

Dissociative Attachment Studies of Halogen-containing Molecules: Problems, Applications and Challenges*

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Abstract

The dissociative attachment (DA) process appears in a surprisingly diverse number of research disciplines. Although gas phase studies have been carried out for approximately 30 years, there are no calculations of the cross sections for this process in molecules larger than diatomics. In this presentation, we review briefly the role of DA in several contexts generally unfamiliar to workers in atomic and molecular physics, and touch on some of the theoretical difficulties. We continue with a discussion of our work, both experimental and theoretical, on compounds containing a single halogen atom and conclude with results showing how the DA process can be used to study intramolecular electron transfer.

1. Introduction

The dissociative attachment (DA) process, $e+AB \Rightarrow AB^{*-} \Rightarrow A+B^{-}$, is important in surprisingly diverse areas of physics, chemistry and engineering. The contexts and jargon in these various fields are often so different that there is very little overlap or communication among the practitioners. As a consequence, the progress of our understanding of this complex and intriguing process has been slowed. In particular it is worth noting that at present there are no complete theoretical treatments, either *ab initio* or empirical, capable of determining the DA cross sections and relative abundances of stable negative ion products for molecules of 'chemical interest'. Existing work has focused on diatomics and has largely been carried out by researchers with backgrounds in physics. Extension of this research to larger systems will call for an interdisciplinary effort incorporating quantum chemistry and electron scattering physics.

In the present brief discussion, our objectives are several-fold. First, we begin by pointing out a few of the many applications of DA in fields that are not likely to be familiar to those in the atomic and molecular physics community. Our choice of examples is unashamedly idiosyncratic and no claim for completeness or priority of reference is made. Rather, they are given to provide indications of the variety of environments in which DA has been invoked, and in which it appears

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to us that continued work on the fundamentals of this process would benefit. We then touch on some of the difficulties encountered in trying to advance our theoretical understanding of the DA process. Again, most of this discussion will reflect our own biases and the pitfalls that we have stumbled into along the way.

Next, we elaborate on our experimental philosophy in which we choose to deal first with a variety of molecules bearing only a single halogen, chlorine, and vary the complexity of the hydrocarbon structure to which it is attached. This approach is founded on our belief that if one cannot make sense of these compounds, then there is little hope for understanding poly-halogenated molecules.

Finally, we finish with a discussion of results in a series of molecules containing a chromophore possessing a temporary negative ion state that is spatially remote from the carbon-chlorine bond which breaks during the DA process. Measurements in such compounds give information about the transfer of electrons across the molecule.

2. Applications

(2a) *Surface Physics and Chemistry*

The role of temporary negative ions in molecules on surfaces and in thin films on substrates is being explored by a rapidly increasing number of groups (Sanche 1990; Palmer and Rous 1992). Comparisons with the results of gas phase studies of the same compounds have proved invaluable in reaching an understanding of the more complex surface environment. The DA process is of particular interest since, in addition to stable anions, it produces free radical species that can bond to the substrate or induce chemical reactions among the molecules on the surface.

Electron collisions with adsorbed molecules and with films have been carried out for some time, however, most of such work has employed electron energies that are too high to form the temporary negative ion states that give rise to large DA cross sections, except through secondary processes. Experiments featuring high energy resolution, low impact energy electron beams are relatively uncommon. It is worth noting that low energy electrons do not penetrate deeply into films, an advantage or disadvantage depending on the objectives of the work.

In the last few years, closely related studies have appeared from a number of groups (for example Marsh *et al.* 1988; Jo and White 1990; Dixon-Warren *et al.* 1993) utilising photoelectrons injected from a conducting substrate into an adsorbed molecular layer or film. Such electrons may be 'free', that is, above the vacuum level, or 'hot', lying below, but in either case they may attach into normally unoccupied molecular orbitals of species near the surface. In films, the strong scattering of these low energy electrons restricts the range of the electrons and causes reactions such as DA to occur near the surface.

In the work of Dixon-Warren *et al.* (1993), for example, a series of chloromethanes, CCl_4 , CHCl_3 , CH_2Cl_2 , CH_3Cl , as well as CCl_3Br , were placed on an $\text{Ag}(111)$ surface and illuminated with laser light. The emission of Cl^- ions was observed. Although the kinetic energy of such a charged fragment produced from CCl_4 in the gas phase is small, the ions in the surface experiment were still able to overcome the image force attracting them to the substrate. The authors proposed that a temporary negative ion was formed by photo-excitation of an electron in the metal into an empty orbital of the chloromethane, and that a subsequent

interaction of the temporary anion/surface complex, forming a new bond with the surface, provided the additional energy needed to free the Cl^- ion. The yield of Cl^- varied with the particular chloromethane in a similar manner to that observed for the DA reaction in the gas phase. It is interesting to note that the photoreaction occurred with photon energies below the work function of the metal, that is, hot 'sub vacuum' level electrons were responsible for the process.

(2b) Surface 'Engineering'

A mechanism similar to that described above has been invoked to explain the bonding of perfluoropolyethers to a variety of substrates by UV light. Vurens *et al.* (1992a) have argued that photo-excitation of substrate electrons creates temporary negative ion states that subsequently undergo DA, resulting in the formation of radicals and F^- ions. The radicals then cross-link the polymer and bond it to the substrate. Because the low energy photo-electrons have a relatively short range in the polymer film, owing to the strong 'resonant' scattering at these energies, the process takes place preferentially in a thin film close to the substrate as desired for a lubricant. The remaining unaltered compound can then be easily removed.

A number of other processes involving lubricants may also have connections with DA. For example, it has been suggested (Vurens *et al.* 1992b) that lubricants may be degraded by microscopic plasmas generated by two surfaces in contact. Such 'tribo-plasmas' (Thiessen *et al.* 1966) contain electrons which can induce fragmentation through formation of temporary negative ion states.

(2c) Liquid Phase

Studies of the DA reaction in solution have been extensive as judged, for example, by the publications of Saveant and co-workers (see for example Savéant 1993). The vocabulary and techniques of electrochemistry, such as cyclic voltammetry, will be unfamiliar to those trained in physics, and for these reasons we make no attempt to do justice to this field in this presentation. One point of terminology is worth noting. In the 'electrochemical reduction' of halides in solution, i.e. the transfer of an electron to these molecules, Saveant distinguishes between the behaviour of alkyl halides, such as methyl or ethyl chloride, and benzyl chloride, a benzene molecule with one hydrogen atom replaced with a $-\text{CH}_2\text{Cl}$ group. In the first case it is argued that transfer of an electron to the molecule and breaking of the C-Cl bond is a 'concerted' one-step process. This terminology seems to imply that the reaction occurs without the formation of a radical anion intermediate. In the second case, a two-step process is invoked in which the electron attaches into an empty π^* orbital on the ring, forming a radical anion which then undergoes dissociation yielding Cl^- by transfer of the electron from the π^* ring orbital to the σ^* orbital associated with the C-Cl bond. Savéant refers to this as an 'intramolecular dissociative-electron-transfer process'.

