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International Journal of Mass Spectrometry 223–224 (2003) 193–204

International Journal of Mass Spectrometry

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Low energy (0–15 eV) electron stimulated reactions in single 1,2-$C_2F_4Cl_2$ molecules and clusters

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Received 2 February 2002; accepted 2 April 2002

Abstract

Formation of negative ions following electron impact to single gas phase $C_2F_4Cl_2$ molecules and to homogeneous $C_2F_4Cl_2$ clusters is studied in crossed beam experiments with mass spectrometric detection of the ionic products. From single molecules a variety of fragment ions are observed arising from dissociative electron attachment (DA) via two low energy resonances located near 0.3 and 2.5 eV. The most abundant product is Cl^- with an estimated DA cross-section of $(2 \pm 1) \times 10^{-15}\,cm^2$. On a comparatively weaker scale the ions F^-, Cl_2^-, $CClF_2^-$, $C_2ClF_4^-$, and ClF^- are observed, with the ion yields all characterized by pronounced resonance profiles. A further very weak and diffuse feature associated with negative ion formation appears in the energy range 8–14 eV. Electron attachment to clusters additionally generates the undissociated complexes M_n^- ($M = C_2F_4Cl_2$) including the stabilized monomer anion, and solvated ions of the form $Cl^-{\cdot}M_n$. The undissociated complexes M_n^- are considerably more abundant than the solvated ions. This mirrors the reaction pathway on an early time scale (femtoseconds to picoseconds) after electron localization in the target cluster indicating that stabilization is preferred over dissociation. The present gas phase and cluster experiments are discussed in relation to recent experiments on electron stimulated desorption and synthesis of Cl_2 from condensed $C_2F_4Cl_2$ [8]. (Int J Mass Spectrom 223–224 (2003) 193–204)

Keywords: Clusters; Electron attachment; Resonances; Negative ions; Solvation effects; Mass spectrometry

1. Introduction

A major process in the interaction of low energy electrons with neutral molecules (M) is formation of transient negative ions ($M^{\#-}$) by resonant electron capture [1–4]. Such transient negative ions $M^{\#-}$ (synonymously called resonances) will reject the extra electron after some time leaving the neutral molecule in the ground state or in an excited state. It is in fact well known that resonant inelastic electron scattering is the only effective way for vibrational excitation of (non-polar) neutral molecules by low energy electron impact. In N_2, for example, vibrational excitation via resonant scattering in the vicinity of the 2.3 eV N_2^- ($^2\Pi_g$) resonance is by several orders of magnitude larger than that via direct electron scattering [5].

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PII S1387-3806(02)00790-X

In the case of halogenated molecules the situation changes in the way that due to the high electron affinity of the halogen atoms dissociation channels become accessible at low energy, i.e., in the range below 3 eV. In that case the unimolecular decomposition of the transient negative ion (formed at low energy) into the halide ion and the corresponding radical competes with the resonant scattering channel (autodetachment). We can hence write for the overall process

$$e^-(\varepsilon) + M \rightarrow M^{\#-} \tag{1a}$$

$$M^{\#-} \rightarrow M^{(*)} + e^-(\varepsilon') \tag{1b}$$

$$M^{\#-} \rightarrow R + X^- \tag{1c}$$

where ε assigns the energy of the initial and ε' that of the scattered electron. $M^{\#-}$ assigns the transient negative ion formed by a Franck–Condon transition from the neutral molecule. Process (1a) is characterized by the electron attachment cross-section σ_0 which exhibits an overall reciprocal dependence from the electron energy [6]. Processes (1b) and (1c) represent the competing decay channels of the transient anion, autodetachment and dissociation, respectively. If the transitory negative ion is coupled to some environment (like in a molecular cluster) stabilization according to

$$M^{\#-} \rightarrow M^- + \text{energy} \tag{1d}$$

by energy dissipation into a level below the dissociation limit may occur. In that case the undissociated anion (or complexes of it) become observable by mass spectrometry.

The cross-section for dissociative electron attachment, σ_{DA} (process (1a) followed by (1c)), can be expressed as

$$\sigma_{DA} = \sigma_0 \times P \tag{2}$$

where P assigns the *survival probability*, expressing the probability that the extra electron will survive in the dissociating system with respect to autodetachment. P is a number between 0 and 1; it usually depends strongly on the electron energy and can come close to unity for DA reactions close to zero eV [7]. Due to the reciprocal energy dependence of the electron attachment cross-section, dissociative electron attachment can be a very effective way to decompose halogenated molecules by low energy electrons.

In a recent publication by our laboratory [8], we have shown that low energy (0–15 eV) electron impact to condensed $C_2F_4Cl_2$ molecules effectively generates molecular chlorine. The cross-section for Cl_2 synthesis showed a pronounced dependence from the primary electron energy with a contribution at energies below 2.5 eV and a resonance-like structure in the vicinity of 8 eV.

In the present study, we investigate electron attachment to single gas phase $C_2F_4Cl_2$ molecules in order to elucidate the intrinsic reaction channels in low energy electron impact. In addition we investigate how the situation changes on proceeding from single molecules under collision-free conditions to homogeneous clusters of $C_2F_4Cl_2$ generated in a supersonic molecular beam. This in turn will help to identify the initial step in the reaction sequence of Cl_2 formation.

2. Experimental

The experiments are performed in two different crossed electron beam/molecular beam arrangements. One set-up uses an effusive molecular beam for the study of single molecules under collision-free conditions and the other is equipped with a supersonic molecular beam source as described in detail earlier [7]. Clusters are produced by adiabatic expansion of $C_2F_4Cl_2$ seeded in Ar through an 80 μm nozzle at room temperature. In both cases the (effusive or the supersonic) molecular beam is crossed at right angle with an electron beam generated by a trochoidal electron monochromator (TEM) [9]. The TEM operates with a homogeneous magnetic field which guides the electrons along the direction of the magnetic field thus preventing spreading of the beam at low electron energies. Negative ions formed by the interaction of the electrons with single molecules or clusters are extracted from the reaction volume by a small electric field ($<1\,\text{V}\,\text{cm}^{-1}$) analyzed by a commercial quadrupole mass spectrometer and detected by single pulse counting. The electron energy resolution is about 0.1 eV (FWHM) at a current of 50 nA for the effusive beam experiments and about 0.2 eV at 80 nA in the cluster experiments. The electron energy scale is calibrated by means of the well known “zero eV” resonance in SF_6 [6]. In addition with reference to the well known thermal electron attachment rate in SF_6, an estimate for the DA cross-section in the present compound can be obtained.

