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Low energy (0–10 eV) electron driven reactions in the halogenated organic acids CCl₃COOH, CClF₂COOH, and CF₃CHNH₂COOH (trifluoroalanine)

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Negative ion formation following resonant electron attachment to the three title molecules is studied by means of a beam experiment with mass spectrometric detection of the anions. All three molecules exhibit a pronounced resonance in the energy range around 1 eV which decomposes by the loss of a neutral hydrogen atom thereby generating the closed shell anion (M–H)⁻ (or RCOO⁻), a reaction which is also a common feature in the non-substituted organic acids. The two chlorine containing molecules CCl₃COOH and CClF₂COOH exhibit an additional strong and narrow resonance at very low energy (close to 0 eV) which decomposes by the cleavage of the C–Cl bond with the excess charge finally localised on either of the two fragments Cl⁻ and (M–Cl)⁻. This reaction is by two to three orders of magnitude more effective than hydrogen loss. Apart from these direct bond cleavages (C–Cl, O–H) resonant attachment of subexcitation electrons trigger additional remarkably complex unimolecular decompositions leading, e.g., to the formation of the bihalide ions ClHCl⁻ and ClHF⁻ from CCl₃COOH and CClF₂COOH, respectively, or the loss of a neutral CF₂ unit from trifluoroalanine thereby generating the fluoroglycine radical anion. These reactions require substantial rearrangement in the transitory negative ion, i.e., the cleavage of different bonds and formation of new bonds. F⁻ from both chlorodifluoroacetic acid and trifluoroalanine is formed at comparatively low intensity (more than three orders of magnitude less than Cl⁻ from the chlorine containing molecules) and predominantly within a broad resonant feature around 7–8 eV characterised as core excited resonance. © *2011 American Institute of Physics*. [doi:10.1063/1.3641479]

I. INTRODUCTION

In organic acids,[1–3] including the amino acids,[4–6] a common feature in electron attachment is the formation of a low energy resonance which decomposes by the loss of a neutral hydrogen atom thereby generating the closed shell anion (M–H)⁻. This dissociative electron attachment (DEA) reaction is characterised by a pronounced resonance at subexcitation energies peaking between 1.0 eV and 1.5 eV. In the case of formic acid, isotope labelling demonstrated that H loss exclusively originates from the OH site.[3] Hydrogen loss triggered by subexcitation electrons is also observed in the DNA bases[7–11] and it thus appears that this low energy DEA process is common to many biologically relevant molecules. In thymine isotope labelling revealed that H loss exclusively takes place at the N-sites.[8]

Electron driven reactions are considered as important initial and decisive steps in the molecular description of radiation damage.[12,13] When high energy radiation (particles or photons) interact with a biological medium it is not the *primary* interaction of the high energy quanta which causes damage but rather a variety of reactive intermediates formed within nanoscopic volumes along the energy track. Due to energy and momentum conservation a high energy photon will in the first step remove electrons within the molecular network of the cell components thus leading to various ionisation/dissociation channels which are indeed responsible for the production of damaging radicals. Such radicals can in turn act on the cell material, thereby becoming the primary cause of cell apoptosis processes.[14] At the same time the primary photon impact produces a great deal of secondary electrons having initial energies in the range of a few tens of eV.[15] These ballistic electrons are quickly slowed down by inelastic scattering events (including further ionisation processes) until they become bound as solvated electrons, then as chemically rather inactive species.

While in gas phase amino acids, these low energy resonances exclusively decompose by hydrogen loss generating the closed shell anion RCOO⁻, the situation changes substantially on going to the halogenated analogues as has recently been demonstrated in the case of CF₃COOH (Ref. 16) and CClF₂COOH.[17,18] Due to the considerable electron affinities of the halogen atoms low energy DEA reactions leading to X⁻ (X = halogen atom) and the corresponding radical become energetically available.

In this contribution we present a comparative study on DEA to the three halogenated organic acids trichloroacetic acid (CCl₃COOH), chlorodifluoroacetic acid (CClF₂COOH) and trifluoroalanine (CF₃CHNH₂COOH). Negative ion formation in gas phase and condensed phase from CClF₂COOH has been studied very recently.[17,18] A few of these results will be quoted and shown for comparison. The experiments show that apart from the direct DEA reactions generating X⁻ and

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the corresponding neutral radical, subexcitation electrons trigger remarkably complex unimolecular reactions, e.g., the formation of the bihalide ion (ClHCl)$^-$ from CCl_3COOH and (ClHF)$^-$ from $CClF_2COOH$ (not reported previously[17, 18]).

