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Nucleophilic displacement (S_N2) reactions in binary van der Waals clusters induced by resonant electron capture

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Abstract

The nucleophilic displacement reactions $F^- + CH_3Y \rightarrow CH_3F + Y^-$ ($Y = Cl, Br, I$) and $Cl^- + OCH_3Br \rightarrow CH_3Cl + Br^-$ are studied in a crossed beam experiment where binary clusters produced by supersonic beam expansion interact with a monochromatized electron beam. The nucleophile (F^-, Cl^-) is generated by resonant dissociative electron attachment (DA) from one component of the cluster and then undergoes an S_N2 reaction with the second component (the "substrate" molecule CH_3Y). Y^- ions carrying the DA resonance profile of the nucleophile are then identified as products of the corresponding S_N2 reaction. Although isolated CH_3Cl has an unmeasurably low DA (Cl^-) cross section ($<10^{-23}$ cm^2 [D.M. Pearl, P.D. Barrow, J. Chem. Phys. 104 (1994) 2940; D.M. Pearl et al., J. Chem. Phys. 102 (1995) 2737]), effective formation of Cl^- from CH_3Cl is observed when the molecule is coupled to C_2F_6 in a binary van der Waals cluster via the respective S_N2 reactions. In addition, the product ion Y^- solvated by CH_3Y molecules and also ion-molecule complexes $(FCH_3Y)^-$ involved in the reaction are observed within the DA resonance of the nucleophile. The relative intensity of the naked product ion with respect to the ion-molecule complexes is a mirror of the exothermicity of the corresponding S_N2 reaction. Because in DA the nuclephile can be created with a defined amount of translational energy, the potential use of the present method to derive information on the energy dependence of the reaction efficiency is discussed. (Int J Mass Spectrom 185/186/187 (1999) 463–475) © 1999 Elsevier Science B.V.

Keywords: Electron attachment; Cluster; S_N2 reaction; Ion-molecule reaction; Negative ions

1. Introduction

In this article we report on bimolecular nucleophilic displacement (S_N2) reactions of the form

$$X^- + RY \rightarrow [XRY]^- \rightarrow XR + Y^- \tag{1}$$

studied in binary clusters by means of a crossed electron/molecular beam experiment equipped with a mass spectrometric detection system.

The idea is to cross a molecular beam containing mixed neutral clusters composed of the components R_1X and R_2Y with an electron beam of well defined, but variable energy (ε). The nucleophile can then be generated by dissociative electron attachment (DA) from the first component

$$e^-(\varepsilon_1) + R_1X \rightarrow R_1X^{-(*)} \rightarrow R_1 + X^- \tag{2}$$

which then undergoes the exchange reaction (1) with the "substrate" molecule, visible by the observation of

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Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

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the leaving group Y^-. The first step [reaction (2)] is generally *resonant* in nature and is operative at a particular energy (ε_1) which is specific for the particular target molecule R_1X.

The necessary requirement for an unambiguous observation of a substitution reaction is then that the substrate molecule R_2Y does either *not* undergo DA to form Y^- at all or at least in an energy range different from ε_1. If then at ε_1 we observe Y^- anions from a mixed cluster, we have strong evidence that they are the result of an S_N2 reaction (1).

The primary step of electron capture inherently implies that (on the basis of the underlying thermodynamics) the energy of the reaction is completely controlled by the energy of the electron. DA processes usually occur within a more or less broad resonant energy region around the maximum position ε_1. The excess energy can hence be varied within the width of the resonance. Moreover, in the case of repulsive DA precursor ions R_1X^-, the translational energy of the nucleophile can eventually be varied on a large scale [1,2].

In this contribution, we restrict to $R = CH_3$ and X, $Y =$ halogen atoms. A gas phase S_N2 reaction is then always exothermic when Y is further down with respect to X in row 7 of the periodic table.

Because in most halogenated hydrocarbons the F^- DA resonances are usually *above* those yielding Cl^-, Br^- or I^- [1] we have also to consider possible inelastic electron scattering events in the target cluster as possible sources for the generation of the "leaving group" Y^-. Any DA reaction is principally subjected to the competition of autodetachment (AD), i.e. re-emission of the extra electron prior to complete dissociation of the transient negative ion (TNI), viz.

$$e^-(\varepsilon_1) + R_1X \rightarrow R_1X^{-(*)} \rightarrow R_1X^{(*)} + e^-(\varepsilon_s) \qquad (\varepsilon_s \le \varepsilon_1) \tag{3}$$

If the energy spectrum of the resonantly scattered electrons include ε_2, then Y^- may also be a product of DA to R_2Y via inelastically scattered electrons.

Inelastic scattering can, in fact, considerably contribute to negative ion formation in homogeneous and heterogeneous clusters [2–5], in particular, in the presence of an effective electron scavenger. As has been shown in a variety of cluster systems, however, a negative ion formed by attachment of secondary electrons usually carries the signature of the electronically excited state(s) of the neutral scatterer and not that of its negative ion resonance, i.e., the relevant *inelastic* scattering events proceed rather through *direct* scattering than *resonant* scattering.

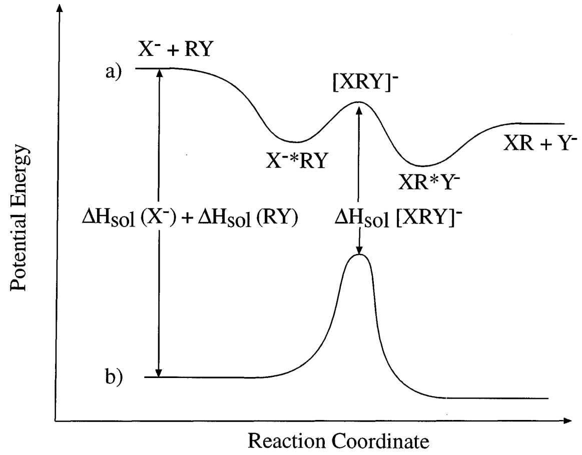

Fig. 1. Comparison of the potential energy surface in the gas phase and in the condensed phase along the reaction coordinate of the collinear S_N2 reaction $F^- + CH_3Y \rightarrow CH_3F^-$.

