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Reactions in clusters of acetone and fluorinated acetones triggered by low energy electrons

Isabel Martin*,[1], Judith Langer[2], Michal Stano[3], Eugen Illenberger

Freie Universität Berlin, Institut für Chemie und Biochemie, Physikalische und Theoretische Chemie, Takustr. 3, D-14195 Berlin, Germany

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ABSTRACT

Electron attachment to clusters of acetone (A), trifluoroacetone (TFA) and hexafluoroacetone (HFA) is studied in a crossed beam experiment with mass spectrometric detection of the anionic products. We find that the electron attachment properties in A change dramatically on going from isolated molecules to clusters. While single acetone is a very weak electron scavenger (via a dissociative electron attachment (DEA) resonance near 8.5 eV), clusters of A capture electrons at very low energy (close to 0 eV). The final ionic products consist of an ensemble of molecules (M) subjected to the loss of two neutral H_2 molecules ($(M_n{-}2H_2)^-$, $n \geq 2$). Their formation at low energies can only be explained by invoking new cyclic structures and polymers. In clusters of TFA, anionic complexes containing non-decomposed molecules ($M_n{}^-$) including the monomer (M^-) and ionic products formed by the loss of one and two HF molecules are observed. Loss of HF units is also interpreted by the formation of new cyclic structures in the anionic system. HFA is a comparatively stronger electron scavenger forming a non-decomposed anion via a narrow resonant feature near 0 eV in the gas phase. In HFA clusters, the non-decomposed parent anion is additionally observed at higher electron energies in the range 3–9 eV. The M^- signal carries signatures of self-scavenging processes, i.e., inelastic scattering by one molecule and capture of the completely slowed down electron by a second molecule within the same cluster. The scavenging spectrum is hence an image of the electronically excited states of the neutral molecule.

1. Introduction

We study reactions in the three homogeneous van der Waals cluster systems acetone (A) CH_3COCH_3, 1,1,1-trifluoroacetone (TFA) CH_3COCF_3 and hexafluoroacetone (HFA) CF_3COCF_3 that are induced by low energy electrons. The basic initial process is the capture of a free electron by the target cluster at a particular energy. To follow the evolution of the negatively charged system the final ionic product is recorded as a function of the initial electron energy. We find that in the present cluster systems low energy electrons induce remarkably complex chemical reactions. Single gas phase molecules usually undergo dissociative electron attachment (DEA) at low energies. This process is characterized by the resonant attachment of the incoming electron generating a metastable transient anion (a resonance) followed by the unimolecular decomposition into one negatively charged and one or more neutral fragments. In competition to fragmentation, the transient anion may also decompose by loss of the attached electron (autodetachment).

On going to clusters the situation becomes considerably more complex with respect to both, the initial step of electron attachment, but also the evolution of the charged complex [1,2]. In clusters, electron capture may still proceed via an individual molecule, now coupled to the environment via polarization forces but the excess charge may also be delocalized over the entire cluster. In van der Waals clusters consisting of polar molecules like water or ammonia only the collective interaction between the molecules provides the situation for the excess charge to be trapped. While the individual molecules cannot bind an excess charge, clusters of water [3] and ammonia [4] exceeding a minimum number of molecules can trap an excess charge in a thermodynamic stable state. The main effect is the preferential orientation of the dipolar molecules around the excess charge generating a so called solvated electron.

In clusters, the *evolution* of the charged system may also strongly be affected by the molecular environment as now energy dissipation from the transient anion and chemical reactions involving sur-

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* Corresponding author.
E-mail address: isabel.martin@u-psud.fr (I. Martin).

[1] Present address: Laboratoire des Collisions Atomiques et Moléculaires (LCAM), Université Paris-Sud, Bâtiment 351, 91405 Orsay, France.

[2] Present address: Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany.

[3] Present address: Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Mlynska dolina F2, 84248 Bratislava, Slovakia.

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rounding molecules become possible [1]. In heterogeneous clusters, this can result in ion–molecule reactions induced by DEA like nucleophilic substitution (S_N2) reactions [5,6] or condensation reactions like the formation of the anhydride in CF_3COOH clusters [7].

