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Dissociative electron attachment in chlorofluoromethanes and the correlation with vertical attachment energies

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Abstract

The total dissociative electron attachment (DEA) cross sections of the chlorofluoromethanes are determined in an electron beam experiment and correlated with the vertical attachment energies (VAEs) for formation of the lowest temporary anion states of these compounds. The latter are determined independently by electron transmission spectroscopy and correspond to the energies of the anions at the equilibrium geometries of the neutral molecules. As we observed previously in the chloroalkanes, the peak DEA cross sections are well correlated with VAEs. For values of VAEs between 0.9 to 3.0 eV, the peak DEA cross sections vary by more than four orders of magnitude. This is attributable in part to the remarkably monotonic variation of the temporary anion widths, arising from their finite lifetimes, over this range of VAE. (Int J Mass Spectrom 205 (2001) 149–161) © 2001 Elsevier Science B.V.

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1. Introduction

The dissociative electron attachment (DEA) process, $e + AB \rightarrow AB^{-*} \rightarrow A + B^{-}$, is extremely sensitive to the characteristics of the intermediate complex, AB^{-*}, the temporary negative ion formed by attachment of the impinging electron into one of the normally unoccupied molecular orbitals of the neutral molecule. DEA cross sections can vary over an enormous range, even in a series of closely related molecules, and there is very little quantitative guidance, either theoretical or experimental to explain the variations. To determine whether empirical relationships could be found that would express the DEA cross sections in terms of easily measurable properties of the temporary anion intermediate, we began studies [1,2] of a simple but important prototypical set of molecules, the chloroalkanes. These compounds contain saturated hydrocarbon backbone structures and one or more Cl leaving groups. The lowest unoccupied molecular orbitals (LUMOs) consist of combinations of the local C–Cl σ^* orbitals. The anion states associated with occupation of these orbitals are readily detected by observing the sharp structures produced in the total scattering cross sections using electron transmission spectroscopy (ETS) [3]. These measurements yield the vertical attachment energy (VAE) of each molecule, that is, the energy required to form the anion state at the equilibrium geometry of

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Dedicated to Professor Alex Stamatovic on the occasion of his 60th birthday and with many fond memories of our time at Yale University.

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the neutral molecule. Beginning with the monochloroalkanes [1] and dichloroalkanes [2], we joined ETS studies with measurements of the total cross section for production of negative ion fragments. These data are combined with studies of selected tri- and tetrachloroalkanes in our most comprehensive ETS [4] and DEA [5] reports.

The major outcome of our previous work was to show that an excellent correlation exists between the maximum values of the DEA cross sections and the VAEs associated with formation of the lowest-lying temporary anion states. The empirical form of this relationship is

$$\sigma_{DEA}^{peak} = 5.41 \times 10^{-(16+0.613VAE^{\,2.01})}\ \mathrm{cm}^2 \qquad (1)$$

The data to which this expression was fit, shown later in this article, consisted of measurements in approximately 30 chloroalkanes having VAEs ranging from 0.6 to 2.8 eV. The standard deviation of the measured cross sections from the best-fit curve was 38%. The cross sections referred to here are those arising from the lowest temporary anion states and having maxima that lie above zero electron energy. As we also discussed [5], *s*-wave attachment of electrons to form these same anion states produces sharp peaks at zero energy as well.

In the present work, we explore the degree to which a similar correlation holds for a much smaller set of compounds in which the chloromethanes are modified by fluorine substitution. In particular, we present total DEA cross sections and VAEs for $CClFH_2$, $CClF_2H$, $CClF_3$, CCl_2FH, CCl_2F_2, and CCl_3F. In the Sec. 2, we outline briefly the experimental methods. Following this, we discuss the ETS measurements, the DEA cross sections, and finally the correlation between these quantities.

2. Experimental methods

2.1. Electron transmission spectroscopy

ETS measurements are carried out in an instrument similar to that described by Sanche and Schulz [3]. The technique and its application to organic molecules have been amply described in the literature [6–8]. Briefly, a magnetically collimated electron beam produced by a trochoidal electron monochromator [9] is passed through a collision cell containing the target gas at a sufficient pressure to partially attenuate the beam. The unscattered, or transmitted, electron current is collected. Discrimination against scattered electrons takes place by applying a retarding voltage on an electrode located between the collision chamber and the electron beam collector. The closer this potential is to that of the electron monochromator, the greater the fraction of scattered electrons that will be rejected. Unless otherwise noted, the ET data were taken in the “high-rejection” mode of operation [10]. A peak in the total scattering cross section arising from the formation of a temporary anion creates a minimum in the transmitted current, and the energy at which this occurs corresponds to the most probable or vertical energy of electron attachment. To enhance the “resonance” structure, the derivative with respect to energy of the transmitted current is acquired [3], and the VAE is assigned to the energy of the midpoint between the two extrema in the derivative signal. The energy scales are calibrated in an admixture of the target compound with N_2 and by reference to the sharp structure arising from formation of the $N_2^{-}(^2\Pi_g)$ state. We assign an overall error of ±0.05 eV to the measured VAEs.

2.2. Dissociative electron attachment

Absolute total DEA cross sections were measured in an apparatus described in more detail elsewhere [1], although a significant change has been made to the electron beam collector since then [5]. This instrument also incorporates a trochoidal monochromator [9] to inject a magnetically collimated beam of electrons into a collision cell, within which is a cylindrical electrode 10 cm in length for collection of stable negative ions produced along the path of the electron beam. The gas pressure in the cell is determined by a temperature-regulated capacitance manometer and corrected for thermal transpiration effects. The temperature of the collision cell is $\simeq 65^\circ$C. Following the collision cell are a number of electrodes used to capture the unscattered portion of the electron beam and minimize the reflection of these electrons back into the cell. As we have emphasized before [1,5], misalignment of the electrodes of the apparatus with the magnetic field, and the return of main beam electrons back into the cell can cause systematic errors. In both of these cases, the apparent cross sections will be too large.

