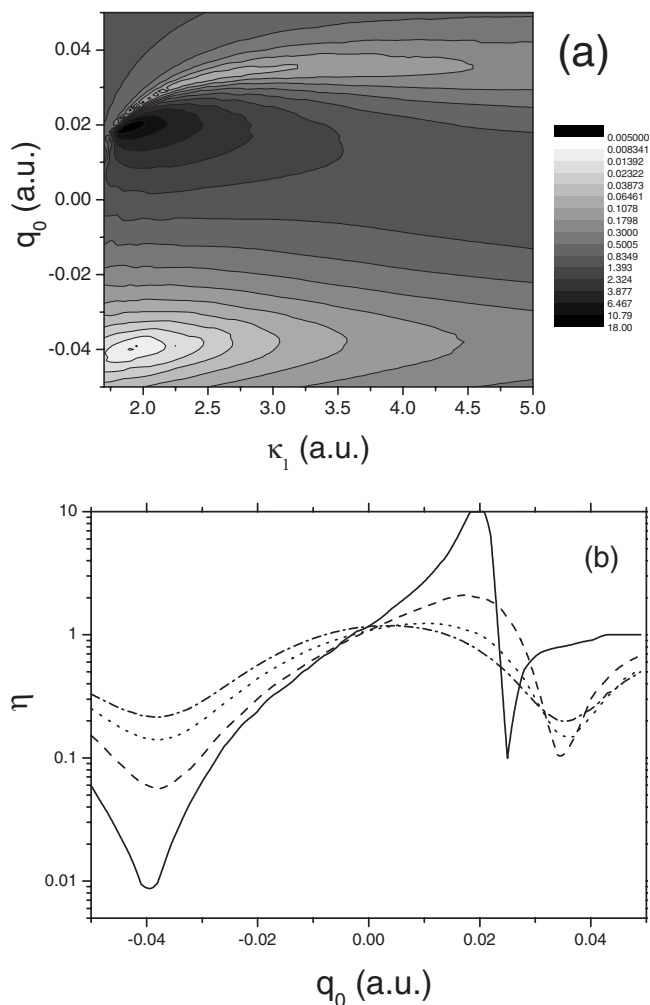


FIG. 2. Upper plate (a) is the density plot of the mean-squared relative error η of the theory fit of the experimental cross section of electron attachment to SF₆ over the 0.1–160 meV energy range. Lighter areas mean better fit. Bottom plate (b) shows η as a function of q_0 for $\kappa_1=2$ (solid curve), 3 (dashed curve), 4 (dotted curve), and 5 (dot-dashed curve).

q_0 instead of κ_0 emphasizes the sensitivity of the attachment cross section to the position of the merging point of the neutral and anion potential curves. To further clarify the magnitude of the relative error, in Fig. 2(b) we show η as a function of q_0 for four values of the other parameter, $\kappa_1=2, 3, 4,$ and 5.

Figure 2 shows that the absolute minimum of η is achieved for $q_0 \approx -0.04$ and $\kappa_1 \approx 2$. A negative value of q_0 means that the electron does form a weakly bound SF₆⁻ state at the equilibrium of the neutral, $q=0$. Figure 1(a) shows the corresponding anion potential curve, $U_0(q)$ from Eq. (7), by the dot-dashed curve. For comparison we also show the SF₆⁻ potential curve calculated in [27]. This potential curve does not reproduce $U_0(q)$ near the merging point [42] but should be reasonably accurate at larger q . Figure 1 also shows that the analytical and numerical potential curves can be matched. The position of the matching point $q_m=0.08$ used in our calculations is indicated by an arrow. Note though, that for $R=0$ the calculation does not require any information

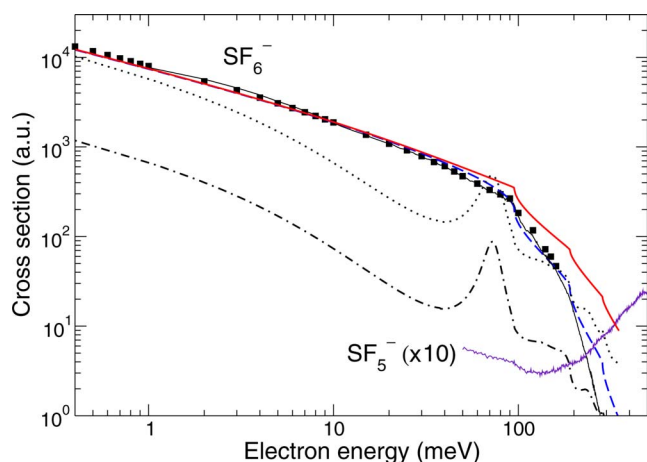


FIG. 3. (Color online) Electron attachment cross sections for SF_6 . Solid squares are the experimental data for metastable SF_6^- obtained by Hotop *et al.* as given in Ref. [1]; thin solid curves show the data for SF_6^- and SF_5^- obtained at the SF_6 nozzle temperature of 300 K [8]. Calculations: $q_0 = -0.04$, $\kappa_1 = 2.0$, $R = 0$ (dashed curve); $q_0 = 0.034$, $\kappa_1 = 4.1$, $R = 0$ (thick solid curve), $R \neq 0$, $\gamma = 0.1\omega_a$ (dotted curve), and $\gamma = 0.01\omega_a$ (dot-dashed curve).

about the anion potential curve far from the merging point, and the choice of the matching point (or the truncation number N) is not critical.

The attachment cross section calculated for $q_0 = -0.04$, $\kappa_1 = 2.0$, and $R = 0$ (dashed curve in Fig. 3) reproduces both the smooth decrease of the measured cross section below the ν_1 vibrational threshold $\varepsilon < \omega$ [43], and its rapid drop for $\varepsilon > \omega$. However, the total cross section calculated with these parameters is noticeably higher than experiment for $\varepsilon \gtrsim \omega$ (see Fig. 4).

The other possibility suggested by Fig. 2 is that $q_0 > 0$, where η has a second local minimum in the form of a narrow “valley.” It corresponds to a virtual electron level at the equilibrium of SF_6 . Here the quality of the fit is not very sensitive

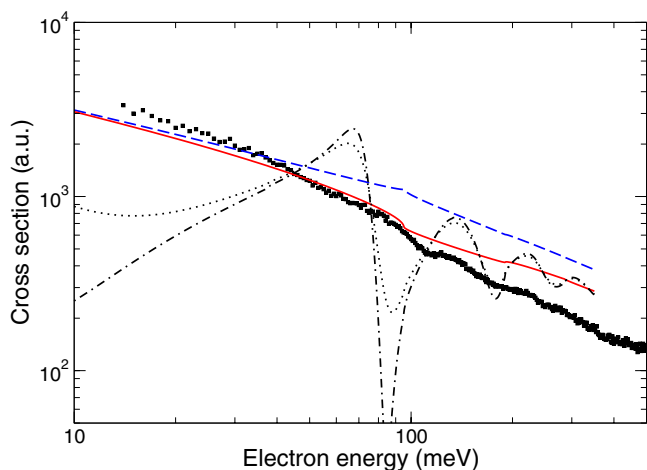


FIG. 4. (Color online) Total cross section for electron scattering from SF_6 . Experimental data: solid squares, Ref. [11]. Calculations: $q_0 = -0.04$, $\kappa_1 = 2.0$, $R = 0$ (dashed curve); $q_0 = 0.034$, $\kappa_1 = 4.1$, $R = 0$ (thick solid curve); $R \neq 0$, $\gamma = 0.1\omega_a$ (dotted curve); and $\gamma = 0.01\omega_a$ (dot-dashed curve).

to the precise value of κ_1 . Choosing $q_0 = 0.034$, $\kappa_1 = 4.1$, and $R = 0$ (thick solid curves in Figs. 3 and 4) we obtain a much better description of the total cross section, while the fit of the attachment data is only slightly worse. In Fig. 1(b) we show the corresponding behavior of the SF_6^- potential curve near the equilibrium. In this case the quadratic curve matches the SF_6^- curve from Ref. [27] even closer at $q \approx q_m = 0.08$. Note though, that due to the proximity of q_m to q_0 , the adiabatic approximation for the nuclear motion is not as accurate here as in the $q_0 < 0$ case (the required truncation N being lower). This means that the actual shape of the SF_6^- potential curve in the vicinity of q_m may have a small effect on the cross section.

