

Laboratoire des Collisions Atomiques et Moléculaires Unité Mixte de Recherche n°8625 - Université Paris Sud - CNRS

Anne LAFOSSE Tel : +33 (0) 1 69 15 76 98

e-mail: lafosse@lcam.u-psud.fr

## **STSM Scientific report**

Reference code: COST-STSM-P9-01854

Electron Stimulated Desorption (ESD) and Temperature Programmed Desorption (TPD) experiments on fluorinated organic acids in the condensed phase have been performed in the laboratory of Pr. Eugen Illenberger at the Freie Universität Berlin. These investigations are part of the initiated experimental program, dealing with the interactions of low energy electrons with small organic acids. These compounds represent building blocks of biomolecules and their behaviour under electron impact is relevant in connection to radiation damage.

Electron interactions with condensed deuterated trifluoroacetic acid CF<sub>3</sub>COOD have been studied. Figure 1 shows the yields of  $F^-$  ions measured by ESD spectroscopy as a function of the incident electron energy for condensed films of CF<sub>3</sub>COOD and methyltrifluoroacetate CF<sub>3</sub>COOCH<sub>3</sub>. In the case of condensed trifluoroacetic acid CF<sub>3</sub>COOD, desorbing  $F^-$  ions are formed via Dissociative Electron Attachment (DEA) mechanisms, whose contributions result in a broad peak located about 10.8 eV, starting at about 8 eV and extending up to 13 eV, as shown in Figure 1. The  $F^-$  ions are formed via DEA involving resonances, which are also present in the gas phase and the ion yield most likely originates from different energetically overlapping resonances with their electronic structure not yet assigned. In the gas phase,  $F^-$  ions are formed via a shape resonance at about 1.3 eV and via DEA mechanisms taking place in the energy range 5-12 eV (with a maximum observed at 7.5 eV)<sup>1</sup>.

Carbon dioxide formation is efficiently induced by electron irradiation of condensed trifluotoacetic acid, as observed by means of TPD (in Berlin) and HREELS (High Resolution Electron Energy Loss Spectroscopy, in Orsay). Two different energy domains have been identified: (i) below 2.5 eV,  $CO_2$  formation proceeds via the formation of a transient negative ion (observed in the gas phase experiment), while above 9 eV, it involves non resonant excited states of the neutral molecule.

Regarding the influence of the molecule environment on the electron induced processes, preliminary experiments have been performed on condensed methyltrifluoroacetate CF<sub>3</sub>COOCH<sub>3</sub>, an ester which is derived from the trifluoroacetic acid. In the condensed phase CF<sub>3</sub>COOD molecules build a network connected by hydrogen bridges in contrast to the ester molecules. The yield of  $F^-$  ions desorbing from a film of CF<sub>3</sub>COOCH<sub>3</sub> (shown in Figures 1 and 2) is characterized by a broad feature between 8 and 16 eV, peaking at about 13.5 eV.  $F^-$  ions are likely formed via overlapping DEA processes. The formation of CO<sub>2</sub> was not

<sup>&</sup>lt;sup>1</sup> J. Langer al., Chem. Phys. Lett. 419 (2005) 228

Laboratoire des Collisions Atomiques et Moléculaires Unité Mixte de Recherche n°8625 - Université Paris Sud - CNRS

observed by TPD after extended electron irradiations of a film of condensed ester molecules. After an irradiation of 32  $\mu$ C at 20 eV of a condensed film of CF<sub>3</sub>COOCH<sub>3</sub>, the F<sup>-</sup> yield is modified, since the broad peak is shifted down to ~12 eV and a shoulder is developing at ~8,5 eV. Obviously the chemical composition of the film has been modified upon electron irradiation. Complementary experiments involving HREEL spectroscopy will be performed in Orsay in order to complete the undertaken work on the electron induced chemistry.

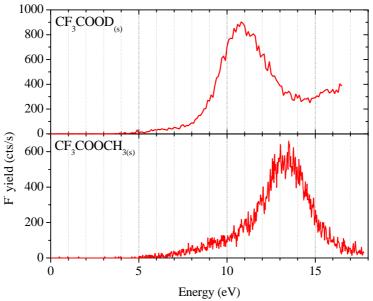


Figure 1: Formation of F<sup>-</sup> versus incident electron energy from deuterated trifluoroacetic acid CF<sub>3</sub>COOD and from methyltrifluoroacetate CF<sub>3</sub>COOCH<sub>3</sub> in the condensed phase (unpublished).

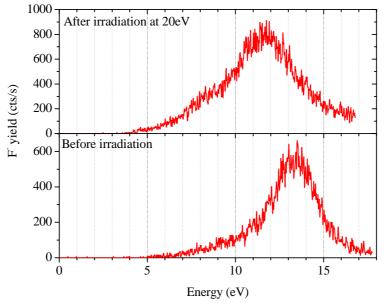


Figure 2: Formation of F<sup>-</sup> versus incident electron energy from a condensed film of methyltrifluoroacetate CF<sub>3</sub>COOCH<sub>3</sub>, before and after electron irradiation at 20 eV (dose: 32 μC) (unpublished).