



Generation of $(M-H)^-$ ions by dissociative electron attachment to simple organic acids M

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Abstract

Low energy ($\sim 0\text{--}3.5\text{ eV}$) dissociative electron attachment to the simplest organic acids (formic, acetic and propanoic) is studied at high electron energy resolution (60 meV) by means of mass spectrometric detection of the product anions. For all $(M-H)^-$ negative fragment ions produced, vibrational structure in the attachment spectra is observed. The energy gaps between the vibrational levels in $HCOO^-$, CH_3COO^- and $CH_3CH_2COO^-$ are derived (ranging from $250 \pm 60\text{ meV}$ up to $350 \pm 60\text{ meV}$).

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1. Introduction

Organic acids are important atmospheric trace gases. These acids are emitted to the atmosphere from biodegradation [1,2], biomass burning as well as from the biosphere and via motor vehicle exhaust [3,4]. They contribute significantly to the acidity of atmospheric condensed water, acid precipitation and also play some role in chemical

processes in the cloud droplets (e.g. liquid phase oxidation of SO_2 by H_2O_2 which depends critically on the pH value of cloud droplets [5]).

The simplest organic acids are prototype molecules for more complex molecules like amino acids and proteins and thus may serve as model systems for the properties of larger biomolecules, e.g. DNA [6]. In this paper we present the results of low energy electron impact on organic acids (formic, acetic and propanoic), leading to the loss of a hydrogen atom from intermediate parent anions and to the formation of $(M-H)^-$ negative fragment ions (where the M and H indicate the molecular organic acid and the hydrogen atom, respectively).

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2. Experimental

The electron attachment spectrometer consists of a trochoidal electron monochromator (TEM), a molecular beam system and a quadrupole mass filter with a pulse counting system for analyzing and detecting the ionic products. The substantially modified TEM has recently been described in detail [7,8]. The anions produced by the electron attachment processes are extracted by a weak electric field into a quadrupole mass filter where they are mass analyzed and then detected. After crossing the collision region, the remaining electrons are collected and the electron current is monitored online during the experiment using a pico-ampèremeter.

The TEM was operated at an energy resolution of 60 meV at full width half maximum.

In the present studies a mixture of organic acid (98% purity purchased from Sigma Aldrich), CCl_4 and argon (as a buffer gas) was used.

3. Results and discussion

Electron attachment to organic acids in the energy range between about 0 and 10 eV leads to the production of various anionic fragments [9–12]. For all of the acids studied here $(\text{M}-\text{H})^-$ anion formation is observed (Fig. 1). The solid lines in these figures are Gaussian fits to the experimental data. A Gaussian peak shape is expected for a situation when the fragment ion yield curve can be represented by the reflection of (the square) vibrational wave function of the ground state of the neutral at the repulsive part of the anionic potential energy surface. Such a situation holds e.g. for diatomic molecules when internal excitation of the atomic fragments can be neglected. In polyatomic molecules the dissociation of the transient negative ion (TNI) does not usually proceed directly along the repulsive part of the potential surface and excitation of internal degrees of freedom in the TNI can take place [13–17].

A closer inspection of the $(\text{M}-\text{H})^-$ ion yields for the organic acids shows weak, but clear, structures

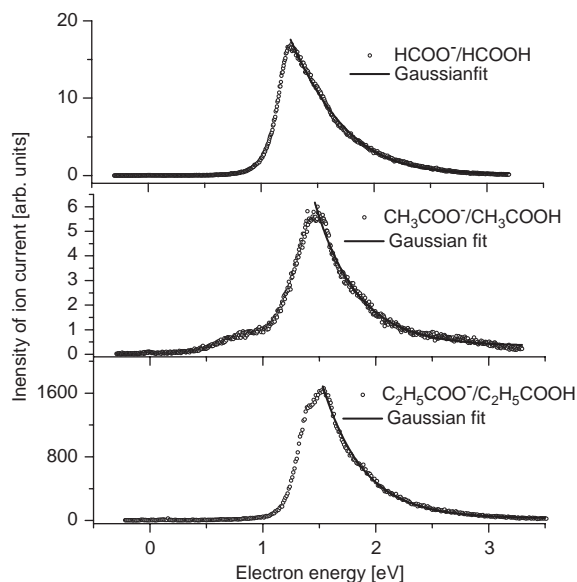


Fig. 1. Formation of $(\text{M}-\text{H})^-$ ions in dissociative electron attachment to the organic acids (formic, acetic and propanoic acid). The solid line in that figure is a Gaussian curve fitted to the experimental data (open circle).

on the high-energy tail of the resonances. In order to highlight the presence of these resonances we plot in Fig. 2 the difference between the experimental data and the fitted Gaussian curve versus the electron energy.

3.1. HCOO^- (from formic acid)

As demonstrated in the previous report [9], electron attachment to formic acid yields the formate HCOO^- anion as the most abundant fragment ion appearing in a prominent resonance peaking at 1.25 eV. The reaction channel is



Process (1) represents a direct cleavage of the $\text{HCOO}-\text{H}$ bond in the TNI with the negative charge remaining on the large fragment. The HCOO^- ion yield exhibits weak structures on the high-energy tail of the resonance [10]. The maxima of this structure are separated by 340 ± 60 meV.

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