High resolution studies of dissociative electron attachment to molecules: dependence on electron and vibrational energy

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Abstract. For several molecules which are important for plasma processing and gaseous dielectrics (CF$_3$I, CF$_3$Br, CH$_3$Br, and SF$_6$), we have studied the dependence of dissociative electron attachment (DEA) on both the electron energy and on the initial vibrational energy. With reference to electron swarm data, we determine highly-resolved absolute DEA cross sections over a broad energy range, using the Laser Photoelectron Attachment (LPA) method ($E = 0-0.2$ eV, $\Delta E \approx 1-3$ meV) and the EXtended Laser Photoelectron Attachment (EXLPA) method ($E = 0-2$ eV, $\Delta E \approx 15-30$ meV). The experimental data are compared with the results of $R$-matrix calculations, involving ab initio information on the potential energy curves and semiempirical autodetachment widths. For CF$_3$I and CF$_3$Br, previous DEA cross sections are found to be substantially too high. For CH$_3$Br, the measurements confirm a predicted vibrational Feshbach resonance, associated with the $v_3 = 4$ vibrational threshold, and the value of the activation energy (due to an intermediate barrier) for this exothermic DEA process. For SF$_6$, we report absolute cross sections for SF$_6^-$ as well as SF$_5^-$ formation for vibrational temperatures ranging from 200 to 500 K. Moreover, the first absolute DEA cross sections (SF$_5^-$ formation) for CO$_2$-laser excited SF$_6$ molecules have been obtained at different initial vibrational temperatures. The results indicate that the effect of the mode-selective energy input into the $v_3$-mode (predominantly $v_3 = 1$) on the enhancement of SF$_5^-$ formation is very similar to that of a corresponding rise of the average vibrational energy by thermal heating; at $E = 2$ meV electron energy, the results indicate an activation energy of about 0.38 eV.

1. Introduction

Attachment of low-energy electrons to molecules [1-4] is an important process in gaseous dielectrics and other environments including excimer lasers, discharges used for etching, and the earth’s atmosphere. Due to the high electron affinity of halogen atoms $Y$ dissociative electron attachment (DEA) to halogen containing molecules $XY$ (short notation $Y/XY$)

$$e^- (E) + XY \rightarrow XY^- \rightarrow X + Y^-$$

may often occur with large cross sections $\sigma(E)$ down to zero electron energy, thus efficiently producing halogen anions as well as halogen atoms or halogen containing radicals which are important precursors for further reactions. Following its formation, the excited, temporary anion $XY^-$ can either decay by autodetachment (corresponding to elastic or inelastic electron scattering) or it may dissociate,
thereby forming stable negative ions $Y^-$. For molecules (such as HF and CH$_3$I) which exhibit sufficiently strong long-range attraction with the colliding electrons (e.g. by the combined polarization and dipolar forces) the electron scattering and the DEA process can be substantially influenced by vibrational Feshbach resonances (VFRs) $XY^-(v \geq 1)$, with the electron weakly bound to vibrationally excited levels $XY(v \geq 1)$ of the neutral molecule [4]. Very sharp VFRs have been observed for anion formation due to attachment of electrons to molecular clusters [4].

In this progress report, we present and discuss highly-resolved DEA cross sections for four important molecules which may be considered as prototypes for the following cases: (i) exothermic DEA where the diabatic anion curve $U(R)$ cuts the neutral potential curve $V(R)$ near the neutral equilibrium distance $R_e$ (CF$_3$I, Figure 1a); (ii) exothermic DEA where $U(R)$ cuts $V(R)$ at distances substantially larger than $R_e$, thus yielding an intermediate reaction barrier (CF$_3$Br, CH$_3$Br; Figure 1b); (iii) endothermic DEA where the strongly-bound diabatic anion curve cuts the neutral curve close to the neutral equilibrium and dissociation is endothermic (SF$_6$, Figure 1c). In all cases, the symmetries are such that s-wave capture is allowed and will thus dominate the attachment process at low energies.

