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Dissociative electron attachment to furan, tetrahydrofuran, and fructose

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We study dissociative electron attachment to furan (FN) (C_4H_4O), tetrahydrofuran (THF) (C_4H_8O), and fructose (FRU) ($C_6H_{12}O_6$) using crossed electron/molecular beams experiments with mass spectrometric detection of the anions. We find that FN and THF are weak electron scavengers and subjected to dissociative electron attachment essentially in the energy range above 5.5 eV via core excited resonances. In striking contrast to that, FRU is very sensitive towards low energy electrons generating a variety of fragment ions via a pronounced low energy feature close to 0 eV. These reactions are associated with the degradation of the ring structure and demonstrate that THF cannot be used as surrogate to model deoxyribose in DNA with respect to the attack of electrons at subexcitation energies (<3 eV). The results support the picture that in DNA the sugar moiety itself is an active part in the initial molecular processes leading to single strand breaks. © 2006 American Institute of Physics. [DOI: 10.1063/1.2222370]

INTRODUCTION

The cyclic compound tetrahydrofuran (THF) has been used to model the deoxyribose ring in DNA (Refs. 1 and 2) with respect to low energy electron interaction. Here we perform a comparative study of dissociative electron attachment (DEA) between the cyclic compounds furan (FN) and tetrahydrofuran (THF) with fructose as a typical representative of a sugar molecule (Fig. 1). The general interest in such a comparative study stems from current attempts to unravel the molecular mechanisms by which low energy electrons damage DNA. In the meantime it is well recognized that in radiation damage of biological material the interaction of secondary electrons (abundantly generated along the ionization track) plays an important role.³⁻⁵ In that context, the intrinsic properties of the DNA building blocks are of fundamental interest. In the meantime, extensive studies have been performed on the DNA bases thymine (T), adenine (A) cytosine (C), and guanine (G) [including also the RNA base uracil (U)],⁶⁻¹¹ demonstrating the sensitivity of these compounds with respect to low energy electrons. It has been shown that

hydrogen loss via DEA is an effective reaction in the energy range below the level of electronic excitation. In contrast to the DNA bases, there is so far less detailed information available on the sugar moiety, which in DNA connects the nucleobase with the phosphate group of the backbone. In DNA, the sugar unit is present in the form of deoxyribose, more precisely, as a five membered ring (furanose form) while in solution deoxyribose and ribose exist in an equilibrium between a linear form and two cyclic forms, namely, the six membered ring (pyranose form) and the five membered ring (furanose form).¹² Experimental and theoretical studies of gas phase D-ribose ($C_5H_{10}O_5$), on the other hand, revealed that the pyranose form of crystalline ribose is preserved in the evaporation process.¹²

For FRU, there is so far no data available in the literature concerning low energy electron interaction. A previous study on deoxyribose revealed that it is subjected to intense DEA reactions already at energies close to 0 eV leading to the loss of H_2O and further neutral molecules.¹³ Accordingly, low energy DEA reactions were also reported for D-ribose. By using isotopically labeled compounds (D, ^{13}C), a remarkable site selectivity was found in the way that neutral units containing the $^{13}C5$ atom are selectively excised from the molecule.¹⁴ While a previous study on FN (obtained with an electron energy resolution of 0.3 eV) reported DEA reactions within a pronounced resonance located near 6 eV,¹⁵ no data concerning DEA with gas phase THF are available.

EXPERIMENT

The experiments on FN and THF were performed within a coordinated study between the Innsbruck laboratory and

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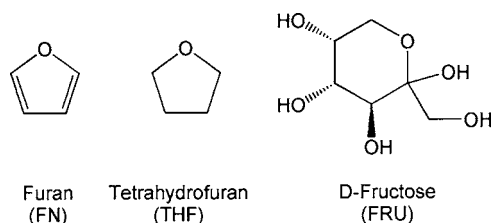


FIG. 1. Schematic geometrical representation of the three compounds under consideration.