During the course of our studies, we have repeatedly measured the DEA cross section for O^-/N_2O as a useful reference to make sure that our apparatus is correctly aligned. At the time of our studies of the monochloroalkanes [1], our peak cross section at 2.25 eV was almost identical to the widely accepted value ($8.6 \pm 0.6 \times 10^{-18}$ cm^2) of Rapp and Briglia [11]. However, following changes to the beam collection configuration [5], we now find $7.64 \pm 0.6 \times 10^{-18}$ cm^2, about 10% below the earlier value. Although the error limits of the measurements overlap, we believe that the new arrangement offers better electron collection efficiency. We urge other experimentalists making total DEA cross-section measurements to include their results in N_2O to act as a reference point, and indeed, to disperse such checks throughout their studies to guarantee the continued alignment of their apparatus. We assign an error of ±10% to our absolute values.

A second apparatus incorporating a crossed electron and molecular beam is also used in these studies and is described elsewhere [12]. This instrument guides the anion fragments to stacked multichannel plates where they are counted. The energy resolution and dynamic range are superior to the total collection apparatus above, and we use it to determine the shapes of the DEA cross sections, especially at very low energy. The relative efficiencies for detection of different fragment masses, however, cannot be trusted. Our energy scales are calibrated in this apparatus with reference to the zero energy peaks associated with the *s*-wave attachment process in the various compounds. In our figures, we have positioned these peaks precisely at zero energy, however, convolution of the sharply varying and asymmetric cross section near zero energy with the electron beam distribution will actually place the peak approximately 20 meV above 0, depending on energy resolution. In this connection, we also note that our negative ion signals have not been normalized near 0 eV where the electron beam current is changing rapidly. The peaks therefore represent effective cross sections convoluted by our energy distribution.

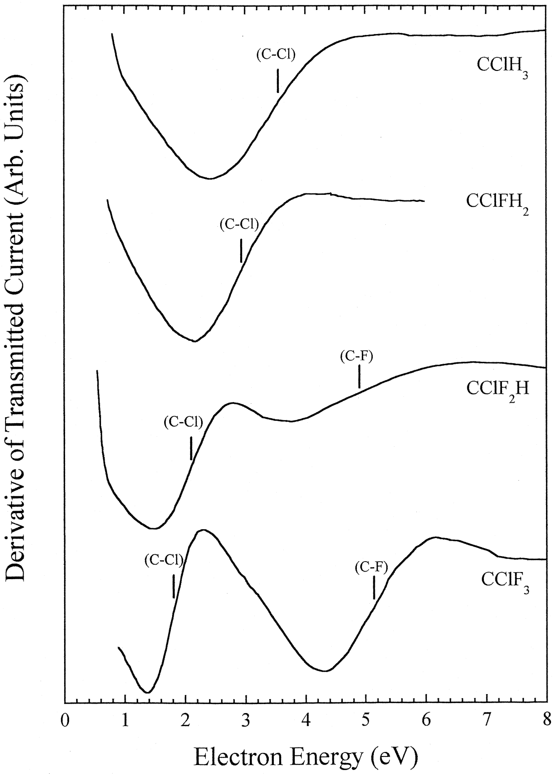

Fig. 1. Derivative with respect to energy of the transmitted electron current as a function of energy in $CClH_3$, $CClFH_2$, $CClF_2H$, and $CClF_3$. The vertical lines indicate the vertical attachment energies and are labeled with the bond giving rise to the σ^* empty orbital.

3. Results

3.1. Electron transmission spectroscopy

Figs. 1–3 show our ETS results, plotting the derivative with respect to energy of the transmitted (unscattered) electron beam current as a function of electron impact energy. The vertical lines indicate the locations of the midpoints of the resonance features

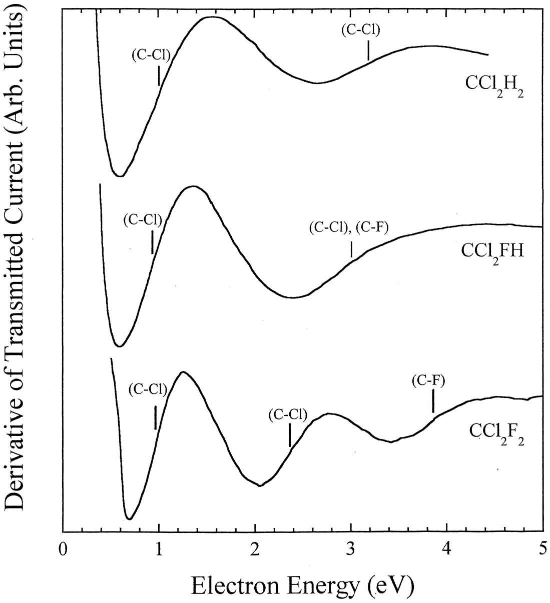

Fig. 2. As in Fig. 1 for CCl_2H_2, CCl_2FH, and CCl_2F_2.

we assign to the vertical attachment energies. The bond giving rise to the normally unoccupied σ^* molecular orbital associated with the anion state is indicated. Table 1 summarizes the VAEs, dip and peak energies, and dip-to-peak energy separations, ΔE_{dp}, of each resonance.

3.1.1.. *Monochlorofluoro compounds*

We begin by discussing the substituted methanes containing a single Cl atom shown in Fig. 1. The ET spectrum of $CClH_3$ is also shown at the top for reference [4,13]. We are not aware of other ETS or total electron scattering cross section measurements for either $CClFH_2$ or $CClF_2H$ that would locate the anion states. $CClF_3$, on the other hand, has been studied extensively by a number of techniques. The total scattering cross section measured by Jones [14] showed peaks at 2.0± 0.04 and 5.94± 0.07 eV, while the measurement of Underwood-Lemons et al.[15] found them at 2.0 and 5.5 eV. We continue to use values obtained from ETS for consistency with our other work. Mann and Linder [16] have examined vibrational excitation proceeding through the resonances in $CClF_3$ and discuss as well the symmetries of the anion states.

