

Low-energy electron scattering cross sections of halofluorocarbons

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The interaction of low-energy electrons with halogenated methanes is important in both their atmospheric and plasma-processing chemistry. In this work, the total electron scattering cross sections of mixed fluorohalomethanes ($\text{CF}_n\text{X}_{4-n}$) were measured for incident electrons in the energy range of 0.3–12 eV using electron transmission spectroscopy. Resonances in the scattering cross sections may be interpreted as the capture of low-energy electrons into unoccupied molecular orbitals. To aid in the assignments of the resulting negative ion states, we performed quantum-mechanical calculations of the electron attachment energies. The effect of halogen substitution on the orbitals participating in electron capture are examined.

I. INTRODUCTION

Collisions of low-energy electrons with halofluorocarbons is a primary step in plasma-processing chemistry and may also play a role in the chemistry of the freon-contaminated atmosphere. The CF_4 plasma is one of the standard etching plasmas in the semiconductor industry. It has been found that the performance of this system with respect to etching anisotropy and polymer formation is modified by the introduction of halogen atoms and ions other than fluorine and fluoride.^{1–3} This can be accomplished by adding mixed halofluorocarbons such as CF_3Br or CF_2Cl_2 . High-temperature plasma processes are being developed for the destruction of intractable wastes including many halogenated alkanes. In addition to simple thermolysis, molecular processes initiated by electron attachment must take part in the complex reactions that occur in these plasmas. In the upper atmosphere the presence of chlorofluorocarbons (CFCs) is responsible in part for the widely publicized depletion of ozone that has been observed in recent years. Because CFCs have a large cross section for electron attachment leading to dissociation, it is possible that ambient electrons should be considered in the formulation of a model of ozone chemistry in the contaminated atmosphere.⁴ Indeed, there has even been a proposal to mitigate ozone depletion by CFCs through the injection of electrons at high altitudes to produce radicals and chlorine anions that can be efficiently consumed in reactions with atmospheric gases.⁵

In this work, we report the measurement of absolute total scattering cross sections for electrons of energies up to 12 eV for the mixed halofluoromethanes CF_3X and CF_2X_2 , where X is Cl, Br, and I. Particular attention is paid to resonant enhancement of the cross sections produced by electron attachment leading to temporary negative-ion states, many of which decay by subsequent dissociation. With the aid of quantum-mechanical calculations, as well as comparisons with previous work, an attempt is made to assign these negative-ion states.

The total cross section of a molecule for scattering electrons in the 0 to 10 eV range basically reflects the physical size of the molecule; the cross section is typically a few tens

of square Ångströms. On the other hand, owing to the fact that electrons in this energy range are moving with velocities comparable to those of the valence electrons of the molecule, there is the opportunity for resonant interactions between the incident and target electrons. Consequently, strong fluctuations in the scattering cross section as a function of incident electron energy are frequently observed. If the potential energy curves for the neutral molecule and negative ion cross near zero electron energy, the cross section is greatly enhanced near threshold, a phenomenon characterized as *s*-wave scattering.^{6–8} For relatively symmetrical molecules, as in atoms, a Ramsauer minimum is seen for electrons near 1 eV. This is a wave-mechanical interference effect that arises because the wavelength of an electron of this energy is of the same dimension as the target. In addition, the scattering cross section may be enhanced by the resonant capture of the incident electron to give a temporary negative ion. From the relatively narrow energy range over which such resonant scattering occurs, it can be surmised that the negative ion typically survives for a period of the order of 10^{-14} s. The ion may decay by reemission of the captured electron or, more importantly for plasma chemistry, the negative ion may fragment to yield a smaller negative ion and a radical. The capture process is termed a *shape resonance* in reference to the trapping potential resulting from the combination of the electron–molecule attractive potential and an angular momentum barrier.^{9,10} A useful model describes the resonance as resulting from the capture of the incident electron into an unoccupied orbital of the molecule. In the spirit of Koopmans' theorem, the energy at which the resonance occurs, termed the *attachment energy*, is identified with the eigenenergy of the orbital. Alternatively, this energy may be thought of as a negative, vertical, electron affinity.