Electron attachment to the three isolated molecules under consideration was studied in a previous beam experiment [8,9]. Acetone appeared to be a very weak electron scavenger exhibiting a resonance at appreciable high energy in the range 8–9 eV associated with several DEA products. TFA showed three resonances near 0.2, 4.2 and 8.5 eV leading to a variety of fragments, among them the bifluoride anion (FHF^-) and the anion $(M–HF)^-$ formed by the loss of neutral HF molecules. HFA finally is a reasonably strong electron scavenger yielding a metastable parent anion M^- by electron capture via a resonance near 0 eV. In an early mass spectrometric work [10], the electron attachment cross-section was reported to be 1/60 of that in SF_6 which itself possesses one of the highest electron capture cross-sections exceeding 10^{-14} cm^2 at electron energies below 0.1 eV [11,12].

2. Experimental

The experiments were performed in a crossed electron/molecular beam setup which has been described in more detail elsewhere [13]. It offers the possibility to study single molecules in the gas phase as well as molecular clusters. Molecular clusters are generated by adiabatic expansion of a mixture of the sample under investigation in an excess of argon (Ar) in a separate expansion chamber. The cluster beam then enters the reaction chamber via a skimmer and interacts in the reaction zone with the electron beam. This electron beam is provided by a trochoidal electron monochromator that offers the advantage to obtain reasonable intensities also at low electron energy. The electron attachment processes are studied in an energy range between 0 and 15 eV with an energy resolution of $\Delta E \approx 500$ meV for A, $\Delta E \approx 200$ meV for TFA and $\Delta E \approx 250$ meV for HFA. The substances were purchased at Sigma–Aldrich with a stated purity of >99% for A and 97% for TFA and HFA. While HFA and TFA are gaseous compounds at standard conditions, A is a colorless liquid with a fairly high vapor pressure of about 0.2 bar at 293 K [14]. In order to remove possible gaseous contaminations the liquid was cleaned by several freeze–pump–thaw cycles. At first, the liquid is frozen in a bath of liquid nitrogen and while slowly warming, the vapor phase containing most volatile compounds will be pumped.

The mixtures of the investigated substances in Ar were prepared at a ratio of 1:20. They are afterwards adiabatically expanded in the vacuum with a stagnation pressure of $p \approx 0.6$ bar for A, $p \approx 1.0$ bar for TFA and $p \approx 1.75$ bar for HFA. Adiabatic expansion generates a distribution of neutral clusters, the average size of which can be controlled to some degree by the experimental parameters (stagnation pressure, nozzle size and temperature, etc.). Consequently, by recording the final ionic product, one cannot directly conclude on the size of the target cluster from which it originates. From the mass spectra we can expect that under the present expansion conditions only relatively small clusters containing up to about 6–10 molecules are present in the beam.

3. Results and discussion

3.1. Chemical reactions in clusters of acetone (A) and 1,1,1-trifluoroacetone (TFA)

3.1.1. Loss of molecular hydrogen in acetone

The previous gas phase experiments [8,9] show that the single acetone molecule is a very weak electron scavenger with ion formation only observed through a resonance in the range 8–9 eV. This resonance leads to the loss of neutral atomic hydrogen ($(M–H)^-$), molecular hydrogen ($(M–H_2)^-$), and the three ionic fragments O^-, OH^- and $HCCO^-$.

