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Temporary Anion States of Dichloroalkanes and Selected Polychloroalkanes

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The electron attachment energies associated with the short-lived occupation of the C−Cl σ^* orbitals of dichloroalkanes and selected polychloroalkanes are measured in the gas phase using electron transmission spectroscopy and compared with those observed previously in monochloroalkanes. In the dichloroalkanes, evidence for two well-resolved anion states is found only in the compounds with both chlorines on the same carbon atom. The effects of methyl substitution on chlorine-bearing carbon atoms are examined in detail and are observed to *stabilize* temporary anion states lying above ∼1.5 eV but to *destabilize* those lying below. The spread in energy of the anion states, attributable to their finite lifetimes, is examined as a function of the vertical attachment energies (VAEs) of the anions and found to vary as $\mathrm{VAE}^{1.5}$, consistent with the relationship expected on theoretical grounds for the monochloroalkanes. Calculated energies of the lowest unoccupied molecular orbitals (LUMOs) are also presented and compared with the measured VAEs.

1. Introduction

The energy of a temporary anion state formed by the short-lived attachment of a free electron into the lowest unoccupied molecular orbital (LUMO) of a compound in the gas phase provides a fundamental measure of the susceptibility of the compound to electron reduction. Because electron attachment is a rapid process relative to the time scale of nuclear motion, such energies characterize this property at the equilibrium geometry of the neutral molecule in its ground electronic state. The energy of such an anion state lies energetically above that of the neutral molecule plus a free electron at infinity, and the state is unstable with respect to autodetachment of the electron. By convention, molecules with these characteristics are said to possess *negative* vertical electron affinities (VEAs). The (positive) kinetic energy of the attaching electron is conveniently denoted as the vertical attachment energy (VAE), and the two quantities are related by VEA = −VAE.

It is important to distinguish these quantities from their adiabatic analogues. Adiabatic electron affinities are given by the difference in energy between the anion and neutral, with each at its equilibrium geometry. Such energies have been measured or estimated by a variety of methods over the years and have been employed as indicators of reducibility.[1] However, they may not be appropriate measures for processes in which an electron is rapidly transferred to a neutral molecule.

In this work, we present measurements of VAEs in a large series of dichloroalkanes and selected mono-, tri-, and tetrachloroalkanes. The reductive properties of this family have been extensively studied in solution, and many of the compounds are of considerable environmental concern. The low-lying temporary anion states we describe here arise from electron occupation of combinations of the C−Cl σ^* molecular orbitals, and in this article, we elaborate on the connections between the structures of the molecules, their VAEs, and the lifetimes of the anion states. Finally, we explore the extent to which quantum-chemical calculations of LUMO energies can replicate measured VAEs. Such computed values are widely used to generate quantitative structure/activity relationships (QSARs) for reactions in which electron transfer occurs.[1]

The present work is a vital part of a comprehensive study of bond breaking induced by electron attachment. In a separate paper,[2] we present measurements of the total cross sections for the dissociative electron attachment (DEA) process, $e^- + AB \rightarrow AB^{-*} \rightarrow A + B^-$, in the dichloroalkanes and selected polychloroalkanes. There, we show the close correlation between the peak DEA cross sections and the properties of the temporary anion states described below. An earlier study[3] describes related work carried out in the monochloroalkanes.

Following a brief discussion of our experimental method, we begin by reviewing previous results for the monochloroalkanes that were obtained by our group and by others. We continue with our new results for the dichloroalkanes and selected polychloroalkanes. In the final section, we relate calculated LUMO energies to our measured VAEs.

2. Electron Transmission Spectroscopy

Electron transmission spectroscopy (ETS), in the format devised by Sanche and Schulz,[4] is a convenient and efficient method for locating the sharp structure in total electron scattering cross sections arising from the formation of temporary anion states. The application of this technique to organic molecules has been reviewed elsewhere.[5−7] Briefly, a magnetically collimated electron beam produced by a trochoidal electron monochromator[8] 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. 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,[4] and the VAE is assigned to the energy of the midpoint between the two extrema. Energy scales are calibrated in an admixture of the target compound with N_2 by reference to the sharp

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TABLE 1: Vertical Attachment Energies and Dip-to-Peak Separations (in parentheses) in the Monochloroalkanes[a]

compound	Guerra et al. ref 11	Burrow et al. ref 10	Modelli et al. ref 12	Pearl et al. ref 3	present work
methyl chloride		3.45 (2.3)			3.45 (3.05)
ethyl chloride	2.35 (1.8)				2.41 (1.72)
1-chloropropane	2.40 (1.8)				
1-chlorobutane	2.39 (1.8)				2.43 (1.67)
1-chloropentane	2.26 (1.78)				
1-chlorooctane				2.24 (1.76)	
1-chlorononane				2.23 (1.75)	
2-chloropropane	1.99 (1.35)				1.97 (1.34)
2-chlorobutane	2.05 (1.4)				
t-butyl chloride			1.80 (1.20)		1.86 (1.18)
cyclobutyl chloride				1.98 (1.4)	
cyclopentyl chloride				1.93 (1.35)	
cyclohexyl chloride				2.31 (1.70)	

[a] All values are in electronvolts.

structure arising from formation of the $N_2^-(^2\Pi_g)$ state. This state, in turn, was previously calibrated against the $He^-(1s2s^2)$ resonance. The energies of the first few positive extrema in the derivative signal in N_2 are found to lie at 1.98, 2.22, 2.46, and 2.69 eV. We assign an overall error of ±0.05 eV to the measured VAEs. 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.[9]

3. Vertical Attachment Energies

A. Monochloroalkanes. We begin by reviewing the low-lying temporary anion states of a number of monochloroalkanes studied by ETS. The dominant feature in the electron scattering cross section of each is a resonance ascribed to temporary occupation of the C−Cl σ^* molecular orbital. Anion states associated with the C−C and C−H σ^* orbitals lie at higher energies, are broad and overlapping, and will not be discussed here. Table 1 summarizes the ETS results for three different groups of molecules. At the top are normal or linear chain chloroalkanes: CH_3Cl by Burrow et al.,[10] $CH_3(CH_2)_nCl$ with $n = 1-4$ by Guerra et al.,[11] and $CH_3(CH_2)_7Cl$ and $CH_3(CH_2)_8Cl$ by Pearl and Burrow.[3] Following this are two secondary alkanes, 2-chloropropane and 2-chlorobutane (Guerra et al.),[11] and a tertiary alkane *tert*-butyl chloride (Modelli et al.).[12] At the bottom are three cyclic compounds, c-$C_nH_{2n-1}Cl$ with $n = 4-6$ (Pearl and Burrow).[3] During the course of the present work, we remeasured a number of these compounds, and our new values are listed in the right-most column. Numbers inside parentheses are the energy spacings between the minimum (dip) and maximum (peak) in the derivative signal of each resonance. This separation, which we label ΔE_{dp}, is a measure of the width of the resonance peak as it appears in the total scattering cross section and, as discussed later, is related in part to the inverse lifetime of the temporary anion state. Within the quoted experimental uncertainties, the VAEs determined by the different groups are in agreement.

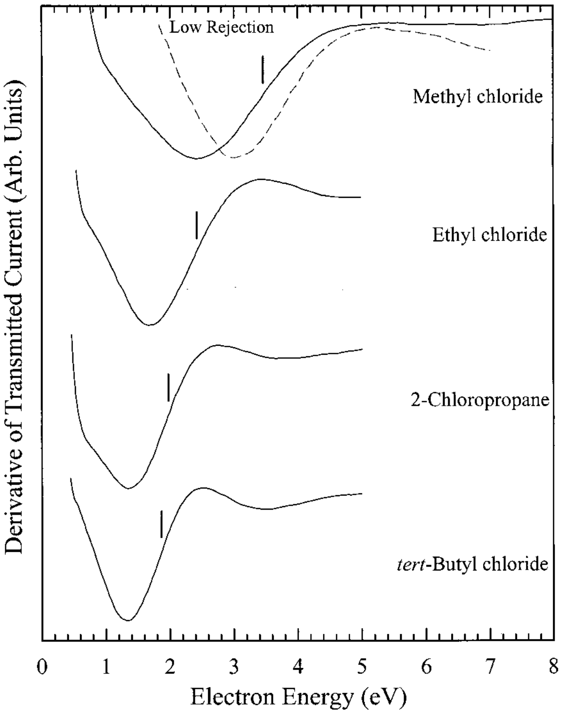

Figure 1. Derivative with respect to energy of the transmitted electron current through several monochloroalkanes as a function of electron energy. The dip and peak structure characterize temporary anion states associated with occupation of the C−Cl σ^* orbitals. The vertical bars indicate the positions of the vertical attachment energies. The dashed curve marked "Low Rejection" is discussed in the text.

