

K and 0.2975×10^{-2} P at 368 K.¹⁹ For these values $\tau_R \approx 600$ ns at 70 °C and 400 ns at 95 °C. The breakpoint between the slow and fast components at 90 °C is ~ 300 ns which is in semi-quantitative agreement with this idealized calculation for vesicle rotation. Recent deuterium nuclear magnetic resonance studies at room temperature have also indicated that vesicle rotation affects the nuclear transverse relaxation time.²⁰⁻²²

D. Temperature Dependence of T_M . Figure 3 shows the temperature dependence of T_M measured for the multibilayers and the vesicles. In the region from 75 to 85 °C the magnitude of T_M for the multibilayers is intermediate between the fast and slow decay values of T_M found in the vesicles. This is as expected if the cholestane nitroxide in the multibilayers undergoes wide angular excursions which average the intrinsic fast and slow decay values of T_M .

The increase of T_M with increasing temperature in the multibilayers has been explained as follows.¹² The hyperfine anisotropy becomes more averaged due to greater molecular reorientation at higher temperature and decreases the relaxation rate. Since T_M is proportional to T_2 , we also note that a T_2 (or T_M) increase with temperature indicates that the electron spin relaxation phenomena can be described by a motionally narrowed formalism.

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A similar temperature dependence is observed for both the fast and slow decay components in the vesicles. However, the increase occurs at higher temperatures in the vesicles which is consistent with a more restrictive environment and greater molecular packing in the vesicles compared to the multibilayers.

In the highest temperature region shown in Figure 3, T_M reaches a maximum and then decreases with increasing temperature. This was previously interpreted for the multibilayer dispersions as the onset of spin dephasing by Heisenberg spin exchange due to increasing translational motion. This interpretation is supported by results on changing the nitroxide probe concentration by twofold in multibilayer dispersions which does affect T_M , particularly in the higher temperature range. An increased nitroxide probe concentration introduces the onset of spin exchange at lower temperatures and tends to partially cancel the increase of T_M with temperature observed at lower spin probe concentrations.

Conclusions

This work demonstrates that *directly* measured transverse electron relaxation times of nitroxide spin probes by time domain techniques can differ between multibilayer dispersions and vesicles. In particular, the anisotropy of the magnetic parameters of the nitroxide is averaged differently in these two types of model membrane preparations. Finally, evidence of vesicle rotation has been directly detected in electron spin echo decay curves.

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Registry No. Cholestane nitroxide, 18353-76-9.

Electron Photodetachment Study of Sulfur Hexafluoride Anion: Comments on the Structure of SF_6^-

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Abstract: Electron photodetachment in the gas phase from the sulfur hexafluoride anion, SF_6^- , has been attempted. When using ion cyclotron resonance spectrometry to generate, trap, and detect ions, no observable photodetachment from SF_6^- was detected upon irradiation with visible light from either broad band arc lamp or laser sources. Theoretical cross-section calculations which have proven reliable in the past indicate that octahedral SF_6^- should possess a large cross section for photodetachment. A model consistent with the lack of photodetachment is one in which SF_6^- has a geometry distorted significantly from that of the neutral. This model is shown to be consistent with the observed kinetic barrier to electron transfer from SF_6^- in gas-phase ion-molecule reactions. Statistical rate theory is used to show that the predicted autodetachment lifetime of a loose, distorted SF_6^- is in the same range as that observed experimentally, while an SF_6^-* which resembles the parent neutral results in a predicted lifetime orders of magnitude too small. Two models consistent with this behavior are (1) an octahedral SF_6^- with sulfur-fluorine bonds weakened significantly from those in the neutral and (2) an SF_6^- that exists as an ion-molecule association complex, $(\text{SF}_5\text{F})^-$. Other negative ions besides SF_6^- also show behavior which may be explained by similar models. The usefulness of SF_6 as a dielectric material in high-voltage electrical equipment is related to its molecular properties.

The negative ion of sulfur hexafluoride, SF_6^- , has been the subject of intensive and continuing investigations. Sulfur hexafluoride has one of the largest low-energy electron-capture cross sections known;¹ it has found extensive applications as an electron scavenger in liquids and gases² and as a high-voltage dielectric material. It is probably the most extensively studied electron-molecule system. In spite of these studies, however, many of the

properties of SF_6^- remain peculiar and inconsistent with what might be expected based on our knowledge of other negative ions. This paper describes our attempts to photodetach electrons from SF_6^- , and we suggest a model which accounts for the unusual properties of this ion.

It was shown³ as early as 1953 that SF_6 is able to capture an electron nondissociatively to form SF_6^- , as well as to undergo a dissociative process to form $\text{SF}_5^- + \text{F}$. The parent ion, SF_6^- , has been observed by a variety of techniques. Among its peculiar

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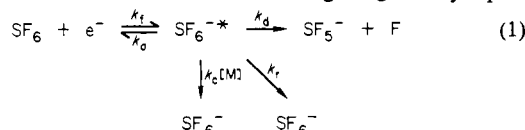
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properties are an anomalous lifetime for autodetachment, its slow reactions with neutral molecules, and the apparent lack of an appreciable cross section for electron photodetachment.

The autodetachment lifetime of SF_6^{-*} has received a great deal of attention. Early work suggested that SF_6^{-} was metastable and existed only transiently. Various workers using time-of-flight (TOF) mass spectrometry initially measured the lifetime⁴ as 10, 25, and 60 μs . Henis and Mable,⁵ however, performing a line shape analysis of SF_6^{-} observed in an ion cyclotron resonance (ICR) spectrometer, placed the lifetime at 500 μs . Due to the large discrepancy with the TOF experiments, the Henis and Mable result was not generally accepted until a study by Futrell et al.,⁶ which showed that the apparent lifetime of SF_6^{-} in an ICR varied significantly with the observation time of the experiment. They found it was possible to measure apparent SF_6^{-} lifetimes ranging from 70 μs to 10 ms. Finally, Beauchamp and Foster⁷ demonstrated that SF_6^{-} could be trapped in an ICR for greater than 300 ms with no discernable decrease in signal intensity. It was postulated that SF_6^{-*} cooled radiatively to form a stable ion; the kinetic scheme consistent with these findings is given by eq 1.



