Highly resolved absolute cross-sections for dissociative electron attachment to SF₅CF₃

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ABSTRACT

Using two complementary experimental methods, we have measured partial (mass-resolved) cross-sections for dissociative electron attachment to the molecule trifluoromethyl sulfurpentafluoride (SF_5CF_3) at the gas temperature $T_G = 300$ K over a broad range of electron energies ($E = 0.001$–12 eV). The absolute scale for these cross-sections was obtained with reference to the thermal ($T = 300$ K) rate coefficient for anion formation ($8.0(3) \times 10^{-8}$ cm^3 s^{-1}). Below 1 eV, SF_5^- is the dominant product anion and formed through the lowest anion state which cuts the neutral SF_5CF_3 potential close to the S–C equilibrium distance. The highly resolved laser photoelectron attachment data exhibit a downward Wigner cusp at 86 meV, indicating that the $\nu_4(a_1)$ vibrational mode is important for the primary attachment dynamics. Both SF_5^- and F^- anions are formed with similar yields through the first excited resonance located near 3.6 eV. Towards higher energies, the anions CF_3^-, SF_4^-, and SF_3^- are also produced. Summation of the partial cross-sections yields a total absolute cross-section for anion formation over the energy range 0.001–12 eV. This is used to calculate the dependence of the rate coefficient for dissociative electron attachment over a broad range of electron temperatures for the fixed gas temperature $T_G = 300$ K; good agreement is found between the calculated values and those obtained in a drift tube experiment. In addition to the experimental work, semiempirical R-matrix calculations have been carried out for the energy dependence of the cross-section for SF_5^- formation. The experimental findings are semi-quantitatively recovered.

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1. Introduction

An analysis of stratospheric air samples by Sturges et al. [1] has indicated that trifluoromethyl sulfurpentafluoride (SF_5CF_3) is present in the stratosphere. The compound is thought to be exclusively anthropogenic in origin; it has been speculated that the source of atmospheric SF_5CF_3 may be the reaction of SF_6 with fluoropolymers in electrical devices (see papers by Huang et al. [2] and by Tsai [3,4]). Although present at a level of only 0.12 ppt in 1999, the atmospheric abundance of SF_5CF_3 is reportedly increasing by 6% per year, tracking the increase of atmospheric SF_6 [1]. This is significant because both SF_6 and SF_5CF_3 are powerful greenhouse gases. The global warming potential (GWP) of SF_5CF_3 is currently estimated at 18,500 times that of CO_2 [5,6], greater than almost any other molecule. The stratospheric profile that was measured by Sturges et al. suggests this compound is long-lived in the atmosphere. Kennedy and Mayhew [7] have recently speculated that, because the compound is not broken down by UV photodissociation, and there are no known atmospheric sinks, ion–molecule reactions and electron attachment reactions must play a significant role in the atmospheric chemistry of SF_5CF_3. Previous reports on the electron attachment rate to SF_5CF_3 place an upper limit of approximately 1000 years on the compound's atmospheric lifetime [7–10]. In addition to its atmospheric relevance, electron attachment studies to SF_5CF_3 are of interest because of the comparisons we can make with SF_6, a molecule used in many technological applications [11,12], and with the similar molecule SF_5Cl for which we recently reported a comprehensive set of partial cross-sections for anion formation [13].

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The findings of Sturges et al. [1] initiated several other studies, including IR spectroscopy [14,15], swarm experiments on electron attachment [7,8,16], and electron beam measurements of the partial cross-sections for anion formation [17,18]. The latter two studies – following pioneering work on the total attachment cross-section for this molecule by Chen et al. [19] – agreed in the observation that the dominant anion at low energies is SF_5^- while the respective findings for other anions were contradictory. Sailer et al. [17] reported a band for CF_3^- formation with a peak cross-section of 0.35×10^{-20} m^2 at 1.2 eV and a band for F$^-$ production peaking at about 0.9 eV (cross-section 0.08×10^{-20} m^2) (in addition a weaker maximum at near-zero energies was seen in the F$^-$ yield). Balog et al. [18] investigated low-energy electron collisions with free SF_5CF_3 molecules and with SF_5CF_3 in homogeneous clusters and in nanofilms. Like Sailer et al., they reported anion yield functions for the fragments SF_5^-, F$^-$, and CF_3^- with relative maximum yields of 1000, 4, and 0.03 while the Innsbruck experiment [17] gave respective maximum yields of 1000, 0.7, and 4. The Berlin measurement for F$^-$ production [18] showed a broad band peaking at about 0.5 eV and a substantially weaker and rather wide band around 3.2 eV; their results for CF_3^- formation indicate the presence of a rather narrow peak near zero energy and a broad band around 3.5 eV.

In the present work, we combine the results from two different beam experiments to determine the partial and the total absolute cross-sections for dissociative electron attachment (DEA) to SF_5CF_3 over the energy range 0.001–12 eV. At energies below 1 eV, the SF_5^- anion is the dominant product, and we measure its DEA cross-section by two versions of the laser photoelectron attachment (LPA) method (LPA and extended laser photoelectron attachment (EXLPA), see Section 2.1) over the range 0.001–1.66 eV with energy widths of 2 meV (LPA) and about 25 meV (EXLPA). The LPA data are put on an absolute cross-section scale with reference to the well-known thermal (T = 300 K) DEA rate coefficient. The other experiment uses a pulsed electron source from a trochoidal electron monochromator with moderate resolution and a time-of-flight mass spectrometer. It yields simultaneously measured relative cross-sections for the relevant product anions with little mass and kinetic energy discrimination over the range 0.2–12 eV. The two sets of cross-section data are combined and thus yield the partial and total cross-sections for anion formation.

