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Associative and dissociative electron attachment by SF_6 and SF_5Cl

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Electron attachment by SF_6 and SF_5Cl in the energy range 0–20 eV has been studied in a beam experiment at room temperature. At low energies (≈ 0 eV) electron attachment to SF_6 yields the well known parent anion SF_6^{-*} (associative attachment) and SF_5^- (dissociative attachment), while other negative ion fragments (F^-, F_2^-, SF_2^-, SF_3^-, and SF_4^-) are generated with comparably low cross sections from various resonances at higher energies. In contrast to that, negative ion formation in SF_5Cl is dominated by dissociative channels (F^-, Cl^-, FCl^-, and SF_5^-) and only a weak SF_5Cl^- signal is observed. A time-of-flight analysis of the ionic fragments reveals that the decomposition of all resonances is characterized by a low translational excess energy release indicating effective energy randomization in the parent ion prior to dissociation. The present results are compared with negative ion formation in halogenated hydrocarbons.

I. INTRODUCTION

Sulfur hexafluoride is a well known compound which has found extensive application as a gaseous dielectric in high-voltage power devices[1] and as an effective electron scavenger in liquids and gases.[2,3] Although the chemical reactivity of SF_6 is low and comparable to that of N_2[4] it captures thermal electrons with one of the highest cross sections known to form a metastable SF_6^{-*} which can be observed by mass spectrometric techniques. The autodetachment lifetime of this ion has received a great deal of attention. Experiments using time-of-flight (TOF) mass spectrometry resulted in lifetimes between 10 and 68 μs[5–7] while workers using ion cyclotron resonance (ICR) spectrometers report lifetimes up to the ms range.[8–10] It has been shown by Futrell *et al.*[9] that the lifetime of SF_6^{-*} in the ICR spectrometer varied with the observation time of the experiment, thus accounting for radiative and collisional cooling of SF_6^{-*}. This question has recently been discussed by Heneghan and Benson.[11] Attachment of free electrons to SF_6 has extensively been studied within the last three decades.[12–17]

It now seems established[16] that the attachment of 0 eV electrons yields both SF_6^{-*} (associative attachment) and SF_5^- by the dissociative attachment reaction

$$e^- + SF_6 \rightarrow F + SF_5^- \,. \tag{1}$$

For the complementary reaction, however,

$$e^- + SF_6 \rightarrow F^- + SF_5 \,; \tag{2}$$

conflicting results can be found in the literature.

In some of the earlier[13,14] and recent[17] works the formation of F^- at 0 eV closely resembling the energy dependence of SF_6^- was reported. This observation has been used (in combination with the known electron affinity of the fluorine atom) to calculate the F_5S–F bond dissociation energy to be 3.38 eV,[18] a value which is frequently cited in standard reference books.[19].

More recent results based on chemiluminescence in the reaction of SF_6 with metastable alkali atoms[20] as well as different flowing afterglow studies[21] derive considerably higher values (3.9 ± 0.15 eV and 4.0 ± 0.14 eV, respectively), thus casting doubt on the dissociative attachment results. In fact, in a later beam experiment performed at room temperature Kline *et al.*[22] demonstrated that the formation of F^- occurs only at electron energies above 2.2 eV.

In this contribution we systematically study the formation of negative ions following electron attachment to SF_6 and SF_5Cl in a beam experiment in the energy range 0–20 eV with particular emphasis on reactions occurring at low electron energies.

From fluorinated methanes and benzenes it is well known that the behavior of these compounds with respect to electron attachment drastically changes when F is replaced by Cl.[23–27] It is generally observed that F^- appears at energies considerably above the thermodynamic threshold while a comparably intense Cl^- signal is observed near threshold. This behavior has been discussed in terms of the "electron capacity" of the halogens which increases with increasing atomic number.[28]

To our knowledge, electron attachment to SF_5Cl has not been reported with the exception of an earlier work by Harland and Thynne[29] where the formation of negative ions has been studied with a conventional TOF mass spectrometer. Although these authors give values for appearance energies and resonance maxima, the explicit ion yield curve is only presented for F^- formation.