Our primary focus in the present work is on the characteristics of the lowest temporary anion state in these compounds. Fig. 1 clearly shows that the state associated with occupation of the C–Cl σ^* orbital is stabilized with increasing fluorination, owing to inductive effects and perturbative coupling with empty CF σ^* orbitals. The higher lying temporary anion states associated with the latter are seen in $CClF_3$ and $CClF_2H$. Our ET data in $CClFH_2$ above 6 eV indicate only a slowly increasing derivative signal and we could not assign a second VAE.

3.1.2. *Dichlorofluoro compounds*

Fig. 2 shows the ET spectra of CCl_2FH and CCl_2F_2, with that for CCl_2H_2 shown at the top for comparison. The ET spectrum for the latter compound was first measured [13] under low scattered electron rejection conditions [10]. Our recent measurement [4] uses high rejection, attempting to emulate the structure as it appears in the total scattering cross section. No ETS or total scattering measurement in CCl_2FH are known to us.

Temporary anion states in CCl_2F_2 have been extensively studied. The initial observation [13] of the

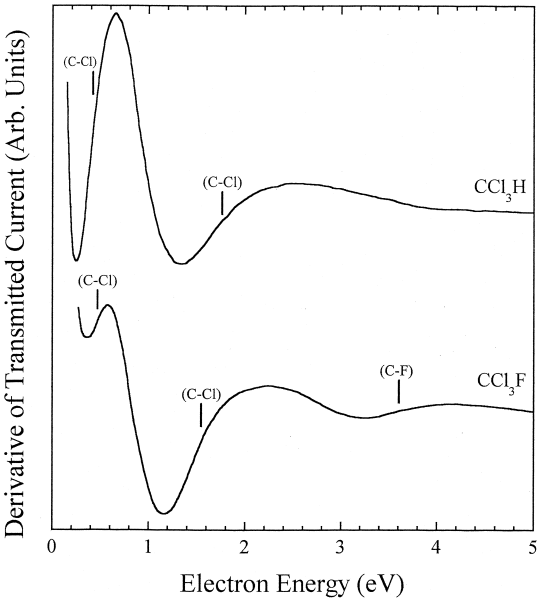

Fig. 3. As in Fig. 1 for CCl_3H and CCl_3F.

Table 1
The vertical attachment energies, dip, peak energies, and dip–peak separations in the chlorofluoromethanes (eV), as determined by electron transmission spectroscopy

Compound	Molecular orbital	VAE (eV)	Dip energy (eV)	Peak energy (eV)	Dip–peak separation (eV)
$CClH_3$	LUMO	3.45	2.38	5.43	3.05
$CClFH_2$	LUMO	2.94	2.14	4.17	2.03
$CClF_2H$	LUMO	2.11	1.46	2.76	1.30
	LUMO + 1	4.91	3.76	6.82	3.06
$CClF_3$	LUMO	1.83	1.39	2.31	0.92
	LUMO + 1	5.14	4.40	6.26	1.86
CCl_2H_2	LUMO	1.01	0.61	1.53	0.92
	LUMO + 1	3.17	2.61	3.90	1.29
CCL_2FH	LUMO + 1	0.94	0.60	1.38	0.78
	LUMO + 1	~3.01	2.39	4.38	1.99
CCl_2F_2	LUMO	0.97	0.70	1.26	0.56
	LUMO + 1	2.36	2.04	2.75	0.71
	LUMO + 2	3.86	3.4	4.5	1.1
CCl_3H	LUMO	0.42	0.25	0.65	0.40
	LUMO + 1,2	1.8	1.3	2.7	1.4
CCl_3F	LUMO	0.47	0.33	0.57	0.24
	LUMO + 1	1.54	1.16	2.26	1.10
	LUMO + 2	3.62	3.27	4.20	0.93

low-lying resonances was by ETS. Total scattering cross section measurements were carried out by Jones [14] and Underwood-Lemons et al. [15]. Vibrational excitation through the resonances was studied by Mann and Linder [17], and a comprehensive review of electron interactions with this molecule has been published by Christophorou et al. [18].

In comparing the ET spectra of CCl_2H_2 and CCl_2F_2, we observe that fluorination stabilizes the upper anion state substantially, as it did the C–Cl σ^* resonance in the monochloromethanes of Fig. 1. The lower of the two C–Cl σ^* anion states, however, is hardly affected. The second feature observed in CCl_2FH, centered roughly at 3 eV, is quite broad, consistent with an overlap of the second C–Cl σ^* anion with a higher lying C–F σ^* anion. In CCl_2F_2, the presence of two F atoms has stabilized the second C–Cl σ^* state sufficiently to separate it from the C–F σ^* anions. The resonance centered at 3.86 eV is primarily associated with the CF_2 moiety. We note that it lies considerably lower in energy than that of the CF_3 component of CF_3Cl (at 5.1 eV), owing to the inductive effect of the two chlorine atoms on CCl_2F_2.

3.1.3. Trichloro compounds

Fig. 3 displays the ET spectra of CCl_3F along with that of CCl_3H for comparison. The latter was first observed in a low-rejection spectrum [13], and Fig. 3 shows the high-rejection spectrum we have remeasured [4]. No other ETS measurements have been made in these compounds to our knowledge. The total scattering cross section of CCl_3F was measured by Jones [14] who observed the second and third resonances. His energy scale did not extend to low enough

