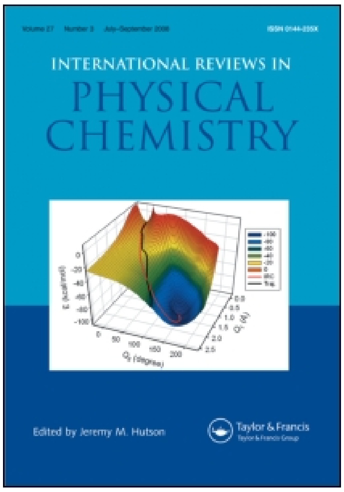

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Formation and decay of negative ion resonances in gaseous and condensed molecules

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Formation of negative ions under low energy electron impact (0–15 eV) is studied from C_6F_6 and C_6F_5Cl at different stages of aggregation: gas phase molecules, free molecular clusters and condensed molecules. The gas phase experiments (molecules, clusters) are performed in a crossed beam apparatus and the condensed phase experiments in a UHV apparatus where the molecules are deposited in definite amounts on a cold (30 K) metallic substrate. In each case the relative cross-section for the formation of a particular anion as a function of the electron energy is recorded mass spectrometrically. Under single-collision conditions, both molecules yield parent anions from a narrow resonance at zero eV and various fragment ions from further resonances at higher energies. In clusters the low energy attachment feature broadens considerably. This is the result of effective intermolecular relaxation which strongly competes with autodetachment. Monomeric anions are also generated from clusters in considerable amounts at higher energies (> 3 eV) via inelastic scattering from one molecule and evaporative capture of the slowed-down electron by another molecule of the same cluster (self-scavenging). In C_6F_5Cl clusters, dissociative attachment is strongly quenched with the exception of a new intense resonance at 6·5 eV yielding Cl^- and $C_6F_5^-$. At this energy, desorption of Cl^- from condensed C_6F_5Cl also has a pronounced maximum. The 6·5 eV feature is interpreted as a core excited open channel resonance which is converted into a closed channel (Feshbach) resonance when coupled to environmental molecules, i.e. any degree of aggregation strongly quenches autodetachment in favour of dissociation.

1. Introduction

The formation and decay of negative ion resonances (NIRs) (or transient negative ions (TNIs)) is a prominent process in the interaction of low energy electrons with molecules (Schulz 1973, Christophorou 1971, Christophorou *et al.* 1984). These reactions play a crucial role in many phenomena where low energy electrons are present, in the gas phase as well as in the condensed phase.

We only mention here resonantly enhanced vibrational excitation of molecules (Mann and Linder 1992), breakdown of discharges by effective attachment of free electrons (Pace and Christophorou 1984) and negative ion resonances as intermediates in photochemical reactions, in particular in the case of molecules adsorbed on solid surfaces. It has been recognized quite recently that the photochemical behaviour of adsorbed molecules may largely be controlled by photoelectrons from the substrate, thereby generating TNIs. These transitory ions can dissociate with the possibility of directly observing the desorbed fragment ions mass spectrometrically (Dixon-Warren *et al.* 1991) In other cases, the TNI can act as the driving force for desorption of the undissociated neutral molecule (Gadzuk *et al.* 1990, Hertel *et al.* 1995). In the spirit of the Menzel–Gomer–Redhead (MGR)-model (Menzel and Gomer 1964) or its modification by Antoniewicz (Antoniewicz 1980), the TNI is first accelerated towards the surface due to polarization or image forces. After transfer of the extra electron into

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the solid or emission into vacuum the neutral system may find itself above the threshold for desorption, i.e. on the repulsive part of the energy surface describing the interaction of the neutral molecule with the solid above the desorption limit. For molecules with large dissociative attachment (DA) cross-sections at low electron energies, this effect can be the source of photochemical activity at energies already near the threshold for photoemission of the solid, i.e. in a wavelength region where the photoabsorption cross-section of the gas phase molecule may still be negligibly small.

It should finally be remembered that any degradation pathway of high energy radiation produces low energy electrons and thereby TNIs via photoionization and further secondary processes (Christophorou 1971, Kimura *et al.* 1993).

In this paper we present and review some recent results concerning the direct formation of TNIs by free electrons. As targets we take C_6F_6 and C_6F_5Cl in different degrees of aggregation: from isolated molecules under collision-free conditions over clusters in the gas phase to condensed molecules. Among many different topics the influence of solvation on chemical reactions has been one of Michael Henchman's favourite problems (Hierl *et al.* 1988, Henchman and Paulson 1988).

Consider a TNI formed by attachment of free electrons of energy E. The molecular ion is then subjected to the following competitive relaxation pathways

$$\begin{aligned} M^-(E) &\rightarrow M^{(*)} + e^- && (1a)\\ &\rightarrow R + X^- && (1b)\\ &\rightarrow M^- + E && (1c) \end{aligned}$$

Reaction (1*a*) represents autodetachment which eventually recovers the neutral molecule in an excited state. In the case of vibrational excitation the excitation function, e.g. for one particular mode, then exhibits a resonance (Mann and Linder 1992). Reaction (1*b*) is dissociative attachment (DA) and (1*c*) is stabilization into the thermodynamically stable ground state of the molecular anion. The latter process requires a positive (adiabatic) electron affinity of the target molecule M.

In isolated molecules under single-collision conditions one usually observes fragment ions through DA (process 1*b*). In this case the ion yield curve (i.e. the intensity of fragment X^- versus electron energy) exhibits pronounced resonances (Christophorou 1971, Oster *et al.* 1989, Illenberger and Momigny 1992). The energy position and width of a particular resonance mirrors the area of the potential energy surfaces of the neutral and anionic system connected by the particular Franck–Condon transition. In larger molecules, metastable parent anions (M^-) can sometimes also be observed mass spectrometrically. They usually appear within a very narrow resonance near zero eV (Christophorou 1971, Oster *et al.* 1989). A remarkable exception is the fullerenes. Electron attachment to C_{60}, for example, yields long-lived C_{60}^- within an unusually broad distribution extending up to 12 eV (Lezius *et al.* 1993, Jaffke *et al.* 1994). In this case electron attachment can be understood by a direct coupling of the energy of the incoming electron with the vibrational degrees of freedom of C_{60}. In other words, the high density of vibrational states in C_{60} allows direct, nonresonant electron attachment (Matejcik *et al.* 1995) in contrast to the usual (electronic) trapping mechanism via shape or Feshbach resonances (Schulz 1973, Illenberger and Momigny 1992).

How does the general situation change on proceeding to clusters or condensed molecules?

With respect to the interacting electrons one is principally faced with a *multiple scattering problem.* Since in the energy range of interest (0–15 eV) the de Broglie wavelength of the electrons may exceed the intermolecular distances (an electron of energy 1 eV has a de Broglie wavelength of 12·4 Å), the electron wave is then simultaneously scattered from different molecules.

Nevertheless, in clusters (Märk 1991, Illenberger 1992) as well as in condensed molecules (Sanche 1990, Meinke and Illenberger 1994, Weik and Illenberger 1995, Azria *et al.* 1994) the DA cross-section often exhibits resonances which can be described on a molecular site, i.e. formation and decay of an individual NIR, coupled to the environmental molecules of the cluster or the molecular film.