II. EXPERIMENT

The experimental approach in our laboratory is a "trochoidal electron monochromator" which generates a beam of quasimonoenergetic and magnetically aligned electrons in conjunction with a quadrupole mass filter for ion identification. The basic apparatus, method of data collection, energy calibration, etc., has been described in detail.[23,30] Briefly, the electron beam is crossed at a right angle with the molecular beam effusing from a capillary near room temperature. Neg-

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ative ions generated in the interaction volume defined by the crossing of the electron beam with the molecular beam are extracted by a small electric field ($\lesssim 1$ V cm^{-1}) and focused onto the entrance hole of a commercial quadrupole mass filter where the ions are analyzed and then detected by single-pulse counting technique. The appearance of a specific ion (*m/e*) vs energy (the ion yield curve) is then recorded. Since in this configuration the electrons are aligned by a homogeneous magnetic field ($\approx$ 160 G), the instrument is particularly suited for studying electron attachment processes at very low energies.

The translational excess energy release is measured by applying a TOF analysis of the ionic fragments as previously described in detail.[24,31] Thermal or near-thermal ions exhibit a Gaussian-like peak shape while ions with considerable translational excess energy generate a doublet in the TOF spectrum due to "direct" and "turn-around" ions, the latter being first reversed by the ion draw-out field and then accelerated towards the detector. Since the low ion draw-out field strongly discriminates against initial velocity components perpendicular to the flight tube axis, only ions ejected along this axis (directly towards and directly away from the detector) will be transmitted to the quadrupole and will thus be detected.

SF_5Cl has been prepared by the high-yield reaction of SF_4 and ClF in the presence of dry ClF at ambient temperature as described in the literature.[32] With the exception of a small amount of SOF_2 arising during the preparation procedure (hydrolysis of SF_4 to SOF_2), positive ion mass spectra did not show any further impurities.

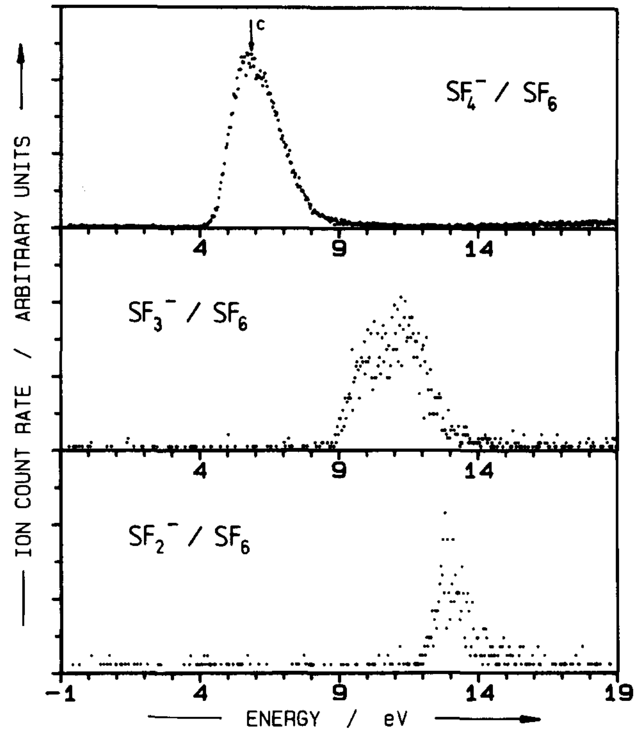

FIG. 2. Negative ion formation in SF_6.