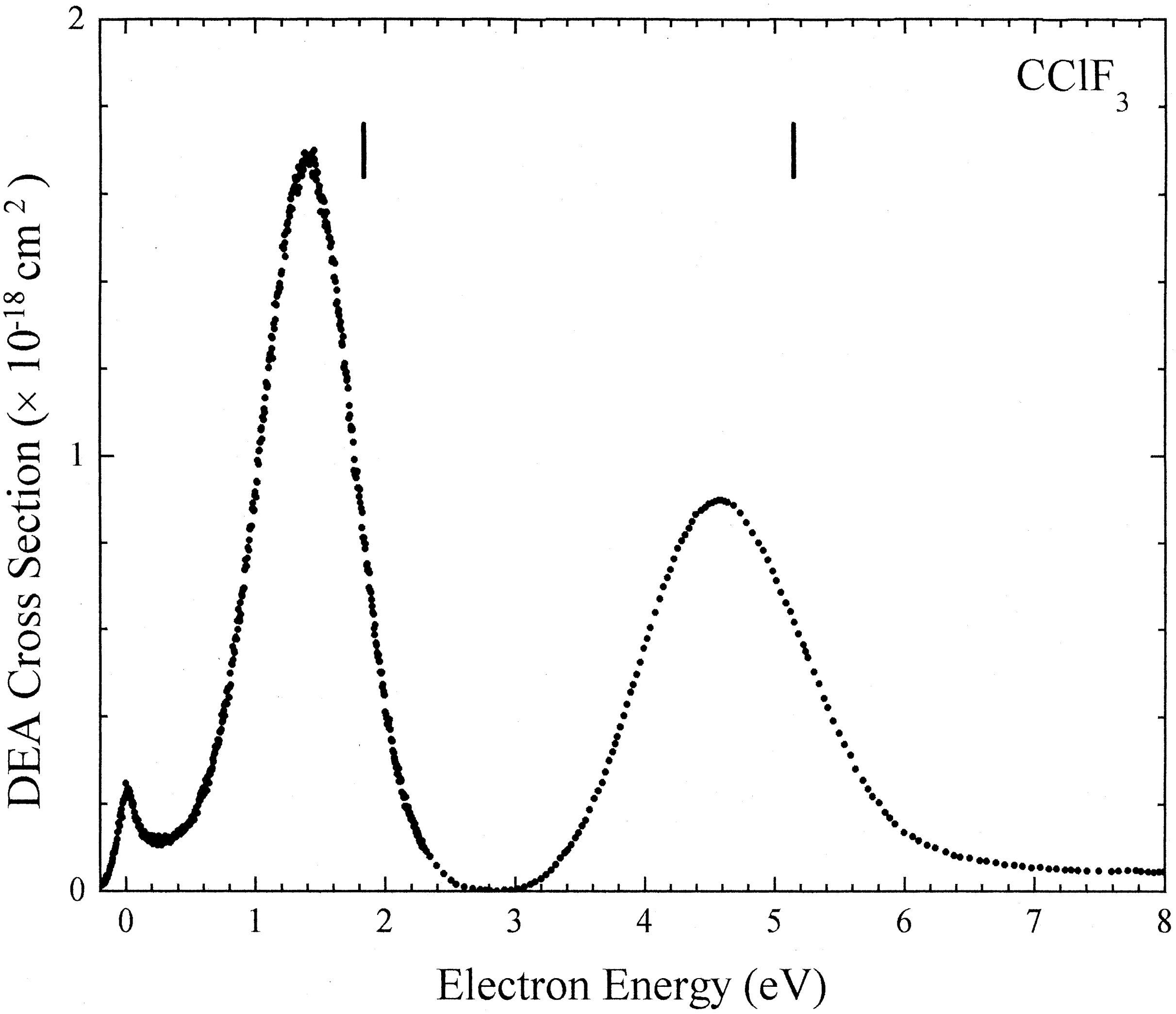

Fig. 4. Total cross section for the dissociative electron attachment process as a function of energy in $CClF_3$. The vertical lines indicate the VAEs for formation of the relevant temporary anion states.

energies to encompass the lowest anion state. Substitution of F for H stabilizes the second (*e*) resonance in CCl_3H similar to its behavior in the dichloromethanes. The ground state (a_1) anion, however is slightly destabilized.

3.2. Dissociative electron attachment

In Figs. 4–9, we plot the total cross sections for the DEA process as a function of the electron energy. For reference, vertical lines in Figs. 4–9 locate the VAEs for the temporary anion states taken from the ET spectra. Unless otherwise noted, the zero energy feature and next higher peak are from our ion counting data and are placed on an absolute scale by normalization at the peak cross section to our absolute measurements. Higher lying peaks, which give rise to other anion fragments in addition to Cl^- and therefore may not be consistent in magnitude in the ion counting apparatus, are from our digitized absolute measurements. The peak DEA cross sections and the energies at which they occur are listed in Table 2.

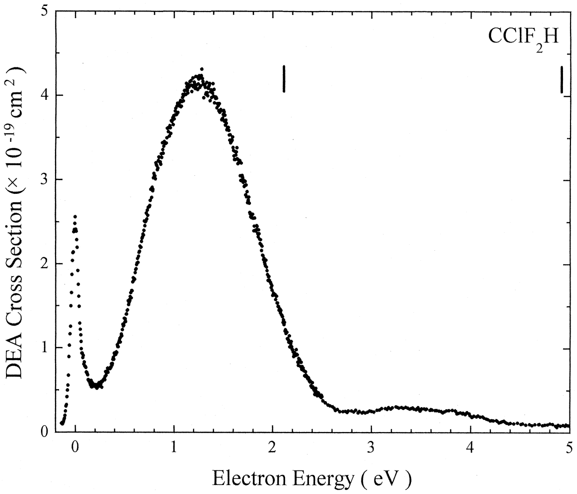

Fig. 5. As in Fig. 4 for CClF$_2$H.

3.2.1. Monochloro compounds

For ease of interpretation, we begin our discussion with CClF$_3$, shown in Fig. 4, and work our way to the less fluorinated compounds with higher VAEs and smaller cross sections. The DEA cross section displays two major peaks below 7 eV, in addition to the small peak at zero energy. There appear to be three measurements, summarized in Table 3, of the total DEA cross section with which to compare our results, an electron beam study by Underwood-Lemons et al. [19], and swarm studies by McCorkle et al. [20] and by Spyrou and Christophorou [21]. The present results are in exceptional agreement with the "swarm-unfolded attachment cross section" of the latter, as

