

Low energy electron driven reactions in single formic acid molecules (HCOOH) and their homogeneous clusters

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Low energy (0–3 eV) electron attachment to single formic acid (FA) and FA clusters is studied in crossed electron/molecular beam experiments. Single FA molecules undergo hydrogen abstraction *via* dissociative electron attachment (DEA) thereby forming HCOO[−] within a low energy resonance peaking at 1.25 eV. Experiments on the isotopomers HCOOD and DCOOH demonstrate that H/D abstraction occurs at the O–H/O–D site. In clusters, electron attachment is strongly enhanced leading to a variety of negatively charged complexes with the dimer M₂[−] (M ≡ HCOOH) and its dehydrogenated form M · (M–H)[−] as the most abundant ones. Apart from the homologous series containing the non-dissociated (M_n[−]) and dehydrogenated complexes (M_{n−1} · (M–H)[−], n ≥ 1) further products are observed indicating that electron attachment at sub-excitation energies (≈ 1 eV) can trigger a variety of chemical reactions. Among these we detect the complex H₂O · (M–H)[−] which is interpreted to arise from a reaction initiated in the cyclic hydrogen bonded dimer target. In competition to hydrogen abstraction yielding the dehydrogenated complex M · (M–H)[−] the abstracted hydrogen atom can react with the opposite FA molecule forming H₂O and HCO with the polar water molecule attached to the closed shell HCOO[−] ion. The FA dimer can thus be used as a model system to study the response of a hydrogen bridge towards dehydrogenation in DEA.

1. Introduction

Formic acid (HCOOH) as the simplest organic acid has recently been identified in the interstellar medium (ISM)^{1,2} and also in the coma of the Hale–Bopp comet.^{3,4} It has been speculated that it may be a key compound in the formation of molecules such as acetic acid (CH₃COOH) or glycine (NH₂CH₂COOH) in the ISM. These molecules^{5,6} are the simplest building blocks of biomolecules and can hence serve as model systems for the properties of larger and more complex amino acids, or proteins, *e.g.*, with respect to their behavior during exposure to high energy radiation.

It is now well accepted that reactions in biological systems induced by secondary electrons constitute an important initial step towards radiation damage.^{7,8} Energy deposition in living cells by high energy quanta creates a variety of reactive intermediates. Among these, electrons are the most abundant secondary species with an initial energy distribution up to about 20 eV.⁹ These *ballistic* electrons are present in the medium for only a short time (fs–ps), during which they are slowed down by collisions thereby initiating further ionization and excitation processes and, consequently, creating reactive species like neutral radicals, ions and electrons. At sufficiently low energies they may be captured at particular molecular sites forming negatively charged transient compounds which can dissociate. The interaction of low energy electrons with biologically relevant molecules (including water as the dominant compound in living tissues¹⁰) is hence crucial to understand the *initial* molecular steps in radiation damage.

The formic acid dimer (FAD) is a prototype for double hydrogen bonded organic complexes^{11,12} with an enthalpy of dimerization of ≈ 14.7 kcal mol^{−1}. Apart from this well known cyclic form of FAD, recent infrared studies in helium nanodroplets at a temperature of 0.37 K¹³ suggested an additional polar acyclic structure dominated by the long-range dipole–dipole interaction.

Recent beam experiments¹⁴ demonstrated that in isolated FA molecules the dominant reaction is dehydrogenation *via* the DEA process



with the maximum of the resonance located at 1.25 eV. HCOOH^{−#} represents the transient negative ion (TNI) formed in the initial Franck–Condon transition. The gas phase DEA cross section at the peak of the resonance was estimated as ≈ 2 × 10^{−22} m² thereby identifying FA as a comparatively weak electron scavenger.

Studies on electron stimulated desorption (ESD) from nanofilms of FA¹⁵ showed an intense H[−] signal appearing within a resonant feature with the maximum at 9 eV while for obvious reasons desorption of HCOO[−] is completely suppressed. The H[−] signal can be regarded to arise from the (condensed phase) complement to the gas phase dehydrogenation reaction (1) with respect to the excess charge, *viz.*,



Both reactions, however, are induced by electrons of rather different energies and hence the involved precursor (TNI) must be of a different nature, *i.e.* in reaction (2) electronic excitation is involved which most likely results in further decomposition of the electronically excited neutral radical.