In the gas phase, a temporary negative ion is viewed as the precursor of the DA reaction in both cases. For the alkyl mono-halides, the anionic potential surface is purely repulsive inside the crossing with the neutral potential surface, yet the anion state is manifested as a clear enhancement of the elastic scattering cross section as well as those for vibrational excitation. The alkyl chlorides have substantially shorter-lived anion states in the gas phase than those formed at

low energies in unsaturated compounds such as benzyl chloride. If the same is true in solution, the radical anions of the alkyl halides would be less likely to be involved in subsequent reactions in solution.

(2d) *Biological Applications*

Certain halogenated hydrocarbons are known to be dehalogenated by transfer of an electron from an enzyme. The free radical thus produced is capable of initiating tissue damage. Because there appears to be a correlation between the rate of reductive metabolism and the ease of electrochemical reduction of the carbon-halogen bond, it has been concluded (Hanzlik 1981) that the reduction potential of a halo-carbon, that is, the energy of attachment of an electron, may therefore be an important determinant indicating whether the process takes place. Such work has stimulated theoretical investigations of the electron affinities of compounds such as chlorofluoromethanes (see for example Luke *et al.* 1988). Such values can be determined experimentally as resonance energies in electron scattering in those compounds that do not have stable negative ions (Jordan and Burrow 1978).

The field of chemical carcinogenesis has a number of possible connections to electron attachment processes. For example, Wachsman *et al.* (1993) reported the outcome of a workshop comparing various methods to screen chemicals for carcinogenicity and decrease the dependence on the expensive and time-consuming assays used currently. One method using experimentally determined electrophilicities (Bakale and McCreary 1992), i.e. attachment rates, did 'surprisingly well'.

(2e) *Analytical Chemistry*

Because of the widespread presence of poly-chlorinated compounds as pesticides, herbicides and solvents, and the concerns with other environmental pollutants, analytical chemists are naturally involved in the development of techniques to determine small quantities of these substances. Electron capture negative ion mass spectroscopy, for example, is widely used and is implemented in a source chamber containing a high pressure of a moderating gas and an electron beam of energy of 50 eV or higher. Because of the broad electron energy distribution that ensues and the multitude of secondary reactions, it is very difficult to untangle any of the fundamental collision processes. Nevertheless, attempts to correlate the mass abundances and even the 'regioselectivity', that is, the location on the molecule from which the Cl^- originated, with calculated orbital energies have been made (Chang *et al.* 1991). More recently the work of Laramée *et al.* (1992) has incorporated an electron monochromator and low pressure source into the mass spectrometer and has shown that the energy dependence of the DA processes can be used to advantage.

The molecules studied in the examples above span an enormous range in complexity. To put things in perspective, the chloromethanes, $\text{CH}_{4-x}\text{Cl}_x$, are most likely the simplest to analyse. In the gas phase, the temporary negative ions of these compounds have been observed (Burrow *et al.* 1982) as they appear in the total scattering cross section using electron transmission spectroscopy (ETS) (Sanche and Schulz 1972) and assigned by means of simple molecular orbital calculations. The temporary anion states have been studied as well using

more sophisticated stabilisation calculations (Falcetta and Jordan 1990), and the assignments and energies are now widely accepted.

The same level of confidence, however, does not exist for the measured DA cross sections. For example, the cross section of methyl chloride is so small at room temperature that it may be masked by impurities (Pearl and Burrow 1993). At the most fundamental level, theoretical calculations of the DA cross sections are not available for any of the chloromethanes except methyl chloride. In the latter, hybrid calculations using a mixture of semi-empirical and *ab initio* methods (Fabrikant 1991*a, b*) have been employed with moderate success in predicting the high temperature behaviour of the DA process (Pearl *et al.* 1995*a*). This study employed a pseudo-diatomic model for the CH₃Cl molecule.

If we consider now the same molecules on surfaces or in films, with the additional complications owing to shifts in temporary anion energies due to image potentials or the stabilisation arising from the polarisability of neighbouring molecules, as well as changes in anion lifetime due to differences in symmetry and anion energy, it is not surprising that little theoretical work has been done on DA on surface or condensed phase systems. In the absence of the key information in the gas phase to serve as tests of theoretical methods, it seems unlikely to us that much progress can be made.

3. Theoretical Challenges

(3*a*) Introduction

As indicated above, the physics of DA seems clear: The electron and the target molecule form a temporary negative ion, producing new forces on the nuclei that result in a non-zero probability for the molecule to dissociate into fragments, one of which is charged. Theoretical treatments of DA roughly reflect this interpretation, dividing the problem into a portion addressing the formation and decay of the temporary electronic state and a portion addressing the nuclear dynamics. The magnitude of the DA cross section depends crucially upon the relative time scales of these two processes. In many ways DA is the *complete* molecular physics problem, involving, as it does, an intimate interplay between electronic and nuclear motion.

The two portions of the problem present significantly different challenges to the theorist. If the molecule is diatomic or reasonably approximated as a pseudodiatomic, the nuclear dynamics depend on only one variable and can be considered solvable given the potential energy curve obtained from the electronic structure problem. On the other hand, theoretical approaches are in their infancy for treating DA when more than one nuclear degree of freedom is important.

The solution of the electronic problem presents profound difficulties. The *ab initio* determination of energies and lifetimes of resonances even for fixed nuclear positions is still accompanied by difficulties involving choice of basis sets and uncertainties concerning background phase shifts. For DA these problems are exacerbated by the requirement that all quantities be known as a function of the nuclear positions. As we see below this brings in a new dimension to the uncertainties.

In the next two subsections we take up these matters, starting with the electronic resonance state.

(3b) *Determination of the Temporary Anion Properties*

The physical picture of the DA process strongly suggests the theoretical separation of the electronic scattering problem into resonant and background parts, and theoretical treatments have focused on this sort of analysis. Many workers have utilised the projection operator techniques of Feshbach (1958, 1962), since these make a formal separation of the resonant and background parts in a rigorous way. An alternative separation using *R*-matrix methods has been utilised by Fabrikant (1994). We take up this method below.