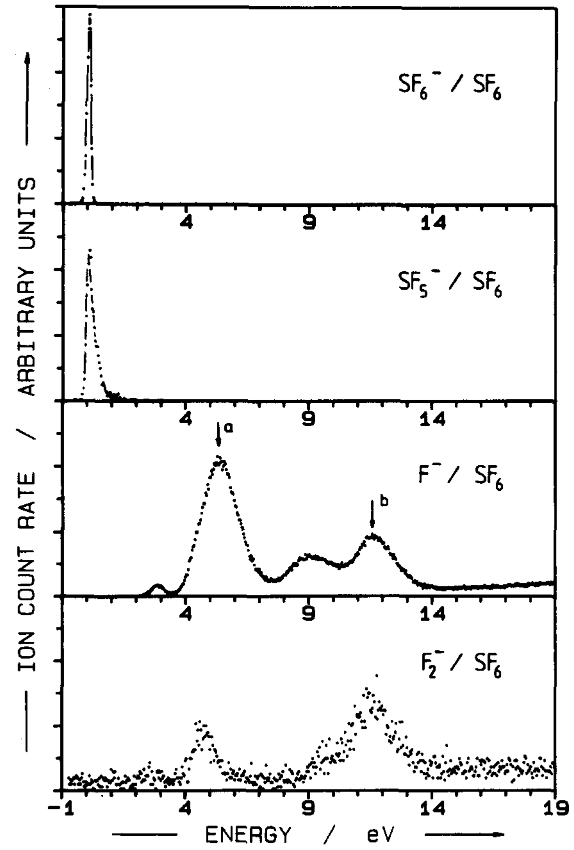

FIG. 1. Negative ion formation in SF_6.

III. RESULTS

A. Negative ion formation

Figures 1–3, 6, and 7 present the ion yield curves for the various negative ions observed on electron attachment to SF_6 and SF_5Cl. Obviously, all curves exhibit pronounced resonance profiles. Since all ion signals show a linear pressure dependence and since it has been established that every ion signal completely vanishes when the electron beam is

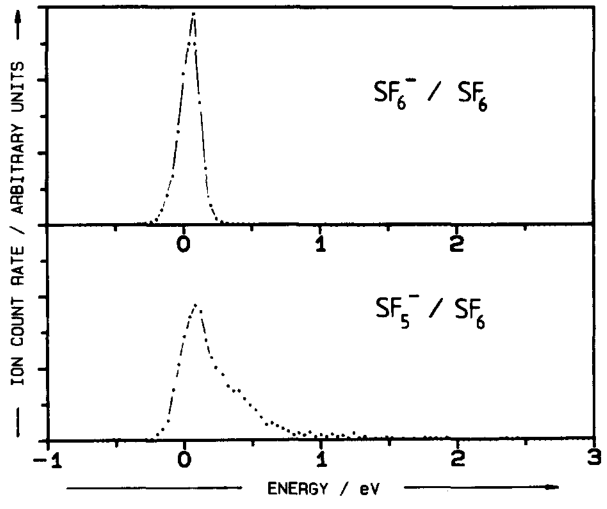

FIG. 3. Enlarged scale for the ion yield curves SF_6^{-*}/SF_6 and SF_5^-/SF_6.

TABLE I. Relative intensities for ion formation in SF_6 and SF_5Cl and absolute cross sections for ion formation in SF_6 (see the text).

	Lehmann (Ref. 15) SF_6 (cm^2)	Kline *et al.* (Ref. 22) SF_6 (cm^2)	This work	
			SF_6 (a.u.)	SF_5Cl (a.u.)
M^-	7.65×10^{-15}	4×10^{-14}	1000	0.5
F^-	5.80×10^{-18}	5×10^{-18}	1.5	40
Cl^-	...	...	...	60
F_2^-	1.41×10^{-19}	1.5×10^{-19}	<0.1	0.1
FCl^-	...	...	...	20
SF_5^-	4.45×10^{-16}	4×10^{-16}	80	10
SF_4^-	5.53×10^{-19}	1×10^{-18}	0.5	<0.1
SF_3^-	$7.7\ \times10^{-20}$	3×10^{-20}	<0.1	<0.1
SF_2^-	$1.7\ \times10^{-20}$	1.5×10^{-20}	<0.1	<0.1

switched off (by applying a stopping voltage to one of the electrodes in front of the reaction volume), all ions observed are considered to be primary products of resonance (dissociative or associative) electron attachment, and not products of possible secondary ion–molecule reactions or reactions at the hot filament.

In Table I the relative intensities of the ions observed from SF_6 and SF_5Cl (taken at the corresponding maximum of the most intense resonance) are given. Although we are aware of the various shortcomings when comparing intensities in a mass spectrometric experiment (mass dependent transmission of the quadrupole, detector efficiency, a general change of experimental conditions when the sample is changed, etc.), the numbers are derived under identical operation conditions (electron current, sample pressure, ion draw-out field, etc.) and should thus be a rough estimate of the relative cross section for the formation of the respective ion. In Table I absolute cross section values for electron attachment to SF_6 (also taken at the respective peak maximum) given by Lehmann[15] and Kline *et al.*[22] are included.