3. Results and discussion

3.1. Electron attachment to single molecules

Figs. 1 and 2 present the ion yield curves of negative ions obtained from electron attachment to single $C_2F_4Cl_2$ molecules in the energy range 0–15 eV with the count rates given in absolute numbers. The experiments where carried out at a pressure of $\approx 10^{-5}$ mbar (reading at the ionization gauge) corresponding to a pressure of $\approx 10^{-2}$ to 10^{-3} mbar directly in the collision region [10]. Under these conditions only fragment ions are observed with Cl^- the most abundant channel.

The ion yield curves indicate two low energy states of the precursor ion, one visible on the Cl^- and on the Cl_2^- yield, with peaks at 0.3 and 1.1 eV, respectively. A second state can be localized near 2.5 eV with the DA peaks slightly dependent on the observation channel. On a much weaker scale we also observe a broad resonance-like structure in the range between 8 and $\approx$14 eV. On the F^- and Cl_2^- channel these structures seem to consist of two overlapping features. It is very likely that the two low energy precursor states can be assigned as one particle resonances where the extra electron occupies one of the first empty MOs. While the lowest MO can be assigned as σ^*(C–Cl), the following MO (in the vicinity of 2.5 eV) may possess some σ^*(C–F) admixture. On the other hand, the high energy features are most likely due to core excited resonances where the incoming electron concommitantly excites an electron resulting in precursor states with two electrons in usually empty MOs. It is interesting to note that desorption from condensed $C_2F_4Cl_2$ molecules is mainly operative in the energy range of these core excited states [8], i.e., in the range where DA from gas phase molecules is only weakly operative. Such a situation is frequently observed when comparing gas phase DA and desorption via DA to a molecule at the surface [10–12].

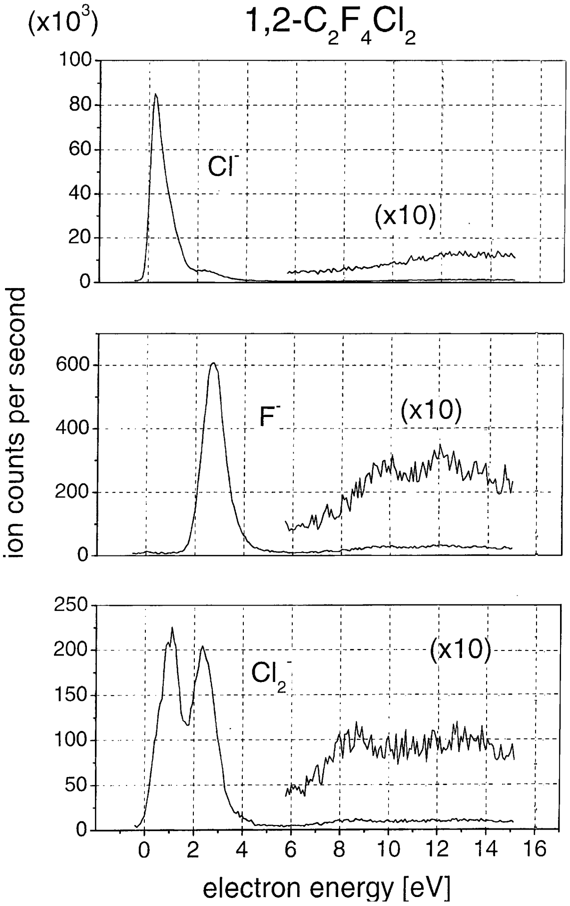

Fig. 1. Formation of Cl^- and F^- and Cl_2^- from single $C_2F_4Cl_2$ molecules (effusive beam) at a pressure of 2×10^{-5} mbar at the ionization gauge. Ion count rates in absolute numbers.

The molecule exhibits a surprisingly large number of different fragment anions which appear from simple bond cleavages but also from more complicated unimolecular reactions involving rearrangement in the precursor anion and the cleavage and formation of different bonds. In the following we shall briefly consider the different DA channels in light of the

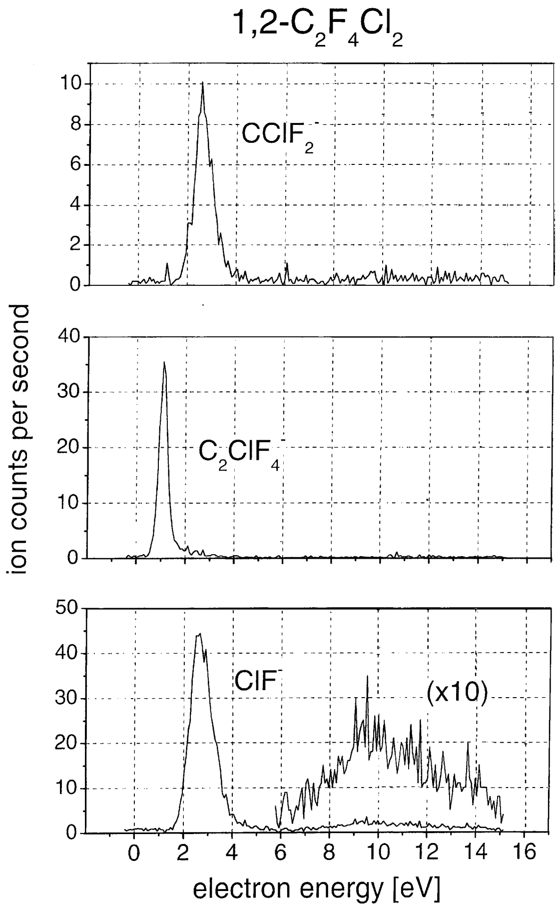

Fig. 2. Formation of $CClF_2^-$, $C_2ClF_4^-$ and ClF^- from single $C_2Cl_4F_2$ molecules (effusive beam) at a pressure of 2×10^{-5} mbar at the ionization gauge. Ion count rates in absolute numbers.

associated reaction, the underlying energetics and also the associated precursor state.