II. EXPERIMENT

The total electron scattering cross section is determined from the attenuation of an electron beam as it passes through the gas-phase sample at low pressure. The apparatus consists of a thermionic electron source followed by a trochoidal electron monochromator,^{11,12} an accelerating lens, a gas cell,

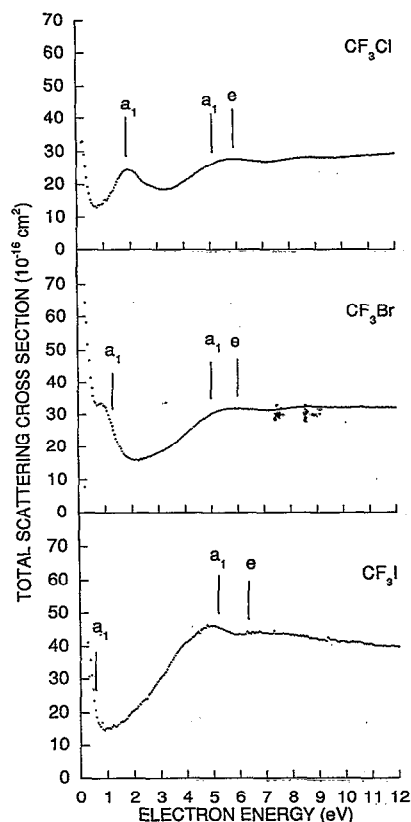


FIG. 1. Total electron scattering cross sections of the halofluorocarbon series CF_3X ($\text{X}=\text{Cl}$, Br , and I). Vertical lines indicate calculated attachment energies for orbitals of the indicated symmetries.

and a retarding potential analyzer that permits only unscattered electrons to be transmitted to an electron collector. The apparatus is immersed in an axial magnetic field of 76 G. The present experiments were implemented with an electron energy resolution of 50 to 80 meV and a target cell temperature of 393 K. The cross section σ is related to the number density of scatterers n and the transmitted electron current with and without gas in the cell, I and I_0 , by Beer's law:

$$\sigma = (nl)^{-1} \ln(I/I_0),$$

where l is the length of the electron trajectory in the target. Target density is determined from a measurement of the gas pressure with a capacitance manometer and the electron current, typically a few nanoamperes in magnitude, is measured with an electrometer. The electrometer output is digitized for storage in the memory of a computer, where the cross section is calculated. The energy scale is obtained by recording and assigning the vibrational features of the $^2\Pi_g$ shape resonance of nitrogen mixed with the sample gas. The uncertainty in the energy scale is estimated to be less than 60 meV. To insure single collision conditions, the cross sections for each compound was measured for several target gas pressures less than 1 mTorr. The cross sections reported in this paper are the averages of several spectra. The statistical uncertainty for each average cross section was less than 10%.

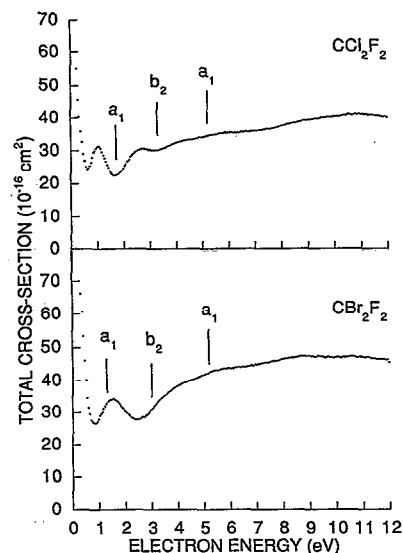


FIG. 2. Total electron scattering cross sections of the halofluorocarbon series CF_2X_2 ($\text{X}=\text{Cl}$ and Br). Vertical lines indicate calculated attachment energies for orbitals of the indicated symmetries.

There are two principal sources of error in determining the magnitude of the cross section. First, the length of the electron trajectory through the target is uncertain, especially at the lowest energies, owing to the helical motion of the electrons in the imposed magnetic field. This effect has been analyzed previously.¹³ The uncertainty in l introduces an uncertainty in the cross section of as much as 43% at 0.2 eV, declining to 17% at 0.5 eV, and to less than 10% above 1 eV. The other major source of uncertainty is in the determination of the target densities. Although the pressure drop at the cell apertures does not seem to be a serious problem, calibration of the capacitance manometer against a McLeod gauge implies an uncertainty of about 11% in the determination of the gas density.