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Recent studies on the gas phase DNA/RNA bases thymine (T), uracil (U), cytosine (C), adenine (A) and guanine (G) demonstrated that any of these nucleobases exhibit a low energy resonance located close to 1 eV and associated with dehydrogenation similar to the presently observed reaction (1), however, at appreciably higher cross sections.^{16–20} Furthermore, isotope experiments⁵ in T demonstrated that hydrogen is abstracted from the N sites. The N3 site in T, on the other hand, is involved in the coupling of the complementary base A within DNA. Dimers of FA can hence serve as a simple model system to study the response of a hydrogen bridge (important in many biological systems) towards electron attack.

In this contribution we study electron attachment to single HCOOH including the two isotopomers DCOOH and HCOOD and to clusters of FA (including the deuterated form HCOOD). It is shown that the attachment behavior is appreciably modified in FA clusters.

2. Experimental

The present experiments were carried out by means of two different crossed electron/molecular beam experiments. Single FA molecules were studied at the Bratislava laboratory using the recently established *effusive molecular beam electron attachment spectrometer*²¹ and FA clusters at the Berlin laboratory by means of the *supersonic molecular beam apparatus*.²² Both equipments consist of an electron beam generated by a *trichoidal electron monochromator* (TEM)²³ which is crossed at right angle with the corresponding molecular beam. In both set ups ions arising from this interaction are extracted and analyzed with a quadrupole mass spectrometer.

The TEM has proven to be particularly suitable for studying reactions at low electron energies since the axial magnetic field prevents spreading of the beam so that sufficient intensities (≈ 30 nA) can be achieved down to very low energies.²⁴ For the present experiments the energy resolution was 0.09 eV in the effusive beam experiment and 0.2 eV in the cluster experiment. The energy is calibrated by the well known standards SF_6^- or Cl^-/CCl_4 .

The supersonic beam is formed by adiabatic expansion of FA seeded in He at a mixing ratio of 1 : 100 at a stagnation pressure of 1 bar through an 80 μm nozzle. The beam then passes a skimmer ($d = 1$ mm) which separates the expansion chamber from the main chamber. In both systems 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.

HCOOH and the deuterated forms are purchased from Sigma Aldrich and used as delivered. The stated purity of the sample was 98%.

3. Results and discussion

Gas phase CHOOH, HCOOD and DCOOH

Fig. 1a shows the DCOO^- fragment from DCOOH and Fig. 1b that of HCOO^- from HCOOD with the SF_6^- calibration peak (1c) and Fig. 2 the two negative ion mass spectra obtained from both isotopomers. HCOO^- and DCOO^- are the only negative ions detected in the energy range below 5 eV. The corresponding TNI can be considered as a shape resonance, with the extra electron occupying the lowest virtual orbital of π^* character localized on the COOH group. Due to the considerable electron affinity of the formyloxyl radical HCOO (3.5 eV)²⁵ the dissociation channel (1) is already accessible from the low energy shape resonance. In contrast to that, the much lower electron affinity of H (0.75 eV)²⁵ makes dissociation into H^- (reaction (2)) energetically inaccessible from the shape resonance.

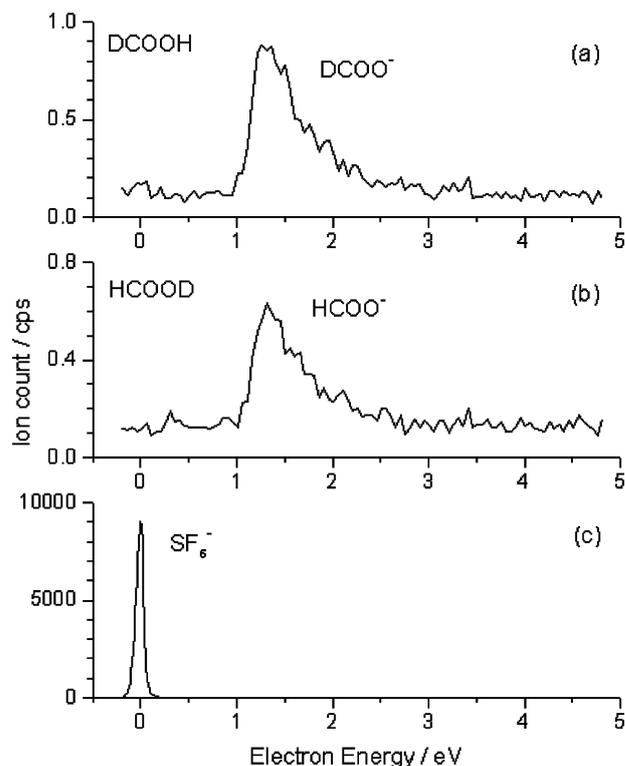


Fig. 1 Ion yields from the isotopomers DCOOH (a) and HCOOD (b), and for comparison the SF_6^- peak used as calibration standard (c).