The most significant changes in VAEs among the monochloroalkanes arise from methyl group substitution on the methyl chloride frame. Figure 1 illustrates this series, plotting the derivative of transmitted current as a function of electron energy. As indicated earlier, the temporary anion states are manifested by a dip followed at higher energy by a peak in the derivative signal. The vertical line locates the midpoint energy that we associate with the VAE. We comment on the dashed curve for CH_3Cl, labeled "Low Rejection", later in this section.

Typical of substituent effects, the first replacement of H by CH_3 produces the largest change in energy. As far as we are aware, a convincing theoretical description of the source of the difference in anion energies between methyl and ethyl chloride has not been given. Pearl and Burrow[3] noted that the C−C σ^* orbital introduced in going from methyl to ethyl chloride lies below that of C−H σ^* but above that of C−Cl σ^* and thus will perturbatively stabilize the latter. Furthermore, each successive H atom replacement reduces the C−Cl bond strength somewhat[13] and increases the equilibrium C−Cl internuclear distance in the neutral molecule.[14] Both of these results effectively bring the potential curve of the neutral at its equilibrium geometry closer to that of the anion, reducing the VAE. Returning to the sequence of normal monochloroalkanes, Table 1 indicates that, from ethyl chloride to 1-chlorononane, only a slight additional stabilization of the VAE occurs.

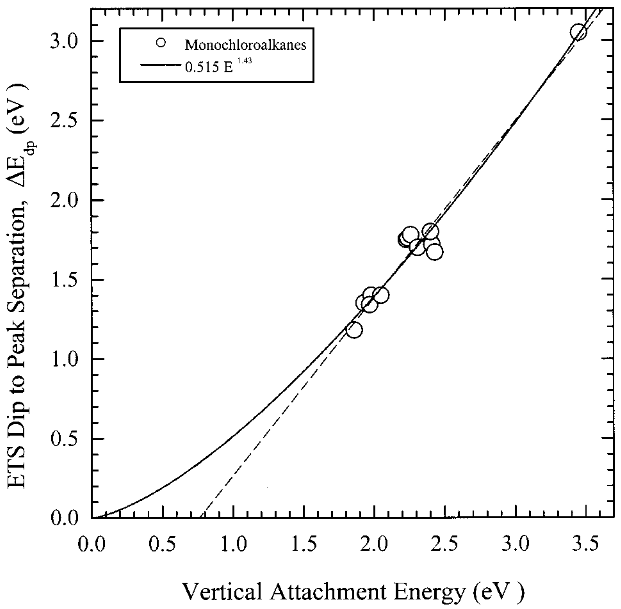

Figure 2. Dip-to-peak separations as a function of the vertical attachment energies of temporary anion states of the monochloroalkanes. The dashed line indicates an earlier linear fit. The solid line shows a fit consistent with known threshold law dependences.

TABLE 2: Vertical Attachment, Dip, and Peak Energies and Dip−Peak Separations in the Dichloroalkanes[a]

compound	molecular orbital	VAE	dip energy	peak energy	dip−peak separation
dichloromethane	LUMO	1.01	0.61	1.53	0.92
	LUMO+1	3.17	2.61	3.90	1.29
1,2-dichloroethane		2.01	1.19	3.33	2.14
	LUMO	1.7 est			
	LUMO+1	2.4 est			
1,3-dichloropropane		1.91	1.22	2.95	1.73
1,4-dichlorobutane		2.07	1.33	3.06	1.73
1,5-dichloropentane		2.04	1.31	3.16	1.85
1,6-dichlorohexane		2.01	1.32	3.15	1.83
1,8-dichlorooctane		2.18	1.47	3.14	1.67
1,9-dichlorononane		2.30	1.56	3.26	1.70
1,1-dichloroethane	LUMO	1.36	1.05	1.73	0.68
	LUMO+1	2.68	2.26	3.18	0.92
1,1-dichloropropane	LUMO	1.39	1.07	1.77	0.70
	LUMO+1	2.62	2.22	3.16	0.94
2,2-dichloropropane	LUMO	1.41	1.07	1.82	0.74
	LUMO+1	<2.5	2.1	∼2.65	>0.6
1,2-dichloropropane		1.64	1.19	2.42	1.23
1,2-dichloro-2-methylpropane		1.40	0.97	1.98	1.01
2,3-dichlorobutane		1.56	1.06	2.32	1.26
trans-1,2-dichlorocyclohexane	LUMO	1.45	1.02	2.03	1.01
	LUMO+1	2.74	2.40	3.18	0.78
1,3-dichlorobutane		1.79	1.24	2.61	1.37

[a] All values are in electronvolts.

Additional information about the temporary anion states is contained in the widths of the resonance peaks. Figure 2 shows the variation of the dip-to-peak separation, ΔE_{dp}, as a function of VAE, where we have used our own measurements where possible. For consistency, we note that earlier ETS results in methyl chloride[10] were determined with lower scattered electron rejection and yielded a ΔE_{dp} value of approximately 2.3 eV. As the dashed curve at the top of Figure 1 indicates, the shape of the signal changes considerably with retarding voltage in this compound. For consistency with the rest of the data presented here, we have used in Figure 2 the width, 3.05 eV, determined with the greatest amount of rejection, thus more closely emulating the structure as it appears in the total scattering cross section. Because of the shape of the profile, however, the width cannot be determined with great accuracy.

Pearl and Burrow[3] pointed out earlier that the dependence in Figure 2 was approximately linear, shown as a dashed line, over the narrow range for which VAEs were available, but noted that this behavior would be unphysical at low values of the VAE. Unfortunately, no one has yet devised an analytic expression that can be fit to the measured ET spectra to determine the factors contributing to the dip-to-peak separation. Because of the short lifetime of an anion state, a portion of the width derives from the spreading in energy attributable to the uncertainty principle. The remainder of the width derives from Franck−Condon (FC) overlap factors between the ground-state nuclear wave function with that of the temporary anion.

For the case of an autodetaching electron tunneling through a spherically symmetric angular momentum barrier, the resonance width, Γ, according to the Wigner threshold law,[15] should behave as $E^{l+1/2}$,where l is the angular momentum quantum number of the electron. In the molecular case, where l is no longer a good quantum number, the dependence is more complicated, although there may be cases in which a single angular momentum component dominates. From the shape of the C−Cl σ^* orbital, we expect that the wave function will have a large component of p_σ character and, thus, that the width should vary as $E^{1.5}$. In a series of molecules of different VAEs positioned in this same angular momentum barrier, we expect that the widths will, therefore, vary as $VAE^{1.5}$. The solid curve in Figure 2 shows a power-law fit to ΔE_{dp} in the monochloroalkanes, which yields a dependence of $E^{1.43}$, in general support of this picture.

To gain insight into the role of FC effects, we generated Morse potential curves for the neutral and anion states of methyl chloride but allowed the VAE to range from 3.45 to 0.80 eV, keeping other parameters the same, thus producing a family of anion curves emulating those of the other monochloroalkanes.[16] The C−Cl bond energy was taken to be approximately equal to the electron affinity of Cl in all cases. By reflecting the Gaussian ground-state wave function onto the anion curves, the full-width at half-maximum (fwhm) of the Franck−Condon "band" could be approximated, and it was found to increase linearly with the VAE. This exercise showed that the major contributor to the total width arises from finite lifetime broadening, rather than from FC factors. Assuming that the widths of the two broadening mechanisms can be added in quadrature to give that of the total, a crude deconvolution can be carried out to determine that portion attributable to the finite lifetime as a function of VAE. The resonance width, Γ, was found to vary as $VAE^{1.45}$, a slightly stronger dependence than that found for ΔE_{dp} and closer to that expected on theoretical grounds. We return to these points later.