Although individual molecular TNIs can obviously be generated in clusters and in the condensed phase, it is clear that their formation and decay mechanisms as well as the resonance energy may significantly differ with respect to the gas phase. This we shall illustrate in the case of the two halogenated benzenes C_6F_6 and C_6F_5Cl.

2. Experimental

The experiments were performed with two different arrangements, one for the gas phase and another for the condensed phase experiments. The 'effusive beam' and 'supersonic beam' techniques as well as the ultrahigh vacuum (UHV) apparatus for the condensed phase studies have previously been described in detail (Kühn and Illenberger 1990, Illenberger 1992, Meinke and Illenberger 1994). In both experiments, the electron beam is generated by a 'trochoidal electron monochromator' (TEM) (Stamatovic and Schulz 1970) which uses a magnetic field to collimate and guide the electron beam. This field is established by a pair of Helmholtz coils which in both cases is mounted outside the vacuum system. The energy resolution is approximately 0·1–0·2 eV (FWHM) with an intensity of 10–50 nA. Due to the magnetic collimation, the beam intensity is fairly constant down to very low energies.

In the gas phase experiments (figure 1), the electron beam is either crossed with a molecular beam *effusing* from a capillary which is directly fitted to the reaction chamber or with a *supersonic cluster beam*. Ions arising from the interaction are then extracted from the reaction volume and detected by a quadrupole mass spectrometer. The supersonic beam is established by adiabatic expansion of the gas seeded in Ar through an 80 μm nozzle. In the present case, the seed gas mixture is prepared by passing Ar through liquid C_6F_6 or C_6F_5Cl using 'bubble tubes' which prevent the liquids from being injected into the apparatus.

The supersonic beam always contains a *distribution of clusters*, eventually also including monomers. Some concentration of monomers is always present in the reaction chamber due to scattered background molecules. The average cluster size can be varied to some extent by varying the stagnation pressure and the nozzle temperature.

Electron stimulated desorption of anions is studied in an UHV apparatus consisting of a TEM, a quadrupole mass spectrometer and a cryogenic cooled substrate mounted on a manipulator (figure 2). For the present experiments, the substrate is polycrystalline platinum which can be cooled down to 30 K and resistively heated up to several hundred K.

The molecules are adsorbed or condensed onto the substrate by exposing it to a volumetrically calibrated gas quantity. The base pressure is in the 10^{-10} mbar range which is sufficiently low to avoid fast contamination of a newly deposited substrate.

While the gas phase spectra are calibrated by the well-known SF_6^- resonance at 0 eV (Oster *et al.* 1989, Illenberger 1992), in the condensed phase experiments the

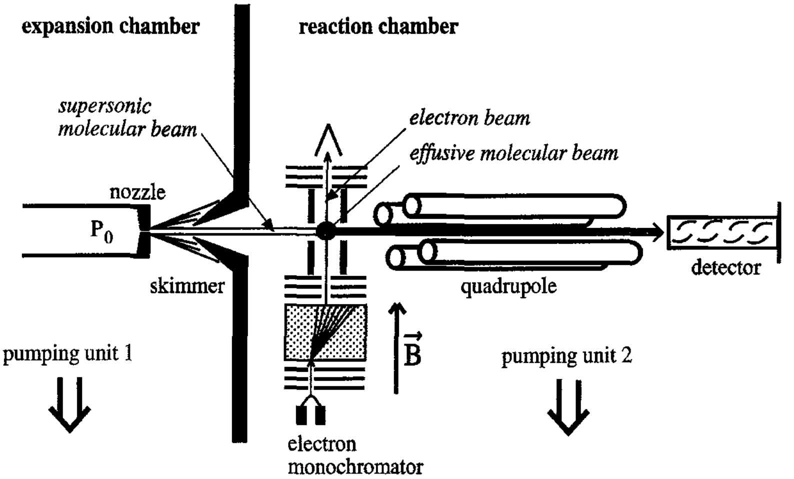

Figure 1. Experimental set-up for the study of electron attachment reactions in isolated molecules and in clusters.

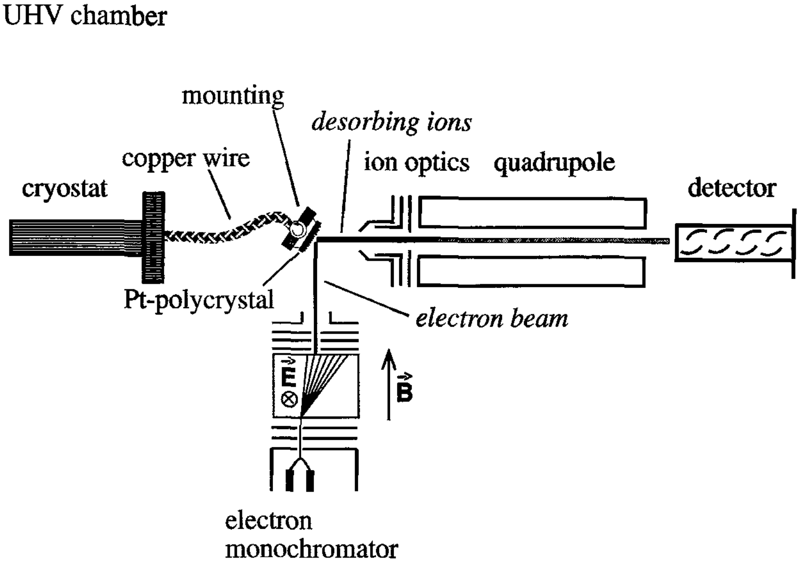

Figure 2. Experimental set-up for the study of electron stimulated desorption (ESD) of anions from condensed and adsorbed molecules.

vacuum level for the electrons (0 eV) is determined from the onset of the electron injection curve (Sanche 1990, Meinke and Illenberger 1994).

Exposition of adsorbed of condensed molecules to the electron beam results in a more or less pronounced charging of the film due to trapped electrons or electrons bound to individual molecules (M^-) or fragments (X^-). This can be seen by a shift of the electron injection curve due to the potential barrier of the accumulated negative charge (Marsolais *et al.* 1989, Meinke and Illenberger 1994). For this reason, all condensed phase spectra presented here are first scans on a newly deposited film. Under these conditions the reproducibility of the spectra presented here is within an accuracy of 0·1 eV.

3. Results and discussion

In this paper we compare the formation and decay of negative ion resonances in C_6F_6 and C_6F_5Cl. Particular emphasis will be placed on the question of how the relevant quantities change on going from isolated molecules over clusters to adsorbed and condensed molecules. While results from gas phase and condensed phase C_6F_6 have been reported previously (Naff *et al.* 1971, Ingólfsson and Illenberger 1995, Weik and Illenberger 1995), to our knowledge, NIRs in clusters of C_6F_5Cl and condensed C_6F_5Cl molecules have not been reported before.

Electron attachment to aromatic systems below 5 eV is usually characterized by involvement of the π system, i.e. formation of shape resonances via accommodation of the extra electron into one of the virtual π^* MOs (Allan 1989, Oster *et al.* 1989). This is usually associated with effective energy randomization in the TNI prior to dissociation.

As will be shown, the overall behaviour concerning the formation and decay of NIRs changes completely on going from C_6F_6 to C_6F_5Cl. This is mainly due to the comparatively high electron capacity of the Cl atom. The electron capacity expresses the ability of an atom in a molecule to accumulate extra negative charge (Olthoff *et al.* 1985).

