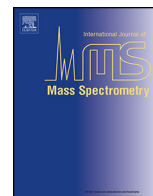




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Partial cross sections for dissociative electron attachment to tetrahydrofuran reveal a dynamics-driven rich fragmentation pattern

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Dedicated to 70th birthday of Prof. Tilmann D. Märk.

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ABSTRACT

We report partial absolute cross sections for dissociative electron attachment (DEA) to tetrahydrofuran C₄H₈O. The high sensitivity of the present setup, quantitative DEA spectrometer with time-of-flight analyzer, led to identification of a number of previously unreported fragments (CH₂⁻, OH⁻, CHO⁻, C₄H₅O⁻, C₃H₃⁻) thus revealing complex dissociation dynamics of the involved resonant states. The chemical composition of fragment anions was assigned by experiments with completely deuterated tetrahydrofuran. We also show that the dominant heavy anionic fragment with $m/z = 41$ is C₃H₅⁻ anion rather than C₂HO⁻ as reported in the previous studies, in spite of the fact that formation of the latter one is energetically more favorable. The dynamics on the resonant state is thus more decisive for the reaction outcome than the asymptotic energetics. The assignment of resonances and their dynamic pathways is discussed by using comparison with recent complementary experiments that characterize electronic states of neutral and ionic tetrahydrofuran.

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1. Introduction

Electron collisions with tetrahydrofuran (THF) attracted a surprising amount of attention during the last 15 years. This interest – which may seem unusual for a small organic molecule – has been part of the line of research in electron collisions with molecules of biological relevance. This line of research aims at elucidating the role of electron-triggered processes in radiation damage. In this respect THF, since it is the simplest saturated furanose ring, can be considered as a prototype for the DNA sugar backbone. Additionally, in contrary to sugars, THF is a liquid at standard laboratory conditions which greatly facilitates the experiments.

The above-mentioned line of research has been triggered by a ground breaking discovery of Sanche and co-workers [1] that low-energy electrons cause single and double strand DNA breaks even at sub-ionization energy. Inspired by this discovery, various research groups started to look at the electron-induced reactions in molecular constituents of DNA. One of the first groups that adopted this direction – and quickly became a beacon in the field – was the group of T.D. Märk in Innsbruck. Märk recognized the high scientific potential in this field and the experiments in his group have greatly contributed to a renewal of the interest in electron-triggered

physics and chemistry, especially the dissociative electron attachment (DEA). This process, which proceeds via formation of a transient resonant state is an effective bond-breaking reaction and the experiments in Innsbruck have elucidated its role in a whole range of molecules with biological relevance: DNA bases [2,3], sugars [4], or amino acids [5]. The experiments have revealed a plethora of phenomena occurring in dissociative electron attachment: site- and bond-selectivity [6] or DEA footprints of vibrational Feshbach resonances in biomolecules [7]. The group of T.D. Märk has been also the first one that looked into DEA process in the molecule of present interest: tetrahydrofuran [8].

Basically all experimentally accessible electron-triggered processes in THF have been characterized in the recent years. The total electron scattering cross sections were reported by Zecca et al. [9], Mozejko et al. [10] and Fuss et al. [11]. The elastic scattering in various energy ranges was probed by Milosavljević et al. [12], Dampc et al. [13], Allan [14], Colyer et al. [15], Baek et al. [16], Chiari et al. [17] and Homem et al. [18]. The vibrational excitation cross sections were reported by Dampc et al. [19] and Allan [14] and electronic excitation was probed by Do et al. [20] and Giuliani et al. [21]. The electron collisions with THF attracted also considerable amount of attention from a theoretical point of view. The scattering processes were characterized by a Schwinger multichannel method [22], complex Kohn variational method [23], or R-matrix method with Born correction [24]. The last study is of special interest here since it identified a number of core-excited resonances. Complementary to the gas phase, series of experiments with THF deposited

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on a surface was performed by Lepage et al. [25], Antic et al. [26,27], Breton et al. [28], Jäggle et al. [29], and Park et al. [30].

The dissociative electron attachment channels in THF have also been the subject of several studies, Sulzer et al. [8] and Ibanescu et al. [31] reported yields of individual DEA fragments as a function of the electron energy and Aflattoni et al. [32] measured total DEA cross section using a total ion collection instrument. Surprisingly, the first two studies only partially agree with each other: they agree on the occurrence of the (strongest) fragment with atomic mass 41, which was assigned by both groups to be the $C_2H_5O^-$ anion. However, Sulzer et al. also reported the occurrence of a parent anion THF $^-$ and a doubly dehydrogenated parent anion (THF-2H) $^-$ around 2 eV, which were not detected by Ibanescu et al. who, on the other hand, reported hydride anion H^- and anion with mass 43 ($C_2H_3O^-$). The occurrence of stable parent anions in DEA at energies considerably higher than 0 eV is very rare, since the excess energy (electron affinity and incident electron energy) has to be stored within internal degrees of freedom. Such situation often leads to metastability of the parent anion in the microsecond time window [33,34]: the excitation energy randomizes over the internal degrees of freedom and the decay of the parent anion results from the concentration of sufficient energy in the relaxation channel.