the Berlin laboratory. The data on FRU have been obtained at the Innsbruck laboratory in the framework of exchange visits within the EU programs Cooperation in the Field of Science and Technical Research (COST) and Electron Induced Processing on a Molecular Level (EIPAM). Both laboratories use crossed electron/molecular beams with mass spectrometric detection of the generated ions. Solid samples can be sublimated by a temperature regulated oven which is connected to the reaction chamber. In the Innsbruck apparatus,¹⁶ the electron beam is produced by an electrostatic hemispherical electron monochromator operated at an energy resolution of 110–130 meV. In the Berlin laboratory¹⁷ the electron beam is generated from a trochoidal electron monochromator¹⁸ operated at an energy resolution of 100–120 meV. In both devices the electron beam intersects orthogonally with the effusive molecular beam and the ions are extracted by a small electric field towards the entrance of a quadrupole mass spectrometer and detected using single pulse counting by a channeltron (Innsbruck) or a secondary electron multiplier (Berlin). The applied extraction field is below 0.5 V cm^{-1} in the Berlin laboratory (magnetically guided electron beam) and below 0.2 V cm^{-1} at the Innsbruck laboratory. In both cases the extraction field does not significantly deteriorate the energy resolution of the beam in the interaction region. The electron energy scale is calibrated by measuring the ion yields of $\text{SF}_6^-/\text{SF}_6$ or Cl^-/CCl_4 both exhibiting a sharp resonance near 0 eV. All measurements were performed in the absence of the calibration gas in order to prevent ion-molecule reactions.

Both FN and THF are liquids under normal conditions with sufficient vapor pressure to generate a molecular beam. D-fructose is a crystalline substance which by heating to 90–100 °C produces a noticeable increase of pressure in the range of $(1-2) \times 10^{-6}$ mbar (recorded by the ion gauge at one of the flanges). Since the shape of the observed ion yields does not change with temperature and also the relative intensity of the observed products was constant in the temperature range of 90–100 °C, we suppose that the gaseous target only consists of intact FRU molecules. The substances were obtained from Sigma Aldrich with stated purities of 99+% (FN), 99.9% (THF), and 99+% (FRU). The liquids FN and THF were subjected to several freeze-pump-thaw cycles prior to use while FRU was used as delivered. The data obtained from FN and THF were in perfect agreement between the two laboratories. Data from FRU were only obtained in the Innsbruck laboratory.

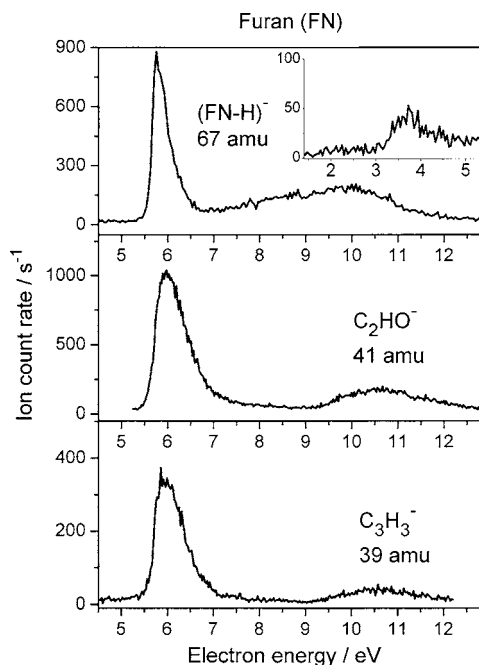


FIG. 2. The three dominant negative ion yields from furan (FN). In the energy range below 5 eV only a small signal due to the furanyl anion is detected (see insert at different intensity scales).

RESULTS AND DISCUSSION

Figures 2–5 present the ion yield curves obtained from the three compounds under consideration. From the data it is immediately obvious that they respond very differently in low energy electron impact. Before discussing the DEA reactions in more detail we shall first address the more general features.

While FRU exhibits a variety of intense low energy DEA reactions close to 0 eV, FN possesses a pronounced

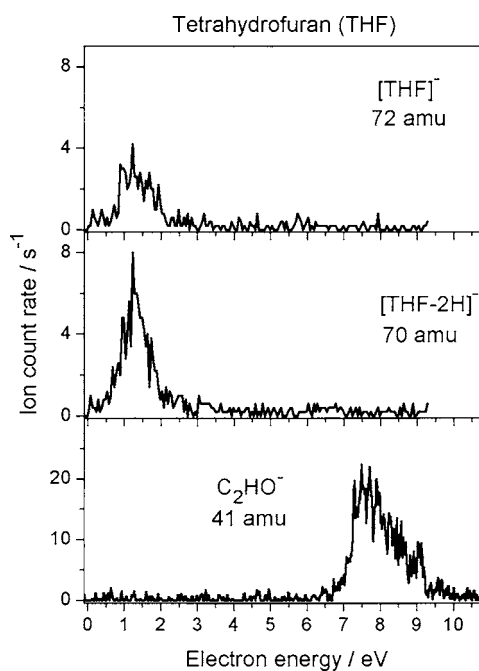


FIG. 3. Negative ion yields from tetrahydrofuran (THF). The weak signal at 72 amu is due to a metastable parent anion (see the text).