The Cl^- ion as the most dominant product can be assigned to the simple bond cleavage process

$$e^- + C_2F_4Cl_2 \rightarrow C_2F_4Cl + Cl^- \tag{3a}$$

when formed at the low energy resonance peaking at 0.3 eV. From the well-established electron affinity of the Cl atom (3.61 eV) and the Cl–CF_2CF_2Cl bond dissociation energy (3.4 ± 0.1 eV) [13] the thermodynamic limit for reaction reaction (3a) becomes slightly exothermic, $\Delta H_0 = -0.2 \pm 0.1$ eV. Cl^- is formed via the lowest TNI (with σ^*(C–Cl) character) but also at lower intensity from the second precursor state near 2.5 eV.

The thermodynamic limit for the multiple fragmentation reaction also generating Cl^-, viz.

$$e^- + C_2F_4Cl_2 \rightarrow C_2F_4 + Cl + Cl^- \tag{3b}$$

becomes 1.8 ± 0.1 eV if we assume that perfluoroethene ($F_2C{=}CF_2$) if formed and use the established enthalpies of formation for the involved compounds, i.e., ΔH_f^{298} ($C_2F_4Cl_2$) $= -937 \pm 7\,kJ\,mol^{-1}$, ΔH_f^{298} (C_2F_4) $= -659\,kJ\,mol^{-1}$ and ΔH_f^{298} (Cl) $= 121.3\,kJ\,mol^{-1}$ [13]. This in turn means that in a sequential process the second C–Cl bond dissociation energy D(Cl–CF_2CF_2) is much weaker compared to the first one (2.0 eV as opposed to 3.4 eV). We can hence assume that in Cl^- formation via the second resonance the multiple fragmentation reaction (3b) contributes to the observed signal.

The ion signal $C_2ClF_4^-$ (Fig. 2) on the other hand, must univocally be assigned to the process

$$e^- + C_2F_4Cl_2 \rightarrow C_2F_4Cl^- + Cl \tag{3c}$$

which is the complement to (3a) with respect to the negative charge. The energy balance of DA into two particles can be expressed as

$$AP(R^-) = D(R - X) - EA(R) + E^* \tag{4}$$

where AP is an experimentally observed appearance energy and E^* is the total excess energy of the reaction. With $AP(C_2F_4Cl^-) = 0.5 \pm 0.1$ eV and the binding energy from above we can extract a *lower limit* for the adiabatic electron affinity of the polyatomic radical as $EA(C_2F_4Cl) \geq 2.9 \pm 0.2$ eV. This relatively high value is not surprising since the associated anion ($C_2F_4Cl^-$) is a closed shell species.

The comparatively sharp onset and narrow shape of this ion signal indicates that it is rather given by the opening of the dissociation channel than the Franck–Condon factors connecting the neutral ground state and the low energy precursor state. In Fig. 3, the situation is illustrated by means of a simple one-dimensional potential energy diagram along the R(C–Cl) axis. This simplification is justified to some degree by the σ^*(C–Cl) character

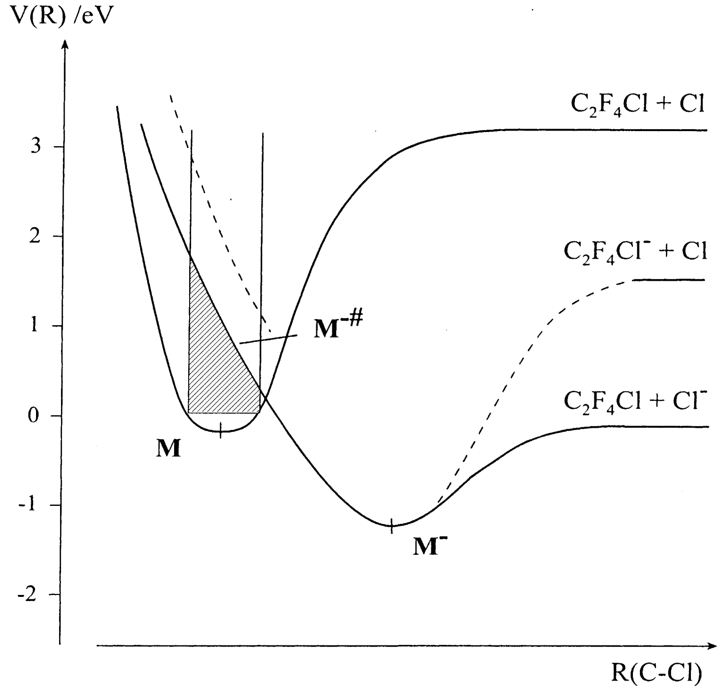

Fig. 3. Schematic one-dimensional potential energy curve illustrating formation of the transient negative ion $M^{-\#}$ ($M = C_2F_4Cl_2$) at low energy by a Franck–Condon transition and dissociation along one of the C–Cl coordinates resulting in the complementary channels $Cl^- + C_2F_4Cl$ and $Cl + C_2F_4Cl^-$. The second dotted curve represents the second negative ion state associated with dissociative attachment.

of the low energy precursor state. We have arbitrarily placed the (so far unknown) adiabatic electron affinity of $C_2F_4Cl_2$ near 1.3 eV which is a reasonable number for a small fluorochlorocompound containing two Cl atoms. Although the transition probability governed by the Franck–Condon overlap has a maximum near 1 eV, the Cl^- signal peaks at 0.3 eV. This shift is caused by the competition of autodetachment which makes DA at low energy more probable (survival probability shift) [12,14,15]. Accordingly, the shape of the $C_2F_4Cl^-$ signal is controlled by the dissociation threshold located *within* the energy range governed by the Franck–Condon transitions. It must be noted, however, that at these low energies a semiclassical description using localized potential energy surfaces (Born–Oppenheimer approximation) may seriously be limited and non-adiabatic effects have to be considered [16,17].

