

Chemical reactions in clusters of trifluoroacetic acid (CF₃COOH) triggered by electrons at sub-excitation energy (<2 eV)

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Abstract

Low energy (<2 eV) electron attachment to clusters of trifluoroacetic acid (CF₃COOH) generates a variety of negatively charged complexes. They are formed via intracuster dissociative electron attachment (DEA) leading to solvated fragment ions, and (evaporative) associative electron attachment resulting in non-decomposed cluster ions including the monomer. The most intense signal is observed at 131 amu and is assigned to the ion–molecule complex CF₃COO⁻·H₂O. It is the result of a chemical reaction initiated by the attachment of electrons at an energy of 0.4 eV to the neutral hydrogen bonded dimer. This reaction exhibits a remarkable size selectivity as it is virtually restricted to the dimer. An alternate pathway, namely expulsion of the neutral water molecule from the negatively charged dimer, thereby forming the anhydride of acetic acid, is also observed at comparatively weaker intensity. These assignments are supported by experiments with clusters of deuterated acetic acid (CF₃COOD). Ion yield curves of different anionic complexes are also presented and discussed in relation to previous experiments on DEA to single CF₃COOH molecules [J. Langer, M. Stano, S. Gohlke, V. Voltin, E. Illenberger, *Phys. Chem. Lett.*, in press].

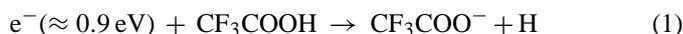
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1. Introduction

Here we present a study of the interaction of low energy electrons with clusters of trifluoroacetic acid (CF₃COOH)_n by means of a crossed beams experiment with mass spectrometric detection of the negatively charged reaction products. CF₃COOH possesses an appreciable dipole moment (2.3 D [1]) and is thereby frequently used as solvent and catalyst for polymerization reactions [2]. The compound can be detected around the globe in soils, plants and waters. It is believed that it is formed from decomposition products of halogenated hydrocarbons [3]. A recent study on low energy electron interaction with single molecules of trifluoroacetic acid [4] identified a shape resonance located near 1 eV and a core excited resonance near 7 eV. The shape resonance was found to decompose into the fragment ions CF₃COO⁻, CF₂COO⁻, and CF₂⁻. While the first ion arises

from a simple bond cleavage



due to the loss of a neutral hydrogen atom with the excess charge remaining on the molecule, the latter two ionic products appear from more complex reaction sequences associated with multiple bond cleavages and formation of new molecules (HF, CO₂) in the corresponding neutral dissociation channel. The core-excited resonance decomposes into F⁻, CF₃⁻, and possibly metastable CO₂⁻.

The present contribution extends the study to clusters of CF₃COOH, which are formed by adiabatic expansion of CF₃COOH molecules seeded in Ar or He. Such an expansion generates a beam of neutral clusters with some size distribution [5,6]. We can expect that among the different sizes and structures the cyclic dimer, bound by two hydrogen bridges, is a representative member within the distribution. The prototype for double hydrogen bonded organic complexes is the formic acid dimer, which has extensively been studied experimentally and theoretically [7–9].

Recent electron attachment experiments to clusters of formic acid [10] have shown that the dehydrogenated dimer anion is

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the dominant mass in the negative ion mass spectrum obtained at an electron energy of 1 eV. In addition, products of various chemical reactions triggered by sub-excitation electrons could be observed. In the present contribution, it is shown that the dominant signal is due to an ion–molecule complex containing a water molecule. The corresponding reaction is initiated by the capture of sub-excitation electrons (≈ 0.4 eV) in the hydrogen bonded dimer target.

2. Experimental

The experiments were carried out in a supersonic molecular beam apparatus, which has been described before [11]. The set up consists of an electron beam generated by a trochoidal electron monochromator [12], which is crossed at right angle with the molecular beam. Ions arising from this interaction are extracted and analyzed with a commercial quadrupole mass spectrometer.