B. Dichloroalkanes. The introduction of a second chlorine atom to the monochloroalkanes produces an additional low-lying C−Cl σ^* orbital, and thus two low-lying temporary anion states are expected. When the two C−Cl bonds are distant from one another in the molecule, these states are expected to be essentially degenerate, whereas at small distances, the interaction of the σ^* orbitals will split the states, and we expect two clearly defined anions. Table 2 summarizes our results for these compounds. Where two anion states could be discerned, the table indicates the assignment to occupation of the LUMO or the second-lowest unoccupied molecular orbital, labeled by LUMO+1. Where not indicated, the VAE gives the midpoint of the composite feature consisting of the two overlapping anion states and ΔE_{dp}, its width.

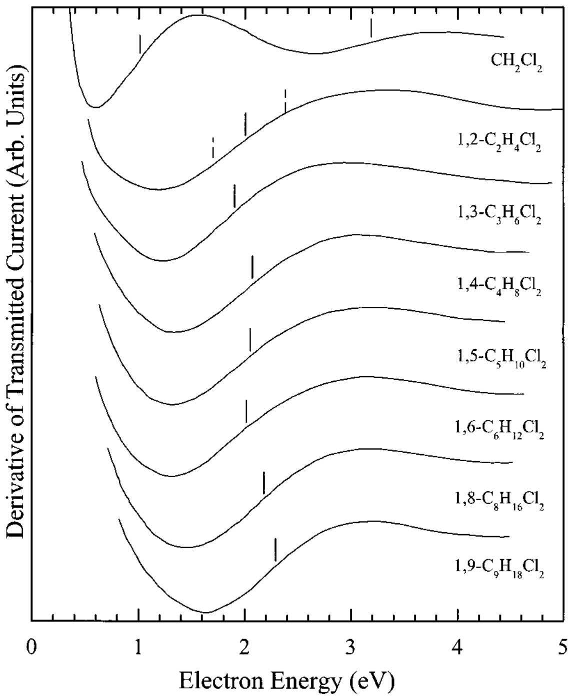

Figure 3. Derivative of transmitted current as a function of electron energy in a series of normal dichloroalkanes with increasing chain length.

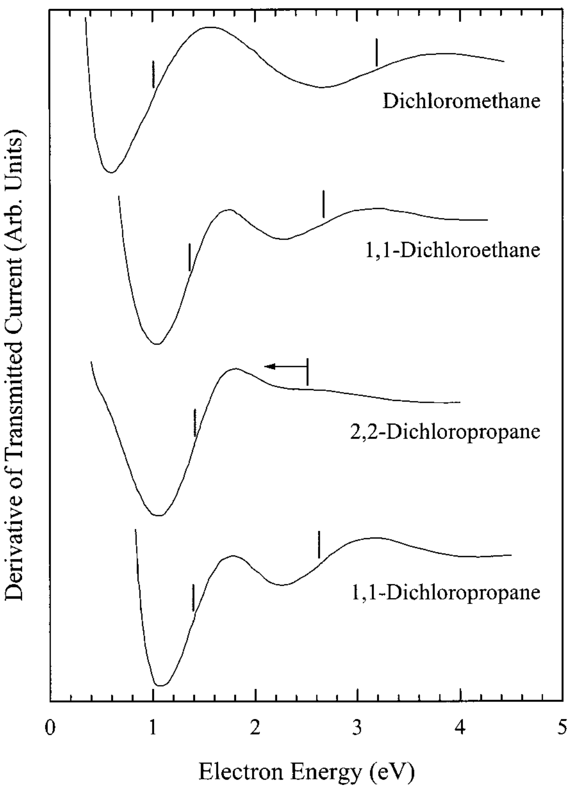

Figure 4. Derivative of transmitted current as a function of electron energy in several geminally substituted dichloroalkanes.

i. Normal Dichloroalkanes. The effect of the overlap of the two C−Cl σ^* orbitals is most clearly seen in Figure 3 in which are plotted the ET spectra of the normal dichloroalkanes Cl(CH$_2$)$_n$Cl with $n = 1-6$, 8, and 9. Only in the smallest member of this series, CH_2Cl_2, where both Cl atoms are attached to the same carbon, is there sufficient interaction of the C−Cl σ^* wave functions to generate two well-separated features. The lower anion state arises from the bonding, or in-phase, combination of the C−Cl σ^* orbitals (a$_1$ symmetry), and the upper from the antibonding combination (b$_2$ symmetry). In the long dichloroalkanes such as 1,8-dichlorooctane and 1,9-dichlorononane, the overlap of the C−Cl σ^* orbitals is minimal, and the two temporary anion states are virtually degenerate. We note also that the experimental results in these cases are an average over all the populated conformers. By comparing the VAEs and the resonance widths of these compounds with those of the normal monochloroalkanes in Table 1, one can see that the anion states in the long dichloroalkanes have essentially the same properties as those in the long monochloro compounds.

Of the remaining compounds in Figure 3, the resonance profile of 1,2-dichloroethane is considerably broader than those of the others, suggesting a substantial splitting. Assuming that each of the anion states has properties similar to those of the corresponding states in the monochloroalkanes, it is possible to make a crude deconvolution of the profile to determine the approximate anion splitting. In a series of monochloroalkanes, we found that the energy of the dip was given approximately by 0.7 × VAE and that of the peak by 1.4 × VAE (see Appendix I). By assuming that the dip in the ET profile of 1,2-dichloroethane is determined primarily by the lower anion state and the peak by the upper state, we estimate a splitting of 0.7 eV between the two anion states. The estimated VAEs of these states are located at 1.7 and 2.4 eV and are indicated by dashed vertical lines in Figure 3. The lower VAE is also in good agreement with the results of quantum-chemical calculations discussed later, adding support to our deconvolution. The splitting in the remaining normal dichloroalkanes is too small to be estimated in this fashion. Table 2 summarizes VAEs and dip and peak energies for these compounds, as well as for the rest discussed below. We note again that, except for CH_2Cl_2, these values are a thermal average over a number of different molecular conformations. The VAEs for CH_2Cl_2 in Table 2 supersede values published earlier[10] in which low scattered electron rejection was employed.

ii. Branched Dichloroalkanes. As shown in Figure 1, methyl substitution on methyl chloride produced the most significant stabilizing change in the VAE. Using dichloromethane as our base, we now examine the influence of methyl substitution on the two anion states associated with temporary occupation of the LUMO and LUMO+1. In the top three curves of Figure 4, we show the ET spectra of dichloromethane, 1,1-dichloroethane, and 2,2-dichloropropane. ETS studies of the latter molecule have also been presented by Modelli et al.[17] The upper anion state, associated with occupation of LUMO+1, is observed to stabilize as in the methyl chloride series. The anion state associated with attaching into the LUMO, on the other hand, is destabilized, with the first methyl group again causing the largest effect. The second methyl substitution appears to saturate the effect near a VAE of 1.4 eV. In 2,2-dichloropropane, we note that the two anion states are heavily overlapped, and only an upper bound to the higher anion state can be estimated. At the bottom of Figure 4, we show the ET spectrum of 1,1-dichloropropane for comparison to that of 1,1-dichloroethane. The two spectra are almost identical, reflecting the small effect of lengthening the alkyl chain, as found in the monochloro compounds.