S_N2 reactions have played a significant role in the development of concepts in physical organic chemistry [6]. While in solution educts and products are separated by an activation barrier (with its height largely controlled by the nature of the solvent), a gas phase S_N2 reaction proceeds through a double minimum potential (Fig. 1) as first suggested by Olmstead and Brauman [7]. The minima represent the ion-molecule complex before ($X^{-\cdot}$ RY) and after electron transfer and rearrangement of the (R–Y) and the (R–X) bonds ($XR^{\cdot}$ Y^-). They are still separated by a central activation barrier, which, however, is considerably lowered with respect to solution.

Gas phase S_N2 reactions reflect the *intrinsic* properties of the involved ions and molecules. In solution, on the other hand, these intrinsic properties interfere with solvent effects.

According to the model introduced by Shaik et al. and Shaik and Pross [6,8,9], the central barrier arises

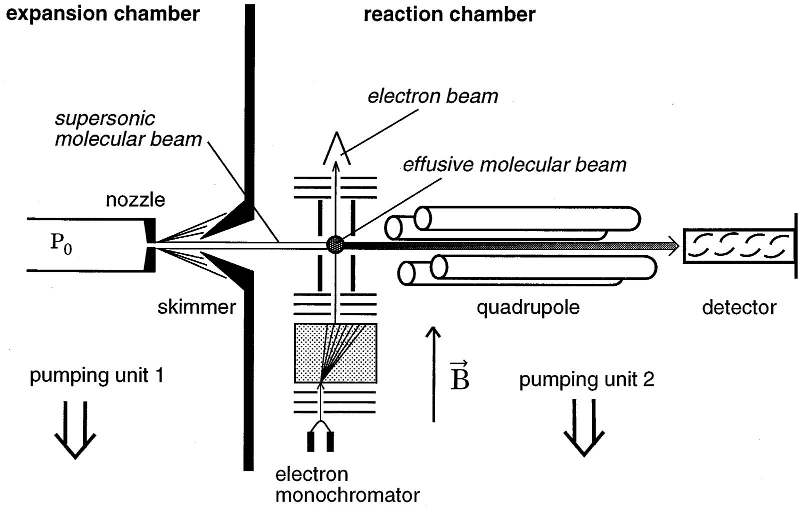

Fig. 2. Schematic of the experimetal set up for the study of S_N2 reactions occurring in free molecule clusters induced by dissociative electron attachment. Reactions with monomers can be observed by means of a capillary for effusive gas inlet which is directly fitted to the reaction chamber.

from an avoided crossing between the two electronic curves containing reactantlike (X^-RY) and productlike (XRY^-) Heitler-London valence bond (VB) forms. These *adiabatic* potential energy curves describe the transfer of the radical R without simultaneous electron transfer. The potential energy curve relevant for the S_N2 reaction is then obtained by introducing an electron transfer matrix element which splits the diabatic curves. The two low lying electronic configurations are then asymptotically identified as $X^- + RY$ and $XR + Y^-$.

It has been known for many years that in the absence of solvation the rate constant can dramatically increase. For the prototype system $R = CH_3$, $X = Cl$ and $Y = Br$, the gas phase rate constant (2.1×10^{-10} cm^3 s^{-1}) is by about 15 orders of magnitude (!) larger than that in water [10,11].

Gas phase S_N2 reactions have been studied for more than two decades. The experimental techniques include ion cyclotron resonance (ICR) mass spectrometry [7,12,13], high pressure mass spectrometry [14], and flow or drift techniques [15–17]. In a drift tube, the mean collision energy can be varied by changing the drift voltage [17].

In the present article we report on S_N2 reactions induced by DA in binary van der Waals clusters using F^- and Cl^- as nucleophiles with CH_3Y ($Y = Cl$, Br, I) as substrate molecules. With the exception of a Short Communication previously reported by our laboratory [18], to our knowledge, this is the first study of an SN2 reaction of the type (1) induced in van der Waals clusters. We mention here related studies, namely, reaction dynamics upon optical excitation of the ion molecule complexes $X^{-\cdot}RY$ which is considered the intermediate for the S_N2 reaction (1) [19,20], reactions of solvated nucleophiles with CH_3Y molecules in the flowing afterglow [21], and S_N2 reactions in mixed cationic cluster systems like $(NH_3/C_6H_5Cl)^+$ generated by resonantly enhanced multiphoton ionization (REMPI) [22].

2. Experimental

S_N2 reactions induced by electron attachment to binary van der Waals clusters are studied in a crossed electron/molecular beam experiment (Fig. 2). The basic configuration has been described in detail [2,23]. In brief, an electron beam is crossed at right angle with a molecular beam and negative ions arising from this interaction are extracted and analyzed with a quadrupole mass spectrometer.

The electron beam is generated by a “Trochoidal Electron Monochromator“ (TEM) [24] where the electrons are aligned by a homogeneous magnetic field. The TEM has proven to be particularly suitable for studying reactions at low electron energies because the axial magnetic field prevents spreading of the beam so that sufficient intensities ($\approx$30 nA) can be achieved down to very low energies. For the present experiments the energy resolution was between 0.1 eV and 0.2 eV. The energy is calibrated by the well known standard SF_6^- [25] or Cl^-/CCl_4 [26].

The supersonic beam is formed by adiabatic expansion of the gas mixture R_1X/R_2Y seeded in Ar up to several bars through an 80 μ nozzle. The beam then passes a skimmer (800 μ) which separates the expansion chamber from the main chamber. In the latter, the molecular beam is crossed with the electron beam and the ions are extracted by a small electric field ($<$1 V cm^{-1}), mass analyzed by a quadrupole mass filter and detected by single pulse counting electronics. The count rate of a particular ion is then recorded as a function of the incident electron energy. This is performed by means of a multichannel scaling (MCS) device plugged into a personal computer.

Alternatively to the supersonic beam, target gas can also be introduced *effusively* by means of a capillary directly mounted to the reaction chamber (Fig 2).

The electron beam can also be pulsed at one of the electrodes before the reaction chamber. In that case it is possible to record time-of-fligh (TOF) spectra of the generated ions. Recording flight times of product ions on their ways between the source and the detector can be used to obtain information on the kinetic excess energy release of the associated reaction and also to separate reactions occurring in in the jet from those occurring in scattered background monomers. We shall use this second possibility in particular to get a more detailed information on the precursor from which the detected ionic product is formed.