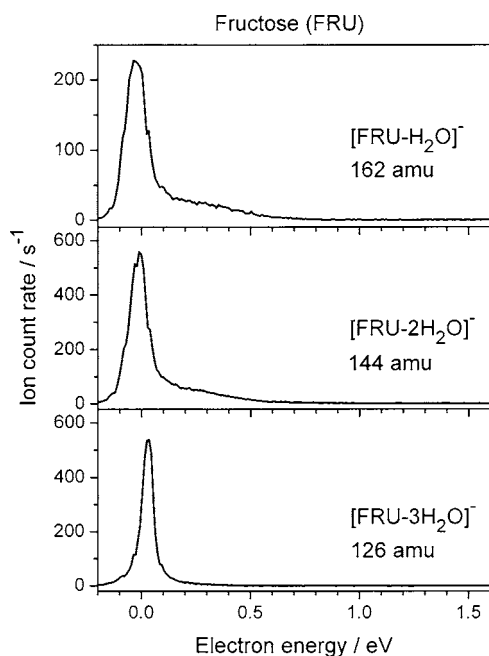


FIG. 4. Fragment anions arising from fructose by the abstraction of one, two, and three neutral water molecules, respectively. Scans on an extended energy scale (up to 12 eV) did not result in detectable signals at these mass units.

DEA resonance at considerably higher energy (6 eV) resulting in different anionic fragments. THF is a very weak electron scavenger showing two resonances, located near 1.25 and 7.5 eV, respectively. In FRU, the intense DEA channels are operative already at energies near 0 eV while at higher energies only signals due to the light fragments OH^- , O^- , and H^- are present. On a first sight one would not expect

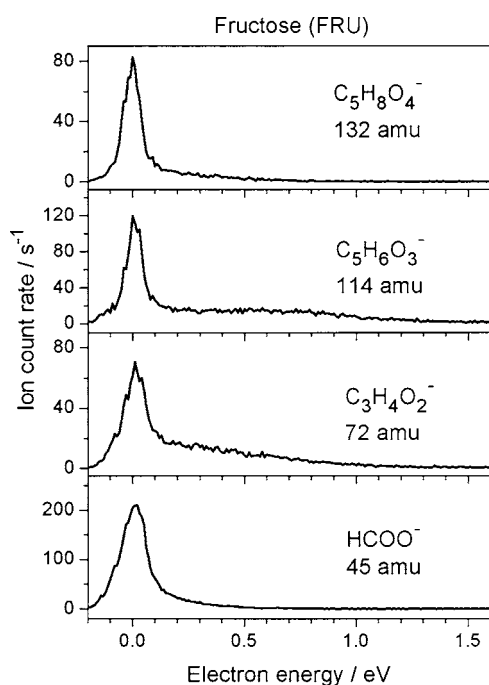


FIG. 5. Mass numbers of fragment ions from fructose arising from complex DEA reactions. For the assignment of the DEA reactions, see the text. Scans on an extended energy scale (up to 12 eV) did not result in detectable signals at these mass units.

TABLE I. Heats of formation (ΔH_f°) for some compounds relevant in the present reactions, taken from Ref. 20.

Compound	ΔH_f° (kJ mol ⁻¹)
C ₆ H ₁₂ O ₆ (D-fructose, FRU, solid)	-1266
C ₆ H ₈ O ₄ (DL-lactide, solid)	-792
H ₂ O	-242
H ₂ O (liquid)	-286
C ₄ H ₄ O [furan (FN), gas]	-35
C ₄ H ₄ O [furanj (FN), liquid]	-62
C ₄ H ₈ O [tetrahydrofuran (THF), gas]	-184
C ₄ H ₈ O [tetrahydrofuran (THF), liquid]	-212
CO ₂	-394
CH ₄	-75
CH ₃ OH (liquid)	-239
CH ₃ OH (gas)	-201
H	218
C ₂ ⁻	527 ± 12
OH	39.0
CH ₃ CHO (acetaldehyde, gas)	-171

such low energy DEA processes, since in fructose only σ^* molecular orbitals (MOs) are available to accommodate an extra electron while FN possesses π^* MOs which are considered to be located at lower energy. In DEA studies to gas phase methanol, e.g., the lowest energy resonance was identified at 6.2 eV.¹⁹

From the thermodynamic point of view, FRU possesses very favorable DEA channels (which is not the case for FN and THF) as is immediately obvious from the thermodynamic properties²⁰ of the involved compounds collected in Table I.