**Figure 1.** Potential energy curves for the prototype cases discussed in the text. (a), (b): neutral (full curve) and anionic (chain curve) potentials are plotted as function of the reaction coordinates C–I and C–Br ($v_3$-mode), respectively. (c): the neutral (full curve) and bound anionic (chain curve) potentials are plotted as function of the symmetric stretch coordinate ($v_1$-mode), whereas the repulsive potential (broken curve) is plotted with respect to the F–SF$_5^-$ reaction coordinate.

For case (i), the Franck-Condon factors for attachment are favorable at low electron energies and low initial vibrational quantum numbers $v$. Thus, one can expect DEA cross sections which monotonically decrease with rising electron energy and depend only weakly on $v$. For case (ii), one expects that the DEA cross section is small for $v = 0$ and strongly rises with $v$ for levels below the crossing point. Correspondingly, the DEA rate coefficient should exhibit Arrhenius-type behavior with an activation energy related to the barrier height. For the endothermic case (iii), the system needs initial rovibrational energy and/or sufficiently high electron energy for DEA to occur. The studied molecule SF$_6$ is sufficiently complex to produce metastable anions at very low energies.
In section 2, we briefly describe the LPA and EXLPA method and the conditions for the experiments with CO\textsubscript{2} laser excitation. In section 3, we summarize the essentials of the $R$-matrix approach for calculating DEA cross sections for different initial vibrational levels of the molecules CF\textsubscript{3}I, CF\textsubscript{3}Br, and CH\textsubscript{3}Br. In section 4, we present, discuss and compare the experimental and theoretical results. We conclude with a brief summary.

2. Experimental

In order to measure highly-resolved cross sections for reaction (1), we used two variants of the Laser Photoelectron Attachment (LPA) method [5-8], as sketched in Figure 2. In the standard LPA method [5,6], energy-variable photoelectrons are created in the reaction region with the target gas (RC) by resonant two-color photoionization of ground-state potassium atoms [6-8]. The electron energy range is limited to about 0–220 meV by the tuning range of the photoionization laser, and resolutions down to 1 meV are obtained. Higher electron energies were accessed by the EXtended Laser Photoelectron Attachment (EXLPA) method [7,8] where near-zero energy photoelectrons are produced in an auxiliary photoionization chamber (PC), accelerated by a weak electric field in a guiding magnetic field (0.002 T), brought to the energy of interest prior to traversal through the target region, and subsequently accelerated and deflected onto a collector plate. The effective resolution in the EXLPA experiment was in the range 15–30 meV. The created anions are mass selected with a quadrupole mass spectrometer and detected with an off-axis channel electron multiplier (CEM).

![Figure 2. Experimental set-up for LPA and EXLPA measurements involving CO\textsubscript{2}-laser excited SF\textsubscript{6} molecules in a collimated, seeded supersonic beam (for details see text and [5-8]).]

With a diffuse target gas (gas temperature $T_G = 300$ K), a pulsed electron production-anion extraction scheme is used [5]. To vary the vibrational temperature of the molecules we used a differentially-pumped, seeded supersonic beam (carrier gas He) from a heatable nozzle ($T_0 = 300–600$ K, nozzle diameter 60 $\mu$m) at a typical stagnation pressure of 1 bar [7-11]. For the supersonic beam target, the experiment was not pulsed, and no anion extraction field was applied. Information on the vibrational temperature $T_V$ of SF\textsubscript{6} molecules in the seeded supersonic beam (12.5% SF\textsubscript{6} in He) has been obtained by a detailed study of SF\textsubscript{5} formation for a broad range of nozzle temperatures and stagnation pressures [7,10]. At $T_0 = 400$ K, the vibrational temperature $T_V$ of SF\textsubscript{6} molecules is close to that for a thermal ensemble at the gas temperature $T_G = 300$ K, as shown by comparison of the SF\textsubscript{5} attachment spectra for SF\textsubscript{6} molecules in a diffuse target gas at $T_G = 300$ K and in the supersonic beam [7,10]. For the discussion of the results in section 4, we assume the relation $T_V = T_0 - 100$ K to be a
good approximation to the vibrational temperature of SF$_6$ molecules in our supersonic beam over the range $T_0 = 300–600$ K.