If decomposition reactions following ionization to a static sample are considered, ions formed with low kinetic energy (e.g., thermal ions) exhibit one peak in the TOF spectrum while ions generated with considerable kinetic energy produce two peaks because of “direct” and “turn around” ions. In the latter case discrimination against velocity components perpendicular to the flight tube axis results in a separation (in time) of ions ejected parallel (direct) or antiparallel (turn around) to the axis. The turn around ions are decelerated, reversed, and then accelerated and reach the detector by some time delay with respect to the direct ions. From the experimentally determined flight time difference the initial kinetic energy release of the product ion can be calculated 1,2,23,27].

In the case of precursors moving in the supersonic beam, the TOF spectrum of a product ion will be shifted to lower flight times due to its initial velocity

$$v_t = \left(\frac{5kT_o}{M}\right)^{1/2}$$

toward the detector [T_o is the temperature in the source and M is the mass of the seed gas (Ar)]. Because all particles in the jet move with approximately the same velocity given by the mass of the seed gas atoms (M) one expects appreciable shifts in the case of large product ions. An inherent shortcoming of the present cluster experiment is its insensitivity to identify the size of the precursor. By recording flight times, however, it is in favourable cases possible to distinguish reactions occurring in the beam from those occurring in scattered background monomers. TOF spectra are recorded by use of a time-to-pulse height converter (TPHC) followed by analog/digital (ADC) ocnversion.

3. Results and discussion

We present experimental results for the displacement reactions of the system F^-/CH_3Y (Y = Cl, Br, I) which in the gas phase are characterized by an appreciable exothermicity. On the basis of the well established thermodynamical data (bond dissociation energies and electron affinities [28,29]), the reaction enthalpies are -1.3 eV (Cl), -1.6 eV (Br) and -1.9 eV (I). In addition we present results for the system Cl^-/CH_3Br where the corresponding reaction is exothermic by only −0.33 eV. As will be shown, the ratio between the "naked" nucleophile and the ion-molecule complexes involved in the reaction (which can be stabilized by intermolecular collisions in a cluster) are a mirror or of the exothermicity of the corresponding S_N2 reaction. A particular interesting problem is the interaction of low energy electrons with mixed clusters composed of C_2F_6 and CH_3Cl. Although isolated CH_3Cl has an unmeasurably low DA cross section into Cl^- [20,21], it generates this fragment ion with appreciable intensity when CH_3Cl is coupled to C_2F_6 molecules via the corresponding S_N2 reaction involving F^-.

3.1 *Observation of the displacement reaction $F^- + CH_3Y \rightarrow CH_3F + Y^-$ (Y = Cl, Br, I) in mixed clusters*

Before identifying possible displacement reactions in binary clusters it is necessary to study the behaviour of the substrate molecules with respect to DA. This is shown in Fig. 3 for the three compounds. The spectra represent the Y^- ion yield obtained from a pure expansion of CH_3Y seeded in Ar at a stagnation pressure of 2.0 bar in each case.

For comparison the count rates are given in absolute numbers. The behavior of CH_3Cl with respect to DA at low energy is still under discussion. This is related to the unusually low cross section which requires an extraordinarily high purity of the sample and the gas inlet system. According to recent experimental and theoretical studies [30,31], the cross section for the DA reaction

$$e^- + CH_3Cl \rightarrow CH_3Cl^{-*} \rightarrow CH_3 + Cl^- \qquad (4)$$

is most likely below 10^{-23} cm². This is many orders of magnitude lower than that of other chlorinated compounds and e.g. about 10 orders of magnitude (!) lower than the DA cross section in CCl_4 [26,32]. It thus appears that in earlier experiments (including those of our laboratory [33] any detected low energy Cl^- signal was obviously because of impurities.

Accordingly, we assign the low energy (<2 eV) Cl^- signal in Fig. 3(a) because of impurities in the sample and/or the gas inlet system. This, however, does not affect any of the further results or conclusions. Under the present experimental conditions and for a cross section of 10^{-23} cm² we would expect a count rate much below 1 s^{-1}. The DA cross sections for the other substrate molecules can be derived from FALP (flowing afterglow Langmiur probe) experiments at thermal energies as 6×10^{-19} cm² (CH_3Br) and 5×10^{-14} cm² for CH_3I [34]. If we compare these numbers with the relative intensities of the present beam experiment one has to consider that (a) the beam consists of clusters and (b) the above cross sections where derived from attachment rate coefficients from the FALP experiment at room temperature. In addition, CH_3Br shows a dramatic temperature effect leading to an activation energy of as large as 300 meV. This explains why the count rates in the beam experiment do not differ by five orders of magnitude between CH_3Br and CH_3I and also explains why Br^- DA peak is above 0 eV.

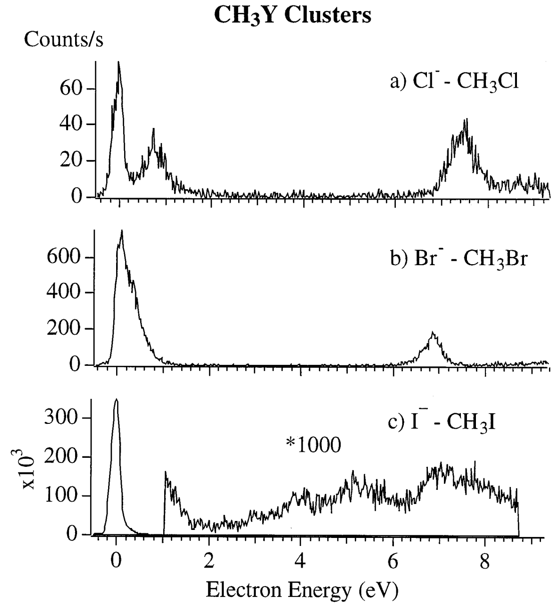

Fig. 3. Y^- ion yields (Y = Cl, Br, I) obtained from the pure expansion of the respective substrate molecules CH_3Y seeded in Ar at a stagnation pressure of 2.0 bar. The following mixing ratios were used: (a) CH_3Cl:Ar = 1:10; (b) CH_3Br:Ar = 1:10; (c) CH_3I:Ar = 1:20.