The yield of the $Cl_2{}^-$ ion exhibits two distinct peaks at 1.1 and 2.3 eV at comparable intensities. It is hence formed from both precursor states which we have assigned as one particle shape resonances. The peak at 1.1 eV, however, is at appreciably higher energy than the corresponding peak of the Cl^- channel (located at 0.3 eV). Formation of $Cl_2{}^-$ can be assigned to

$$e^- + C_2F_4Cl_2 \rightarrow C_2F_4 + Cl_2{}^- \quad (5)$$

with the thermodynamic limit of $\Delta H_0 = 0.5 \pm 0.1$ eV based on $EA(Cl_2) = 2.38 \pm 0.1$ eV [13] and the enthalpies of formation from above. A closer inspection of the $Cl_2{}^-$ yield indicates that the appearance energy is close to 0 eV which is considerably below the calculated threshold (also in light of the limited energy resolution). It is possible that in the very low energy region (i.e., below the thermodynamic threshold) *hot band* transitions contribute to the $Cl_2{}^-$ signal. Such transitions can significantly modify the overall ion signal due to the particular situation in DA, namely the reciprocal energy dependence of the attachment cross-section and also the energy dependence of the survival probability [14,15,18].

In any case, formation of Cl_2^- results from the cleavage of two C–Cl bonds at different C atoms. If the neutral counterpart is perfluoroethene, then reaction (5) also involves considerable electronic rearrangement. Fragmentation into more than two particles can be excluded due to the comparatively strong C–F bond energy (see below).

Formation of F^- is obviously the result of the simple C–F bond cleavage

$$e^- + C_2F_4Cl_2 \rightarrow C_2F_3Cl_2 + F^- \qquad (6)$$

with a thermodynamic threshold of $\Delta H_0 \approx 1.6\,eV$ based on the well-established electron affinity of the fluorine atom (3.40 eV) [13] and taking the estimated bond dissociation energy $D(F–CFClCF_2Cl) \approx 5.1\,eV$ [8].

The CF_2Cl^- ion must arise from the symmetric C–C bond cleavage process

$$e^- + C_2F_4Cl_2 \rightarrow CF_2Cl^- + CF_2Cl \qquad (7)$$

From the available thermodynamic data (ΔH_f^{298} $(C_2F_4Cl_2) = -937 \pm 7\,kJ\,mol^{-1}$ and ΔH_f^{298} $(CF_2Cl) = -279 \pm 7\,kJ\,mol^{-1}$ [13] we obtain the C–C bond dissociation energy as $3.9 \pm 0.3\,eV$. With the energy balance from above (Eq. (4)) and $AP(CF_2Cl^-) \approx 1.8\,eV$ we derive the lower limit $EA(CF_2Cl) = 2.1\,eV$.

The fragment ClF^-, finally, involves cleavage of a C–Cl and a C–F bond, either from the same or from different C atoms

$$e^- + C_2F_4Cl_2 \rightarrow C_2F_3Cl + FCl^- \qquad (8)$$

Similar to the situation for Cl_2^- formation, the neutral counterpart (C_2F_3Cl) is likely to have the ethene structure. The energetic situation for this reaction is not well established. For ΔH_f^{298} (C_2F_3Cl) we find values between -510 and $-565\,kJ\,mol^{-1}$ [19] and there is no accurate number available for the electron affinity of FCl from a direct experiment like photodetachment. Taking the average value with the appropriate uncertainty (ΔH_f^{298} $(C_2F_3Cl) = -537 \pm 30\,kJ\,mol^{-1}$), and ΔH_f^{298} $(FCl) = -50.3\,kJ\,mol^{-1}$ [19] the reaction enthalpy into the *neutral* particles of (8) becomes $3.6 \pm 0.4\,eV$. With $AP(FCl^-) = 1.8 \pm 0.1\,eV$ we can then derive the lower limit for the electron affinity as $EA(FCl) = 1.8 \pm 0.5\,eV$. The values given in the *NIST WebBook* scatter between 1.5 and 3 eV. For comparison, the values for the homogeneous counterparts are $EA(Cl_2) = 2.38\,eV$ and $EA(F_2) = 3.08\,eV$ [13].

In summary for the experiments under single collision conditions only *dissociative* electron attachment and into various channels is observed with Cl^- due to reaction (3a) by far the dominant process. Since in each spectrum we used SF_6 for calibration we can obtain an estimate of the absolute cross-section for DA into Cl^- at the peak (0.3 eV) by using the recommended value for the thermal (300 K) electron attachment rate in SF_6 ($2.25 \times 10^{-7}\,cm^3\,s^{-1}$ [20]). This rate corresponds to an average attachment cross-section of $\approx 2.2 \times 10^{-14}\,cm^2$ in the thermal energy range. Although our electron energy distribution is broader than that of thermal electrons at 300 K (kT (300 K) = 26 meV) a comparison of the pressure normalized count rates (SF_6^- near 0 eV and Cl^- at 0.3 eV) allows an estimate for the absolute DA cross-section. This procedure yields $\sigma_{DA}(Cl^-) = (2 \pm 1) \times 10^{-15}\,cm^2$ at 0.3 eV.

3.2. Electron attachment to clusters

The cluster beam is generated by adiabatic expansion of $C_2F_4Cl_2$ seeded in Ar (1:10) at stagnation pressures up to several bars. The beam contains a *size distribution* of clusters, including monomers, the latter also present in the scattered background gas. The background pressure in the main chamber during expansion is in the 10^{-5} mbar range. The exact size of the target cluster is not known since in the present method an ionic product is detected as a result of a reaction initiated by electron capture of some target cluster of unknown size.