Obviously, negative ion formation in SF_6 is dominated by associative electron attachment leading to SF_6^{-*} while in SF_5Cl dissociative channels leading to Cl^-, F^-, and FCl^- are the prominent processes. Since the measured intensity of the parent anion depends on its autodetachment lifetime, we note that for our experimental arrangement and for the present operation conditions the flight time of an ion from the source through the quadrupole to the detector is given by $T(\mu s) = 3.18\,[m_i(\text{a.u.})]^{1/2}$.[31]

B. Translational excess energy release

We have applied a TOF technique in order to study the translational excess energy release in the dissociative electron attachment reactions presently studied. In short, the TOF spectra taken at different electron energies revealed Gaussian peak shapes for all the fragments observed indicating thermal or near-thermal translational excess energy distributions. This is illustrated for the fragments F^- and SF_4^- arising from SF_6 (Fig. 4). Zero in the relative time scale in Fig. 4 refers to an ion (of the respective mass) and zero initial kinetic energy.

For low initial translational energy, all ions are extracted and focused onto the entrance hole of the mass filter; the width [full width at half-maximum (FWHM)] of the TOF peak $T_{1/2}$ and the mean kinetic energy of the ions E_i are then related by the expression[31]

$$E_i = \frac{(\epsilon q T_{1/2})^2}{3.7 m_i} \tag{3}$$

with ϵ the ion draw-out field ($\epsilon = 4\ \text{V cm}^{-1}$ when applying TOF analysis) and q the charge of the ion. Expression (3) is based on a standard Maxwell–Boltzmann distribution.

Figure 4 shows that the TOF peak for F^- is Gaussian

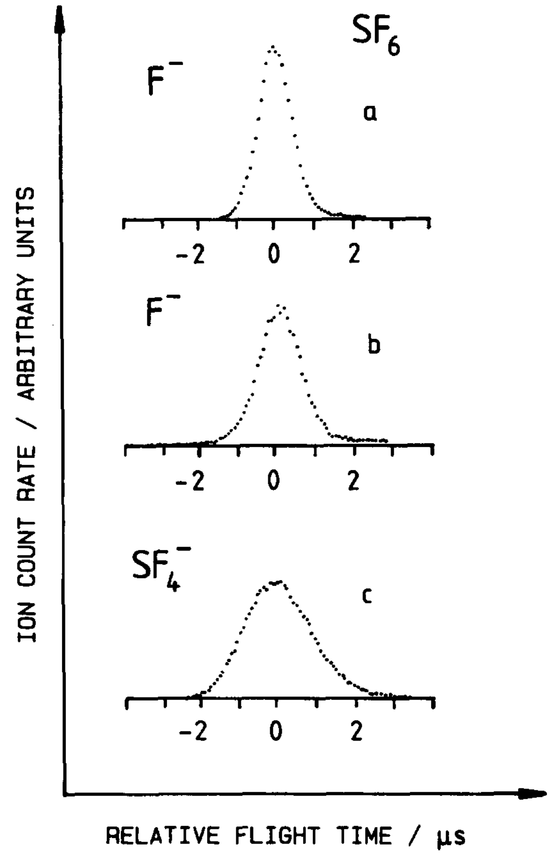

FIG. 4. Illustrative examples for TOF spectra taken at the electron energies marked by the arrows in Figs. 1 and 2.

shaped and virtually independent of the electron energy with a width of $\sim 1\ \mu s$ (FWHM) while the width of the SF_4^- peak is $\sim 2.0\ \mu s$ (also nearly independent of electron energy). Since the gate width of the pulsed electron beam is $0.7\ \mu s$, the different widths of the time-of-flight spectra (F^- and SF_4^-) only reflect the different masses of the ions. We can thus conclude that the translational excess distribution is thermal or quasithermal with a mean value below 0.15 eV [according to expression (3)]. A qualitatively similar result is obtained for all ionic fragments arising from SF_6 and SF_5Cl at any energy between 0 and 20 eV. It should be noted, however, that the relatively high ion draw-out field during TOF analysis ($4\ V\ cm^{-1}$ instead of $< 1\ V\ cm^{-1}$) discriminates against very low energy electrons so that a TOF analysis is not rigorously possible for processes occurring at thermal or near-thermal electron energies.

