Formation of $(M-H)^-$ Ions from OH-group-Containing Molecules: Dissociative Electron Attachment to Perfluorinated Octanoic Acid $C_7F_{15}COOH$ (PFOA)

Valery G.Voinov, Yury V.Vasil'ev, Douglas F. Barofsky, Max .L. Deinzer
Department of Chemistry, Oregon State University, Corvallis, OR 97331

Overview

Purpose

To check whether the formation of $(M-H)^-$ ions from pentadecafluorooctanoic acid $C_7F_{15}COOH$ (as a model molecule containing a hydroxy-group) is a statistical process.

Method

- Trochoidal monochromator for selecting electrons with specific energy;
- Monochromator controller allows 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;
- Synchronization of ToF extractions with energy ramping.

Result

Data obtained have proved that $[M-H]^-$ ions form through a nonergodic predissociative process.

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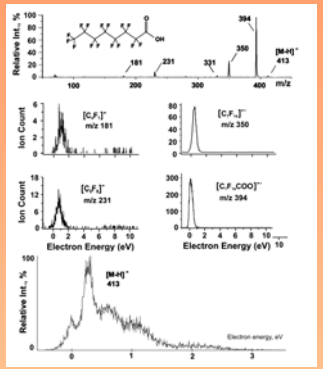
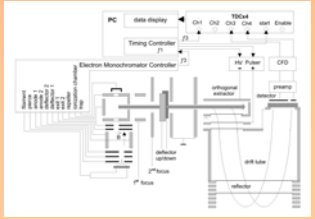
Introduction

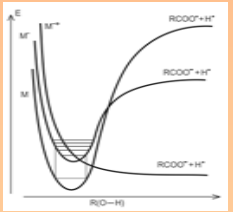
As it is known, the process of decomposition of positive ions is well described by statistical theories since these processes are ergodic in nature. The situation for negative ions is different. First, the formation of negative ions is a resonance process, i.e. it is a mode-selective process. Second, these molecular negative ions are metastable with respect to electron autodetachment and because of the short lifetimes, result in poor energy randomization over the molecular vibrational modes. Both of these characteristics lead to the possibility of fast fragmentation of parent anions, i.e. fragmentation by nonergodic processes. The formation of $(M-H)^-$ ions from molecules containing a hydroxy-group was used to investigate whether the process is statistical [1,2] or not [3,4]. Using a trochoidal electron monochromator-mass spectrometer, we performed a study of this process with perfluorooctanoic acid ($C_7F_{15}COOH$). This molecule possesses a large number of available vibrational modes with only one H atom so that only one high frequency vibrational mode, ν(O-H), is available and thus looked at explicitly.

Experimental

The experimental set up has been described in detail [5]. This particular experiment was performed under the following conditions. Sample (perfluorooctanoic acid $C_8F_{15}O_2H$ (98%,), **PFOA**, purchased from Aldrich Chem. Co.) was introduced into the ion source by a direct insertion probe. The probe temperature was held at 100 °C. The ionization chamber was kept at 120 °C. 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. At this acquisition rate, the *m/z*-range is nominally 550, and the resolving power is ~1000.







Results

The effective yield curve of the $[M-H]^-$ ion from **PFOA** exhibits fine structure consisting of three prominent peaks with maxima at 0.03, 0.31, 0.66 and 1.15 eV. The first resonance peak is particularly temperature-sensitive, and is not related to the problem under discussion [4]. The next three peaks should be associated with excitation of ν(O-H) vibrational mode since this mode is the only high-frequency vibration present in the PFOA molecule. The occurrence of the vibrations ν(O-H) observed in the curve of $[M-H]^-$ are explained by formation of these ions through a predissociation process.

References

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