J. Phys. Chem. A **2001,** *105,* 8403−8412

Fragmentation of Energy-Selected $SF_5CF_3^+$ Probed by Threshold Photoelectron Photoion Coincidence Spectroscopy: Bond Dissociation Energy of SF_{5}–CF_3 and Its Atmospheric Implications

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Received: April 26, 2001; In Final Form: June 20, 2001

Using tunable vacuum-UV radiation from a synchrotron in the range 12−26 eV, we have measured the threshold photoelectron and threshold photoelectron−photoion coincidence spectrum of SF_5CF_3, a new anthropogenic greenhouse gas. The ground state of $SF_5CF_3^+$ is repulsive in the Franck−Condon region, the parent ion is not observed, and the onset of ionization can only give an upper limit to the energy of the first dissociative ionization pathway of SF_5CF_3, to $CF_3^+ + SF_5 + e^-$. We have determined the kinetic energy released into the two fragments over a range of photon energies in the Franck−Condon region of the ground state of $SF_5CF_3^+$. Using an impulsive model, the data has been extrapolated to zero kinetic energy to obtain a value for the first dissociative ionization energy for SF_5CF_3 of 12.9 ± 0.4 eV. A similar experiment for CF_4 (to $CF_3^+ + F + e^-$) and SF_6 (to $SF_5^+ + F + e^-$) yielded values for their dissociative ionization energies of 14.45 ± 0.20 and 13.6 ± 0.1 eV, respectively, in agreement with previous data on the CF_3 and SF_5 free radicals. The enthalpy of formation at 0 K of SF_5CF_3 is determined to be −1770 ± 47 kJ mol^{-1}, and the dissociation energy of the SF_5–CF_3 bond at 0 K to be 392 ± 43 kJ mol^{-1} or 4.06 ± 0.45 eV. The implication of this bond strength is that SF_5CF_3 is very unlikely to be broken down by UV radiation in the stratosphere. In addition, over the complete energy range of 12−26 eV, coincidence ion yields of SF_5CF_3 have been determined. CF_3^+ and SF_3^+ are the most intense fragment ions, with SF_5^+, SF_4^+, and CF_2^+ observed very weakly. Energetic constraints require that SF_3^+, SF_4^+, and CF_2^+ can only form with CF_4 + F, CF_4, and SF_6, respectively, so that fragmentation of $SF_5CF_3^+$ to these ions involves migration of a fluorine atom across the S−C bond.

1. Introduction

The greenhouse effect is usually associated with small polyatomic molecules such as CO_2, H_2O, CH_4, N_2O, and O_3. The “natural” greenhouse gases, mainly CO_2 and H_2O, have been responsible for hundreds of years for maintaining the temperature of the earth at ca.290 K, suitable for habitation. The “enhanced” greenhouse gases, mainly CH_4, N_2O, and O_3, have concentrations in the atmosphere which have increased dramatically in the last 50−100 years, have infrared (IR) absorptions where CO_2 and H_2O do not absorb, and are believed to be the main culprits for global warming. It is now clear, however, that there are larger polyatomic gases of low concentrations in the atmosphere which can contribute significantly to global warming because of their exceptionally strong IR absorption in the parts of the 5−25 μm region where other greenhouse gases do not absorb. A notable example is SF_6, which has a global warming potential (GWP) of 22 200 relative to CO_2 over a time horizon of 100 years. In a very recent paper,[1] Sturges et al. have detected SF_5CF_3 in the atmosphere. Previously unreported, it is believed to be anthropogenic in nature, a breakdown product of SF_6 in high-voltage equipment. IR absorption measurements have shown that it has the highest radiative forcing per molecule of any gas found in the atmosphere to date (0.57 W m^{-2} ppb^{-1}). Antarctic firn measurements suggest that it has grown from a concentration of near zero in the late 1960s to ca. 0.12 parts per trillion in 1999, and stratospheric profiles suggest that the lifetime of this species in the atmosphere is between several hundred and a few thousand years. It is estimated that the GWP of SF_5CF_3 is 18 000 relative to CO_2, with only SF_6 having a higher value.

From an applied, atmospheric viewpoint, one of the main questions to answer is whether SF_{5}–CF_3 can be broken down by UV photodissociation in the stratosphere, or whether the loss of this species from the atmosphere is governed by bimolecular ionic reactions (i.e. electron attachment and ion−molecule reactions) and vacuum-UV photodissociation processes in the mesosphere. The strength of the SF_{5}–CF_3 bond is needed to answer this question. Photodissociation generally occurs through excitation of a molecule to a repulsive state. Close to the energy threshold, the cross section for photodissociation is negligibly small. Thus, CF_4 has a dissociation energy (to CF_3 + F) of 5.61

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10.1021/jp0116050 CCC: $20.00

eV,[2] but VUV photons with energies in excess of 12 eV are required to photodissociate CF_4.[3] Likewise, the bond dissociation energy of SF_6 (to SF_5 + F) is 3.82 eV,[4] but photodissociation is not observed until the photon energy exceeds ca. 10 eV.[5] In the lower stratosphere, the highest-energy photons have an energy of ca. 4.0 eV. It seems unlikely, therefore, that SF_5CF_3 will be destroyed in this region through photolytic cleavage of either a C−F or a S−F bond. If the S−C bond in SF_5CF_3 is relatively weak (<2.5 eV or 250 kJ mol^{-1}), SF_5CF_3 could, in principle, be broken down by UV photolysis. However, although an absorption spectrum has not been recorded, there is no evidence from electron energy loss spectroscopy for dissociative excited states of SF_5CF_3 lying ca. 3−8 eV above its ground state.[6] If the bond strength is rather greater, then the removal of SF_5CF_3 from the atmosphere will, like CF_4 and SF_6, be governed by ionic or vacuum-UV processes occurring in the mesosphere.[7]

We report a study of the fragmentation of the parent cation of SF_5CF_3 excited by photons in the range 12−26 eV by threshold photoelectron−photoion coincidence (TPEPICO) spectroscopy. It follows from our previous studies of CF_4^+ and SF_6^+.[8,9] We use a technique, developed for recent work on SeF_6 and TeF_6 and described in section 2,[10] to deduce the dissociative ionization energy of CF_4 (to $CF_3^+ + F + e^-$), SF_6 (to $SF_5^+ + F + e^-$), and SF_5CF_3 (to $CF_3^+ + SF_5 + e^-$) at 0 K. In this paper, these thresholds are called the *first* dissociative ionization energies of these molecules, although we should note that the dissociation channel $SF_5CF_3 \rightarrow SF_4^+ + CF_4 + e^-$ lies lower in energy than $CF_3^+ + SF_5 + e^-$ (section 6). We are then able to determine the SF_5–CF_3 bond dissociation energy and the enthalpy of formation of SF_5CF_3 at 0 K. We also report the threshold photoelectron spectrum of SF_5CF_3 in the range 12−26 eV, the coincidence ion yields over this energy range, and the mean translational kinetic energy (KE) release into the fragment ions. Some indication of the dynamics of photodissociation of excited electronic states of $SF_5CF_3^+$ can be inferred.

2. First Dissociative Ionization Energy (DIE) of CF_4, SF_6, and SF_5CF_3

The parent cations of CF_4, SF_6, and SF_5CF_3 have the common property that the parent ion is not observed in a conventional 70 eV electron-impact mass spectrum.[11] In other words, the ground electronic state of these cations is repulsive in the Franck−Condon region, dissociating on a time scale that is very much faster than the transit time of the ion through a magnetic or quadrupole mass spectrometer. For CF_4^+ and SF_6^+, it is obvious that dissociation must occur by cleavage of a C−F or S−F bond to form CF_3^+ or SF_5^+ + F. With $SF_5CF_3^+$, we assume that cleavage of the S−C bond will occur. Since the $CF_3^+ + SF_5 + e^-$ threshold lies ca.0.8 eV below that of $SF_5^+ + CF_3 + e^-$ (section 5.2), the former products are expected to be produced from photoionization of SF_5CF_3 through the repulsive ground state of the parent cation. We define the first DIE of CF_4, SF_6, and SF_5CF_3 to be the 0 K energy of $CF_3^+ + F + e^-$, $SF_5^+ + F + e^-$, and $CF_3^+ + SF_5 + e^-$ relative to the ground vibronic state of CF_4, SF_6, and SF_5CF_3, respectively.