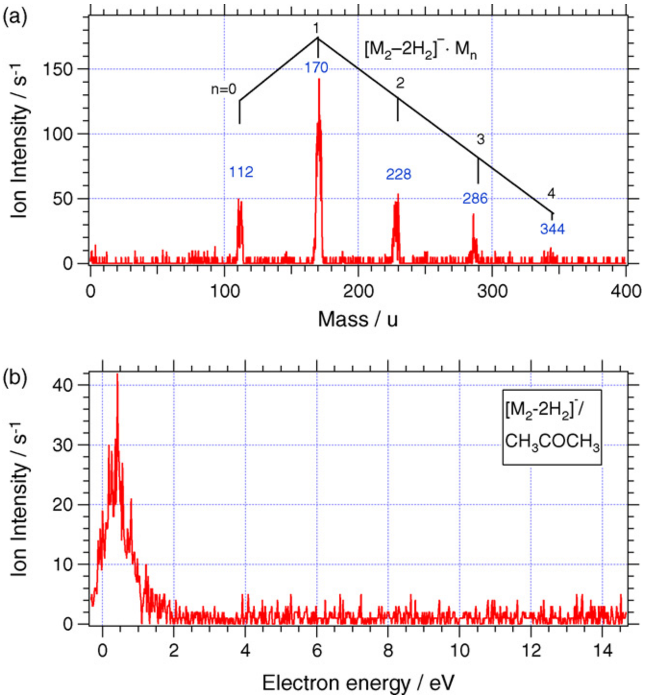

Fig. 1. (a) Negative ion mass spectrum from acetone clusters recorded at ≈0.5 eV electron energy and (b) an ion yield showing the formation of an anionic complex arising from the loss of four hydrogen atoms from acetone (mixture 1:20 in Ar, $p = 0.6$ bar, $\Delta E \approx 500$ meV).

On going to clusters of acetone the situation completely changes as now a new and comparatively stronger feature appears at low energy (0.5 eV) yielding a series of ionic products. Fig. 1 (a) displays a mass spectrum recorded at an electron energy of ≈0.5 eV showing signals at 112, 170, 228, 286 and 346 u. Below (b) the ion yield of the product at 112 u is shown in the range from 0 to 15 eV. From stoichiometry the signals can be assigned to ionic complexes of the form $(M–2H_2)^-{\cdot}M_m$ ($m = 1–5$) or $(M_2–2H_2)^-{\cdot}M_n$ ($n = 0–4$) with $M = A$. By considering the underlying energetics it becomes obvious that formation of complexes of the type $(M–2H_2)^-{\cdot}M_m$ may not be accessible at low energies. Formation of $(M–2H_2)^-{\cdot}M$ at 112 u, e.g., would imply that DEA within the cluster can be described on a molecular site, i.e., electron attachment to an individual acetone molecule subjected to the loss of two hydrogen molecules, *viz.*

$$e^- + M_p \rightarrow (M–2H_2)^-{\cdot}M + (p\text{-}2)M + 2H_2 \quad (1)$$

leaving an ion–molecule complex as the final ionic product. The energy threshold for such a reaction is given by $E_0 = 4D(C–H) - 2D(H–H) - EA(M–2H_2)$, where D assigns the bond dissociation energy and EA the electron affinity. It further requires evaporation (in part or complete) of the (p-2) remaining neutral molecule(s) minus the binding energy in the ion–molecule complex. If we take $D(H–CH_2COCH_3) = 4.3$ eV [14] and $D(H–H) = 4.5$ eV [14] and assume that the evaporation energy is counterbalanced by the binding energy in the ion–molecule complex, we arrive at a threshold for process (1) of $E_0 = 8.2\ eV - EA(M–2H_2)$. Since the reaction is observed at 0.5 eV (Fig. 1), it would require an unreasonable value for electron affinity for the radical $(M–2H_2)$ larger than 7.7 eV. We therefore conclude that electron attachment to clusters of acetone triggers chemical reactions which provide the

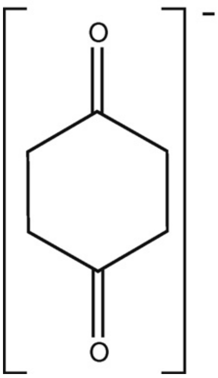

Fig. 2. Possible structure for the complex $(M_2–2H_2)^-$ in clusters of acetone.

necessary energy for observing the corresponding ions at that low energy.

A possible structure for the 112 u ion is shown in Fig. 2 representing a six-membered cyclic diketone structure (cyclohexane-1,4-dione) which is associated with an intermolecular chemical reaction forming two new C–C single bonds whereas *two* different reaction centers are involved. In the simplest case, this ion may be formed by electron attachment to a dimer.

$$e^- + M_2 \rightarrow (M_2–2H_2)^- + 2H_2 \qquad (2)$$

The threshold energy from above is then lowered by the binding energy of the two newly formed C–C bonds. If we take a typical value of about 3.5 eV for a C–C bond the threshold for reaction (2) becomes 1.2 eV − EA(c-M_2–$2H_2$) where (c-M_2–$2H_2$) represents the cyclic diketone new molecule which may possess sufficient electron affinity to drive the reaction at 0.5 eV. Another possible path could be the formation an open chain hex-3-ene-2,5-dione. In contrast to cyclic isomer formation, here the C–C coupling occurs via C=C double bond formation at the same reaction center. With a typical binding energy of the newly formed double bond of (D(C=C) = 6.3 eV) the threshold of reaction (2) becomes 1.9 eV − EA(M_2–$2H_2$) where (M_2–$2H_2$) represents the open chain species.

