

# Uncommon Features of Monomolecular Decay for Perfluorinated Carboxylic Acids under Resonance Electron Capture Conditions.

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**Novel Aspect:** Particularity of PFC's interaction with low energy (0-2 eV) electrons.

## Introduction

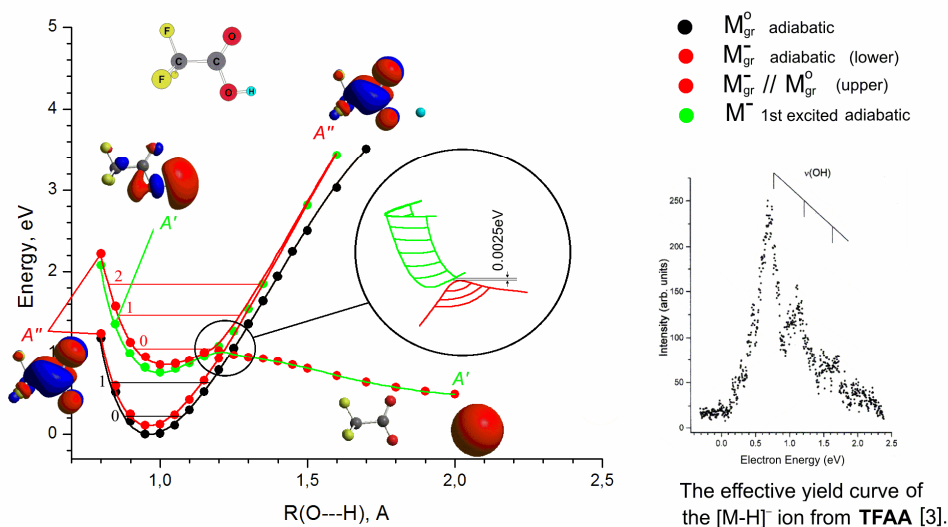
An earlier study [1] involving a series of perfluorinated carboxylic acids (PFCA's,  $C_nF_{2n+1}COOH$  with  $n=7-11$ ) by resonance electron capture MS (REC MS) has revealed some interesting observations, namely the fine structure on the effective yield curves for  $[M-H]^-$  ions and the presence of low abundant diffuse peaks in REC TOF spectra. The present work explains these observations.

## Methods

Resonance electron capture (REC) MS was performed on a custom-made electron monochromator-TOF mass spectrometer [2] and metastable decomposition was followed on a JEOL MSRoute mass spectrometer. The samples (perfluorocarboxylic acids, 98%) were purchased from Aldrich Chem. Co. (Milwaukee, WI). In computations, CBS-Q for ground states and UCIS(D)/D95+(d,p) for excited state were used for energy calculations and CASSCF for the crossing region analysis. Calculations were performed on trifluoroacetic acid.

## Results

First, the effective yield curve for  $[M-H]^-$  ions exhibits fine structure corresponding to the  $\nu(O-H)$  stretching modes [1] upon electron capture. The quantum chemical calculations explain (Figure 1) this structure by electron capture on the vibrational levels in the molecular anion ground state  $A''$  (bound state



corresponding to the lowest unoccupied  $\pi^*$ -orbital), followed by iso-energetic (horizontal) transfer from the  $M^-$  ion channel to another electronic-state surface  $A'$  (decay state corresponding to the next unoccupied  $\sigma^*$ -orbital) from which dissociation occurs with formation of the carboxylate anion and H-radical, i.e. by a pre-dissociation process.

Secondly, REC mass spectra of PFCA's obtained with a reflectron/TOF and double focusing/magnetic sector analyzer consist of low intensive and diffuse peaks (Figure 2). In spite of the fact that these diffuse peaks look like those corresponding to metastable decay, they cannot be attributed by their mass to any metastable decomposition. Yet they correspond to fragment ions with the composition  $C_nF_{2n-2}$ . A possible explanation for the diffuse shapes of these peaks is that a large amount of kinetic energy is released in the process of their formation.

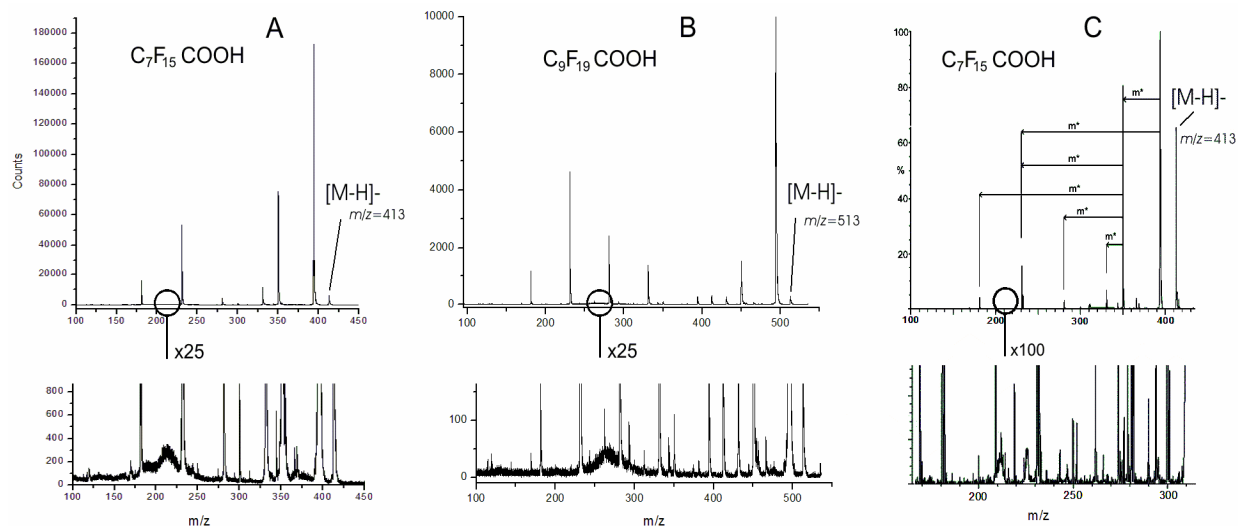


Figure 2. REC-TOF spectra of perfluorooctanoic acid (A) and perfluorodecanoic acid (B), and REC-EB spectrum of perfluorooctanoic acid (C).

### Acknowledgement

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### References:

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