Generally, the ZRP model is expected to provide a more accurate description of the attachment cross section than the total cross section. Due to the symmetry of the negative ion state and the role played by the symmetric stretch mode, the low-energy attachment model can be restricted to the electron s wave. However, contributions of higher partial waves to the total cross section (in particular, due to excitation of the strong infrared-active ν_3 mode), may become sizable even at low energies. This is indicated by the observed anisotropy of the total cross section [11] (see also Ref. [9]). Since the present ZRP model does not take into account any of these contributions, one could expect that the cross section (18) would be a lower bound for the true total cross section. Hence, we believe that the parameters $q_0 = 0.034$ and $\kappa_1 = 4.1$ are more realistic, in spite of a less accurate fit of the attachment cross section than that for $q_0 = -0.04$, $\kappa_1 = 2.0$.

As a final check of the model for $R = 0$, in Fig. 5 we compare the calculated cross sections with the ν_1 and $2\nu_1$ vibrational excitation differential cross sections measured at the scattering angles of 30° and 135° [9]. Since the ZRP model cross sections, Eq. (17), are isotropic, the differential cross sections are found as $d\sigma_n/d\Omega = \sigma_n/(4\pi)$. As in Figs. 3 and 4, the two sets of theory curves in Fig. 5 correspond to $q_0 = -0.04$, $\kappa_1 = 2.0$, and $q_0 = 0.034$, $\kappa_1 = 4.1$. The experimental cross sections for the two angles are very different close to the threshold. However, the data within 30 meV of the threshold may not be reliable [44], while beyond this region the anisotropy of the differential cross section is greatly reduced. Here the experiment is clearly in much better agreement with the calculation for a positive value of q_0 (i.e., that for which the anion state is virtual at the equilibrium of the neutral). This is especially clear for the $n = 2$ excitation. The calculation for $q_0 = 0.034$ and $\kappa_1 = 4.1$ also shows the same cusps at higher vibrational thresholds as the experiment. We thus conclude that the experimental data for the low-energy attachment and scattering favor the potential curve scheme shown in Fig. 1(b).

2. Incomplete IVR ($R \neq 0$)

In the calculations above we used $R = 0$, i.e., we neglected the reflected wave $\chi^{(-)}$ in the anion wave function (13). In general, the size of the reflection amplitude R is determined by the rate of IVR, which depends on the coupling between the vibrational modes. A full calculation of the vibrational dynamics of highly excited SF_6^- is a nontrivial task well beyond the scope of the present work. Hence, we introduce

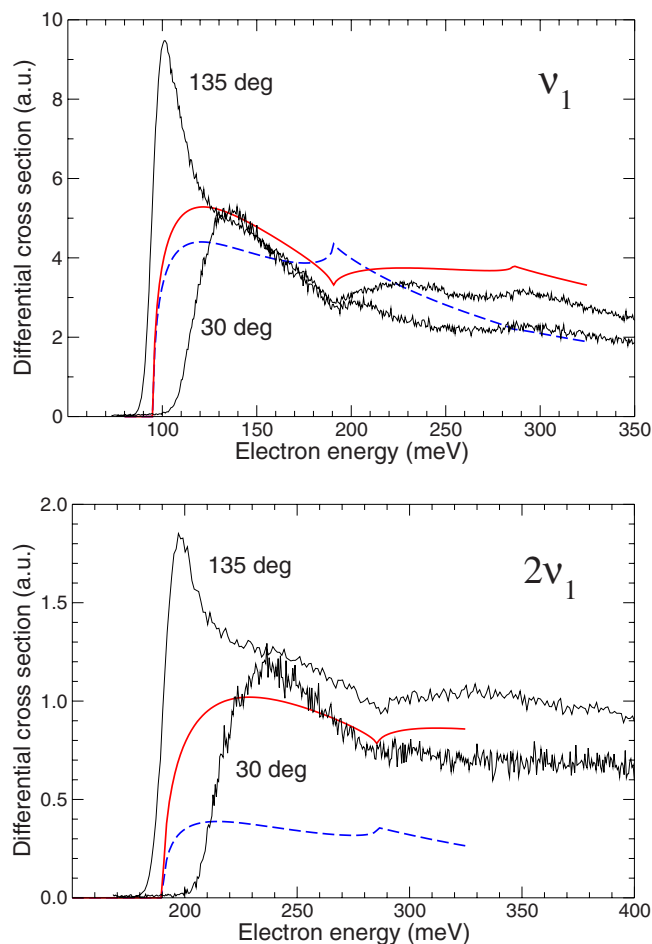


FIG. 5. (Color online) Differential vibrational excitation cross sections of the symmetric stretch mode of SF₆ (top, ν_1 ; bottom, $2\nu_1$). Thin solid lines are the experimental results of Ref. [9] obtained at 30° and 135°. Dashed curves are the cross sections calculated for $q_0 = -0.04$ and $\kappa_1 = 2.0$, and thick solid curves are those for $q_0 = 0.034$ and $\kappa_1 = 4.1$ (both for $R = 0$).

the IVR rate phenomenologically as a width γ of the breathing mode. This is done by adding a small imaginary part $-i\gamma/2$ to the anion potential energy $U_0(q)$. The reflection amplitude R is then obtained semiclassically as outlined in Appendix A.

In the numerical calculations we treat the anion potential curve for $q > q_m$ in the harmonic approximation. The IVR damping of the reflected wave is then proportional to γ/ω_a , Eq. (A19), where ω_a is the anion breathing mode frequency. For strong damping, e.g., $\gamma/\omega_a = 1$, the results are very close to those obtained with $R = 0$. The reflected wave here is suppressed by a factor of about $e^{-\pi} \approx 0.05$. In contrast, smaller IVR rates lead to drastic changes in the cross sections. In Figs. 3 and 4 we show the cross sections for $q_0 = 0.034$, $\kappa_1 = 4.1$, and two values of the damping parameter: $\gamma/\omega_a = 0.1$ and 0.01 [45]. (The effect of damping on the cross sections for $q_0 < 0$ is broadly similar.)

We see that allowing for a sizable reflected wave results in the emergence of anion vibrational Feshbach resonances and overall suppression of the attachment cross section. Both effects spoil the good agreement with experiment achieved in

the calculations with $R = 0$. We thus conclude that the IVR in SF₆⁻ is very rapid, $\gamma \gtrsim \omega_a$. It takes place over the time of one vibrational period of the breathing mode, that indicates strong coupling between the breathing mode and other nuclear degrees of freedom in SF₆⁻.