Total cross sections for electron energies from 0.3 to 12 eV for the series CF_3Cl , CF_3Br , and CF_3I are shown in Fig. 1 and for CF_2Cl_2 and CF_2Br_2 are shown in Fig. 2. Our results for the chlorine-substituted compounds are roughly 25% smaller than those measured previously.¹⁴ Negative-ion resonances appear in every case. These are especially apparent for electron energies below 5 eV. Ramsauer minima near 1 eV are also observed in the spectra, particularly for CF_3Cl . Finally, the enhancement associated with a negative-ion state near threshold is readily apparent in the cross sections for CF_3Br and CF_2Br_2 .

III. CALCULATIONS AND DISCUSSION

A variety of experimental and theoretical means can be, and have been, applied to determine the symmetry and chemical nature of the extremely short-lived negative-ion states arising from electron attachment to molecules. In the event that electron capture leads to dissociation, the bonding and charge distribution in the negative ion can be inferred from the fragmentation pattern.¹⁵ The most elegant experi-

ments involve the observation of resonantly enhanced electron-impact vibrational excitation.^{16–18} From a consideration of the symmetry of the modes excited and the associated angular scattering distributions it is possible to both deduce the symmetry of the negative-ion state and to learn about the bonding in the negative ion.^{19,20} Drawbacks to this approach are that the experiments require relatively high-resolution electron spectroscopy and that the interpretation requires large quantities of data (cross sections differential in energy and angle) to make an unambiguous assignment.

Resonant electron scattering processes give rise to negative ions which are metastable with respect to electron detachment. A rigorous theoretical description of the state of such a negative ion is a time-dependent problem; however, a dynamical treatment of scattering for a complex polyatomic molecule is very difficult. On the other hand, a static calculation of the energy and wave function of a metastable negative ion is unreliable since the usual variational approach with a sufficiently flexible trial wave function can be expected to converge to the ground state of the neutral molecule plus an electron at an infinite distance. In spite of this basic difficulty, static calculations employing a variety of approximations have proven to be useful. These approaches adopt the model which describes the scattering resonance in terms of electron capture into an unfilled orbital of the neutral target. The goal is to determine the energy, symmetry, and bonding character of this orbital. The most simple approach is to assume that the attached electron is independent of all other electrons in the molecule. This is analogous to the application of Koopmans' theorem in describing positive-ion states arising from photoionization. A self-consistent-field (SCF) calculation is performed on the neutral molecule and the positive eigenenergies are identified with resonant attachment energies. Because most neutral, ground-state molecules are in closed-shell Σ states, the symmetry of the negative-ion resonant state is the same as that of the corresponding unoccupied orbital. This approach appears to give reasonable results with minimum-basis-set wave functions as demonstrated by Burrow *et al.*²¹ for some of the halogenated methanes; however, if the basis set is expanded, these calculations invariably yield a plethora of low-lying unoccupied orbitals. The lowest-energy orbital obtained from such calculations is typically a reasonable description of the orbital occupied to give the ground state of the negative ion. The energies of orbitals above the first are very sensitive to the details of the basis set chosen. There is no obvious correspondence between these energies and the observed energies of negative-ion excited states since many of these orbitals are very diffuse, essentially artifacts of the expanded basis set. An accurate estimate of the attachment energy (AE) for electron capture into the lowest unoccupied orbital (LUMO) of the neutral can be obtained from the difference ΔE_{SCF} of the total SCF energies of the negative ion and the neutral.

Another approach to predicting the energy of a metastable negative ion is to carry out calculations on an analogous system which is stable—a legitimate application of the variational method—and then add back an energy increment to account for the stabilization. One method involves the introduction of positive point charges around the negative

ion or the immersion of the negative ion in a cloud of positive charge (a “Watson sphere”) in order to create a stable system.²² The calculation is done on this system and the energy associated with the positive charge is added to that calculated. In this so-called stabilization method, calculations are done on both the neutral molecule and the anion positioned in point charge arrays (with the point charges located far from the terminal atoms). The energy of the anion is then corrected for the Coulombic attraction of the point charge array and the additional electron, and this corrected anion energy is compared to the calculated energy for the neutral molecule in the point charge array to obtain the attachment energy. Although this method is more sound in principle than the unstabilized approach, it gives very similar results. For example, in CF_3Cl , the stabilized and unstabilized AEs for the LUMO were 1.93 and 2.03 eV, respectively.