IV. DISCUSSION

A. Sulfur hexafluoride

After years of uncertainty the adiabatic electron affinity now seems to have been stabilized at 1.05 ± 0.1 eV.[33,37] The mechanism of electron attachment by SF_6 to form SF_6^{-*} and the structure of this anion, however, is not yet totally clear. Recent theoretical calculations[34-37] consistently show that the HOMO in SF_6^- is $6a_{1g}(Oh)$ (totally symmetric) with S–F antibonding character resulting in a substantial increase of the S–F bond length when going from the neutral to the anion.

Compton and co-workers[38] have discussed the initial formation of SF_6^{-*} in terms of electron capture into degenerate MOs (with lower than a_{1g} symmetry) leading to a Jahn–Teller distortion in the negative ion and thus providing the strong coupling of electronic and nuclear motion necessary to trap the extra electron. Lack of any photodetachment signal from SF_6^- also suggests a structure of SF_6^- considerably different from that of the neutral.[39] Apart from a loose octahedral SF_6^-, an ion molecule association complex $(SF_5 \cdot F)^-$ has also been suggested.[39]

Figure 1 clearly demonstrates that the attachment of low-energy (< 1 eV) electrons only yields SF_6^{-*} and SF_5^-, while F^- is generated only at energies above 2.4 eV. The present result is thus consistent with the work of Kline *et al.*[22] It has, in fact, been shown by Chen and Chantry[40] that at zero electron energy F^- is only generated at temperatures above 600 K. Appearance energies and resonance maxima observed in the present study are in good agreement with the data of Kline *et al.*[22] We therefore suggest that the earlier observations of F^- formation at thermal energy[7,13,17] were probably due to undefined conditions in the ion source (reactions at the hot filament, presence of scattered electrons, etc.) or sample impurities.

The energy balance for a dissociative electron attachment reaction leading to two fragments

$$e^- + AB \rightarrow A + B^- \quad (4)$$

may be expressed as

$$AE(B^-) = D(A\text{–}B) - EA(B) + E^* \quad (5)$$

with AE the appearance energy of the negative ion (B^-), D the bond dissociation energy in the neutral, EA the electron affinity, and E^* the total available excess energy of the process.

With the most recent value for the $(F_5S\text{–}F)$ bond dissociation energy (4.0 ± 0.14 eV[21]) and the well known electron affinity of F (3.399 eV[41]) the thermodynamic threshold for F^- formation, i.e., reaction (2),

$$e^- + SF_6 \rightarrow SF_5 + F^-$$

becomes $\Delta H_0 = 0.65 \pm 0.14$ eV. F^- formation at thermal electron energies and at room temperature is thus not expected by simple thermodynamic considerations. The experimentally observed appearance energy (Fig. 1) is 2.4 ± 0.2 eV. F^- predominantly arises from a resonance centered around 5.4 eV. This resonance is also associated with the formation of F_2^- and SF_4^-. While the first low-intensity resonance leading to F^- (around 2.9 eV) is unambiguously associated with reaction (2), the following resonance peaking at 5.4 eV may be associated with the channels

$$e^- + SF_6 SF_6^{*-}\ (5.4\ \text{eV}) \rightarrow SF_4 + F + F^- \quad (6a)$$

$$\rightarrow SF_4^- + F_2 \quad (6b)$$

$$\rightarrow SF_4 + F_2^- \quad (6c)$$

[We assign SF_6^{*-} for the electronically excited negative ion and SF_6^{-*} for the ion in its electronic ground state and internal (vibrational) energy.] Taking the average F–S bond dissociation energy in SF_6 [3.41 eV, known from the well established heat of formation (− 12.65 eV[42])] for the cleavage of two fluorine atoms, ΔH_0 for reaction (6a) becomes 3.42 eV.