The supersonic beam is formed by adiabatic expansion of CF_3COOH seeded in Ar (mixing ratio 1:30) or in He (mixing ratio 1:100) at stagnation pressures between 0.5 and 1.5 bar through a $50\ \mu\text{m}$ nozzle. The beam then passes a skimmer ($\varnothing = 0.4$ mm), which separates the expansion chamber from the main chamber. The ions are extracted by a small electric field ($< 1\ \text{V cm}^{-1}$), towards the 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.

In the course of the present experiments the energy resolution was ≈ 0.15 – 0.2 eV, the electron energy was calibrated by the well-known standard SF_6^- . The samples CF_3COOH and CF_3COOD were purchased from Sigma–Aldrich (stated purity $> 99\%$), and used as delivered.

3. Results and discussion

3.1. Negative ion mass spectra and associated reactions

Fig. 1 shows a survey of the negative ion mass spectrum (NIMS) obtained from attachment of electrons at 0.3 eV to clusters of CF_3COOH . As already known from the previous gas phase experiments [4], the single molecule exhibits a pronounced shape resonance near 1 eV (the exact location of the dissociative electron attachment (DEA) resonance being dependent on the particular observation channel). In electron attachment to clusters, the maximum of the yield curves of particular negatively charged complexes can be shifted to energies distinctly below 1 eV. This shift will be considered below in connection, which some selected yield curves of ionic products.

As can already be seen from the survey mass spectrum, electron attachment to clusters generates ions at the mass of the monomer (114 amu), the dimer (228 amu), the trimer (342 amu) and the tetramer (456 amu), in Fig. 1 assigned as M_n^- ($n = 1$ – 4), $M = \text{CF}_3\text{COOH}$. A closer inspection of the spectrum at improved mass resolution will reveal that these peaks also contain contributions from the corresponding complexes, subjected to the loss of an H atom (see below). In addition, there are three more

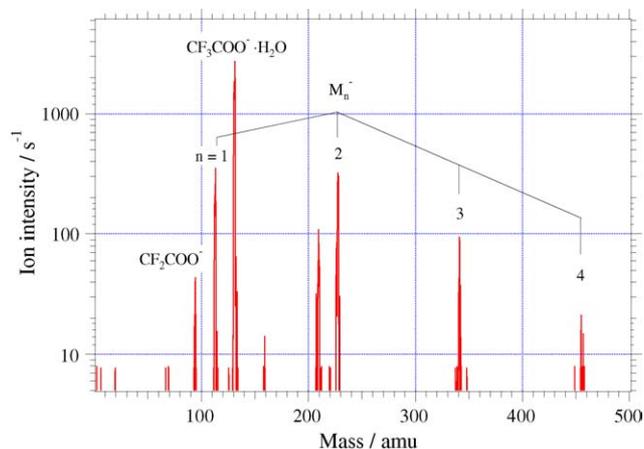


Fig. 1. Survey of the negative ion mass spectrum (NIMS) from an expansion of CF_3COOH seeded in Ar (1:30, stagnation pressure 1 bar) recorded at an electron energy of 0.3 eV. The peaks assigned to M_n^- ($M = \text{CF}_3\text{COOH}$) also contain contributions of the dehydrogenated form $(M-H)^-(M)_{n-1}$ (see the text).

prominent peaks in the NIMS. The signal at 94 amu can be assigned to CF_2COO^- , which is due to HF abstraction from the monomer (also observed from the isolated target molecule [4]). In the present experiment we cannot distinguish whether this ion results from DEA to a monomer travelling in the beam or to a larger cluster. The strong peaks at 131 and 210 amu are due to interesting chemical reactions and will also be discussed below by means of spectra recorded at an improved mass resolution. In electron capture by the isolate molecule [4] only fragment ions were observed, with the most abundant signals at 113 and 94 amu are due to the dehydrogenation reaction (1) and the loss of HF, respectively.