The series of the larger products at 170, 228, 286 and 344 u can then accordingly be assigned as $(M_2–2H_2)^-\cdot M_n$ (n = 1–4), i.e., ion–molecule complexes containing the cyclic diketone ion. The exceptionally strong signal (under the present expansion conditions) at 170 u could equally arise from a "condensation" reaction in the trimer of the type

$$e^- + M_3 \rightarrow [CH_3COCH_2–CH_2COCH_2–CH_2COCH_3]^- + 2H_2 \qquad (3)$$

where, in analogy to (2), the formation of two new C–C single bonds provides the energy to drive the reaction leading to an open chain triketone. The energy gain forming two new C–C single bonds in (3) is estimated to a similar value as for the cyclic isomer in (2) so that the threshold for (3) differs from (2) mainly by the difference in the EA of the involved radical species (c-M_2–$2H_2$) and $CH_3COCH_2CH_2COCH_2CH_2COCH_3$.

3.1.2. Collisional stabilization and loss of HF in clusters of 1,1,1-trifluoroacetone (TFA)

The gas phase results [8,9] clearly show that TFA possesses an appreciably higher cross-section for dissociative electron attachment than acetone. A broad variety of anionic fragments were obtained from three pronounced resonances located near 0.2, 4.2 and 8.5 eV. In the gas phase most of the ion intensity ($(M–H)^-$, $(M–F)^-$, F^-, O^-, OH^-, CF_3^-, $HCCO^-$, C_2H^-) is still channeled into ionic products arising from the two resonances at higher energy (4.2 and 8.5 eV) and only the bifluoride anion FHF^- and the anion due to loss of HF ($(M–HF)^-$) are formed from the low energy resonance.

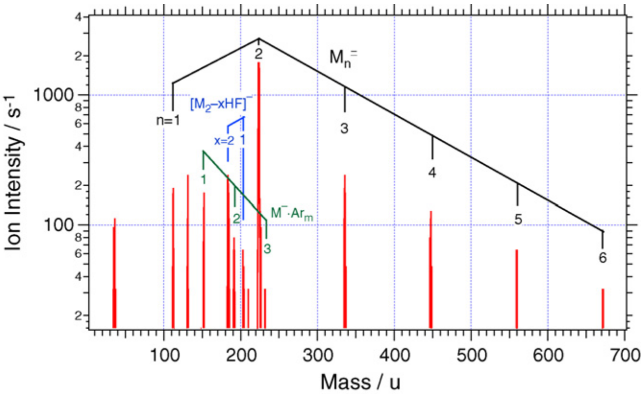

Fig. 3. Negative ion mass spectrum from 1,1,1-trifluoroacetone clusters recorded at ≈0 eV electron energy (mixture 1:50 in Ar, p = 2.0 bar).

In contrast to the gas phase, ionic products from clusters are nearly exclusively formed from a narrow resonant feature near 0 eV. The strongest signals are due to the non-decomposed anionic complexes M_m^- (m = 1–6) with the dimer as the most abundant one (see Fig. 3). Even under various expansion conditions the dimer remains always the product with the highest intensity. Thus we can assume that the dimer conformation is particularly stable. Fig. 4 shows the ion yield for the monomer and the dimer anion. Irrespective of the electronic structure of the complex initially formed by electron capture, collisional stabilization can generate the corresponding non-decomposed ionic complexes in their thermodynamically stable configuration. This goes along with the evaporation of neutral molecules from the target cluster according to

$$e^- + M_n \rightarrow M^-{}_m + (n-m)M \qquad (4)$$

The monomer radical anion is probably a dipole bound state as observed in Rydberg electron transfer to TFA [15]. The dipole moment of TFA (2.9 D) is appreciably above the critical value (1.8 D) to create a dipole supported state.