3.1. *Hexafluorobenzene*

Figure 3 displays the energy profile of the four anions obtained from gas phase C_6F_6 under single-collision conditions. Hexafluorobenzene belongs to the class of molecules yielding metastable parent anions. As mentioned above, these ions usually appear within a narrow resonance at zero eV. Further resonances at higher energy are associated with DA reactions leading to the ionic fragments F^-, $C_6F_5^-$ and $C_5F_3^-$.

The electronic configuration of the two lowest resonances (at 0·0 and 4·5 eV) are assigned as Π single particle resonances, namely ${}^2E_{2u}$ (0·0 eV, doubly degenerate) and ${}^2B_{2g}$ (4·5 eV) (Ingólfsson and Illenberger 1995).

From ESR coupling constants (Symons *et al.* 1977) and *ab initio* calculations (Hiraoka *et al.* 1990) $C_6F_6^-$ in its ground state is predicted as a planar carbon structure containing out of plane C–F bonds. Strictly speaking, the extra electron then resides in a π^*–σ^* combination orbital with π^* the dominant component.

Some σ^* admixture is also necessary to explain DA (e.g. F^- formation at 4·5 eV). Dissociation of a pure Π resonance into $F^- + C_6F_5$ would be symmetry forbidden (Clarke and Coulson 1969).

In clusters (figure 4) three significant new features are apparent: (i) formation of ionic clusters of the form $(C_6F_6)_n^-$, $n \geqslant 1$, (ii) a broader low energy attachment profile with the peak definitely above zero eV and (iii) formation of the parent anion M^- (and the homologs M_n^-) in large quantities at higher electron energies (> 3 eV). The fragment ions F^-, $C_6F_5^-$ and $C_5F_3^-$ are also observed from clusters with resonance profiles close to those from isolated molecules.

As pointed out recently (Ingólfsson and Illenberger 1995), the broader attachment profile near zero eV is a mirror of the additional relaxation pathways in clusters.

It has been known for some time that C_6F_6 has a positive adiabatic electron affinity (0·52 eV from electron transfer equilibria, Chowdhury *et al.* 1986). On the other hand, electron transmission (ET) on C_6F_6 exhibits a resonance at 0·43 eV (Frazier *et al.* 1978) indicating a 'negative vertical attachment energy', while electron attachment gives a narrow $C_6F_6^-$ peak near zero eV (figure 3).

This seeming contradiction, however, is a question of the different experimental methods and the different ways in which the ions are produced and observed.

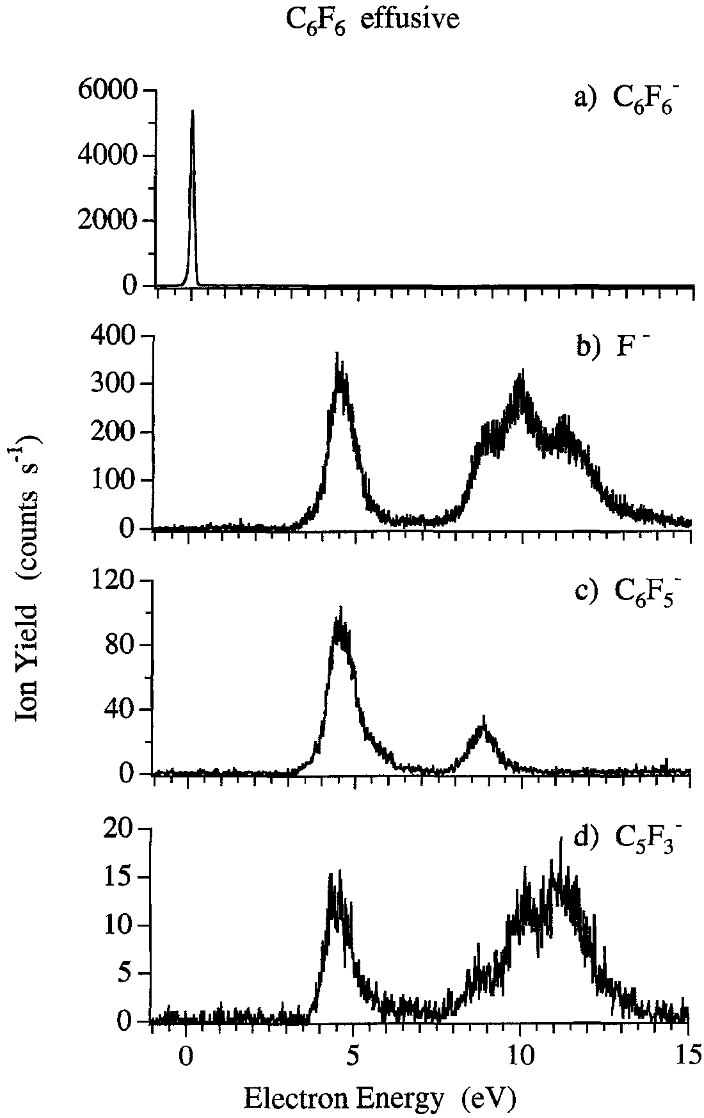

Figure 3. Ion yield curves for electron attachment to gas phase C_6F_6 under single-collision conditions ($p = 5 \times 10^{-5}$ mbar).

While electron transfer equilibria simply lead to thermodynamic values, the structure in ET is associated with the vertical Franck–Condon transition with no *direct* information on the fate of the TNI. In mass spectrometry, on the other hand, one detects ions which must have survived the flight between source and detector ($\geqslant 10$ μs).

Under collision-free conditions, the width of the $C_6F_6^-$ resonance in a mass spectrometric experiment can then be totally controlled by the autodetachment lifetime which rapidly decreases with electron energy hence giving a narrow peak at zero eV (figure 3(*a*)). It has, in fact, been shown in a direct time-of-flight experiment that $C_6F_6^-$ formed by thermal electron attachment has a lifetime of 12 μs (Naff *et al.* 1968) which is in the range of the ion flight times in the present experiment (see below).