Fig. 4 shows the negative ion mass spectrum recorded at an electron energy of 0.3 eV and a

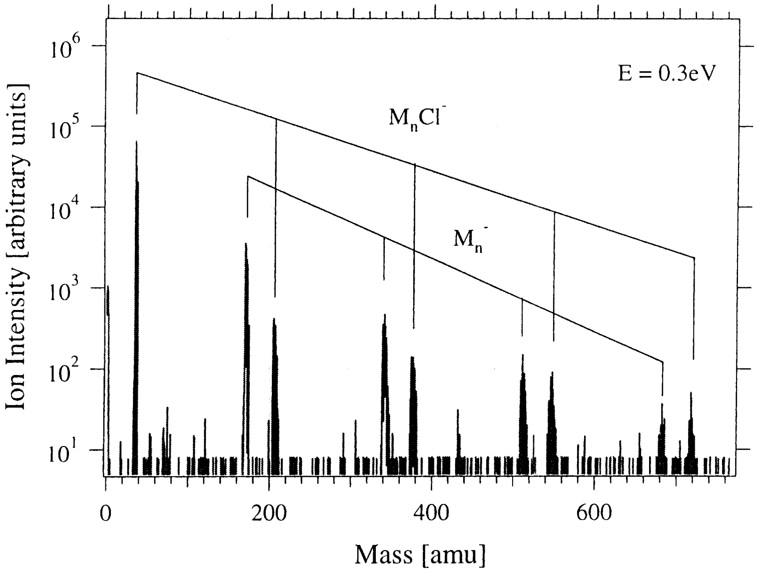

Fig. 4. Negative ion mass spectra obtained from an expansion of $C_2F_4Cl_2$ seeded in Ar (1:20), at an electron energy of 0.3 eV and a stagnation pressure of 1 bar. The mass peaks consist of a series of unresolved peaks due to the ^{35}Cl and ^{37}Cl isotopes.

stagnation pressure of 1 bar. In addition to the fragments obtained from isolated molecules we detect the undissociated complexes M_n^- ($M = C_2F_4Cl_2$) including the stabilized monomer $C_2F_4Cl_2^-$ as well as solvated ions of the form $M_n{\cdot}Cl^-$. At higher electron energies the solvated ion $M{\cdot}F^-$ is also observed. Undissociated complexes and solvated ions $M_n{\cdot}Cl^-$ are observed up to $n = 4$. As stated above the negative ion mass spectrum is no direct mirror of the size distribution in the neutral cluster beam (apart from experimental restrictions like mass-dependent transmission, detection probabilities, etc. which we shall not discuss here). From energy considerations, however, one can estimate an upper limit for the size of the target cluster, M_m, from which the product, $Cl^-{\cdot}M_n$, can be generated. The reaction can be expressed as

$$\begin{aligned} &e^-(\varepsilon = 0.3\,\mathrm{eV}) + M_m \rightarrow M^{\#-} \cdot M_{m-1} \\ &\quad \rightarrow Cl^- \cdot M_n + R + (m-n-1)M \end{aligned} \tag{9}$$

where $R = C_2F_4Cl$ assuming that electron localization occurs on an individual molecule. In isolated molecules, the analogue to (9) is dissociative electron attachment into Cl^- (reaction (3b)) which is exothermic by −0.2 eV. Under the reasonable assumption that only single monomer units are vaporized the reaction enthalpy for intracluster DA (9) is modified with respect to gas phase DA (3a) by subtracting the binding energy in the ionic complex and adding the energy to evaporate the neutral $(m - n - 1)$ monomers M. We do not have any accurate information on the binding energies in the ionic complex, but we can reasonably assume that for the ionic complex $Cl^-{\cdot}M_n$ around the size $n = 4$ the average binding energy per particle is roughly twice of that in the neutral cluster. Formation of an ionic complex $Cl^-{\cdot}M_n$ thus gains sufficient energy to evaporate $\approx 2n = m - n - 1$ and hence $m \approx 3n + 1$ monomer units. Finally, taking into account the exothermicity of the gas phase DA reaction (−0.2 eV) and considering processes recorded at the energy of the peak maximum (0.3 eV), an additional amount of 0.5 eV excess energy is supported which can be used to evaporate neutral units. An absolute value for the binding energy in neutral clusters can be estimated from the enthalpy of vaporization in bulk material. For the present molecule, however, no value is given in the standard literature [13,19]. If we take 23.8 kJ mol^{-1} which is the interpolated value for the enthalpy of vaporization between the related compounds C_2F_5Cl (19.4 kJ mol^{-1}) and $C_2F_3Cl_3$ (1,1,2-trichlorotrifluoroethane, 27.0 kJ mol^{-1}) [13] we arrive at ≈240 meV binding energy per monomer unit in the neutral $C_2F_4Cl_2$ cluster. We then finally arrive at $m \approx 3n + 3$, i.e., observation of the complex $Cl^-{\cdot}M_n$ ($n = 4$) yields $m \approx 15$ as an upper limit for the size of the target cluster M_n from which by energy reasons the ionic product can be observed.

This situation does not appreciably change with the expansion conditions (gas mixture or stagnation pressure): while with increasing stagnation pressure the relative intensity of larger ionic products increases, the absolute number decreases. It appears that a mixing ratio of 10:1 and a stagnation pressure around 1 bar produces the maximum signal of cluster ions.