In the past, the IVR in highly vibrationally excited SF₆ molecules was studied in multiphoton laser excitation experiments (see, e.g., [46], and references therein). These and other studies [47] indicate that the IVR rate of the strong infrared-active ν_3 mode is noticeably smaller than our estimate. However, the two situations are quite different. In the capture process the amount of energy equal to the electron affinity of SF₆, $E_a = 1.06$ eV (recommended value [1]), is instantaneously deposited into a single mode. This mode then has a much higher effective vibrational quantum number $n \sim E_a/\omega_a \approx 14$, than those in multiphoton excitation experiments where the energy is distributed between many modes. At the energies at which it is formed, SF₆⁻ also has a stronger anharmonicity related to the proximity of dissociation thresholds.

The vibronic state of SF₆⁻ at the instant of capture, Ψ_{att} , Eq. (12), is embedded in the dense multimode vibrational spectrum. The average level spacing of the SF₆⁻ vibrational spectrum at the $e^- + \text{SF}_6$ threshold is about 10^{-10} a.u. (see Sec. III). In the process of IVR, the initial state Ψ_{att} spreads over a large number of multiple vibrational excitations of SF₆⁻. For a weak coupling (i.e., small γ), Ψ_{att} would describe a simple single-mode vibrational Feshbach resonance. In the actual case of strong coupling, Ψ_{att} plays the role of a doorway for the final multimode vibrational resonances. Therefore, the ultimate states of SF₆⁻ populated in electron attachment are extremely closely spaced metastable vibrational resonances with very large but finite lifetimes. In the next section we consider their decay via electron autodetachment and estimate the corresponding lifetimes.

III. DECAY OF THE METASTABLE NEGATIVE ION

A. Evaluation of decay widths

The metastable negative ion species SF₆^{-*} formed by electron attachment can decay via the reverse, autodetachment process, Eq. (4). Another decay channel open at low energies, see, e.g., Refs. [34–36], is dissociation, Eq. (3). To analyze these possibilities, compare the dissociative attachment cross section with the measured cross section for the production of SF₆⁻ and calculated σ_{att} , Fig. 3. The relatively small SF₅⁻ signal at $\varepsilon < 150$ meV (below the dissociation threshold) is due to electron attachment to thermally activated SF₆. It depends strongly on the target molecule vibrational temperature and has been used as a “thermometer” [8]. At larger energies the SF₅⁻ cross section rises rapidly and at $\varepsilon > 0.3$ eV it becomes the dominant contribution to the total electron attachment cross section.

In our view this picture indicates that for most of its part dissociation does not occur as a decay of SF₆^{-*} formed via the resonant doorway state Ψ_{att} . If the latter were true, the calculated cross section σ_{att} , which is actually the cross section of formation of metastable SF₆^{-*}, would follow the total attachment cross section, i.e., the sum of the dissociative

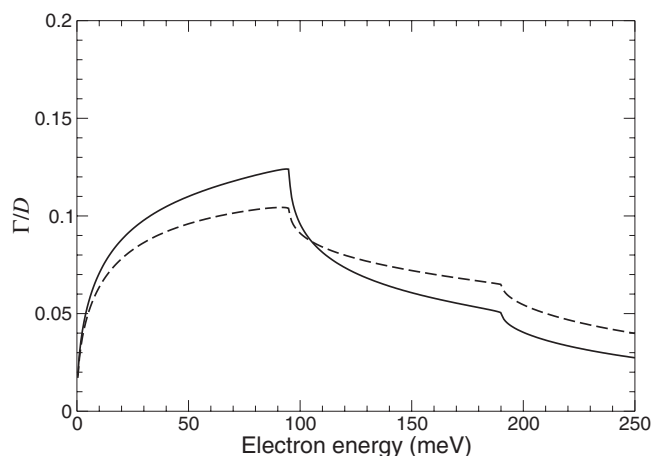


FIG. 6. Ratio of the mean resonance width to the level spacing evaluated from the attachment cross section, Eq. (20), for $q_0 = 0.034$ and $\kappa_1 = 4.1$, $n_0 = 0$ (solid curve) and $n_0 = 1$ (dashed curve).

attachment cross section and that of SF_6^- production. We conclude that at low energies, dissociation does not proceed via the intermediate multimode vibrational resonances formed in s -wave electron attachment described by Ψ_{att} . Hence, autodetachment is the main process responsible for the decay of SF_6^{*-} [48].

The situation when a projectile forms a very dense spectrum of resonant states with the target (“compound states”) is well known in nuclear physics [49]. In this case it is useful to consider the cross section averaged over an energy interval containing many resonances. Such average cross section is described by the optical model [40]. In this model the resonant cross section, in our case σ_{att} , accounts for all processes occurring via intermediate resonant states (i.e., SF_6^{*-}), including their contribution to elastic scattering. If the mean energy spacing between the resonances, D , is much larger than the resonance widths, the cross section of electron capture by the SF_6 target in the initial vibrational state ν can be written as

$$\sigma_{\text{att}}(\varepsilon, \nu) = \frac{2\pi^2 \bar{\Gamma}_\nu}{k^2 D}, \quad (20)$$

where $\bar{\Gamma}_\nu$ is the average partial elastic width at a given energy [40]. It determines the average detachment rate leading to a free electron with energy $\varepsilon = k^2/2$ and neutral SF_6 in state ν . In our approach σ_{att} depends only on the number of breathing vibrational quanta in the state ν , i.e., on n_0 (see Sec. II A). Figure 6 shows the ratio $\bar{\Gamma}_\nu/D$ obtained from Eq. (20), as a function of the electron energy for $n_0 = 0$ and 1.

Since $\bar{\Gamma}_\nu/D \ll 1$, the assumption of nonoverlapping resonances is valid. Hence, we can evaluate D as the reciprocal of the level density of resonances ($\rho = D^{-1}$), and use Eq. (20) to estimate the lifetimes of the metastable states, $\tau = \hbar/\Gamma$. In this context, Eq. (20) is sometimes referred to as the principle of detailed balance [18]. In addition to finding $\bar{\Gamma}_\nu$, one also needs to take into account level-to-level fluctuations of the widths, which affect the shapes of the SF_6^{*-} decay curves (see Sec. III B).

TABLE I. Vibrational modes and frequencies of SF_6 and SF_6^- .

Mode	Symmetry	Frequencies (cm^{-1})		
		SF_6^{a}	$\text{SF}_6^{-\text{b}}$	$\text{SF}_6^{-\text{c}}$
1	A_{1g}	774	700	626
2	E_g	642	625	447
3	T_{1u}	948	925	722
4	T_{1u}	616	594	306
5	T_{2g}	525	500	336
6	T_{2u}	347	325	237

^aExperimental data from Ref. [50].

^bFrequencies used in Ref. [35] and earlier in Ref. [51].

^cMBPT(2) calculation, Ref. [3].

Apart from the total energy, the process of electron attachment and detachment considered here conserves the total angular momentum J , its projection M , and parity. The electronic part ψ_0 of the doorway state Ψ_{att} , Eq. (12), is spherically symmetric, and the continuum electron is represented by the s wave. Hence, the angular momenta of the SF_6 target and SF_6^{*-} resonances coincide. These resonances also have the same parity as the initial and final vibrational states of SF_6 . Therefore, D in Eq. (20) refers to the average spacing between the SF_6^- levels with definite J , M , and parity. The SF_6 molecule is a spherical top, and its rotational states with a given J and M are $2J+1$ times degenerate with respect to the quantum number K [40]. For the highly excited SF_6^- this degeneracy can be lifted by rovibrational interactions. The rotational energies of the anion and neutral molecule are close, and much smaller than the total vibrational energy of SF_6^- ,

$$E = E_a + E_{v_i} + \frac{k^2}{2}, \quad (21)$$

where E_{v_i} is the target initial vibrational energy. Hence, we can write

$$D^{-1} = \frac{1}{2}(2J+1)\rho(E), \quad (22)$$

where ρ is the total density of vibrational states of SF_6^- , and $\frac{1}{2}$ accounts for parity.