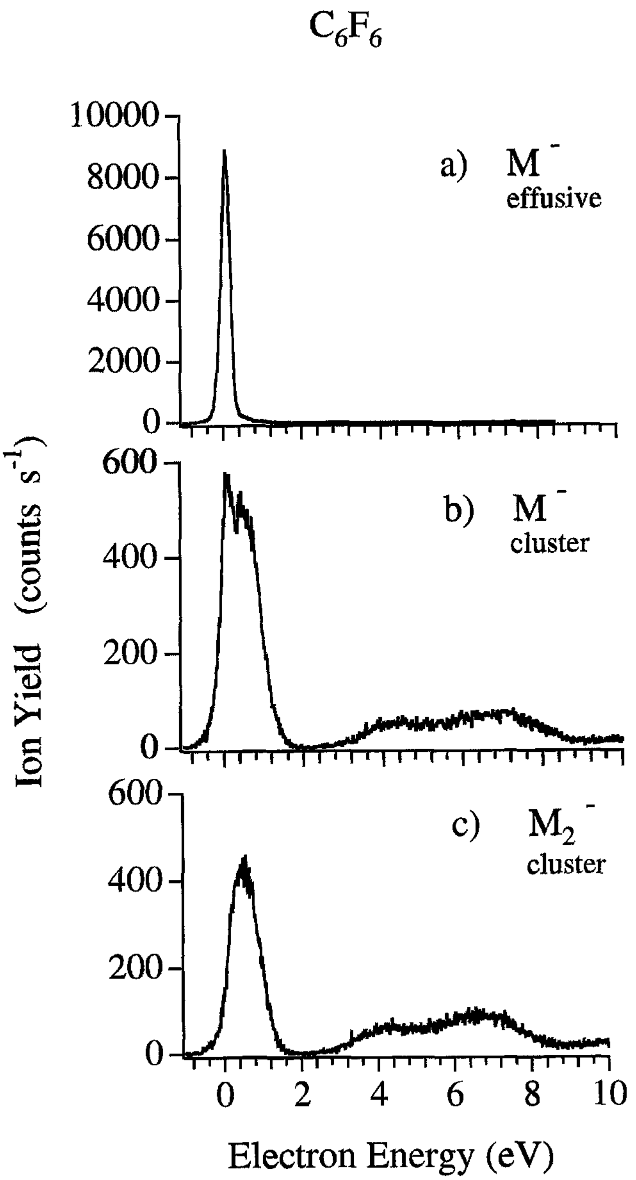

Figure 4. Ion yield curves obtained from electron attachment to single C_6F_6 molecules and clusters of C_6F_6. (*a*) $C_6F_6^-$ (M^-) from single molecules at collision-free conditions ($p = 5 \times 10^{-5}$ mbar); (*b*) (M^-) from clusters; (*c*) (M_2^-) from clusters. The cluster experiments were recorded at a stagnation pressure of 2 bar.

If a TNI is created within a cluster, it is subjected to intermolecular collisions on a ps scale. This opens effective additional relaxation pathways which strongly compete with autodetachment. Figure 5 illustrates the process in a simplified scheme. The Franck–Condon transition creates the ion in a vibrationally excited state. In single molecules under collision-free conditions, the ion remains unstable with respect to autodetachment, although vibrational coupling can remove energy from the relevant coordinate Q. In clusters, however, intramolecular collisions quickly relax the anion to

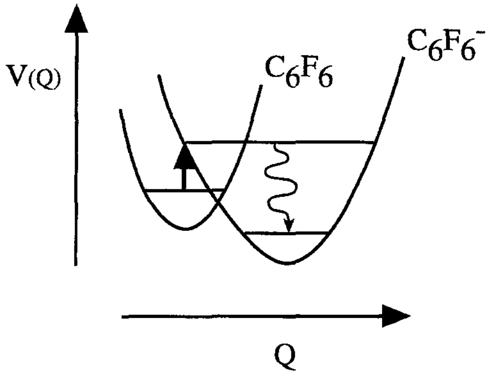

Figure 5. Schematic representation of $C_6F_6^-$ (M^-) formation in a cluster. Intramolecular collisions quickly stabilize the TNI to an energy below the crossing of the two potential curves. In single molecules only Franck–Condon transitions close to 0 eV create metastable $C_6F_6^-$.

an energy below the crossing point of the two potential energy surfaces, where it remains stable toward autodetachment.

In actual practice the problem is complicated by the solvation energy and further complicated by the Jahn–Teller effect, leading to an elongated and compressed ground state $C_6F_6^-$ ($^2E_{1g}$) anion.

In the cluster experiment, the low energy resonance observed on the monomer anion $C_6F_6^-$ (M^-) displays a doublet structure (figure 4(*b*)). While the first peak of this doublet is simply due to electron capture by monomeric neutrals (M) which are always present in the reaction volume, the second peak closely resembles that of the dimer anion (figure 4(*c*)). These dimer anions (and the larger homologs, not shown in figure 4) are necessary products of electron attachment to pre-existing neutral clusters. Their resonance peak approximately reflects the *primary* shape of the resonance characterized by the particular Franck–Condon transition. Of course, a complete description of the M_n^- resonance profile also requires consideration of the shift of the resonance energy due to solvation and the cross-section behaviour to form a particular product ion M_m^- from electron attachment to a particular neutral cluster M_n ($n \geqslant m$).

From figure 4 it can also be seen that the parent anion $C_6F_6^-$ (and the larger homologs) are also formed from clusters in considerable amounts above 3 eV. The mechanism is either (a) direct capture of the fast electron via a core excited (shape or Feshbach) resonance and subsequent stabilization by intermolecular collisions or (b) inelastic scattering of the fast primary electron from one molecule and capture of the slowed down electron by another molecule of the same cluster (self-scavenging).

The shape of the M^- ion yield curve above 3 eV correlates with the energies of electronically excited states in neutral C_6F_6 as documented from optical absorption spectroscopy (Robin 1985), electron energy loss spectroscopy (EELS) (Frueholz *et al.* 1979) and threshold electron excitation spectra (TEES) (Ingólfsson and Illenberger 1995). Thus, the self-scavenging mechanism is likely to be responsible for M^- (and M_n^-) formation above 3 eV reflecting the three states $^1B_{2u}$ (4·8 eV), $^1B_{1u}$ (6·4 eV) and $^1E_{1u}$ (7·1 eV) of the first order benzene transitions $1e_{1g}$ (π) → $1e_{2u}$ (π^*).

Figure 6 displays the F^- desorption yield from condensed C_6F_6. F^- is the only observable desorption product. Appreciable desorption only occurs in the resonance range between 8 and 14 eV. At the energy where the π^* system is involved (near 4·5 eV) however, desorption is barely visible.

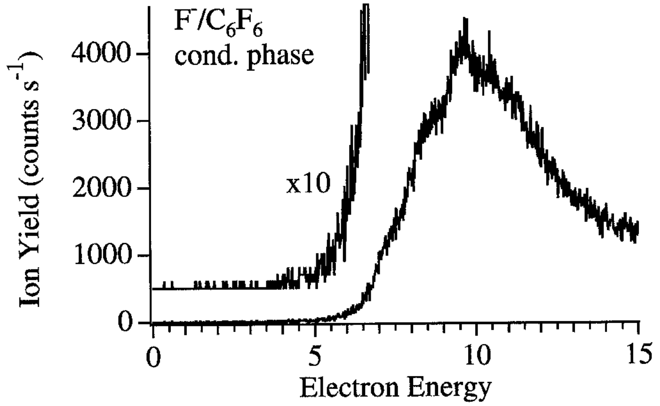

Figure 6. Desorption of F^- from a submonolayer C_6F_6 adsorbed on a multilayer Xe film as spacer to the metallic substrate.

The spectrum in figure 6 is recorded from a submonolayer of C_6F_6 deposited on a multilayer Xe film as spacer. The desorption yield drops further when C_6F_6 is deposited directly on the metal.

Desorption of an ionic fragment requires some translational energy in order to overcome the solvation (or polarization) energy of the negative charge. This leads to an expression for the *desorption threshold* ($\varepsilon_{\mathrm{th}}$) of a fragment of mass m_i (Meinke and Illenberger 1994)

$$\varepsilon_{\mathrm{th}} = \Delta H_0 + \left(\frac{m_i}{m}\right) V_p \tag{2}$$

where m expresses the mass of the neutral fragment, ΔH_0 the thermodynamic threshold for the gas phase DA process and V_p the polarization energy. Note that in this context V_p is defined as a *positive number*. An estimation of the bulk solvation energy can be obtained from the Born equation (Born 1920)

$$V_p = \frac{e^2}{8\pi\varepsilon_0 R}\left(1 - \frac{1}{\varepsilon_d}\right), \tag{3}$$

with R the ionic radius and ε_d the dielectric constant of the medium. For dielectric films a value near 1 eV has been estimated as a reasonable number for the solvation energy of an ion at the surface (Michaud and Sanche 1990, Meinke and Illenberger 1994, Weik and Illenberger 1995).