Fig. 5 shows the ion yields of a series of complexes associated with the abstraction of HF. While the ion $(M–HF)^-$ can also be formed from a monomer traveling in the molecular beam, the prod-

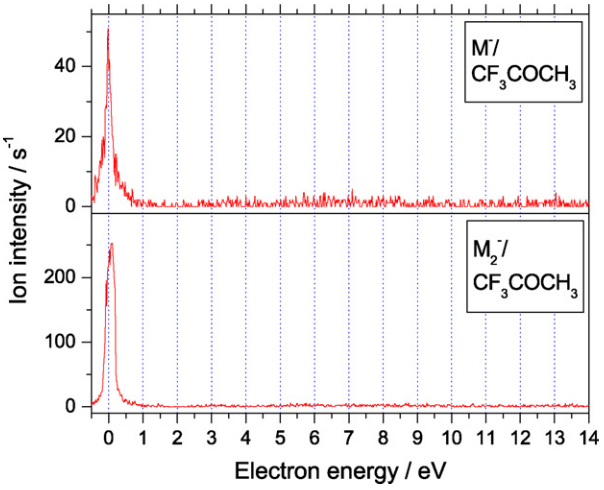

Fig. 4. Ion yields showing the formation of the intact molecular anions M^- and M_2^- in clusters of 1,1,1-trifluoroacetone (mixture 1:20 in Ar, p = 1.0 bar, $\Delta E \approx$ 200 meV).

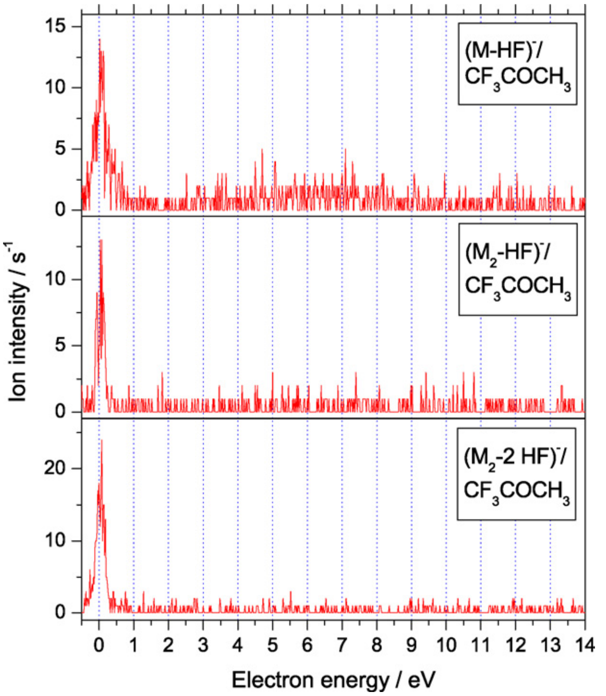

Fig. 5. Ion yields showing the formation of various anionic complexes due to the loss of HF following electron attachment to 1,1,1-trifluoroacetone (mixture 1:20 in Ar, $p = 1.0$ bar, $\Delta E \approx 200$ meV).

ucts $(M_2–HF)^-$ and $(M_2–2HF)^-$ must necessarily originate from an electron attachment process to a TFA cluster.

The ion $(M_2–HF)^-$ is either formed by loss of HF from one molecule thereby forming the ion $(M–HF)^-$ as in the gas phase now solvated by an intact TFA molecule, or it can be abstracted from two different molecules in the cluster. In the latter case, two molecules can be linked by a new C–C bond to form a hexane-2,5-dione compound (see Fig. 6a). Similar to the situation discussed above, the second reaction is energetically more favorable. Taking into account the average binding energies of C–F bonds (D(C–F) = 5.0 eV), C–H bonds (D(C–H) = 4.3 eV) and of HF (D(H–F) = 5.9 eV) a threshold of 3.4 eV – EA(M–HF) can be established for HF loss from one TFA molecule disregarding the ion–molecule binding energy of $D((M–HF)^-\cdot M)$. Considering the loss of HF from two different molecules and the formation of a new C–C bond (D(C–C) = 3.5 eV) the threshold becomes −0.1 – EA(M_2–HF) and the reaction is thus exothermic.