Fig. 2 shows two sections of a NIMS recorded at improved mass resolution indicating that the peaks assigned as M_n^- always contain both the contributions of the non-dissociated anionic complex, M_n^- , and their dehydrogenated form,

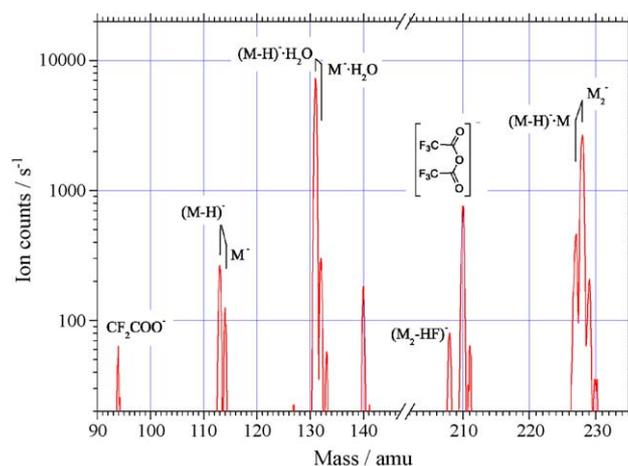


Fig. 2. Two sections of the NIMS recorded at an improved mass resolution. The dominant peak at 131 amu is assigned to the complex $\text{H}_2\text{O}\cdot\text{CF}_3\text{COO}^-$ arising from electron capture by a dimer and the peak at 210 amu is assigned to the acid anhydride anion, formed by expulsion of a neutral H_2O from the dimer anion (see the text).

Table 1
Heats of formation (ΔH_f°) and electron affinities (EA) for compounds relevant for the present DEA reactions [16]

Compound	ΔH_f° (kJmol ⁻¹)	Compound	EA (eV)
CF ₃ COOH	-1031.4	CF ₃	1.8
CHF ₃	-697	CF ₃ COO	4.46 ^a
CF ₃ COO ⁻	-1206*		
HF	-273		
CF ₃	-470		
CF ₂ ⁻	-202 ± 9		

^a Calculated from the reaction enthalpy of the reaction CF₃COOH → H⁺ + CF₃COO⁻ [17].

(M-H)⁻ · (M)_{n-1}. This is shown for the mass range in the vicinity of the monomer and the dimer.

Generally, the dehydrogenated complexes are due to hydrogen loss according to



while their non-decomposed counterparts arise from processes of the form



($m = k + n$) which is called evaporative attachment [14,15]. In this case, a number of k neutral molecules are evaporated from the target cluster thereby stabilizing the remaining ionic complex. The fact that also the monomer anion is observed suggests that CF₃COOH possesses a positive adiabatic electron affinity, while the vertical attachment energy is close to 1 eV. From that and on the basis of the available thermochemical data (Table 1 [4,16–18]) we propose an energetic situation schematically shown in Fig. 3 relevant for the DEA reaction (1) in the isolate molecule. The potential energy curve of the anion in the vicinity of the Franck–Condon region is shown dashed in order to emphasize that this representation is schematic. In reality,

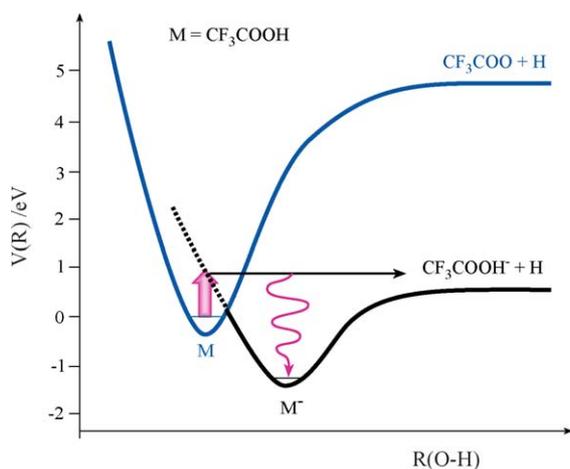


Fig. 3. Schematic representation of the potential energy surface along the O–H coordinate for neutral CF₃COOH and its anion. The anionic curve is shown dashed near the Franck–Condon region indicating that H-abstraction is not considered to proceed directly along a repulsive potential energy curve. The curved arrow symbolises energy dissipation following electron capture in a cluster accessing the ion in its relaxed geometry (see the text).

the reaction may not proceed via direct electronic dissociation along a repulsive potential energy surface. It is rather a pre-dissociation mechanism in which the excess electron is localized in a π^* -type virtual MO (shape resonance) resulting in vibrational excitation of the precursor ion with transfer of the energy into the relevant O–H coordinate. In fact, electron transmission experiments on formic acid [19] revealed a series of more than 12 peaks separated by about 65 meV and assigned to the population of OCO-bending levels (having a separation of 65 meV in neutral HCOOH [16]).