Equation (2) indicates that desorption becomes less favourable with increasing mass (m_i) of the ionic fragment. This is simply due to conservation of linear momentum in the dissociation of the precursor resulting in less translational energy for the large fragment ion. Thus, polarization of the environment acts as a *translational energy filter* for desorbing ions.

Gas phase measurements indicated (Fenzlaff and Illenberger 1989) that in C_6F_6 the Π resonances decompose with low kinetic energy while in the region above 8 eV decompositions giving considerable translational energy are observed. These latter precursor TNIs are most likely to be of the core excited type having some σ* (C–F) nature, which would also explain the appreciable desorption intensity in this energy range.

In the gas phase, both complementary DA channels with respect to the negative charge

$$C_6F_6^{*-} \rightarrow F^- + C_6F_5 \qquad (4a)$$

$$F + C_6F_5^- \qquad (4b)$$

are observed from two resonances peaking at 4·5 and 8·8 eV (figure 3).

Desorption of F^- is the result of the DA process

$$C_6F_6^{*-}(\text{cond}) \rightarrow F^-(\text{gas}) + C_6F_5(\text{cond}) \qquad (5a)$$

in analogy to the gas phase reaction (4*a*). It should be mentioned that in the condensed phase the alternate channel

$$C_6F_6^{*-}(\text{cond}) \rightarrow F^-(\text{cond}) + C_6F_5(\text{gas}) \qquad (5b)$$

is energetically more favourable. With the present experimental arrangement, the detection of desorbed *neutral* fragments, however, is not yet possible.

The desorption process

$$C_6F_6^{*-}(\text{cond}) \rightarrow F(\text{cond}) + C_6F_5^-(\text{gas}) \qquad (5c)$$

is not observed. This is due to the translational energy filter which makes desorption of heavy ions unlikely (*supra vide*).

However, even for the light ion F^- the desorption cross-section is low when compared to different halomethanes (Oster *et al.* 1993, Weik and Illenberger 1995, Meinke and Illenberger 1994).

Principally, the desorption cross-section of a fragment from a TNI at or near the surface is controlled by the geometry of the precursor ion relative to the surface as well as the amount of translational energy imparted to the fragments. From the energetic point of view, DA to gas phase C_6F_6 yields fragments with comparatively low kinetic energy, at least in the range below 7 eV where π^* MOs are involved (Fenzlaff and Illenberger 1989). In contrast to the present system, electron capture by halomethanes is often characterized by involvement of σ^* (C–X) MOs (X = halogen) and consequently by more impulsive dissociation mechanisms due to the release of considerable translational energy (Oster *et al.* 1989). Such systems can then have large desorption cross-sections.

3.2. *Chloropentafluorobenzene*

Electron capture by C_6F_5Cl shows remarkable features when going from single molecules to aggregates or to the condensed phase.

Figure 7 first displays the ion yield curves from gaseous C_6F_5Cl. Similar to perfluorobenzene, one observes the parent anion as a narrow peak at zero eV and further resonances yielding the different DA products. The lifetime of the $C_6F_5Cl^-$ parent anion formed upon thermal electron attachment ($\approx$ 30 meV) was determined as 17·5 μs (Naff *et al.* 1968).

The most striking difference from the previous system is that now DA (into Cl^-) is the dominant process while in C_6F_6 it was formation of the parent anion $C_6F_6^-$. Furthermore, in C_6F_5Cl the DA process yielding F^- is remarkably low in intensity (figure 7(*d*)).

Replacing one F by Cl in C_6F_6 lowers the symmetry from D_{6h} to C_{2v}. Consequently, the degeneracy of the two lowest unoccupied MOs is also removed on going from C_6F_6 to C_6F_5Cl. Due to the comparatively high electron capacity of Cl one expects appreciable admixture of σ^*(C–Cl) components to the π^* system.

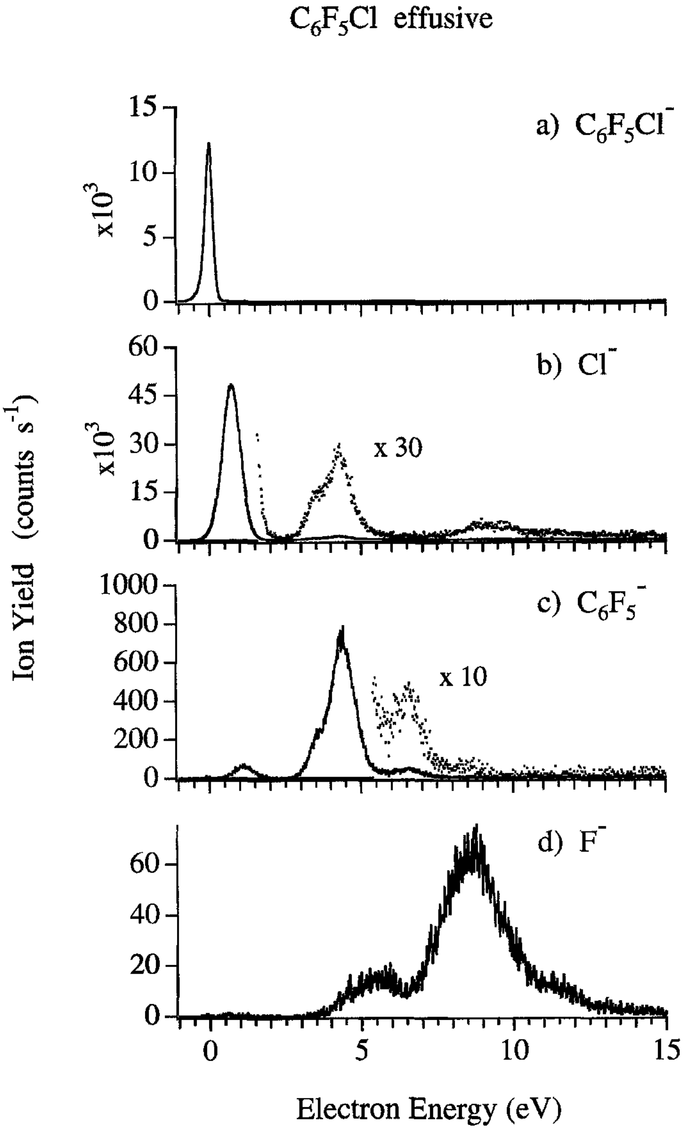

Figure 7. Ion yield curves for the different products observed in electron attachment to gas phase C_6F_5Cl molecules under single-collision conditions ($p = 5 \times 10^{-5}$ mbar).

From the energetic point of view, formation of Cl^- is also considerably favoured over F^-. From thermochemical data ($D(C_6F_5\text{–}Cl) = 4{\cdot}0$ eV (McMillen and Golden 1982), *EA* (Cl = 3·615 eV, *EA*(F) = 3·399 eV (Mead *et al.* 1984)) one calculates the threshold for Cl^- formation as 0·4 eV and that for F^- formation as 1·5 eV (assuming the same C–F bond dissociation energy in C_6F_5Cl as in C_6F_6, $D(C_6F_5\text{–}F) = 4{\cdot}9$ eV (Choo *et al.* 1974)).