II. EXPERIMENTAL

The DEA experiments were carried out by means of a crossed electron-molecular beams apparatus that has already been described in detail elsewhere.[19] In brief, an incident electron beam of well-defined energy (FWHM $\approx$ 0.2 eV, electron current $\approx$ 10 nA) generated from a trochoidal electron monochromator[20] orthogonally intersects with an effusive molecular beam containing the respective target molecule. Under ambient temperatures, the samples are solid (trichloroacetic acid and trfifluoroalanine) or near the transition between solid and liquid (chlorodifluoroacetic acid, melting temperature 22 °C) so that the material was directly deposited into a small vessel inside the vacuum system. The vessel itself is directly connected with the reaction zone by a capillary. The overall system can be heated by two *in vacuo* halogen bulbs to temperatures which are sufficient to generate an effusive molecular beam of the respective target molecule emanating from the capillary. During the experiments the pressure reading by means of an ionisation gauge mounted at one of the flanges was in the range of 10^{-6} mbar, the background pressure in the UHV system (no sample) is in the 10^{-8} mbar range.

Negative ions formed in electron-molecule collisions are extracted from the reaction volume towards a quadrupole mass analyser, and are detected by a single pulse counting technique The intensity of a particular anion as a function of the incident electron energy (assigned as the ion yield function or relative cross section curve) is then recorded. The electron energy scale is calibrated by measuring the formation of SF_6^- ions, which exhibits a sharp peak of known cross section located near 0 eV. The samples were obtained from Sigma Aldrich at a stated purity of 98% ($CClF_2COOH$ and CF_3CHNH_2COOH) and 99% (CCl_3COOH) and used as delivered.

III. RESULTS AND DISCUSSION

Figures 1–6 present yields of fragment ions obtained from the three halogenated acids. A detailed study on electron attachment to $CClF_2COOH$ has previously been published[17, 18] and we hence present just for comparison only the ion yields arising from the cleavage of the C–X (X = Cl, F) bond. The count rates are given in absolute numbers under the corresponding experimental conditions indicated in the figure captions. Within the present experimental conditions (pumping speed, geometry of the collision area) the pressure directly in the collision zone can be estimated to be two to three orders of magnitude higher than the pressure reading at the gauge. The experiments are hence operated safely within single collision conditions.

Among the three halogenated molecules only $CClF_2COOH$ does form a long-lived non-decomposed parent radical anion $CClF_2COOH^-$. As discussed previously,[17] it is
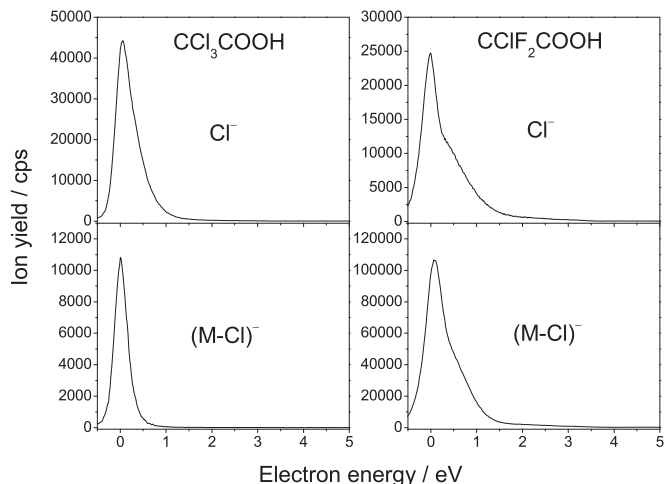

FIG. 1. Relative cross section curves for the complementary ions Cl$^-$ and (M–Cl)$^-$ from chlorodifluoroacetic acid and trichloroacetic acid (partly adapted from Ref. 17).

formed within a resonance peaking at 0.75 eV which is quite unusual as metastable non-decomposed parent radical anions are usually formed (if at all) within a narrow resonance at energies close to zero energy.[19]