Our primary motivation to study THF was the eventual occurrence of such metastability, which can be detected with a time-of-flight setup such as the one available in our laboratory. We report negative evidence for metastable processes in our time window, however, we have discovered several surprising aspects of the DEA to THF. The high sensitivity of our instrument enabled identification of a number of previously unreported anionic fragments, thus revealing much more complex fragmentation dynamics. We also provide new assignment of the strongest heavy anionic fragments with the mass 41, which turned out to be $C_3H_5^-$. We provide absolute partial DEA cross sections for all reported fragments and discuss the possible origins of resonant states leading to the reported dissociation pattern.

2. Experiment

The quantitative DEA spectrometer has been described in detail previously [35–37]. The electron beam is produced by a trochoidal electron monochromator, passes through a collision cell filled with the sample gas and is collected by a Faraday cup. Anions created by DEA are extracted through a narrow slit in the cell's wall to a time-of-flight mass (TOF) spectrometer. The experiment works in a pulsed mode. The electron beam passes through the collision cell for 200 ns while it is field-free. After another 200 ns (so that the electrons are allowed to leave the cell) a voltage pulse of -300 V is applied across the cell to expel the anions. They are detected by a microchannel plate coupled with phosphorus screen and photomultiplier, counted and their arrival times are analyzed using a delayed coincidence scheme. The spectra are recorded as a two-dimensional map of the ion signal as a function of electron energy and the flight time (which reflects the anion mass). The repetition rate is 50 kHz. The pressure in the collision cell is controlled by a needle valve and monitored by a capacitance manometer. It was kept in the range of 3×10^{-4} to 6×10^{-4} Torr. Since the previous studies did not reveal any fine structures in DEA ion yields, the electron monochromator was operated to yield high electron current (around 100 nA in the CW mode) and thus a total high sensitivity. The electron energy resolution during the present measurements was 250 meV.

The TOF setup has two acceleration regions and a drift region. The first acceleration region is between the pulsed pusher and the wall of the collision chamber, the second acceleration region is between the wall of the chamber and the front plate of the

time-of-flight tube. The TOF tube (drift region) is not entirely field-free, it is constructed as a focusing ion lens and the entire setup was designed to keep the extraction and detection efficiency independent of the mass and initial kinetic energy of the detected anions [37]. Additionally, its first part has a deflecting capacity in order to compensate for the effect of the magnetic field. It has been shown by simulations and extensive tests that only two types of voltage settings are necessary for the proper collection: 'light ion settings' for H^- and D^- ions and 'heavy ion settings' for ions with larger masses. The mass scale is calibrated with ions of known masses from other compounds (O^- from O_2 , H^- , C_2^- and C_2H^- from acetylene) and the calibration is based on the fact that the time-of-flight is directly proportional to the square root of mass. The mass assignment is verified by the fact that all assigned masses fit perfectly on the calibration curve.

The electron energy scale was calibrated using the 4.4 eV O^-/CO_2 peak. The shape of this band (with a threshold at 3.99 eV) has been measured with high electron-energy resolution [38]. We determine both the energy scale calibration and the electron energy resolution by fitting the convoluted high-resolution data to our measurement. Absolute magnitudes of the cross sections were calibrated on the same O^-/CO_2 band with a peak cross-section value of 14 pm^2 [35]. The error of the absolute measurements (two standard deviations) is taken to be $\pm 25\%$. This is the combined error of $\pm 20\%$ of the relative measurements with the $\pm 15\%$ error of the O^-/CO_2 absolute cross section. We have shown recently [39] that this calibration approach is not appropriate if there are narrow bands in the DEA spectra due to effect of electron beam resolution on the peak width, however, it is perfectly suitable for the present molecule since only broad bands appear in the spectra (see below).

3. Results and discussion

3.1. Anionic fragments and partial cross sections

Fig. 1 (top) shows the negative ion mass spectrum of tetrahydrofuran originating from the impact of 8.5 eV electrons. One can observe a rich fragmentation pattern with a number of previously unreported anionic fragments. The chemical composition of all

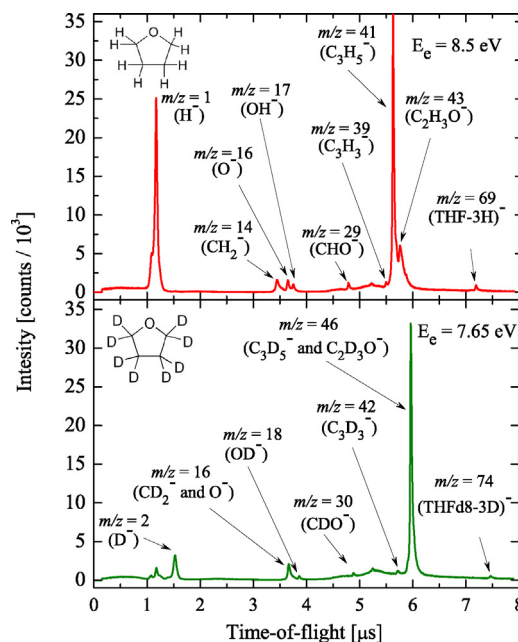


Fig. 1. Negative ion TOF mass spectrum of tetrahydrofuran (top) and fully deuterated tetrahydrofuran THF-d8 (bottom).

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