Accordingly, for the loss of two HF molecules leading to $(M_2–2HF)^-$ the energetically favorable reaction is that they arise from the combination of two different TFA molecules. The resulting ion possesses either a cyclic structure of the cyclohexane-dione type similar to that proposed for the loss of two H_2 molecules from the dimer of acetone or a chain-like structure (hex-3-ene-2,5-dion type anion) (see Fig. 6b and c). The energetic thresholds can be estimated to −0.2 eV – EA(c-M_2–2HF) for the cyclic product and to 0.6 eV – EA(M_2–2HF) for the linear product. The abstraction of one or two molecules of HF is not observed from higher order clusters; therefore we conclude that a specific configuration of the molecules (only present in the dimers) is necessary to allow HF loss.

Fig. 7 shows the ion $(M–H)^-$ and two products with the stoichiometric composition $[C_3F_4H_3O]^-$ and $[C_3F_3H_4O]^-$. The anion $(M–H)^-$ is likely to possess the enolate structure, and the signal may be composed from electron attachment to clusters and also to single molecules traveling in the beam.

Possible structures of the entity $[C_3F_4H_3O]^-$ are $F^-\cdot M$, $(M–F)^-\cdot F_2$ and $(M–H)^-\cdot HF$. Since the typical C–F binding energy (5 eV) is larger than the electron affinity of F (3.40 eV), formation of the complex $F^-\cdot M$ can be excluded near 0 eV as the threshold is calculated to 1.6 eV. In order to generate the product $(M–F)^-\cdot F_2$ two C–F bonds have to be broken whereas a comparatively weak F–F bond (D = 1.6 eV [14]) is formed. The threshold can then be calculated to 8.4 eV – EA(M–F). Alternatively, the localization of the negative charge on the F_2 forming $F_2{}^-\cdot(M–F)$ with EA(F_2) = 3.1 eV leads to a threshold of approx. 5.3 eV so that both ions are also not accessible from the low energy resonance. On the other hand for a reaction forming $(M–H)^-\cdot HF$ initiated in a dimer

$$e^- + M_2 \rightarrow (M–H)^-\cdot HF + (M–F) \qquad (5)$$

the energy threshold can be expressed as

$$E_0 = D(C–F) + D(C–H) - D(HF) - EA(M–H) + \delta \qquad (6)$$

where δ assigns the difference between the binding energy in the neutral dimer minus that in the ion–molecule complex. Taking D(H–F) = 5.9 eV, the C–F and C–H binding energies from above and the electron affinity of the TFA enolate radical

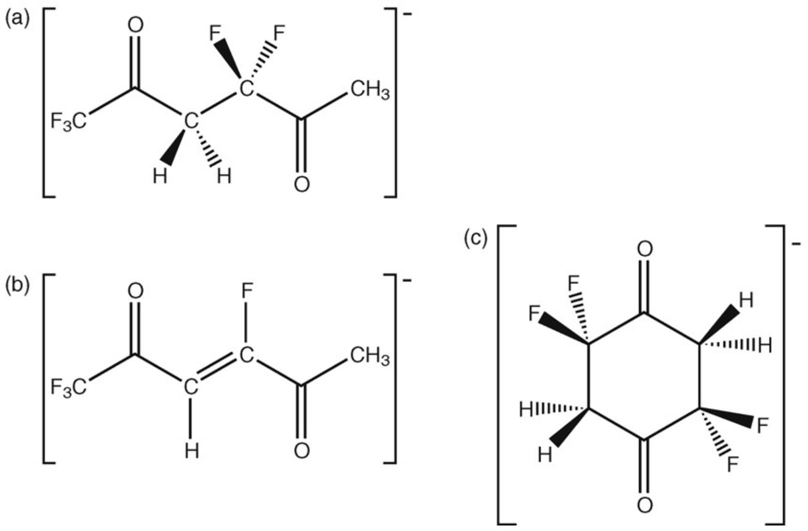

Fig. 6. Possible structures for the complexes (a) $(M_2–HF)^-$, (b) and (c) $(M_2–2HF)^-$.