The ions Cl^- and $C_6F_5^-$ arise from the complementary processes

$$C_6F_5Cl^- \rightarrow Cl^- + C_6F_5 \qquad (6a)$$

$$\rightarrow Cl + C_6F_5^-. \qquad (6b)$$

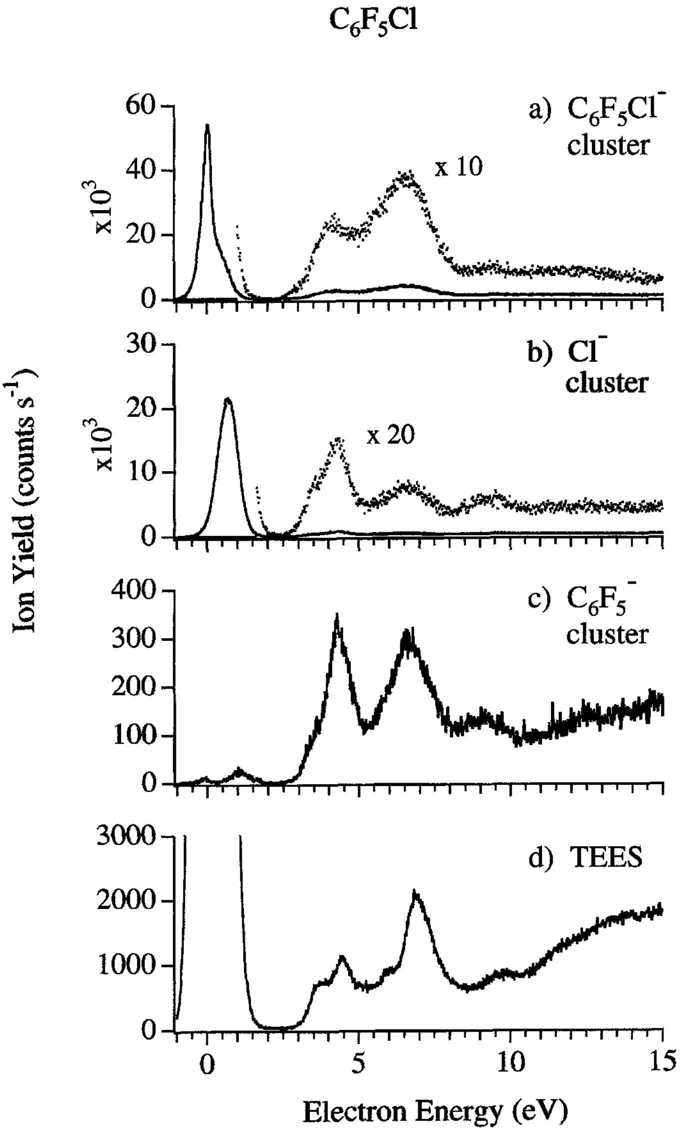

Figure 8. (*a*)–(*c*) Ion yield curves for some selected products from C_6F_5Cl clusters, stagnation pressure 1 bar; (*d*) threshold electron excitation spectrum (TEES) recorded on $C_6F_5Cl^-$, effusive gas inlet, $p = 6 \times 10^{-4}$ mbar.

In the 3–6 eV energy range both ions have a similar energy profile while the low energy $C_6F_5^-$ peak is at significantly higher energy compared to Cl^-. This simply reflects the lower electron affinity of C_6F_5 (~ 2·75 eV, Herd *et al.* (1989)) as compared to Cl (3·615 eV) which makes channel (6*b*) only accessible for energies above ~ 1·2 eV.

Figure 8 displays a selection of product ions obtained from electron attachment to clusters. For the monomeric anion $C_6F_5Cl^-$ (M^-) (figure 8(*a*)) and the homologs M_n^- (for the dimer M_2^-, see figure 9(*a*)) we have a situation comparable to the previous system C_6F_6, namely (i) a broadening of the low energy peak due to effective relaxation which suppresses autodetachment and (ii) additional contributions above 3 eV due to

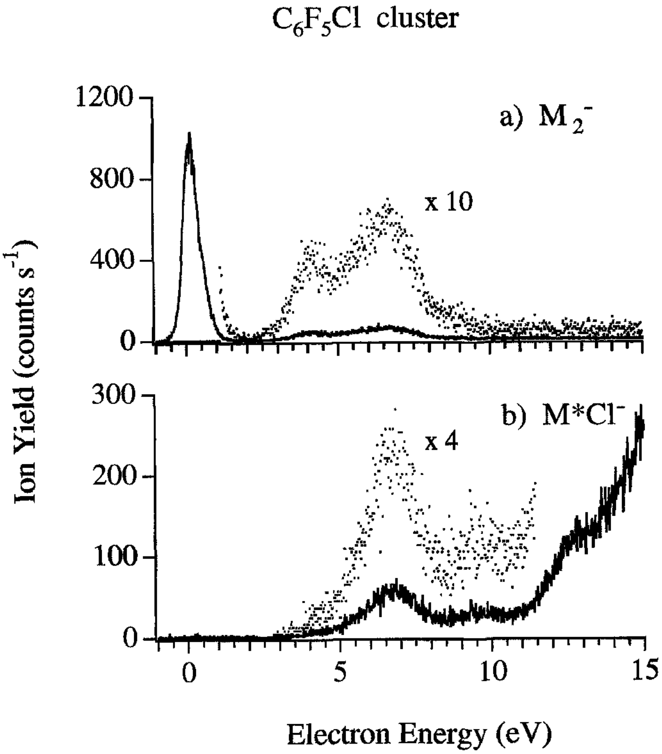

Figure 9. Ion yield curves for (*a*) the dimer ion M_2^- ($M = C_6F_5Cl$) and (*b*) the product $M \cdot Cl^-$ from C_6F_5Cl clusters.

inelastic scattering prior to electron attachment. The M^- peak in figure 8(*a*) displays a shoulder toward higher energies. In contrast, the M_2^- resonance is a necessary product from a *cluster* peak at 0·2 eV and also has an asymmetric profile toward higher energies (figure 9(*a*)).

In figure 8(*d*) we additionally present a threshold electron excitation spectrum (TEES) of C_6F_5Cl. A TEES is obtained by scanning the electron energy and recording the $C_6F_5Cl^-$ ion *under effusive gas inlet* but at a pressure (6×10^{-4} mbar) beyond single-collision conditions. The TEES reflects (electronic) excitations (including resonances) in isolated C_6F_5Cl molecules which slow the primary electron down completely. The slow electron is then captured by a second, *uncorrelated* C_6F_5Cl molecule. For this reason, a TEES is also called a *scavenging spectrum*. A *self-scavenging spectrum*, on the other hand, mirrors the corresponding process between two *correlated* molecules of the same cluster. As can be seen from figures 8(*a*) and 8(*d*) there is a close correlation between the scavenging and self-scavenging spectrums with the latter less structured due to intermolecular interactions in the ionized cluster. A similar situation was observed in perfluorobenzene (Ingólfsson and Illenberger 1995).