There is a further resonant contribution yield near

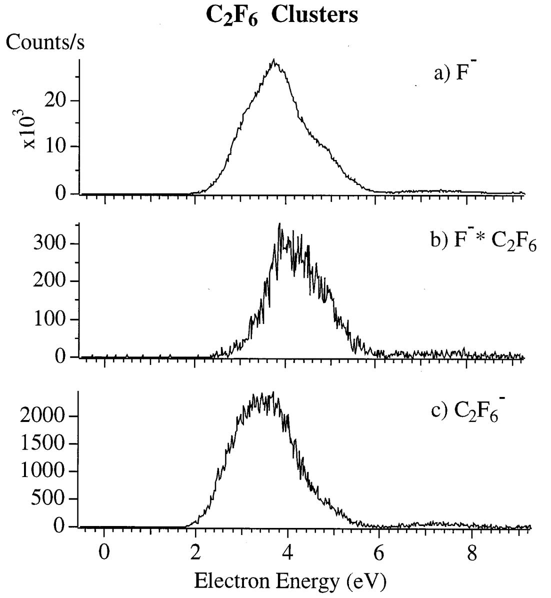

Fig. 4. Some ion yields obtained from a pure expansion of the nucleophile delivering component C_2F_6 seeded in Ar (1:10) at a stagnation pressure of 2.5 bar. (a) isolated DA product F^-; (b) solvated fragment ion $F^{-\cdot}$ C_2F_6 and (c) stabilized parent ion $C_2F_6^-$.

7.4 eV (CH_3Cl) and 6.9 eV (CH_3Br). In the recent DA studies to CH_3Cl [30] the cross section for this second Cl^- contribution was determined as 5×10^{-20} cm^2. This high energy signal (Cl^-, Br^-) is most likely the result of a multiple fragmentation reaction involving a core excited resonance. In the system (CH_3I) some I^- contribution is already observed above ~3.4 eV which is not seen from the isolated molecule. This signal can be interpreted as *self-scavenging*, i.e. inelastic scattering of the fast electron creating an electronically excited molecule and dissociative attachment by a second molecule of the same cluster. Such self-scavenging processes are always present when a cluster contains strong electron scavengers [2–5,23] as in the present case.

We have chosen C_2F_6 as the F^- donating compound for the following reason: from Fig. 4(a) it can be seen that F^- is formed from a DA resonance peaking at 3.8. eV and hence at an energy where the substrate molecule does not undergo DA at all. Fig. 4 (b) and 4 (c) show further products resulting from electron attachment to a pure C_2F_6 expansion seeded in Ar (1:10 at a stagnation pressure of 2.5 bar). Although isolated C_2F_6 is exclusively subjected to DA with F^- by far the dominant ion [35], from C_2F_6 clusters we also observe ionic complexes of the form $(C_2F_6)_{\dot{n}}$ including the monomer and also solvated fragment ions $F^{-\cdot}$ $(C_2F_6)_n$. The F^- signal obtained from a pure C_2F_6 expansion, on the other hand, is the result of DA reactions from (1) C_2F_6 clusters traveling in the molecular beam, (2) C_2F_6 monomers traveling in the molecular beam and, finally, (3) C_2F_6 monomers representing the scattered background gas. In favourable cases it is possible to separate products resulting from reactions in the molecular beam from those in the scattered background gas by means of a TOF technique (see below).

Fig. 5 presents an overview for the three substrate molecules concerning potential S_N2 reactions from the mixed C_2F_6/CH_3Y expansions. For comparison, Fig. 5(a) again shows the F^- contribution from a pure C_2F_6 expansion. From the mixed clusters the F^- profile is virtually identical to that from the pure expansion with roughly 50% of the original intensity.

However, from each of the mixed cluster systems we observe in the Y^- yield now a relatively strong contribution in the vicinity around 3.8 eV, which we ascribe to the S_N2 reaction

$$F^- + CH_3Y \rightarrow CH_3F + Y^- \tag{5}$$

As already mentioned above, apart from the reaction (5) we have to consider two further possible processes which could be a source of some Y^- signal, namely (a) inelastic electron scattering from C_2F_6 in the mixed cluster and capture of the slow electron by the second component which then undergoes DA forming Y^- and (b) reactions occurring in the scattered background or gas, i.e. either an S_N2 reaction between F^- (generated from an isolated C_2F_6) and gas phase CH_3Cl or the ineleastic scattering sequence described in (a) occurring between uncorrelated monomers.

The latter possibility (b) can easily be checked by effusing the two compounds at a pressure corresponding to the background pressure of the supersonic beam experiment (10^{-5} mbar). This did not result in any

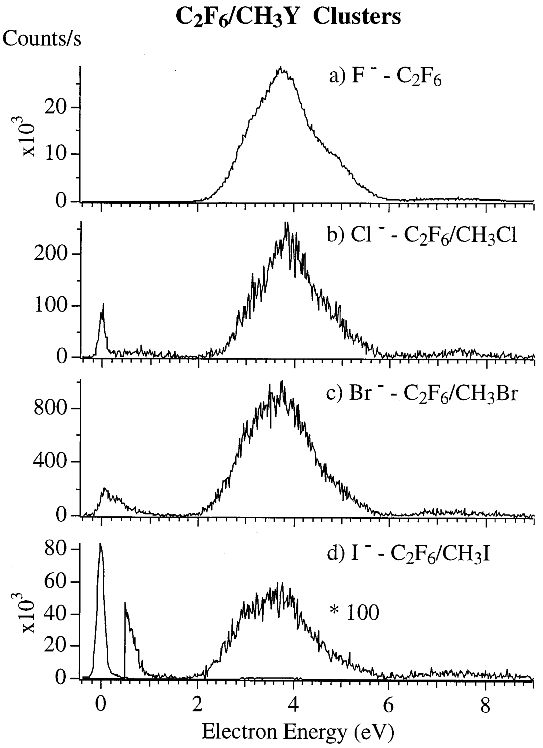

Fig. 5. Energy profile of the nucleophile F^- observed from a pure C_2F_6 expansion compared to the energy profiles of the respective naked product ions Y^- (Y = Cl, Br, I) observed from expansion of the mixture C_2F_6/CH_3Y seeded in Ar at a stagnation pressure of 2.5 bar. The following mixing ratios were used: (a) C_2F_6:Ar = 1:10; (b) C_2F_6:CH_3Cl:Ar = 3:1:40; (c) C_2F_6:CH_3Br:Ar = 10:1:100; (d) C_2F_6:CH_3CI:Ar = 10:1:100.

detectable Y^- signal at energies near 4 eV, not even by increasing the pressure into the 10^{-4} mbar region. We will show below by means of TOF measurements, that in fact any Y^- signal detected in the vicinity of 4 eV must be attributed to reactions occuring in the jet. Because the Y^- ion in every case carries the profile of the C_2F_6 DA resonance, only inelastic scattering via the $C_2F_6^-$ resonance has to be considered.