Here, k_f is the electron-attachment rate constant, k_a is the autodetachment rate constant, k_d is the rate constant for dissociation, and k_r and k_c are the rate constants for cooling by radiative and collisional means, respectively. In retrospect, the known stability of SF_6^{-} from flowing afterglow studies⁸ clearly required some such scheme, since its lifetime at high pressure is essentially infinite.

The autodetachment lifetime has been treated theoretically by a number of workers. The first analysis by Compton et al.^{4b} showed that a SF_6^{-*} lifetime of 25 μs was consistent with an electron affinity (EA) of 1.1 eV. (The only measured value for the EA of SF_6 at that time was⁹ 1.49 eV.) Later treatments by Klots^{10a} and by Christophorou et al.^{10b} showed that the autodetachment lifetime for SF_6 should decrease markedly with increasing energy of the anion, but that the measured lifetimes were still consistent with an EA greater than 1 eV.

Since that time, a number of determinations¹¹ of the SF_6 electron affinity have been carried out, and the true value is now believed to lie much lower than originally thought. The most recent determination by Compton et al.^{11a} places the EA at 0.54 eV at 300 K. When this value is used in the calculation of the SF_6^{-} autodetachment lifetime, the predicted lifetime drops to well below 1 μs . This is clearly inconsistent with the TOF experiments, which show lifetimes one to two orders of magnitude larger than this new calculated value. Klots¹² has been able to use this electron affinity to calculate an autodetachment lifetime of 50 μs , but only by making the arbitrary assumption that each of the vibrational frequencies in SF_6^{-} is one-half in the neutral. For a moderately sized molecule like SF_6 , there is little physical basis for such an assumption.

The gas-phase ion-molecule chemistry of SF_6^{-} has been extensively studied, and many rather surprising results have been

obtained. Of the main group hexafluorides, SF_6 has by far the largest cross section for electron capture, even though the electron affinities of its analogues (SeF_6 , TeF_6) are more than 2 eV higher than that of SF_6 . SF_6 is also the only main group hexafluoride that will nondissociatively capture an electron.¹³ Once SF_6^{-} is formed, there appears to be a large kinetic barrier to charge transfer to neutrals. SF_6^{-} will transfer an electron efficiently if the reaction is highly exothermic¹³ (e.g., $\text{SF}_6^{-} + \text{SeF}_6 \rightarrow \text{SF}_6 + \text{SeF}_6^{-}$, $\Delta H^\circ = -2.3$ eV), but the rate is much less than unit efficient for moderately exothermic (≤ 1 eV) reactions.¹⁴ Electron transfer to SF_6 from other anions is also seen to be slow.^{14,15} Very often, fluoride transfer rather than electron transfer is the dominant pathway in reactions of¹⁶ SF_6^{-} . In addition, resonant charge transfer from SF_6^{-} to SF_6 is not observable^{7,14} (efficiency $< 10^{-3}$), even though such a process might be expected to be very efficient. Indeed, such resonant charge transfer is found to be very efficient for ions such^{17,18} as NO_2^{-} , SO_2^{-} , CS_2^{-} , and $\text{C}_6\text{H}_5\text{Br}^+$.

Finally, there have been indications that electron photodetachment from SF_6^{-} is very inefficient, even when it is irradiated with light of energy and intensity that would cause substantial photodetachment in anions with similar electron affinities. Such behavior would not be consistent with the large number of negative ions which have been studied by photodetachment in the past. However, there has not yet been reported any detailed study of the photodetachment spectrum of SF_6^{-} .

In summary, there remain major unanswered questions concerning the lifetime, reactions, and photophysics of SF_6^{-} . The model of an anion that closely resembles neutral SF_6 is inadequate to explain many properties of this ion. We believe these problems can be resolved if an appropriate model for SF_6^{-} is chosen.

Experimental Section

Sulfur hexafluoride (Matheson, >99.8% purity) was subjected to several freeze-pump-thaw cycles before use. SF_6^{-} was generated, trapped, and detected in a modified Varian V-5900 ion cyclotron resonance spectrometer. Its mode of production was electron impact on SF_6 . While SF_6^{-} was observed under a wide range of electron energies, the most stable signals were with electron energy ca. 50 eV and a SF_6 pressure of 10^{-6} torr. Since SF_6 has an appreciable nondissociative electron capture cross section only near 0 eV, presumably the majority of electrons captured are those which are initially inelastically scattered by the neutral molecules in the cell and then trapped in the ICR potential well.⁷ In order to obviate the possibility that photodetached electrons might also become trapped and then recaptured by SF_6 giving no apparent signal decrease, we ejected electrons from the cell by placing an oscillating radio frequency potential on the trapping plates of our system.¹⁹ Under conditions similar to our own, it has been shown that 99% of the electrons are removed from the cell within a few microseconds, and that the probability of an electron being recaptured by SF_6 is less⁶ than 1%. This electron ejection does not directly affect the behavior of other ions in the cell. All photodetachment experiments involving the broad band arc lamps were used in conjunction with a 300 nm long wavelength pass filter in front of the ICR cell window. It was found that light at wavelengths shorter than 300 nm produced photoelectrons (from the rhodium cell walls) which were rapidly captured by SF_6 . With the electron current off, no SF_6^{-} was detected upon irradiation when the filter was used, as compared to a sizable signal when no filter was used.

Concurrent with the generation of SF_6^{-} was the appearance of an SF_5^{-} signal, which had an intensity of 5–10% of the SF_6^{-} signal. Fluoride anion was never detected in the ICR under any conditions. Trapping times of 400 ms for SF_6^{-} in the ICR cell were routinely achieved.