It is interesting to note that under any expansion conditions the intensity of the undissociated unit M^- is by nearly one order of magnitude larger than that of the solvated ion $Cl^-{\cdot}M$. This is considerably different to the previously studied cluster systems C_2F_5I [21] CF_3Cl [22], and CF_3I [23], where the signal due to solvated ions was much higher than that due to the undissociated monomer. As pointed out previously [21] the corresponding branching ratio is a mirror of the preferential pathway in the short time domain after electron localization and formation in the transitory ion in the target cluster. In the present case the ion $C_2F_4Cl_2^{\#-}$ in the first step prefers stabilization into a state below the dissociation limit than dissociation into $C_2F_4Cl + Cl^-$. This preference, however, becomes smaller with the size of the observed complexes and at $n = 4$ both ions are at comparable level (Fig. 4). The rate of stabilization depends on the excess energy: in the present case the transitory negative ion is created not far above the dissociation limit, but separated by an appreciable potential energy minimum, see Fig. 3. We note that an extreme of such a situation was recently observed in electron attachment to the benzene derivatives C_6F_5X ($X = Cl$, Br, I) [7,24]. In those systems any clustering quantitatively suppressed DA into X^- in favor of associative electron attachment. These compounds are characterized by a remarkably slow DA reaction: low energy attachment (≈0 eV) to single molecules generates X^- and M^- competing on the mass spectrometric time scale. The systems CF_3Cl, CF_3I and C_2F_5I (showing only a weak M^- signal), on the other hand, are characterized by more available excess energy and also a pronounced *impulsive* dissociation as obvious from the energy analysis of the X^- ions. In the present system, clustering suppresses bond cleavage in favor of associative attachment, but by far not quantitatively. In addition, the mass spectrum (Fig. 4) clearly indicates that the intensity ratio $M_n{}^-/Cl^-{\cdot}M_n$ decreases with n and levels off at $n = 4$. This can be explained by the available excess energy of the corresponding reaction which is appreciably higher in forming undissociated complexes (see Fig. 3): we can then assume that the average size of the target cluster resulting in $M_n{}^-$ is larger than that for $Cl^-{\cdot}M_n$. For a neutral cluster distribution extending to $m \approx 15$ one then expects a decrease of the ratio $M_n{}^-/Cl^-{\cdot}M_n$ with n.

In Fig. 5, the ion yield curves of the products Cl^-, $Cl^-{\cdot}M$ and M^- from an expansion at 1 bar are shown. The shape of the Cl^- signal is virtually identical to that obtained from the effusive beam (the Cl^- signal in fact also arises from monomers in the beam and scattered background gas) and the ion yield curve due to the solvated ion $Cl^-{\cdot}M$ closely resembles that of the single ion, however, with the peak shifted to 0.7 eV. The relatively stronger diffuse signal in the range 8–12 eV on the $Cl^-{\cdot}M$ signal is probably the result of inelastic electron scattering in the target cluster involving electronically excited neutral or anion states.

Electron attachment to clusters can (like for single molecules) be pictured by means of the schematic potential energy curve representation of Fig. 3. On proceeding to clusters, the ionic curve is shifted to lower energy by the solvation energy which also shifts the initial Franck–Condon transition (the electron attachment energy) to lower values since the ionic state is more influenced by aggregation than the neutral molecule (vide supra). By observing a *dissociation* product (Cl^- or $Cl^-{\cdot}M$) this shift may be counterbalanced by the energy-dependent dissociation dynamics of the corresponding process. This is obviously the

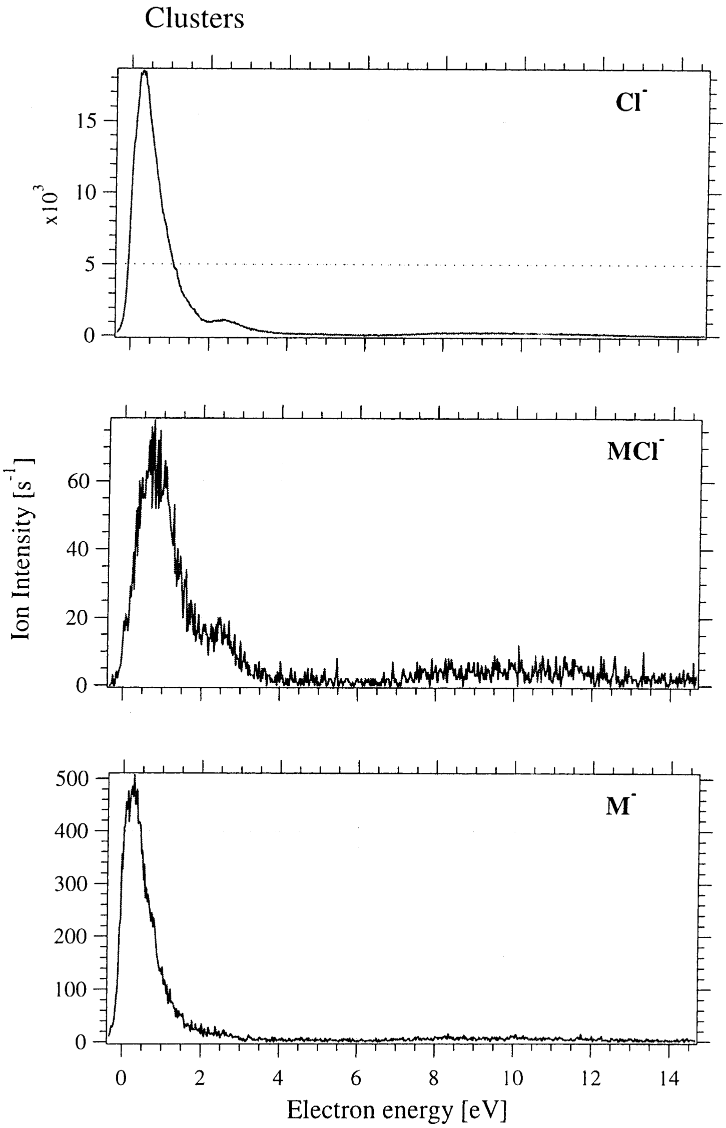

Fig. 5. Yields of the product ions Cl$^-$, M·Cl$^-$, and M$^-$ recorded from the beam generated by an expansion of $C_2F_4Cl_2$ seeded in Ar (1:10) at a stagnation pressure of 1 bar. The resonance maximum for the solvated ion is shifted to higher energy with respect to the naked ion Cl$^-$ (see the text). DA to monomers also contributes to the signal of the naked Cl$^-$ ion.

case on the channel Cl$^-$·M. Comparing DA curves between single molecules and clusters hence do not contain any *direct* information on solvation shifts in the cluster. The peak maxima of the M_n^- ion yields are shifted to lower energy and the shape becomes narrower with increasing n (Figs. 6 and 7). Since formation of undissociated complexes requires the dissipation of sufficient energy to a level below the dissociation asymptode Cl$^-$ + C_2F_4Cl it is clear that this process becomes more probable towards low energy.