For a DEA reaction generating two fragments,



[$M^{\#-}$ assigns the transient negative ion (TNI) formed by electron attachment], the appearance energy of the negative fragment X^- can be expressed as

$$AE(X^-) = D(R-X) - EA(X) + E^*, \quad (2)$$

where D is the bond dissociation energy in the neutral system, $EA(X)$ the electron affinity of fragment X , and E^* the total excess energy of the reaction due to the initial transition creating the transient anion at energy E^* above the dissociation limit. The energy threshold for the DEA reaction (1) (the reaction enthalpy) is then

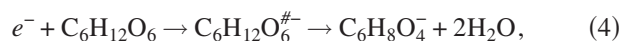
$$\Delta H_R = D(R-X) - EA(X). \quad (3a)$$

Equation (3a) is appropriate for a simple bond cleavage along the coordinate $R-X$. Most of the present DEA reactions are appreciably more complex and associated with multiple bond cleavages, electronic, and structural rearrangements associated with the formation of new bonds. In such cases it is more adequate to express the standard reaction enthalpy by means of the standard heats of formation (ΔH_f°) of the involved compounds. Equation (3a) is then equivalent to

$$\Delta H_R = \Delta H_f^0(R) + \Delta H_f^0(X^-) - \Delta H_f^0(RX), \quad (3b)$$

where $\Delta H_f^0(X^-) = \Delta H_f^0(X) - EA(X)$.

If we apply (3b) to the DEA reaction in FRU generating an anion at 144 amu which is due to the loss of two neutral water units, viz,



and assume that the anion of cyclic DL-lactide is formed, the enthalpy for the DEA reaction (4) can be calculated (in the condensed phase, Table I) according to (3b) within the limit of the unknown electron affinity of $C_6H_8O_4$ as $\Delta H_R = 2\Delta H_f^0(H_2O) + \Delta H_f^0(C_6H_8O_4) - \Delta H_f^0(C_6H_{12}O_6) - EA(C_6H_8O_4) = -98 \text{ kJ mol}^{-1} - EA(C_6H_8O_4)$. This demonstrates that from the *thermodynamic point of view* the loss of two water units from fructose is exothermic *even in the neutral* system, but kinetically strongly hindered due to the presence of large activation barriers. Fructose can hence certainly be viewed as stable compound on a macroscopic time scale as many other compounds which are only kinetically stable. Obviously, this situation is dramatically changed by the presence of an electron. The electron affinity of the created fragment may then energetically further drive the reaction.

DEA is usually pictured as a two-step process, i.e., formation of a resonance, thereby accommodating an extra electron (of particular energy) into one of the virtual MOs (via a Franck-Condon transition) which then decomposes.²¹ As mentioned above, one would rather expect low energy DEA processes in FN (due to the availability of π^* MOs) than in the saturated compound FRU. It has to be noted, however, that the energy of the first unoccupied MO in the *neutral molecule* cannot directly be correlated to the attachment energy (i.e., the energy of the transient *anion*). Low-lying σ^* MOs (near 0 eV) are in fact well known for saturated halocarbons containing the larger halogen atoms Cl, Br, and I.^{21–25} We may hence conclude, that the transient negative ion $FRU^{\#-}$ either possesses low-lying σ^* MOs (with respect to the vacuum level) or that the mechanism for DEA has to be described beyond the Born-Oppenheimer approximation and vertical Franck-Condon transitions. We further note that the energy of a transient negative ion cannot directly be calculated by standard quantum chemistry methods based on energy minimalization, since they represent discrete states embedded in the electron detachment continuum. Any minimalization procedure using large basis sets would ultimately accommodate the extra charge into diffuse and specially extended orbitals thereby approaching the energy of the neutral molecule. Such quasi-bound-states are, e.g., accessible through scattering calculations²⁶ or the *R*-matrix method.¹

Furan (FN) (C_4H_4O , 68 amu)

This compound generates several fragment anions appearing from a pronounced resonance located near 6 eV (Fig. 2) with the exact position slightly depending from the observation channel. The following fragment ions were observed: 67 amu ($(FN-H)^-$), 49 amu (C_4H^-), 41 amu ($HCCO^-$), 39 amu ($C_3H_3^-$), and 25 amu (C_2H^-). In this notation $(FN-H)^-$ assigns the (closed shell) negative ion of furan, subjected to the loss of a neutral hydrogen atom. Fig-

ure 2 shows the yields of the three most abundant ions. The complete set of data is collected from the diploma thesis of Bald.²⁷