The effects of methyl substitution on the 1,2-dichloroethane frame are illustrated in Figure 5. The two dashed vertical lines on the top spectrum indicate the estimated deconvoluted energies of the two anion states of 1,2-dichloroethane mentioned earlier. The width of the feature in 1,2-dichloropropane is greatly reduced, indicating that the two anion states are much closer in energy. The midpoint of the overall feature lies below that of

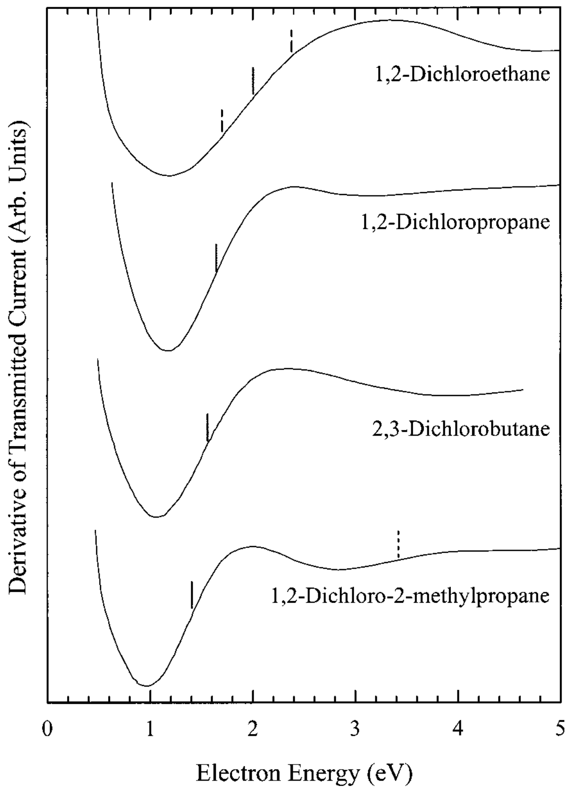

Figure 5. Derivative of transmitted current as a function of electron energy in several vicinally substituted dichloroalkanes.

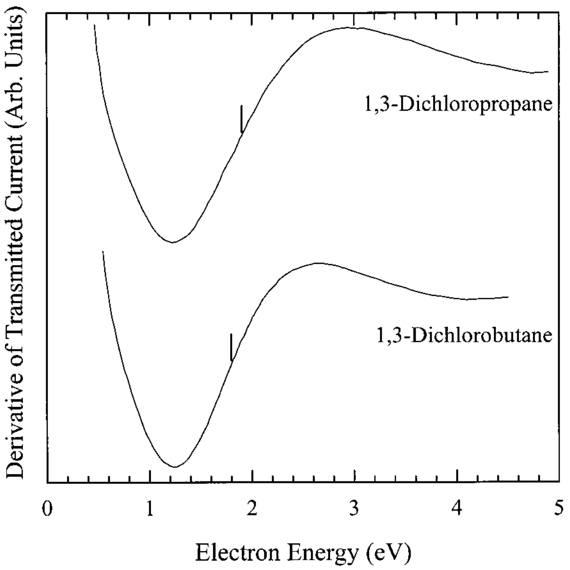

Figure 6. Derivative of transmitted current as a function of electron energy in 1,3-dichloropropane and 1,3-dichlorobutane.

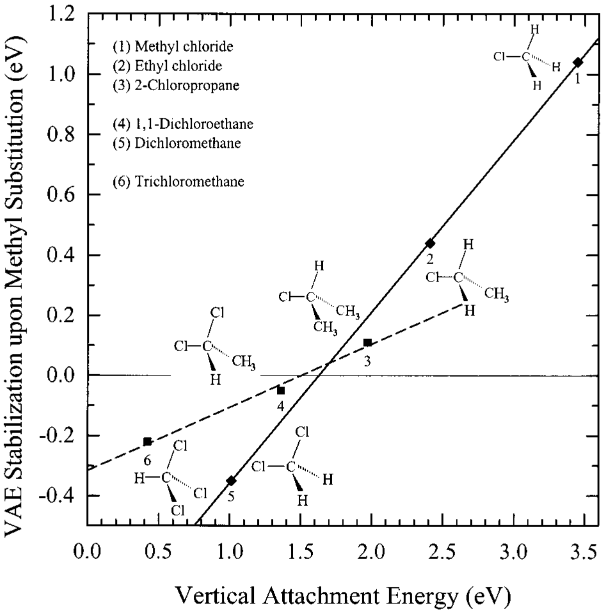

Figure 7. Stabilization of temporary anion energy upon methyl substitution on the indicated molecules as a function of the vertical attachment energies of the same molecules. The dashed line connects compounds having only a single hydrogen atom on the central carbon. The solid line connects compounds having two or three hydrogens.

the estimated energy of the LUMO anion of 1,2-dichloroethane, suggesting that both anion states are stabilized, but the upper is stabilized by much more than the lower. Substitution of a methyl group on C1 to produce 2,3-dichlorobutane results in only a very modest stabilization of the midpoint. Substitution on C2 to produce 1,2-dichloro-2-methylpropane yields a larger stabilization, leaving the midpoint near the value of 1.4 eV. Given that methyl substitution stabilizes the upper anion state, a resonance appearing near 3.4 eV in this compound is likely due to occupation of the C−C σ^* orbitals, stabilized by the inductive effects of the two chlorine atoms.

In 1,3-dichloropropane, shown in Figure 6, the splitting of the two anion states is sufficient to broaden the profile by ~0.4−0.5 eV over that expected for a monochloroalkane at the same VAE. Methyl substitution on C3 to produce 1,3-dichlorobutane causes narrowing of the profile and stabilization of the overall feature, consistent with stabilization of both anion states, but of the upper state by a greater amount.

iii. Summary of Methyl Substituent Effects. In the compounds presented here, methyl group substitution is observed to function as both a stabilizing and a destabilizing agent on the anion states associated with the C−Cl σ^* orbitals. We find that anion states lying above ~1.5 eV before substitution are stabilized; those below this energy are destabilized.

The general behavior observed in our studies of methyl substitution is easiest to rationalize using a perturbational picture, although steric factors must also play a role. The addition of a methyl group introduces a number of occupied and unoccupied molecular orbitals that can couple with the original C−Cl σ^* orbital. The new C−C and C−H σ^* orbitals lie above C−Cl σ^*, and overlap with these orbitals will tend to stabilize the anion state. The new filled orbitals, primarily the pseudo-π orbitals on the methyl group, lie below C−Cl σ^* and will destabilize it. At some value of the VAE, these two effects must approximately balance. Thus, we find that anion states with VAE > 1.4−1.6 eV, lying closer to the empty orbitals, are stabilized, whereas those with lower VAEs, falling closer to the filled orbitals, are destabilized.

For anion states corresponding to filling of the LUMO, there are six clear-cut examples of the methyl group shifts, if we include the ETS results for $CHCl_3$ and 1,1,1-trichloroethane discussed later. In Figure 7, we summarize these examples by plotting the stabilization in energy that occurs upon methyl substitution on a given compound as a function of the VAE *of that same compound.* For example, the VAE of compound 2, ethyl chloride, at 2.41 eV, is stabilized by 0.44 eV upon methyl substitution to form 2-chloropropane (VAE = 1.97 eV). For convenience, each starting compound is accompanied by a sketch of its structure.

The solid line passing through points 1−5, with the result for trichloromethane considered as an outlier, is the most

TABLE 3: Vertical Attachment, Dip, and Peak Energies and Dip−Peak Separations in the Tri- and Tetrachloroalkanes[a]

compound	molecular orbital	VAE	dip energy	peak energy	dip−peak separation
trichloromethane	LUMO	0.42	0.25	0.65	0.40
	LUMO+1,2	1.8	1.3	2.7	1.4
1,1,1-trichloroethane	LUMO	0.64	0.40	0.87	0.47
	LUMO+1,2	1.51	1.21	1.99	0.78
1,1,1,2-tetrachloroethane	LUMO	0.63	0.52	0.78	0.26
		1.32	1.05	1.67	0.62
1,2,3-trichloropropane	LUMO	1.40 1.23 est	0.86	2.37	1.51
1,1,2-trichloroethane	LUMO	0.94 0.83 est	0.58	1.46	0.88
1,1,2-trichloro-2-methylpropane	LUMO	1.02 0.90 est	0.63	1.58	0.95
1,1,2,2-tetrachloroethane	LUMO	~0.5	0.41	~0.6	~0.2
	LUMO	0.6 est ~0.8	~0.6	1.33	~0.7

[a] All values are in electronvolts.

obvious interpretation of these data, which indicate a “balance point” in the substitution effect near VAE = 1.6 eV. We cannot resist suggesting an alternate possibility, noting that compounds 3, 4, and 6 lie on a reasonably straight line (dashed) and that 1, 2, and 5 fall very well on the solid line. The only distinction between these groups that we can determine is that compounds 3, 4, and 6 contain only a single hydrogen atom connected to the central carbon, whereas compounds 1, 2, and 5 contain two or, in the case of methyl chloride, three hydrogen atoms. The fact that the methyl group can give rise to only two pseudo-π type orbitals, thus matching the number for 2 and 5, may explain why 1 falls on a common line with them. The quality of the fit to each of these two smaller data sets is quite good but may well be fortuitous. At present, we have no further explanation for the difference in slope, nor any justification for fitting two lines to the data.