The total vibrational energy E is large (≥ 1 eV), but the mean energy per vibrational mode is comparable to their frequencies, and we calculate the vibrational spectrum of SF_6^- using the harmonic approximation (see Appendix B). Table I lists the mode frequencies of SF_6 and SF_6^- . In contrast to SF_6 , the fundamentals of SF_6^- are not well known. In the past these frequencies were assumed to be equal to those of the neutral, or slightly softer [18,33–36]. For example, the first set of anion frequencies in Table I was used in Refs. [35,51]. The second set is from Ref. [3], which is probably the best calculation of SF_6 and SF_6^- by the coupled-cluster and many-body perturbation theory (MBPT) methods. These lower anion frequencies are supported by a recent photodetachment study of SF_6^- [52], and we regard them as more

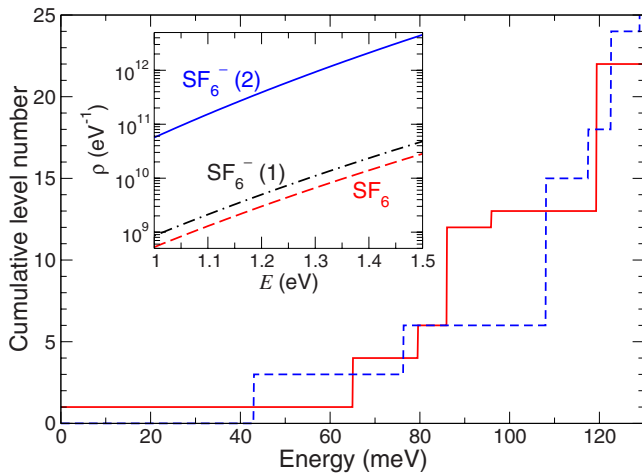


FIG. 7. (Color online) Cumulative level numbers of even (solid) and odd (dashed) vibrational states of SF₆. The inset shows the vibrational spectrum density of SF₆ (dashed) and SF₆⁻ (dot-dashed and solid) obtained using the frequency sets from Table I.

accurate. In the inset of Fig. 7 we show the total vibrational level densities in the energy range relevant to metastable SF₆^{-*}. As expected, the density obtained using the second set of anion frequencies is much greater than the density given by the first set.

The average total resonance width Γ is the sum of partial widths $\bar{\Gamma}_\nu$ for all open decay channels ν allowed by the conservation of energy, angular momentum, and parity. Equations (20) and (22) give

$$\Gamma(E) = \sum_\nu \frac{\sigma_{\text{att}}(\varepsilon_\nu, \nu) k_\nu^2}{\pi^2 \rho(E)}, \quad (23)$$

where the energy ε_ν and momentum k_ν of the emitted electron are determined by $\varepsilon_\nu = k_\nu^2/2 = k^2/2 + E_{\nu_i} - E_\nu$. The sum in Eq. (23) is over the open-channel vibrational states of neutral SF₆. Summation over $2J+1$ states with different K gives an additional factor $2J+1$, which is canceled by the same factor in Eq. (22). To compare with experiment, the width (23) can also be averaged over the distribution of the initial target states and incident electron energies.

To within a factor of 2 related to parity selection, Eq. (23) coincides with that derived by Klots [33] using equilibrium considerations. It has a simple physical meaning. The decay rate in each channel is given by the probability per unit time for SF₆^{-*} to enter the doorway state Ψ_{att} , which is equal to the classical frequency $D/2\pi$, times the probability P of detachment at each attempt. The latter quantity is determined by the capture cross section, $P = \sigma_{\text{att}}(\varepsilon, \nu) k^2/\pi$, as follows from the detailed balance relations [18].

To show how the number of open decay channels affects the width, we plot in Fig. 7 the cumulative number of SF₆ vibrational excitations for both parities. The parity of the final SF₆ must be the same as that of its initial state. Besides the ground state, at room temperature only the lowest excited states, T_{2u} , T_{2g} , and T_{1u} , are populated with probabilities $w_\nu > 0.05$. These are shown in the inset of Fig. 8. In this figure we also show the energy dependence of the mean reso-

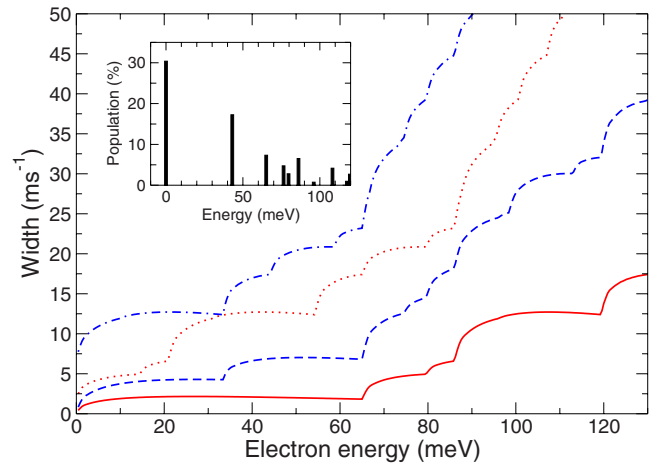


FIG. 8. (Color online) Mean resonance width Γ as a function of the incident electron energy ε for different initial target states: ground state (solid curve), T_{2u} (dashed curve), T_{2g} (dotted curve), and T_{1u} (dot-dashed line). Shown on the inset are the populations of a few lower vibrational states of SF₆ at room temperature.

nance width Γ , Eq. (23), for each of the above target states. The dependence of Γ on ε is steplike, each step related to the opening of a new decay channel. The width is also bigger for higher-lying target states, as more channels are open.

The widths in Fig. 8 are given in reciprocal time units, i.e., they represent the decay rates Γ/\hbar . The smallest of the widths, for the electron capture by the ground state SF₆, is about 2 ms⁻¹ below 65 meV. This indicates a lifetime of 0.5 ms, which is comparable to the values observed in traps [23–26]. Note however, that the widths are very sensitive to the SF₆⁻ vibrational spectrum. Thus, if we used the first set of anion frequencies from Table I, the widths given by Eq. (23) would be about 10² times larger, since they are inversely proportional to the vibrational level density of SF₆⁻ shown in Fig. 7. The smallest width would then be about 10 μs, i.e., in the range of values from time-of-flight experiments [17–22]. In fact, the earliest of such studies, Ref. [18], which analyzed the lifetimes theoretically in a way similar to Eq. (23), using SF₆ fundamentals and disregarding parity, concluded that the lifetime of 25 μs corresponded to the electron affinity of ~1.1 eV.

It should also be noted that due to the strong energy dependence of $\rho(E)$, the widths and lifetimes are sensitive to the value of the electron affinity. A change of 0.1 eV in E_a changes the lifetimes by a factor of 3. In addition, our calculation of the density neglects anharmonic effects in the anion vibrational spectrum. The amount of energy deposited in each mode is relatively small, but the total vibrational energy E is close to the dissociation threshold. In this case anharmonicity can increase $\rho(E)$, and hence the lifetimes, by a factor of 2 or 3.