In the following, we shall present the ion yields due to dissociative electron attachment (DEA) to the three compounds first comparing common reactions like the direct cleavage of the C–Cl bond or loss of a neutral hydrogen atom before considering some specific DEA reactions.
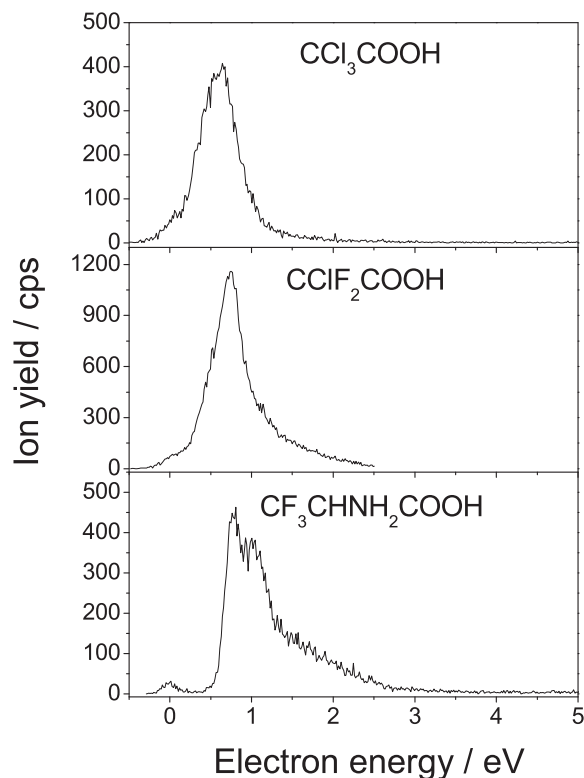

FIG. 2. Relative cross section curves for the DEA reaction resulting in the loss of a neutral hydrogen atom thereby generating the closed shell anions (M–H)$^-$ or RCOO$^-$.
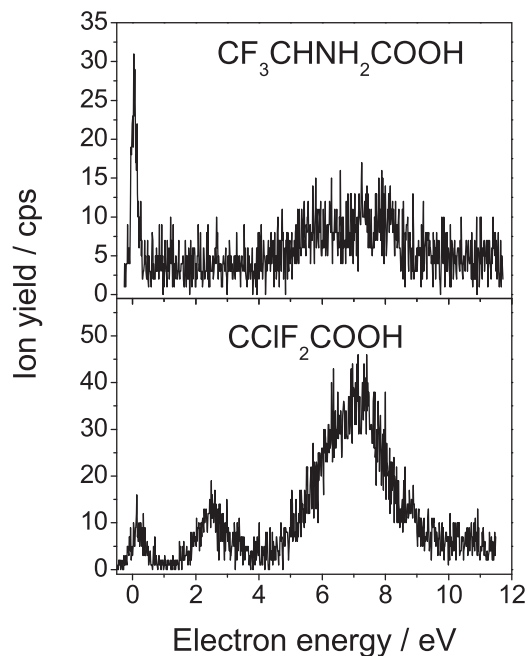
FIG. 3. Relative cross section curves for the formation of F⁻ from trifluoroalanine and chlorodiflouroacetic acid. The narrow peak close zero is not a product of DEA to the corresponding ground state molecule but due to a very small impurity present in the reaction volume (possibly from thermal decomposition at the hot filament, see the text).
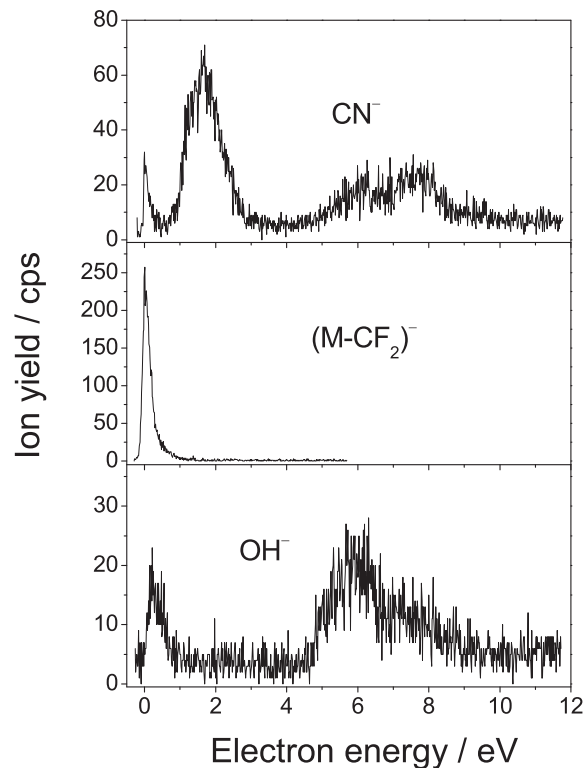