Broad band light sources consisted of 1000-W high-pressure xenon and xenon-mercury arc lamps. Laser sources were a Coherent CR-12 argon ion laser and a Coherent CR-590 tunable dye laser pumped by the argon ion laser. All laser light used was expanded to the size of the ICR cell

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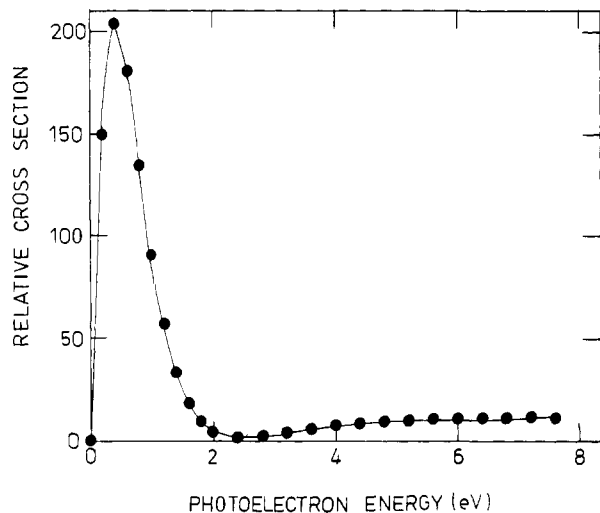


Figure 1. Theoretical photodetachment cross section for SF₆⁻ vs. photoelectron energy.

window (2.5 cm diameter). In the photodetachment experiments involving the argon ion laser, the cell could be irradiated with all visible output lines, or individual lines could be selected by use of an intracavity prism. The dye employed in the dye laser was rhodamine 6G (Eastman) pumped by 4 W for all lines to give 500 mW maximum output over 600–640 nm. Light intensity was measured by an uncalibrated Coherent 210 power meter.

Photodetachment Results

Under a variety of conditions, the SF₆⁻ signal change upon irradiation with broad band light from the arc lamps was often zero; occasionally, small, nonreproducible signal decreases were observed. When signal changes were observed, they were usually less than 3% of the SF₆⁻ signal. When decreases in the SF₆⁻ signal were observed, they were always accompanied by a rise in the SF₅⁻ signal. The use of electron ejection decreased the size of the initial SF₆⁻ signal, but did not seem to have an effect on the magnitude of the signal decrease, implying that the small signal changes seen were not due to photodetachment. In a typical arc lamp experiment, the light intensity entering the ICR cell was determined to be ca. 4 W for the xenon lamp and 1 W for the xenon-mercury lamp.

Lasers were also used as high intensity light sources. Irradiation with up to 5 W by the argon ion laser produced small, irreproducible decreases and often had no apparent effect on the SF₆⁻ signal. There did not seem to be any difference whether one line or all lines from the laser were used. Light of such energy and intensity would be expected to bleach completely anions possessing comparable electron affinities. In addition, irradiation by up to 500 mW of red light from the argon ion pumped dye laser had little to no effect on the SF₆⁻ signal.

In conclusion, we find experimentally that SF₆⁻ has an extremely low cross section for electron photodetachment. The small signal changes sometimes observed are not understood and may be artifacts. We have previously carried out enough experiments of this general kind to say with certainty that were photodetachment occurring with a cross section comparable to those of other negative ions, we would have observed it.

Photodetachment Theory

The photodetachment cross section as a function of energy was calculated for octahedral SF₆⁻ in order to see if there is any theoretical reason why photodetachment should not be expected under the conditions of our experiment. This calculation is based on the assumption that the photodetachment process is a dipole-allowed transition from the highest occupied molecular orbital of the anion to a continuum electron described by a plane wave.²⁰ This theory has shown good agreement with experiment for a

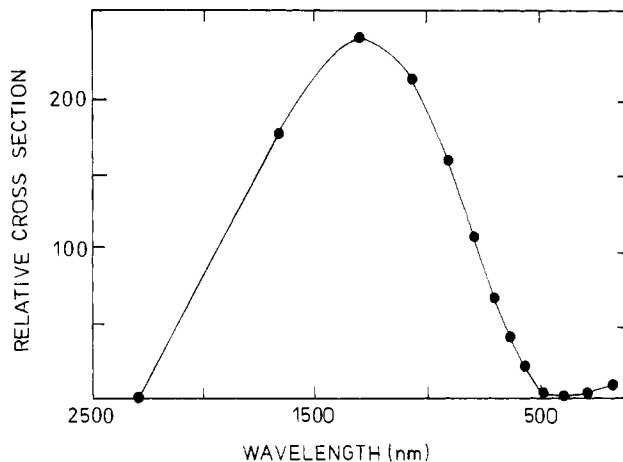


Figure 2. Theoretical photodetachment cross section for SF₆⁻ vs. wavelength of incident photon assuming a threshold of 2300 nm (0.54 eV).

variety of ions. The molecular orbital coefficients used were determined by means of a CNDO calculation on SF₆. The results of this calculation indicate that the highest occupied molecular orbital of SF₆⁻ is σ antibonding with A_{1g} symmetry. This is in good agreement with past theoretical treatments²¹ of SF₆.

The calculated cross section for SF₆⁻ (Figure 1) shows a sizable photodetachment cross section a few tenths of an electron volt above threshold. The maximum cross-section value, 2×10^{-16} cm², is very large relative to other anions studied in the past. The shape of the curve is also very interesting, as the usual behavior for a cross section is to rise to and remain at some constant value. In the SF₆⁻ case, the theoretical curve rises rapidly to a maximum, drops sharply to a value near zero, and then slowly rises to a value ca. 5% of the initial maximum.

A cross-section vs. wavelength curve will obviously depend on the photodetachment threshold, equal to the adiabatic electron affinity (EA) of the neutral. The electron affinity of SF₆ is believed from collisional ionization experiments to be¹¹ ≥ 0.54 eV at 300 K. The cross-section vs. wavelength curve for this EA is shown in Figure 2.