Figure 8 shows that if the electrons and SF₆ molecules possess broad thermal energy distributions, e.g., when the anions are formed in a trap, the decay of SF₆^{-*} will be characterized by a set of average widths rather than a single detachment width. This was indeed observed by Delmore and Appelhans [20,21], who detected several lifetimes or bunches of lifetimes depending on the temperature (in the

10 μs range, though). For monoenergetic electrons with $\varepsilon < 65$ meV and vibrationally cold SF_6 , the decay process is governed by a single average width. Such experiment was done by Garrec *et al.* [22], who did report a single lifetime $\tau \approx 19$ μs . However, the corresponding width would be close to the values found using the neutral or similar vibrational frequencies [35]. It is incompatible with the more accurate softer anion vibrational spectrum, unless a much lower electron affinity is used.

In our view, the present calculation does explain observations of sizable SF_6^{-*} signals at millisecond and greater times, and its slow nonexponential decay [24–26], at least qualitatively. Equations (20) and (23) yield the widths *averaged* over large numbers of closely spaced resonances. Given the large density $\rho(E)$, these resonances cannot be resolved experimentally, even with a highly monoenergetic electron beam. As a result, one always observes an ensemble of such states. Some of them may have widths much smaller than the average. Such states will form a tail of long-lived anions, as was first suggested by Odom *et al.* [24]. Therefore, to determine the survival curve of SF_6^{-*} , one must take into account the *distribution* of resonance widths.

B. Fluctuations of the widths and nonexponential decay

The width of a particular multimode vibrational resonance is determined by the size of the doorway state Ψ_{att} component in its wave function. This component is extremely small since Ψ_{att} spreads over a large number of such resonances, which can be estimated as $\gamma\rho(E) \sim \omega_a\rho(E) \sim 10^{10}$ (Sec. II B 2). Physically, this situation is similar to that of neutron capture by heavy nuclei, where each of the narrow compound resonances contains only a small fraction of the “neutron+target” state, which allows their coupling to the continuum. Due to strong mixing between the basis states that make up the compound states, the statistics of their components becomes Gaussian (see, e.g., Ref. [53]). This leads to the following probability density for the partial widths Γ_ν ,

$$f(\Gamma_\nu) = \frac{e^{-\Gamma_\nu/2\bar{\Gamma}_\nu}}{\sqrt{2\pi\Gamma_\nu\bar{\Gamma}_\nu}}, \quad (24)$$

where $\bar{\Gamma}_\nu$ is the mean. Equation (24) is known as the Porter-Thomas distribution [49,54].

If only one decay channel is open, every resonance decays exponentially as $e^{-\Gamma_\nu t}$. However, it is easy to see that fluctuations of Γ_ν result in a nonexponential time dependence of the survival probability $P(t)$ for the ensemble. Assuming that at $t=0$ all levels in the ensemble have equal populations and using Eq. (24), one obtains,

$$P(t) = \int_0^\infty e^{-\Gamma_\nu t} f(\Gamma_\nu) d\Gamma_\nu = (1 + 2\bar{\Gamma}_\nu t)^{-1/2}. \quad (25)$$

For more than one decay channel, the survival probability is given by (see, e.g., [55,56])

$$P(t) = \prod_\nu (1 + 2\bar{\Gamma}_\nu t)^{-1/2}, \quad (26)$$

where the product includes all open channels. When the number of open channels, N_c , is large, then for $\bar{\Gamma}_\nu t \ll 1$ one can use $(1 + 2\bar{\Gamma}_\nu t)^{-1/2} \approx e^{-\bar{\Gamma}_\nu t}$ in Eq. (26), which gives

$$P(t) \approx e^{-\Gamma t}, \quad (27)$$

where $\Gamma = \sum_\nu \bar{\Gamma}_\nu \sim N_c \bar{\Gamma}_\nu$ is the total width. The exponential behavior that holds for $\Gamma t < \Gamma/\bar{\Gamma}_\nu \sim N_c$ is a consequence of suppression of fluctuations in the total width. The case of $N_c \gg 1$ in fact corresponds to the classical limit of the decay process of a compound system with a dense spectrum of states. The parameter N_c determines whether the decay process is classical with an exponential behavior, or quantum where sizable deviations from the pure exponent can be expected (see, e.g., [57]).

Besides the fluctuations of the partial widths described by Eq. (24), the distribution of resonance widths in the negative ion ensemble depends on the conditions of its formation. Thus, SF_6^{-*} formed in a trap will have a different distribution of autodetachment widths and hence, different decay curves, to SF_6^{-*} formed with a high-resolution electron beam. In particular, the population of SF_6^{-} resonances created in a beam experiment at time $t=0$ is proportional to the level density and their elastic (entrance) widths. For a single decay channel ν (identical to the entrance channel), the number of ions that have survived to time t is found as

$$N(t) \propto \rho(E) \int \Gamma_\nu e^{-\Gamma_\nu t} f(\Gamma_\nu) d\Gamma_\nu = \frac{\bar{\Gamma}_\nu \rho(E)}{(1 + 2\bar{\Gamma}_\nu t)^{3/2}}. \quad (28)$$

Note that compared with Eq. (25), the account of the initial resonance population has resulted in an additional factor $(1 + 2\bar{\Gamma}_\nu t)^{-1}$. For more than one decay channel, Eq. (26) will be similarly modified,

$$N(t) \propto \frac{\bar{\Gamma}_{\nu_i} \rho(E)}{1 + 2\bar{\Gamma}_{\nu_i} t} \prod_\nu (1 + 2\bar{\Gamma}_\nu t)^{-1/2}, \quad (29)$$

where ν_i is the initial vibrational state of the target molecule.

If the target molecules are characterized by a distribution of initial states with vibrational and rotational quantum numbers ν_i and J , with probabilities $w_{\nu_i J}$, the decay curves must be averaged over these. This gives

$$N(t) \propto \sum_{\nu_i J} \frac{w_{\nu_i J} \bar{\Gamma}_{\nu_i} \rho(E)}{1 + 2\bar{\Gamma}_{\nu_i} t/N_J} \prod_\nu \left(1 + \frac{2\bar{\Gamma}_\nu t}{N_J}\right)^{-N_J/2}, \quad (30)$$

where N_J is the number of channels with different rotational quantum numbers K' of the final SF_6 that can be populated for a given K of the target molecule. If the K quantum number is not conserved then $N_J = 2J + 1$, while if K were conserved, one would have $N_J = 1$. In the former case the decay should be close to exponential for room temperature (or even much colder) SF_6 , since typical J and N_J are large. Indeed, the probabilities for a thermal ensemble of SF_6 molecules are