A second method involving calculations on stable systems is based on the observation of a simple correlation between shape resonances observed in low-energy electron scattering and resonances associated with the excitation of inner-shell electrons into low-lying unoccupied valence orbitals analogous to those involved in low-energy electron capture. The latter are observed in x-ray absorption spectra and inner-shell electron energy-loss spectra (ISEELS) and appear as features near the inner-shell ionization edge. Such resonant states are stabilized by the positive hole created by the promotion of the inner-shell electron. The energy of the resonant state relative to the nearby ionization edge is specified as the *term value* (TV), the difference between the ionization energy and the energy of excitation of the inner-shell electron to the valence orbital. The correlation between a core-excited resonant state and a negative-ion resonant state involving an analogous orbital is parameterized in terms of a measure of the stabilization attributed to the positive core hole: A *stabilization energy* (SE) defined by $\text{SE} = \text{TV} + \text{AE}$. It has been observed that the stabilization energy for resonances observed in an homologous series of molecules is constant within about 1 eV, with typical values between 6 and 8 eV. It follows that attachment energies for a series of molecules can be predicted from calculations of term values for inner-shell excitation. Of course, an inner-shell excited state is metastable and its energy cannot be directly calculated. This problem is dealt with in the equivalent ionic core virtual orbital model (EICVOM), or $Z+1$ analogy, wherein the calculation is performed after replacing the nucleus of the core-excited atom with the nucleus of the atom having an atomic number one higher. The negative of the eigenvalues for the unoccupied orbitals are then taken as the corresponding term values. A stabilization energy can be determined from the sum of the highest term value and the attachment energy for the ground state of the negative ion calculated as described above. Assuming the constancy of the stabilization energy, attachment energies to excited negative-ion states can be predicted from the lower term values. Of course it is also possible to predict attachment energies from term values obtained from experiments.