Irrespective of the detailed DEA mechanism, the initial Franck–Condon transition creates the anion considerably *off* its relaxed geometry, and energetically *above* the dissociation limit of reaction (1), which is at 0.45 eV (calculated from the thermochemical values of Table 1). Due to the lack of efficient mechanisms to withdraw energy from the isolated system, the transient negative ion will dissociate (Fig. 3). On the contrary, in a transient anionic cluster, the excess energy can easily be dissipated by evaporation of neutral units, symbolised by the curved arrow in Fig. 3. Otherwise Fig. 3 illustrates the energetic situation for the *isolated* molecule and does include any solvation shifts present in clusters. The contribution of associative (evaporative) attachment increases with the size of the observed complex as already seen for the monomer and dimer in Fig. 2. While the dehydrogenated monomer (113 amu) is more intense than the intact anion M⁻ (114 amu), the non-decomposed dimer (228 amu) is appreciably more intense than its dehydrogenated form at 227 amu. At the quadramer (tetramer) (not shown here) virtually the entire signal is due to the non-dissociated complex M₄⁻. This behaviour simply mirrors the increase of possibilities for energy dissipation with the size of the system. The intensity of signal at 229 amu is 7% of that at 228 and is partly due to the contribution of the ¹³C isotopes (4%) plus possible contributions of reactions not yet identified. One can speculate on various possibilities like formation of CF₃COO⁻ · CF₃H · HCOOH from electron attachment to a larger cluster.

More interesting is the origin of the peak at 131 amu, which is the strongest signal in the low energy NIMS. It corresponds to an ion with the stoichiometric composition C₂F₃H₂O₃⁻ with the likely electronic structures OH⁻ · CF₃COOH or CF₃COO⁻ · H₂O. By considering the underlying energetics [4], it becomes immediately obvious that at energies near 1 eV only the second structure can be generated from electron attachment to CF₃COOH clusters. A corresponding result was obtained in clusters of formic acid (HCOOH) yielding a signal at 63 amu (although at much less intensity), assigned to HCOO⁻ · H₂O. This complex was considered to be the result of a chemical reaction initiated by electron attachment to the formic acid dimer. Along the same line we interpret the complex CF₃COO⁻ · H₂O to arise from electron attachment to (CF₃COOH)₂. In a first approximation the reaction can be pictured to be initiated by hydrogen loss (in analogy to the dominant process in the monomer) in which the hydrogen atom runs into the OH group of the adjacent CF₃COOH molecule thereby forming H₂O (see Fig. 4a). The polar water molecule is then bound to the dehydrogenated anion and detected as the ion–molecule complex CF₃COO⁻ · H₂O in the mass spectrometer. The overall reaction