C. Selected Polychloroalkanes. The data discussed in this section consist of ETS results for a small selection of compounds to illustrate the trends encountered in the more heavily chlorinated alkanes. The results are summarized in Table 3. The lowest VAE encountered in the dichloroalkanes was that of CH_2Cl_2 at 1.01 eV. Further stabilization of the anion state associated with the filling of the LUMO is known to take place upon additional substitution of chlorines on the central carbon to form $CHCl_3$ and CCl_4.[10,11]

i. Trichloromethane, 1,1,1-Trichloroethane, and 1,1,1,2-Tetrachloroethane. For consistency with our present work, the ET spectrum of $CHCl_3$ was remeasured and is shown at the top of Figure 8. The earlier study,[10] as in the case of CH_2Cl_2, was not carried out with the high rejection mode used here. VAEs of 0.42 and 1.76 eV were found for the lowest two resonances, previously assigned to the $^2A_1$ and ^2E anion states, respectively.[10,11]

The ET spectrum of 1,1,1-trichloroethane, shown in the middle of Figure 8, was acquired for comparison with that of $CHCl_3$. It has also been presented by Modelli et al.[17] at energies below 6 eV. Consistent with our earlier discussion of methyl substitution effects, the $^2A_1$ anion state of $CHCl_3$, at 0.42 eV, is *destabilized* to 0.64 eV, and the ^2E state, at 1.76 eV, is *stabilized* to 1.51 eV upon addition of the methyl group. Because the symmetry of this compound is the same as that of $CHCl_3$, the two lower features are also ^2A and ^2E states, in agreement with Modelli et al.[17] The additional anion states near 4.28 and 7.30 eV are likely to be associated with the C−C $\sigma^*(a_1)$ and C−H $\sigma^*(a_1, e)$ orbitals, respectively, substantially stabilized by the presence of three chlorine atoms.

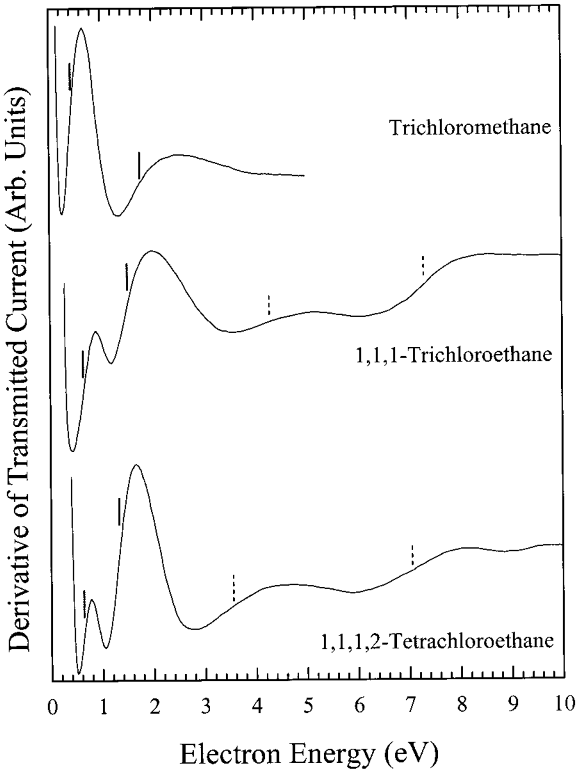

Figure 8. Derivative of transmitted current as a function of electron energy in $CHCl_3$, 1,1,1-trichloroethane, and 1,1,1,2-tetrachloroethane.

Substitution of a chlorine atom on the C2 carbon of 1,1,1-trichloroethane gives rise to the tetrachloro compound whose spectrum is shown at the bottom of Figure 8. Although the symmetry of the former is now broken, the ET spectra are quite similar. The second composite feature, nominally centered at 1.32 eV, has been stabilized by almost 0.2 eV relative to that in 1,1,1-trichloroethane by the addition of the chlorine atom.

ii. 1,2,3-Trichloropropane. In polychloroalkanes with only one or two chlorines on any particular carbon atom, the features in the ET spectra are heavily overlapped, making it difficult to assign VAEs. However, with some approximations derived from our studies of the monochloroalkanes, we can suggest values for the first VAE in some of the compounds.

The ET spectrum of 1,2,3-trichloropropane, shown at the top of Figure 9, displays at low energy only a single broad feature centered at 1.40 eV, as might be expected from three weakly interacting C−Cl σ^* orbitals. Although we cannot deconvolute these anion states, we can give a rough estimate of the energy of the anion associated with the LUMO. As mentioned earlier, and discussed in Appendix I, we found in a series of monochloroalkanes that the dip energy was given by 0.7 × VAE. If we assume that the minimum of the feature in the 1,2,3-trichloropropane ET spectrum can be associated solely with the lowest-lying anion state, and further, that its characteristics are identical to those in the monochloroalkanes, we can estimate the lowest VAE to be 1.2 eV.

iii. 1,1,2-Trichloroethane and 1,1,2-Trichloro-2-methylpropane. The ET spectra of these compounds are shown in the middle portion of Figure 9. Again, the anion states are heavily overlapped. Using the above approach, the lowest VAE is estimated to lie at 0.8 eV in 1,1,2-trichloroethane and 0.9 eV in the propane analogue. There is some evidence that a weak structure on the high-energy side of the main feature in the 1,1,2-trichloroethane spectrum has been stabilized by the methyl

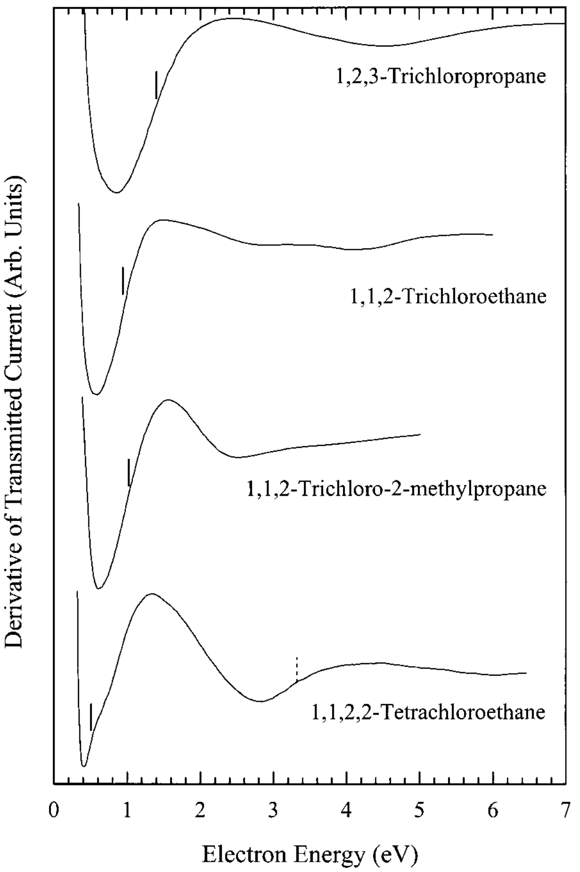

Figure 9. Derivative of transmitted current as a function of electron energy in several trichloroalkanes and 1,1,2,2-tetrachloroethane.

substitution, giving rise to the more symmetrical dip and peak seen in the propane compound.

iv. 1,1,2,2-Tetrachloroethane. At the bottom of Figure 9, we show the ET spectrum of this tetrachloroalkane. In this compound, the lowest anion state is almost separated from the larger feature. Although the peak of this lower state cannot be clearly discerned, the center of this anion state would appear to be near 0.5 eV. Applying our monochloroalkane approach, we estimate a VAE of about 0.6 eV, in good agreement with this value. A pronounced resonance is also observed near 3.5 eV, likely due to the C−C σ^* orbital inductively stabilized by the four chlorine atoms.