FIG. 5. Relative cross sections for the formation of CN⁻, the ion arising from the loss of a neutral CF₂ unit ((M-CF₂)⁻), and OH⁻ from trifluoroalanine. (M-CF₂)⁻ is assigned as the fluoroglycine radical anion.
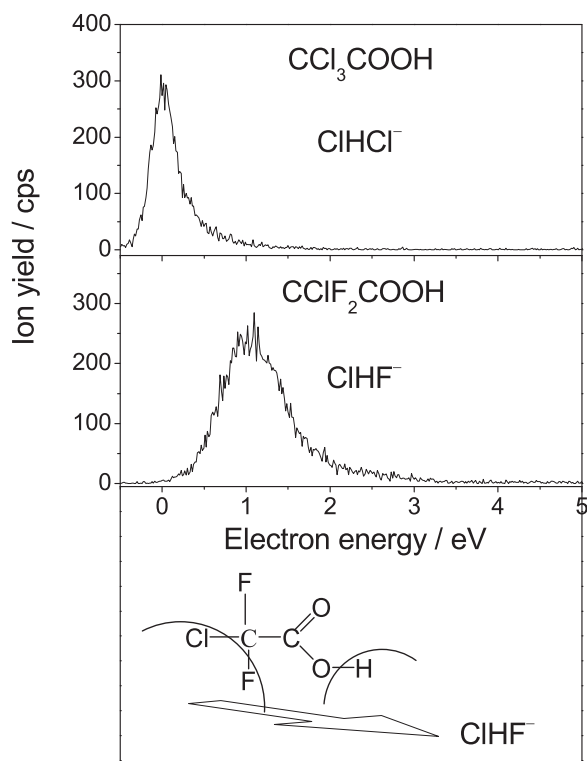
FIG. 4. Relative cross section for the formation of the bihalide ion ClHCl⁻ from trichloroacetic acid (top) and ClHF⁻ from chlorodifluoroacetic acid (centre). Bottom: Cartoon illustrating the formation of ClHF⁻ from chlorodifluoroacetic acid.

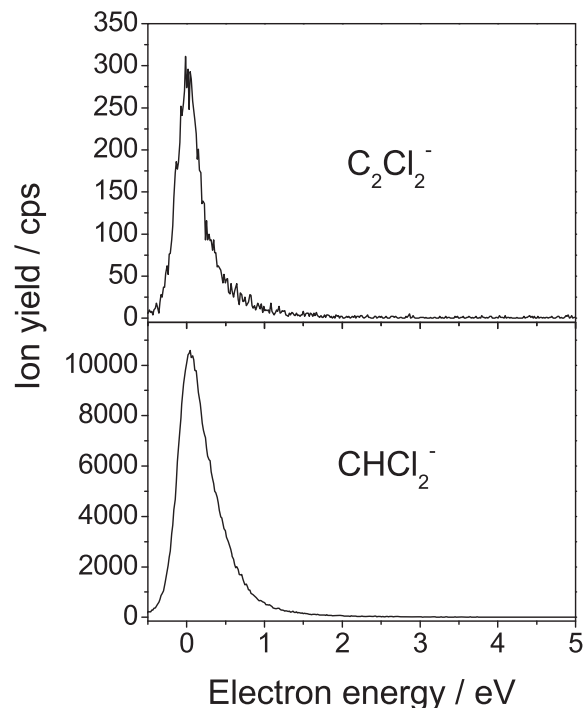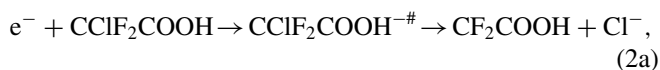FIG. 6. Relative cross sections for the formation of C₂Cl₂⁻ and CHCl₂⁻ from trichloroacetic acid. C₂Cl₂⁻ is considered to have the vinylidene structure and CHCl₂⁻ is the closed shell dichlorovinyl anion (see the text).