The determination of the DIE of species whose ground state of the parent ion is repulsive in the Franck−Condon region is a notoriously difficult problem, because its value is likely to be significantly less than the energy corresponding to the onset of ionization of the neutral precursor. Thus, the photoelectron spectrum of the precursor molecule can only give an upper bound to its first DIE. This problem is well-known for both CF_4 and SF_6, and the DIE of these species has been the subject of controversy. The DIE of a molecule AB is given by

$$\mathrm{DIE(AB)} = D_0(\mathrm{A{-}B}) + \mathrm{AIE(A)} \qquad (1)$$

where A−B refers to CF_3–F, SF_5–F, or CF_3–SF_5, D_0(A−B) is the dissociation energy of the A−B bond, and AIE(A) is the adiabatic ionization energy of the A free radical. The principal unknown in the estimation of the DIE of CF_4 and SF_6 is the AIE of the CF_3 and SF_5 radicals. While the CF_3–F and SF_5–F bond dissociation energies are known to an accuracy of ca. 10 kJ mol^{-1} or 0.1 eV,[2,4] the experimental values for the AIE of the CF_3 and SF_5 radicals are still uncertain at the level of ca. ±0.3 and ±1.0 eV, respectively. The problem with CF_3 arises essentially due to the change from pyramidal to planar geometry upon ionization. A consensus has emerged that the AIE of CF_3 lies between 8.8 and 9.1 eV,[12,13] with the most complete ab initio calculation giving 9.05 eV.[14] Experimental values for the AIE of SF_5 lie in the larger range 9.6−11.5 eV, a review being given in ref 4. The consensus now is that the high values are in error, and the value of 9.60 ± 0.05 eV [4] obtained from a guided ion beam study of the charge-transfer reaction of SF_5^+ with Xe is probably correct; the most complete ab initio study to date gives 9.71 eV.[15] For SF_5CF_3, the estimation of its first DIE needs a knowledge of both the SF_5–CF_3 bond dissociation energy and the AIE of the CF_3 radical. Neither is well characterized.

One method to determine the DIE of CF_4, SF_6, and SF_5CF_3 directly is to use the fact that, in the Franck−Condon region, the ground state of the parent cation lies above the DIE and perform a photoelectron−photoion coincidence experiment to measure the translational KE released into the A^+ + B fragments. From an analysis of the width and shape of the fragment ion (A^+) time-of-flight distribution in the (T)PEPICO spectrum measured at a photon energy $h\nu$, it is possible to determine the kinetic energy released in fragmentation at that one energy. This will correspond to some fraction of the available energy, where

$$E_{\mathrm{avail}} = h\nu + (\text{thermal energy of AB}) - \mathrm{DIE(AB)} \qquad (2)$$

The size of the fraction is governed by the dynamics of the decay mechanism.[16] The mechanism cannot unambiguously be determined from a measurement at one single photon energy. By measurement of the KE release continuously as a function of photon energy, however, and assumption that the fractional KE release is independent of energy, an extrapolation to a KE release of zero gives an intercept corresponding to the DIE of AB. We used this method to determine the DIE of SeF_6 and TeF_6[10] and obtained values for the 0 K enthalpy of formation of SeF_5^+ and TeF_5^+. However, there were no other data with which to compare our results, so the method could not be validated. Here, we demonstrate its use to estimate the DIE of CF_4 and SF_6. From the former result, we deduce the 0 K enthalpy of formation of CF_3^+ and, via $\Delta_f H^o{}_0(CF_3)$,[2] the AIE of CF_3. Our AIE value, 8.84 ± 0.20 eV, is in good agreement with recent experimental determinations[12,13,17] and theory.[14,18] The SF_6 result determines $\Delta_f H^o{}_0(SF_5^+)$. Using the recommended value for $\Delta_f H^o{}_0(SF_5)$ from the ion beam study of Fisher et al.,[4] we obtain a value for the AIE of SF_5 of 9.8 ± 0.2 eV. This value is at the lower end of the wide range of values in the literature and, within error limits, is in agreement with the guided ion beam result.[4] Following these "test" experiments, we have measured the first DIE of SF_5CF_3. Using the AIE (CF_3) result above, we have been able to determine, in an indirect manner, the dissociation energy of the SF_5−CF_3 bond.

3. Experimental Section

The apparatus for the acquisition of TPEPICO data has been described in detail elsewhere.[16,19] In brief, monoenergetic photons are selected using a 1 m Seya-Namioka vacuum-UV monochromator (range 40−150 nm or 8−30 eV) attached to the synchrotron storage ring at Daresbury, U.K. Light enters the apparatus via a glass capillary, providing differential pumping between the monochromator (ca. 10^{-9} Torr) and the interaction region (ca.10^{-4} Torr). The photon beam interacts with an effusive jet of sample gas and is monitored by a photomultiplier tube via the visible fluorescence provided by a sodium salicilate window. A threshold electron analyzer and a linear ion time-of-flight (TOF) drift tube are mounted collinearly and orthogonal to the direction of the photon beam, detecting threshold electrons and cations, respectively. The photon beam is plane-polarized, with its electric field vector also perpendicular to the direction of flight of both electrons and ions. An extraction field of 20 V cm^{-1} draws the products of photoionization out of the interaction region to their respective detectors. The first lens of the threshold electron analyzer is designed with high chromatic aberrations and serves to focus zero-energy electrons to the 2 mm diameter entrance aperture of a 127° postanalyzer. The postanalyzer discriminates against energetic electrons that enter it on axis. In this configuration, the threshold analyzer provides a collection efficiency of ca. 30% and a resolution of 10 meV, ensuring that only zero-kinetic-energy electrons reach the channeltron electron detector. In all experiments, the resolution of the VUV monochromator was 0.3 nm, a factor of ca. 4−20 times inferior to that of the threshold analyzer; hence, the resolution of these experiments is governed primarily by the monochromaticity of the photon beam. The ion TOF analyzer is configured to satisfy the space-focusing condition.[20] It consists of two accelerating regions and a 186 mm field-free region. Ions are detected by a pair of microchannel plates arranged in the chevron configuration. The TOF resolution is sufficient to allow measurement of kinetic energy releases from photoionization processes, while the analyzer still maintains a high collection efficiency.

Raw signals from both the electron and ion detectors pass through discriminating and pulse-shaping circuits to a dedicated data-acquisition PC equipped with a time-to-digital converter (TDC, highest time resolution 8 ns) and a counter card. The PC also controls the scanning of the vacuum-UV monochromator. The TDC operates in the multihit mode, with the electrons providing the "start" and the ions the "stop" pulses, and threshold electrons and ions are then detected in time-delayed coincidence. The counter card can record the threshold electron, total ion, and photon flux signals. The TDC and counter card operate simultaneously, thus flux-normalized TPEPICO, threshold photoelectron, and total ion yield spectra can be measured concurrently.

Experiments can be performed as a function of VUV photon energy or at a fixed photon energy. In the scanning photon energy mode, flux-normalized TPEPICO spectra are obtained as three-dimensional histograms where the coincidence count is plotted against both the photon energy and the ion TOF. A low time resolution of the TDC, 128 ns per channel, is used, with the TOF window extending from 0 to 32.7 μs so that all ions in the mass range 0 to ca.340 u are detected. A cut through the histogram at fixed photon energies gives the TOF of the ions which are coincident with threshold electrons at those energies. Since the ion TOF is dependent only on its mass (TOF $\propto m^{1/2}$) and known drift tube parameters, in most cases its identity can unambiguously be determined; problems only arise when two possible ions differ in mass by less than 2 u,[21] which does not arise for the fragment ions of $SF_5CF_3^+$. Ion yields and breakdown diagrams as a function of photon energy may be obtained from cuts taken at fixed ion TOFs. False coincidences are removed by subtracting a cut of the same width, taken over a TOF range which differs from any of the observed ions. The monochromator is calibrated by recording the TPES of Ar through the two ...$(3s)^2(3p)^5$ ionic states of Ar^+, $^2P_{3/2}$ and $^2P_{1/2}$, at 15.759 and 15.937 eV, respectively.[22] For the measurement of the DIEs of CF_4, SF_6, and SF_5CF_3, the TOF spectrum was recorded over a narrower time window (13.6−15.6 μs for CF_3^+, 18.8−20.8 μs for SF_5^+) with a resolution of 16 ns. In the fixed photon energy mode, recorded with a TDC resolution of 16 ns, the TPEPICO spectra are two-dimensional graphs of coincidence count vs ion TOF. This mode is used to measure accurate values of the total mean translational kinetic energy, $\langle KE \rangle_t$, for a single-bond cleavage such as the production of $CF_3^+ + SF_5$.

SF_5CF_3 was manufactured by Flura Corp. (99.99%), Newport, TN, and used without further purification.