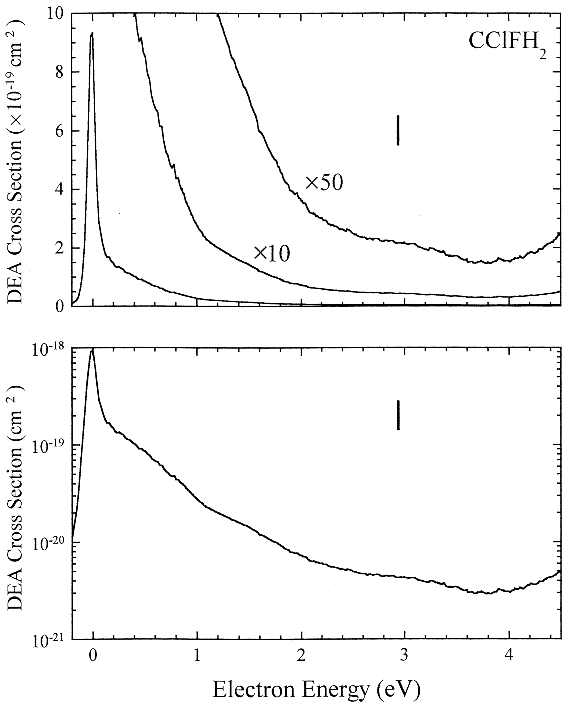

Fig. 6. As in Fig. 4 for CClFH$_2$. The lower panel shows the same data on a semilog plot.

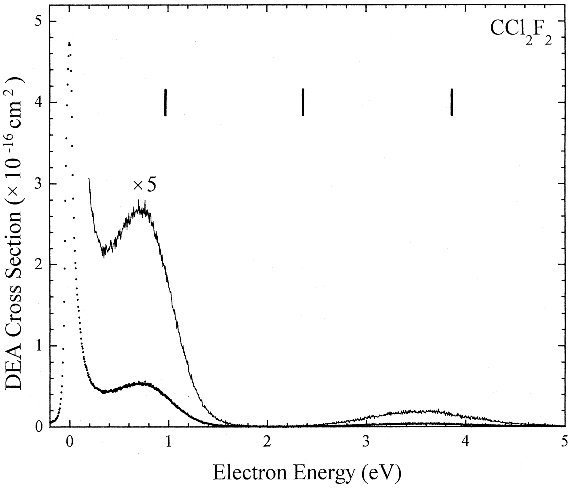

Fig. 7. As in Fig. 4 for CCl$_2$F$_2$.

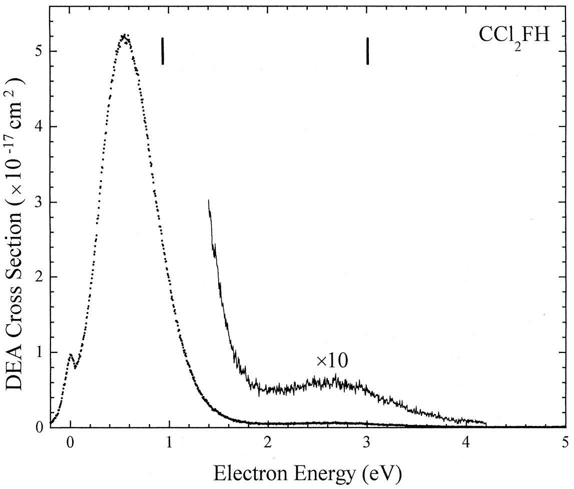

Fig. 8. As in Fig. 4 for CCl$_2$FH.

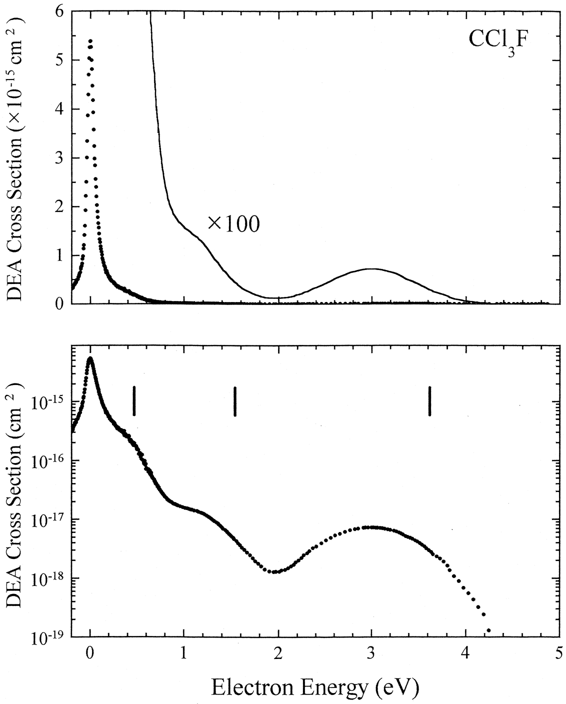

Fig. 9. As in Fig. 4 for CCl$_3$F. The lower panel shows the same data on a semilog plot.

read from Fig. 10 in [21], with respect to both peaks. The earlier work of McCorkle et al. [20] for the lower peak only, lies a factor of 1.2 higher. The electron beam results of Underwood-Lemons et al. [19] are in substantial disagreement with the present work and that of Spyrou and Christophorou [21], lying a factor of 2.3 higher for both peaks. Although the work was carried out at a somewhat higher temperature (393 K), this does not appear to account for the difference in cross sections. Temperature studies in CClF$_3$ have been made by Spyrou and Christophorou [21] and Hahndorf et al. [22], and both show that the second peak is relatively insensitive to temperature variation.