The mass spectra in Fig. 2 demonstrate that H/D abstraction almost exclusively operates from the O–H/O–D site. In both mass spectra we detect a small contribution ($\approx 20\%$) on the $\text{DCOO}^-/\text{HCOOD}$ and $\text{HCOO}^-/\text{DCOOH}$ signal which may arise from either some H/D exchange in the precursor ion and/or incomplete isotope purity of the sample. We note that in

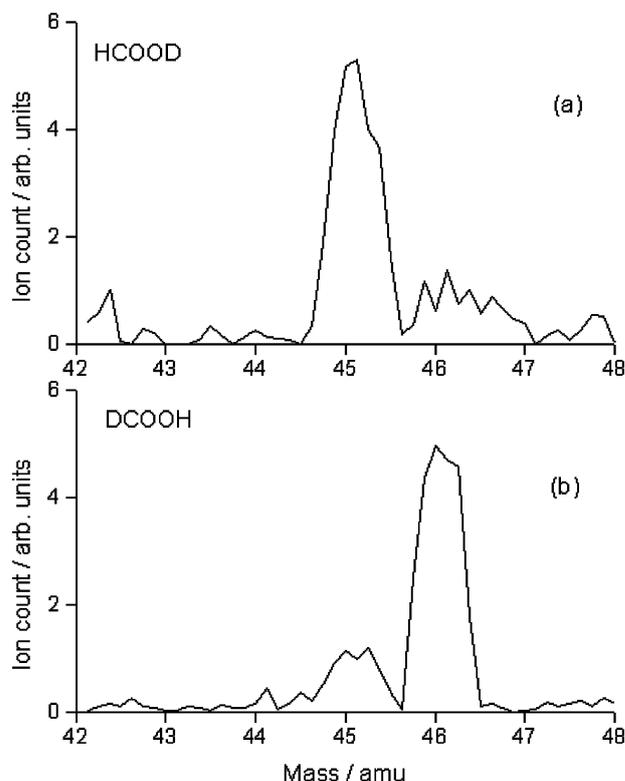


Fig. 2 Mass spectra from the isotopomers HCOOD and DCOOH. The small intensity at 47 amu (DCOOH) and 45 amu (HCOOD) is due to hydrogen transfer in the precursor ion or/isotope impurity.

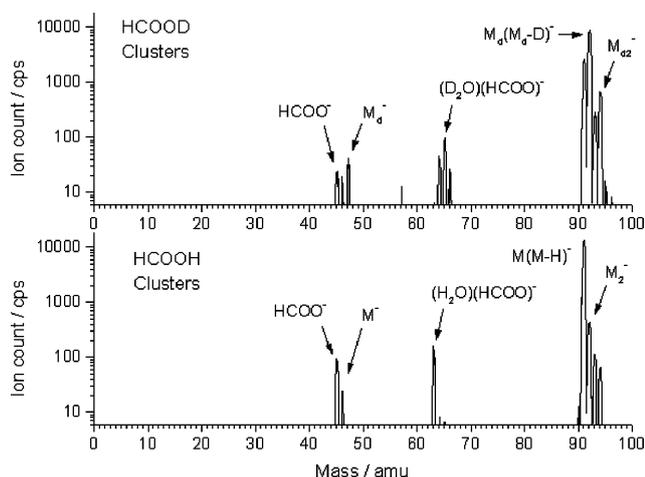


Fig. 3 Lower part of the negative ion mass spectra obtained from an expansion of HCOOH and HCOOD seeded in He, recorded at 1 eV electron energy.

electron stimulated desorption (ESD) from FA nanofilms (including the isotopomers HCOOD and DCOOH) the situation is completely different as the excited TNI responsible for H^-/D^- desorption is subjected to strong H/D scrambling, *i.e.*, the particular isotopomer loses its original identity following attachment of electrons at 9 eV, in striking contrast to the site selectivity of neutral hydrogen abstraction at low energy.