4. Widths of the Temporary Anion States

Having completed our discussion of the VAEs of the dichloro- and polychloroalkanes and the variation of these energies with methyl group substitution, we turn next to an examination of the widths of these anion states and comparisons with those found earlier in the monochloroalkanes and shown in Figure 2. Figure 10 collects the dip-to-peak separations, ΔE_{dp}, found in the ET spectra and plots them as a function of VAE. The dichloro- and polychloroalkane data are coded by symbol to several chemical families, including those with geminally or vicinally substituted chlorines, the long chain alkanes, and trichloroalkanes, as well as a few specific molecules. The numbers indicate the compounds identified in the figure caption. In the compounds for which more than one anion state is observed by ETS, only the width of the anion state associated with the LUMO is shown. In the examples in which a feature consisting of overlapping anion states is observed, we use the center of the composite feature for the VAE. In these cases, it is clear that the values of both the VAE and ΔE_{dp} are *upper* bounds to the true properties of the lowest temporary anion states. The solid line represents a best fit of the form $A \times (\mathrm{VAE})^n$, as used in Figure 2, to data in the 19 compounds in which a well-isolated lowest anion state is observed. The dependence is found to be $\Delta E_{dp} = 0.51 \times \mathrm{VAE}^{1.44}$, quite close to that for the monochloroalkanes alone.

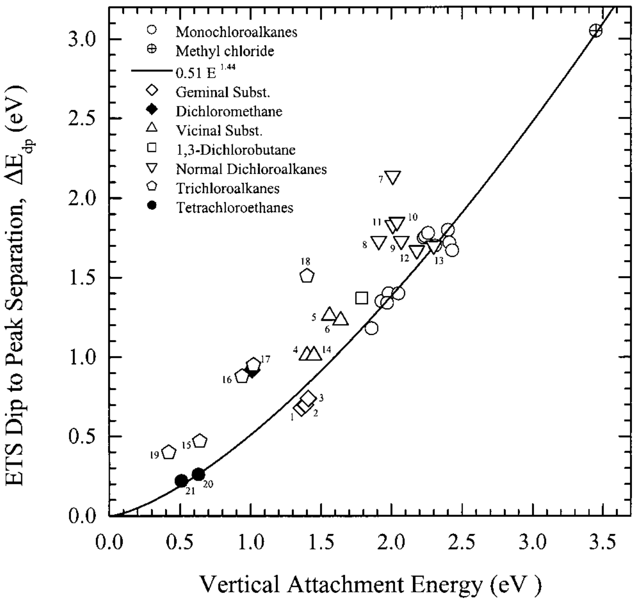

Figure 10. Dip-to-peak energy separations of the temporary anion states associated with occupation of the lowest unoccupied molecular orbital as a function of vertical attachment energy in a number of polychloroalkanes coded by symbol. The solid line shows the power-law fit to the compounds with clearly isolated lowest anion states. The numbers refer to the following compounds: (1) 1,1-dichloroethane, (2) 1,1-dichloropropane, (3) 2,2-dichloropropane, (4) 1,2-dichloro-2-methylpropane, (5) 2,3-dichlorobutane, (6) 1,2-dichloropropane, (7) 1,2-dichloroethane, (8) 1,3-dichloropropane, (9) 1,4-dichlorobutane, (10) 1,5-dichloropentane, (11) 1,6-dichlorohexane, (12) 1,8-dichlorooctane, (13) 1,9-dichlorononane, (14) *trans*-1,2-dichlorocyclohexane, (15) 1,1,1-trichloroethane, (16) 1,1,2-trichloroethane, (17) 1,1,2-trichloro-2-methylpropane, (18) 1,2,3-trichloropropane, (19) trichloromethane, (20) 1,1,1,2-tetrachloroethane, and (21) 1,1,2,2-tetrachloroethane.

Consider first the normal dichloroalkanes, compounds 7−13, shown as open, downward-pointing triangles. In the longest of these, 1,9-dichlorononane, compound 13, the two anion states are essentially degenerate, and we see that the width of the feature is identical to that of a monochloroalkane of the same VAE. Compound 12, 1,8-dichlorooctane, also has a width quite close to that given by the monochloro line. As the chain length decreases, the widths of the composite features arising from overlap between the two anion states increase, and these data fall above the line. The extreme case is that of compound 7, 1,2-dichloroethane, in which we estimated the splitting to be 0.7 eV. The width of the composite lies 0.74 eV above the monochloro line.

A group of vicinally substituted compounds (4−6 and 14), open, upward pointing triangles, as well as 1,3-dichlorobutane, open square, all fall in close proximity to but above the monochloroalkane line. The anion states in these compounds are likely to be split by a smaller amount than those in 1,2-dichloroethane because of stabilization of the upper anion state by the methyl groups (4−6) or the carbon ring (14).

Of the trichloro-compounds, the lowest feature in the ET spectra of compounds 16−18, open pentagons, clearly arises from overlapping temporary anion states. The widths of these features, in common with the shorter normal compounds, lie well above the monochloro line.

Of the two tetrachloro compounds in Figures 8 and 9, only the anion state arising from occupation of the LUMO of 1,1,1,2-tetrachloroethane, compound 20, can be clearly resolved in the ET spectrum. The width of this state is in excellent agreement with that predicted on the basis of the monochloroalkanes. The width of the lowest anion state in 1,1,2,2-tetrachloroethane, compound 21, can only be approximately determined from its ET spectrum but also appears to be in good agreement.

We are left with three examples of compounds in which the lowest anion state is well-separated, but its associated width is not in good agreement with that predicted by the line.

Dichloromethane, shown as a filled diamond in Figure 10, has the largest observed splitting between its two C−Cl σ^* anion states. Thus, the width of the lower anion state should not be altered by overlap effects. Nevertheless, it lies substantially above the line. We have noted elsewhere[18] that the dissociative attachment cross section of dichloromethane is approximately a factor of 30 *smaller* than would be expected given the value of its VAE. This result is consistent with an anomalously shorter anion lifetime and thus a greater profile width. At present, this is not understood, although ongoing measurements in the mixed fluorochloro methanes may provide some clues. The widths of the lowest anion states of $CHCl_3$, compound 19, and 1,1,1-trichloroethane, compound 15, also lie above the line but not in such substantial disagreement as CH_2Cl_2.

As discussed in section 3A, ΔE_{dp} is made up of two components, the natural lifetime broadening, Γ, and contributions from Franck−Condon factors. For VAEs > 1 eV, our modeling of Franck−Condon overlaps suggested that the contribution from Γ was the dominant effect. A crude deconvolution shows that Γ varies as a somewhat higher power than that found for ΔE_{dp}. In view of the approximate nature of these estimates, we conclude that our results are consistent with $\Gamma \propto \mathrm{VAE}^{1.5}$, in good agreement with the relationship predicted from the p_σ local symmetry of a C−Cl σ^* orbital.

For VAEs < 1 eV, the interpretation is not as straightforward because the contributions from Franck−Condon overlaps become an increasingly larger part of the total width. Indeed, given that, for finite angular momentum, Γ must go to zero as the energy of the autodetaching electron goes to zero because of threshold law requirements,[15] it is clear that the total widths must reflect the Franck−Condon overlaps between neutral and anion as VAE → 0.