There are particular molecules where resonances in the DA cross section have their counterpart in the inelastic scattering cross section. This is generally the case when autodetachment strongly competes with dissociation in the decay of the transient negative ion formed upon resonant electron capture. In the case of CF_3Cl, e.g. it has been shown by Mann and Linder [36] that the inelastic scattering cross section exhibits a resonance at 2 eV with a cross section value of more than 10^{-16} cm^2, nearly two orders of magnitude larger than the DA cross section. However, the intensity of the inelastically scattered electrons decreases rapidly with the amount of energy loss, which is a general phenomenon in electron scattering. For the present problem the primary electron has to be scattered nearly completely down from about 4 eV (to be dissociatively captured by the second component) which is a most unlikely event. In addition, only CF_3I is is a reasonable electron scavenger and the inelastic scattering cross section of C_2F_6 does not show any pronounced enhancement near 4 eV [37].

We therefore conclude that the observed Y^- signal around 4 eV in fact is the result of the exchange reaction (5). For the CH_3Cl molecule we have thus the remarkable phenomenon that the interaction of single molecules with low energy electrons does not result in a detectable Cl^- signal, whereas from mixed C_2F_6/CH_3Cl clusters, effective generation of Cl^- via the ion-molecule reaction (5) takes place.

Interestingly the count rate of the leaving group is in the same order of magnitude for all the three systems with the intensity ratio Y^-/F^- in the order of a few percent. Superficially, one would thus expect that the effectivity of a reaction in a mixed cluster is not high. This number, however, is not a direct mirror of the reaction efficiency in the target cluster as Y^- represents the "naked" product leaving the target cluster and accordingly F^- the "naked" DA product from C_2F_6. We have performed time-of-flight experiments in order to get some idea to which degree observed ions arise from events in the background gas or in the jet. Because the quadrupole axis is mounted *in line* to the supersonic beam, ions arising from reactions in the beam carry the additional velocity component and can be distinguished from the randomly moving background gas. These TOF experiments showed that under the present experimental conditions most of the F^- signal arises from scattered background C_2F_6 molecules. This is always the observation for an expansion of a gas of low condensation temperature (195 K for C_2F_6 under standard conditions) when no cooling of the nozzle is applied

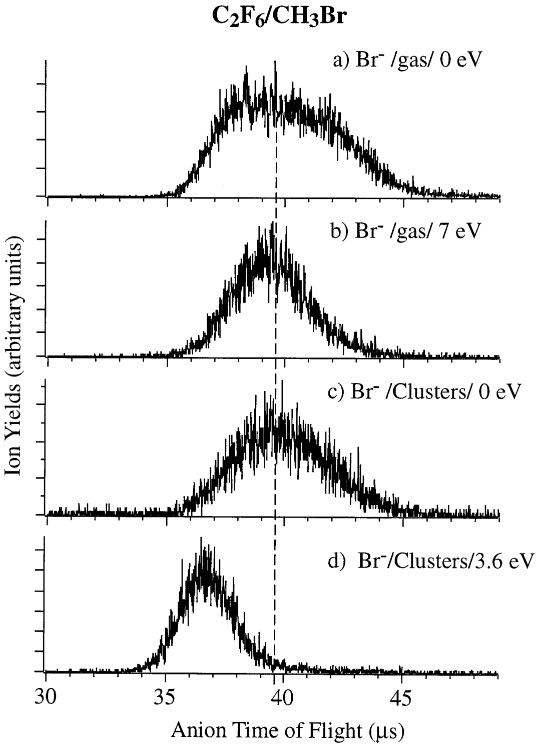

Fig. 6. TOF distributions of the product ion Br^- obtained from effusive gas inlet [(a) and (b)] and from an expansion of the C_2F_6:CH_3Br:Ar mixture (3:1:40) at a stagnation pressure of 2.5 bar [(c) and (d)] recorded at the indicated electron energies. Ion draw out field 2.8 Vcm^{-1} (see text).

as in the present experiments; it also indicates the weak tendency of C_2F_6 to form aggregates (although in the expansion mixture used in considerable excess) and is also a mirror of the fact that no differential pumping is used in the present arrangement. Apart from mixed clusters, the molecular beam may also contain homogeneous clusters and probably monomers. We can hence conclude that an F^- DA event in a mixed C_2F_6/CH_3Y cluster must have a much higher probability to undergo an S_N2 reaction than suggested by the small intensity ratio Br^-/F^-. From the spectra of the naked products Br^-, on the other hand, it is clear that they virtually must arise from precursors in the supersonic beam.

To illustrate the TOF principle, Fig. 6 shows spectra for the Br^- product from a C_2F_6/CH_3Br mixture recorded at different inlet conditions and electron energies. Figs. 6(a) and 6(b) show the TOF spectra obtained at ≈0 eV and ≈7 eV, respectively, when the gas is effusing from the capillary directly fitted to the reaction volume. Near 0 eV one observes an uncompletely resolved TOF doublet because of ions emitted along the quadrupole axis either directly towards or directly away from the detector. This indicates that near 0 eV the precursor ion CH_3Br^- obviously dissociates impulsively via direct electronic decomposition along a repulsive potential energy surface. Near 7 eV, on the other hand, only one peak appears which indicates the formation of Br^- ions with only thermal or near thermal energy. The associated decomposition reaction is obviously less direct and most likely associated with the appearance of more than one neutral fragment. Figure 6(c) and 6(d) show the TOF spectra obtained from the mixed expansion through the nozzle at a stagnation pressure of 2.5 bar near 0 eV and 3.6 eV, respectively. The spectrum near 0 eV resembles that from the effusive inlet although the unresolved doublet is less pronounced which may be related to the fact that the reaction volume (defined by the crossing of the electron beam with the gas) is now less localized with respect to the effusive gas inlet by means of the capillary.