Accordingly, with the electron affinities for SF_4 (2.34 ± 0.1 eV) and F_2 (3.08 ± 0.1 eV) derived from flowing afterglow charge transfer reactions[43] and endothermic charge transfer reactions,[44] respectively, the energetic threshold is $\Delta H_0 = 2.8 \pm 0.1$ eV for reaction (6b) and $\Delta H_0 = 2.1 \pm 0.1$ eV for reaction (6c). Since SF_4^- and F_2^- are generated from the prominent resonance between 4 and ~ 8 eV we cannot definitely exclude that the formation of these ions is associated with multiple fragmentation reactions (i.e., $F_2^- + SF_3 + F$ and $SF_4^- + F + F$, at least at the high energy side of the resonance). As mentioned above, all dissociative attachment reactions exhibit thermal or quasithermal kinetic excess energy release, the decomposition of SF_6^- into the various ionic fragments must therefore be associated with a very effective energy randomization in the parent ion prior to dissociation (vibrational predissociation). This is different from many other systems. In halogenated methanes, e.g.,[24,31] the extra electron occupies an antibonding σ^* MO resulting in a rather direct dissociation along a repulsive potential energy surface with considerable kinetic excess energy in the fragments. We therefore suggest that the molecular orbitals involved in dissociative electron capture by SF_6 do not have a significant valence character (with the possible exception of electron attachment near 0 eV) and may probably be characterized as core excited resonances, i.e., electronic states with two electrons occupying a normally empty MO. At this point, however, we note that even in neutral SF_6 electronic excitation, although repeatedly studied within the last years, remains confusing.[45]

The formation of SF_5^- at low electron energies is well

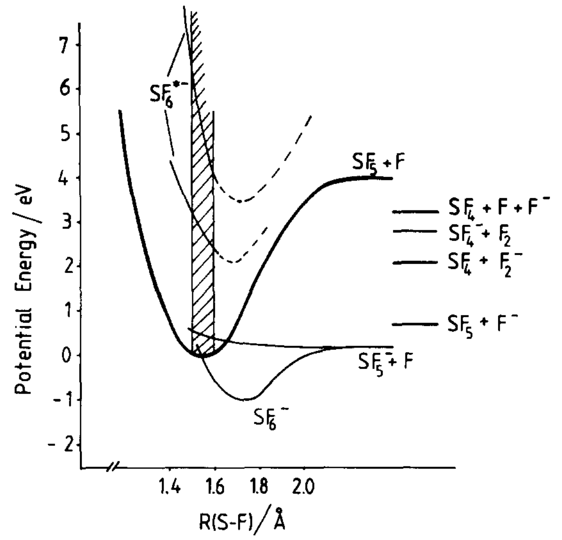

FIG. 5. Schematic potential energy diagram illustrating electron attachment to SF_6 (see the text).

established[16,40,46] and a dramatic temperature effect has been reported. Chen and Chantry[16] demonstrated that the ion yield curve for SF_5^- consists of two overlapping resonances peaking at 0.0 and 0.38 eV, the first resonance being enhanced by two orders of magnitude when going from room temperature to 800 K and also being enhanced when SF_6 is vibrationally excited by infrared laser excitation prior to electron attachment. From this temperature dependence, an activation energy of 0.2 eV for SF_5^- formation has been derived.

SF_5^- evidently arises from the process (1):

$$e^- + SF_6 \rightarrow SF_5^- + F.$$

With the abovementioned activation energy (0.2 eV) and the known F_5S–F bond dissociation energy (4.05 ± 0.14 eV), the electron affinity of the SF_5 radical becomes $EA(SF_5) = 3.8 \pm 0.14$ eV. Values available from the literature range from 2.7 to 3.7 eV.[47]

Figure 3 shows SF_6^{-*} and SF_5^- formation on an enlarged scale (temperature of the reaction chamber ~400 K). The situation for electron attachment to SF_6 is schematically illustrated in Fig. 5 in a one-dimensional potential energy diagram. For the diagram we used the now established electron affinity of SF_6[33] and the model for SF_5^- formation suggested by Chen and Chantry.[16] The equilibrium distances were taken from recent theoretical calculations.[36,37] In the diagram the energies of some dissociation channels available from the prominent resonance (peaking near 5 eV) are also included.

Finally, SF_3^- and SF_2^- (Fig. 2) arise from resonances at very high energies where multiple fragmentation reactions are obviously possible.