Until more realistic calculations of the anion potential curves are available, it will not be possible to extract values for Γ for anions with low VAEs. Considering how well the $\mathrm{VAE}^{1.5}$ dependence seems to account for the widths at VAE > 1 eV, however, it is reasonable to use this as an approximation to the Γ behavior below 1 eV. This gives rise to a simple picture in which the angular momentum barrier through which the electron must tunnel is essentially the same for all of the compounds, and the various intramolecular orbital interactions such as those arising from methyl and chlorine substitutions serve primarily to determine the VAE, thereby positioning the anion state higher or lower inside the barrier. This model is certainly oversimplified with respect to the nature of the barrier and will have to be tested with rigorous scattering calculations. Nevertheless, it provides a simple way to view the connection between VAE and anion lifetime. As we show elsewhere,[2] this relationship is key to an understanding of the dissociative electron attachment process.

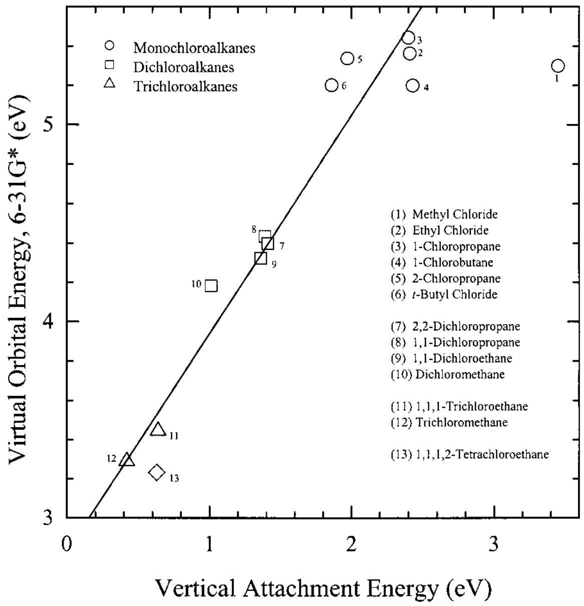

Figure 11. Virtual orbital energies obtained from the 6-31G* basis set as a function of vertical attachment energies. Geometry optimizations were also carried out at this level. The solid line shows a best fit to the data, excluding the point for methyl chloride.

5. Calculations of LUMO Energies

In the final portion of this work, we examine the connections between quantum chemical calculations of LUMO energies and measured VAEs. LUMO energies are widely used to correlate molecular structure to chemical processes in which a likely key step is electron transfer to a neutral molecule.[1] There are obvious advantages in establishing such quantitative structure/activity relationships (QSARs), as computations in large numbers of related compounds can be carried out consistently and expeditiously with modern computers.

LUMO energies are generally computed in the optimized geometry of the electronic ground state of the neutral molecule. Thus, they are characteristic of a vertical process in which the geometry of the anion does not relax. It does not appear to be widely appreciated that such LUMO energies are approximations to the VAEs discussed here. Comparisons of LUMO energies and VAEs in *unsaturated* compounds have been made by several groups.[19−23] Considerably less has been done for saturated hydrocarbons,[24] although LUMO calculations in the chloromethanes were carried out by Burrow et al.[10] to aid in the assignment of their ETS data. Heinrich et al.[19] also included these compounds in their study and found that the slope of the line correlating the LUMO energies with VAEs differed from that in unsaturated compounds. The most detailed treatment of empty orbital energies, the corresponding anion states, and VAEs is that of Falcetta and Jordan[25] for the CH_3Cl−CCl_4 series. This study utilized a variant of the stabilization method in conjunction with the Koopmans' theorem approximation to distinguish physically meaningful orbital energies from those that arise from diffuse quasi-continuum orbitals. We illustrate some of these aspects below. In Appendix II, we provide additional theoretical comments on the connections between LUMO energies and VAEs.

Our present ab initio SCF calculations have been carried out using the GAMESS program.[26] Geometries of the neutral molecules were optimized using the 6-31G* basis set, and virtual orbital energies were obtained from the same basis set. In Figure 11, we plot the calculated empty orbital energies, LUMOs only, as a function of measured VAEs. We include only those

TABLE 4: Calculated Virtual Orbital Energies in the 6-31G* Basis Set and Predicted and Measured Vertical Attachment Energies[a]

compound	VOE 6-31G*	predicted VAE[b]	VAE expt
Monochloroalkanes			
methyl chloride	5.299	2.229	3.45
ethyl chloride	5.362	2.286	2.41
2-chloropropane	5.337	2.264	1.97
t-butyl chloride	5.202	2.140	1.86
1-chloropropane	5.443	2.360	2.4
1-chlorobutane	5.200	2.139	2.43
Dichloroalkanes			
dichloromethane	4.184	1.212	1.01
1,1-dichloroethane	4.323	1.339	1.36
1,1-dichloropropane	4.435	1.441	1.39
2,2-dichloropropane	4.398	1.407	1.41
Trichloroalkanes			
trichloromethane	3.290	0.396	0.42
1,1,1-trichloroethane	3.446	0.538	0.64
Tetrachloroalkanes			
1,1,1,2-tetrachloroethane	3.233	0.344	0.63

[a] All values are in electronvolts. [b] Predicted VAE = (VOE − 2.856)/1.096.

compounds in which well-isolated anion states are observed. The data fall into three clusters, as expected, associated with the monochloro, dichloro, and trichloro compounds. One example of a tetrachloroalkane is also provided in the latter. As we have noted elsewhere, a striking problem seen in Figure 11 is the failure of the calculations to describe properly the virtual orbital energy of methyl chloride, compound 1. In contrast to experimental results, methyl chloride, ethyl chloride, and 2-chloropropane have almost identical calculated C−Cl (σ^*) LUMO energies in this basis set. Excluding the result for methyl chloride, a regression to the remaining compounds is shown as a solid line in Figure 11. The relationship is found to be VOE = 2.83 + 1.11 × VAE, where VOE is the virtual orbital energy in electronvolts.

The correlation for the LUMO anions associated with the filling of the C−Cl σ^* orbitals differs substantially from those for π^* orbitals in unsaturated compounds. For example, using a 6-31G basis set, Chen and Gallup[20] found, for the LUMO anions of the unsaturated compounds listed by Heinrich et al.,[19] the relationship VOE = 2.33 + 1.31 × VAE. Similarly, in a small number of aromatic compounds used to emulate the DNA bases, namely, benzene, naphthalene, pyridine, and pyrimidine, Aflatooni et al.,[27] in their ref 14, found the correlation to be VOE = 2.555 + 1.375 × VAE, using the 6-31G* basis set.

These results indicate that the same shifting/scaling relationship *cannot* be used for both saturated and unsaturated compounds and that, even within unsaturated compounds, differences occur within various families of molecules. However, it is clear that, by empirically adjusting the LUMO energies to match VAEs *within a given family*, the predictive use of LUMOs in QSAR studies would be greatly improved for other members of the same family. An example of this approach applied to environmentally important molecules and their degradation on iron surfaces has been noted elsewhere.[28] Table 4 summarizes the calculated 6-31G* VOEs, the predicted VAEs using the best-fit line, and the experimentally determined VAEs. We note in addition that the predicted VAE of the lowest anion state of 1,2-dichloroethane is 1.72 eV, in excellent agreement with the estimated value of 1.7 eV obtained using the experimental method discussed in Appendix I.

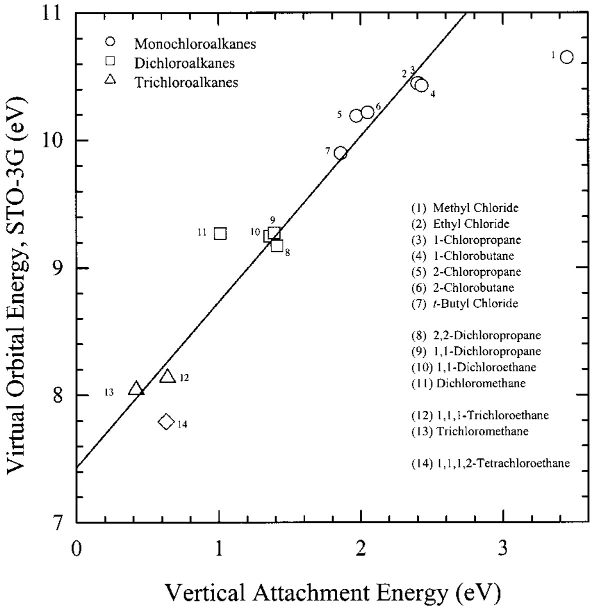

Figure 12. Virtual orbital energies obtained from the STO-3G basis set as a function of vertical attachment energies. Geometry optimizations were carried out at the 6-31G* level. The solid line shows a best fit to the data, excluding the point for methyl chloride.