The total DEA cross section of CClF$_2$H is shown in Fig. 5. In contrast to CClF$_3$, the contribution from the anion state associated with the C–F σ^* orbitals is greatly reduced with respect to that from the lowest anion state. Bruening et al. [23] have carried out a study of the mass-analyzed anion fragments as a function of electron energy, finding a maximum in the production of Cl$^-$ at 1.1 eV and of F$^-$ at 3.4 eV, in rather good agreement with the present work. A crude estimate of the cross section for the 1.1 eV feature was made by comparison to the SF$_6^-$ calibration peak. This yielded a value of $\approx 2 \times 10^{-18}$ cm^2, about 4.8 times larger than we measured but reasonably close considering the many assumptions involved in this approach. A nonthermal swarm measurement by Jarvis et al. [24] found a maximum cross section of

Table 2
Peak DEA energies and cross sections in chlorofluoromethanes

Compound	Molecular orbital	DEA peak energy (eV)	DEA peak cross section (cm^2)
CClFH$_2$	LUMO	~1.4[a]	7.2×10^{-21} [a]
CClF$_2$H	LUMO	1.27	4.17×10^{-19}
	LUMO + 1	3.36	3.4×10^{-20}
CClF$_3$	LUMO	1.40	1.68×10^{-18}
	LUMO + 1	4.56	9.00×10^{-19}
CClF$_2$FH	LUMO	0.55	5.22×10^{-17}
	LUMO + 1	2.61	5.63×10^{-19}
CCl$_2$F$_2$	LUMO	0.71	5.44×10^{-17}
	LUMO + 1	3.55	4.27×10^{-18}
CCl$_3$F	LUMO	0.15[a]	4.2×10^{-16} [a]
	LUMO + 1	1.0[a]	1.2×10^{-17} [a]

[a] Peak fitting result.

Table 3
Peak DEA cross sections (cm^2) in CClF$_3$, CCl$_2$F$_2$, and CCl$_3$F

CClF$_3$ Peak energy (eV)	Present work	Spyrou and Christophorou[a] (Swarm)	McCorkle et al.[b] (Swarm)	Underwood-Lemon et al.[c] (Beam)
1.40	1.68×10^{-18}	1.63×10^{-18}	2.09×10^{-18}	3.8×10^{-18} (393 K)
4.56	0.90×10^{-18}	0.91×10^{-18}		2.1×10^{-18} (393 K)
CCl$_2$F$_2$ Peak energy (eV)	Present work	Pejcev et al.[d] (Beam)	McCorkle et al.[b] (Swarm)	Underwood-Lemon et al.[c] (Beam)
0.71	5.44×10^{-17}	$\sim 7.2 \times 10^{-17}$	8.9×10^{-17} (0.9 eV)	6.0×10^{-17} (393 K)
3.55	4.27×10^{-18}	7.0×10^{-18}		$\sim 6 \times 10^{-18}$ (393 K)
CCl$_3$F Peak energy (eV)	Present work		McCorkle et al.[b] (Swarm)	
0.15	4.2×10^{-16}		9.46×10^{-16} (0.25 eV)	
1.0	1.2×10^{-17}		6.70×10^{-16} (0.75 eV)	

[a] See [21].
[b] See [20].
[c] See [19].
[d] See [28].

4.8×10^{-19} cm^2, in very good agreement, but peaking at an energy of 2.0 eV, substantially above that found here.

Fig. 6 gives our data in CClFH$_2$, the most problematic result in the series we are investigating here. The lower panel shows the results on a semilog scale. The high VAE of this compound, coupled with the rapid rate of decrease of the cross section magnitudes with VAE encountered in the monochloroalkanes [1,2] suggests a very small DEA cross section. In this regard, it is useful to recapitulate what is known about DEA in methyl chloride (CClH$_3$) for comparison. Semiempirical calculations by Fabrikant [25] have shown that the cross section from the ground vibrational level is extremely small, 4×10^{-23} cm^2 at 1.9 eV, with a smaller peak near 0.8 eV. At room temperature, on the other hand, the yield of Cl$^-$ is entirely dominated by that from the sparsely populated excited levels. The DEA cross section of the latter, according to theory, has its maximum value at low energy, approximately 0.7 eV. As the temperature increases, this low energy peak is greatly enhanced [26].

The data in Fig. 6 suggest that the DEA cross section of CClFH$_2$ has characteristics that are intermediate between the behavior of CClH$_3$ and the other monochloro compounds with lower VAEs. Below 4 eV, Fig. 6 shows evidence for three DEA processes, in addition to the peak at zero energy that may arise in part from impurities. There is a shoulder or unresolved peak in the region of a few hundred millielectron volts above the zero energy peak, a second feature between 1 and 2 eV, and a third near 3 eV. The first of these we ascribe to DEA from thermally populated vibrational levels, as in the case of CClH$_3$. The small contribution located between 1 and 2 eV we interpret as arising from same mechanism that produces the major peak in Figs. 4 and 5, namely vertical electron attachment into the LUMO followed by DEA. This peak is appropriately shifted to much lower energy from the indicated VAE because of the short temporary anion lifetime. In contrast to the other molecules and again by analogy to CClH$_3$, it is very likely that a portion of the cross section arises from $v > 0$. An attempt at peak fitting to the data in Fig. 6

was carried out and yielded a cross section of 7.2×10^{-21} cm^2 at an energy of 1.4 eV. This is the cross section we will correlate with the measured VAEs in Sec. 4, but it should be viewed as an upper bound to the cross section from $v = 0$. The peak at 3.1 eV we interpret as arising from a resonance (not observed in ETS) associated with occupation of the higher lying C–F σ^* orbital.

3.2.2. Dichloro compounds

Fig. 7 shows the DEA cross section of CCl_2F_2. Electron interactions with this compound have been reviewed extensively by Christophorou et al. [27]. With regard to the two cross section maxima lying above zero energy, there are two absolute measurements using electron beams, the earlier by Pejcev et al. [28] and the more recent by Underwood-Lemons et al. [19]. A swarm study of the lower peak was carried out by McCorkle et al. [20]. The cross section maxima are summarized in Table 3, where we have used our measured energies to designate the peak locations. Agreement between the present work and that of Underwood-Lemons et al. is much better than in $CClF_3$ discussed earlier, falling within the experimental error. The swarm result [20] for the lower peak is a factor of 1.6 higher than ours.

Mann and Linder [29] have noted that the second C–Cl σ^* resonance (b_2 symmetry) that we locate at 2.36 eV does not appear to give rise to negative ion fragments. Given the correlations between VAE and peak cross section we describe elsewhere [1,2,5] and below, it is likely that the second resonance contributes only approximately 1% as much as the first resonance (a_1 symmetry), and thus is swamped by the latter.