4. Determination of the Total Mean Translational Kinetic Energy Release, $\langle KE \rangle_t$

The kinetic energy release distribution (KERD) and hence the total, mean translational kinetic energy release, $\langle KE \rangle_t$, were determined from the fragment ion peak shape obtained in the fixed photon energy experiment by the method described in detail elsewhere.[21] Each spectrum is fitted to a basis set of KE releases, the KERD, given by $\epsilon_t(n) = (2n - 1)^2\Delta E$, with $n = 1, 2, 3, ...$ ΔE, the minimum energy release in the basis set, depends primarily on the statistical quality of the data; the higher the signal-to-noise ratio of the spectrum, the lower ΔE and the higher n can be set to obtain the best fit.[21] The thermal energy of the parent molecule is convoluted into each component of the KERD. Each computed peak in the KERD spans the range of energies $4(n - 1)^2\Delta E$ to $4n^2\Delta E$. The reduced probability of each discrete energy, $P[\epsilon_t(n)]$, is varied to minimize the least-squared errors between the simulated and experimental TOF spectra. From the derived $P[(\epsilon_t(n)]$ vs $\epsilon_t(n)$ distribution, it is simple to calculate the total mean translational KE release, $\langle KE \rangle_t$. The analysis assumes a two-body process, corresponding to the cleavage of one bond only, and conservation of linear momentum. This method is clearly applicable for fragmentation of CF_4^+, SF_6^+, and $SF_5CF_3^+$ to $CF_3^+ + F$, $SF_5^+ + F$, and $CF_3^+ + SF_5$, respectively, but not for three-body processes such as dissociation of $SF_5CF_3^+$ to $SF_3^+ + CF_4 + F$. The analysis does not allow for anisotropy in the dissociation. The values of $\langle KE \rangle_t$ can be compared with E_{avail} (defined in eq 2) to determine the fraction of the available energy being channeled into translational energy of the fragments. In the experiments to determine the DIEs of CF_4, SF_6, and SF_5CF_3, this procedure is simplified by constraining n to 1 and only varying ΔE (section 5.1). The single peak in the KERD, convoluted with the thermal energy of the parent molecule prior to ionization, then spans the range of energies from 0 to $4\Delta E$, with a mean value of $2\Delta E$. The probability is constant within this range and zero outside. This mean value is likely to be very similar to the value of $\langle KE \rangle_t$ obtained from the full KERD.

For a pure impulsive dissociation, applicable to the ground states of CF_4^+, SF_6^+, and $SF_5CF_3^+$, the release of energy occurs after the fragment ion has relaxed to its final geometry.[23,24] The repulsion of the atoms as the bond breaks is then so great that intramolecular collisions result between the recoiling atoms and the remainder of their recoiling fragments and transfer of energy occurs to vibrational modes of the fragments. If the dissociation applies a torque to the fragments, rotation may also be excited. Under these circumstances, $\langle \mathrm{KE} \rangle_t$ and E_{avail} are related by simple kinematics: [23]

$$\frac{\langle \mathrm{KE} \rangle_t}{E_{\mathrm{avail}}} = \frac{\mu_b}{\mu_f} \tag{3}$$

Here μ_b is the reduced mass of the two atoms whose connecting bond is broken and μ_f is the reduced mass of the two products of the dissociation. This model was developed for dissociation of polyatomic ions to a fragment molecular ion and neutral atom,[23] but it is simple to show that it is valid also for a *molecular* neutral fragment. The maximum fraction of the available energy that can be channeled into translational energy of the products is predicted by this model; for cleavage of the C−F bond in CF_4^+, S−F bond in SF_6^+, and S−C bond in $SF_5CF_3^+$, this fraction is 0.49, 0.72, and 0.20, respectively. The model predicts a linear dependence of $\langle \mathrm{KE} \rangle_t$ with E_{avail}. Within the approximation that the experimental mean value of the kinetic energy is equivalent to $\langle \mathrm{KE} \rangle_t$, the DIE can be deduced by extrapolating the plot of the mean KE release vs $h\nu$ to a release of zero. Being a classical model, the extrapolation should be linear even for very low values of the mean KE release.

By comparison, the minimum fraction of the available energy is channeled into translation for a statistical dissociation. Klots[25] has then shown that, for dissociation of a parent ion to a daughter ion plus neutral atom, $\langle \mathrm{KE} \rangle_t$ and E_{avail} are related by

$$E_{\mathrm{avail}} = \frac{r-1}{2}\langle \mathrm{KE} \rangle_t + \langle \mathrm{KE} \rangle_t + \sum_i \frac{h\nu_i}{\exp(h\nu_i/\langle \mathrm{KE} \rangle_t) - 1} \tag{4}$$

where r and ν_i are the number of rotational degrees of freedom and the vibrational frequency of the ith vibrational mode of the daughter ion. Such dissociations assume that the ground electronic state of the parent ion is bound, at least in some regions of its multidimensional potential energy surface, and knowledge of the vibrational frequencies of the daughter ion is required. If these values are not known, it is possible to estimate a lower limit to the fractional release by

$$\frac{\langle \mathrm{KE} \rangle_t}{E_{\mathrm{avail}}} = \frac{1}{x+1} \tag{5}$$

where x is the number of vibrational degrees of freedom in the transition state.[26] For $SF_5CF_3^+$, $x = 24$, leading to a fractional release > 0.04. From eq 4, $\langle \mathrm{KE} \rangle_t$ is approximately proportional to E_{avail}. The extrapolation to zero $\langle \mathrm{KE} \rangle_t$, however, is not completely linear, with a higher slope when approaching threshold as quantum effects become important. A linear extrapolation can therefore give a value for the DIE which is too low and an underestimation of the AIE of the A radical.

5. Results

5.1. Measurement of the First Dissociative Ionization Energy of CF_4 and SF_6. To validate the method for determining the first DIE of SF_5CF_3, we have recorded the TPEPICO spectrum of CF_4 and SF_6 in the scanning photon energy mode from the onset of ionization (ca.15.5 and 15.3 eV, respectively) over the range of energies of the ground and low-lying excited states of the parent ion. For CF_4, the spectrum was recorded from 66 to 88 nm (15.5 to 18.8 eV) in 64 channels. The integrated accumulation time per wavelength channel ranged from ca. 20−40 min. This energy range encompasses the onset of ionization of CF_4 through the $\tilde{X}\ ^2T_1$, $\tilde{A}\ ^2T_2$, and $\tilde{B}\ ^2E$ states of CF_4^+. These three ionic states all dissociate to CF_3^+. The dissociation mechanism of the $\tilde{A}\ ^2T_2$ and $\tilde{B}\ ^2E$ states is uncertain.[8,24] However, it seems likely that the low-energy parts of the $\tilde{X}\ ^2T_1$ state dissociate directly in an impulsive manner from its repulsive potential energy surface to CF_3^+ + F.

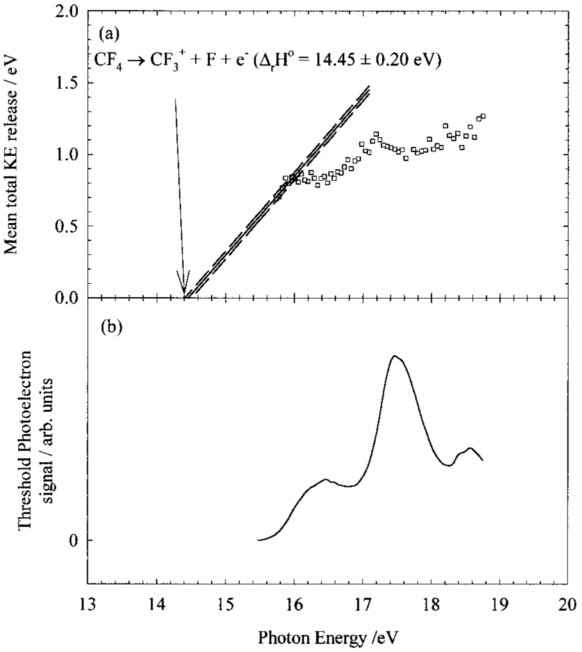

Figure 1. (a) Mean total kinetic energy released in the reaction $CF_4 + h\nu \rightarrow CF_3^+ + F + e^-$ for photon energies in the range 15.5−18.8 eV. A linear extrapolation to zero kinetic energy gives the dissociative ionization energy of CF_4, 14.45 ± 0.20 eV. The error in each value of the kinetic energy release is ca. 20%. (b) Threshold photoelectron spectrum of CF_4 over the same range of energies.