In electron transmission experiments,²⁸ two low lying resonances located at 1.73 and 3.15 eV were identified and assigned to the shape resonances $\pi_4^*(b_1)$ and $\pi_5^*(a_2)$ occupying LUMO 1 and LUMO 2, respectively. We only detect a very small $(FN-H)^-$ signal in that energy regime (see insert to Fig. 2). From the enthalpy of the deprotonation reaction in FN [$FN \rightarrow (FN-H)^- + H^+$, $\Delta H_R = 1636 \text{ kJ mol}^{-1}$ (Ref. 21)], one can calculate the reaction enthalpy for DEA yielding $(FN-H)^-$ as 3.35 eV. This indicates, that $(FN-H)^-$ is only accessible within the high-energy tail of the π_5^* resonance which also explains its comparatively low intensity. Other DEA channels are possibly not accessible from the π^* shape resonances. The presumably lowest energy DEA channel is $C_2^- + CH_2CHO$ (acetaldehyde) with a thermodynamic threshold of 3.25 eV (Table I). It would require appreciable rearrangement in the temporary anion and is not observed.

Electronically excited states in FN involving the two highest occupied MOs (π_2 and π_3) were identified at 5.80 and 6.04 eV (Ref. 29) and we therefore suggest that the DEA resonance is a core excited resonance associated with these electronically excited states. It has to be noted that in the excitation function of the C–H stretch vibration, a broad resonance feature was found³⁰ which was associated with a single particle σ^* (C–H) resonance. Since the presently observed DEA feature is considerably narrower, however, we assume that it is a core excited two particle resonance associated with a $\pi \rightarrow \pi^*$ transition.

The decomposition products of this TNI are due to complex reactions involving multiple bond cleavage and also formation of new bonds. Only the 67 amu fragment creating the closed shell furanyl anion $(FN-H)^-$ is formed by the loss of a neutral hydrogen atom. $HCCO^-$ is known as a stable anion for which photoelectron spectra were recorded.³¹ Its formation can be considered by the cleavage of a C–C and a C–O bond accompanied with hydrogen transfer. Accordingly, $C_3H_3^-$ (allenyl anion) is formed by cleavage of the C=C and a C–O bond thereby forming the HCO radical as neutral complement. $C_3H_3^-$ has been characterized in photoelectron spectroscopy^{32,33} having an electron binding energy near 0.9 eV. The C_2H^- anion, finally, is known as an appreciably stable compound with an electron binding energy of 2.97 eV,³⁴ corresponding to the electron affinity of C_2H^- .

The molecule exhibits a second and comparatively broader resonance at higher energy possible composed of different electronic states. Since they are located above the ionization energy of FN [8.88 eV (Ref. 21)] they may be viewed as core excited shape resonances involving Rydberg states.

Tetrahydrofuran (THF) (C_4H_8O , 72 amu)

This molecule has been considered as surrogate for deoxyribose in DNA.^{1,2} As can be seen from the count rates in Fig. 3 it is an extremely weak electron scavenger showing two resonances located at 1.25 and 7.6 eV. *R*-matrix calculation do not give evidence of one particle shape resonances

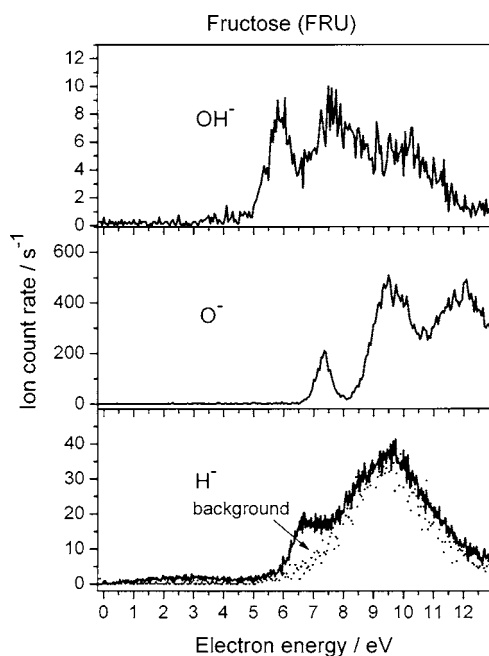


FIG. 6. Fragment ions from fructose appearing at higher energies. H^- and OH^- can be formed via a single bond rupture while O^- is expelled from the C–O–H group. The H^- spectrum contains the background signal which is also present in the UHV apparatus, when the sample is switched off (see the text).

but core excited resonances in the area between 6.5 and 8 eV,¹ which is the range where the product HCCO^- is observed. H^- has also been observed in electron stimulated desorption (ESD) from condensed THF,² but not in the present gas phase study, reflecting the particular sensitivity of ESD experiments in detecting light ions. From the low energy feature we find a signal at 70 amu due to anion subjected to the loss of two H atoms.