Use of the Feshbach approach has been pioneered by Bardsley *et al.* (1966) and O'Malley (1966) and more recently reviewed by Domcke (1991). If, for the moment, we ignore relatively minor inelastic effects and assume that one partial wave predominates ($l = 1$ for definiteness), the Feshbach approach leads to an expression for the transition matrix element T

$$-\pi T = e^{i\delta_0(E)} \sin \delta_0(E) - e^{2i\delta_0(E)} \frac{\Gamma_b(E)/2}{E - E_b - \Delta_b(E) + i\Gamma_b(E)/2}, \quad (1)$$

where $\delta_0(E)$ is the background phase shift, E_b is the energy of the quasibound resonant state, and $\Gamma_b(E)$ and $\Delta_b(E)$ are the width and energy shift of the resonant state respectively. These quantities are also functions of R but, for simplicity, this dependence has been suppressed. Furthermore they are not all independent since $\Gamma_b(E)$ and $\Delta_b(E)$ are connected by the equation:

$$\Delta_b(E) = \frac{1}{2\pi} \int \Gamma_b(E')(E - E')dE'. \quad (2)$$

All of the quantities in equation (1) are fixed, once a quasibound state function ϕ_b , designed to represent the inner portion of the scattering wave function at the resonance energy, is selected. Many uncertainties accompany the determination of this function.

As molecular structure calculations using Gaussian basis sets became common, it developed that useful correlations could be made between resonance energies and the *virtual orbital* energies from these calculations using Koopmans' theorem (Jordan and Burrow 1978, 1987). Further studies of Heinrich *et al.* (1986), Howard and Staley (1984) and Staley and Strnad (1992, 1994) have demonstrated that a number of different substances show a linear relationship between the measured shape resonance energies and the virtual orbital energies obtained using the standard 6-31G Gaussian basis set (Binkley and Pople 1977; Gordon *et al.* 1982). Chen and Gallup (1990) showed how this linear relationship could be deduced from the Feshbach procedure and, in particular, how the virtual orbitals provide an appropriate *zeroth order* ϕ_b function for the Feshbach treatment.

The STO-3G basis set has also been used and produces ϕ_b functions rather less diffuse than does the 6-31G basis set. The result is that the STO-3G basis set yields higher values of E_b . The relationship between the quantities

in equation (1) is intricate. As ϕ_b is changed, $\delta_0(E)$, $\Gamma_b(E)$, E_b and $\Delta_b(E)$ must all change in concert to produce an unchanged T -matrix element, since its true value depends only upon the system treated. Since the inflexibility and uncertainties of *ab initio* treatments make understanding the physics underlying the interrelationship of these quantities difficult, we have attempted to fill out some of the details by performing model calculations. Using a simple spherical model potential, one may solve the Feshbach problem exactly, in the numerical sense. These calculations show that, as ϕ_b is changed from more to less diffuse, $\delta_0(E)$ (<0) and $\delta_b(E)$ (<0) decrease while E_b (>0) and $\Gamma_b(E)$ (>0) increase (Gallup 1994). These trends hold for energies in the vicinity of the resonance position, but may not hold far from that feature. Since the resonance energy is the solution of $E_{\text{res}} - E_b - \Delta_b(E_{\text{res}}) = 0$, $\Delta_b(E)$ must become more negative to compensate for the rise in E_b , and $\Gamma_b(E)$ must rise significantly at larger values of E when ϕ_b contracts. A careful analysis of these results shows, unfortunately, that securing desirable values of all of the parameters produces conflicting criteria for choosing ϕ_b .

When considering basis sets for the ϕ_b function, another pitfall must be avoided. High quality calculations on bound electronic states of molecules require one to use flexible basis sets, and increasing the flexibility can improve the results substantially. In electronic structure calculations on bound anion states, it is necessary to employ flexible basis sets in order to obtain accurate energies and other properties. Accurate calculations on temporary anion states require basis sets at least as flexible as those used in calculations on bound anion states. Unfortunately, straightforward calculations with such basis sets lead to variational collapse. The virtual orbital with the *lowest* energy is no longer a good representation of the inner part of the resonance state, and E_b is much too low. In principle, stabilisation methods (Hazi and Taylor 1970; Nestmann and Peyerimhoff 1985; Chao *et al.* 1990) could be used to arrive at a 'buoyed up' state, but we are unaware of any attempts to do this in connection with the Feshbach procedure and DA.

As indicated above, the electronic scattering problem may be separated into resonant and background parts within the R -matrix framework by writing the R -matrix as two terms, a simple pole plus a constant background term. In calculations at UNL we have taken a hybrid semi-empirical *ab initio* approach, determining the R -matrix semi-empirically from measured energies, lifetimes, and vibrational excitation cross sections and utilising *ab initio* calculations of the potential curves as described above in the Feshbach context. The R -matrix representation of the electronic state has the great advantage that the effects of long-range dipole and polarisation potentials may be easily included semi-empirically.

Here we are using work based on the quasiclassical resonant R -matrix theory as developed by Fabrikant (1991*a*, 1991*b*) and Fabrikant *et al.* (1991). As was proposed in the conventional R -matrix theory (Schneider *et al.* 1979) we introduce an electron-molecule distance r_0 beyond which the electron-molecule interaction can be described by a local potential that typically exhibits some long-range behaviour, i.e. includes the electron-dipole (for polar molecules) and long-range polarisation potential. The short-range interaction at $r < r_0$ is taken care of by an appropriate matching condition containing the R -matrix as a function of

internuclear coordinates. The major assumption of the resonant theory is that the R -matrix may be written with only one resonant term, i.e.

$$R(\rho) = \frac{\gamma^2(\rho)}{W(\rho) - E_e} + R_r, \quad (3)$$

where ρ is the set of internuclear coordinates, E_e is the electron energy, $W(\rho)$ and $\gamma(\rho)$ are the standard parameters of the R -matrix theory, and R_r is a background term that weakly depends on both ρ and E_e .

