

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

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Overview

Purpose

To explain observed peculiarities in the interaction of low energy electrons with perfluorinated carboxylic acids [1].

Method

REC MS by custom-built TOF mass-spectrometer [2] with:

- trochoidal monochromator for selecting electrons with specific energy;
- monochromator controller for scanning of the electron energy with frequency up to 40 ms in the full range 0-12 V;
- orthogonal ToF analyzer with extraction frequency up to 80 kHz;

Metastable decomposition analysis by *EB* JEOL MS ;

QC: CBS-Q for ground states and UCIS(D)/D95+(d,p) for excited state were used for energy calculations. A state-average CASSCF calculations with averaging two lowest states of MNI on the basis set D95(3df,2p). Wave function used in the CASSCF calculation is characterized by an active space of 7 electrons in 8 orbitals.

Result

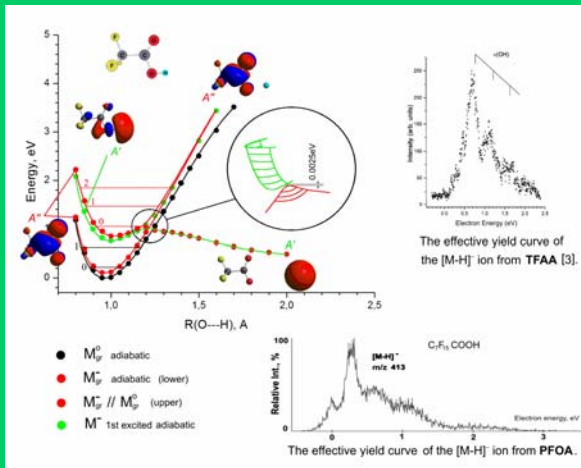
- QC results prove that $[M-H]^-$ ions are formed by predissociative process.
- Diffuse peaks of the same masses in TOF and *EB* spectra are explained by the high kinetic energy contents of these ions.

QC

The effective yield curve for $[M-H]^-$ ions exhibits fine structure corresponding to the $\nu(O-H)$ stretching modes upon electron capture [4]. The quantum chemical calculations explain the presence of this structure by electron capture on the vibrational levels in the molecular anion ground state A'' (bound state corresponding to the lowest unoccupied π^* -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 σ^* -orbital) from which dissociation occurs with formation of the carboxylate anion and H-radical, i.e. by a pre-dissociation process.

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References

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MS

Samples $C_8F_{15}O_2H$ and $C_{10}F_{19}O_2H$ (98%) purchased from Aldrich Chem. Co., were introduced into the ion source by a direct insertion probe.

TOF: The electron energy was ramped from -1.7 eV to 3.3 eV at a frequency of 10 Hz, and the energy spread of the 15 nA electron beam was 110 meV. Ions were extracted orthogonally into the TOF analyzer at a frequency of 60 kHz.

EB: The electron energy was tuned to provide the highest yield of $[M-HF]^-$ ions.

REC mass spectra of PFCA's obtained with reflectron/TOF or double focus/magnetic sector analyzer consist of low intense diffuse peaks but they can not be attributed by their mass to any metastable decomposition. At the same time they correspond to fragment ions with the composition of C_nF_{2n-2} . A feasible explanation for diffuse shapes of these peak can be the high kinetic energy contents of these ions.