Electron attachment to FA clusters

Fig. 3 and Fig. 4 show negative ion mass spectra (NIMS) from expansions of HCOOH and HCOOD seeded in He and recorded at 1 eV electron energy. Just by looking at these spectra it is obvious that the situation changes dramatically on going from the single molecule to clusters, namely (a) an appreciable enhancement in the intensity of negative ion formation (b) the formation of non-dissociated anionic complexes including the FA monomer anion and (c) indications that sub-excitation electrons (≈ 1 eV) induce interesting chemical reactions in FA clusters.

Fig. 3 shows the negative ion mass spectrum in the range up to 100 amu for HCOOH $\equiv M$ and HCOOD $\equiv M_d$ and Fig. 4 shows the same arrangement for the mass domain between 100 amu and 200 amu. In the supersonic beam experiment the reaction chamber is at about 7 cm distance from the skimmer,

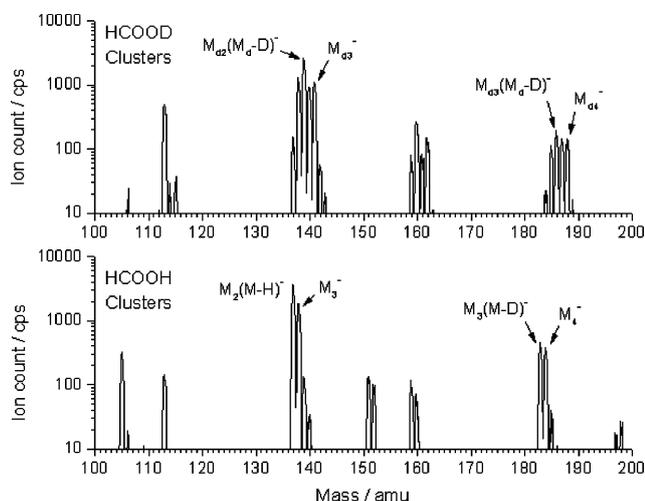


Fig. 4 Negative ion mass spectra in the range 100 amu to 200 amu obtained from an expansion of HCOOH and HCOOD seeded in He, recorded at 1 eV electron energy.

so that the particle density in the collision zone is expected to be below that of the effusive beam experiment. Also, due to the fact that FA molecules are diluted in the propellant we can conclude that (by just comparing the count rates) the cross section for electron attachment to FA clusters is at least 3 orders of magnitude higher of that to single molecules. In a supersonic expansion we do not have direct control on the size of the clusters in the beam and in the present experiments the stagnation pressure was simply adjusted for a maximum signal on small cluster anions.

From the negative ion mass spectra we immediately identify the prominent peaks of the homologous groups around the monomer (M^-), dimer (M_2^-) trimer (M_3^-) and tetramer (M_4^-), but also prominent peaks between these groups. Some remarkable differences in the mass spectra between the isotopes are also evident.

From Fig. 3 it can be seen that apart from $HCOO^-$ (45 amu) also the non-dissociated parent ion (M^-) is formed (46 amu) which is not observed in electron capture by single FA. It can be formed as a product from electron capture to a larger FA clusters with subsequent collisional stabilization (evaporative attachment). Observation of $M^- \equiv HCOOH^-$ may indicate that the neutral compound possesses a positive electron affinity. Strictly speaking, the present experiment cannot prove that $HCOOH^-$ exists in a thermodynamically stable state, it only indicates that the anion exists on the mass spectrometric time scale (tens of μs). While M^- is most likely a product of electron attachment to a FA cluster (*e.g.* a dimer) the dehydrogenated anion $HCOO^-$ (or $(M-H)^-$) can be a product from either a monomer (traveling in the molecular beam) or a cluster.

Accordingly, from the deuterated compound we observe $HCOO^-$ (45 amu) and $HCOOD^- \equiv M_d^-$ (47 amu) with the intensity ratio now reversed with respect to the non-deuterated compound. The relatively small signal at 46 amu is either $(M_d-H)^-$ or M^- , with the first arising from some hydrogen exchange and the latter due to incomplete purity of the isotope sample, respectively.