An important consideration in our approach is the choice of the R -matrix radius in the electron coordinate r_0 . If chosen too small, an overestimate of the role of the long-range forces in the region $r > r_0$ will occur. If chosen too large, several terms will be required in the partial fraction R -matrix expansion as in the standard R -matrix approach (Schneider *et al.* 1979). If we retain but one term in the expansion while keeping r_0 large, some unphysical effects appear. Namely, in the absence of long-range forces the background phase shift of the one-pole, one-channel R -matrix theory equals $-kr_0$, where k is the electron's wavenumber. (Of course, an inclusion of the long-range interaction modifies the background phase shift, but this does not change our qualitative arguments.) It is obvious that for a large enough r_0 , we would obtain the unphysical effect of a very rapid variation of the background phase shift. The influence of this term, however, is smaller for inelastic processes than for elastic scattering. We conclude that using the resonant R -matrix theory we are more capable of describing inelastic processes in the vicinity of an isolated resonance than in describing elastic scattering or scattering in a broad energy range. We note, however, that the resonant R -matrix theory describes eigenphases for elastic e-HCl (Fabrikant 1985) and e-HF (Fabrikant *et al.* 1992) scattering in a satisfactory way.

(3c) Resonance Properties for Moving Nuclei

Determining the resonance parameters as functions of the nuclear positions permits the treatment of processes such as vibrational excitation and DA. Since DA implies substantial, long-distance motion of the nuclei, it presents more of a challenge. Considering for the present a diatomic molecule, it is useful to divide the range of R into a portion outside the neutral potential surface, where autodetachment of the electron is not possible, and an inner region, where the anion must be described as a resonance. One needs to choose a ϕ_b function that provides a good representation of the anion state at all internuclear separations. The resulting value of $E_b(R)$ is the potential function for the nuclear motion in the outer region. In the inner region, however, $E_b(R)$ is modified by addition of $\Delta_b(E, R) - i\Gamma_b(E, R)/2$ to provide a complex potential.

Well known techniques for calculating anionic bound states dictate that the outer portion of the potential be determined with as flexible a basis set as is practical. But, as discussed in the last subsection, in the inner region use of flexible basis sets leads to variational collapse when applied to virtual orbital techniques that have been useful in treating resonances in larger molecules. At present there appears to be no completely satisfactory method to bridge the conflicting requirements for basis sets in the inner and outer regions.

CH₃Cl is an example of a polyatomic molecule for which the DA process appears to be well described by a pseudo-diatomic model. Even within this

model, however, in determining the potential surface there remains the question as to whether it is more appropriate to treat the CH₃ group as a rigid entity or whether it should be allowed to relax. In the latter case, the CH bond lengths and the HCCl angles are reoptimised (under a constraint of C_{3v} symmetry) at each C–Cl distance considered. The calculations done to date have used a ‘relaxed’ CH₃ group. This is justified with the following argument: The H atoms are less massive than a C or Cl atom and can be considered to ‘keep up’ with the motion of the more massive atoms. The magnitude of the error in the calculated DA cross section using potentials with fully relaxed CH₃ groups is, however, not known. A general answer to the question of dealing with relaxation is not at hand, either. DA in CCl₄, for example, occurs in a system where the masses of all of the peripheral atoms are the same. In this system complete relaxation of the CCl₃ group at each C–Cl distance might be inappropriate.

(3d) Nuclear Dynamics

As we noted above, the problem of the nuclear dynamics of DA for diatomic molecules and polyatomic molecules that are well described as pseudo-diatomic can be considered solved since it is a one-dimensional system. The situation for polyatomic molecules is much more difficult. Although vibration in polyatomic molecules has long been treated approximately with the theory of small vibrations and the harmonic model, DA is not a small motion and displays the ultimate degree of anharmonicity in the motion. Since the initial states in the DA process are the low-lying vibrational levels of the ground electronic state of the neutral molecule, it is useful to represent the nuclear positions as functions of the harmonic normal modes of that state. Since they completely span the space of internal nuclear motions, this may be done whether or not anharmonicity is considered. They have the additional advantage of simplifying the Franck–Condon problem in the DA process. Nevertheless, other complications arise. During the DA process, the leaving of the Cl[−], expressed in terms of the harmonic normal modes, will generally require that the values of more than one of them increase to infinity in the asymptotic region. The forces inducing the motion come from the antibonding orbital temporarily occupied, and the surface crossing region where the electron becomes bound can be very complex. We know of no successful attack on these problems in DA.

To avoid all these difficulties we employ the pseudo-diatomic model described in Section 3b. To include vibrational dynamics as suggested by Schneider *et al.* (1979), we consider, instead of equation (3), the operator

$$R(\rho) = \gamma(\rho)[H_I - E]^{-1}\gamma(\rho) + R_r, \quad (4)$$

where

$$H_I(\rho) = T(\rho) + V(\rho), \quad (5)$$

$$V(\rho) = V_0(\rho) + W(\rho), \quad (6)$$

and where $T(\rho)$ is the kinetic energy operator for the nuclear motion, V_0 is the potential energy function of the target molecule, and E is the total energy.

The function $V(\rho)$ can be identified, with some modifications (Fabrikant 1991*a, b*), as a negative-ion surface.

The matching procedure incorporating the R -matrix in the form of equation (4) leads to an integro-differential equation that is completely equivalent (Fabrikant 1990) to that of the non-local complex potential theory (Bardsley 1968) and can be solved in the same way. The R -matrix theory, however, allows the incorporation of the long-range (dipole and polarisation) interaction between the electron and incident molecule in an easier way. The quasiclassical approach (Kalin and Kazansky 1990) to solving the basic equation allows, in an efficient way, inclusion of many vibrational channels, which is necessary for a correct account of the survival probability of the intermediate negative ion. This is especially important for relatively heavy molecules having a large number of vibrational levels. Our previous calculations for methylchloride (Fabrikant 1991*a, b*) have shown that if fewer than 35 vibrational channels are included, DA cross sections exhibit a qualitatively wrong behaviour. Our theory can easily take into account 50 or more vibrational channels of the neutral molecule interacting with the intermediate negative ion state.

4. Experimental Challenges

A number of technical problems, some unique to electron beam studies of DA in large molecules, tend to slow further progress. Perhaps the most straightforward measurement to make in this field is that of the total DA cross section, summing over all final charged fragment species. Although such studies have been carried out for many years in smaller molecules, there exists no commonly accepted benchmark cross section with which to calibrate or test the apparatus. DA in N_2O perhaps comes the closest to this although there remains some scatter in published values. The cross section of Rapp and Briglia (1965) may be the most reliable in this regard. Energy scale calibration of DA peaks has also suffered from a lack of consensus. Measurement of peak energies to better than 50 meV is desirable.

Proceeding to larger molecules, generally consisting of liquids or solids with low vapor pressures, presents additional problems with determination of gas densities in the scattering region. Particular attention will have to be focused on the maintenance of uniform, or at the least, known temperatures in the gas cell and the manometer. The times required for such vapours to reach equilibrium may also be lengthy.