The very weak signal at 72 amu (distinctly above the detection limit and readily separable from the 70 amu signal) is due to the nondissociated THF radical anion. Such metastable parent anions are sometimes observed in larger polyatomic systems but usually at energies close to 0 eV, such as SF_6^- and other perfluorinated compounds.^{26,35–37} Only in C_{60} (including the higher fullerenes) intact parent anions C_{60}^- can be observed up to electron energies extending 12 eV.^{38,39} The general understanding is that effective coupling with the vibrational degrees of freedom removes electronic energy thereby delaying autodetachment. Since the presently observed signal is distinctly above 0 eV and very weak we cannot exclude that it is generated via secondary processes (ion-molecule reactions).

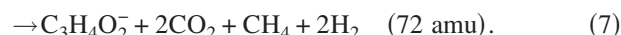
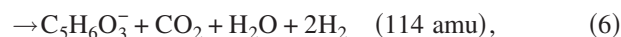
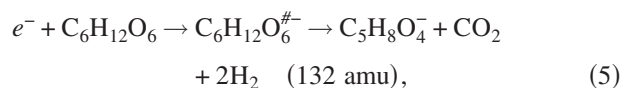
Fructose (FN) ($\text{C}_6\text{H}_{12}\text{O}_6$, 180 amu)

Figures 4 and 5 present the ion signals observed at very low energies and Fig. 6 the ion yields of the lighter fragments OH^- , O^- , and H^- appearing from structured features in the energy range between 6 and about 12 eV. It has to be noted that for the ions shown in Figs. 4 and 5 no further signal is detected upon extended energy scans up to 12 eV.

The ions at 162, 144, and 126 amu can be assigned to the loss of one, two, and three neutral water units, respec-

tively. Stoichiometrically, the loss of two water units would also correspond to the loss of C_3 which is chemically very unreasonable. Accordingly, the assignment of the anionic fragments in Fig. 5 is not in every case unambiguous, but it follows reasonable decomposition pathways, some of which are very similar to those recently observed in ribose.¹⁴ In this case isotope labeling (D, ^{13}C) enabled an unambiguous stoichiometric assignment.

Along that line we tentatively assign the product ions shown in Fig. 5 to the following DEA reactions:



Formation of the fragment at 72 amu may equally be associated with the neutral channel $\text{CO}_2 + 2\text{CH}_3\text{OH}$ which is, however, energetically appreciably less favorable with respect to (7).

The lightest ion along the series of fragments formed at very low energy appears at 45 amu which is either HCOO^- or COOH^- . Both anions exist in the gas phase and their potential energy surfaces (including that of the neutral systems) have been explored by photoelectron spectroscopy and *ab initio* calculations.^{40–42} From that, it appears that the HCOO radical is less stable than COOH , while in the anionic system the configuration HCOO^- is more stable having a binding energy for the excess electron (corresponding to the electron affinity of HCOO) of 3.51 eV. Irrespective of the structure, formation of the fragment anion at 45 amu represents the excision of a larger unit from FRU which may degrade the ring structure.

In contrast to these complex processes, the light anions OH^- and H^- can be formed by simple bond cleavage (eventually leaving the rest of the fructose molecule unchanged). The energy threshold for such a reaction can be expressed by Eq. (3). For the typical bond dissociation energies $D(\text{C–OH})=4.5$ eV and $D(\text{O–H})=5.0$ eV and the known electron affinities $\text{EA}(\text{OH})=1.83$ eV and $\text{EA}(\text{H})=0.75$ eV,²¹ the threshold for the appearance of OH^- and H^- becomes 2.77 and 3.25 eV, respectively.

The O^- ion, finally, must be expelled from the C–O–H unit. The energetically lowest pathway is expulsion of O^- ion and concomitant formation of a new C–H bond. In methanol, such a reaction creates CH_4 having an energy threshold of 2.4 eV.³⁵ It is interesting to note that expulsion of the O^- unit is more effective than the simple bond cleavage creating OH^- and O^- . These light ions show a more or less structured profile in the energy range above 5 eV. It is clear that the associated states of the precursor ion are of the core excited type. Since they all appear appreciably above the thermodynamic limit for a corresponding simple bond cleavage one can suppose that also the neutral complement is subjected to further decompositions.