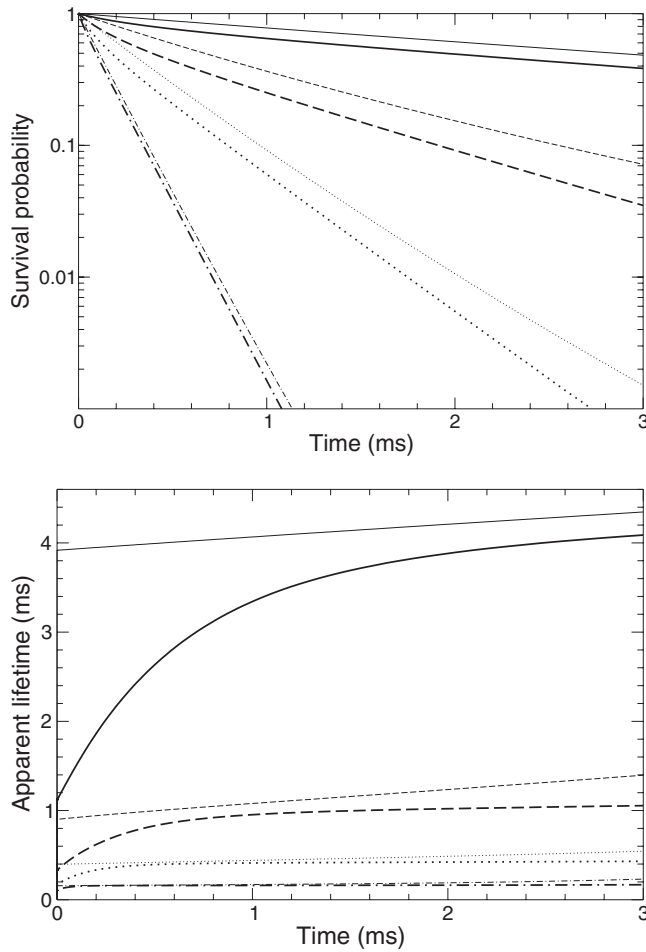


FIG. 9. Time evolution of the survival probability of SF₆^{-*}, $N(t)/N(0)$ (top) and apparent lifetimes, τ (bottom) calculated for two target temperatures $T=300$ K (thick curves) and $T=10$ K (thin curves), and different electron energies: 0.45 meV (solid), 44 meV (dashed), 79 meV (dotted), and 113 meV (dot-dashed).

$w_{v_i J} \propto \exp\{-[E_{v_i} + J(J+1)/2I]/T\}$, where T is the temperature in energy units, and $I=1.23 \times 10^6$ a.u. is the moment of inertia of SF₆. Hence, from $J(J+1)/2I \sim \frac{3}{2}T$ we have $J \sim 50$ at room temperature.

The widths in Eq. (30) depend on the initial vibrational state of the target and the incident electron energy. For SF₆^{-*} formed in a trap in equilibrium with thermal electrons, the resonances will be populated uniformly, with Boltzmann probabilities $\propto e^{-E/T}$. In this case the decay curve is given by the right-hand side of Eq. (30) without the factor $w_{v_i J} \bar{\Gamma}_{v_i} / (1 + 2\bar{\Gamma}_{v_i} t/N_J)$, averaged over the Boltzmann anion energy distribution.

Figures 9 and 10 show the results of our modeling of the decay curves of SF₆^{-*} formed under different conditions. In both figures the bottom plates show the apparent lifetime τ estimated from the instantaneous decay rate $\tau^{-1} = (dN/dt)/N$. This quantity should be constant for a purely exponential decay, but in general, given Eqs. (28)–(30), increases with time. The rate of such increase is asymptotically linear, $\tau \propto t$, since the fraction of long-lived ions increases with time.

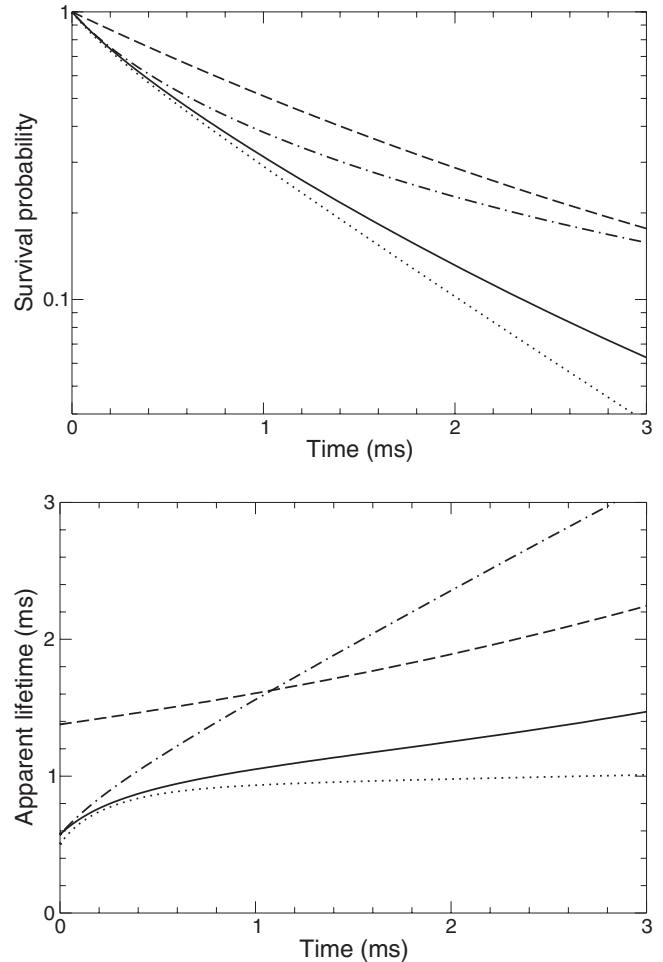


FIG. 10. Time evolution of the survival probability of SF₆^{-*}, $N(t)/N(0)$ (top) and apparent lifetimes, τ (bottom), calculated for anions formed at equilibrium conditions at two trap temperatures, $T=300$ K (solid) and $T=77$ K (dashed). The dotted curve corresponds to the decay of SF₆^{-*} produced by the capture of electrons with fixed energy $\varepsilon=38$ meV, equal to the mean energy at room temperature. The dot-dashed curve shows τ obtained assuming conservation of the angular quantum number K (i.e., for $N_J=1$).

In Fig. 9 we assume that the anions are produced in collisions of monochromatic electrons with four different energies with the SF₆ gas at $T=300$ and 10 K. As expected from the energy dependence of the widths, Fig. 8, the decay becomes much faster with the increase of the electron energy. However, even at the highest energy the lifetime remains greater than 100 μ s, which is compatible with the laser photoelectron attachment experiments [5,8]. Nonexponential features clearly seen in Fig. 9 at small times are due to the contribution of short-lived anions formed by vibrationally excited target molecules. Naturally, this effect is more pronounced at higher temperatures. The nonexponential decay at large times is caused by the Porter-Thomas fluctuations of the autodetachment widths. This effect is greater at small molecular temperatures, where the number of rotational channels is not too large. However, at room temperature $N_J \sim 50$, and the decay is close to exponential over the time interval shown.

The curves that model the decay of SF_6^{-*} formed in a trap at two temperatures, $T=300$ and 77 K, are shown in Fig. 10. In addition to nonexponential features at small times, the presence of long-lived anions formed by low-energy electrons leads to a nonexponential decay at large times. To illustrate this effect, we show for comparison in Fig. 10 the decay curve for anions formed by monoenergetic electrons with the energy of $\frac{3}{2}T$. Also shown in Fig. 10 is the decay curve calculated assuming that K is conserved (i.e., neglecting the effect of the rotational motion on the number of decay channels). As expected, this decay curve is strongly nonexponential, with the apparent lifetime growing as $\tau \sim t$. This feature of the SF_6^- decay was observed experimentally in Refs. [24,26]. It is a consequence of the fact that the fraction of surviving long-lived ions increases with t . On the other hand, allowing for the mixing of the rotational quantum number K makes for a faster (exponential) depletion of SF_6^- , which makes it hard to explain how the anion signal can be observed at much longer times.

There is another effect that molecular rotations can have on the SF_6^{-*} lifetimes, and that has not been taken into account in the present consideration. Due to a difference between the equilibrium S-F bond lengths of the neutral and anion, the moment of inertia of SF_6^- is about 20% greater than that of the neutral. This means that the contribution of the rotational energy $J(J+1)/2I$ in SF_6 and SF_6^- differs by 20% as well. At room temperatures this difference is close to 10 meV, which means that the amount of energy available for IVR in different rotational states is different, and is larger for higher J . This is another source of fluctuations in the detachment widths, which can, in principle, affect the anion decay curves.