Figures 8(*b*) and 8(*c*) indicate that the energy profiles of the complementary DA products Cl^- and $C_6F_5^-$ significantly change when going to clusters. Most striking is the evolution of a peak at 6·5 eV, where we have a strong self-scavenging feature (figure 8(*a*)). At a slightly higher energy (6·8 eV) one observes a prominent TEES peak (figure 8(*d*)), while in isolated molecules DA contributions on the complementary ions $Cl^-/C_6F_5^-$ are barely visible as resonances at that energy (figures 7(*b*) and 7(*c*)).

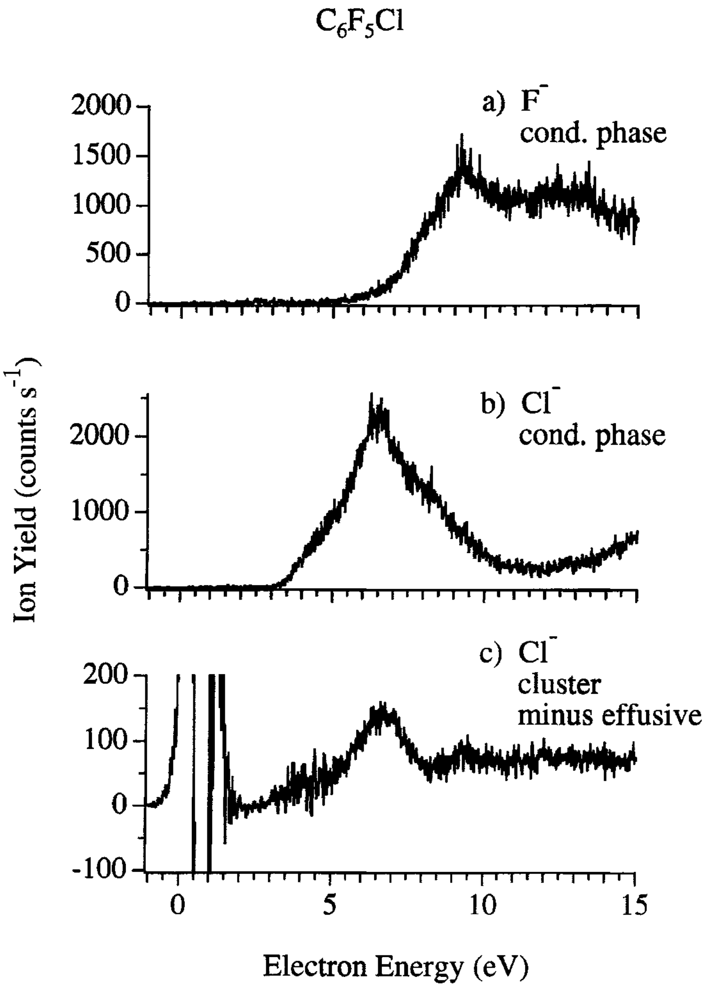

Figure 10. (*a*) and (*b*) Desorption of F^- and Cl^- from an 8-layer C_6F_5Cl film; (*c*) difference spectrum of the Cl^- yield between supersonic beam and effusive beam normalized at the low energy resonance.

Figure 9 displays the energy profile for the products M_2^- and $M \cdot Cl^-$. The solvated fragment ion $M \cdot Cl^-$ shows a completely different feature as compared to Cl^- formation from single C_6F_5Cl molecules (figure 7(*b*)). This is a very unique behaviour since solvated ions $X^- \cdot M_n$ generally carry the signature of the X^- DA fragment (Illenberger 1992). On the $M \cdot Cl^-$ product we have a significant contribution at 6·5 eV while the strong DA resonance yielding Cl^- at 0·7 eV and the weaker one around 4·5 eV is completely quenched. In the present system, we obviously have very effective relaxation mechanisms in the ionized clusters which strongly quench dissociation in favour of undissociated products like M_2^- (figure 9(*a*)). Furthermore the DA process at 6·5 eV is strongly enhanced in clusters (see also figure 10(*c*)). We also mention here that solvated ions of the form $F^- \cdot M_n$ could not be detected from either compound.

Figure 10(*c*) finally displays a difference spectrum of the Cl^- intensity between supersonic and effusive beam, normalized to the intensity of the low energy peak. The dominant contribution is now at 6·5 eV. The strong positive and negative enhancements around 0·7 eV integrate to zero intensity. They simply arise from the fact that around 0·7 eV the difference of two large numbers is taken and that both original spectra were recorded with a slightly different energy resolution.

Figures 10(*a*) and 10(*b*) display the desorption spectra obtained from condensed C_6F_5Cl. While F^- desorption shows some correlation with the gas phase DA spectrum (peaks at 9·5 and around 11·5 eV with the low energy peak at 5·5 eV quenched in the condensed phase), desorption of Cl^- is virtually restricted to a distribution peaking at 6·5 eV with flat shoulders on both sides.

In short the situation in C_6F_5Cl can be summarized as follows: (i) the strong Cl^- DA channel at low energy is quantitatively quenched in clusters in favour of undissociated products M_n^-; (ii) in clusters a new resonance at 6·5 eV evolutes yielding the complementary ions Cl^- and $C_6F_5^-$; (iii) the corresponding state in the isolated molecule appears as a strong peak at 6·8 eV in the TEES spectrum, which is, however, barely visible on the DA products; and (iv) desorption of Cl^- from condensed C_6F_5Cl is virtually restricted to a resonance around 6·5 eV.

What is the nature of the electronic state at 6·5 eV and how can this behaviour be understood? The high intensity of the Cl^- desorption at 6·5 eV suggests an electronic state with C–Cl antibonding nature, or at least effective coupling to some other repulsive state. In the gas phase the intensity is too low to perform a time-of-flight (TOF) analysis of the ionic products at 6·5 eV. From clusters, however, some intriguing features concerning Cl^- formation can be obtained from the TOF spectra.

Figure 11 displays the $C_6F_5Cl^-(M^-)$ and Cl^- TOF spectra from isolated molecules and clusters. The spectra were recorded by pulsing the electron beam at one of the electrodes before the reaction volume (Lotter and Illenberger 1990, Illenberger 1992).

Figure 11(*a*) compares the M^- TOF spectrum from effusive gas inlet at 0 eV with the M^- TOF spectrum from clusters at 4·5 eV. From the discussion about it is clear that at 4·5 eV the parent ion M^- is necessarily a product from electron attachment to a cluster (self-scavenging). The lower flight time of the 'cluster' TOF peak is essentially due to the supersonic beam with all particles travelling with the *seeded beam velocity* (~ 560 m s^{-1} in the case of Ar) toward the detector (Lotter and Illenberger 1990).

Figure 11(*b*) compares the Cl^- TOF spectrum at 0·7 eV energy (effusive) and 6·5 eV (supersonic beam) now taken at a lower draw out field ($\varepsilon = 0{\cdot}6$ eV) in order to better visualize the difference between effusive and supersonic beam inlets.

For a static target gas having a Maxwell–Boltzmann distribution, mean kinetic energy (E_T) and full width at half maximum of the TOF peak (ΔT) are related by

$$\Delta T = \frac{(m_i \frac{16}{3} E_T \ln 2)^{1/2}}{\varepsilon}$$

with m_i the mass of the ion (Illenberger 1982). For effusive gas inlet we have ΔT $(C_6F_5Cl^-) = 3{\cdot}3$ μs at 0 eV and $\Delta T(Cl^-) = 4{\cdot}5$ μs at 0·7 eV corresponding to $E_T(C_6F_5Cl^-) = 37$ meV and $E_T(Cl^-) = 56$ meV. The DA fragment thus has a slightly overthermal energy ($3/2kT = 41$ meV at $T = 300$ K).