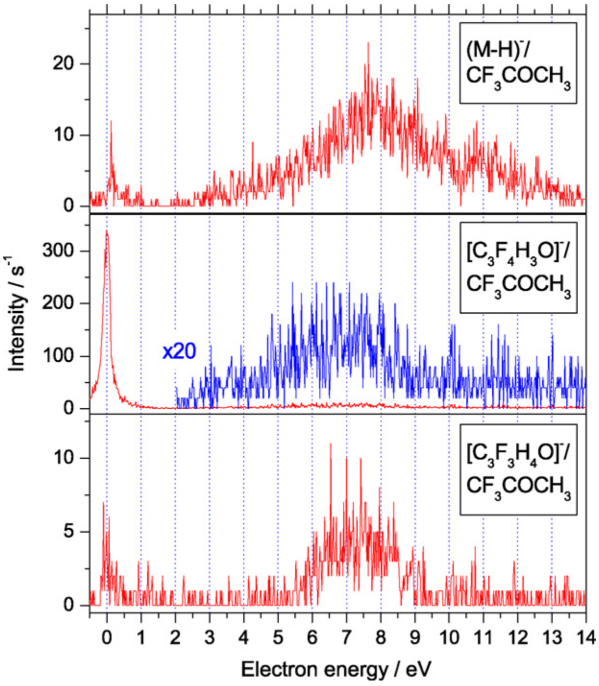

Fig. 7. Ion yields showing the formation of the dehydrogenated trifluoroacetone anion (M–H)$^-$ and the complexes $[C_3F_3H_4O]^-$ and $[C_3F_4H_3O]^-$ in clusters of 1,1,1-trifluoroacetone (mixture 1:20 in Ar, $p = 1.0$ bar, $\Delta E \approx 200$ meV).

EA(F_3C–$COCH_2$) = 2.65 eV [16] we arrive at an estimated threshold of $E_0 = 0.75\,\text{eV} + \delta$. Since δ is a negative number, the reaction may be accessible near zero eV. We hence suggest that (M–H)$^-$·HF is generated via the narrow low energy resonance. The dissociation into the complementary ions F^- and (M–F)$^-$ (initial steps for formation of F^-·M and (M–F)$^-$·F_2) from resonances in single TFA molecules can be observed from overlapping states between 3 and 9 eV [8,9]. Because of the considerably high threshold for the formation of (M–F)$^-$·F_2 we conclude that F^-·M is formed in the region between 3 and 9 eV while contributions of (M–F)$^-$·F_2 or $F_2{}^-$·(M–F) can only be expected on the high energetic flank.

Accordingly, the compound $[C_3F_3H_4O]^-$ can be assigned to the structures H^-·M, (M–H)$^-$·H_2 and (M–F)$^-$·HF with the latter probably the most stable complex. In analogy to (5) the reaction may already be initiated in the dimer, in this case leading to the products (M–F)$^-$·HF + (M–H). The fact, that in this compound we observe appreciably less signal near 0 eV suggests that the electron affinity of the (M–F) radical may be lower than that of the (M–H) radical. Also, the high energy feature suggests that it may rather be formed in a concerted rearrangement reaction within an electronically excited dimer transient anion, than via intracluster DEA like in the compound above $[C_3F_4H_3O]^-$.

3.1.3. Electron interaction with clusters of HFA

In contrast to A and TFA no comparable loss of a neutral molecule (in this case F_2) is observed for HFA. This change in reactivity may originate from the fact that the binding energy of fluorine (1.6 eV) is considerably lower than the ones of molecular hydrogen and hydrogen fluoride. The energetic threshold for the abstraction of two F_2 molecules from the dimer combined with two intermolecular C–C coupling reactions leading to an hypothetical cyclic product (c-M_2–$2F_2$)$^-$ analog to reaction (2) is estimated to 9.8 eV – EA(c-M_2–$2F_2$). Accordingly, the formation of this cyclic product is not expected at low energy. This further indicates that the C–C coupling reactions at low energies are driven by the (thermodynamic) stability of the formed byproducts.