At a distance of 5 cm before the attachment volume, the $v_3$ mode of SF$_6$ in the target beam could be transversely excited by radiation in the 10.6 $\mu$m band of a line-tunable CO$_2$-laser (intensities up to 400 W/cm$^2$). The normalized photon-induced change of the anion yield is defined as $\varepsilon \equiv (Y_f - Y_0)/Y_0$. For SF$_6$ formation, the enhancement $\varepsilon$ was found to depend on the photon wave number $1/\lambda_0$, on the laser intensity $I_L$, on the electron energy $E$, and on the initial vibrational temperature $T_v$. From the measured enhancement $\varepsilon$ and the fraction $F$ of laser-excited molecules one can determine the cross section $\sigma_f$ for anion formation involving laser-excited molecules in terms of the cross section $\sigma_0$ for molecules in the absence of laser excitation by the simple formula $\sigma_f/\sigma_0 = 1 + dF$. The fraction $F$ (up to 5%) was determined with reference to earlier work, as described in detail in [10].

3. $R$-matrix calculation of absolute DEA cross sections

DEA to the quasi-diatomic molecules CH$_3$X or CF$_3$X (X = Cl, Br, I) in the low-energy region proceeds through electron capture into the lowest unoccupied molecular orbital of $a_1$ symmetry. To calculate DEA cross sections, we employ the resonance $R$-matrix theory in the approximation of one isolated resonance, as reviewed by Lane and Thomas [12]. The $R$-matrix in the fixed-nuclei approximation has the form

$$R(\rho) = \gamma^2(\rho)/[W(\rho) - E] + R_0$$

(2)

where $\rho$ is the C–X distance relative to the equilibrium separation in the neutral molecule, $W(\rho)$ is the lowest $R$-matrix pole, $\gamma(\rho)$ is the surface amplitude and $R_0$ is a background term independent of $\rho$ and electron energy $E$. The relation between the surface amplitude $\gamma$ and the resonance width $\Gamma$ is given in [12]; basically $\Gamma$ is proportional to $\gamma^2$. The physical significance of $W(\rho)$ is that it represents the energy of the resonance state. It is given by the equation $W(\rho) = U(\rho) - V(\rho)$, where $V(\rho)$ is the potential energy curve for the neutral molecule, and $U(\rho)$ the potential energy curve for the intermediate negative ion state. The surface amplitude $\gamma$ is typically a slowly varying function of $\rho$, we parameterize it in the following form:

$$\gamma(\rho) = \gamma_l/[\exp(\zeta \rho) + \eta].$$

(3)

The parameters $\gamma_l$, $\zeta$, and $\eta$ are adjusted semiempirically to provide a realistic description of the thermal rate coefficients.

The neutral potential energy curve is determined from reliable experimental data on the dissociation energy and vibrational spacing for the C–X stretch vibrational mode $v_3$. The anion curve is taken from $ab initio$ calculations available in the literature or calculated using quantum chemistry codes. The parameters of the potential energy curves for the molecules CF$_3$I, CF$_3$Br, and CH$_3$Br are given in [8,9,11].

To calculate DEA cross sections, we incorporate nuclear dynamics and solve the basic equations of the resonance $R$-matrix theory in the quasiclassical approximation [13]. As part of this procedure, we calculate electron scattering wave functions outside the $R$-matrix sphere, which include dipolar and polarization interactions. For the electric dipole moment and the dipole polarizability of the neutral molecule in the equilibrium geometry we use the best experimental values [8,9,11]. For the dipole moment dependence on the C–X distance we assume the function used in calculations [14] for hydrogen halides. Typically we adopt the results for HX, however we use the correct equilibrium dipole moment for CH$_3$X/CF$_3$X and adjust the function to reproduce the correct value of the transition dipole moment, obtained from data on the intensities for infrared transitions [15]. Additional calculations for CH$_3$Br, using a multiconfigurational valence bond method [16], have generated a dipole moment function which is close to the model function.
4. Results and discussion

In this section we present essential results obtained for the four prototype molecules CF₃I, CF₃Br, CH₃Br, and SF₆. We concentrate on the absolute cross sections for anion formation as a function of electron and initial vibrational energy. We note that in our recent papers [8,9,11] we also dwell on the rate coefficients for attachment of Rydberg electrons (as a function of principal quantum number n) as well as of a Maxwellian ensemble of electrons (as a function electron temperature $T_e$). Moreover, we have predicted cross sections for vibrational excitation (VE) of these molecules, using theoretical parameters which were found to provide a reasonable description of the DEA cross sections.