The largest intensity is observed at the peaks associated with the dimer M_2^- . In the HCOOH expansion we assign the 92 amu peak to the dimer M_2^- and the 91 amu peak to the dimer with one hydrogen atom missing, $(M_2-H)^-$, having the electronic structure $M \cdot (M-H)^-$. The intensity of the two further peaks at 93 and 94 amu is in the range of a few % and may be attributed to the ^{13}C isotope (93 amu) and eventually to an ion-molecule complex arising from a reaction in a larger cluster (94 amu, see below). Accordingly, expansion of the HCOOD compound leads M_{d2}^- (94 amu) and $(M_{d2}-D)^-$ (92 amu) as the dominant peak with the ion having the electronic structure $M_d \cdot (M_d-D)^-$. This peak may also contain ions of the form $M_d \cdot (M_d-H)^-$ or $M_d \cdot (M-H)^-$, again arising from hydrogen scrambling or isotope impurity. Along the same line the 93 amu peak may be due to $M_d \cdot (M_d-H)^-$, $M_d \cdot (M-D)^-$, or $M_d \cdot (M_d-D)^-$ while the 91 amu peak must unambiguously be assigned to $M \cdot (M-H)^-$. The intensity of this latter peak is about 30% of the deuterated analogue $M_d \cdot (M_d-D)^-$ (at 92 amu) also indicating some isotope impurity.

An analogous assignment can be made for the group of trimers and tetramers. From the non-deuterated compound we observe M_3^- (138 amu) and $(M_3-H)^-$ (137 amu), the latter again with the most likely structure $M_2 \cdot (M-H)^-$ and finally M_4^- (184 amu) and $(M_4-H)^-$ (183 amu). For the expansion of the deuterated compound we observe M_{d3}^- (141 amu) and M_{d4}^- (188 amu). Within these groups the peaks corresponding to $M_{d2} \cdot (M-D)^-$ (139 amu) and $M_{d3} \cdot (M-D)^-$ (186 amu) are dominant (with the possibility that non-deuterated molecules and hydrogen abstraction may also contribute to that signal, see above). Again the dominant peaks at 139 amu and 186 amu, suggest that the reaction is primarily initiated at the O-D site.

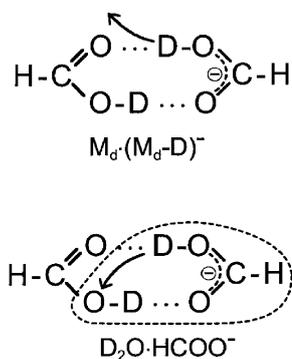
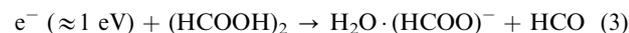


Fig. 5 Cartoon of two possible reaction channels triggered by a slow electron in the deuterated dimer, (i) abstraction of D generating $M_d \cdot (HCOO)^-$ (92 amu), and (ii) intracuster reaction generating the complex $D_2O \cdot (HCOO)^-$ (65 amu).

Chemical reactions triggered by sub-excitation electrons

The 63 amu peak in the $HCOOH$ expansion can be assigned to an ion of the stoichiometric composition $H_3CO_3^-$ with the likely electronic structure $M \cdot (OH)^-$ or $H_2O \cdot (M-H)^-$. A closer look at the energetic situation immediately reveals that only the second complex is energetically accessible by 1 eV electrons (basically irrespective of the size of the target cluster). For a reaction initiated in the hydrogen-bonded dimer, the dehydrogenation process (already known from the isolated molecule) is then modified in FAD in the way that the neutral hydrogen (deuterium) either leaves the complex leading to the ionic product $M \cdot (M-H)^-$, or it runs into the OH/OD group of the opposite FA molecule forming $H_2O/(D_2O)$ which is bound to the $HCOO^-$ unit and detected as an ion–molecule complex in the mass spectrum. This reaction is illustrated for the case of the deuterated dimer in Fig. 5. The overall reaction (expressed on the $HCOOH$ system) can be expressed as



which is reduction of FAD thereby generating H_2O at sub-excitation energy.