Knowing the cross section and photon intensity, it is possible to calculate the signal decrease upon photodetachment by applying a steady-state kinetic model to ions in the ICR cell.²² This model yields kinetic eq 2, where I_w and I_{w_0} are the ion signal intensities with the light on and the light off, respectively. In eq 2, k_2 is

$$I_w/I_{w_0} = k_2 t / [k_p(\lambda) + k_2] t \quad (2)$$

the pseudo-first-order rate constant for nonreactive ion loss from the cell, and is approximately equal to $1/\tau$, where τ is the trapping time for SF₆⁻ in the cell (400 ms). The rate constant, k_p , for ion loss due to photodetachment averaged over the spectral range used can be calculated from eq 3, in which $\sigma(\lambda)$ is the photodetachment cross section, $F(\lambda)$ is the spectral distribution function, and ρ is the total photon flux incident on the sample.

$$k_p = \rho \int \sigma(\lambda) F(\lambda) d\lambda \quad (3)$$

Our model predicts extensive photodetachment from SF₆⁻ under the conditions of our experiment. We obtain essentially identical results for any photodetachment threshold chosen in the range 0.5–1.2 eV. The results of our calculation are consistent with our past experience with other negative ions. Although our method

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tends to overestimate the absolute value of the cross section,²² other negative ions with smaller calculated cross sections undergo extensive photodetachment under conditions similar to those employed here. Thus, we expect a neutral-like, octahedral SF₆⁻ to exhibit "normal" behavior. The only instances in the past where such a serious discrepancy between the experimental and theoretical behavior of an ion with respect to photodetachment has occurred has been in systems such as CF₃⁻ and NO₂⁻, which have very poor Franck-Condon factors for electron photodetachment.

Discussion

The model of an SF₆⁻ that structurally resembles neutral SF₆ is not consistent with the lack of photodetachment we find in our experiments. This implies that the SF₆⁻ we observe has a structure much different from that of the neutral. Indeed, we can rationalize a low photodetachment cross section from a distorted SF₆⁻ as a result of poor Franck-Condon overlap for the transition from a distorted anion to a ground-state neutral (plus electron).

One possibility is an SF₆⁻ which has all of its sulfur-fluorine bonds lengthened and weakened. Such a system would still be octahedral, but vertical photodetachment would result in a vibrationally excited SF₆ neutral. Photodetachment to the ground-state SF₆ neutral would be weak due to small Franck-Condon factors.

A second, intriguing model is one in which SF₆⁻ exists predominantly as an ion-molecule association complex (SF₅F)⁻. Such a complex would have very poor Franck-Condon factors for adiabatic photodetachment. The strong Franck-Condon transition would give SF₅ plus F plus a free electron in the limiting distorted case. We would not expect to see photodetachment giving SF₅ + F + e⁻, since this would require photons with energy greater than 4.4 eV, well above the energies available in our experiments.

If we assume that a sulfur-fluorine bond is broken in the electron-capture process, the SF₆⁻ formed by attachment of a zero-energy electron does not contain enough energy to dissociate into two fragments; the lowest energy process SF₆ + e⁻ → SF₅⁻ + F requires an activation energy⁸ of 0.43 eV. The main attractive force in such a complex is the interaction of the negative charge of the anion with the ion-induced dipole of the neutral. Since SF₅ is much more polarizable than F, we might expect that the negative charge in the complex resides mainly on the fluorine, despite the somewhat larger electron affinity of SF₅. The energy of binding F⁻ to SF₅, ca. 1 eV, is not unreasonable for this suggested model. A driving force for complex formation would be the large electron affinity (>3.4 eV) of the product fragments, as well as the resulting ion-dipole interaction.

We find that both models are consistent with the peculiar properties associated with SF₆⁻. In the remainder of this paper we show that the ion-molecule chemistry and the autodetachment lifetime of SF₆⁻ fit well with the suggestion of a distorted (loose) structure for this ion, but not for a neutral-like (tight) model. We will also compare the two proposed models for loose SF₆⁻.

Ion-Molecule Reactions

The gas-phase ion-molecule chemistry of SF₆⁻ is peculiar in that there appears to be a kinetic barrier to electron transfer from the anion to a neutral collision partner. One indication of this is the failure to observe resonant charge transfer between SF₆⁻ and neutral SF₆. For example, Lifshitz et al.¹⁴ failed to detect any electron transfer between isotopes of SF₆ in a tandem mass spectrometer. Beauchamp and Foster⁷ obtained similar results in an ICR study. From these experiments, the efficiency of resonant charge transfer must be ≤10⁻³. In contrast, resonant charge transfer for the polyatomic ions CS₂⁻, NO₂⁻, SO₂⁻, and C₆H₃Br⁺ proceeds^{17,18} with high efficiency.

A kinetic barrier also exists for some exothermic SF₆⁻ charge-transfer reactions.^{14,15} No electron transfer is observed to SO₂, despite the fact that the reaction would be 0.45 eV exothermic. Electron transfer from SF₆⁻ to NO₂ (Δ*H*^o = -1.9 eV) is two orders of magnitude slower than the analogous transfer from O⁻ to NO₂ (Δ*H*^o = -0.9 eV), despite the difference in exothermicities. Efficient charge transfer from SF₆⁻ is observed only when the reaction becomes much more exothermic; reactions with SeF₆,

TeF₆, and UF₆ (EA = 2.9, 3.3, and ≥5.1 eV, respectively) proceed readily¹³ to generate the corresponding molecular negative ions.

The model of a distorted SF₆⁻ provides an explanation for the observed slow electron transfer. Direct transfer of an electron from ground-state SF₆⁻ to ground-state SF₆ would produce both a neutral and an anion distorted by considerable amounts from their equilibrium geometries. This process is substantially endothermic and cannot occur. Alternatively, in the Marcus electron-transfer formalism,²⁶ we can distort both ion and neutral to the point at which they have equal energy and then the electron transfer will be rapid. Such distortion, however, requires energy, so that the reaction will be slow for this thermoneutral reaction.

A sizable fraction of the SF₆⁻ in the mass spectral experiments should be vibrationally hot, owing to the short time scale (μs) of the experiment. If a tight SF₆⁻ is a true intermediate in the electron-capture process, one might expect some sort of steady-state concentration of this species within the mass spectrometer. Since no resonant charge transfer is observed even for this activated SF₆^{-*}, we infer that SF₆^{-*} with a geometry close to that of the neutral exists at most only transiently in the electron capture and detachment processes.

Autodetachment Lifetimes

The earliest determinations of the SF₆^{-*} autodetachment lifetime were performed with time-of-flight (TOF) mass spectrometers employing a retarding potential difference technique. The time scale of this technique is fast enough that relaxation of SF₆^{-*} is only a minor process. Autodetachment lifetimes determined in this manner have been reported⁴ as 10, 25, and 60 μs.