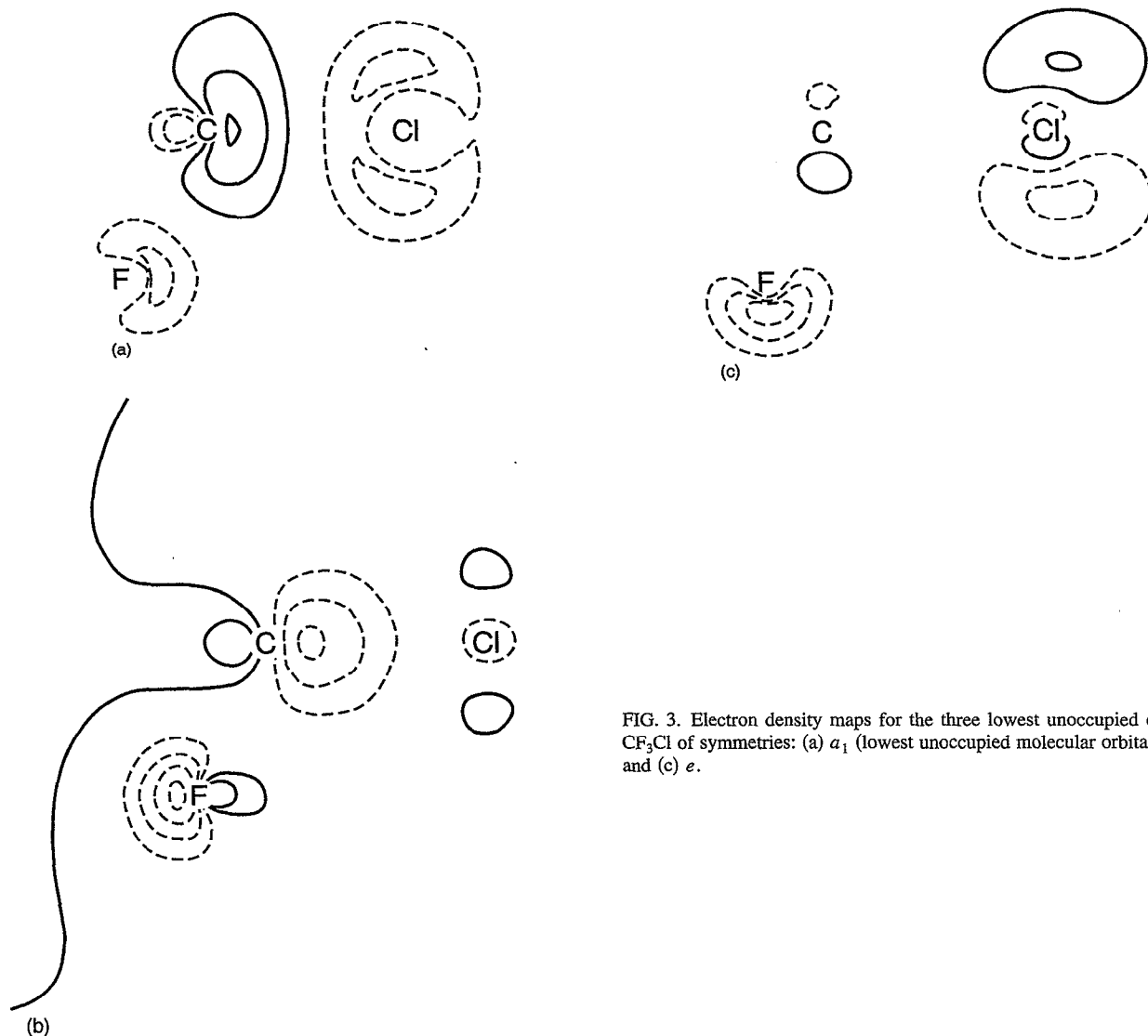


FIG. 3. Electron density maps for the three lowest unoccupied orbitals of CF_3Cl of symmetries: (a) a_1 (lowest unoccupied molecular orbital); (b) a_1 ; and (c) e .

A. Assignment of resonances in CF_3X

In CF_3Cl , resonant enhancement of the total electron scattering cross section is observed in our data at 2.0, 5.5, and 8.5 eV. From measurements of differential cross sections for elastic scattering and a study of the resonantly enhanced vibrational excitation at these energies, Mann and Linder¹⁶ associated these resonances with occupation of valence orbitals of the type $a_1(\text{C}-\text{Cl}\sigma^*)$, $e(\text{C}-\text{F}\sigma^*)$, and $a_1(\text{C}-\text{F}\sigma^*)$, respectively. Illenberger and co-workers⁴ observed dissociation of Cl^- upon attachment of electrons with energies near 1.3 and 4.8 eV, an indication of the formation of a C-Cl antibonding state at these energies. Indications of a C-F antibonding state, the dissociation of F^- and CF_2Cl^- , were observed for the capture of electrons with energies of 4.1 eV. A calculation for neutral CF_3Cl using a minimum basis set of STO-3G orbitals predicts attachment energies of 2.0, 7.9, and 9.7 eV for capture into orbitals of type a_1 , e , and a_1 , respectively. Given the simplicity of this calculation, this result may be considered in reasonable agreement with the results of Mann and Linder. We have carried out much more rigor-

ous calculations for each member of the CF_3X series, and the results of these calculations are discussed below.

Ab initio self-consistent-field calculations were implemented using the general atomic and molecular electronic structure system (GAMESS). The 3-21G split valence functions of Binkley *et al.*,²³ augmented with *s* and *p* diffuse, and *d* polarization functions, provided the basis for each atom. An energy-minimized geometry for each neutral molecule was calculated. Computed and measured^{24,25} bond lengths and angles agree to within 0.03 Å and 1.5 deg, respectively. The electron density maps of the unoccupied orbitals of the neutral molecules, such as those shown in Fig. 3 for the three lowest unoccupied orbitals of CF_3Cl , were also generated. From Fig. 3, the a_1 LUMO certainly appears to be a $\sigma^*(\text{C}-\text{Cl})$ orbital, while the next a_1 orbital has mostly $\pi^*(\text{C}-\text{F})$ character, and the lowest e orbital has mostly Cl 3*p* character with some $\pi^*(\text{C}-\text{Cl})$ character. This is qualitatively consistent with Cl^- production from the a_1 LUMO and the e state and F^- production from the higher a_1 state.

