

SCIENTIFIC REPORT

Title: Reactions in halo-substituted molecules driven by low energy electrons

REFERENCE: Short Term Scientific Mission, COST CM0601

Beneficiary: Dr Janina Kopyra, University of Podlasie

Host: Prof. Dr. Eugen Illenberger, Freie Universität Berlin

Period: from 01.04.2008 to 30.04.2008 Place: Berlin (DE)

Reference code: COST-STSM-CM0601-03408

Purpose of the visit

The purpose of the visit was to investigate interaction of the low energy electrons with some organic halides in the gas phase by means of a crossed electron-molecular beams technique. Many of these molecules are of wide technological interest. Due to their particular physical properties they have been used as a specialized solvents, refrigerant, foam blowing etc. but first of all in the microelectronics industry in the plasma etching of integrated circuits. In order to understand many types of plasma, knowledge is required of the behavior of electrons and neutral molecules mixed under define conditions of molecule density and temperature. Therefore the aim of this project was to investigate the LEE interactions with halo-substituted (simple) organic acids in the gas phase by means of crossed electron/molecular beams.

Description of the work carried out

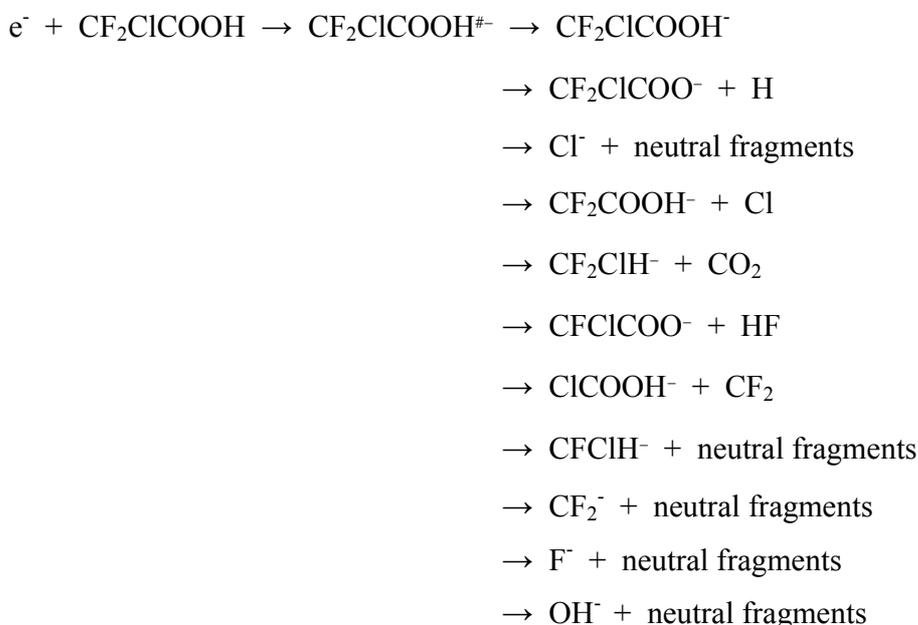
The experiments were performed using the crossed electron-molecular beams technique. The apparatus consists of an electron source (tungsten filament), an oven, a quadrupole mass analyzer and a detection system. The electron beam of a defined energy is generated by a trochoidal electron monochromator and crossed perpendicularly with the molecular beam under investigation. The generated negative ions are extracted by

a weak electric field in the order of 1V/cm and accelerated by a series of parallel electrodes onto the entrance hole of quadrupole mass analyzer and detected by a single pulse counting technique as a function of incident electron energy. The energy scale was calibrated using the well known resonance in SF₆ near 0 eV generating metastable SF₆⁻.

Description of the main results obtained

During my stay in the laboratory in Berlin I was involved in the studies of electron attachment by chlorodifluoroacetic acid and trichloroacetic acid. It appeared that these halo-substituted organic acids are very sensitive towards low energy electrons (LEEs). This can be ascribed to the so-called electron capacity of the halo-substituents which rises in oppose to the electron affinity and electronegativity as well as to the presence of low lying virtual π^*_{COOH} MO. An indirect collision of LEEs with those molecules lead to the formation of various negatively charged ions (parent and fragment ions).

The observed anionic products from chlorodifluoroacetic acid CF₂ClCOOH are caused by following reaction pathways:



Electron attachment investigation reveals that CF_2ClCOOH forms a stable parent molecular anion within an intensive resonance peaking at about 0,7 eV. At the same energy domain the molecular anion after abstraction of the neutral hydrogen atom ($(\text{M-H})^-$) was observed.