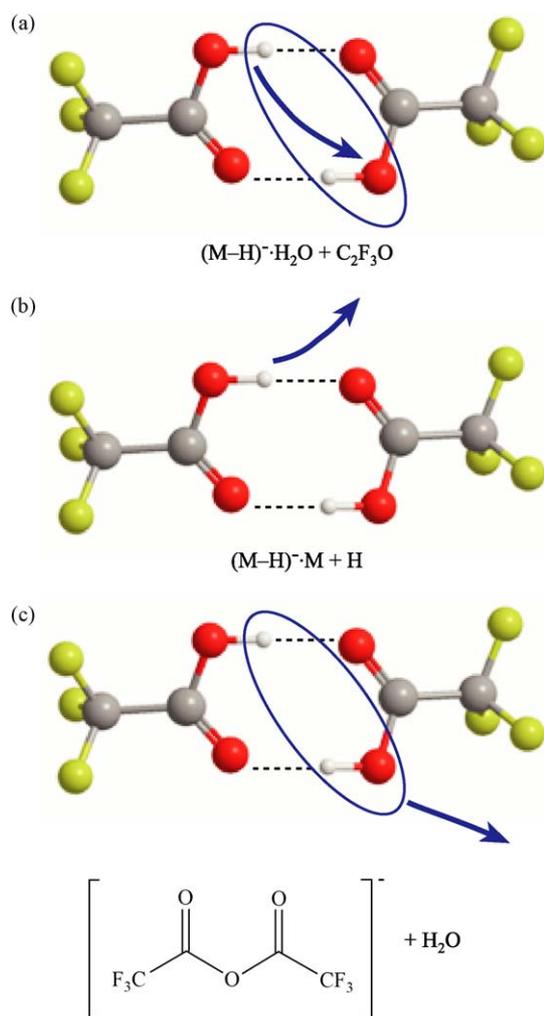


Fig. 4. Cartoon illustrating the main reactions following electron capture by a dimer (a) formation of the complex $H_2O \cdot CF_3COO^-$ (b) loss of hydrogen creating the complex $CF_3COOH \cdot CF_3COO^-$ (c) expulsion of neutral water resulting in the anion of the acid anhydride $(CF_3CO)_2O^-$.

can be expressed as



it is immediately obvious that this reaction is energetically accessible once the neutral hydrogen is cleaved, since the C–OH binding energy ($\approx 390 \text{ kJ mol}^{-1}$) is weaker than the H–OH binding energy (498 kJ mol^{-1}) [1]. In actual practice, the peak of the ion yield curve associated with this chemical reaction (131 amu) is located at even lower energy than the DEA reaction associated with dehydrogenation (1), see also below. We note that this is probably an oversimplified and mechanistic picture based on the reaction in an isolated molecule, not taking into account possible new electronic states which may appear in the relevant energy range ($<1 \text{ eV}$) when the two molecules are coupled via the two hydrogen bridges [13].

The alternate route is dehydrogenation with the neutral H atom leaving the cluster unit (Fig. 4b) according to



giving rise to the signal at 227 amu.

One point remains worth to be emphasised: Generation of water is exclusively seen on the product $CF_3COO^- \cdot H_2O$, while complexes of the form $CF_3COO^- \cdot M_n \cdot H_2O$ $n > 0$ are not observed. This strongly suggests that the reaction is mainly initiated in dimers, in analogy to the system formic acid [4]. The conclusion then is, that in a larger cluster, energy dissipation suppresses water formation. This suppression may not be *complete* as the signal at 132 amu contains contributions from $CF_3COOH \cdot H_2O$, which can only arise from a reaction initiated in a larger cluster. This contribution, however, is very small since the signal at 132 amu is about 4% of that at 131 amu and also contains the ^{13}C isotopes from $CF_3COO^- \cdot H_2O$ (2%). From that we can conclude that water formation is virtually restricted to the dimer and hence exhibits a remarkable *size selectivity*.

From the mass spectrum it can be seen that within the alternate routes illustrated in Fig. 4a and b the reaction leading to $CF_3COO^- \cdot H_2O$ is considerably more intense than that leading to $CF_3COO^- \cdot CF_3COOH$. This strongly contrasts the situation in the system formic acid in which the compound $HCOO^- \cdot H_2O$ was by more than one order of magnitude less intense than $HCOO^- \cdot HCOOH$. One can speculate why the signal from $CF_3COO^- \cdot H_2O$ is the most intense within the low energy NIMS since for the underlying reaction (formation of H_2O in the dimer) one expects an appreciable activation energy. On the other hand, one can suppose that the binding energy of the complex $CF_3COO^- \cdot H_2O$ is larger than in $HCOO^- \cdot H_2O$, (owing to the large dipole moment of CF_3COOH (2.3 D) [1] and the large electron affinity of CF_3COO^- (4.46 eV) [17], which thermodynamically favours its formation within the complex.

The signal at 210 amu can be assigned to the loss of a water molecule (H_2O) from the dimer anion. The resulting anion is likely to represent the anhydride of trifluoroacetic acid $[(CF_3CO)_2O]^-$. Its formation can be viewed as an additional pathway following water formation (Fig. 4c). In this case the water molecule is expelled from the transitory complex with the anion rearranging to the anhydride. Finally, the 208 amu signal can be assigned to the dimer anion, subjected to the loss of HF while the signal at 140 amu remains to be interpreted; a possible structure is $(CHF_3)_2^-$. Such a signal is not observed when the deuterated compound is expanded.