The DEA cross section of CCl_2FH is shown in Fig. 8. Tegeder et al. [30] have recently published mass-selected relative cross sections with shapes that are consistent with our work, although our measurements indicate a small zero energy peak that is not present in their data. They find that the feature near 2.7 eV is primarily due to F^-. As in the case of CCl_2F_2, this contribution arises from the C–F σ^* resonance rather than the upper C–Cl σ^* anion. The nonthermal swarm results found by Jarvis et al. [24] in CCl_2FH are difficult to reconcile with the present work. They find two peaks, the lower of which lies near 0.4 eV with a magnitude of $\approx 3 \times 10^{-17}$ cm^2. This could reasonably be associated with our peak at 0.55 eV of magnitude 5.22×10^{-17} cm^2. However, we find no evidence in Fig. 8 for their still larger second peak lying at 1.25 eV with a magnitude of 4.5×10^{-17} cm^2.

3.2.3. CCl_3F

Fig. 9 shows our results in CCl_3F, with the DEA cross section on a linear scale in the upper panel and a semilog plot in the lower. The enormous zero energy peak in this compound tends to obscure the feature we are most interested in here, although it can be clearly seen as a shoulder just below the lowest VAE in the lower panel of Fig. 9. The peak at 3 eV, however, could be accurately measured in the total ion collection system. The data from the ion counting apparatus was joined near 0.8 eV. Because the range of overlap (200 meV) was small, the magnitude of the cross section below this energy is not as accurate.

Peak fitting routines were carried out to determine the cross section of the contribution below 1 eV and suggested a peak value of 4.2×10^{-16} cm^2 at an energy of 0.15 eV. In similar fashion, the peak near 1.0 eV had a maximum value of 1.2×10^{-17} cm^2. The results are given in Table 3 and compared with the swarm data of McCorkle et al. [20]

4. Correlation

Having acquired the VAEs and DEA cross sections of the chlorofluoromethanes, we now consider the correlation between the VAEs of the lowest C–Cl σ^* anion states and the peak values of the associated DEA cross sections giving rise to Cl^- from these temporary anions. In particular, we are curious to see the extent to which the present compounds obey the same dependence that we observed [Eq. (1)] in the polychloroalkanes [5]. The latter, tabulated elsewhere [1,4,5], are shown as filled circles in Fig. 10 in which we plot the peak cross sections versus VAE. The dashed line shows the best-fit [Eq. (1)] to the polychloroalkane data for compounds having $0.6 < \text{VAE} < 2.8$ eV, ex-

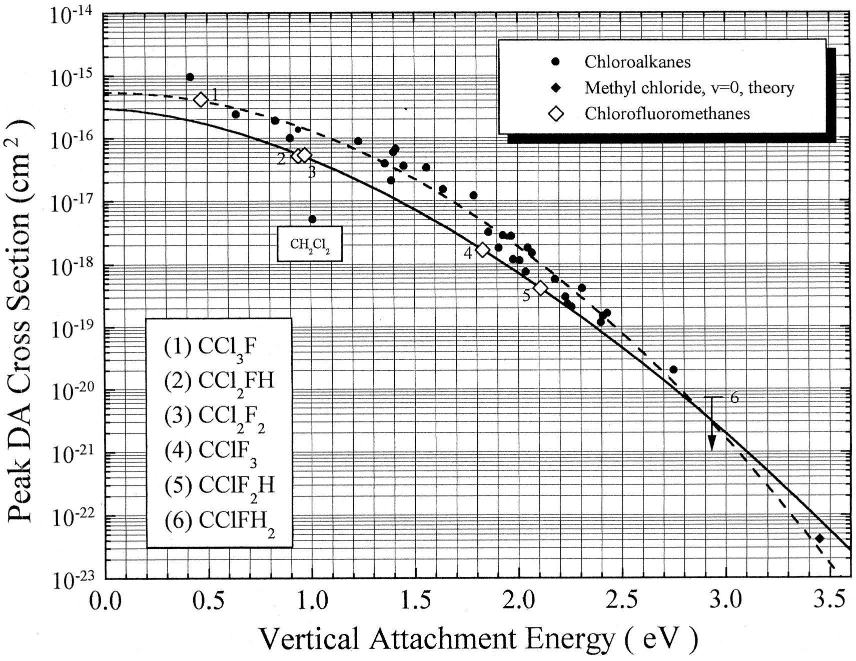

Fig. 10. Peak values of the DEA cross sections as a function of VAE. The dashed line and filled circles refer to the chloroalkanes [5]; the solid line and open diamonds to the chlorofluoromethanes. In all cases the cross sections are those peaking above 0 eV and not those arising from the *s*-wave attachment at 0 eV.

cluding CCl_2H_2 [5]. As noted earlier, the latter yields the only anomalous result we have found in this range among the more than 30 compounds we investigated. Our result for CCl_3H, at VAE = 0.42 eV, has also not been included in this fit, for reasons discussed in more detail elsewhere [5]. Our data in the chloroalkanes are sparse at high VAEs where the DEA cross sections are small. We include one theoretical cross section computed by Fabrikant [25] for the $v = 0$ level of $CClH_3$ at the experimental value of its VAE = 3.45 eV. The dashed best-fit line passes gratifyingly close to this point although it was not included in the fit.

Our present data in the chlorofluoromethanes are shown as open diamonds in Fig. 10. The result for $CClFH_2$ is shown as an upper bound, as described earlier. The peak cross sections fall uniformly below those of the chloroalkanes and generally outside the ±38% average deviation from the best-fit line to the chloroalkanes. On the other hand, the overall dependence on VAE is quite similar. The solid line shows a best-fit of the same general form ($\log \sigma_{\mathrm{DEA}}^{\mathrm{peak}} = A \times \mathrm{VAE}^n + B$) through the chlorofluoromethane data from $0.9 < \mathrm{VAE} < 2.2$ eV, that is, excluding CCl_3F and $CClFH_2$, yielding

$$\sigma_{DEA}^{peak} = 2.97 \times 10^{-(16+0.81 VAE^{1.69})}\ \mathrm{cm}^2 \qquad (2)$$

for comparison with Eq. (1).