A. Cleavage of the C–Cl bond

Figure 1 shows the reaction products arising from the cleavage of the C–Cl bond in the two Cl-containing compounds with the excess charge localised on either of fragments Cl$^-$ and (M–Cl)$^-$ according to the DEA reactions

$$e^- + CCl_3COOH \rightarrow CCl_3COOH^{-\#} \rightarrow CCl_2COOH + Cl^-,$$
(1a)

$$e^- + CCl_3COOH \rightarrow CCl_3COOH^{-\#} \rightarrow CCl_2COOH^- + Cl,$$
(1b)

$$e^- + CClF_2COOH \rightarrow CClF_2COOH^{-\#} \rightarrow CF_2COOH + Cl^-,$$
(2a)

$$e^- + CClF_2COOH \rightarrow CClF_2COOH^{-\#} \rightarrow CF_2COOH^- + Cl,$$
(2b)

where CCl$_3$COOH$^{-\#}$ and CClF$_2$COOH$^{-\#}$ assign the transient negative ions (TNI) formed in the first step of electron attachment to the corresponding neutral molecule.

As expected, the presence of one or more chlorine atoms results in a situation that the total cross section for DEA is considerably increased (compared to acetic acid) and that most of the intensity is channelled into the fragment ions arising from the cleavage of the C–Cl bond. Also, the total intensity increases with the number of Cl atoms. The DEA reaction leading to the loss of a neutral hydrogen atom (the dominant DEA reaction in acetic acid[2]) is also an effective reaction in the haloacids (see Fig. 2) but more than two orders of magnitude less intense than the products arising from the cleavage of the C–Cl bond.

Within the two complementary reactions in CCl$_3$COOH, the Cl$^-$ signal (process (1a)) is considerably more intense than its complement (M–Cl)$^-$ (1b) while it is the other way round in CClF$_2$COOH which is presumably a consequence of the different energetic situation.

The thermodynamic threshold for a DEA reaction associated with the cleavage of the C–Cl bond is given by the value of the C–Cl bond enthalpy (D(C–Cl)) minus the electron affinity of the fragment, on which the excess charge becomes localised. The fact that from both compounds Cl$^-$ is observed already directly at threshold (near zero energy) indicates that D(C–Cl) equals or is lower than the electron affinity of Cl (3.60 eV (Ref. 21)). Accordingly, from the fact that the ion (M–Cl)$^-$ from both molecules is also observed already at threshold it follows that the electron affinity of the corresponding radicals (M-X) must be equal or exceed the C–Cl binding enthalpy, but there are no explicit values available so far. The different relative intensities between X$^-$ and (M-X)$^-$ among the two target molecules CCl$_3$COOH and CClF$_2$COOH may then be based on the different energetics, i.e., reaction (1a) is more favourable than (1b) and (2b) more favourable than (2a).

B. Loss of a neutral hydrogen atom, cleavage of the C–F bond and character of the resonances involved in DEA

Figure 2 shows formation of the closed shell anion (M–H)$^-$ arising from the loss of a neutral hydrogen atom which is observed in all three compounds as an appreciably effective reaction. As mentioned above, in the (non-halogenated) organic acids hydrogen loss is the only DEA reaction operative at subexcitation energies. In the halogenated acids studied here, although an effective reaction, it is considerably weaker than those associated with cleavage of the C–Cl bond as obvious from Fig. 1. Figure 3 presents the ion yields of F$^-$ from the two fluorine containing compounds indicating that from both molecules the F$^-$ ion intensity is surprisingly weak and also the complementary ion (M-F)$^-$ is not observed within the detection limit of the present experiment.

We can assume that hydrogen loss takes place at the O–H site thereby generating the RCOO$^-$ anion (which is obvious for CCl$_3$COOH and CClF$_2$COOH) but not in CF$_3$CHNH$_2$COOH. While this assumption might be intuitive from a chemical point of view (considering reactions in a liquid environment) it is not *a priori* obvious for a gas phase reaction as the O–H bond dissociation enthalpy may even be higher than that of C-H as can be shown by using the relevant thermochemical data in the case of the simplest organic acid (HCOOH).[21–23] On the other hand, the anion HCOO$^-$ is considerably more stable than COOH$^-$ so that the overall DEA reaction *via* cleavage of the O–H bond is energetically more favourable.