Both the naked F$^-$ ion recorded from the cluster beam and the solvated ion F$^-$·M closely resemble F$^-$ formation from the isolated molecules. Only the Cl_2^-

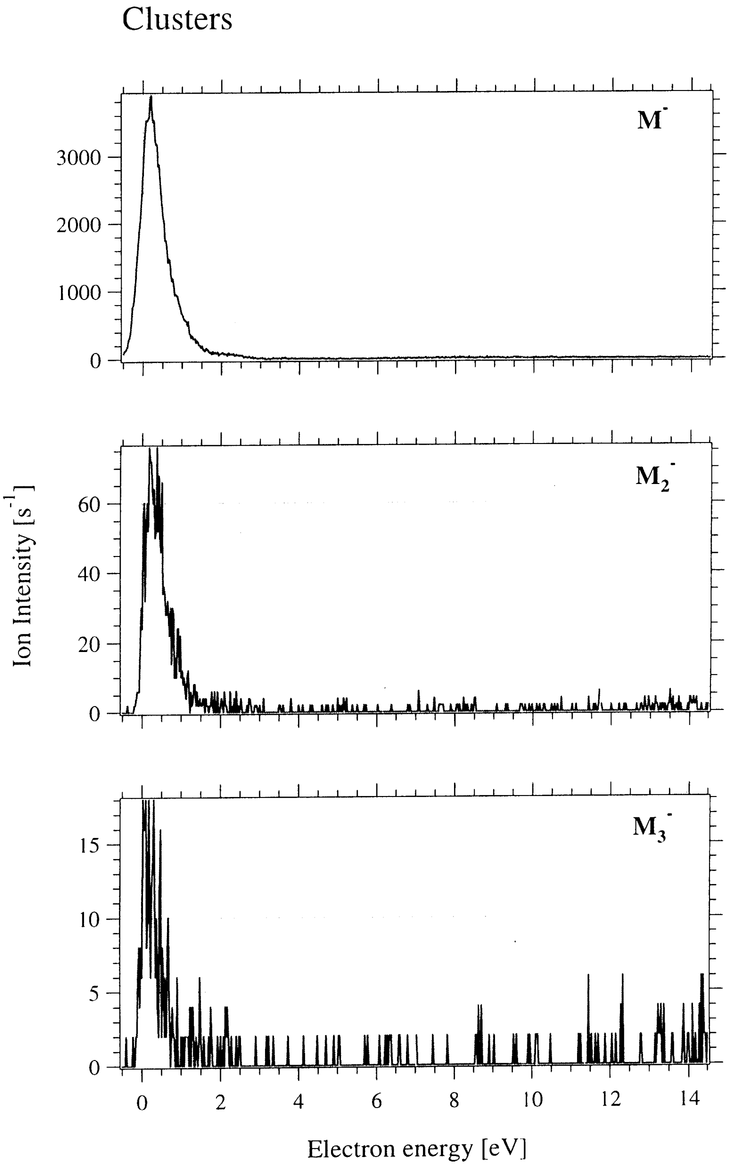

Fig. 6. Ion yields of the undissociated complexes M_n^- (n = 1–3) recorded from the supersonic beam at the conditions of the spectra in Fig. 5.

ion yield shows a significant difference compared to the gas phase DA analogue in that the contribution at higher energy (where excited states are involved) is relatively enhanced. In that energy range electron stimulated desorption from condensed $C_2F_4Cl_2$ and electron-induced synthesis of Cl_2 is at maximum.

3.3. Relation to electron-induced processes in the condensed phase

In a very recent publication by our laboratory [8], it was demonstrated that molecular chlorine is very effectively synthesized by electron impact to condensed

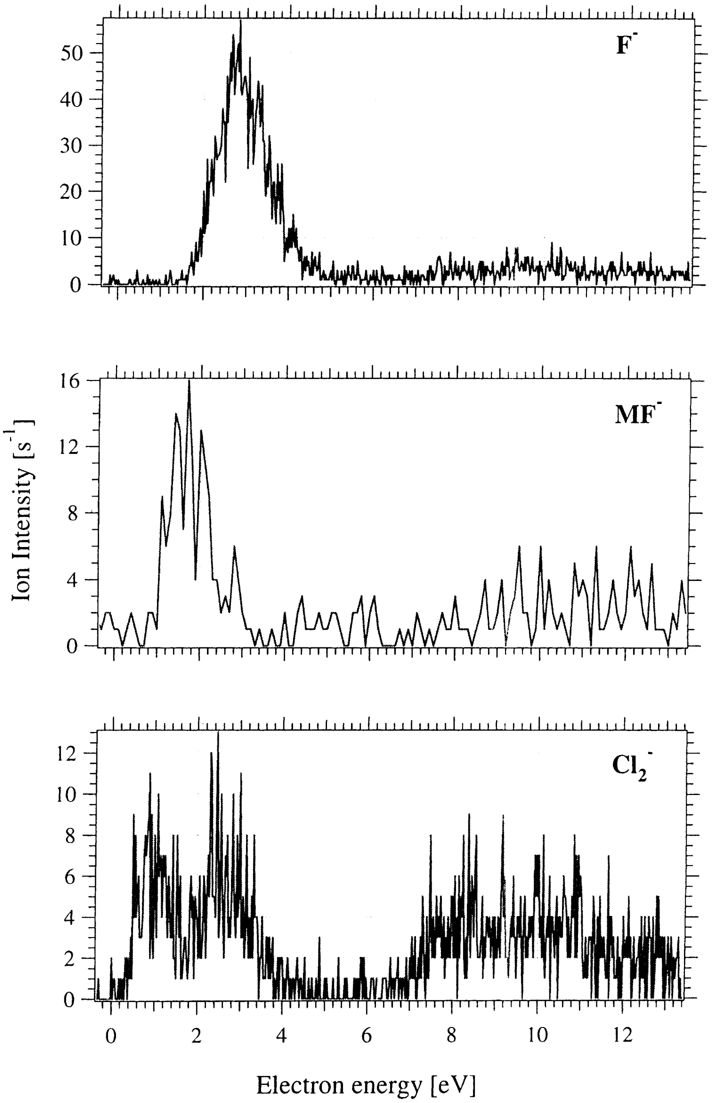

Fig. 7. Ion yields of the atomic fragment F^-, the solvated ion $M{\cdot}F^-$. Note the relatively enhancement of the $Cl_2{}^-$ signal in the vicinity of the core excited resonances.