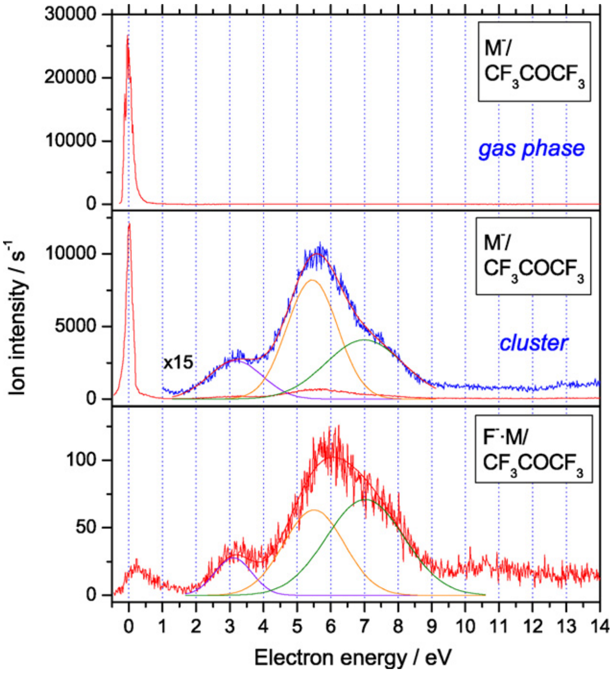

Fig. 8. Ion yield curves showing the formation of M^- in electron attachment experiments to gas phase hexafluoroacetone (top), the formation of M^- in molecular clusters of hexafluoroacetone (middle) and the production of an anionic complex F^-·M in hexafluoroacetone clusters (bottom). Gas phase: $p = 5 \times 10^{-6}$ mbar, $\Delta E \approx 210$ meV; Clusters: mixture 1:20 in Ar, $p = 1.75$ bar, $\Delta E \approx 250$ meV. Some Gaussian fits are added to clarify that the broad feature between 2 and 9 eV most likely consists of several overlapping resonances.

Electron interaction with HFA clusters only leads to the formation of the intact molecular anion (see below) and the ion–molecule complex M·F^- (see Fig. 8).

3.2. Self-scavenging processes in clusters of hexafluoroacetone (HFA)

The formation of a metastable, non-decomposed anion M^- in single HFA via a narrow resonance near 0 eV is well established [8–10,17]. The adiabatic electron affinity of HFA has been derived from ion–molecule reactions involving $O_2{}^-$ to be larger than that of O_2, namely EA (HFA) > 0.44 eV [18]. Single HFA exhibits comparatively weaker DEA resonances located near 4 and 6 eV associated with the formation of the fragment ions F^-, $CF_3{}^-$, (M–F)$^-$ and CF_3CO^- [8,9]. Fig. 8 shows spectra of M^- formation in single TFA (upper panel) and M^- from clusters. The cluster spectrum reveals structures at higher energy which can be assigned to inelastic scattering processes in the target cluster (self-scavenging). Such features are often observed when a strong scavenger for electrons at energies close to 0 eV is present [2].

In a first step the electron is inelastically scattered from one molecule and the slowed down electron is then captured by another molecule of the same cluster which is then stabilized by intracluster collisions. Together with the excitation energy of the neutral it is possible that the final products then consist of the stabilized anion and the completely vaporized target cluster. Since only such scattering events are detected which result in a considerable loss of the initial electron energy the structures in the M^- ion yield hence represent so called threshold electron excitation spectra (TEES). The TEES spectrum mirrors the excited states of neutral HFA including triplet states which are present in that energy region [19]. It is *a priori* not evident whether the inelastic scattering processes proceeds via *direct* or *resonant* scattering. In Fig. 8 (low panel) we present the spectrum of the fragment ion F^- solvated by a neutral HFA molecule ($F^-{\cdot}M$). This complex is formed by the initial DEA reaction generating F^-. Since the scavenging features have appreciable similarity with the $F^-{\cdot}M$ profile, one can assume that DEA resonances contribute to the inelastic scattering processes. More precisely, the involved resonances decay by DEA into F^- competing with autodetachment into the associated electronically excited state of the neutral. The latter process then is responsible for the scavenging features seen on the M^- signal.

Within the comparison of the three different acetones such self-scavenging processes are only observed for HFA. For A and TFA no indication for a similar process was obtained.

4. Conclusions

Acetone is a strong example of a system in which the electron attachment properties dramatically change on going from single molecules to clusters. While single acetone is virtually transparent for electrons below 7 eV clusters of A do capture low energy electrons via a resonance near 0.5 eV. The additional charge triggers remarkably complex chemical reactions involving multiple bond cleavages and the formation of new molecules. In clusters of trifluoroacetone, non-decomposed ionic complexes of the form M_n^- appear which are stabilized by intermolecular collisions. The loss of one and two HF units following low energy attachment is (as for acetone) explained by the formation of new chemical bonds in the ionic system. The hexafluoroacetone parent ion exhibits strong self-scavenging features mirroring the electronically excited state of the neutral molecule.

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