In the H^- spectrum we have included the H^- background which is present under conditions when no sample is intro-

duced or present in the UHV chamber. H^- can be formed from many molecules such as water and hydrocarbons and hence even under UHV conditions there is always some H^- background signal in the range of 50 counts s^{-1} (present in both the Berlin and Innsbruck apparatus).

CONCLUSIONS

The comparative study between FN, THF, and FRU demonstrates that that FRU is sensitive to the interaction of low energy electrons (subexcitation electrons), thereby undergoing a series of complex decomposition reactions leading to the degradation of the ring system. In contrast to that, FN and THF are comparatively weak electron scavengers undergoing DEA mainly via core excited resonances at appreciably higher energies. This directly shows that THF cannot be viewed as a model for the deoxyribose ring in DNA, at least not with respect to DEA at subexcitation energies. The present results on FRU support the picture that at low energies the deoxyribose ring itself plays an active role in the initial steps towards single strand breaks. At subexcitation energies, only single strand breaks are observed in plasmid DNA.⁴³ The situation is different at energies above 5 eV where electrons induce single and double strand breaks.³ In that domain, the sugars only undergo DEA reactions generating the light fragments OH^- , O^- , and H^- , and the DNA bases can in fact be viewed as active centers for the attachment of electrons with subsequent decompositions like the degradation of the ring structure⁶ or the cleavage of the glycosidic N1–C1 bond as very recently demonstrated in DEA studies to thymidin, representing a thymine coupled to a deoxyribose unit.⁴⁴

The mechanisms of the low energy DEA reactions in fructose remain to be explored. The question is whether low lying σ^* MOs are accessible in electron attachment and/or whether non-Born-Oppenheimer effects provide pathways for the anionic system to access the energetically low-lying DEA channels.

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¹D. Bouchiha, J. D. Gorfinkiel, L. G. Caron, and L. Sanche, *J. Phys. B* **39**, 975 (2006).

²D. Antic, L. Lepage, and L. Sanche, *J. Phys. Chem. B* **103**, 6611 (1999).

³B. Boudaiffa, P. Cloutier, D. Hunting, M. A. Huels, and L. Sanche, *Science* **287**, 1658 (2000).

⁴L. Sanche, *Eur. Phys. J. D* **35**, 367 (2005).

⁵L. Sanche, *Mass Spectrom. Rev.* **21**, 349 (2002).