For the description of H loss from formic acid (and other organic acids) there is not yet complete consensus on the underlying mechanism. In a theoretical study,[24] the DEA process has been attributed to initial electron attachment into the COOH π^* MO followed by out-of-plane distortions thereby coupling the π^* MO to the σ^* MO ultimately generating HCOO$^-$ + H. In contrast to that, in a recent R-matrix study[25] the DEA cross section curves were explicitly calculated for both formic acid and glycine using a one-dimensional model invoking a single σ^* valence anion state in which the excess electron is largely localised on the O–H bond. Surprisingly good agreement with the experimental results could be obtained by taking some kind of extreme properties of the σ^* state, namely a resonance energy of 5.5 eV and a width of 5.8 eV. Structures in the experimental cross section appear as cusps and steps in the calculated cross section at the vibrational excitation thresholds in good agreement with the experimental results which strongly supports the σ^* resonance model. It should further be noted that the isotope labelling experiments mentioned above[3] do not indicate any hydrogen scrambling in the TNI which further supports the picture of a direct decomposition along a repulsive surface rather than an indirect reaction involving the π^* resonance and coupling to the σ^* state.

Within the present molecules only the (M–H)$^-$ signal from trifluoroalanine indicates pronounced and clearly reproducible structures (Fig. 2, bottom). In the spirit of the previous study to formic acide and glycine[25] the peak at 0.8 eV and the structures near 1.0 and 1.7 eV can be interpreted as cusps arising from the onsets of the v = 2, 3, and 4 vibrational excitation of the O–H stretch. The (M–H)$^-$ cross section curves from the other compounds apparently do not show such pronounced structures.

Formation of F$^-$ from the two fluorine containing compounds is surprisingly weak (Fig. 3) and occurs mainly at

considerably higher energies. The thermodynamic threshold for F^- formation can be estimated to be located at the range 0.6–1.6 eV on the basis of typical C–F bond dissociation enthalpies (4–5 eV (Refs. [21] and [26])) and the well established electron affinity of F (3.4 eV (Ref. [21])). The narrow peak near zero energy can hence not arise from DEA to the corresponding ground state molecules. At that point it must be noted that electron attachment experiments in the range close to zero energy are particularly delicate as different phenomena and mechanisms (in addition to DEA) may contribute to (more or less intense) negative ion signals. Possible scenarios are negligibly small impurities of the sample or electron attachment to vibrationally excited neutral molecules. Such *hot band* transitions are well known in spectroscopy and seen as very weak features reflecting the Boltzmann-like population of excited levels.[27] However, due to the reciprocal energy dependence of the attachment cross section, such hot band transition can be quite intense in DEA.[28,29] For the present molecules the likely scenario is a spurious impurity in the reaction volume arising from some thermal decomposition of the respective sample molecule at the hot filament generating F_2 or FCl. Negligibly small amounts of these products may reach the reaction volume thereby generating a noticeably F^- signal close to zero energy due to the strongly increasing attachment cross section towards low energies (*vide supra*).

The F^- yield from both fluorinated compounds extends over a broad resonance located near 8 eV while a weaker feature near 2.5 eV is clearly present in $CClF_2COOH$ but barely visible in trifluoro-alanine. We can assume that this low energy feature is due to a $\sigma*$ resonance with antibonding (C–F) character, while the broad structure in the energy range between 4 and 10 eV is composed of core excited resonances (two electrons in normally unoccupied MOs and a hole in one of the usually occupied MOs) with possible contributions of higher energy shape resonances.