However, the most intensive anionic fragment Cl^- is formed at about 0 eV and is found to extend up to $\approx 3,8$ eV, as is obvious from the logarithmic plot in Figure 1. The Cl^- fragment as well as its complementary fragment CF_2COOH^- ($(\text{M-Cl})^-$) arise from the chlorodifluoroacetic acid due to the direct breakage of the C-Cl bond.

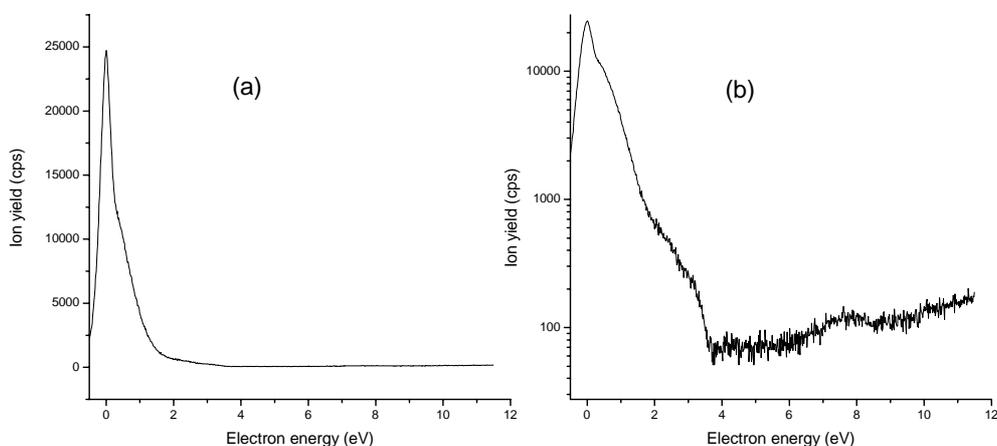


Figure 1 (a): Formation of Cl^- from chlorodifluoroacetic acid, (b): Same anion as in (a) panel but on a logarithmic scale.

Additionally, in the low energy range 0-1,5 eV a series of fragment ions, CF_2ClH^- , CFCIH^- , CFCICOO^- and ClCOOH^- , was observed (Figure 2). All of them were created due to multiple bond cleavages. The ClCOOH^- resonance with a maximum at about 0 eV is followed by the second distinct contribution at around 0,7 eV.

The remaining anions, i.e. OH^- and F^- , are created via broad resonances at the energy range 6-9 eV (Figure 3) and hence attributed to the core excited resonances. The latter one is preceded by the low energy resonance peaking at about 2,5 eV.