Near 3.6 eV, however, the Br^- TOF spectrum is now distinctly shifted to lower flight times. This is because of the additional velocity component of the particles in the jet (see Sec. 2, Experimental). This is a further proof that Br^- ions formed around 3.6 eV arise from *reactions in the molecular beam and not from scattered background molecules*. Br^- formation from the mixed expansion close to 0 eV, on the other hand, arises from (or is due to) DA from scattered background CH_3Br molecules.

In the mixed cluster systems studied here, a variety of ion-molecule complexes arising from electron attachment to the respective target cluster can be observed. Fig. 7 shows the energy profiles of ions with the stoichiometric composition $(FCH_3Br)^-$ and $(BrCH_3Br)^-$ together with that of the nucleophile F^- and the product ion Br^-. In both complexes the localization of the excess charge is not directly obvious. In the case of $(BrCH_3Br)^-$ it is rather $Br^{-\cdot}$

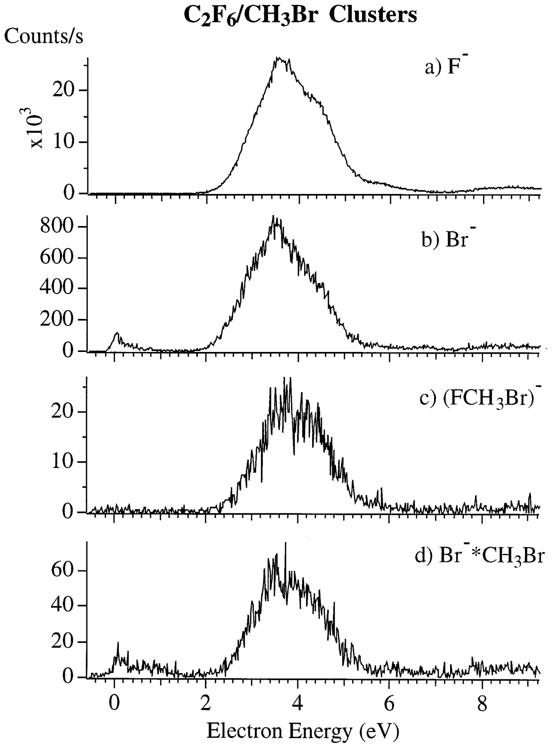

Fig. 7. Energy profiles of two ion molecule complexes obtained from the expansion of C_2F_6:CH_3Br seeded in Ar (10:1:100) at a stagnation pressure of 2.5 bar. For comparison the energy profiles of the nucleopile (F^-) and the naked product ion (Br^-) is also shown.

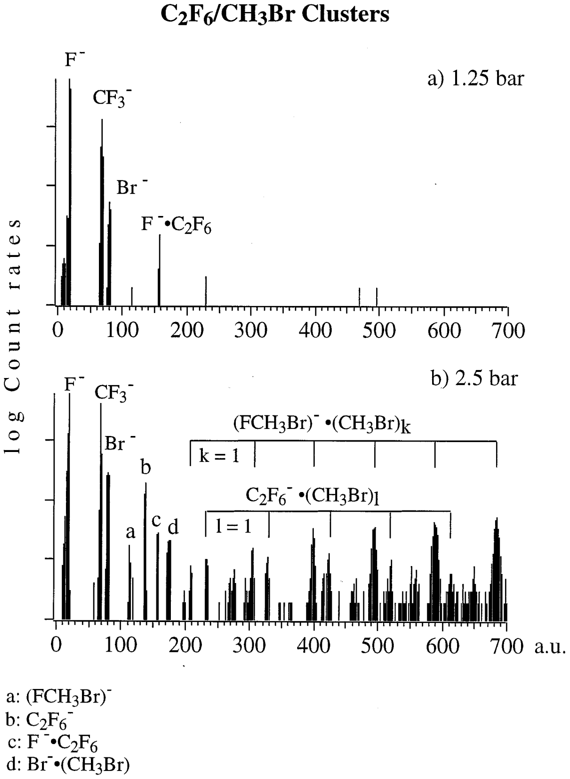

Fig. 8. Evolution of th mass spectrum recorded from the expansion of C_2F_6:CH_3Br seeded in Ar (10:1:100) with increasing stagnation pressure (see text).

CH_3Br than $Br^{\cdot}$ $(CH_3Br)^-$ because of the much larger electron affinity of Br as compared to CH_3Br. In any case, because the energy profile of the complex $Br^{-\cdot}$ CH_3Br resembles that of the nucleophile F^-, it must be formed in the course of a completed S_N2 reaction in the target cluster. The ion $(FCH_3Br)^-$, on the other hand, is either the ion-molecule complex before ($F^{-\cdot}$ CH_3Br) or after the S_N2 reaction ($FCH_3^{\cdot}$ Br^-).

Fig. 8 shows the evolution of the mass spectrum on a log intensity scale obtained from a mixed C_2F_6/CH_3Br expansion at two different stagnation pressures recorded at an electron energy of 3.6 eV where the generation of the nucleophile has its maximum. At the low stagnation pressure of 1.2 bar we have small clusters in the beam and we observe the DA products F^- and CF_3^- from C_2F_6, the ion Br^- arising from the S_N2 reaction and also the solvated fragment $Br^{-\cdot}$ C_2F_6. At the higher stagnation pressure of 2.5 bar, the ion molecule complex $(FCH_3Br)^-$ solvated by CH_3Br becomes very significant. It is possible that the charge localization in the complex $(FCH_3Br)^-$ is shifted towards $F^{-\cdot}$ CH_3Br as the cluster size increases. Note that the intensity of the $(FCH_3Br)^{-\cdot}$ $(CH_3Br)_k$ compounds increases with k in spite of the discrimination of the quadrupole towards higher masses. The other homologous series consists of stabilized $C_2F_6^-$ ions solvated by methylbromide molecules. A further series (for clarity not directly assigned in Fig. 8) consists of the S_N2 product Br^- solvated by CH_3Br. The intensity of these solvated ions also slightly increase with the number of CH_3Br units and thus demonstrate that S_N2 reactions in larger clusters are rather manifested by the formation of complex ions than generation of the single production

Br^-. The mass spectrum does not indicate the formation of product ions containing of more than one C_2F_6 unit. The weak tendency of C_2F_6 to form aggregates has already been mentioned above and from these results it seems that the mixed clusters generally only contain one C_2F_6 molecule with the rest consisting of methylbromide units.