Figure 3. Absolute cross sections for I⁻ formation due to DEA to CF₃I ($T_G = 300$ K). Open circles: LPA/EXLPA. Full curve: optimized R-matrix calculation. Full squares: DEA cross sections suggested in [17]. See text for details.

Figure 4. R-matrix DEA cross sections for several initial vibrational levels of CF₃I and comparison of our LPA/EXLPA cross section (open circles) with the R-matrix vibrational average calculated for $T_G = 300$ K (full curve).

4.1. Dissociative electron attachment to CF₃I

In Figure 3 we present absolute cross sections for DEA to CF₃I molecules (I⁻ formation) with a gas temperature of $T_G = 300$ K over the electron energy range 0.2–1500 meV; the absolute scale of our data (open circles) was established with reference to the thermal rate coefficient $1.9\times 10^{-7}$ cm³/s ($T_e = T_G = 300$ K) [8,17]. At very low energies, s-wave attachment behavior $\sigma(E) \propto E^{-\alpha}$, where $\frac{1}{2} < \alpha < 1$ due to dipolar interaction [4,8], is observed. At the onsets for VE of one and two quanta of the C–I stretch mode $v_3$, downward cusps appear which are due to the coupling of the attachment channel with the VE channels [4]; the latter exhibit steep onsets near threshold [8]. The broken curve in Figure 3 represents the cross section, derived from fits to attachment yields which were measured with a VUV photoelectron attachment method (TPSA) at an optical resolution of about 6 meV [18], using the thermal rate coefficient listed above for absolute normalization. The shape of this cross section differs from our LPA cross section in a characteristic way, as observed before e.g. for SF₆ and CCl₄ [4]; it can be attributed to the influence of electric fields and the choice of a non-optimal analytical fit function in [18]. The DEA cross section suggested by Christophorou and Olthoff [17] (full squares) is substantially higher than our DEA cross section; it even exceeds the unitarity limit $\pi k^2$ (chain curve; $k =$ electron wave vector) for s-wave attachment [4] in the range 20–100 meV. Moreover, it is not compatible with the size of DEA rate coefficients obtained consistently (to within ±15%) by several
groups in different types of electron swarm experiments [8,17]. The size of our DEA cross section at very low energies is supported by the values of rate coefficients for Rydberg electron transfer, as explained in [8].

The calculated cross section (full curve) agrees very well with the combined LPA/EXLPA cross section over the range 0.2–500 meV. We emphasize that the potential energy curves were taken from experiment (neutral) and ab initio theory (anion) while the surface amplitude was chosen to yield agreement with the thermal rate coefficient and adjusted to also reproduce the strong decline of the DEA cross section towards higher energy. In this sense the agreement with the experimental data is not so surprising. But it is remarkable to see the detailed agreement in the cross section shapes and in the cusp structure at the VE thresholds. It would be interesting to have experimental tests of our VE cross sections predicted in [8].

In Figure 4 we present calculated DEA cross sections for single initial vibrational levels \( v_3 = 0 \text{--} 4 \) and compare the resulting thermal average for \( T_G = 300 \) K with our experimental cross section. The DEA cross sections for \( v_3 = 0 \text{--} 4 \) have similar shapes and their sizes agree to within a factor of three or less (see also inset). CF\(_3\)I is thus a prototype molecule for which the DEA cross sections depend only weakly on vibrational energy or temperature, as also reflected in measurements of the rate coefficients as a function of temperature [17].