The behavior of SF₆^{-*} has also been studied using ICR techniques. The SF₆⁻ formation is achieved through the capture of electrons that have been scattered and then trapped in the ICR potential well. However, electrons that autodetach are also trapped in this well, and are rapidly recaptured by SF₆. Consequently, SF₆^{-*} is maintained at a high steady-state concentration. The TOF experiments differ in that autodetached electrons are not recaptured. In addition, since the time scale of an ICR experiment is longer than that of a TOF experiment, it is possible for SF₆^{-*} to stabilize radiatively during the experiment, as proposed by Beauchamp.^{7,24} Thus, a simple first-order rate law is not adequate to describe the behavior of SF₆⁻ in an ICR, and attempts to interpret data in this manner will yield ambiguous results. This was elegantly demonstrated by Odom, Smith, and Futrell,⁶ who were able to extract autodetachment lifetimes ranging from 50 μs to 10 ms by applying a first-order rate law to their ICR data.

Statistical rate theory has been used^{4,10} in order to predict the autodetachment lifetime of SF₆^{-*}. Assuming that SF₆^{-*} exists in equilibrium with neutral SF₆ and free electrons, the principle of detailed balance leads to expression 4. Here, *k_a* and τ_a are

$$k_a(E) = 1/\tau_a = \frac{\rho_0(E)}{\rho_-(E)} \sigma(v)v \quad (4)$$

the rate constant and lifetime for autodetachment, ρ₀ is the density of states for the neutral and electron, ρ₋ is the density of states for the anion, and σ(*v*) is the cross section for the capture of an electron with velocity *v*. This expression gives only a lower limit for the autodetachment rate constant, as the ρ₋ appropriate to this calculation may be smaller than the theoretical maximum, if all states of the negative ion at a given energy are not active or accessible after electron capture.

In this calculation, the neutral molecule is assumed to be in its nondegenerate ground state, so that ρ₀ is equal to the state density of a free electron. The electron-capture cross section for SF₆ has been measured,¹ so that only the density of states of the anion is needed in order to predict a lifetime. The density of states in the anion may be estimated using the Whitten-Rabinovitch²⁷

(26) Christe, K. O.; Curtis, E. C.; Schack, C. J.; Pilipovich, D. *Inorg. Chem.* **1972**, *11*, 1679.

(27) Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley-Interscience: London, 1972; p 133.

Table I. Calculated SF₆⁻ * Lifetime (μs)

model	statistical rate theory
neutral SF ₆	0.02
SF ₆ w/vibrations loosened 100 cm ⁻¹	0.20
SF ₅ ⁻ w/extra 200, 200, and 100 cm ⁻¹ vibrations	8.0
SF ₅ ⁻ w/extra 100, 100, and 100 cm ⁻¹ vibrations	26
SF ₅ ⁻ w/extra 200, 200, and 20 cm ⁻¹ vibrations	36

approximation which requires the knowledge of the vibrational frequencies of the anion. Since octahedral SF₆⁻ is a large molecule, it is not expected that the addition of a single electron to a σ* orbital would change the vibrational frequencies drastically from those of neutral SF₆. The state density will depend strongly on the SF₆ electron affinity, as a larger electron affinity results in a more highly energized anion.

The initial use of this formulation assumed that the vibrational frequencies of SF₆⁻ were the same as those of the neutral. It was determined^{4b} that a lifetime of 25 μs was consistent with an SF₆ electron affinity greater than 1 eV. The theory seemed to fit well with the experiment, as the only measured value of the SF₆ electron affinity at that time was⁹ 1.49 eV. Klots^{10a} and Christophorou et al.^{10b} later showed that the predicted lifetime depends strongly on the internal energy of the anion, as well as on the electron affinity of the neutral. For an SF₆ electron affinity of 1.5 eV, they calculated autodetachment lifetimes in the 50–200 μs range.

However, extensive experimental work since that time indicates that the early SF₆ electron affinity value was in error, and that the true value may lie well under 1 eV. With the use of Compton's most recent value^{11a} of 0.54 eV, the predicted autodetachment lifetime drops into the tens of nanoseconds range, three orders of magnitude smaller than experimentally measured.

From eq 4, we see it is necessary to raise either the SF₆ electron affinity or the negative ion density of states value in order to bring the theoretical lifetime into line with the experimental determination. The negative ion state density would be higher if the vibrational frequencies in the anion were lower than those of the neutral, i.e., the ion is "loosened up". Stock et al.²⁵ have reproduced the experimental lifetime by reducing all vibrational frequencies in SF₆ by one-half and using those values in the calculation, and alternatively by using an SF₆ model where a few key vibrations are drastically reduced in energy. Klots¹² has achieved similar results by reducing the SF₆ frequencies by one-half.

The notion of an SF₆⁻ that is distorted from the parent neutral nicely rationalizes the higher density of states required to make the theoretical autodetachment lifetime consistent with experiment. In the case of the octahedral anion model, longer (weaker) bonds result in a higher state density than in the neutral. As noted, the simplest consistent octahedral model requires that the anion has all of its vibrational frequencies halved relative to SF₆. Alternatively, a "tight" SF₆⁻ model is supported only if the electron affinity of SF₆ lies near 1 eV (see Note Added in Proof).

The ion-molecule complex model of SF₆⁻ also provides a rationale for a much higher density of states. The interaction between SF₅ and F fragments in a negative ion association complex is of much lower energy than in an analogous bonding situation. In addition, SF₅⁻ is known²⁶ to have much lower vibrational frequencies than SF₆.²⁷

Because we do not know its exact structure or frequencies, we cannot determine the exact state density for a molecular complex (SF₅·F)⁻. However, we are able to calculate state density values for a number of models which we believe approximate the interactions of the two fragments. (SF₅·F)⁻ has 15 vibrational degrees of freedom, and we will assume that 12 correspond to the vibrational frequencies of SF₅⁻, which have been measured.²⁶ We modeled the three remaining degrees of freedom as low-frequency vibrations involving SF₅ and F. Different values for these vibrations were used in conjunction with the SF₅⁻ frequencies in a Whitten-Rabinovitch formulation²⁸ to generate state densities

for the complex. An SF₆ EA of 0.54 eV was used in the calculation.