Returning to the calculation of the LUMO virtual orbital energy of CH_3Cl, Falcetta and Jordan[25] have argued that its energy is stabilized because of strong mixing with a nearby virtual orbital with considerable continuum character. In general, this is a problem to which high-lying orbitals will be particularly susceptible. It is thus of interest to consider the degree to which the other monochloroalkanes (compounds 2−6) in Figure 11 also suffer from this effect. Falcetta and Jordan state that minimal basis sets are not affected by mixing with “discretized continuum” states and that, in particular, the STO-3G level of theory is better at predicting relative anion energies than the 3-21G or 4-31G levels. To explore this issue, we have carried out STO-3G calculations of the VOEs of the molecules shown in Figure 11 and plotted these as a function of the VAE in Figure 12. All geometry optimizations were made using 6-31G* bases. In contrast to the scatter observed for the monochloro compounds in Figure 11, an improved and almost monotonic dependence of the VOE on the VAE is observed in Figure 12 for these compounds. However, the results suggest that a change in slope occurs above VAE ≈ 2.0 eV, with the higher-lying VOEs depressed. This issue requires further theoretical input. This behavior may result simply from insufficient flexibility in such a basis set. On the other hand, as we note in Appendix II, the Koopmans’ approach is an approximation that omits a number of interactions. The most significant of these may be the absence of coupling to the continuum and the concomitant shift in energy. For completeness, a straight-line fit to the data in Figure 12, excluding that for CH_3Cl, is expressed by VOE = 7.43 + 1.30 × VAE (eV). The STO-3G data are summarized in Table 5.

6. Conclusions

We have provided a comprehensive set of measurements characterizing the energies and lifetimes of the temporary anion states associated with the short-lived occupation of the C−Cl σ^* orbitals of the dichloroalkanes and selected tri- and tetrachloroalkanes. Because our measurements are carried out in the gas phase, the anion energies are characteristic of the isolated molecules in their equilibrium ground states. Such VAEs serve,

TABLE 5: Calculated Virtual Orbital Energies in the STO-3G Basis Set, and Predicted and Measured Vertical Attachment Energies[a]

compound	VOE STO-3G	predicted VAE	VAE expt
	Monochloroalkanes		
methyl chloride	10.648	2.484	3.45
ethyl chloride	10.447	2.327	2.41
2-chloropropane	10.191	2.127	1.97
t-butyl chloride	9.897	1.898	1.86
1-chloropropane	10.447	2.327	2.40
1-chlorobutane	10.428	2.312	2.43
2-chlorobutane	10.218	2.148	2.05
	Dichloroalkanes		
dichloromethane	9.271	1.409	1.01
1,1-dichloroethane	9.249	1.392	1.36
1,1-dichloropropane	9.276	1.413	1.39
2,2-dichloropropane	9.173	1.333	1.41
	Trichloroalkanes		
trichloromethane	8.044	0.451	0.42
1,1,1-trichloroethane	8.139	0.525	0.64
	Tetrachloroalkanes		
1,1,1,2-tetrachloroethane	7.793	0.255	0.63

[a] All values are in electronvolts. [b] Predicted VAE = (VOE − 7.466)/1.281.

therefore, as reference points from which solvation and nuclear relaxation effects that alter the anion energies must take place. In particular, we have examined the role of methyl substitution on the anion energies and found that it serves to stabilize higher-lying anions but to destabilize those at lower energies. A simple relationship between the VAE and the temporary anion lifetime was observed that holds, on average, over a wide range of chloroalkanes with only one significant exception. This dependence is consistent with the threshold law for electron tunneling through a barrier associated with one unit of angular momentum. Although temporary anion states are observed that correspond to attaching into higher-lying orbitals, primarily C−C σ^*, we have not attempted to analyze them. Preliminary calculations indicate that the energy ordering of the C−C σ^* and C−H σ^* orbitals is basis-set dependent and greatly influenced by interaction with continuum orbitals.

The correlations between measured VAEs and the calculated LUMO energies of C−Cl σ^* orbitals using two basis sets were explored. By shifting and scaling the calculated energies to match one or more experimental values of the VAE, the predictive power of the LUMO calculations can be greatly improved. However, there remain problems with the energies of the higher-lying empty orbitals.

Appendix I

As shown in Figure 2, the dip-to-peak energy separation of the C−Cl σ^* structures in the ET spectra of the monochloroalkanes varies approximately linearly over the range that they can be measured. In Figure 13, we plot the dip and peak energies separately against the VAE for the monochloroalkanes and see that they also vary linearly. Extrapolating straight lines through these two data sets to pass through the origin yields the expressions relating either peak or dip energy to VAE shown in the insets of the figure. Because of the difficulty of accurately determining the peak energy in CH_3Cl, we have not included it in the fit, but show the data for reference. The dip energy, although not included in the fit, is in excellent agreement with that of the other monochloroalkanes.

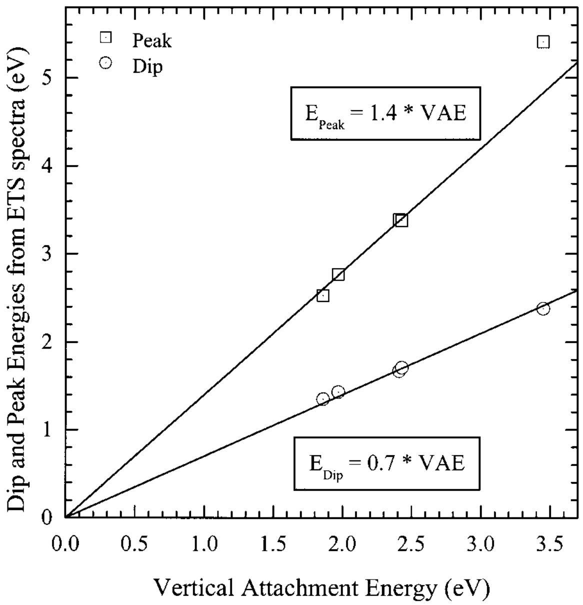

Figure 13. Dip and peak energies of the electron transmission structures of several monochloroalkanes plotted as a function of the vertical attachment energy. The equations were used to determine the estimated energy of the lowest anion state in compounds with overlapping anion states.

In a composite ETS feature consisting of two or more overlapping anion states, the observed dip energy will be, at most, an upper bound to the dip energy of the lowest anion state in the composite. Assuming that the characteristics of this resonance are the same as those for the monochloroalkanes, we have used the lower line in Figure 13 to make an estimate of the associated VAE, as carried out in the text.

Appendix II

The VAEs we measure are properties of the true scattering (continuum) states of the molecules, whereas the calculated unoccupied orbital energies in their unshifted form are, in part, the result of artifacts depending upon the basis used. (This is over and above any inaccuracies caused by the limitations of the basis in producing an accurate representation of the neutral molecule.) The unoccupied orbitals may be said to be a “discretization” of the scattering states of the $(N + 1)$st electron actually involved in the scattering. Because the basis is finite from practical necessity, the unoccupied orbital energies are approximate (in the Koopmans’ theorem sense) eigenvalues of the Hamiltonian for this discretized basis. The number and positions of these eigenvalues are determined by the size and nature of the basis used. As we have seen, restricted minimal bases such as STO-3G give fairly high orbital energies, whereas more extended ones such as 6-31G* give lower values.

Two methods that have been used to make the calculated LUMO energies more directly comparable to experiment are stabilization[29] and Fano-Feshbach resonance theory.[30] In cases where these have been applied, a much better comparison with experiment has resulted. (Some further adjustments are frequently needed because of limitations of the Hartree−Fock procedure in producing the effects of polarization and relaxation.) In the present work, our empirical shifting and scaling compensates in part for the discrepancies between the unmodified LUMO energies and the true VAEs.

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