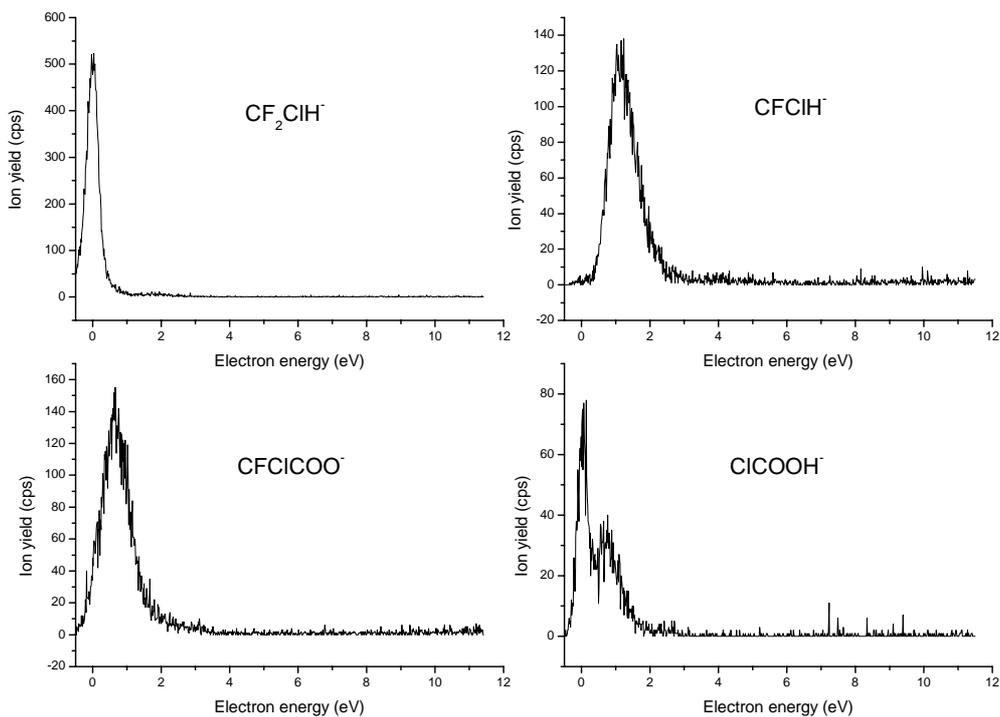


Figure 2 Yields of CF_2CIH^- , CFCIH^- , CFCICOO^- and ClCOOH^- anions following DEA to chlorodifluoroacetic acid.

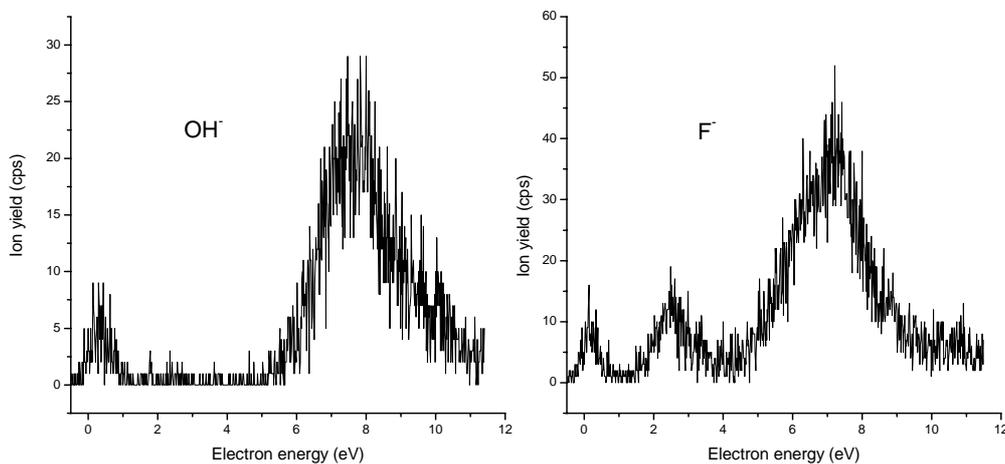
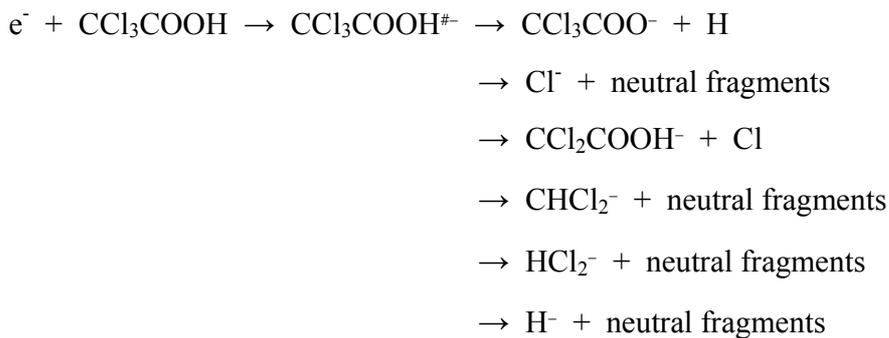


Figure 3 Ion yield for OH^- and F^- in the chlorodifluoroacetic acid as a function of incident electron energy.

In the case of trichloroacetic acid CCl_3COOH electron attachment is a purely dissociative process with the production of the six anionic fragments. The dissociation products of electron attachment partly arise from simple bond cleavage (e.g. CCl_3COO^- , Cl^- , $\text{CCl}_2\text{COOH}^-$, H^-), but there are also more complicated reaction pathways that go along with multiple bond cleavage and the formation of new molecules. The fragments are formed via the following reaction mechanisms:



The characteristic ion efficiency curves from trichloroacetic acid are shown in Figure 4. The studies reveal that different fragments leading to the decomposition of CCl_3COOH are formed via the low energy single particle shape resonances near zero eV. Additionally, in the spectrum of H^- two weak and broad structures are visible at high energy domain - the first located at around 7-8 eV and the second one in the energy range 9-11 eV.