The results of this modeling are shown in the first column of Table I. The models assuming complex ion behavior (SF₅⁻ vibrations, low-frequency SF₅-F stretch, to low frequency SF₅-F bends) yield lifetimes in the same range as the experimental values (i.e., tens of μs). It is seen that the predicted lifetimes do not vary drastically with the three SF₅-F vibrations chosen. In contrast, moderate weakening of the neutral SF₆ frequencies (100 cm⁻¹ less for each vibration) results in a lifetime still two orders of magnitude smaller than experiment. Only drastic weakening of the neutral SF₆ frequencies gives autodetachment lifetimes comparable to experiment.^{12,25}

Neither the theoretical treatments nor any of the experimental evidence speak to the mechanism by which the electron attaches to the neutral and is detached from the negative ion. Nevertheless the hypothesis of a distorted SF₆⁻ structure and the very large²⁹ electron-capture cross section suggest that the "transition state" for capture-autodissociation may look like ground-state SF₆ plus a localized electron.

Other Studies Involving SF₆⁻

Little experimental information concerning the structure of SF₆⁻ is presently available. Electron spin resonance techniques have been used to probe SF₆⁻ formed by irradiation of SF₆ matrices with high-energy electrons³⁰ or γ irradiation.³¹ These studies indicate that the sulfur center is surrounded by six fluorines which are equivalent on the ESR time scale. This may be due to either an octahedral SF₆⁻ or to a system with six rapidly interconverting fluorine ligands.

Matrix-isolated SF₆⁻ has also been the subject of other spectroscopic studies. Bhattacharya and Willard³² have measured the optical absorption spectrum of SF₆⁻ trapped in a 3-methylpentane matrix. They attributed to SF₆⁻ a broad, featureless absorption starting at 540 nm and rising with photon energy. In another study, Barefield and Guillory³³ measured the infrared absorption spectrum of the products from irradiation-initiated charge transfer from NO or alkali atoms to SF₆ in an argon matrix. After irradiation, they found a new 594-cm⁻¹ absorption of 10 K which disappeared upon annealing to 30 K. They were not able to match this absorption with any other previously measured SF_n species, so the 594-cm⁻¹ absorption was tentatively assigned to SF₆⁻. This corresponds to the red-shifted 613-cm⁻¹ ν₄ mode of SF₆. While they also expected to see a red-shifted peak corresponding to the ν₃ mode of SF₆, no such absorption was found in their system.

Many other studies have taken advantage of the unique properties of SF₆ and its negative ion. SF₆ has frequently been employed as an electron scavenger both in the gas phase and solution. In pulse radiolysis experiments, SF₆ rapidly captures solvated electrons, dissociating^{2a} to SF₅ and F⁻. In the gas phase, SF₆⁻ is found to be a very good fluoride donor in ion-molecule reactions.¹⁶ But while these experiments shed light on the behavior and reactivity of SF₆⁻, the actual structure of the gas-phase ion has not been experimentally resolved.

Comparison with Other Systems

There are many halogenated systems besides SF₆⁻ which capture low-energy electrons, but the majority of these yield dissociation products rather than the parent negative ion. The SF₆ analogues SeF₆ and TeF₆ yield only fragmentation products (e.g., SeF₅⁻ + F) upon electron capture.¹³ Other halogenated species such as CCl₄, CCl₃F, and CF₃Cl also capture low-energy electrons,^{34,35} but yield only chloride anion and the corresponding neutral as products.

(29) Compton, R. N.; Huebner, R. H. *Adv. Rad. Chem.* **1970**, *2*, 366.

(30) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1966**, *45*, 1845.

(31) Morton, J. R.; Preston, K. F.; Tait, J. C. *J. Chem. Phys.* **1975**, *62*, 2029.

(32) Bhattacharya, D.; Willard, J. E. *J. Phys. Chem.* **1980**, *84*, 146.

(33) Barefield, J. E.; Guillory, W. A. *J. Phys. Chem.* **1977**, *81*, 634.

(34) Christophorou, L. G.; Stockdale, J. A. D. *J. Chem. Phys.* **1968**, *48*, 1956.

(35) Drzalic, P. S., unpublished results.

One important difference that sets SF₆ apart from these species is its thermochemistry. The behavior of an anion after electron capture depends strongly on the internal energy of the ion and the reaction pathways available to it. Dissociative electron capture for SF₆ is 0.4 eV endothermic, whereas dissociation is exothermic for the other species mentioned. Since dissociation is rapid compared to any sort of relaxation mechanism available to these ions, an accessible dissociative channel would be the dominant pathway after electron capture. Such behavior is reflected by the observation that dissociative electron capture by SF₆ (SF₆ + e⁻ → SF₅⁻ + F) increases rapidly with increasing temperature of the gas.³⁶ This is consistent with a larger Boltzmann distribution of SF₆ molecules having the necessary 0.4 eV internal energy to dissociate after electron capture. Additionally, the ratio of SF₅⁻/SF₆⁻ formed in flowing afterglow studies of SF₆ electron attachment is much smaller than in studies done at much lower pressures.⁸ In the afterglow studies, collisional stabilization of SF₆^{-*} presumably occurs fast enough to compete with dissociation and decrease the amount of SF₅⁻ formed.