B. Sulfur pentafluorochloride

SF_5Cl forms negative ions dominantly via dissociative attachment into F^-, Cl^-, FCl^-, and SF_5^-, and only a small amount of SF_5Cl^- is observed under our experimental conditions (flight time from the source to the detector is 40 μs for SF_5Cl^-). At higher energies the fragments F_2^-, SF_2^-, SF_3^-, and SF_4^- are also observed. In the early work of Harland and Thynne[29] the formation of F^-, Cl^-, FCl^-, SF_3^-, SF_4^-, and SF_5^- above zero electron energy was reported (without presenting explicit ion yield curves). Some ion formation at 0 eV was interpreted as a result of thermal decomposition of the gas at the hot filament. Their tabulated appearance energies and peak maxima (above 0 eV) agree passably well with the present results when we shift their data to lower energies by 0.5–0.8 eV.

From electron diffraction[48] and other techniques it is known that the S–Cl bond length is ≈ 2.05 Å and the S–F bond length is 1.57 Å and thus comparable to that in SF_6.

We expected Cl^- to dominate in dissociative electron attachment by SF_5Cl. A salient feature in various fluorochlorocarbons recently studied is the formation of Cl^- with high intensity near the energetic threshold and the formation of F^- significantly above threshold with low intensity.[14,23,27,47] MNDO calculations applied to these systems[49,50] clearly revealed that in the anion's electronic ground state the additional charge is readily localized at the chlorine atom, the extra electron thus occupying a localized MO with σ^* (C–Cl) character. This can be interpreted in terms of the electron capacity of the halogens which is larger for Cl than for F.[51] It has already been mentioned by Moore and co-workers[28] that in electron attachment the important property is not the electron affinity of the halogen but the electron capacity.

Since in SF_5Cl the ions F^-, Cl^-, FCl^-, and SF_5^- are observed near 0 eV with an intensity in the same order of magnitude, we suggest that the HOMO in SF_5Cl^- consists of both antibonding S–F and S–Cl components.

SF_5Cl has already been studied in infrared multiphoton dissociation;[52,53] to our knowledge, however, a direct experimental value for the S–Cl or S–F bond dissociation energy has not been reported. When we use the known F_5S–F dissociation energy (4.05 ± 0.14 eV[21]) and the heat of formation for SF_5Cl (-10.86 eV[42]) we derive $D(F_5S\text{–}Cl) = 2.70 \pm 0.15$ eV.

The formation of F^-, Cl^-, FCl^-, and SF_5^- occurs at thermal or near-thermal energies. These fragments are likely to be associated with the reactions

$$e^- + SF_5Cl \rightarrow Cl^- + SF_5 \qquad (7a)$$

$$\rightarrow F^- + SF_4Cl \qquad (7b)$$

$$\rightarrow FCl^- + SF_4 \qquad (7c)$$

$$\rightarrow SF_5^- + Cl. \qquad (7d)$$

Reactions (7a) and (7d) are then exothermic by roughly 1 eV. The energetic threshold for reaction (7c) is given by

$$\Delta H_0 = D(\text{S–Cl}) + D(\text{S–F}) - D(\text{FCl}) - EA(\text{FCl}). \qquad (8)$$

With $D(\text{F–Cl}) = 2.7$ eV[54] and $D(\text{S–Cl}) = 2.7$ eV from the above equation we have

$$\Delta H_0 = D(\text{S–F}) - EA(\text{FCl}) \qquad (9)$$

for the "thermodynamic" appearance energy of FCl^- ($E^* = 0$). Since the experimental appearance energy is ~0 eV it follows that $D(\text{S–F}) < EA(\text{FCl})$.