Although F possesses an appreciable electron affinity and the thermodynamic threshold for F^- formation is in the range between 0.6 and 1.6 eV, the ion intensity is remarkably low in comparison to Cl^- (and the complementary ions $(M–Cl)^-$). This fact is a consequence of the considerably lower polarizability of F (0.55 a_o^3) as compared to Cl (2.4 a_o^3).[21] The polarizability is, besides the electron energy, the essential quantity which determines the absolute value of the electron attachment cross section.[30,31] For the corresponding atom or subunit bound within a molecule it then reflects the ability of this component *within* the molecule to accommodate extra charge. Thus in halogenated molecules, the ability to accommodate extra charge increases on going down row 7 of the periodic table which is also well established by the general behaviour of the DEA cross section in halogenated compounds.[32]

From Fig. [3] it is also obvious that the F^- intensity is larger at the broad resonance around 8 eV while the feature near 2.5 eV is less intense. This is contrary to the energy dependence of the electron attachment cross section which is expected to increase with decreasing electron energy. Such a behaviour indicates that the low energy $\sigma*$ shape resonance near 2.5 eV is subjected to a relatively stronger autodetachment, thereby suppressing the formation of fragment F^- ions.

A similar situation has previously been observed and analysed in CF_3Cl.[33,34]

C. Formation of the bihalide ions (ClHF)⁻ and (ClHCl)⁻

Figure [4] shows the relative cross section curve for the formation of $ClHF^-$ from $CClF_2COOH$ (not reported in the previous study on electron attachment to $CClF_2COOH$ (Refs. [17] and [18])) and $ClHCl^-$ from CCl_3COOH. The bihalide ions XHY^- are well known as hydrogen bonded ionic complexes possessing a considerable stability with respect to both the bond dissociation energy and in particular the binding energy of the extra electron. Detachment of the extra electron creates the corresponding neutral $XHY^\#$ which is a thermodynamically unstable state and which can be regarded as the transition state for the hydrogen transfer reaction

$$X + HY \rightarrow (XHY)^\# \rightarrow XH + Y. \qquad (3)$$
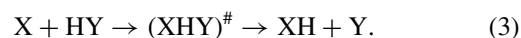
Photodetachment from the thermodynamically stable anions has been considered as a so called *transition state spectroscopy* by which the properties of the transition state $XHY^\#$ (energy, structure, lifetime, etc.) could directly be accessed. Experiments have been performed not only in isolated gas phase compounds but also in clusters.[35–37]

From Fig. [4], it can be seen that the bichloride ion $ClHCl^-$ appears within a very narrow resonance close to zero eV while the $ClHF^-$ ion is generated at higher energy with the cross section curve peaking near 1 eV. We mention that the ion $(FHF)^-$ could not be detected from trifluoroalanine within the detection limit of the present experiment. The formation of both bihalide ions from the corresponding organic acids is a surprisingly complex reaction as the O–H and two C–X bonds must concomitantly be cleaved with reorganisation to $(XHY)^-$ with the excess charge finally localised on the bihalide as illustrated in the cartoon on Fig. [4] (bottom). From the present experiments we have no information on the molecular structure of neutral counterparts but one can assume that at the correspondingly low electron energy one radical of the structure CClCOO and CFCOO, respectively, is formed. With the exceedingly large electron affinity (4.9 eV for ClHCl) and the low value for the standard heat of formation (ΔH_f° $(ClHCl)^- < -5.4$ eV)[21] one can estimate that such a reaction is indeed thermodynamically accessible at subexcitation energies. One would, however, expect some appreciable activation energy (three bonds have to be cleaved prior to the formation of $ClHCl^-$ or $ClHF^-$) so that the comparatively high intensity of both ions is a rather unexpected observation. In the case of $(ClHCl)^-$ it is likely that the low energy shape resonance having $\sigma*$(C–Cl) character is the precursor. Apart from the dominant decomposition processes (cleavage of the C–Cl bond), the anionic potential energy surface may also possess further gradients (in addition to that along the C–Cl axis) thereby triggering substantial rearrangement in the TNI which finally leads to $ClHCl^-$. In the previous study on $CClF_2COOH$,[17] a resonance near 1 eV was identified not only decomposing into a variety of negative ions $((M–HF)^-$, CF_2^-, $(M-CF_2)^-$ and $CHFCl^-$) but also leading to the formation of

the long lived-non decomposed parent anion M$^-$. An additional decomposition pathway of this transient anion (and not reported previously[17]) apparently also leads to the bihalide ion ClHF$^-$.