At this point we shall not extend the discussion to the other mixed expansions concerning the formation of solvated ions and ion molecules complexes following electron attachment. We only note that a variety of complex ions are formed from C_2F_6/CH_3I (similar to C_2F_6/CH_3Br described above with even a stronger tendency of complex formation relative to I^-). From the system C_2F_6/CH_3Cl we observe the compounds $Cl^{-\cdot}$ $(CH_3Cl)_n$ ($n = 1, 2$), which carry the profile of the nucleophile (not shown here) and are hence also considered as the result of the corresponding S_N2 reaction. The methylchloride parent anion CH_3Cl^- has probably a very shallow minimum along the CH_3Cl^- axis [30,31]. To our knowledge, however, a stabilized CH_3Cl^- has yet not been observed.

3.2 Energy dependence of the reaction efficiency

Reactions of F^- with CH_3Y ($Y = Cl, Br, I$) as prototype S_N2 reactions have been the subject of numerous investigations in the gas phase [6,11,38]. The rate of these exothermic reactions decreases with collision energy and is only weakly sensitive on the temperature of the substrate molecule. We mention here, e.g. a recent study on the system F^- with CH_3Cl [42] indicating that the *rate constant* for the S_N2 reaction decreases from 1×10^{-9} cm^3 s^{-1} to 2×10^{-10} cm^3 s^{-1} on increasing the collision energy from 0.3 eV to 1eV.

It appears that in the gas phase the internal barrier for the S_N2 reactions studied here are in each case below the energy of the entrance channel which generally explains why the reactivity decreases with collision energy.

The question arises whether from the present results information on the energy dependence of the reaction efficiency can be extracted. We note that the amount of energy deposited in the system and hence the excess energy of the S_N2 reaction is (on the basis of the underlying thermodynamics for the reaction) entirely controlled by the energy of the attaching electron. This energy can be varied over the range of the respective DA resonance, in the present case between approximately 2 eV and 6 eV. From gas phase measurements the distribution of the excess energy in the DA reaction of the nucleophile donating compound is often known [1,2,23,27]. In C_2F_6 most of the available excess energy appears as internal energy of the neutral radical (C_2F_5) wheres the translational energy of the nucleophile only slightly increases over the resonance up to 250 meV [39]. There are, however, also systems (e.g. CF_4 [1]) that decompose into F^- via strongly repulsive precursor states and hence with the release of appreciable kinetic energy.

The question is whether from the explicit comparison between the F^- and the Y^- energy profile the energy dependence of the respective S_N2 reaction can be extracted. To reveal this problem we return to the system C_2F_6/CH_3Br. Fig. 9(a) shows that by increasing the energy accross the resonance the relative intensity of the reaction product (Br^-) decreases with

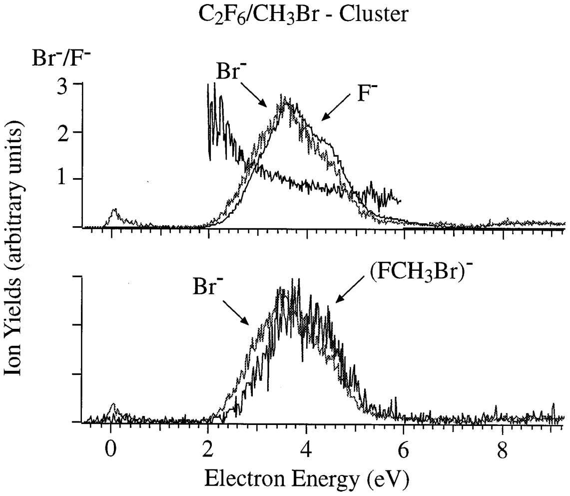

Fig. 9. (a) Comparison of the energy profile of the nucleophile (F^-) with the naked product ion (Br^-) and energy dependence of the ratio Br^-/F^-; (b) comparison of the energy profile between the naked product ion Br^- and the ion-molecule complex $(FCH_3Br)^-$ (see text).

respect to that of of the nucleophile (F^-). This suggests a *negative energy dependence* for the S_N2 reaction. In Fig. 9(b) it can be seen that the ratio Br^-/F^- drops to below 25% when the electron energy is increased from 2 eV–5eV.

To which extend does this number reflect the energy dependence of the underlying S_N2 reaction occurring in the respective *target cluster*? It must be remembered that F^- represents the free DA product from C_2F_6 and Br^- the "naked" product emitted from the target cluster. It has already been discussed above that in the case of F^- only a minor amount of the detected signal arises from DA processes in the cluster beam. In any case, the observed F^- ion represents a *free* DA fragment, either formed from scattered background molecules or ejected from clusters moving in the jet. Electron capture by an aggregated molecule, on the other hand, is subjected to polarization interaction with the neighbouring molecules that will modify the DA resonance profile to some extend [2]. We can thus conclude that the F^- resonance profile obtained in the present experiment is not an *exact* mirror of the formation probability of the nucleophile within the cluster. Similar arguments apply for the energy dependence of Br^- which represents a particular product ion of a completed S_N2 reaction. Other products are the ion-molecule complexes $Br^{-\cdot}$ CH_3F, isolated or solvated by methylbromide molecules (see Fig. 8). These latter products cannot be distinguished by mass spectrometry from their isomer $F^{-\cdot}$ CH_3Br *before* the reaction. Interestingly the formation probability of this unspecified complex $(FC\dot{H}_3Br)^-$ shows a slight shift to *higher* energies with respect to the isolated product ion Br^-. This result has been reproduced many times and we have no simple explanation for that kind of behaviour. From simple arguments (energy dependence of the Langevin capture cross section to form the initial complex $F^{-\cdot}$ CH_3Br and energy dependence for the stabilization of such a complex) one would rather expect the opposite behaviour, namely a shift of the resonance of the ion-molecule complex to lower energy with respect to the nucleophile. One has to be aware, however, that formation of the *isolated* ion-molecule complex $(FCH_3Br)^-$ as in Fig. 9(b) requires evaporation of a target cluster of eventually appreciable size. This probability depends on the cluster size and is expected to increase with the excess energy deposited in the system. In contrast to that, owing to the appreciable excess energy in the S_N2 reaction we do not expect that ejection of the isolated product ion Br^- is generally accompanied by a *complete* evaporation of the target cluster.