To study the role of molecular structure in the DA process, it is increasingly likely that the synthesis of desired compounds will have to be carried out. Purification processes are also essential because certain contaminants such as CCl_4 may have cross sections that are enormously larger than that of the desired molecule. Synthesis and purification are very labor intensive, and the net result is that only small samples are generally available. This puts strong constraints on the available running time and the checks necessary for confidence in the outcome.

By far the most difficult experimental hurdle concerns measurement of the absolute DA cross section of each mass selected anion fragment in compounds which have multiple stable fragments. The problems in this area are well known but have been studied mostly with regard to positive ion fragmentation

and multiple ionisation. Very little reliable information is available for DA in halogenated hydrocarbons.

5. Recent DA Studies

In the final part of this paper, we briefly describe recent and on-going DA studies at the University of Nebraska and with other collaborators. Our philosophy has been to simplify the problem by considering molecules in which there is only one halogen. In saturated hydrocarbons, i.e. those with no double or triple bonds, but with one C-X bond, there will exist only a single low-lying temporary negative ion that is associated with occupation of the C-X antibonding σ^* orbital. Temporary anion states associated with the empty C-C and C-H orbitals, although they have not been studied extensively, will generally lie at higher energies, typically above 4 eV. A second advantage of these mono-halide compounds is that there will be only a single stable anion product, namely X^- , at the low electron energies we will be using. For all our studies thus far, we have chosen to use chlorine as the halogen of choice. ETS measurements have shown that the temporary negative ion state associated with the C-Cl σ^* orbital lies in a convenient energy range for electron beam studies. The heavier halogens tend to produce peaks in the DA cross sections which lie closer to zero energy and thus present more difficulties in determining their absolute values. In Section 5a we discuss measurements in a series of mono-chloroalkanes and in Section 5b recent progress in understanding these measurements theoretically. In Section 5c we explore the influence on the DA cross section of a region of unsaturation in the molecule, that is, a double bond placed close to or distant from the C-Cl bond.

(5a) Monochloroalkanes

The monochloroalkanes present the simplest possible hydrocarbon system in which to study the DA process. The smaller compounds such as methyl and ethyl chloride therefore are important prototypes. As noted earlier, the C-Cl σ^* orbital lies well below other unfilled orbitals and thus only a single temporary negative ion state is of importance. By considering various substituents on the carbon atom to which the chlorine is attached, however, considerable variety in the hydrocarbon framework is possible. In the 'normal' alkanes, a single carbon is attached to the central carbon; in the 'secondary' and 'tertiary' compounds, two or three carbons are attached, respectively. Further variation in structure is possible by attachment of the chlorine to saturated hydrocarbon ring compounds.

The measured DA cross sections of these compounds (Pearl and Burrow 1994) vary by more than an order of magnitude, even excluding methyl chloride, which appears to be a very special case and possesses a cross section orders of magnitude smaller than the rest. The details of the rather subtle differences in C-Cl σ^* orbital energies due to the different structures of the hydrocarbon framework will not be pursued here. Rather, we focus on the systematic variation of the cross sections with resonance energy to reveal the most important aspects of the DA process.

The key ingredients determining the DA cross section are the lifetime of the temporary negative ion, determined primarily by its energy and the nature of the barrier through which the electron must tunnel back to the continuum,

and the time required for the C–Cl separation to increase to the value at the crossing with the potential surface of the neutral molecule. In the simplest possible model, which will be entirely adequate for our purposes, the DA cross section may be viewed (see for example Bardsley *et al.* 1966) as the product of a capture cross section and a survival probability that depends exponentially on the separation time t_{sep} and the resonance lifetime τ_{ave} , averaged over the internuclear coordinate from its equilibrium value to that at the crossing with the neutral potential curve:

$$\sigma_{\text{DA}} = \sigma_{\text{cap}} \exp(-t_{\text{sep}}/\tau_{\text{ave}}). \quad (7)$$

The lifetime, of course, is inversely proportional to Γ_{ave} , the average spread in energy of the resonance.

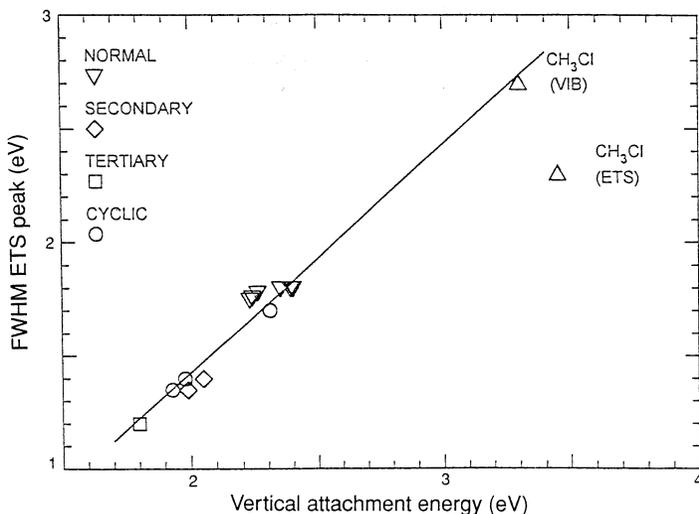


Fig. 1. Full-width at half-maximum of the resonance peaks in the chloroalkanes as a function of vertical attachment energy, as measured using electron transmission spectroscopy. [Taken from Pearl and Burrow (1994).]

The variation in resonance width among these closely related molecules may therefore play the major role in determining the relative DA cross sections. The approximate widths and energies of the temporary negative ion states may be determined experimentally using ETS, by observing the resonance peaks in the total scattering cross sections. Fig. 1, taken from Pearl and Burrow (1994), summarises these data in the chloroalkanes, plotting the width as a function of the resonance energy, that is, the vertical attachment energy, VAE. We note that the width of the resonance in CH₃Cl is very large and a measurement using the total cross section is subject to error because of changes in the non-resonant portion of the scattering. A more reliable assessment, labeled ‘VIB’, is obtained from the resonance peak as it appears in the vibrational excitation cross section (Shi *et al.* 1995), which does not suffer from a non-resonant contribution at large scattering angles. The data points are coded by different symbols to indicate the various molecular structures.