Other systems with behavior similar to that of SF₆⁻ suggest that the ideas presented here may be applicable to a variety of systems. For example, UF₆⁻ has been reported not to undergo resonant charge transfer to neutral UF₆,³⁷ in analogy to the SF₆⁻/SF₆ system. Another possibility is CF₃Cl⁻, which does not appear to photodetach an electron when irradiated by visible light,^{35,38} despite the fact that its electron affinity should be³⁹ under 1 eV. A third example is CF₃O⁻, which also does not photodetach under irradiation with visible light.³⁵ In addition, we have found^{40a} that CF₂O is efficient relative to other neutral gases in collisionally relaxing CF₃O^{-*}. While this may be due to near resonant V-V coupling in a CF₃O⁻·CF₂O collision complex, it might also be attributed to a degenerate fluoride transfer mechanism. Such fluoride transfer would be expected to be efficient from a CF₂O·F⁻ complex.^{40b}

There are a number of matrix-isolated halogenated species which form stable negative ions upon irradiation. Williams⁴¹ has found the CF₃X system (X = Cl, Br, I) forms stable negative ions upon γ irradiation at 77 K. ESR spectra indicate that the spin density for these species lies partially on the unique halogen, indicating a strong interaction between the halogen and the carbon center. Similar results are found for the (CF₃)₃CI system.⁴² In contrast, many alkyl halides undergo dissociative electron capture under similar conditions, yielding only the weakly bound system⁴³ R·---X⁻. Why these systems behave differently is still subject to discussion, and the nature of the interactions within these radical anion species remains to be explored.

Models for SF₆⁻

Based on the present photodetachment results and the autodetachment and electron-transfer experiments cited, we believe that SF₆⁻ exists as a structure that differs in geometry and has much weaker bonding than that in neutral SF₆. Two simple models are consistent with the above criteria. One is an SF₆⁻ which has all of its sulfur-fluorine bonds lengthened, but still retains an octahedral structure. The other model assumes that SF₆⁻ exists as an association complex, (SF₅·F)⁻, where the attractive force between the fragments is at best a weak chemical bond, and largely an electrostatic interaction between the ion and the induced dipole of the neutral.

(36) Spence, D.; Schulz, G. J. *J. Chem. Phys.* **1973**, *58*, 1800.

(37) Beauchamp, J. L. *J. Chem. Phys.* **1976**, *64*, 929.

(38) The CF₃Cl⁻ observed in these experiments was formed by electron impact on CF₃COCl, see: Asublojo, O. I.; Blair, L. K.; Brauman, J. I. *J. Am. Chem. Soc.* **1975**, *97*, 6685.

(39) The electron affinities of CF₃I and CF₃Br have been measured as 1.57 and 0.91 eV, respectively. See: Compton, R. N.; Reinhardt, P. W.; Cooper, C. D. *J. Chem. Phys.* **1978**, *68*, 4360.

(40) (a) Jasinski, J. M.; Brauman, J. I. *J. Chem. Phys.* **1980**, *73*, 6191. (b) CF₃O⁻ has been shown to transfer fluoride readily to carboxylic acids. See: Clair, R. L.; McMahan, T. B. *Can. J. Chem.* **1979**, *57*, 473.

(41) Hasegawa, A.; Williams, F. *J. Chem. Phys. Lett.* **1977**, *46*, 66.

(42) Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1980**, *102*, 2860.

(43) Symons, M. "Chemical and Biochemical Aspects of ESR Spectroscopy"; Halsted Press: New York, 1978; pp 73-77.

While we cannot distinguish experimentally between the two structures, we do find it difficult to reconcile the octahedral ion with the requirements of the autodetachment lifetime and a low electron affinity (but see Noted Added in Proof). As noted (vide supra), vibrational frequencies of the anion need to be approximately one-half of those in the neutral. This means the addition of an electron to a sulfur-fluorine σ antibonding orbital weakens all ion bonds by a substantial amount.

There are studies on some simple σ-bonded systems that seem to make such drastic reductions unlikely. For example, Andrews⁴⁴ has shown that the fundamental vibrational frequencies of F₂⁻ and Cl₂⁻ correspond to roughly one-half the frequencies of the parent neutrals. Thus, addition of an electron to a σ* orbital reduces both the bond order and vibrational frequency by one-half. However, in SF₆⁻ the σ-bonding molecular orbitals correspond to six sulfur-fluorine bonds. Because the σ* orbital involves all the atoms, we expect the average bond order to decrease only slightly. Consequently, we expect that the vibrational frequencies in an octahedral SF₆⁻ should not be too much weaker than those in the neutral.

Alternatively, it is possible to reconcile the autodetachment lifetime without halving all frequencies if one or two of the low-frequency vibrations is lowered by a substantial amount (i.e., 1/5 to 1/10). However, it is again difficult to imagine one electron affecting any one of the SF₆ vibrational modes by such a significant amount.

The association complex model for SF₆⁻ presents no such difficulties in rationalizing a large state density, as the interaction between the two fragments is weak compared to chemical bonding. While the idea of this anion existing as an ion-molecule complex is novel, it does have a relationship to other halogenated species and their electron-capture characteristics. A large number of halogenated molecules undergo dissociative electron capture (vide supra). This process may be thought of as formation of an ion-molecule complex which contains enough internal energy to dissociate into ionic and neutral fragments. SF₆⁻ is a special case where the interaction is very strong, and dissociation after electron capture is still 0.4 eV endothermic. As mentioned, many halogenated systems besides SF₆⁻ exhibit anomalously slow electron transfer and photodetachment rates, and it will be interesting to discover whether the proper model for SF₆⁻ also rationalizes the behavior of these other systems.⁴⁵

SF₆ in High-Voltage Devices

Sulfur hexafluoride has seen extensive use as a dielectric material in high-voltage electrical devices.⁴⁶ The ability of SF₆ to extinguish arcing as well as its chemical inertness makes it useful in this regard. These macroscopic properties may be related to the microscopic electron-capture properties of SF₆ and the stability of the resulting anion.

Sulfur hexafluoride quickly scatters and captures discharged electrons. Consideration of the electron attachment and detachment rate constants for SF₆ at 300 K shows that even the equilibrium process SF₆ + e⁻ ⇌ SF₆^{-*} reduces the free-electron concentration by a factor of 10⁶ at an SF₆ pressure of 10 torr. Dissociative attachment is endothermic and not an important process at ambient temperatures. Since SF₆^{-*} has a lifetime of tens of microseconds, collisional relaxation of the vibrationally excited anion rapidly leads to stable SF₆⁻. At this point, propagation of charge through the medium is slowed owing to the low mobility of the large SF₆⁻ system. Since SF₆⁻ does not undergo

(44) Howard, W. F., Jr.; Andrews, L. *J. Am. Chem. Soc.* **1973**, *95*, 2056, 3045.