Figure 1a shows the mean translational KE released for fragmentation to CF_3^+ + F, while Figure 1b shows the threshold photoelectron spectrum (TPES) of CF_4 over the energy range 15.5−18.8 eV. The KE data were extracted from the multiple TOF spectra by the simplified way described in section 4. As an example, Figure 2a shows the TOF spectrum for CF_3^+ from CF_4 recorded at a photon energy of 16.05 eV, for which a mean KE release of 0.81 ± 0.11 eV was obtained. A few TOF spectra were checked more rigorously by determining the full KE release distribution (section 4), but the $\langle \mathrm{KE} \rangle_t$ values showed little deviation from the values shown in Figure 1a. Values of the mean KE release range from 0.7 to 1.3 eV, with a general trend of an increasing KE release as the photon energy increases. However, the increase is not linear, suggesting that the dissociation mechanism varies for different parts of the $\tilde{X}$-, $\tilde{A}$-, and $\tilde{B}$-state potentials of CF_4^+. There appears to be a linear increase in the KE release when $h\nu$ corresponds to energies below the Franck−Condon maximum of each of these three states of CF_4^+. As the photon energy passes through each Franck−Condon maximum, the KE release then appears to decrease. This phenomenon is also observed in the $\tilde{X}$, $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$ states of SF_6^+ (see below). One explanation for this effect is that as the photon energy is increased across a photoelectron band, symmetric vibrations are excited. If these modes do not couple efficiently to the reaction coordinate, the additional energy will not necessarily appear as an increase in the translational energy of the products. We should also note that these effects are only observed due to the high signal-to-noise ratio of the TPEPICO spectra. In particular, the spectra are superior to those of SeF_6^+ and TeF_6^+,[10] where no such effects were observed. Only a linear increase in the mean KE release

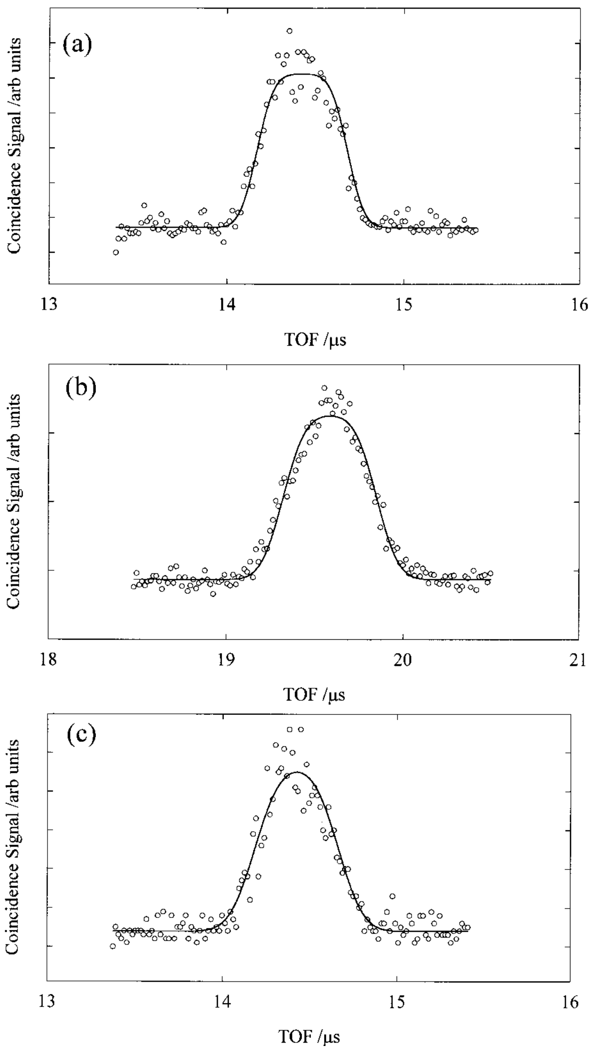

Figure 2. TPEPICO−TOF spectra (open circles) for (a) CF_3^+/CF_4, (b) SF_5^+/SF_6, and (c) CF_3^+/SF_5CF_3 recorded at photon energies of 16.05, 15.72, and 14.09 eV, respectively. Shown as solid lines, the data fit to mean kinetic energy releases of 0.81 ± 0.11, 0.83 ± 0.07, and 0.24 ± 0.05 eV, respectively (see text).

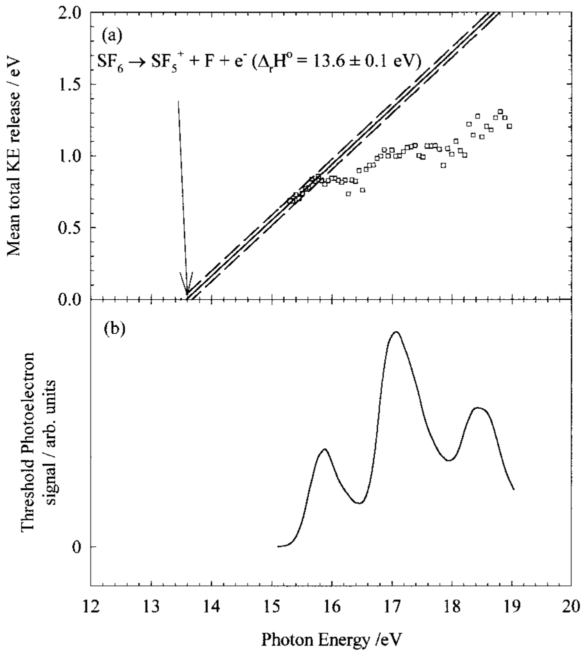

Figure 3. (a) Mean total kinetic energy released in the reaction $SF_6 + h\nu \rightarrow SF_5^+ + F + e^-$ for photon energies in the range 15.1−19.1 eV. A linear extrapolation to zero kinetic energy gives the dissociative ionization energy of SF_6, 13.6 ± 0.1 eV. The error in each value of the kinetic energy release is ca. 20%. (b) Threshold photoelectron spectrum of SF_6 over the same range of energies.

with increasing photon energy over the range of the ground and first three excited electronic states was observed for SeF_6^+ and TeF_6^+,[10] with any small deviations being obscured by the limited signal-to-noise ratio of these spectra.

To deduce the DIE of CF_4, we have extrapolated the mean KE releases from only the eight lowest photon energies of Figure 1a, since impulsive dissociation is most likely to pertain for these points. These data points lie on a straight line with a positive slope of 0.55. This value for the fractional energy release is consistent with the prediction of the pure-impulsive dissociation model, 0.49. Assuming that the decay mechanism of the $\tilde{X}\ ^2T_1$ state of CF_4^+ does not change if it were possible to access the potential energy curve below 15.5 eV, the extrapolation of this linear region to zero KE gives the first DIE of CF_4 to be 14.45 ± 0.20 eV. Using enthalpies of formation at 0 K for CF_4 (−927 kJ mol^{-1}) and F (+77 kJ mol^{-1}),[27] we determine $\Delta_fH^o(CF_3^+)$ at 0 K to be 390 ± 19 kJ mol^{-1}. Constraining $\Delta_fH^o_0(CF_3)$ to be −463 ± 4 kJ mol^{-1},[2] we determine the adiabatic ionization energy (AIE) of the CF_3 radical to be 853 ± 19 kJ mol^{-1} or 8.84 ± 0.20 eV. We comment that the linear region of the graph (Figure 1a) leading to the Franck−Condon maximum of the $\tilde{A}$ state of CF_4^+ also appears to extrapolate to an intercept of 14.45 eV but with a reduced slope

A similar experiment was performed for SF_6 over the range 65−82 nm (15.1−9.1 eV). This energy range encompasses the $\tilde{X}\ ^2T_{1g}$, $\tilde{A}\ ^2T_{1u}$, $\tilde{B}\ ^2T_{2u}$, and $\tilde{C}\ ^2E$ states of SF_6^+, all of which dissociate solely to SF_5^+.[8] Figure 3a shows the mean KE measured for fragmentation to $SF_5^+ + F$ as a function of photon energy, while Figure 3b shows the TPES of SF_6. Only one isotopomer of the daughter ion ($^{32}S^{19}F_5^+$) was used to determine the mean KE releases. As an example, Figure 2b shows the TOF spectrum of SF_5^+/SF_6 recorded at 15.72 eV, from which a mean KE release of 0.83 ± 0.07 eV was determined. The general trend of an increasing KE release with increasing photon energy is observed, but as in CF_4, the increase is not linear. Data from the eleven lowest photon energies fit to a straight line with a slope of 0.39, whereas the pure-impulsive model predicts a fractional energy release of 0.72. This discepancy may relate to the nonplanarity of the fragment SF_5^+ cation. Indeed, there is even uncertainty in the geometry of this ion, with two isomers (one square pyramidal C_{4v}, one trigonal bipyramid D_{3h}) predicted to have comparable energies,[28] although this prediction has been disputed.[15,29] Extrapolation to a mean KE release of zero yields the DIE of SF_6 to $SF_5^+ + F + e^-$ to be 13.6 ± 0.1 eV. (We comment that this value is significantly lower than a recent determination of 14.11 ± 0.08 eV from an analysis of the *maximum* peak width of SF_5^+/SF_6 in a TPEPICO−TOF spectrum,[30] a procedure now recognized to be fraught with uncertainties.) Using the 0 K enthalpy of formation for SF_6 (−1206 kJ mol^{-1}), we determine directly $\Delta_fH^o_0(SF_5^+)$ to be 29 ± 10 kJ mol^{-1}. Constraining $\Delta_fH^o_0(SF_5)$ to the value of −915 ± 18 kJ mol^{-1} recommended by Fisher et al.,[4] we determine the AIE of the SF_5 radical to be 944 ± 21 kJ mol^{-1} or 9.8 ± 0.2 eV. Again, we note that the linear region of Figure 3a below the Franck−Condon maximum of the $\tilde{A}$ state of SF_6^+ at 17.0 eV appears to extrapolate back to the same intercept of 13.6 eV.