### 4.2. Dissociative electron attachment to CF\(_3\)Br and CH\(_3\)Br

In Figure 5 we show absolute cross sections for DEA to CF\(_3\)Br molecules (Br\(^-\) formation) with a gas temperature of \( T_G = 300 \) K over the electron energy range 1–2000 meV; the absolute scale of our data (open circles) was established with reference to the thermal rate coefficient \( 1.4 \times 10^{-6} \text{cm}^3/\text{s} \) \( (T_e = T_G = 300 \) K, see discussion in [9,19]). At low energies, s-wave attachment behavior is observed. At the onsets for VE of one and two quanta of the C–Br stretch mode \( v_3 \), downward cusps appear which are due to the coupling of the attachment channel with the VE channels [4,9]; the latter show steep onsets near threshold [9]. The broken curve in Figure 5 represents the TPSA cross section [20], using the same thermal rate coefficient for absolute normalization. The shape of this cross section differs from our LPA cross section in a characteristic way, as observed and discussed above for CF\(_3\)I. The DEA cross section measured with a magnetically-guided electron beam by Underwood-Lemons et al. [21] at the gas temperature \( T_G = 393 \) K (full squares) is substantially higher than our DEA cross section. Only a minor part of this deviation can be attributed to the higher gas temperature in [21], and it was proposed in [9] that the DEA experiments on both CF\(_3\)I and CF\(_3\)Br described in [21] were influenced by a systematic error leading to too large cross sections.

The calculated cross section (full curve) shows good overall agreement with our combined LPA/EXLPA cross section over the range 1–500 meV; at higher energies it stays below the measured cross section. As explained for CF\(_3\)I, the potential energy curves were taken from experiment (neutral) and ab initio theory (anion) while the surface amplitude was chosen to yield agreement with the thermal rate coefficient and adjusted to reproduce the strong decline of the DEA cross section towards higher energy.

In Figure 6 we present DEA cross sections for CF\(_3\)Br, as calculated for seven different vibrational temperatures in the range 50–600 K, and compare them with our experimental results for \( T_G = 300 \) K. The cross section calculated for 50 K gas is nearly that for the vibrational ground level \( v_3 = 0 \) and is (at energies below 30 meV) almost a factor of 100 lower than that for 300 K, reflecting a strong dependence on vibrational temperature. This is caused by the effects of the intermediate barrier (the diabatic anion curve cuts the neutral curve at an energy of 121 meV above the energy of the neutral vibrational ground state, see Figure 1b), leading to very low Franck-Condon factors for \( v_3 = 0 \). The dependence of the DEA cross section on initial vibrational level is even stronger for the molecule CH\(_3\)Br for which the diabatic anion curve is displaced even further to larger distances and cuts the neutral curve about 372 meV above the neutral vibrational ground state [11]. For CH\(_3\)Br, the DEA
cross section for \( v_3 = 0 \) at near-zero electron energies is about \( 10^{13} \) times lower than that for \( v_3 = 4 \) (the level with the highest DEA cross section) [11].

![Graph](image1.png)

**Figure 5.** Absolute cross sections for Br\(^-\) formation due to DEA to CF\(_3\)Br. Open circles: LPA/EXLPA \((T_G = 300 \, \text{K})\). Full curve: optimized \( R \)-matrix calculation. Full squares: beam data of [21]. See text for details.

![Graph](image2.png)

**Figure 6.** Calculated absolute cross sections for Br\(^-\) formation due to DEA to CF\(_3\)Br for vibrational temperatures from 50 to 600 K. For comparison the LPA/EXLPA absolute DEA cross section determined at 300 K is shown.

A prominent VFR, associated with the \( v_3 = 4 \) level, was predicted for CH\(_3\)Br some time ago [22]. This prediction has been verified in our recent LPA experiment [11], carried out at a gas temperature of 600 K, thus producing some population in higher vibrational levels. The occurrence of the VFR for CH\(_3\)Br (as compared to CF\(_3\)Br) is mainly due to the much higher dipole moment of CH\(_3\)Br which – in combination with the polarization force – results in a weakly-bound diffuse anion state at shorter internuclear distances. The VFR leads to a strong enhancement of the DEA cross section at energies just below the \( v_3 = 4 \) threshold and has a characteristic shape with a steep rise below the threshold, a peak and a slower drop to lower energies, as seen most clearly for CH\(_3\)I [22,23] where the VFR is attached to the \( v_3 = 1 \) level.

It would be of interest to measure the DEA cross sections for the molecules CF\(_3\)Br and CH\(_3\)Br over a broad range of vibrational temperatures at sufficiently high electron energy resolution to test the theoretical predictions in more detail. For CF\(_3\)Br, comparisons have been be made with the results of swarm measurements in which the gas temperature \( T_G \) and the electron temperature \( T_e \) could be varied independently over a rather wide range [9]. Good qualitative agreement between the measured and the predicted dependences of the DEA rate coefficients on \( T_G \) and \( T_e \) was observed; some quantitative differences may indicate that the DEA process is influenced by other vibrational modes which were not taken into account in the calculations [9].