Term values for inner-shell electron excitation into low-

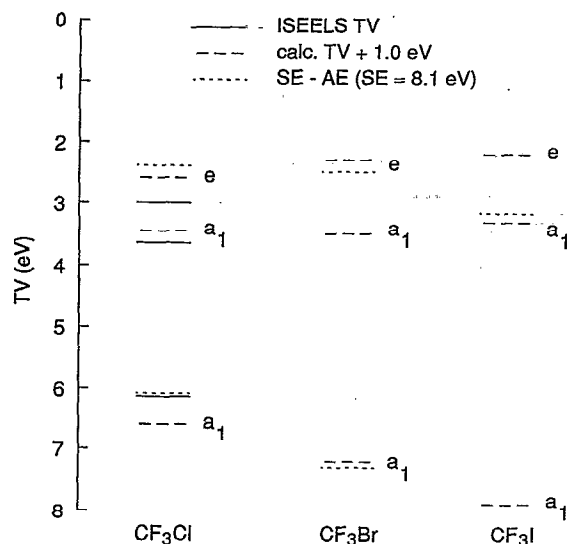


FIG. 4. Calculated term values (long dashed line) and term values obtained from inner-shell electron excitation spectroscopy (solid line) compared to term values estimated from attachment energies obtained from the measurement of low-energy electrons scattered from the halofluorocarbon series CF_3X (short dashed line).

lying unoccupied valence orbitals for each member of the series were calculated in the EICVOM approximation. For CF_3Cl these can be compared with the experimental observations of Zhang *et al.*²⁶ who report term values for $\text{Cl}1s$ excitation to the lowest three molecular orbitals of 6.15, 3.65, and 3.0 eV. The calculated term values are 5.6, 2.4, and 1.6 eV; an incremental adjustment of 1.0 eV brings calculation and experiment into agreement to within 0.5 eV. An underestimation of term values of this order is typical at this level of calculation. For example, in a theoretical study of the ISEELS of sulfur-containing compounds,²⁷ term values calculated in this way were consistently smaller than experiment by about 1 eV. Consequently we have adjusted all calculated term values upward by 1.0 eV. The symmetry of these first three orbitals from the calculation are a_1 , a_1 , and e , respectively, suggesting, contrary to the tentative assignment of Zhang *et al.*, that the final orbital assignment for the first features in the $\text{Cl}1s$ excitation spectra are $11a_1$, $12a_1$, and $8e$, respectively.

Calculations at the same basis set level were used to determine ΔE_{SCF} values for attachment energies. For the series CF_3Cl , CF_3Br , and CF_3I , the lowest unoccupied molecular orbital (LUMO) is of $a_1(\text{C}-\text{X}\sigma^*)$ character with calculated attachment energies of the ΔE_{SCF} level of 2.0, 1.5, and 0.4 eV, respectively. In the total cross section measurements, resonant enhancements are observed at 2.0 eV in CF_3Cl and 0.9 eV in CF_3Br . This suggests that the calculation slightly underestimates the stabilization of the LUMO with successive substitution of a heavier halogen. The LUMO in CF_3I can thus be expected to lie near threshold. Indeed, the observation of I^- for the dissociative attachment of near-threshold energy electrons is consistent with this supposition.²⁸

The theoretical stabilization energy (SE) can be taken as the sum of the highest calculated term value (TV) and the

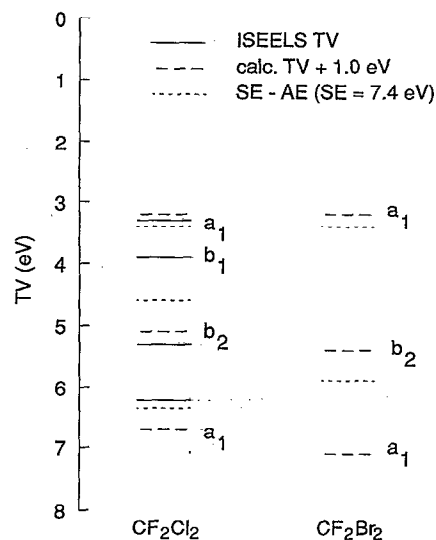


FIG. 5. Calculated term values (long dashed line) and term values obtained from inner-shell electron excitation spectroscopy (solid line) compared to term values estimated from attachment energies obtained from the measurement of low-energy electrons scattered from the halofluorocarbon series CF_2X_2 (short dashed line).