IV. CONCLUSIONS

Comparison of calculated cross sections with experimental data demonstrates that low-energy electron attachment to SF_6 proceeds via capture into a virtual state with a strong coupling to the breathing vibrational mode. The model provides an accurate description of the attachment cross section, and is in agreement with the measured total and vibrational excitation cross sections. From this comparison, we have determined the two parameters of the model which describe the behavior of the SF_6 and SF_6^- potential curves near the equilibrium of the neutral. This behavior is in accord with the quantum chemistry calculations of the potential curves.

By allowing a reflected wave in the nuclear dynamics of the SF_6 breathing mode, we have studied the effect of the IVR rate on the cross sections. Comparison with experiment indicates that the IVR in SF_6^- formed by electron attachment is very fast, its rate being comparable to the frequency of the breathing mode.

We have evaluated the autodetachment widths of metastable SF_6^{-*} resonances, assuming statistical distribution of the energy over the vibrational spectrum of the molecule. The magnitude of the widths depends strongly on the set of SF_6^- vibrational frequencies used, as well as on the adiabatic electron affinity of SF_6 . Using the recommended value of

1.06 eV together with the best calculated fundamentals we obtain estimates of SF_6^{-*} lifetimes in the 100 μs to 1 ms range, shorter lifetimes corresponding to the anions formed by higher-energy electrons. These lifetimes are broadly in agreement with the values inferred in laser photoelectron attachment experiments and found in ion-cyclotron-resonance experiments and in traps. At the same time, we cannot explain the observation of tens of μs lifetimes in time-of-flight experiments. Such values would be compatible with a much stiffer set of SF_6^- fundamentals (similar to the neutral), or smaller electron affinity values.

By using the Porter-Thomas distribution we have modeled the effect of fluctuations of autodetachment widths due to the statistical (“chaotic”) nature of highly excited vibrational states of SF_6^- . We have also investigated the effect of SF_6 temperature and electron energy on the SF_6^{-*} decay curves. Fluctuations of the widths result in nonexponential decay of SF_6^{-*} . However, the presence of a large number of rotational channels for all but very low temperatures of the neutral molecule makes these effects relatively small.

Finally, dissociative attachment into $\text{SF}_5^- + \text{F}$ has been largely ignored in the present work. We believe that it can have only a very small effect on the lifetimes of metastable SF_6^- formed at low electron energies. It appears that for electron energies below 0.2 eV the SF_5^- ions originate from (thermally activated) metastable SF_6^- . However, the dissociation signal is low due to a small branching ratio in comparison with autodetachment. At higher electron energies the SF_5^- signal has a large peak. Here the dissociation cross section exceeds that of the s -wave attachment model. In our view this means that the main dissociation mechanism at these energies is different from that responsible for the long-lived SF_6^- .

When this work was completed, we became aware of two very recent studies of the electron- SF_6 problem. In the first of these [58], the autodetachment lifetimes of metastable SF_6^- were studied with a time-of-flight and Penning ion trap techniques, for very low (~ 1 meV) electron energies as a function of the gas temperature. At room temperature only long-lived SF_6^{-*} with $\tau \geq 1$ ms were seen. At higher temperatures shorter lifetimes were observed (~ 0.4 ms), together with a small signal of short-lived anions (≤ 10 μs). These values are broadly in agreement with our decay curve modeling. The second set of papers [59] used kinetic modeling within the framework of the statistical unimolecular rate theory. It analyzed the attachment and dissociation data in a wide range of target and electron temperatures, as well as SF_6 and carrier gas pressures, allowing for additional effects (e.g., the rate of IVR as a function of the incident electron energy) by model factors and fitting parameters. One of the results of this analysis is an indication of a larger electron affinity of 1.20 ± 0.05 eV. This value would result in a factor of 3–5 decrease of our autodetachment widths, and a corresponding increase of the lifetimes. Given the sensitivity of the decay curves to the conditions under which SF_6^{-*} are formed, such change still leaves the lifetimes in the 1–10 ms range, for the conditions similar to those used in Ref. [58].

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APPENDIX A: MATCHING OF THE WAVE FUNCTION

Here we show how the total wave function $\Psi(\mathbf{r}, q)$ of the $e^- + \text{SF}_6$ system, Eq. (8), with the amplitudes satisfying Eq. (10), matches the adiabatic wave function $\Psi_{\text{att}}(\mathbf{r}, q)$, Eq. (12), of SF_6^- , in the range of nuclear coordinates where the incident electron is bound. In order to do this, we project Ψ_{att} onto the SF_6 breathing vibrational states $\chi_n(q)$ with large n . This allows us to determine the asymptotic behavior of f_n corresponding to the two terms on the right-hand side of Eq. (13) and obtain an explicit relation between f_n and the amplitudes A and B .

Consider the wave function $\Psi_{\text{att}}(\mathbf{r}, q)$ far from the merging point of the neutral and anion potential curves. Here its nuclear part (13) can be written explicitly using the semiclassical (WKB) approximation [40]. Let us first consider the contribution of the outgoing wave term,

$$\chi(q) = \frac{A}{\sqrt{v(q)}} \exp\left(i \int_a^q p(q) dq\right), \quad (\text{A1})$$

where $p(q) = \sqrt{2M[E - U_0(q)]}$, $v(q) = p(q)/M$ is the corresponding velocity, $E = \frac{1}{2}k^2 + E_{n_0}$ is the energy of the system, and a is in the classically allowed region (its choice only affecting the phase of A).

Let us now demonstrate that the projection of $\Psi_{\text{att}} = \psi_0(\mathbf{r}, q)\chi(q)$ onto $\chi_n(q)$,

$$g_n(\mathbf{r}) = \int \Psi_{\text{att}}(\mathbf{r}, q)\chi_n(q) dq, \quad (\text{A2})$$

matches the electronic part of the terms in the sum over n in Eq. (8).

For a large n , we can use a normalized semiclassical expression for $\chi_n(q)$ [60],

$$\chi_n(q) = \sqrt{\frac{2\omega}{\pi v_n(q)}} \cos\left(\int_a^{q_n} p_n(q) dq - \frac{\pi}{4}\right), \quad (\text{A3})$$

where $p_n = \sqrt{2ME_n - (M\omega q)^2}$, $v_n(q) = p_n(q)/M$, and $a_n = \sqrt{2E_n/M\omega^2}$ is the classical turning point. Using Eqs. (A1) and (A3) in Eq. (A2), we obtain

$$g_n(\mathbf{r}) = \frac{A\sqrt{\omega}}{\pi r} \int \frac{\sqrt{\kappa(q)} e^{-\kappa(q)r}}{\sqrt{v(q)v_n(q)}} \times \exp\left(i \int_a^q p(q) dq\right) \cos\left(\int_a^{q_n} p_n(q) dq - \frac{\pi}{4}\right) dq. \quad (\text{A4})$$

The integral above contains rapidly oscillating functions. It can be evaluated in the saddle-point approximation, and the main contribution is due to the incoming wave component of the cosine. Hence, the oscillatory factor in the integrand is of the form $\exp[i\varphi_n(q)]$, where

$$\varphi_n(q) = \int_a^q p(q) dq + \int_q^{a_n} p_n(q) dq. \quad (\text{A5})$$

The equation for the saddle point $\partial\varphi_n/\partial q=0$ gives $p(q) = p_n(q)$, i.e., the ‘‘transition’’ between the nuclear vibrational state of the neutral and that of the anion takes place when the momenta are equal. This gives the following equation for the saddle point q_n :

$$E - \varepsilon_0(q_n) = E_n. \quad (\text{A6})$$

It immediately follows that

$$\kappa(q_n) = \sqrt{-2\varepsilon(q_n)} = \sqrt{2(n - n_0)\omega - k^2} \equiv |k_n|, \quad (\text{A7})$$

which shows that $g_n(\mathbf{r}) \propto e^{-|k_n|r}/r$, exactly as that of the n th term in Eq. (8) for closed channels. Note also that the saddle point, found using Eq. (A6), as

$$q_n = \frac{|k_n| - \kappa_0}{\kappa_1} \sim \frac{\sqrt{2\omega n}}{\kappa_1}, \quad (\text{A8})$$

lies in the classically allowed region of the oscillator, which justifies the use of Eq. (A3).