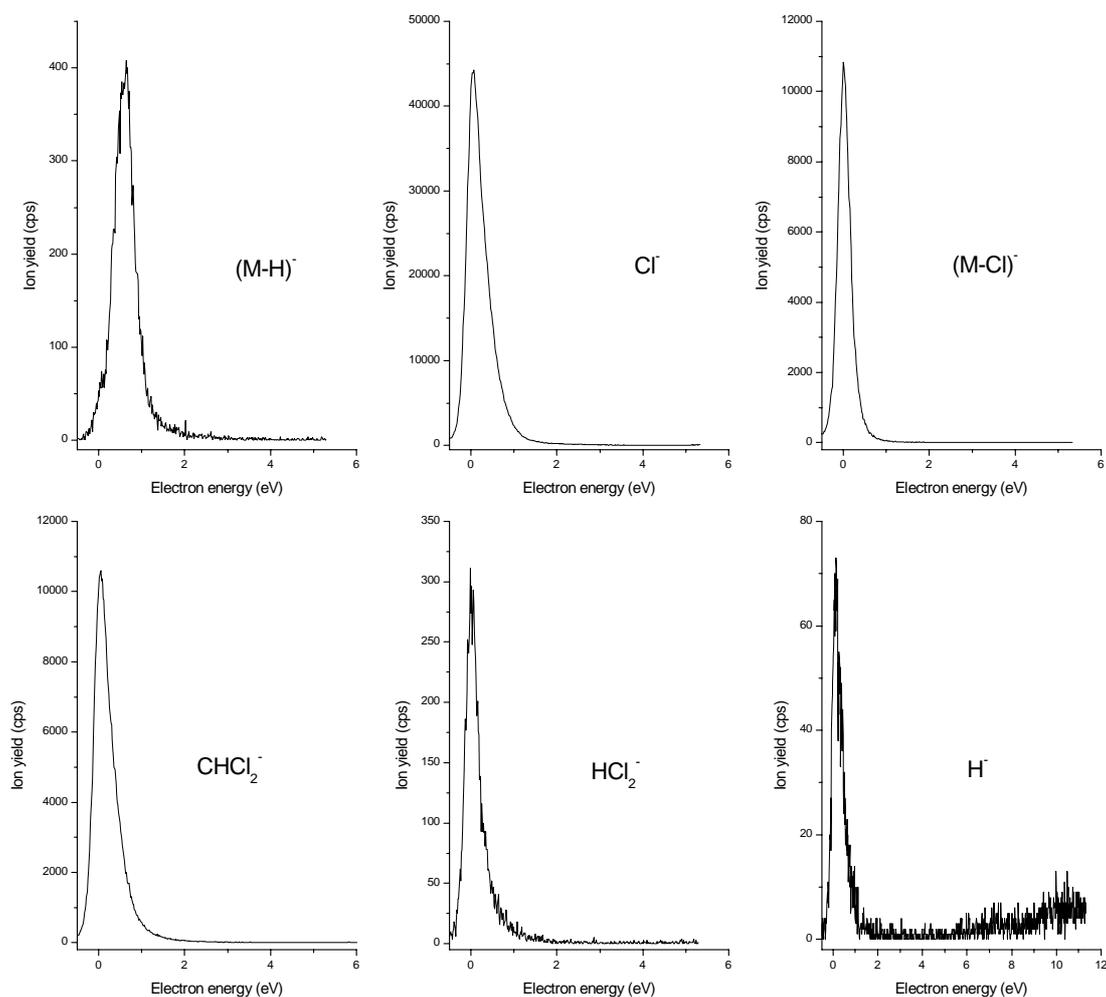


Figure 4 Ion yield for CCl_3COO^- , Cl^- , $\text{CCl}_2\text{COOH}^-$, CHCl_2^- , HCl_2^- and H^- in the trichloroacetic acid as a function of incident electron energy.

Future collaboration with host institution

It is expected to continue the collaboration in the area of electron spectroscopy.

Projected publications resulting from the grant

It is planned to publish the results of chlorodifluoroacetic acid studies as soon as the data analysis will be finished.

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20 May 2008

Host Confirmation for Dr. Janina Kopyra

COST Action

I herewith confirm that Janina Kopyra visited the Berlin laboratory during the period 01 April to 30 April 2008. She performed experiments on electron attachment to halogenated acids using the gas phase electron attachment spectrometer.

I approve her written report.

Dr. Eugen Illenberger
Professor of Physical Chemistry