(45) A referee has suggested that the Franck-Condon factor for photodissociation of an (SF₅·F)⁻ complex should be large, and the apparent lack of photodissociation might argue against this model. However, the photodissociation cross section generally is appreciable only if an excited state of the system is involved. [See: Dunbar, R. C. "Gas Phase Ion Chemistry", Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2.] Consequently, one does not usually expect to observe photodissociation at the thermochemical threshold unless this occurs at an energy above the onset of transitions to excited states.

(46) Rieder, W. *Sci. Am.* **1974**, *224* (1), 76.

efficient resonant charge transfer, electrons are not able to hop from one SF₆ to another, again inhibiting rapid propagation of charge.

Conclusion

We have shown that many of the properties of the negative ion SF₆⁻ are not consistent with a structure resembling the parent neutral. The lack of photodetachment and the kinetic barrier associated with SF₆⁻ ion-molecule reactions are consistent with a highly distorted anionic structure. The autodetachment lifetime calculated from statistical rate theory implies that SF₆⁻ is much less tightly bonded than the parent neutral. While the model of a loose octahedral SF₆⁻ and the model of an ion-molecule association complex for SF₆⁻ are both consistent with these observations, we find the bonding changes required by the octahedral system difficult to rationalize. There are hints that other halogenated systems besides SF₆⁻ exhibit behavior which may be explained by similar models. Whether these models are a general

phenomena or are specific to SF₆⁻ remains to be explored.

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Note Added in Proof. Recent experimental⁴⁷ and theoretical⁴⁸ work supports an SF₆ electron affinity of roughly 1 eV. As noted, the statistical autodetachment lifetime is consistent with a "tight" SF₆⁻ if the SF₆ EA is this high, and the distorted octahedral model becomes acceptable. The complex model remains consistent as well.

The infrared multiphoton photochemistry of SF₆⁻ also suggests a distorted structure.⁴⁹

(47) Streit, G. E. *J. Chem. Phys.*, submitted for publication.

(48) Hay, P. J. *J. Chem. Phys.*, in press.

(49) Drzagic, P. S.; Brauman, J. I. *Chem. Phys. Lett.* 1981, 83, 508.

Chloronium Ions as Alkylating Agents in the Gas-Phase Ion-Molecule Reactions with Negative Temperature Dependence

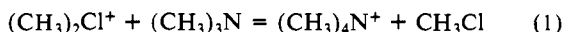
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Abstract: The kinetics of the reactions Me₂Cl⁺ + B = MeB⁺ + MeCl and MeEtCl⁺ + B = MeB⁺ or (EtB⁺) + EtCl (or MeCl) were studied with a pulsed-electron-beam, high-pressure mass spectrometer. At room temperature the rate constants were found to increase in the order B = benzene, toluene, isopropylbenzene, EtOH, Me₂O, Et₂O. At this point *k* became equal to the orbiting capture rate constant *k*_L ≈ 10⁻⁹ molecule⁻¹ cm³ s⁻¹. NH₃ and Me₃N were alkylated at orbiting capture rates. The temperature dependence of the rate constants for B = toluene, Me₂O, and Et₂O was examined. The rate constants were found to increase with decrease of temperature. This increase continued until the rate constants reached the magnitude of the orbiting rate constants *k*_L. The rates remained approximately independent of temperature below this temperature. At low temperatures the collision-stabilized Me₂Cl⁺B and MeEtCl⁺B could be observed. The temperature dependence of the equilibrium Me₂Cl⁺ + toluene = (Me₂Cl-toluene)⁺ was measured and led to the corresponding Δ*H*^o and Δ*S*^o. The reaction Me₂Cl⁺ + benzene = Me-benzene⁺ + MeCl was found to have positive temperature dependence. On the basis of the above data it is suggested that the reactions Me₂Cl⁺ + B = MeB⁺ + MeCl have an internal barrier in the potential energy of the reaction coordinate. This barrier protrudes above the energy level of the reactants (Me₂Cl⁺ + B) for B = benzene. This leads to positive temperature dependence. For all other B, the top of the internal barrier lies below the level of the reactants and sinks lower, roughly in the order of increasing basicity of B. This leads to negative temperature dependence (toluene, isopropylbenzene, Me₂O, Et₂O). For B = NH₃, Me₂NH₂, Me₃N, the barrier is so low that the reactions have orbiting capture rates equal to *k*_L. Alkylation of bases B by chloronium ions like Me₂Cl⁺ might have considerable utility in mass spectrometric analysis by chemical ionization. Ethers can be distinguished from alcohols and tertiary amines from primary and secondary amines. The alkylated ethers and the tertiary amines have no protic hydrogens and therefore do not form strongly hydrogen-bonded adducts.

Introduction

This work represents a continuation of studies of the gas-phase chemistry of halonium ions. Earlier work^{1,2} provided binding energies R⁺-XR' from measurement of the equilibria R⁺ + XR' = (RXR')⁺. The present report deals with alkylation of bases B by alkylchloronium ions. An example of such a reaction is shown in eq 1. We have examined the methylation and ethylation



of a number of π and n donor bases. Alkylbromonium and -chloronium ions are often used as alkylating agents in solution and have synthetic utility.³ We thought it of interest to examine

whether the same reactions occur in the gas phase. These reactions can have a certain utility in the gas phase, for example, as a convenient route to the preparation of tertiary oxonium and quaternary ammonium ions.

The rates of exothermic ion-molecule reactions in the gas phase are generally chemically featureless since the rate constants can be predicted from the Langevin or ADO orbiting capture rates.⁴ These depend on reduced mass, polarizability, and dipole moment and are always close to *k*_L ≈ 10⁻⁹ molecule⁻¹ cm³ s⁻¹. Furthermore, there is only a very weak temperature dependence. The alkylation rates by chloronium ions, observed in the present work, showed very different behavior. Some reactions showed negative tem-

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(3) Olah, G. A. "Halonium Ions"; Wiley: New York, 1975.

(4) "Gas Phase Ion Chemistry"; Bowers, M. D., Ed.; Academic Press: New York, 1979.