At this stage, we comment on the assumptions and limitations of this extrapolation method. The quoted errors for CF_4 and SF_6 arise from random statistical errors in the data. Three factors, which have been ignored in our analysis, might produce systematic errors. First, if the extrapolation to zero mean KE release is not linear, an error will result in the DIE. Second, the single-value KE release determined at each photon energy from the multiple CF_3^+ or SF_5^+ TOF spectra represents a mean value; each $P[\epsilon_t(n)]$ vs $\epsilon_t(n)$ distribution is constrained to $n = 1$. Given the broad distribution of $P[\epsilon_t(n)]$ vs $\epsilon_t(n)$ when each TOF spectrum is fitted to the full KE release distribution, $\langle KE \rangle_t$ may be slightly different from the mean KE release. Third, anisotropic effects have been observed for F-atom loss from the $\tilde{X}$ $^2T_{1g}$ state of SF_6^+ with β parameters ranging from 0.9 to 1.3.[31] Likewise, fragment ion anisotropy has been demonstrated both in the F 1s core ionization and the valence ionization of CF_4.[32,33] In our experiments, the polarization of the VUV photon beam is perpendicular to the TOF axis. The energy releases are determined from the flight times of the fragment ions, or a projection of the recoil velocity on to the TOF axis. It is therefore possible that anisotropy in the fragmentation may lead to a consistent under- or overestimation of the mean KE release, which could cause a small systematic error in the intercept when extrapolating these values to zero. However, this effect is difficult to quantify, and it is not even obvious whether it under- or overestimates the DIE. Our justification for ignoring all three factors is that the enthalpies of fomation at 0 K of CF_3^+ and SF_5^+ which we determine directly from the DIE data, 390 ± 19 and 29 ± 10 kJ mol^{-1}, agree within experimental error with the previous best estimates, namely 410 ± 4 and 11 ± 18 kJ mol^{-1}, respectively.[2,4]

5.2. Measurement of the First Dissociative Ionization Energy of SF_5CF_3. The onset of ionization of SF_5CF_3, ca.12.9 eV, lies significantly lower in energy than that in either CF_4 or SF_6. This arises because its highest-occupied molecular orbital (HOMO) has a very different character to that of CF_4 or SF_6. With SF_5CF_3, it is essentially a S−C σ-bonding orbital,[34] whereas the HOMO of both CF_4 and SF_6 is a F 2pπ nonbonding orbital with an ionization energy similar to that of an isolated fluorine atom.[8,35] Over the range 80−97 nm (12.8−15.5 eV), which encompasses all the ground state and the lower-lying part of the first excited state of the parent cation (Figure 4b), SF_5CF_3 dissociates exclusively to CF_3^+ (see also section 5.4). We have recorded the scanning-energy TPEPICO spectrum of SF_5CF_3 over this range in 64 channels. The mean KE releases are much smaller than in CF_4 and SF_6, ranging from 0.05 to 0.4 eV (Figure 4a). Figure 2c show the TOF spectrum of CF_3^+/SF_5CF_3 recorded at 14.09 eV from which a mean KE release of 0.24 ± 0.05 eV was determined. Within experimental error, the 35 lowest-energy data points fit to a straight line with a slope of 0.19, in excellent agreement with the prediction of the pure-impulsive model of 0.20.[23] Extrapolation to a mean KE release of zero yields the first DIE of SF_5CF_3 to $CF_3^+ + SF_5 + e^-$ to be 12.9 ± 0.4 eV. The relatively large error in the DIE reflects the small slope of the KE release vs photon energy graph and the shallow nature of the extrapolation. We should note that the DIE, unlike that of CF_4 and SF_6, is coincidentally isoenergetic with the ionization onset of the first photoelectron band of SF_5CF_3. Two important thermochemical data can now be determined. First, using values for the 0 K enthalpies of formation of CF_3^+ (390 ± 19 kJ mol^{-1}) (section 5.1) and SF_5 (−915 ± 18 kJ mol^{-1}),[4] we determine $\Delta_f H^o{}_0(SF_5CF_3)$ to be −1770 ± 47 kJ mol^{-1}. This value is significantly lower than that quoted in the most recent JANAF tables, −1700 ± 63 kJ mol^{-1}.[27] Second, using the value for AIE (CF_3) determined in section 5.1, 8.84 ± 0.20 eV, we determine the dissociation energy of the SF_5−CF_3 bond at 0 K to be 4.06 ± 0.45 eV or 392 ± 43 kJ mol^{-1}. Using the value for the AIE(SF_5) from Fisher et al.,[4] 9.60 ± 0.05 eV, the *second* DIE of SF_5CF_3 (defined here to be $SF_5^+ + CF_3 + e^-$) is calculated to be 13.66 ± 0.45 eV. This energy is ca. 0.8 eV higher than the first DIE to $SF_5 + CF_3^+ + e^-$ and explains why only CF_3^+ is observed for dissociation of the low-energy regions of the ground-state potential of $SF_5CF_3^+$.

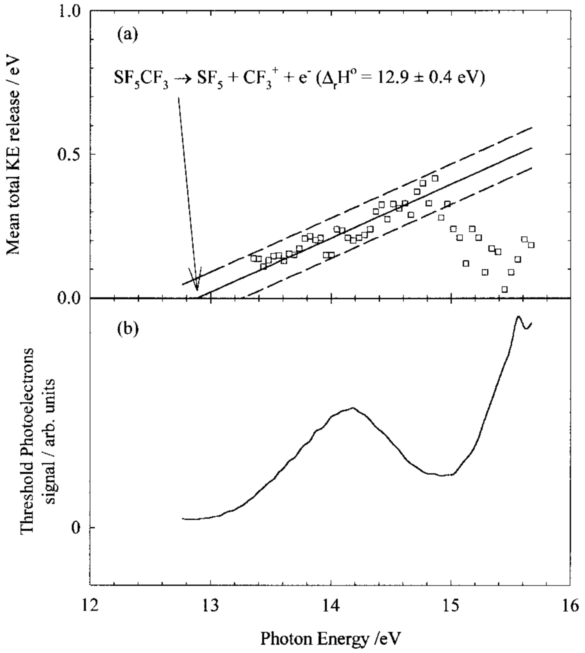

Figure 4. (a) Mean total kinetic energy released in the reaction $SF_5CF_3 + h\nu \rightarrow CF_3^+ + SF_5 + e^-$ for photon energies in the range 13.3−15.5 eV. A linear extrapolation to zero kinetic energy gives the first dissociative ionization energy of SF_5CF_3, 12.9 ± 0.4 eV. The error in each value of the kinetic energy release is ca. 20%. (b) Threshold photoelectron spectrum of SF_5CF_3 over the same range of energies.

5.3. Threshold Photoelectron Spectrum of SF_5CF_3. The threshold photoelectron spectrum (TPES) of SF_5CF_3 was measured from 12.7 to 26.4 eV with a constant wavelength resolution of 0.3 nm (Figure 5a). No vibrational structure was observed. The onset of ionization, defined as the energy at which signal is first observed above the level of background noise, is 12.92 ± 0.18 eV. The vertical ionization energy of this first band occurs at 14.13 eV. The low value of this vertical IE, ca. 2 eV lower than that in both CF_4 and SF_6 where the HOMO has F 2pπ nonbonding character, has already been noted. The large difference between the onset of ionization and the vertical IE suggests a significant change in geometry between neutral and cation, probably in the S−C bond length, compatible with a repulsive ground state of the parent cation along this coordinate. Ab initio calculations on the structure of SF_5CF_3 at the Hartree−Fock level predict bond angles close to either 90.0° (e.g. FSF) or 109.4° (e.g. FCS), a S−F bond length of 1.58 Å, a S−C length of 1.87 Å, and a C−F length of 1.30 Å,[34] in good agreement with the experimental structure from gas-phase electron diffraction.[36] No other structures of molecules with stoichiometry $C_1S_1F_8$ are stable. The HOMO of SF_5CF_3 has a large S−C σ-bonding character, whereas the next three orbitals lie ca. 0.1 au or 2.7 eV lower in energy and are F 2pπ nonbonding in character. No minimum-energy geometry of the ground state of $SF_5CF_3^+$ can be obtained at either the Hartree−

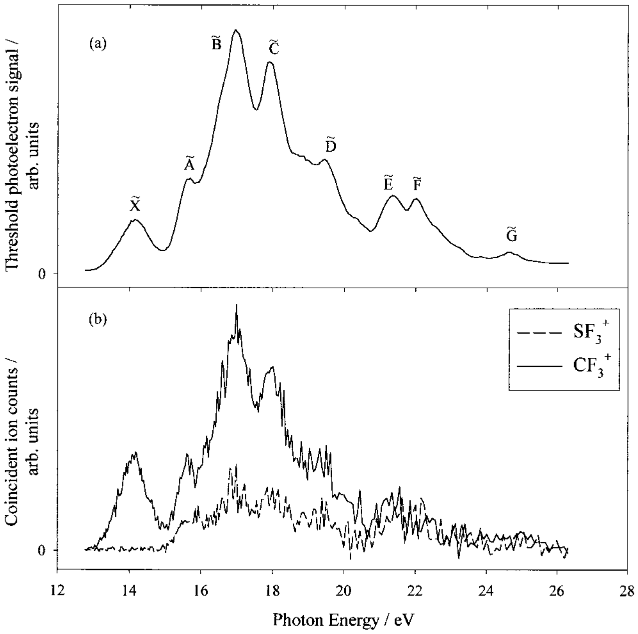

Figure 5. (a) Threshold photoelectron spectrum of SF_5CF_3 at a resolution of 0.3 nm. The electronic states of the parent cation are labeled $\tilde{X}$ through $\tilde{G}$ (Table 2). (b) Coincidence ion yields of CF_3^+ and SF_3^+, the two most intense fragment ions.