3.2. Negative ion mass spectra from $(CF_3COOD)_n$

Additional experiments on the deuterated compound CF_3COOD were performed in order to confirm that the complex $CF_3COO^- \cdot H_2O$ is in fact due to a reaction in the dimer and not an artefact, e.g., arising from some pick-up of water from the background gas in the expansion zone of the molecular beam, or contamination of the sample by water. However, in using deuterated compounds one is faced to the problem that by passing the deuterated sample through the gas inlet system, it is effectively transformed into the non-deuterated analogue due to H–D exchange by collisions with hydrocarbons sticking at the walls. This problem can be reduced by applying a series of *fill*

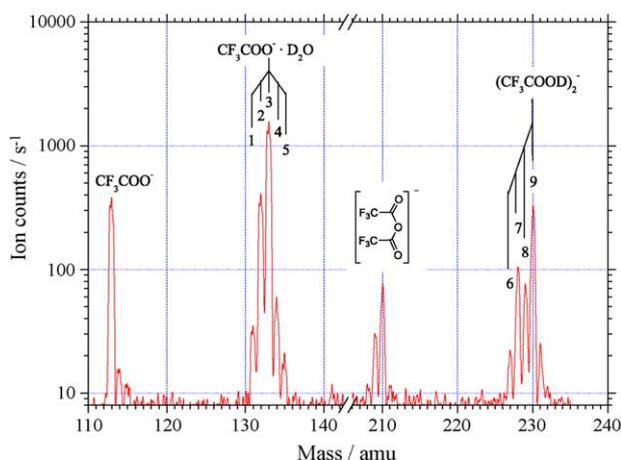


Fig. 5. Two sections of the NIMS from an expansion of deuterated acetic acid (CF_3COOD) seeded in He (1:100). The dominant peak at 133 amu is assigned to the complex $\text{D}_2\text{O}\cdot\text{CF}_3\text{COO}^-$.

and pump out cycles during which the walls will increasingly be covered with the deuterated compound.

Fig. 5 shows two sections of the negative ion mass spectrum in the vicinity of the water containing complex (131 amu) and in the vicinity of the dimer (228 amu). The series of five peaks in the range 131–135 enumerated from 1 to 5 can be assigned to complexes containing a water molecule attached to the dehydrogenated ion or the parent anion and their respective deuterated forms. The small signal at 131 amu (1) can unambiguously be assigned to $\text{CF}_3\text{COO}^- \cdot \text{H}_2\text{O}$. By just comparing the signal intensity of $\text{CF}_3\text{COO}^- \cdot \text{H}_2\text{O}$ between Figs. 2 and 4 it becomes obvious that in these experiments the deuterated compound was present in the beam in considerable excess (over the non-deuterated). The signal at 135 amu (5) contains the ^{13}C isotopes of 134 amu (2%) and additionally $\text{CF}_3\text{COOD}^- \cdot \text{D}_2\text{O}$. The dominant signal at 133 amu (3) virtually consists of $\text{CF}_3\text{COO}^- \cdot \text{D}_2\text{O}$ (with some minor contributions from $\text{CF}_3\text{COOH}^- \cdot \text{HDO}$ and possibly $\text{CF}_3\text{COOD}^- \cdot \text{H}_2\text{O}$). From that we conclude that water is in fact formed in a chemical reaction, following electron attachment to the dimer.

Following the discussion from above the series of peaks ranging from 227 amu (6) to 230 amu (9) can be assigned to the dimer anion and its dehydrogenated form in the different H/D combinations. The signal at 227 amu (6) can unambiguously be assigned to $\text{CF}_3\text{COO}^- \cdot \text{CF}_3\text{COOH}$, and the dominant signal at 230 amu (9) to the deuterated dimer anion $(\text{CF}_3\text{COOD})_2^-$ while the two peaks between contain the different isotopic combinations, namely at 228 amu (7) a mixture of $\text{CF}_3\text{COO}^- \cdot \text{CF}_3\text{COOD}$ and $(\text{CF}_3\text{COOH})_2$, and at 229 (8) amu the non-decomposed dimer $(\text{CF}_3\text{COOH}\cdot\text{CF}_3\text{COOD})^-$. The small signal at 231 amu is only about 5% of that at 230 amu and can mainly be attributed to the ^{13}C isotope with a relative abundance of 4%.