In our work on the chloroalkanes [5], we related the dependence on VAE in Eq. (1) to the variation of the temporary anion survival factor over this series of compounds. In the simplest formulation of the DEA cross section by O'Malley [31],

$$\sigma_{\mathrm{DEA}} = \sigma_{\mathrm{cap}} \times \exp(-t_{\mathrm{sep}}\hbar),$$

where σ_{cap} is the capture cross section for formation of the anion, Γ is the average spread in energy of the anion owing to its finite lifetime, and t_{sep} is the time required for the vertically formed anion to move along its potential surface and reach the crossing point with the potential curve of the neutral molecule. Over a class of related molecules, both factors in the expo-

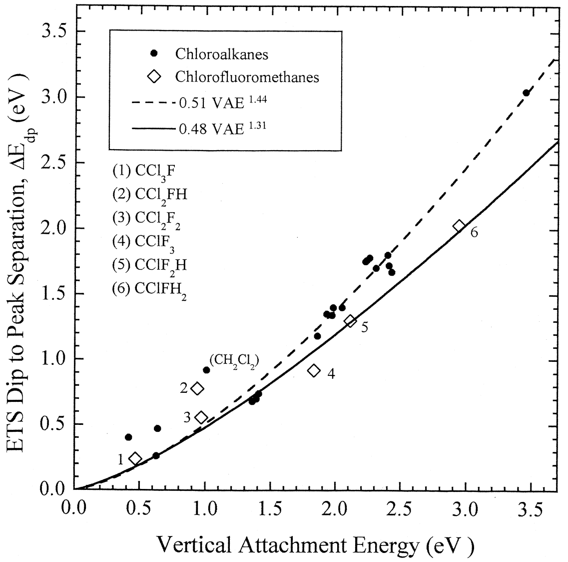

Fig. 11. Dip-to-peak energy separation of the ETS features as a function of VAE. The dashed line and filled circles refer to the chloroalkanes [4]; the solid line and open diamonds to the chlorofluoromethanes.

nential can be viewed as functions of VAE, and our measurements [5] [Eq. (1)] suggested that t_{sep} $\Gamma \propto \mathrm{VAE}^{2.01}$, whereas in the chlorofluoromethanes, it appears that t_{sep} $\Gamma \propto \mathrm{VAE}^{1.69}$.

Information on the variation of Γ alone may be obtained from the widths of the structures in the ET spectra. The dip-to-peak energy separations, ΔE_{dp}, for those compounds having clearly isolated lowest anion states are plotted as a function of VAE in Fig. 11. The chloroalkanes are shown as filled circles and the chlorofluoromethanes as open diamonds. The dashed and solid lines show a best-fit to these respective data of the form $A \times \mathrm{VAE}^n$, (excluding CCl_2H_2). ΔE_{dp} contains a contribution from Franck-Condon (FC) widths arising from the overlap between the ground state of the neutral and the anion curve as well as the broadening Γ owing to the finite anion lifetime. In the chloroalkanes [4], a family of simple Morse potentials curves representing the anions were generated to provide estimates of the FC widths as a function of VAE. From these it was concluded that Γ is the dominant contributor for VAE $>$ 1 eV. If the precise energy dependence of the resonance profiles in the total scattering cross sections were known, they could be fit with analytic functions. Unfortunately this is not the case. Nevertheless a crude unfolding of ΔE_{dp} to estimate Γ(VAE) was carried out. We concluded that the dependence was consistent with $\Gamma \propto \mathrm{VAE}^{1.5}$, as would be predicted by the Wigner threshold law [32] for tunneling through a *p*-wave angular momentum barrier. Given that the C–Cl σ* local orbitals appear to be largely p_σ in character, this interpretation seems satisfactory. This result then implied that $t_{sep} \propto \mathrm{VAE}^{0.5}$. This weak dependence, as well, appears to be consistent with our simple Morse potential models [5].

As Fig. 11 shows, the variation of ΔE_{dp} with VAE in the chlorofluoromethanes is somewhat weaker than that in the chloroalkanes. Although the slightly smaller widths could imply smaller Γ's and thus longer temporary anion lifetimes, this would be at odds with the peak DEA cross sections which are smaller than those in the chloroalkanes for given values of VAE. Alternatively, the smaller ΔE_{dp} of Fig. 11 may imply smaller contributions from FC factors over this class of molecules. This in turn would suggest less steep anion potential curves in the FC region, and thus longer separation times and consequently smaller DEA cross sections, consistent with our measurements. Theoretical input on the anion curves would be useful to confirm this conjecture.

The strong dependence of $\sigma_{DEA}{}^{peak}$ on VAE in both Eqs. (1) and (2) supports the dominant role of the survival factor, and more specifically Γ(VAE), in determining the DEA cross section over the range of VAE $>$ 0.6 eV. For lower values of VAE, the survival factor changes more slowly and variations in the capture cross section become significant, particularly the shape and location of the anion curve with respect to the neutral. We note in this context that $\sigma_{DEA}{}^{peak}$ for both CCl_3H and CCl_3F, having VAEs $<$ 0.5 eV, appears to depart from the dependence in Eqs. (1) and (2).

Regarding the anomalous behavior of CCl_2H_2 in Fig. 10, we note that its analog, CCl_2F_2, does not share this property. Although successive fluorination does not alter VAE very much as shown in Fig. 11, it decreases ΔE_{dp} substantially, and CCl_2F_2 appears to lie on the lines characteristic of both families of compounds. The specific property of CCl_2H_2 accounting for its behavior is still unclear.

From a practical point of view, the correlations observed here provide a means to predict peak DEA cross sections if VAEs are known or can be accurately calculated. For such applications, knowledge of the extent to which the energy-integrated cross sections correlate with VAE will be important, and this work is underway. Future efforts will also require achieving a deeper understanding of the shapes of the cross sections and the factors that determine the energies at which the peaks occur. Finally, the data set for the chlorofluoromethanes is small, and its extention to the substituted ethanes is clearly worthwhile to confirm the correlation observed in Fig. 10.

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