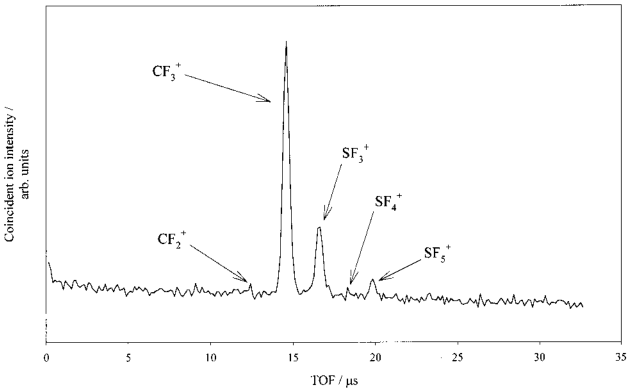

Figure 6. Time-of-flight spectrum of the fragment ions from SF_5CF_3, summed over the photoexcitation energies 12.7−26.4 eV.

Fock or the MP2(full)/6-31g(d) level, giving further evidence that this state is unbound.

Higher-energy peaks in the TPES are observed at 15.68, 16.94, 17.86, 19.44, 21.34, 22.01, and 24.67 eV. The broad peak at 16.94 eV, ca.2.7 eV above the ground state, probably corresponds to several bands produced by removal of a F 2pπ nonbonding electron. No attempt has been made to assign the other peaks in the TPES.

5.4. Scanning-Energy TPEPICO Spectrum of SF_5CF_3. The TPEPICO spectrum of SF_5CF_3 was measured from 12.7 to 26.4 eV with an optical resolution of 0.3 nm. Figure 6 shows the ions produced from the TPEPICO spectrum, summed over this range of energies. The parent ion is not observed. The five fragment ions observed are, in order of increasing mass, CF_2^+, CF_3^+, SF_3^+, SF_4^+, and SF_5^+. CF_3^+ and SF_3^+ are the dominant ions, with CF_2^+ and SF_4^+ very weak. The relative intensities of the most intense ions (CF_3^+, SF_3^+, and SF_5^+) are ca. 38:13:1, and we note that these three ions are also the most intense and formed in approximately this ratio in the 70 eV electron-impact mass spectrum of SF_5CF_3.[11] The coincident ion yields of CF_3^+ and SF_3^+ are shown in Figure 5b. The appearance energies (AE) at 298 K of these two ions are determined to be 12.92 ± 0.18 eV (for CF_3^+) and 14.94 ± 0.13 eV (for SF_3^+). The average internal energy of SF_5CF_3 at 298 K is calculated to be 0.17 eV,[27] so this corresponds to AEs at 0 K of 13.09 ± 0.18 eV (CF_3^+) and 15.11 ± 0.13 eV (SF_3^+). The weakness of the signals for the other three fragment ions is reflected in large uncertainties in their AEs. We measure AEs at 298 K of 13.9 ± 1.2, 13.5 ± 1.5, and 16.0 ± 2.0 eV for SF_5^+, SF_4^+, and CF_2^+, respectively.

The shape of the CF_3^+ ion yield follows that of the TPES of SF_5CF_3 from the onset of ionization to ca.20 eV, and clearly the states of the parent ion with vertical energies below 20 eV dissociate predominantly to CF_3^+. The AE at 298 K of CF_3^+ corresponds to the onset of ionization of SF_5CF_3, which is close to its first DIE to $CF_3^+ + SF_5 + e^-$. The AE of SF_5^+, 13.9 eV with relatively large errors, also corresponds closely to the calculated second DIE of SF_5CF_3 to $SF_5^+ + CF_3 + e^-$, 13.66 ± 0.45 eV. The SF_5^+ signal is so weak that it is not possible to say whether there is any correlation between its ion yield and the electronic states of $SF_5CF_3^+$ as revealed in the TPES. The thermochemical threshold for dissociative ionization of SF_5CF_3 to SF_3^+ ($+ CF_4 + F$) is 13.01 eV (section 6), considerably below the observed AE at 298 K of SF_3^+, 14.94 ± 0.13 eV. In fact, this AE appears to correspond to the onset of ionization to the $\tilde{A}$ state of $SF_5CF_3^+$, indicating electronic state specificity in the fragmentation of $SF_5CF_3^+$ to form SF_3^+. Furthermore, peaks in the SF_3^+ ion yield also correlate weakly with peaks in the TPES of SF_5CF_3 at 16.94, 17.86, 19.44, 21.34, and 22.01 eV. Thermochemistry shows that, at energies between threshold and 17.02 eV, SF_3^+ can only form in association with the neutral products $CF_4 + F$ (see section 6). The ion yields of CF_2^+ and SF_4^+ are extremely weak. As with SF_5^+, it is not possible to say whether there is any correlation between their ion yields and peaks in the TPES of SF_5CF_3. Thermochemistry, however, shows that, certainly at low energies above threshold, CF_2^+ can only form in conjunction with SF_6 and SF_4^+ with CF_4 (section 6). Thus, for the three fragment ions formed involving more than one bond cleavage (CF_2^+, SF_3^+, and SF_4^+), a fluorine migration must occur across the S−C bond to produce the necessary neutral partner(s). Such intramolecular rearrangements, involving migration of a fluorine atom across a C−X bond, have been observed in the fragmentation of perfluorocarbon cations, $C_xF_y^+$.[37,38]

5.5. Fixed-Energy TPEPICO Spectra of SF_5CF_3. TPEPICO−TOF spectra of SF_5CF_3 were recorded at a resolution of 16 ns for the CF_3^+ fragment at photon energies of 14.25, 15.69, 16.98, 17.97, and 19.07 eV, corresponding to the first five peaks in the TPES of SF_5CF_3. Accumulation times per spectrum ranged between 2 and 8 h. Figure 7 shows the TPEPICO−TOF spectrum of CF_3^+/SF_5CF_3 at an excitation energy of 14.25 eV, corresponding to the vertical ionization energy to the ground state of the parent ion. The spectrum is fitted with $\Delta E = 0.03$ eV and $n = 3$, and $\langle KE\rangle_t$ is determined to be 0.32 ± 0.05 eV (Table 1). This value of $\langle KE\rangle_t$ corresponds to 21% of the available energy, in excellent agreement with the prediction of the pure-impulsive model.[23] This is to be expected, because the ground state of $SF_5CF_3^+$ at the Franck−Condon maximum lies over 1 eV higher in energy than the dissociative limit to $CF_3^+ + SF_5 + e^-$. Dissociation from this repulsive potential energy surface is therefore expected to occur rapidly, probably on a subpicosecond time scale, with a relatively large amount of the available energy released into translation of the two fragments. The $\langle KE\rangle_t$ values determined for the other CF_3^+/SF_5CF_3 spectra are shown in Table 1. As the photon energy increases from 14.25 to 19.07 eV, the values of $\langle KE\rangle_t$ only increase by ca. 0.1 eV, so

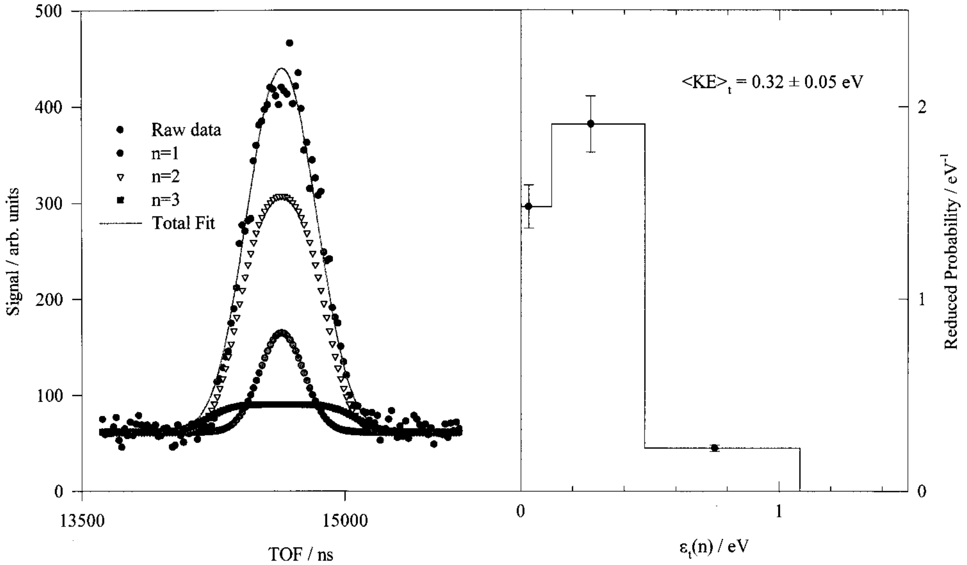

Figure 7. (a) Coincidence TOF spectrum (dots) of CF_3^+ from SF_5CF_3 photoionized at 14.25 eV into the ground, $\tilde{X}$ state of the parent cation. The solid line gives the best fit to the data, comprised of three contributions ($n = 1-3$) in the basis set for $\epsilon_t(n)$. The reduced probability of each contribution is shown in (b). The fit yields a total mean translational kinetic energy into $CF_3^+ + SF_5$ of 0.32 ± 0.05 eV, which constitutes 21% of the available energy.