As above, the signal at 210 amu can be assigned to the loss of a water molecule (in the present case D_2O , HDO and H_2O) from the dimer anion (with its different isotopes). Accordingly, the peak at 209 amu can be assigned as $\text{CF}_2\text{COO}^- \cdot \text{CF}_3\text{COOD}$, which formally is formed by the abstraction of DF from the deuterated dimer.

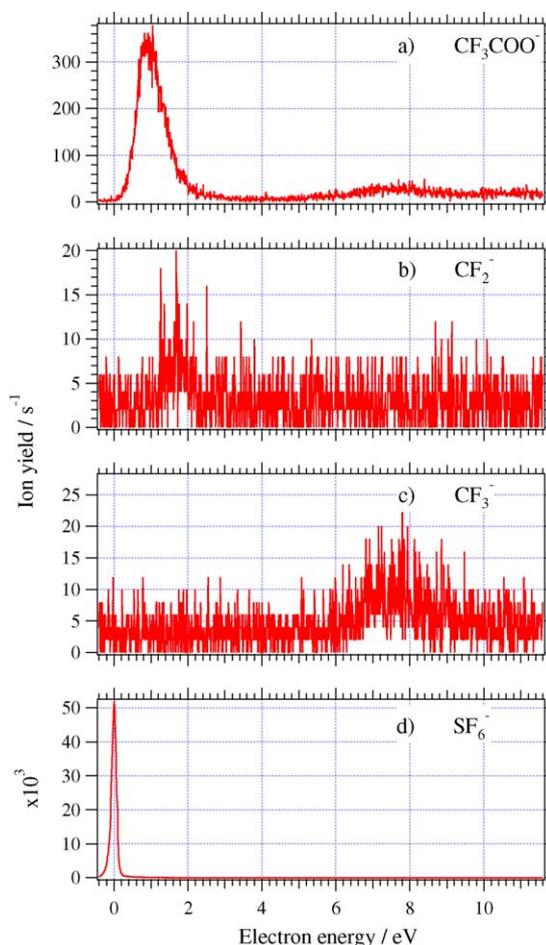


Fig. 6. Yield curves of selected fragment ions arising from electron attachment to a cluster beam off CF_3COOH .

3.3. Ion yield curves

We finally present some ion yield curves of a few selected product ions obtained from electron attachment to clusters of CF_3COOH . Fig. 6 shows fragment anions, which arise from either electron capture by clusters or by monomers, which may also be present in the molecular beam. Also shown is the SF_6^- signal, which reflects the energy resolution and serves to calibrate the electron energy scale.

The obvious difference to the results obtained from single CF_3COOH molecules is manifested in a strong change in the relative intensity for some ions. While the intensity ratio $\text{CF}_3\text{COO}^- : \text{CF}_2^-$ is about 2:1 in isolate CF_3COOH , it is about 50:1 in clusters. Along the same line, the ions CF_3COO^- (H loss) and CF_2COO^- (HF loss) appear at approximately the same intensity from the isolate molecule, while CF_2COO^- (not shown here) is strongly suppressed from clusters. This behaviour indicates that: (i) complex reactions connected with some rearrangement in the precursor ion are considerably suppressed in clusters (due to effective intermolecular energy transfer) and (ii) the abundance of monomers in the beam must be very low, if they are present at all. Fig. 6 also shows the yield of CF_3^- appearing at higher energy via