- ⁶G. Hanel, B. Gstir, S. Denifl, P. Scheier, B. Farizon, M. Farizon, E. Illenberger, and T. D. Märk, *Phys. Rev. Lett.* **90**, 188104 (2003).
- ⁷S. Ptasinska, S. Denifl, V. Grill, P. Scheier, T. D. Märk, S. Gohlke, M. A. Huels, and E. Illenberger, *Angew. Chem., Int. Ed.* **44**, 1647 (2005).
- ⁸S. Ptasinska, S. Denifl, V. Grill, T. D. Märk, E. Illenberger, and P. Scheier, *Phys. Rev. Lett.* **95**, 093201 (2005).
- ⁹H. Abdoul-Carime, S. Gohlke, and E. Illenberger, *Phys. Rev. Lett.* **92**, 168103 (2004).
- ¹⁰R. Abouaf and H. Dunet, *Eur. Phys. J. D* **35**, 405 (2005).
- ¹¹A. M. Scheer, K. Aflatooni, G. A. Gallup, and P. D. Burrow, *Phys. Rev. Lett.* **92**, 068102 (2004).
- ¹²L.-P. Guler, Y.-Q. Yu, and H. I. Kenttämä, *J. Phys. Chem. A* **106**, 6754 (2002).
- ¹³S. Ptasinska, S. Denifl, P. Scheier, and T. D. Märk, *J. Chem. Phys.* **120**, 8505 (2004).
- ¹⁴I. Bald, J. Kopyra, and E. Illenberger, *Angew. Chem., Int. Ed.* **45**, 4851 (2006).
- ¹⁵M. V. Muftakhov, N. L. Asfandiarov, and V. I. Khvostenov, *J. Electron Spectrosc. Relat. Phenom.* **69**, 165 (1995).
- ¹⁶D. Muigg, G. Denifl, A. Stamatovic, and T. D. Märk, *Chem. Phys.* **239**, 409 (1998).
- ¹⁷R. Balog, J. Langer, S. Gohlke, M. Stano, H. Abdoul-Carime, and E. Illenberger, *Int. J. Mass. Spectrom.* **233**, 267 (2004).
- ¹⁸A. Stamatovic and G. J. Schulz, *Rev. Sci. Instrum.* **41**, 423 (1970).
- ¹⁹A. Kühn, H.-P. Fenzlaff, and E. Illenberger, *J. Chem. Phys.* **88**, 7453 (1988).
- ²⁰NIST Chemistry webbook, <http://webbook.nist.gov/chemistry>
- ²¹E. Illenberger, *Gaseous Molecular Ions: An Introduction to Elementary Processes Induced by Ionization* (Steinkopff, Darmstadt/Springer, New York, 1992).
- ²²L. G. Christophorou and J. K. Olthoff, *Fundamental Electron Interactions with Plasma Processing Gases* (Kluwer Academic, Dordrecht/Plenum, New York, 2004).
- ²³E. Illenberger, *Photoionization and Photodetachment*, Advanced Series in Physical Chemistry Vol. 10B, edited by C. Y. Ng (World Scientific, Singapore, 2000), pt. II, pp. 1063–1160.
- ²⁴L. G. Christophorou, *Atomic and Molecular Radiation Physics* (Wiley-Interscience, New York, 1971).
- ²⁵L. G. Christophorou, D. L. McCorkle, and A. A. Christodoulides, in *Electron-Molecule Interactions and Their Applications*, edited by L. G. Christophorou (Academic, Orlando, 1984), Vol. I.
- ²⁶R. R. Lucchese, F. A. Gianturco, *Int. Rev. Phys. Chem.* **15**, 429 (1996).
- ²⁷I. Bald, Diplomarbeit, Freie Universität Berlin, 2005.
- ²⁸A. Modelli and P. B. Burrow, *J. Phys. Chem. A* **108**, 5271 (2004).
- ²⁹M. H. Palmer, I. C. Walker, C. C. Ballard, and M. F. Guest, *Chem. Phys.* **192**, 11 (1994).
- ³⁰F. Motte-Tollet, F. Eustaciu, and D. Roy, *J. Chem. Phys.* **105**, 7448 (1996).
- ³¹B. Schafer-Bung, B. Engels, T. R. Taylor, D. M. Neumark, P. Botschwina, and M. Peric, *J. Chem. Phys.* **115**, 1777 (2001).
- ³²J. M. Oakes and B. G. Ellison, *J. Am. Chem. Soc.* **105**, 2969 (1983).
- ³³M. S. Robinson, M. L. Pollak, V. M. Bierbaum, C. De Puy, and W. C. Lineberger, *J. Am. Chem. Soc.* **117**, 6766 (1995).
- ³⁴K. M. Ervin and W. C. Lineberger, *J. Phys. Chem.* **95**, 1167 (1991).
- ³⁵D. Klar, M.-W. Ruf, and H. Hotop, *Aust. J. Phys.* **45**, 263 (1992).
- ³⁶M. Fenzlaff and E. Illenberger, *Chem. Phys.* **136**, 443 (1989).
- ³⁷S. Spyrou, I. Sauers, and L. G. Christophorou, *J. Chem. Phys.* **78**, 7200 (1983).
- ³⁸Th. Jaffke, E. Illenberger, M. Lezius, St. Matejcik, D. Smith, and T. D. Märk, *Chem. Phys. Lett.* **226**, 213 (1994).
- ³⁹O. Elhamidi, J. Pommier, and R. Abouaf, *J. Phys. B* **30**, 4633 (1997).
- ⁴⁰T. G. Clements and R. E. Continetti, *J. Chem. Phys.* **115**, 5345 (2001).
- ⁴¹E. H. Kim, S. E. Bradforth, D. W. Arnold, R. B. Metz, and D. M. Neumark, *J. Chem. Phys.* **103**, 7801 (1995).
- ⁴²T. G. Clements and R. E. Continetti, *J. Chem. Phys.* **117**, 6478 (2002).
- ⁴³F. Martin, P. D. Burrow, Z. Cai, P. Cloutier, D. J. Hunting, and L. Sanche, *Phys. Rev. Lett.* **93**, 068101 (2004).
- ⁴⁴S. Ptasinska, S. Denifl, S. Gohlke, P. Scheier, E. Illenberger, and T. D. Märk, *Angew. Chem., Int. Ed.* **45**, 1893 (2006).