TABLE 1: Total Mean Translational Kinetic Energy Release, $\langle KE \rangle_t$, of the Two-Body Fragmentation of the Valence States of $SF_5CF_3^+$

parent ion	daughter ion	E/eV	E_{avail}/eV[a]	$\langle KE \rangle_t$/eV	$\langle f \rangle_{t,exp}$[b]	$\langle f \rangle_{t,stat}$	$\langle f \rangle_{t,imp}$
$SF_5CF_3^+$	CF_3^+	19.07	6.34	0.37 ± 0.01	0.06	0.04	0.20
	CF_3^+	17.97	5.24	0.40 ± 0.01	0.08	0.04	0.20
	CF_3^+	16.98	4.25	0.38 ± 0.01	0.09	0.04	0.20
	CF_3^+	15.69	2.96	0.29 ± 0.02	0.10	0.04	0.20
	CF_3^+	14.25	1.52	0.32 ± 0.05	0.21	0.04	0.20
$SF_5CF_3^+$	SF_3^+	16.98[c]					

[a] E_{avail} is defined in eq 2. [b] Given by $\langle KE \rangle_t / E_{avail}$. [c] The peak shape of the SF_3^+ daughter ion at this photon energy fits to a mean KE release of 0.17 ± 0.01 eV.

the fractional release into translational energy of the $CF_3^+ + SF_5$ products decreases. It appears, therefore, that as higher-lying electronic states of $SF_5CF_3^+$ are populated, there is a reduced coupling of the initially excited vibrational modes to the reaction coordinate. This phenomenon, that the value of $\langle KE \rangle_t$ does not increase as rapidly with photon energy as a pure-impulsive model would predict, has also been observed in CF_3^+/CF_4 and SF_5^+/SF_6[8] and for single bond cleavages in the CCl_3X^+ and $CF_2X_2^+$ series of molecules.[39,40] In all these cases, the ground state of the parent cation in the Franck−Condon region lies above the first dissociative ionization energy.

One TPEPICO−TOF spectrum was measured for SF_3^+ with a resolution of 16 ns at a photon energy of 16.98 eV. The peak shape of the daughter ion fits to a KE release of 0.17 ± 0.01 eV into SF_3^+. A value of $\langle KE \rangle_t$ cannot be determined since dissociation involves more than one bond cleavage. No other fragment ions were measured as signal levels were too weak.

6. Thermochemistry

The 0 K energies of various dissociation channels of $SF_5CF_3^+$ can now be determined (Table 2). We use values for the first DIE of SF_5CF_3 (12.9 eV), adiabatic IEs for CF_3 (8.84 eV) and SF_5 (9.60 eV) determined by this work and by Fisher et al.,[4] respectively, and the bond dissociation energies for SF_x^+-F from the guided ion beam study.[4] The CF_3–F bond dissociation energy (5.61 eV) is taken from Asher and Ruscic,[2] while that of CF_2^+-F (6.32 eV) is calculated assuming an IE for CF_2 of 11.44 eV.[41] The largest uncertainty in these energies occurs in channels involving SF_3^+ and SF_4^+, at the level of ca. 0.3−0.5 eV. The interpretation of the mechanism of reactions which form these ions, however, does not depend on the precise values of the bond dissociation energies.

Products formed by cleavage of the S−C bond are easy to understand. As shown earlier, the onset of ionization of SF_5CF_3 at 298 K, 12.92 ± 0.18 eV corresponding to 13.1 ± 0.2 eV at 0 K, lies slightly higher in energy than the experimentally deduced value for the first DIE of 12.9 ± 0.4 eV. The KE releases from $SF_5CF_3^+ \ \tilde{X} \rightarrow CF_3^+ + SF_5$ are therefore relatively small, making an accurate extrapolation to zero KE difficult to achieve. The calculated dissociation threshold of SF_5CF_3 to $SF_5^+ + CF_3 + e^-$, 13.66 eV, lies within error at the same energy as the experimentally determined threshold of 13.9 ± 1.2 eV. In other words, SF_5^+ turns on, albeit very weakly, at its thermochemical threshold. For photon energies above this threshold, dissociation to $CF_3^+ + SF_5 + e^-$ dominates that to $CF_3 + SF_5^+ + e^-$. This effect has also been observed for reactions of cations with recombination energies in excess of 13.66 eV with SF_5CF_3, where the CF_3^+ product dominates SF_5^+.[42]

Channels involving more complicated photodissociation processes are perhaps more interesting. The threshold for production of SF_3^+ at 298 K is measured to be 14.94 ± 0.13 eV. This threshold corresponds to the onset of ionization to the second band in the TPES of SF_5CF_3 and suggests a nonstatistical electronic state-selective fragmentation of the $\tilde{A}$ state of $SF_5CF_3^+$ is occurring. Even with allowance for a significant uncertainty in the enthalpy of formation of SF_3^+, it is clear from Table 2 that this channel is energetically only open if SF_3^+ forms in conjunction with $CF_4 + F + e^-$ (dissociation energy 13.01

TABLE 2: Energetics of Important Dissociation Channels and Ionization Energies of SF_5CF_3

neutral/ parent ion	dissociation channel	dissociation energy/eV[a]	vertical ionization energy/eV
$SF_5CF_3^+$ $\tilde{G}$			24.67
$SF_5CF_3^+$ $\tilde{F}$			22.01
$SF_5CF_3^+$ $\tilde{E}$			21.34
$SF_5CF_3^+$ $\tilde{D}$			19.44
	$CF_3^+ + SF_3 + 2F + e^-$	19.28	
	$CF_2^+ + SF_5 + F + e^-$	19.22	
	$SF_3^+ + CF_3 + 2F + e^-$	18.62	
	$SF_4^+ + CF_3 + F + e^-$	18.26	
$SF_5CF_3^+$ $\tilde{C}$			17.86
	$SF_5^+ + CF_2 + F + e^-$	17.37	
	$SF_3^+ + CF_3 + F_2 + e^-$	17.02	
$SF_5CF_3^+$ $\tilde{B}$			16.94
$SF_5CF_3^+$ $\tilde{A}$			15.68
	$CF_3^+ + SF_4 + F + e^-$	15.41	
	$CF_2^+ + SF_6 + e^-$	15.40	
$SF_5CF_3^+$ $\tilde{X}$			14.13
	$SF_5^+ + CF_3 + e^-$	13.66	
	$SF_3^+ + CF_4 + F + e^-$	13.01	
	$CF_3^+ + SF_5 + e^-$	12.90	
	$SF_4^+ + CF_4 + e^-$	12.65	
	$SF_5 + CF_3$	4.06	
SF_5CF_3 $\tilde{X}$			0

[a] Dissociation energies of channels involving CF_3^+ and SF_x^+ ($x = 3-5$) are calculated from the experimental DIE of SF_5CF_3 to $CF_3^+ + SF_5 + e^-$ (12.9 eV), bond dissociation energies at 0 K of SF_x^+ from Fisher et al.,[4] adiabatic IEs for CF_3 and SF_5 of 8.84 and 9.60 eV (see text), and a bond dissociation energy for CF_3-F of 5.61 eV.[2] Channels involving CF_2^+ are calculated using an enthalpy of formation for this ion of 922 kJ mol^{-1}.[41]

eV). SF_3^+ cannot form with CF_3 and either F_2 or 2F, since these channels lie ca. 2.1 or 3.7 eV above the experimentally determined AE of SF_3^+. Likewise, SF_4^+ and CF_2^+ form very weakly with AEs of 13.5 and 16.0 eV. Table 2 shows that SF_4^+ can only form with CF_4, and CF_2^+ with SF_6 at energies close to their respective thresholds. Thus, all these three fragmentation channels must involve a fluorine atom migration across the S−C bond to form the requisite neutral partner.