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}).²⁵ In addition, with the heats of formation from Table 1 one obtains a reaction enthalpy of $+95 \text{ kJ mol}^{-1}$ (neglecting the binding energy in the FA dimer and in the ionic complex) which is approximately balanced by the energy of the attaching electron. It is interesting to note that this kind of reaction is restricted to the unit $H_2O \cdot (M-H)^-$ which suggests that the target cluster in fact is exclusively the dimer. We also note that a similar observation was made in the fluorinated acetic acid, where the corresponding complex $H_2O \cdot (M-H)^-$ is the strongest peak in the negative ion mass spectrum recorded at sub-excitation energies ($M \equiv CF_3COOH$).²⁶ Note that in the mass spectrum of the deuterated compound the peak at 65 amu representing $D_2O \cdot HCOO^-$ is the strongest, which shows that water formation in fact preferentially occurs at the site of the hydrogen bridges as indicated in Fig. 5. Interestingly, we detect an ion at 65 amu ($D_2O \cdot DCOO^-$) but not at 63 amu ($H_2O \cdot HCOO^-$).

The peaks between the dimer–trimer and trimer–tetramer groups exhibit a regular structure insofar as their separation (in the spectrum of the non-deuterated expansion) is 14 amu and 22 amu above the dimer and trimer unit or 32 amu and 24 amu below the trimer and tetramer unit. This can be interpreted by a complex consisting of ionic dimer or trimer where a unit of 14 amu and/or 22 amu is attached to a complex where ionic trimer and tetramer were subjected to the evaporation of neutral compounds with 24 amu and 32 amu, respectively. Formation of O_2 (32 amu) C_2 (24 amu) or CH_2 (14 amu) can be excluded

Table 1 Gas phase standard heats of formation relevant for the decomposition of formic acid clusters. All values from ref. 25

Compound	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
$HCOOH$	-379
H_2COH (hydroxy methyl radical)	-9 ± 4
H_3CO (methoxy radical)	$+17 \pm 4$
H_2CO (formaldehyde)	-116
$HCOO^-$	-464 ± 10
H_2O	-242
CO_2	-393.5
HCO (formyl radical)	+43.5
CO	-110.5
H	+218

from energy reasons since such channels are by far not accessible *via* DEA near 1 eV. In searching for other possible products note that, from the thermodynamic point of view, FA is a rather unstable compound as the decomposition reaction



is slightly exothermic ($-14.5 \text{ kJ mol}^{-1}$) and the reaction



slightly endothermic ($+26 \text{ kJ mol}^{-1}$). While in neutral gas phase FA these reactions may not play a particular role due to the considerable activation energy, the presence of an excess charge can change the situation considerably. In clusters the charge can open new and energetically favorable reaction pathways. The dimer, *e.g.*, can react upon electron attachment along the routes



Reaction (6) is endothermic by 119 kJ mol^{-1} while (7) is (on the basis of (4) and dependent on the electron affinity of $HCOOH$) expected to be exothermic. In larger clusters it is possible to find a variety of energetically favorable pathways containing the ionic units $(M-H)^-$ and M^- , and neutral compounds of the form H_2O , CO_2 , H_2 , CO and H_2CO (with H_2CO and $H_2 + CO$ energetically at a comparable energy level (see Table 1)). These neutrals may then either be attached to some ionic complex or evaporated from an ionic complex in a reaction following electron attachment.

In that spirit, the compound at 151 amu and 152 amu (which for some reason is missing in the spectrum of $HCOOD$ (!)) can be interpreted as the complex $(M_4-H)^-$ and M_4^- , respectively, subjected to the evaporation of neutral units of 32 amu which can be either $CO + 2H_2$ or $H_2CO + H_2$. Accordingly, the 159 amu and 160 amu peaks can be interpreted as $(M_3-H)^-$ and M_3^- , respectively, with neutrals of 22 amu attached ($H_2O + 2H_2$), or alternatively, as $(M_4-H)^-$ and M_4^- with the loss of neutral units of 24 amu (which could correspond to the loss of formaldehyde and an attached H_2).

We shall not extend this rather speculative discussion but state that larger clusters can decompose into a variety of favorable channels following low energy electron attachment, including cyclic oxygen containing molecules.

In conclusion, from the results presented here it can be seen that single formic acid is a weak electron scavenger, thereby abstracting hydrogen from the $O-H$ site. The only negative ion observed at low energy is $HCOO^-/DCOO^-$ arising from dehydrogenation of FA. In clusters the electron capture cross section is strongly enhanced and the mass spectrum shows a variety of ionic products. Apart from dehydrogenation, low energy electrons trigger interesting reactions including the formation of H_2O in the dimer, which is detected as the reaction product attached to $HCOO^-$.

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