lowest predicted attachment energy ΔE_{SCF} . For the series CF_3Cl , CF_3Br , and CF_3I , this gives SEs of 8.7, 8.8, and 8.4 eV—essentially constant across the series. Taking $\text{SE}=8.6$ eV, attachment energies for orbitals above the LUMO can be predicted from calculated term values as indicated in Fig. 1, or, as shown in Fig. 4, term values can be predicted from the position of observed electron capture resonances. This suggests that the broad resonances centered at 5.5 eV in CF_3Cl and CF_3Br and at 4.9 eV in the total cross section for CF_3I are possibly comprised of two resonances of $a_1(\text{C}-\text{F}\sigma^*)$ and $e(\text{C}-\text{Cl}\pi^*)$ symmetry. The observation of fluoride fragments for CF_3Cl and CF_3I for electron impact energies of 4.1 and 3.8 eV, respectively, support the existence of the a_1 resonances. The observation of CF_3^- fragments when 3.8 eV electrons are incident on CF_3I prompted Oster *et al.*²⁹ to analyze the decomposition dynamics of the reaction. They conclude that the corresponding temporary negative-ion state has a significant CF_3-I repulsive character resulting from a two-particle (core excited) resonance associated with occupation of the LUMO of the neutral molecule. Our calculations suggest that the repulsive state is probably produced by electron capture into the $e(\text{Cl}3p, \text{C}-\text{Cl}\pi^*)$ orbital. Omitted from the spectra of each compound is an additional a_1 orbital which is almost degenerate with the e orbital.

B. Assignment of resonances in CF_2X_2

For CF_2Cl_2 and CF_2Br_2 the calculated stabilization energies are 8.7 and 8.1 eV. Taking a mean value of 8.4 eV, attachment energies are predicted from calculated term values (Fig. 2) and term values are predicted from observed attachment energies (Fig. 5). The calculated term values for CF_2Cl_2 confirm the tentative assignment of the first two features in the ISEELS spectrum to inner-shell excitation to the

$13a_1(C-Cl\sigma^*)$ and $9b_2(C-Cl\pi^*)$ valence orbitals.²⁶ (Note that the bonding characteristics of these orbitals are obtained from electron density maps generated in this work.) The third peak was assigned to a blend of the $7b_1$ and $14a_1$, however, the calculation places the b_1 orbital approximately 1 eV above the a_1 . Predicted attachment energies agree to within 1.5 eV with the position of the relatively broad enhancements observed in the total cross section. The assignments agree in order and moderately well in energy with the virtual orbitals given in the small-basis-set calculation of Burrow *et al.*²¹ As for the CF_3X series, the calculated LUMOs are not stabilized sufficiently. With this in mind, we predict that the LUMO of CF_2Br_2 is near threshold. In addition, a preliminary measurement in our laboratory indicates a large cross section for dissociative attachment near threshold. The first observed resonance is thus assigned to electron capture into a b_2 orbital.

IV. CONCLUSIONS

Overall, we see that the ground state of the negative ion of CF_4 is stabilized as one or more of the fluorines is replaced with heavier halogens. This trend is the opposite effect one might anticipate when considering the electronegativity of the substituted halogens; however, the increased charge capacity of the halogen with atomic number could produce such a stabilization. In contrast, the excited states for the CF_3X series are less sensitive to the exchange. However, the first excited state of the CF_2X_2 series is affected to the same degree as the LUMO with increase in the atomic number of the halogen, while the energy of the second excited state remains virtually constant.

The vertical electron affinities obtained in this work are consistent with the measured adiabatic electron affinities reported for some of the compounds. The vertical electron affinity is usually less positive than the adiabatic electron affinity. Our results suggest that CF_3I will have a small positive vertical electron affinity and that CF_3Br has a negative vertical electron affinity of 0.82 eV. The adiabatic attachment energies for these two compounds are 1.57 and 0.91 eV, respectively.³⁰

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