For both CF\(_3\)Br and CH\(_3\)Br, we also calculated VE cross sections, and it would be of interest to have experimental results for comparison, desirably for several gas temperatures.

### 4.3. Dissociative electron attachment to SF\(_6\) with thermal and laser heating

Sulfurhexafluoride (SF\(_6\)) is a molecule with many industrial applications [1,2,24,25]. One of the most important properties of SF\(_6\) is its high cross section for the capture of low-energy electrons, forming predominantly long-lived SF\(_6^+\) ions by non-dissociative attachment [1-5,7,25] and – towards higher energies – SF\(_5^+\) + F by DEA [1,7,10,25,26]. It is generally understood that the primary collision
process at very low energies proceeds through non-adiabatic s-wave electron capture involving nuclear motion along the symmetric stretch normal coordinate $v_1$ and a temporary negative ion (TNI) state with $A_1$ symmetry:

$$\begin{align*}
\text{e}^-(E) + \text{SF}_6(T_G) & \rightarrow \text{SF}_6^-(\text{TNI}; A_1) \\
(\text{TNI}) & \rightarrow \text{SF}_6 + \text{e}^-(E) \quad \text{elastic scattering (4a)} \\
(\text{TNI}) & \rightarrow \text{SF}_6(v > 0) + \text{e}^-(E < E) \quad \text{vibrational excitation (4b)} \\
(\text{TNI}) & \rightarrow \text{SF}_6^-(\text{metastable}) \quad \text{IVR (4c)}
\end{align*}$$

On the one hand, the primary TNI is coupled to the elementary paths of elastic scattering (4a) and VE (4b) via autodetachment. On the other hand, fast and efficient intramolecular vibrational redistribution (IVR) (4c) within the TNI leads to a reorganized anion complex which is immune to autodetachment in view of the high vibrational level density of the anion at energies of at least 1.2 eV above the SF$_6^-$ ground state (see Figure 1c; the adiabatic electron affinity of SF$_6$ is 1.20(5) eV [27]). Recent work [28] demonstrated that attachment of near-zero energy electrons to SF$_6$ molecules at a gas temperature of $T_G = 300$ K leads to metastable SF$_6^-$ anions with lifetimes in the millisecond range. Further evolution of the metastable anion complex may proceed by autodetachment on a long time scale, by dissociation towards SF$_5^- + F$, or – for times above several milliseconds – by emission of infrared photons yielding a stabilized SF$_6^-$ anion. The quantitative details of this evolution depend more or less strongly on the energy $E$ of the captured electron and on the internal rovibrational energy of the initial SF$_6$ molecule (which depends on $T_G$) [7,10,25,27].

**Figure 7.** Absolute cross sections for SF$_5^-$ formation in electron-SF$_6$ collisions. Full symbols: LPA/EXLPA cross sections obtained with a seeded supersonic beam for energies up to 1300 meV ($T_0 = 300–600$ K). Open symbols: cross sections for CO$_2$-laser excited SF$_6$ (multiplied by 2 for clarity) over the range $E = 1–200$ meV (for details see text).
Here, we present new experimental results for SF$_6^-$ formation due to low-energy electron attachment to thermally and CO$_2$-laser excited SF$_6$. In contrast to the previous DEA work involving CO$_2$-laser pumping [29,30], very high electron energy resolution is achieved by the LPA/EXLPA method. Moreover, SF$_6$ molecules in a collimated seeded supersonic beam are used (nozzle temperatures $T_0$ = 300–600 K, corresponding to vibrational temperatures $T_v \approx T_0 - 100$ K [7,10]) and transversely excited by lines in the 10PX branch of a line-tunable CO$_2$-laser (see above). The IR photon induced enhancement of the SF$_6^-$ yield is found to be optimal on the 10P28 line (936.8 cm$^{-1}$) at all nozzle temperatures (with the maximum reached for $T_0 \approx 390$ K) and to monotonically decrease with rising electron energy from 0 to about 300 meV. With reference to previous work on the excitation of supersonic SF$_6$ beams by CO$_2$-laser light, the fraction of laser-excited SF$_6^-$($v_3 \geq 1$) molecules is estimated [10], and absolute cross sections $\sigma(E)$ for SF$_6^-$ formation involving the IR-excited molecules are determined for the first time. In Figure 7, we summarize the DEA cross sections without ($\sigma_0(E)$) and with laser excitation ($\sigma_1(E)$), as determined for different nozzle temperatures $T_0$. At fixed $T_0$, the cross section $\sigma_1$ exceeds the cross section $\sigma_0$ for thermal molecules in a way which strongly depends on electron energy and initial vibrational energy. In contrast, the cross section for SF$_6^-$ formation is found to be almost independent of laser-excitation and temperature [10] in the studied energy range.