7. Discussion

The TPEPICO data in both the scanning photon and the fixed photon energy modes have been discussed in sections 5.4 and 5.5. Here, we discuss only the results to deduce the dissociative ionization energy of CF_4, SF_6, and SF_5CF_3. The value of the AIE of the CF_3 radical, and hence the DIE of CF_4, have been controversial for many years. As described in section 2, the difficulty in measuring accurately the AIE of CF_3 arises because of the change in geometry between the neutral (pyramidal, C_{3v}) and ionized (planar, D_{3h}) forms of the radical, resulting in a negligibly small Franck−Condon overlap factor at threshold.[18] The experimental data up to 1998 were reviewed,[12] and an upper limit of 8.8 ± 0.2 eV for the AIE of CF_3 was recommended. Since then, a new ab initio calculation[14] and further photoionization experiments on $CF_3Br \rightarrow CF_3^+ + Br + e^-$ [17] both suggest that the AIE (CF_3) is somewhat higher, between 9.0 and 9.1 eV. In addition, Irikura[13] has suggested that some of the low values of the AIE (<8.6 eV) from ion−molecule chemical reactions may be in doubt, because entropy effects have been ignored in determining whether such reactions may proceed at a reasonable rate. Our result does not add significantly to this controversy. However, it is gratifying that the extrapolation method (Figure 1a) gives a value for the DIE of CF_4, 14.45 ± 0.20 eV, which leads to a value for the AIE of the CF_3 radical, 8.84 ± 0.20 eV, which is consistent with the recommendations of two recent reviews.[12,13] It seems unlikely that this method will ever be able to give an accuracy in the DIE better than ca. ± 0.1 eV, when an extrapolation of over 1 eV, as here, is involved.

The range of values in the recent literature for the AIE of the SF_5 radical is even greater, with values spanning ca. 9.6−11.5 eV.[4] The lowest value of 9.60 ± 0.05 eV, and probably the most reliable because it is a *direct* measurement, comes from a guided ion beam mass spectrometric study.[4] Both our new value for the first DIE of SF_6, 13.6 ± 0.1 eV, and that derived for the AIE of SF_5, 9.8 ± 0.2 eV, are in excellent agreement with the results of Fisher et al.[4] The AIE result is also in good agreement with two independent Gaussian-2 ab initio calculations.[15,43] All three values are slightly higher that that calculated, 9.52 eV, at the CCSD(T) level of theory.[44]

The purpose of these CF_4 and SF_6 experiments was *not* to measure new values for the ionization energies of the CF_3 and SF_5 radicals but rather to validate the extrapolation method described in section 2. The results show that this has been achieved. Within the limitations of this method described in section 5.1, we therefore have confidence in the KE extrapolation data for SF_5CF_3 (Figure 4a) and the determination of its first DIE to $CF_3^+ + SF_5 + e^-$. From this value, we have been able to determine the 0 K enthalpy of formation of SF_5CF_3 and $D_0(SF_5-CF_3)$. The strength of the SF_5-CF_3 bond, 4.06 ± 0.45 eV, is slightly greater than that of the SF_5-F bond in SF_6, 3.82 eV.[4] The atmospheric implication of this measurement is that SF_5CF_3, like SF_6 and CF_4, is very unlikely to be broken down by UV radiation in the stratosphere. Also like CF_4 and SF_6,[7] the reactions of O (^{1}D) and the OH radical with SF_5CF_3 are likely to be very slow. Taken together, these data are consistent with the observed atmospheric profile of SF_5CF_3 in the stratosphere, which has been interpreted to indicate a lifetime of the order of 1000 years.[1] Its removal from the atmosphere is likely to be determined by ionic processes (i.e. electron attachment and ion−molecule reactions) and possibly VUV photodissociation with Lyman-α radiation occurring in the mesosphere. The rate constant for electron attachment to SF_5CF_3 at room temperature in a Swarm apparatus has recently been measured.[45] Its value suggests a lifetime of SF_5CF_3 in the atmosphere of less than 1000 years.

8. Conclusions

Using tunable VUV radiation from a synchrotron source and threshold photoion−photoelectron coincidence spectroscopy, we have studied the fragmentation of the valence states of $SF_5CF_3^+$ over the energy range 12−26 eV. Threshold electron spectra and coincidence ion yields have been recorded with the experiment operating in the scanning photon energy mode. CF_3^+ is the most intense fragment ion over this range of energies, and its ion yield follows that of the TPES of SF_5CF_3 from ca. 12−20 eV. SF_3^+ is the second most intense fragment ion. Its yield shows some evidence for state-selective fragmentation. The ion yields of SF_5^+, SF_4^+, and CF_2^+ are weak. SF_5^+ turns on at the thermochemical dissociation energy of $SF_5^+ + CF_3 + e^-$. Like SF_3^+, SF_4^+ and CF_2^+ turn on at energies which are only compatible with the lowest-energy dissociation channel involving that ion. Thus SF_3^+ can only form in conjunction with $CF_4 + F + e^-$, SF_4^+ with $CF_4 + e^-$, and CF_2^+ with $SF_6 + e^-$. In all cases, a fluorine atom must migrate across the S−C bond.

In the fixed photon energy mode, the translational kinetic energy released into $CF_3^+ + SF_5$ has been measured at five different excitation energies over the range 14−19 eV. The values of ⟨KE⟩$_t$ range from 0.29 to 0.40 eV. Whereas dissociation of the ground state of $SF_5CF_3^+$ appears to follow a pure-impulsive model with a fractional release into translational energy of 0.19, that from excited states shows a lower fractional release. This phenomenon has been observed in other molecules (e.g. CF_4 and SF_6),[8] where the ground state of the parent ion in the Franck−Condon region lies above the first DIE.

We have also used the scanning photon energy TPEPICO experiment to deduce the first DIE of CF_4 (to $CF_3^+ + F + e^-$), SF_6 (to $SF_5^+ + F + e^-$), and SF_5CF_3 (to $CF_3^+ + SF_5 + e^-$), obtaining values of 14.45 ± 0.20, 13.6 ± 0.1, and 12.9 ± 0.4 eV, respectively. From the first two results, we determine values for the adiabatic IE of the CF_3 and SF_5 free radicals to be 8.84 ± 0.20 and 9.8 ± 0.2 eV, respectively. These results are in good agreement with what we believe to be the most reliable values in the recent literature. The fractional kinetic energy release from $SF_6^+ \rightarrow SF_5^+ + F$ is significantly less than that predicted by the pure-impulsive model,[23] whereas that from CF_4^+ or $SF_5CF_3^+ \rightarrow CF_3^+ + F$ or SF_5 is in good agreement with this model. This result may relate to uncertainty in the geometry of SF_5^+.[28] From the first DIE of SF_5CF_3, we are able to determine the enthalpy of formation at 0 K of SF_5CF_3 (−1770 ± 47 kJ mol^{-1}) and the dissociation energy of the $SF_5{-}CF_3$ bond at 0 K (4.06 ± 0.45 eV). These errors are dominated by the uncertainty in the first DIE of SF_5CF_3. The new value for the enthalpy of formation of SF_5CF_3 is 70 kJ mol^{-1} lower than that given in the JANAF tables.[27] Its value has already been used to determine possible product channels for reactions of small atmospheric cations (e.g. N^+, N_2^+, O_2^+) with SF_5CF_3.[42] This type of reaction is just one of several bimolecular processes which could remove this molecule from the atmosphere. Indeed, the electron attachment data strongly suggest that dissociative electron attachment is the dominant removal process.[45]

The high value of the $SF_5{-}CF_3$ bond dissociation energy suggests that it is unlikely to be broken down by UV photodissociation in the stratosphere. Furthermore, from a low-resolution electron energy loss spectrum (i.e. a pseudo-VUV absorption spectrum),[6] there is no evidence for excited states of SF_5CF_3 lying ca. 3−8 eV above its ground state with appreciable absorption cross sections. If photon-induced processes dominate the removal of SF_5CF_3 from the earth's atmosphere, vacuum-UV photodissociation with Lyman-α radiation in the mesosphere seems more likely. We suggest that measurement of the absorption cross section of SF_5CF_3 at 121.6 nm, similar to that made for CF_4 and SF_6,[7] would be useful additional data in determining more accurately the lifetime of SF_5CF_3 in the atmosphere.

Acknowledgment. We thank EPSRC for research grants (GR/L82083 and GR/M42794), postdoctoral fellowships (W.Z., G.K.J.) and a research studentship (D.J.C.) and the University of Birmingham for a research studentship (R.Y.L.C.). We thank Professor K. P. Shine (University of Reading, Reading, U.K.) and Dr. W. T. Sturges (University of East Anglia, East Anglia, U.K.) for bringing to our attention their work on the atmospheric importance of SF_5CF_3 and for the SF_5CF_3 gas sample. Finally, we thank Professor P. J. Knowles (University of Birmingham, Birmingham, U.K.) for running ab initio calculations on SF_5-CF_3 and Drs. I. Powis (University of Nottingham, Nottingham, U.K.) and N. J. Mason (UC London, London, U.K.) for communicating unpublished data.

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