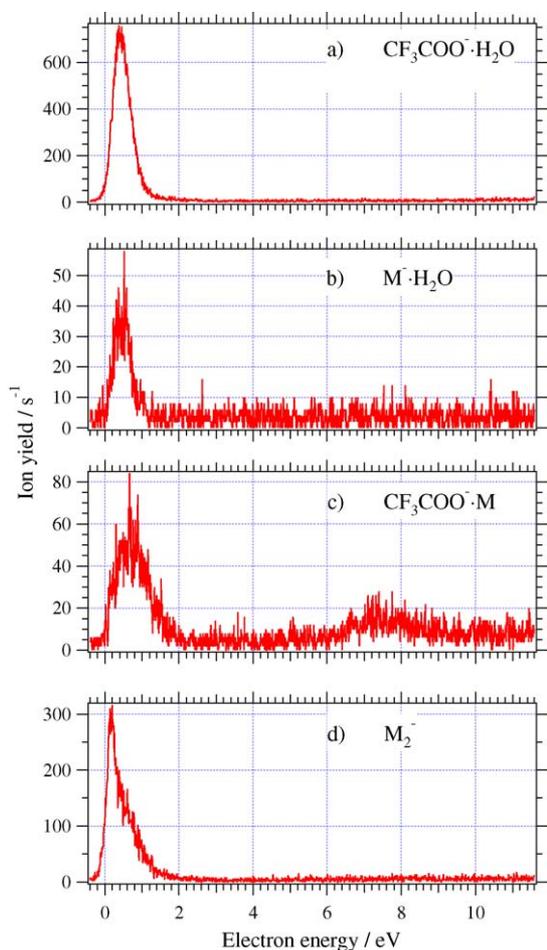


Fig. 7. Yield curves of selected anionic complexes arising from electron attachment to a cluster beam of CF_3COOH .

a core-excited resonance (similar to the situation in the isolate molecule).

A further interesting point concerns the additional appearance of CF_3COO^- in the vicinity of the core-excited resonance (Fig. 6a), which is not the case in the isolated molecule. In the present experiment we a priori cannot distinguish whether it is a direct product of DEA from the core-excited resonance (modified to some extent in the cluster) or from an inelastic scattering effect in the target cluster. In the latter case the fast electron would undergo inelastic electron scattering from one molecule (leaving it in an electronically excited state) and the slowed down electron is subsequently captured by a second molecule of the same cluster subjected to DEA, reaction (1). For strong electron scavenging molecules, such features can directly mirror a so-called threshold electron excitation spectrum (TEES) [14,19].

Fig. 7 presents some ion yields of products, which necessarily arise from an attachment event to a cluster. The yield of the complex consisting of water attached to the dehydrogenated ion, $\text{CF}_3\text{COO}^- \cdot \text{H}_2\text{O}$ peaks at 0.4 eV and is hence shifted to lower energy with respect to that of CF_3COO^- .

Such a shift principally reflects the effect of solvation for an ion coupled to neighbouring molecules. Strictly speaking,

the initial Franck–Condon transition creating the cluster anion is subjected to some solvation shift with respect to the isolated molecule. The ion yield of a particular product then reflects the initial transition, which is weighted by the energy dependent decomposition probability into the particular ion under observation. From that, the shift of the $\text{H}_2\text{O} \cdot \text{CF}_3\text{COO}^-$ yield maximum to lower energy is contra-intuitive since H_2O formation should be subjected to an appreciable activation energy and one would consequently expect the probability for its formation to be shifted to the higher side of the resonance.

At that point, however, we again emphasise that electron attachment to the present system may no longer appropriately be described on a molecular site, i.e. localisation of the excess electron on an individual molecule which is coupled to its environment. Such a picture is often appropriate for molecular van der Waals clusters [14], while in the present system a stronger coupling via hydrogen bonds is present. Although the resonance positions observed from clusters do not substantially differ from those observed from isolate molecules, recent scattering calculations by Gianturco et al. on the hydrogen bridged formic acid dimer [13] indicated the appearance of additional resonances in which the density of the excess charge is distributed over the entire dimer. One can then speculate on the existence of low lying potential energy surfaces connected to the product $\text{CF}_3\text{COO}^- \cdot \text{H}_2\text{O}$.

A comparison between the ion yield of $\text{CF}_3\text{COO}^- \cdot \text{M}$, and M_2^- , again shows that the non-decomposed dimer is considerably more intense than its dehydrogenated form, with the peak of the ion yield as low as 0.2 eV. It is a signature of the considerable solvation shift and indicates an appreciable stability of the dimer anion.

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