The paper is organized as follows: in Section 2, we describe the two experimental setups. In Section 3, we summarize some of the relevant structural and energetic properties of SF_5CF_3 and its anion, and we describe briefly the R-matrix method used to calculate the energy dependence of the DEA cross-section at low energies (<1 eV). In Section 4, we report the partial and total cross-sections and compare with the calculated cross-section and with the previous experimental results [17–19]. In addition, we calculate the dependence of the DEA rate coefficient on electron temperature for a Maxwellian electron gas at the fixed gas temperature T_G = 300 K and compare with a previous drift tube experiment [7]. We conclude with a brief summary.

2. Experimental

2.1. Laser photoelectron attachment experiment (Kaiserslautern)

In order to measure highly resolved cross-sections for anion formation in low-energy electron collisions with SF_5CF_3, we used two variants of the laser photoelectron attachment method, as discussed elsewhere in detail [20–22]. The energy range 1–200 meV was covered at resolutions of about 2 meV by the standard LPA method [20]: energy-variable photoelectrons (typical current 40 pA) are created in the reaction region with the target gas by resonant two-color photoionization of ground state potassium atoms

via the excited K($4p_{3/2}$) level [21]. Higher electron energies were accessed by the extended laser photoelectron attachment method [22]: here near-zero energy photoelectrons are produced in an auxiliary photoionization chamber (distance from reaction centre about 5 cm), 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. Care was taken to align the exciting and the focused ionizing laser (diameter 0.12 mm) to avoid any collisions of the electron beam with surfaces on its way from the photoionization chamber to the collector since these would yield spurious low-energy electrons and thus lead to unwanted attachment processes. This is especially critical in energy ranges where the attachment cross-section is small. In this way, the drop of the SF_6^- cross-section, for example, could be followed over five orders of magnitude towards higher electron energies [22]. The effective resolution in the EXLPA experiment was about 25 meV.

Both the LPA and the EXLPA experiment were pulsed at a rate of 100 kHz: following each photoelectron production and attachment period, the infrared laser (767 nm), exciting the K($4s$–$4p_{3/2}$) transition, was switched off by an acousto-optical modulator, and a voltage pulse was initiated to extract the anions. A stack of electrodes imaged the anions onto the entrance hole of a quadrupole mass filter which mass selected the species of interest. The transmitted anions were detected by a channel electron multiplier (Fa. Sjuts, background 0.02 s^{-1}).

A diffuse low-density target of SF_5CF_3 molecules (Apollo Scientific, Ltd., stated purity 99%) at the gas temperature T_G = 300 K was used without further purification. An anion mass spectrum taken at very low electron energies (using electron transfer from highly excited $K^{**}(nd)$ Rydberg atoms with $n \approx 140$; see, e.g., [21]) yielded SF_5^- as the dominant anion product. SF_6^- anions were detected at a relative intensity level of about 3.5% and attributed to a minor SF_6 impurity (relative density about 1%); correspondingly, SF_5^- anions resulting from DEA to SF_6 contribute to the SF_5^- yield at a negligible level (see Ref. [22] for the energy dependent cross-section for SF_5^- formation from SF_6). Other anions in the mass spectrum had intensities ≤10^{-4} relative to that for SF_5^-.

The LPA/EXLPA experiment provides a highly resolved yield $Y(E)$ for anion formation. This yield is proportional to the absolute DEA cross-section, i.e., $\sigma(E) = NY(E)$ where N is a normalization factor, assumed to be independent of electron energy E. The size of the normalization factor is established with reference to a known thermal DEA rate coefficient for the same process. The thermal rate coefficient $k = \langle v_{rel}\sigma(v_{rel})\rangle$, ($v_{rel}$ = relative collision velocity of the electron–molecule system) is given by the average:

$$k(T_e, T_G) = (2/m)^{1/2} \int E^{1/2} \sigma_{tot}(E; T_G) f(E; T_e)\, dE \qquad (1)$$

Here, T_G denotes the rovibrational temperature of the target gas, T_e the electron temperature and $f(E;T_e)$ the electron distribution function. Note that the velocity of the gas molecules at T_G = 300 K is much smaller than the electron velocity even at electron energies as low as 0.1 meV, and the relative collision velocity v_{rel} can be replaced by the electron velocity. In calculating the rate coefficient, we use a Maxwellian distribution function which is given by

$$f(E; T_e) = 2\left(\frac{E}{\pi}\right)^{1/2} \beta^{-3/2} \exp\left(-\frac{E}{\beta}\right) \qquad (2)$$

with $\beta = k_B T_e$ (k_B = Boltzmann constant). The usual thermal average in Eq. (1) requires $T_e = T_G$. In the calibration of the absolute DEA cross-section scale, we have used the thermal rate coefficient $k(T)$ measured for $T = T_e = T_G$ = 300 K.