From this short discussion we may conclude that the energy dependence of the ratio (Br^-/F^-) *alone* is no reliable measure of the energy dependence of the corresponding S_N2 reaction. A more detailed information is eventually possible via extended experiments of the energy profiles of all product ions related to the reaction in dependence of the stagnation pressure.

We are currently preparing experiments using CF_4 as nucleophile delivering component. From gas phas experiments [1,27] it is known that the kinetic energy of F^- varies between 0.5 eV and 1.6 eV across the fairly broad DA resonance in CF_4.

3.3. *Displacement reaction $Cl^- + CH_3Br \rightarrow CH_3Cl + Br^-$ in binary clusters*

In this last section we will study the exchange reaction of Cl^- with methyl-bromide in the mixed cluster system CCl_4/CH_3Br. Compared to the systems studied above, this reaction is (in the gas phase) exothermic by only 0.3 eV. As nucleophile donating compound we use CCl_4, which has an exceedingly high cross section for dissociative electron capture at very low energies. According to recent high resolution experiments [25,26,40], the attachment behaviour towards very low energies can be described by the "s wave" cross section, which is the theoretical upper cross section limit in electron scattering. At thermal electron energies, the absolute value of the attachment cross section is in the range of 10^{-14} cm^2 [41].

Figs. 10(a) and (b) show the Cl^- and Br^- yield from a pure expansion of CCl_4 and CH_3Br, respectively. Apart from the intense contribution near 0 eV, the Cl^- yield exhibits an additional weak resonant contribution peaking at 0.8 eV, which is also present in gas phase experiments [26]. The Br^- signal exhibits only one weak resonance to 0 eV [see also Fig.

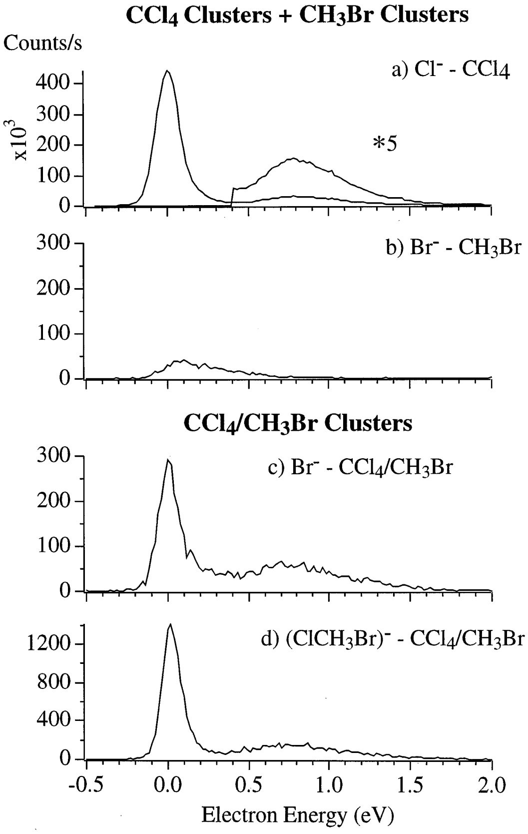

Fig. 10. Energy profiles of ions involved in the S_N2 reaction $Cl^- + CH_3Br \rightarrow CH_3Cl + Br^-$. (a) Cl^- profile obtained from a pure expansion of CCl_4 seeded in Ar (1:20) at a stagnation pressure of 1 bar; (b) Br^- profile obtained from a pure expansion of (CH_3Br) seeded in Ar (1:10) at a stagnation pressure of 2 bar, intensity scale adopted to (c); (c) energy profile of naked product ion Br^- recorded from a mixed CCl_4:CH_3Br expansion seeded in Ar (1:1:80); (d) energy profile of the ion-molecule complex $(ClCH_3Br)^-$, expansion conditions as in (c).

3(b)]. In Fig. 10(b) the scale has been adopted to Fig. 10(c) showing the Br^- yield from the mixed CCl_4/CH_3Br expansion. In the present system we have no clear separation between the Cl^- and the Br^- energy profile and different resonant profiles.

The following observations can be made: (a) the Br^- count rate is now much higher than from the pure CH_3Br expansion, (b) its energy profile closely resembles that of Cl^-, in particular, the resonance at 0.8 eV now also appears in the Br^- channel and (c) TOF distributions like those described above demonstrate that the Br^- signal in Fig. 10(c) exclusively arises from processes occurring in the molecular beam [42].

From these observations it is clear that the Br^- signal is essentially a result of the exchange reaction. It is obvious from Fig. 10 that the relative intensity of the Br^- yield is significantly higher than that in the nucleophile Cl^-. In spite of the difficulties discussed above in deriving energy dependent reaction efficiencies, one may speculate that the significantly higher (relative) intensity of the product ion at 0.8 eV reflects some positive energy dependence for the underlying S_N2 reaction in the mixed clusters. Because of the appreciably lower exothermicity of the present reaction compared to those discussed above one expects a considerably higher activation barrier which may come close to the energy of the entrance channel. Such a picture is also confirmed by *ab initio* calculations [43]. In that case, solvation by only a few molecules in the cluster can shift the activation barrier above the energy of the entrance channel which would then result in a positive energy dependence of the reaction.

Finally from Fig. 10(d) it can be seen that the intensity of the complex $(ClCH_3Br)^-$ is now more than four times higher than that of the naked product ion Br^-. In addition, the complex solvated by methylbromide molecule is also present in appreciable amounts in the mass spectrum recorded near 0 eV (not shown here). In the system C_2F_6/CH_3Br the abundance of $(FCH_3Br)^-$ amounts to only about 3% of Br^-. This is a direct mirror of the different reaction exothermicities. Whereas in the system C_2F_6/CH_3Br a considerable amount of Br^- ions can leave the target cluster, it is much less in the case of CCl_4/CH_3Br. Hence, we may also conclude that the majority of the complexes $(FCH_3Br)^-$ have the structure $(FCH_3^{\cdot}Br^-)$, whereas for the complexes $(ClCH_3Br)^-$ it is $Cl^{-\cdot}$ CH_3Br.

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