$C_2F_4Cl_2$. The cross-section for Cl_2 production showed a strong variation with the primary electron energy yielding two resonance like structures with maxima near 1 and 10 eV. Between these maxima (in the energy range around 5 eV) the cross-section effectively dropped to zero.

Electron-induced formation of Cl_2 at higher energy (around 10 eV) proceeds along complex pathways involving electronically excited states. It may also be initiated to some degree by electronically excited negative ion resonance which are weakly seen in the gas phase and which strongly contribute in electron-induced desorption.

At low energy, i.e., below the energy of electronic excitation and dissociation into neutral particles the only effective way to induce a chemical reaction must be initiated by dissociative electron attachment. As demonstrated in this contribution, by far the most effective process is formation of Cl^- which is operative between ≈0 and ≈4 eV. In light of this it is very likely that electron-induced formation of Cl_2 at low energies (below 3 eV) in the condensed phase occurs through reactive scattering of Cl^- with the surrounding $C_2F_4Cl_2$ molecules

$$Cl^- + C_2F_4Cl_2 \rightarrow C_2F_4Cl^- + Cl_2 \quad (10)$$

initiated by the very effective DA process at low energies. With $D(\text{Cl–Cl}) = 2.53\,\text{eV}$ [13] and the thermodynamic data from above, the (gas phase) reaction enthalpy becomes 0.8 eV minus the (unknown) electron affinity of the C_2F_4Cl radical. Since the corresponding anion ($C_2F_4Cl^-$) is a closed shell species one expects an electron affinity of a few eV which makes reaction (10) considerably exothermic.

Acknowledgements

This work has been supported by the Volkswagen Siftung (I/73593), the Deutsche Forschungsgemeinschaft (Il 16/15-1), the Fonds der Chemischen Industrie and the Freie Universität Berlin. One of us (W.B.) thanks the State Committee for Scientific Research Poland (Grant No. 3 T09A01018) for support.

References

[1] H.S.W. Massey, Negative Ions, Cambridge University Press, Cambridge, 1976.

[2] B.M. Smirnov, Negative Ions, McGraw-Hill, New York, 1982.

[3] L.G. Christophorou (Ed.), Electron–Molecule Interactions and their Applications, Vol. I, Academic Press, Orlando, FL, 1984.

[4] E. Illenberger, J. Momigny, Gaseous Molecular Ions: An Introduction to Elementary Processes Induced by Ionization, Springer, New York, 1992.

[5] M. Allan, J. Electron Spectrosc. Relat. Phenom. 48 (1989) 219 (review).

[6] D. Klar, M.-W. Ruf, H. Hotop, Aust. J. Phys. 45 (1992) 263.

[7] O. Ingólfsson, F. Weik, E. Illenberger, Int. J. Mass Spectrom. Ion Process. 155 (1996) 1 (review).

[8] R. Balog, M.N. Hedhili, F. Bournel, M. Penno, M. Tronc, R. Azria, E. Illenberger, Phys. Chem. Chem. Phys. 4 (2002) 3350.

[9] A. Stamatovic, G.J. Schulz, Rev. Sci. Instrum. 41 (1970) 423.

[10] Y. Le Coat, N.M. Hedhili, R. Azria, M. Tronc, O. Ingólfsson, E. Illenberger, Chem. Phys. Lett. 296 (1998) 208.

[11] F. Brüning, P. Tegeder, J. Langer, E. Illenberger, Int. J. Mass Spectrom. 195/196 (2000) 507.

[12] E. Illenberger, Electron capture processes by free and bound electrons, in: C.Y. Ng (Ed.), Advanced Series in Physical Chemistry, Vol. 10B, Photoionization and Photodetachment, Part II, World Scientific, Singapore, 2000.

[13] D.R. Lide (Ed.), Handbook of Chemistry and Physics, 78th Edition, CRC Press, Boca Raton, FL, 1997.

[14] I. Hahndorf, E. Illenberger, L. Lehr, J. Manz, Chem. Phys. Lett. 231 (1994) 460.

[15] L. Lehr, W.H. Miller, Chem. Phys. Lett. 250 (1996) 515.

[16] I.I. Fabrikant, Commun. Atom. Mol. Phys. 24 (1990) 37.

[17] A. Schramm, I.I. Fabrikant, J.M. Weber, E. Leber, M.-W. Ruf, H. Hotop, J. Phys. B 32 (1999) 2153.

[18] I. Hahndorf, E. Illenberger, Int. J. Mass Spectrom. Ion Process. 176/177 (1997) 78.

[19] NIST Chemistry WebBook (http://webbook.nist.gov/).

[20] L.G. Christophorou, J.K. Olthoff, J. Phys. Chem. Ref. Data 29 (2000) 267.

[21] J. Langer, S. Matejcik, E. Illenberger, Phys. Chem. Chem. Phys., in press.

[22] E. Illenberger, Chem. Rev. 92 (1992) 1589.

[23] T. Oster, O. Ingólfsson, T. Jaffke, M. Meinke, E. Illenberger, J. Chem. Phys. 99 (1993) 5141.

[24] P. Tegeder, L. Lehmann, O. Ingólfsson, E. Illenberger, Zeitschr. Phys. Chem. 196 (1996) 217.