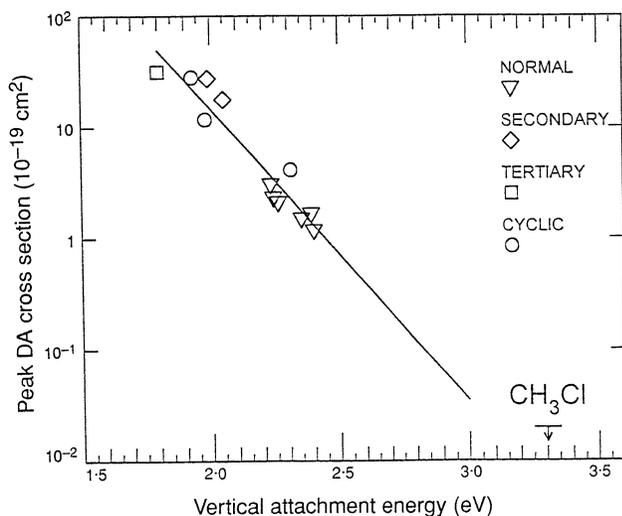


Fig. 2. Peak DA cross section in the chloroalkanes as a function of the vertical attachment energy. [Taken from Pearl and Burrow (1994).]

Over the limited range of VAEs shown in Fig. 1, the widths are rather well represented by a linear relationship. We assume here that the contribution from the variation in the Franck–Condon overlaps is not strong. Putting this functional dependence into equation (7) leads to the prediction that the DA cross sections will decrease exponentially with increasing VAE. Fig. 2 illustrates the experimental data (Pearl and Burrow 1994), plotting on a semi-log scale the peak DA cross section versus VAE. The straight line gives a best fit to the data, excluding that for CH_3Cl for which only an upper bound exists. This figure provides compelling evidence that in a closely related series of molecules, the resonance lifetime, through its dependence on resonance energy, is the most important property determining the variations in the DA cross sections. The scatter among the points, which is greater than the experimental uncertainties, indicates that other factors, as yet unanalysed, also play a role.

Fig. 2 provides an interesting insight into the way in which placing one of these compounds on a surface or in a film might affect its DA cross section. In the gas phase, attachment occurs into the empty C–Cl σ^* orbital of each of the compounds. By changing the hydrocarbon framework, we are in a sense ‘tuning’ the energy of this orbital. Fig. 2 shows that these shifts in energy cause an exponential variation in the DA cross section. In a similar way we can anticipate that shifts in the resonance energy of a given compound caused by polarisation effects in a film or image forces near a conducting surface will cause dramatic increases in the DA cross section.

As illustrated in Fig. 3, we note that the same simple relationship of Fig. 2 does not exist between the peak DA cross sections and the energies of the peaks in the yield of Cl^- ions (Pearl and Burrow 1994). In compounds with short temporary negative ion lifetimes, the energy of the resonance and that of the peak in the DA cross section do not coincide. We illustrate this in Fig. 4 which

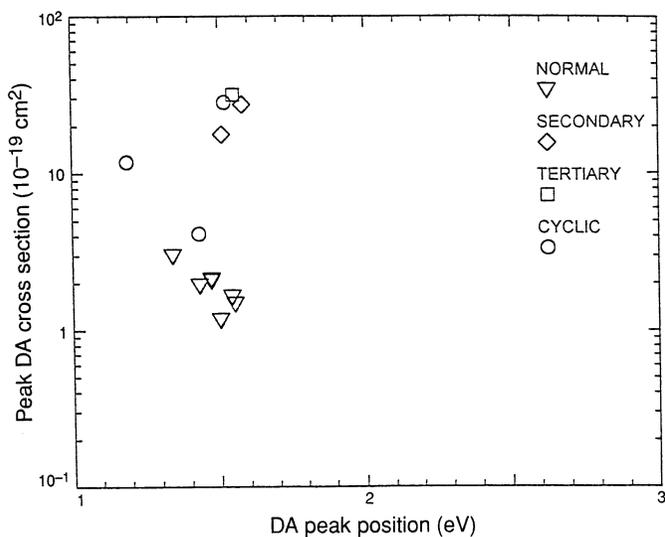


Fig. 3. Peak DA cross section in the chloroalkanes as a function of the energy of the DA peak. [Taken from Pearl and Burrow (1994).]

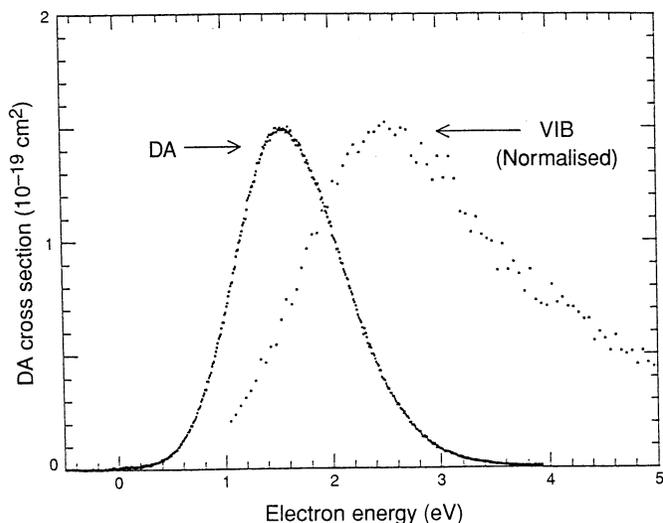


Fig. 4. DA cross section of ethyl chloride as a function of electron energy (Pearl and Burrow 1994) and the differential cross section for excitation of the C–Cl stretching mode as a function of energy (Chan and Burrow 1995) normalised to the DA data for purposes of comparison.

shows the DA cross section of ethyl chloride along with the differential cross section for excitation of the C–Cl stretch mode (Chan and Burrow 1995). The latter peak lies quite close to the resonance peak in the total scattering cross section. In the figure, the vibrational cross section is normalised to the DA cross

section for comparison purposes. In fact, it is approximately three orders of magnitude larger. A substantial difference in the peak positions is evident, owing to the proportionally higher rate of autodetachment of the electron taking place on the high energy side of the resonance compared to the rate on the low side.

(5b) Theoretical Efforts

Methyl chloride, the simplest of the chloroalkanes, and the prototypical compound one would assume could be understood most readily, has proved to be a challenge from an experimental point of view (Pearl and Burrow 1993). As noted in Figs 1 and 2, the width of the temporary negative ion associated with the C-Cl σ^* orbital is quite large and, consequently, the DA cross section so small that there is concern that the observed signal may derive from impurities. Fabrikant (1991*a, b*) has employed the hybrid approach mentioned earlier that utilises experimental data for the resonance energy and lifetime, obtained by fitting to the cross section for vibrational excitation, along with *ab initio* calculations of the anionic potential curve in the stable region, and the *R*-matrix method for the scattering portion of the problem. As noted before, the molecule is assumed to be a quasi-diatomic. In the most recent version of these calculations (Pearl *et al.* 1995*a*), the calculated DA cross section for methyl chloride at room temperature was found to be about 4.4×10^{-23} cm² at 0.66 eV, smaller than the upper bound determined in our experiments, rendering a test of the theory inconclusive. As an alternate approach, the temperature dependence of the DA process was measured and computed by the same means. A peak in the cross section near zero energy was found to grow rapidly with increasing temperature and was easily observable above 500°C. The agreement between theory and experiment was quite gratifying, although the possibility of systematic errors make a conclusive comparison difficult.