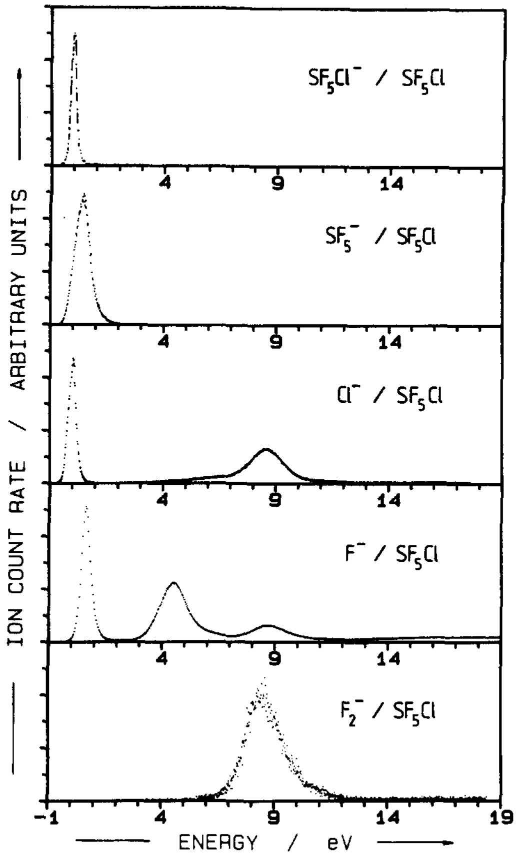

FIG. 6. Negative ion formation in SF_5Cl.

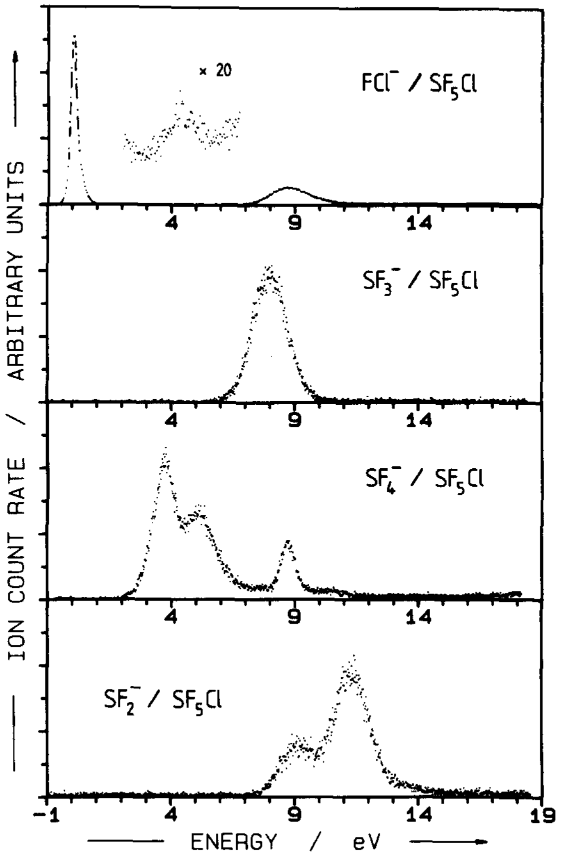

FIG. 7. Negative ion formation in SF_5Cl.

For the electron affinity of FCl, values ranging from 1.5 to 2.4 eV (mostly derived from dissociative electron attachment) can be found in the literature.[47] Reliable values for some bihalogens are 2.6 eV (IBr), 3.08 eV (F_2), and 2.4 eV (Cl_2).[55] A value between 2 and 3 eV might thus be reasonable for the electron affinity of FCl and therefore indicating a lower S–F bond dissociation energy in SF_5Cl than in SF_6.

Returning to Figs. 6 and 7, it can be seen that SF_5Cl exhibits a pronounced resonance around 9 eV which decomposes into all ionic fragments observed from this compound, except SF_5^- which is only formed near 0 eV. It is very likely that this resonance of high energy decomposes in more than two fragments and may thus unlikely generate $SF_5^- + Cl$.

In conclusion, from the results presented here it can be seen that

(1) Negative ion formation in SF_6 is strongly dominated by associative attachment of thermal electrons to form SF_6^- while the cross section for dissociative attachment occurring via various resonances at higher energies is remarkably low.

(2) F^- is formed from different resonances above 2.4 eV. This result is in agreement with a recent beam experiment, but in contrast to earlier works where F^- formation at 0 eV (probably due to experimental shortcomings) was reported.

(3) Negative ion formation in SF_5Cl occurs dominantly via dissociative attachment of low-energy electrons into F^-, Cl^-, FCl^-, and SF_5^-.

(4) The decomposition of the various resonances in both compounds is characterized by a uniformly low translational energy release.

ACKNOWLEDGMENTS

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