Completing the saddle-point calculation of the integral (A4), we obtain an expression for the amplitude f_n at large n , for the case when $\chi(q)$ is an outgoing wave as follows:

$$f_n = A \sqrt{\frac{\omega}{2\pi v(q_n)\kappa_1}} \exp[i\varphi_n(q_n)] \quad (\text{A9})$$

$$\simeq A \sqrt{\frac{\omega}{2\pi\kappa_1}} \left[\frac{2\omega n}{M} \left(1 - \frac{M\omega^2}{\kappa_1^2} \right) \right]^{-1/4} \exp[i\varphi_n(q_n)]. \quad (\text{A10})$$

In the last equation we used an asymptotic expression for the velocity $v(q_n) = \sqrt{2[E - U_0(q_n)]}/M$ obtained for large n using Eq. (7).

Thus we see that apart from a slowly varying prefactor, the successive amplitudes differ by their phase, so that

$$\xi = \frac{f_{n+1}}{f_n} \simeq \exp\left[i \frac{d}{dn} \varphi_n(q_n)\right]. \quad (\text{A11})$$

Using Eq. (A5) and taking into account the fact that $\partial\varphi_n(q)/\partial q=0$ at $q=q_n$, we obtain

$$\frac{d}{dn} \varphi_n(q_n) = \omega \int_{q_n}^{a_n} \frac{dq}{v_n(q)} \equiv \omega\tau_n, \quad (\text{A12})$$

where τ_n is the time it takes the oscillator with energy E_n to pass from q_n to a_n . Hence, we obtain

$$\xi = \cos \omega\tau_n + i \sin \omega\tau_n = \frac{q_n}{a_n} + i \sqrt{1 - \frac{q_n^2}{a_n^2}}, \quad (\text{A13})$$

where

$$\frac{q_n}{a_n} = \sqrt{\frac{M\omega}{2n+1} \frac{|k_n| - \kappa_0}{\kappa_1}}. \quad (\text{A14})$$

We can see that expression (A13) coincides with ξ_+ from Eq. (15) for large $n=N$. This proves that the solution of the recurrence relation (10) with the boundary condition $f_{N+1}^{(+)} / f_N^{(+)} = \xi_+$ corresponds to the outgoing wave in the anion nuclear wave function.

If instead of Eq. (A1) we consider the contribution of the incoming wave in $\chi(q)$, Eq. (13), the coefficients f_n will be given by the complex conjugate of Eqs. (A9) and (A10) with A replaced by B . The corresponding phase factor f_{n+1}/f_n is the complex conjugate of Eq. (A13), asymptotically equal to $\xi_- = \xi_+^*$ from Eq. (15). Hence, the incoming wave contribution is obtained by solving Eq. (10) with $f_{N+1}^{(-)} / f_N^{(-)} = \xi_-$.

The relation between the behavior of $\Psi_{\text{att}}(\mathbf{r}, q)$ at large q and the asymptotic form of the amplitudes f_n for closed channels allows one to find the attachment cross section σ_{att} directly from f_n . Thus, for the pure outgoing wave case, calculating the flux for $\chi(q)$ from Eq. (A1), and using Eq. (A9), we have

$$\sigma_{\text{att}} = \frac{|A|^2}{k} = 2\pi \frac{|f_n|^2 \kappa_1}{k\omega} v(q_n), \quad (\text{A15})$$

where the last expression is independent of n for large n .

Finally, the reflection coefficient R is evaluated by following the semiclassical wave Eq. (A1) along the anion potential curve $U_0(q)$ from the matching point $a=q_m$ to the right turning point b and back. Here we assume that due to IVR the potential also acquires a small negative imaginary part $-i\gamma/2$. This gives

$$R = -i \exp \left[2i \int_{q_m}^b p(q) dq - \gamma \int_{q_m}^b \frac{dq}{v(q)} \right], \quad (\text{A16})$$

where the momentum $p(q)$ and velocity $v(q)$ are calculated as in Eq. (A1) using $U_0(q)$, and the imaginary part of the potential results in damping at the rate γ . If the anion potential curve for $q > q_m$ is described in the harmonic approximation,

$$U_0(q) = U_a + \frac{1}{2} M \omega_a^2 (q - q_a)^2, \quad (\text{A17})$$

the integrals in Eq. (A16) are given by

$$\int_{q_m}^b p(q) dq = \frac{E - U_a}{\omega_a} \left[\frac{\pi}{2} - \arcsin \alpha - \alpha \sqrt{1 - \alpha^2} \right], \quad (\text{A18})$$

$$\gamma \int_{q_m}^b \frac{dq}{v(q)} = \frac{\gamma}{\omega_a} \left[\frac{\pi}{2} - \arcsin \alpha \right], \quad (\text{A19})$$

where $\alpha = (q_m - q_a) / (b - q_a)$, $b - q_a = \sqrt{(E - U_a) / (M \omega_a^2)}$, ω_a is the frequency of the SF_6^- breathing mode, and $|U_a|$ is the adiabatic electron affinity (neglecting the zero-point energy).

The reflection coefficient that relates the amplitudes corresponding to the outgoing and incoming waves, $R_f = f_{N+1}^{(-)} / f_N^{(+)}$, is obtained with the help of Eq. (A9), and contains an additional phase factor as follows:

$$R_f = R \exp \left[-2i \int_{q_N}^{a_n} p_n(q) dq \right]. \quad (\text{A20})$$

In the matching procedure the coordinate q_m is chosen equal to q_N , Eq. (A8), where N is the truncation number of the recurrence relation (10).

APPENDIX B: VIBRATIONAL SPECTRUM DENSITY

Let us calculate $\rho(E)$ as the density of states for an ensemble of s harmonic oscillators with frequencies ω_i for a fixed temperature T ,

$$\rho(E) = \frac{e^S}{\sqrt{2\pi \langle \Delta E^2 \rangle}}, \quad (\text{B1})$$

where

$$S = \frac{E}{T} - \sum_{i=1}^s \ln(1 - e^{-\omega_i/T}) \quad (\text{B2})$$

is the entropy of the ensemble,

$$\langle \Delta E^2 \rangle = \sum_{i=1}^s \frac{\omega_i^2 e^{-\omega_i/T}}{(1 - e^{-\omega_i/T})^2}, \quad (\text{B3})$$

is the variance of the energy, and T is measured in the units of energy. To find the density for a given energy, the temperature must be chosen so that the mean energy of the ensemble (measured from the ground state) is equal to E as follows:

$$E = \sum_{i=1}^s \frac{\omega_i}{e^{\omega_i/T} - 1}. \quad (\text{B4})$$

The density of states calculated in this way is in excellent agreement with that obtained by directly counting the multi-mode vibrationally excited states.

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