Because the DA cross section of ethyl chloride is readily measurable at room temperature and absolute cross sections for vibrational excitation have now been measured (Chan and Burrow 1995), it appears to us that this compound, even though more complex, may be more suitable for a closer test of theory. We report here a few preliminary findings.

As carried out earlier in methyl chloride, the first task is to fit the theoretical expression for the cross section for vibrational excitation of the fundamental of the C-Cl stretching mode of ethyl chloride to that measured by experiment to obtain the resonance energy and the width of the resonance at the equilibrium geometry of the neutral molecule. The quality of the fit is also a function of the way in which the width of the resonance varies with the C-Cl internuclear separation, although not in a strongly sensitive manner. This is illustrated in Fig. 5 which displays the theoretical and experimental vibrational cross sections for two different models, labeled M0 and M2, of the width versus C-Cl distance dependence. The latter is shown in Fig. 6 in which is plotted the adiabatic width as a function of the C-Cl distance measured from the equilibrium separation. In all cases the same width at the equilibrium separation was used.

The parameters employed in M0 yield a DA cross section in ethyl chloride which is in excellent agreement with experiment. As seen in the upper panel of Fig. 5, the theoretical cross section for vibrational excitation reproduces the energy and width of the resonance fairly accurately, although overestimating

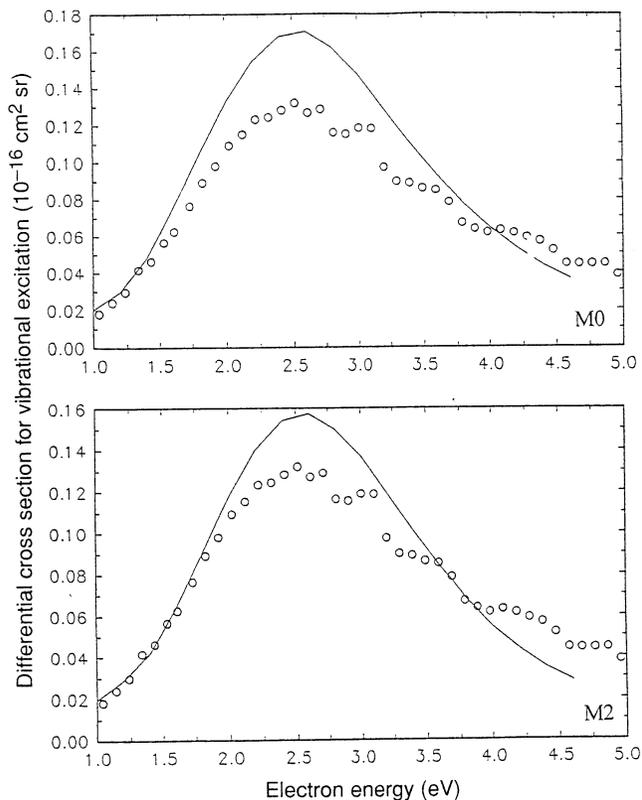


Fig. 5. The curves display the theoretical fit to the experimental data (open circles) for the cross section for excitation of the C-Cl fundamental stretching mode. The upper and lower panels show the results for two different models for the variation of the resonance width with C-Cl separation.

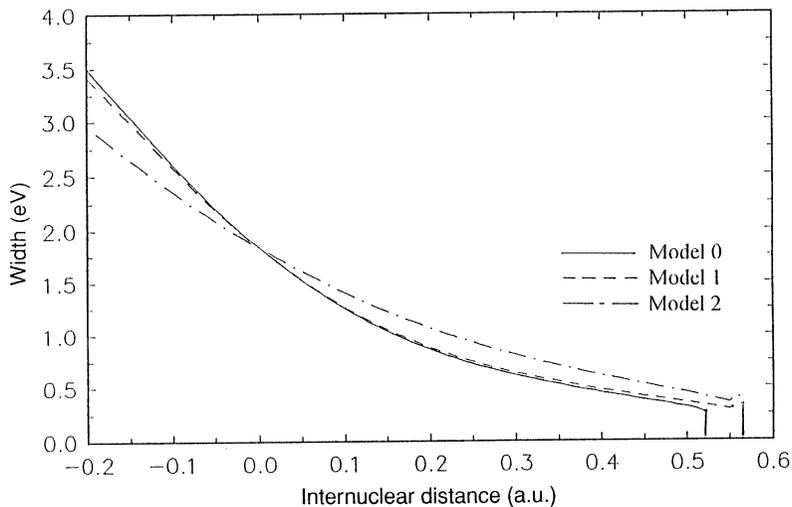


Fig. 6. Three theoretical models for the variation of the resonance width with C-Cl separation measured from the equilibrium position. In all cases the width of the resonance at the equilibrium position was taken to be the same.

the magnitude by approximately 30%. The theoretical method also permits the calculation of the magnitudes of the higher harmonics of the C-Cl stretching mode which are excited through the temporary negative ion state. This information is also available from experiment, and the various models shown in Fig. 6 represent an attempt to fit the measured ratio for excitation of the second harmonic of the C-Cl mode to the fundamental. The experimental value for this ratio is 0.067. For model M0, which gives an excellent DA cross section, this ratio is 0.117. Model M2 improves this ratio to 0.090 and displays the vibrational cross section shown in the lower panel of Fig. 5 which is also improved over that of M0. Unfortunately, the DA cross section given by M2 lies a factor of 10 lower than that found in experiment. We note again that these results are preliminary, in that fitting to the experimental cross sections for vibrational excitation involves the exploration of a multidimensional 'phase space' which has not yet been carried out systematically. There is no question, however, that the extreme sensitivity to the resonance width function will make it difficult to extract a unique DA cross section.

The eventual goal of the theoretical portion of this program, of course, is to replace the empirically determined parameters with values calculated from first principles. The results reported here stress again the importance of accurate determinations of the resonance lifetimes if an understanding of the DA process is to be obtained.

