Scientific report on my visit in FU Berlin
COST Action P9

During the period from June 15th to June 28th I have visited the laboratory of Prof. Dr. E. Illenberger in Freie Universität Berlin within the COST Action P9 network. During this stay I have done experimental studies of dissociative electron attachment on formic and formic acid clusters. This molecule has been chosen as a model for hydrogen-bonded systems like DNA bases. In previous measurements it has been shown that dehydrogenation is dominant reaction induced by slow electrons on DNA bases in gas phase. Experiments on deuterated thymine showed that dehydrogenation is exclusively operative from the N-sites of the isolate DNA bases.

In present studies we have studied electron attachment to isolated molecule of HCOOH and to molecular clusters of HCOOH. It has been shown before that electron attachment to isolated molecule of formic acid leads to dehydrogenation. However it was not clear which H-atom is being split off. To answer this question we have study electron attachment to deuterated formic acid with deuterium on O-site and looked which of following reactions takes place:

$$\begin{aligned} e^- + \mathrm{HCOOD} &\rightarrow \mathrm{HCOO}^- + \mathrm{D} \\ &\rightarrow \mathrm{COOD}^- + \mathrm{H} \end{aligned}$$

The first reaction will produce ions with mass 45 amu, while the second one ions with mass 46 amu. At these measurements only HCOO^- ions have been observed with best yield at 1eV electron energy. No production of COOD^- has been observed that means dehydrogenation is operative on O-site. However, small ion signal and relatively high noise of the apparatus would make small production of COOD^-, say 1% of the signal of HCOO^- unobservable.

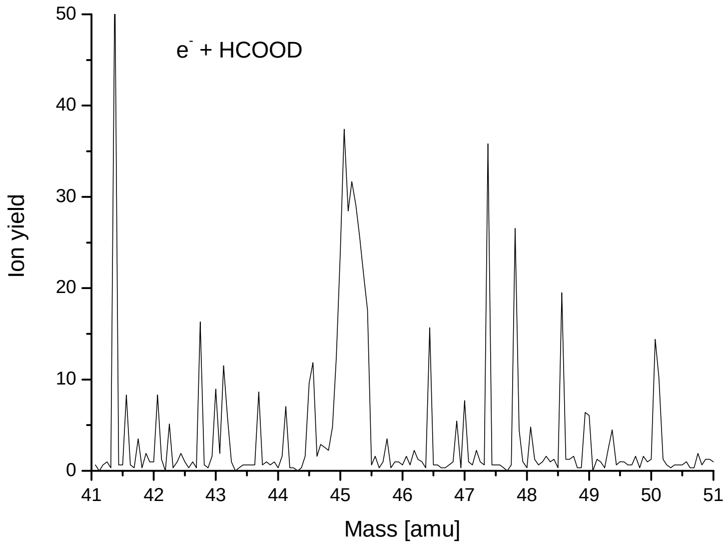

Fig.1. Mass spectrum of negative ions obtained by 1eV electrons to isolated molecule of HCOOD. Mass 45 corresponds to HCOO$^-$ ions.

To see how can hydrogen bonding influence behavior of electron attachment we have studied electron attachment to formic acid clusters. Small molecular clusters were produced by supersonic expansion of formic acid vapor mixed with argon (1:100) through a 70 µm nozzle into the vacuum. In these measurements deuterated form HCOOD of formic acid has been used.

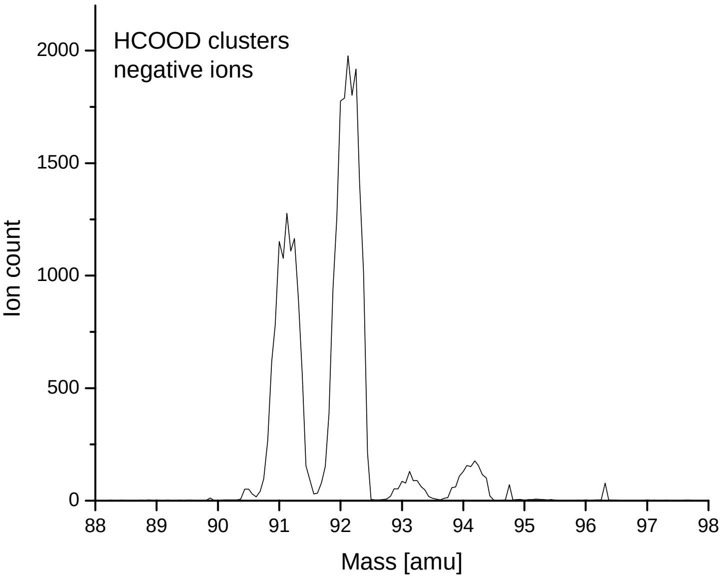

Fig. 2. Mass spectrum of negative ions obtained by 1eV electrons to molecular clusters of HCOOD. Mass 92 is HCOOD●HCOO$^-$ ion signal.

Fig.2. shows mass spectrum of products obtained. Best yield obtained on mass 92 corresponds to dehydrogenation on O-site and production of HCOOD●HCOO$^-$. Product with mass 94 amu is probably undissociated dimmer anion HCOOD●HCOOD$^-$. However strong signal was found also at mass 91 and only explanation seems to be that significant (40%) impurity of nondeuterated formic acid has been present. That would lead to production of HCOOH●HCOO$^-$ on mass 91 and HCOOH●HCOOD$^-$ on mass 93. On mass 93 there is also contribution of HCOOD●HCOO$^-$ ions with one ^{13}C carbon isotope.

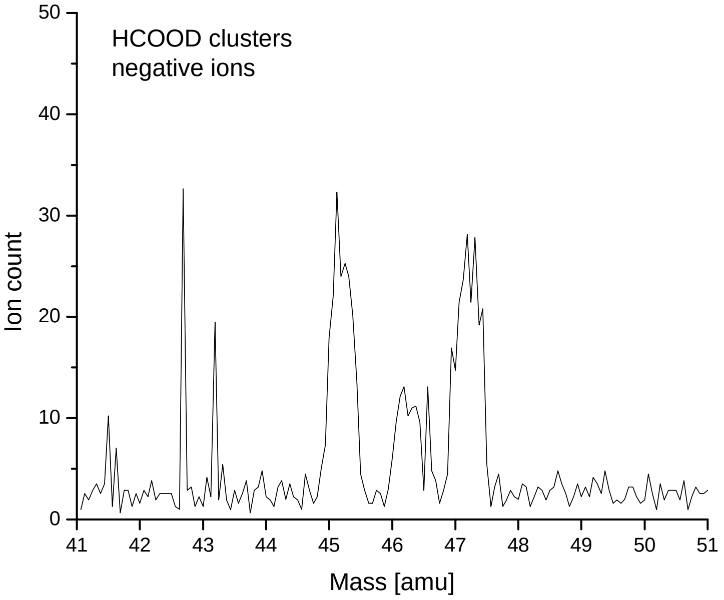

Fig.3. Mass spectrum of negative ions obtained by 1eV electrons to molecular clusters of HCOOD. Mass 45 corresponds to HCOO$^-$ ions, mass 47 to parent ions HCOOD$^-$.

Fig.3 shows products obtained at the same conditions in mass range 41 – 51 amu. In these measurements also production of parent negative ion (mass 47) has been observed. Signal on mass 46 which is about 40% of that on mass 47 may also be result of impurity of HCOOH corresponding to parent ions HCOOH$^-$.

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