In Figure 8, we plot the DEA cross sections for thermal (full circles) and laser-excited (open circles) SF$_6$ molecules, measured at the electron energy $E = 2$ meV, as a function of the inverse effective vibrational temperature $1/T_{v,eff}$ (for the laser excitation process it was found that on average one IR photon (116.15 meV) is absorbed [10]). The experimental data are fitted with an Arrhenius-type expression for the DEA cross section (full curve) which includes an additive constant [10] (this constant with a cross section about 3x10$^{-4}$ times smaller than that for SF$_6^-$ formation at $E = 2$ meV accounts for the possibility of processes involving DEA to a small fraction of SF$_6$ molecules which do not participate in cooling during the supersonic expansion). The full curve corresponds to an ‘activation energy’ of 0.38 eV. This value is close to the new endothermicity (0.41 eV [27]) of the SF$_6^--+F(2P_{3/2})$ limit relative to the SF$_6$ rovibrational ground state plus a zero energy electron. The branching ratios $R(E) = \sigma(SF_6^-)/[\sigma(SF_6^-) + \sigma(SF_6^0)]$ as a function of electron energy rise monotonically with increasing electron energy and reach values near unity between about 0.3 and 0.4 eV [10]. If unimolecular decay of the metastable SF$_6^-$ ions resulting from the IRV process (4c) is the only source for SF$_6^-$ formation, i.e. if a direct process via attachment to a repulsive potential energy surface (broken curve in Figure 1c) with prompt dissociation is negligible, the ratios $R(E)$ would simply reflect the energy-dependent dissociation probabilities (after correction for losses due to long-time autodetachment processes). Troe et al. [27] have recently modeled SF$_6^-$ and SF$_6^0$ formation and concluded that a direct process is not needed. Some features in our cross sections for SF$_6^-$ and SF$_6^0$ formation indicate, however, that anion formation via a repulsive surface plays a certain role, as will be described elsewhere in detail (see also the discussion in [7,10]).

5. Summary

For the prototype molecules CF$_3$I, CF$_2$Br/CH$_3$Br, and SF$_6$ we have measured highly-resolved absolute cross sections for DEA and investigated the role of the initial internal energy of the molecules on the anion formation process. For the molecules CF$_3$I, CF$_2$Br, and CH$_3$Br the experimental data are compared with the results of R-matrix calculations, involving ab initio information on the potential energy curves and semiempirical autodetachment widths. The calculations are particularly useful in that they uncover the dependence of the DEA cross section on the initial vibrational level for the mode which is primarily responsible for the dissociation process. For CH$_3$Br, the measurements confirm a predicted VFR, associated with the $v_3 = 4$ vibrational threshold, and the value of the activation energy (due to an intermediate barrier) for this exothermic DEA process. For SF$_6$, we report absolute cross sections for SF$_6^-$ as well as SF$_6^0$ formation for vibrational temperatures ranging from 200 to 500 K. Moreover, the first absolute DEA cross sections (SF$_6^-$ formation) for CO$_2$-laser excited SF$_6$ molecules

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have been obtained at different initial vibrational temperatures. The results indicate that the effect of mode-selective energy input into the \( \nu_3 \)-mode (predominantly \( \nu_3 = 1 \)) on the enhancement of \( \text{SF}_5^- \) formation is very similar to that of a corresponding rise of the average vibrational energy by thermal heating; at \( E = 2 \) meV electron energy, the results indicate an activation energy of about 0.38 eV.

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