(5c) DA in Unsaturated Mono-halides

The existence of an unsaturated bond or bonds in a molecule introduces one or more empty π^* orbitals which, at the equilibrium geometry of the neutral molecule, generally lie lower in energy than the C-Cl σ^* orbital (Burrow *et al.* 1982). In contrast to the anion states formed by filling the latter, electrons in π^* orbitals experience a much higher angular momentum barrier and the lifetimes of such anion states are substantially longer. In some cases the scattering cross section may even show fine structure due to quasi-vibrational motion of the anion. These orbitals therefore provide a means to localise the electron on the molecule for a much longer time than in saturated compounds. Coupling between π^* and σ^* orbitals, and here we use these terms to describe the local symmetries, may therefore greatly enhance the DA cross section.

The strength of π^*/σ^* coupling will depend on the separation and orientation of the relevant bonds and the nature of the framework separating them. Effects of the coupling are directly observable in total scattering cross sections in which the energies of the resonances are shifted from the values in the unsubstituted molecules. In molecules such as allyl and benzyl chloride, in which the C-Cl bond is separated from the unsaturated moiety by a single C-C bond, the couplings are quite strong and the DA cross sections are roughly three orders of magnitude larger than that of ethyl chloride (Stricklett *et al.* 1986). Furthermore they are observed to have their peak values quite close to the energies attributed to the nominally π^* orbitals (Dressler *et al.* 1985; Olthoff *et al.* 1985; Stricklett *et al.* 1986). In fact, the mixing of the π^* and σ^* orbitals is so strong in these compounds that the view that the electron is captured into the π^* orbital and transfers into the σ^* orbital is not a realistic model. There is no doubt however that the admixture permits attachment to take place at lower energy and with

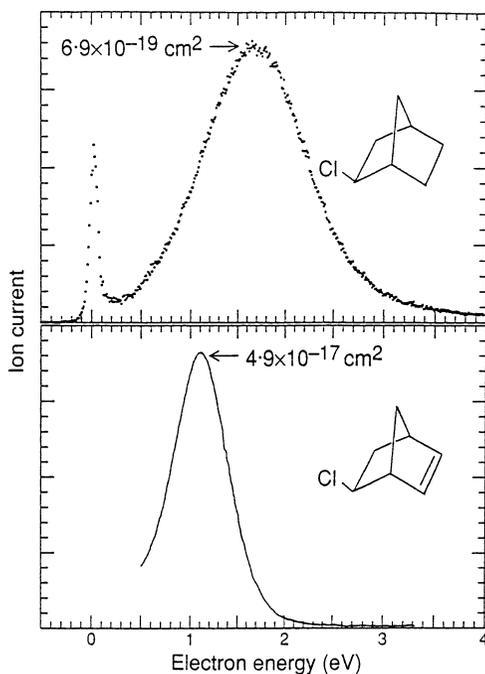


Fig. 7. DA cross sections for the saturated compound, exo-2-chloronorbornane (upper panel) and the unsaturated compound, exo-5-chloro-2-norbornene (lower panel) as a function of electron impact energy. [Taken from Pearl *et al.* (1993).]

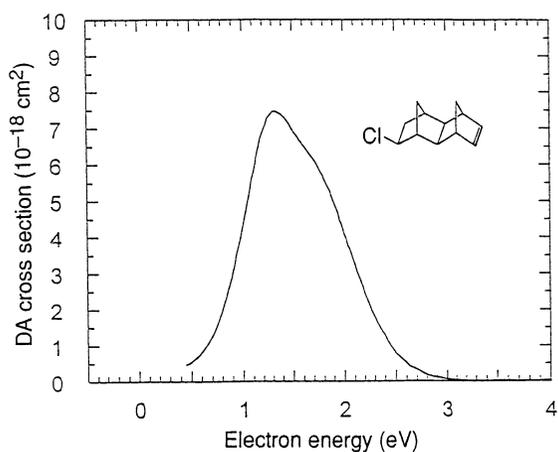


Fig. 8. DA cross section as a function of electron impact energy of the unsaturated compound in which the C-Cl bond is separated from the ethylenic group by four C-C bonds. [Taken from Pearl *et al.* (1995b).]

an effectively increased resonance lifetime. Both of these effects will create larger DA cross sections.

In planar compounds such as vinyl chloride and chlorobenzene in which the Cl atom is directly attached to a C=C or phenyl group respectively, the DA cross sections are also large although smaller than in the related allyl and benzyl chloride compounds (Stricklett *et al.* 1986). The DA process is forbidden by symmetry if the molecules remain planar. Out-of-plane distortion induced in the temporary negative ions apparently permits the reaction to take place. Theoretical treatment of this process in such molecules would be very illuminating.

Compounds in which the unsaturated portion of the molecule and the C-Cl bond are further separated permit a study of the distance dependence of the coupling between the π^* and σ^* orbitals, as well as insight about the *intramolecular* transfer of electrons. For the clearest interpretation, it is important that the molecules be rigid so that the distances are well determined. Inspired by a series of molecules based on norbornyl structures synthesised and studied by Paddon-Row (1993), the DA cross sections of the compounds illustrated in Fig. 7 have been measured (Pearl *et al.* 1993). The upper panel displays the yield of Cl^- from the fully saturated compound. The magnitude, shape and peak energy are all characteristic of the chloro-alkanes discussed earlier. (The sharp peak at zero energy is due to an impurity.) In the lower panel, the DA cross section for a molecule with similar structure except for the presence of a double bond is shown. The cross section is enhanced by a factor of 71. Furthermore, the peak in the cross section is shifted to a lower energy coincident with that of the peak in the total scattering cross section associated with the empty π^* orbital.

In more recent studies (Pearl *et al.* 1995*b*), the DA cross section from the molecule shown in Fig. 8 has been obtained. In this case the double bond and C-Cl bond are separated by four single bonds. The DA cross section is reduced from that shown in the lower panel of Fig. 7, but still exceeds the values found in the saturated compounds. Again the main peak occurs at the energy of the π^* resonance in the total cross section as observed using ETS. The yield of Cl^- also indicates a shoulder near 1.8 eV. This energy is consistent with DA taking place directly through formation of the C-Cl σ^* anion. Thus the DA process appears to take place both in a direct fashion as well as through capture into the π^* orbital and subsequent transfer to the σ^* orbital.

Studies in molecules of this type have the potential to refine greatly our understanding of the DA process, particularly with regard to the three different time scales involved, i.e. the lifetime of the π^* negative ion, the time for electron transfer from the π^* to the σ^* orbital, and the time for separation of the C and Cl atoms.

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