The Cl^- TOF peak recorded at 6·5 eV is purely due to Cl^- emission from a cluster travelling with the seeded beam velocity. Under the present experimental conditions we calculate a shift of 6·0 μs ($C_6F_5Cl^-$) and 3·0 μs (Cl^-) for the flight time of the respective ion ($E_T = 0$) generated in the supersonic beam compared with a static gas. Figure 11 indicates that this is very close to the experimental values.

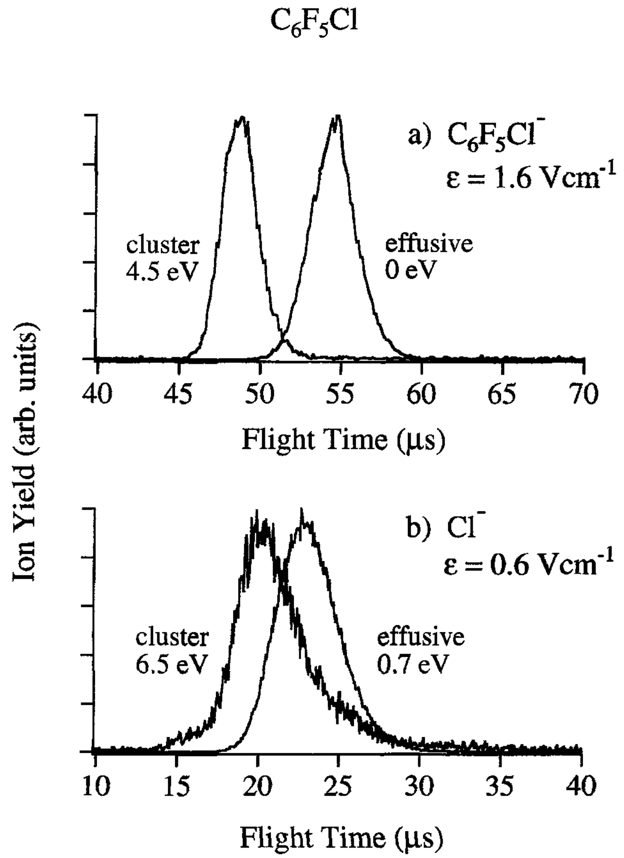

Figure 11. TOF spectra of (*a*) $C_6F_5Cl^-$ and (*b*) Cl^- obtained from the cluster beam and the effusive beam at the electron energies indicated.

The significantly larger base width of the Cl^- TOF peak recorded at 6·5 eV indicates emission of Cl^- having some translational energy.

More interesting is the observation that the Cl^- TOF peak recorded at 0·7 eV is virtually identical between effusive beam and supersonic beam inlets. This directly shows that any Cl^- signal at 0·7 eV arises from the static background gas, i.e. Cl^- emission is *quantitatively quenched in clusters*. Furthermore, it indicates that the *supersonic beam only contains clusters*. This is at least the case under the present expansion conditions (stagnation pressure $p_0 = 1$ bar). The $C_6F_5Cl^-$ signal from the supersonic beam recorded at 0 eV, on the other hand, displays *two* peaks at 49 and 55 μs (not shown in figure 11, it is essentially the sum of both peaks in figure 11(*a*)) with the relative heights varying with stagnation pressure.

Based on the experimental observations, we propose the following mechanisms to be operative in electron attachment to $C_6F_5Cl^-$: the intense Cl^- DA channel at 0·7 eV is quantitatively quenched in clusters due to very effective intermolecular relaxation processes. Capture of electrons near 6·8 eV by single molecules generates a core excited (open channel) resonance. Under single-collision conditions, this TNI primarily decays via autodetachment into the associated electronically excited neutral state slightly below 6·8 eV as corroborated by the strong feature in the TEES.

In clusters, the 6·8 eV core excited resonance is red shifted due to the attractive interaction of the negative charge with the molecules of the cluster (polarization or solvation energy), possibly *below* the energy of the associated excited neutral state. This results in an increase in the dissociation probability yielding the complementary ions $Cl^-/C_6F_5^-$. In this case, effective intermolecular relaxation does not prevent dissociation, but slows down the ejected ion considerably. Although the emission of *free* electrons is no longer possible from the core excited resonance solvated in a cluster, there is still some possibility of transferring a bound electron to a C_6F_5Cl molecule generating ground state $C_6F_5Cl^-$. This is enabled by the electron affinity of C_6F_5Cl (1·8 eV predicted from semiempirical MO calculations (Glidewell 1985)). As can be seen from figure 8(*a*), there is, in fact, a prominent feature at 6·5 eV due to self-scavenging. For the present system, however, formation of undissociated products M_n^- at 6·5 eV via the core excited resonance and subsequent intermolecular relaxation (one of the two possible mechanisms discussed above) may in fact compete with self-scavenging.

The interaction of electrons with condensed C_6F_5Cl molecules results in Cl^- as the dominant desorption product. This process is exclusively observed at 6·5 eV due to the repulsive character of the electronic state. As expected, desorption of the complementary ion $C_6F_5^-$ is completely suppressed due to its large mass in combination with the translational energy filter inherent in the desorption of ions.

4. Conclusion

Electron capture by both C_6F_6 and C_6F_5Cl gas phase molecules under collision-free conditions yields long-lived parent anions M^- which are exclusively observed from a narrow resonance at 0 eV. At higher energies, additional resonances appear which relax via dissociation into different fragment ions. In perfluorobenzene, M^- is by far the dominant ion while in C_6F_5Cl DA into $C_6F_5+Cl^-$ prevails over associative attachment. In clusters the low energy resonance (now yielding the parent anion M^- *and* the solvated ions M_n^- in both systems) is considerably broadened, having a maximum above 0 eV. This is the result of intermolecular relaxation processes which strongly suppress autodetachment in the ionized cluster. In single molecules under collision-free conditions, on the other hand, only parent anions M^- formed close to 0 eV live long enough to be detected mass spectrometrically.

In both cluster systems, M^- (and M_n^-) also appear in appreciable amounts at energies above 3 eV. The structures in the corresponding ion yields correlate with the threshold electron excitation spectra (TEES) indicating inelastic scattering from one molecule and capture of the slowed down electron by another molecule of the same cluster (self-scavenging).

C_6F_5Cl clusters show a unique behaviour in that an additional resonance at 6·5 eV appears, observable on the complementary ions $Cl^-/C_6F_5^-$. While this DA resonance is strongly mediated by the cluster, the other DA resonances are quantitatively quenched. From condensed C_6F_5Cl, desorption of Cl^- is exclusively observed from the resonance at 6·5 eV.

The 6·5 eV resonance in clusters and condensed C_6F_5Cl molecules is related to a gas phase open channel resonance at 6·8 eV with σ^*(C–Cl) antibonding nature, which predominantly decays via autodetachment into an associated electronically excited neutral molecule as documented by the strong TEES intensity and a weak DA signal at that energy. In clusters and in the condensed phase the polarization interaction shifts the energy of the core excited resonance below that of the associated neutral thereby suppressing autodetachment in favour of DA. Due to conservation of linear momentum in combination with the kinetic energy filter inherent in the desorption of ions, only the light fragment Cl^- is observed as the ionic desorption product from the resonance at 6·5 eV.

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