D. Further fragment ions observed from trichloroacetic acid and trifluoroalanine

Figure 5 presents the relative cross section curves for the formation of three more fragment ions from trifluoroalanine, namely CN$^-$, an ion due to the loss of a neutral CF$_2$ ((M-CF$_2$)$^-$) and OH$^-$. Similar to other amino acids,[4–7] CN$^-$ is generated from a resonance near 2 eV and a further broad feature at higher energy. It is the result of a rather complex reaction sequence as the unit has to be excised from the central part of the target molecule with rearrangement of the neutral counterpart. The most direct low energy decomposition pathway is

$$e^- + CF_3CHNH_2COOH \rightarrow CN^- + CF_3COOH + H_2 + H,$$
(4)
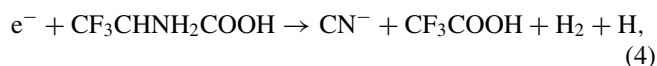
which generates the neutral molecule of trifluoroacetic acid. Along reaction (4) the number of bonds is decreased by three while the bond order is increased. Hence the energetic driving force of the reaction is the appreciably stable cyanide anion with its triple bond and its exceedingly high electron affinity of 3.8 eV.[21]

The loss of a neutral CF$_2$ unit also takes place at subexcitation energies. The lowest energy pathway is

$$e^- + CF_3CHNH_2COOH \rightarrow CHFNH_2COOH^- + CF_2,$$
(5)
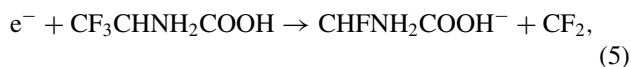
thereby generating the fluoroglycine radical anion (CHFNH$_2$COOH$^-$). We do not have information on the stability of this radical anion, i.e., whether it exists with the extra electron bound in a valence orbital. Anyhow, one can assume that in any case a loosely bound anion state exists, supported by dipole and/or polarization forces. A similar process has been recently reported for N,N,N-trimethylglycine[38] and the formation of the glycine radical anion was observed already at the threshold with a small contribution in the energy range 1–2 eV.

OH$^-$ finally appears as a very weak fragment ion at higher energies. It is likely to originate from a direct cleavage of the C–OH bond. With the C–OH bond dissociation enthalpy of about 4.0 eV and the electron affinity of OH (1.83 eV (Ref. 21)) the thermodynamic threshold is located near 2.2 eV and hence the experimental appearance energy is considerably above the thermodynamic threshold.

From trichloroacetic acid reasonably strong signals are due to ions C$_2$Cl$_2^-$ and CHCl$_2^-$ both of which appear within a narrow resonance close to zero energy (Fig. 6). CHCl$_2^-$ is likely to be the (closed shell) dichlorovinyl anion and, with an electron binding energy of 1.48 eV (Ref. 21) thereby representing a considerably stable negative ion.

The ion C$_2$Cl$_2^-$ is likely to have the vinylidene structure Cl$_2$C=C$^-$ similar to H$_2$C=C$^-$ (Ref. 39), HFC=C$^-$ and F$_2$C=C$^-$.[40,41] Its formation requires the cleavage of three bonds. The neutral counterparts may rearrange to HClO$_2$ or the two stable diatomics HCl + O$_2$. The different isomers of

HClO$_2$ were discussed as intermediates in the cycles of the stratospheric ozone depletion and have been identified in low temperature matrix isolation spectroscopy.[42,43]

IV. CONCLUSIONS

Similar to the non-substituted organic acids also the halogenated acids studied here exhibit a low energy resonance around 1 eV associated with the loss of a hydrogen atom thereby generating the closed shell anion RCOO$^-$. The halogen containing molecules exhibit a further narrow resonance close to zero energy decomposing by the cleavage of the C–Cl bond. This reaction is much more effective than the loss of a neutral hydrogen atom. Further low energy reactions are triggered by resonant attachment of subexcitation electrons like formation of the bihalide ions ClHCl$^-$ from CCl$_3$COOH and ClHF$^-$ from CClF$_2$COOH, or CN$^-$ formation and the loss of a neutral CF$_2$ unit from trifluoroalanine (thereby forming the fluoroglycine radical anion).

The signal of F$^-$ is surprisingly weak and occurs from both fluorine containing molecules predominantly from a broad resonance around 7 eV and hence far above the thermodynamic threshold.

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