Doorway mechanism for dissociative electron attachment to fructose

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Recently, the three sugars ribose, deoxyribose, and fructose have been shown to undergo dissociative electron attachment at threshold, that is, to fragment upon capture of a zero-energy electron. Here the electron acceptor properties of three fructose isomers are investigated in view of a doorway mechanism. Two key ingredients for a doorway mechanism, a weakly bound state able to support a vibrational Feshbach resonance, and a valence anion more stable than neutral fructose are characterized. Moreover, possible structures for the observed fragment anion (fructose-H_2O)$^-$ are suggested. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2710275]

I. INTRODUCTION

As high-energy radiation passes through tissue, it creates a trace of reactive "secondary" species, excited molecules, radicals, and free electrons. These secondary species cause two-thirds of the damage associated with the primary radiation.[1] Secondary electrons are the most abundant radiolytic species,[2] and, in particular, since Sanche and coworkers demonstrated that low-energy (0–5 eV) electrons can induce single-strand and double-strand breaks of plasmid DNA,[3,4] electron-induced reactions of many single molecules that either are, or model, building blocks of DNA have been investigated (see, e.g., the recent review[4] and other articles in Ref. 37.

One building block of the DNA backbone is the sugar 2-deoxyribose that adopts in DNA a furanose (five-membered ring) structure. Dissociative electron attachment (DEA) of deoxyribose,[5] ribose,[6] and fructose[7] molecules has recently been studied. However, since all these sugars exist in the gas phase predominately in their pyranose forms, i.e., as six-membered rings, in addition furan and tetrahydrofuran have been considered as models for the furanose form of deoxyribose in DNA.[7–9] Both furanose models, furan and tetrahydrofuran, were found to be comparably inefficient electron scavengers and to fragment dominantly through relatively high lying resonances above 5 eV.[7] In contrast, all three sugars, deoxyribose, ribose, and fructose, undergo a rich fragmentation pattern at much lower energies, where, in particular, fragment anions (fructose-$(H_2O)_n$)$^-$ corresponding to the loss of one or more water units were observed.[5–7] Moreover, all three sugars exhibit pronounced threshold peaks, i.e., the sugars fragment efficiently upon capture of essentially zero-energy electrons.

Here we study electron attachment properties of different fructose isomers related to the mechanism of DEA at threshold using *ab initio* methods. To be specific, we concentrate on fructose, yet, our findings are expected to be transferable to ribose and other sugars. After outlining the doorway mechanism[10–12] usually invoked to explain DEA with zero-energy electrons, we investigate different conformers of three fructose isomers focusing on the prerequisites for the doorway mechanism, a weakly bound diffuse state strongly coupled with a valence state. We characterize a dipole-bound state as well as a stable valence anion of fructose, and we suggest possible products for the observed (fructose-H_2O)$^-$ anion.

II. COMPUTATIONAL DETAILS

Different isomers of neutral fructose, the fructose anion, and radical anions associated with loss of a water molecule from the fructose anion are studied using standard *ab initio* methods. Gaussian-3 theory with reduced Møller-Plesset order[13] [G3(MP2)] is used to compare different isomers of neutral fructose and to access the energetics of electron-induced fragmentation into water and a remaining radical anion. To investigate electron attachment to the fructose molecule, different species have been optimized at the second-order Møller-Plesset perturbation theory level (MP2) using the 6-31G* basis set[14] for neutrals and the 6-31+G* basis set[14] for anions. At the optimized geometries the MP2 energy was recalculated with the larger aug-cc-pVDZ basis set.[15] The 1*s* core electrons were frozen in their Hartree-Fock orbitals in all MP2 calculations, and the MP2 calculations for open-shell molecules are based on spin-unrestricted Hartree-Fock calculations ($s^2 < 0.77$ in most calculations). To characterize dipole-bound states the aug-cc-pVDZ basis was further augmented with a (6*s*6*p*3*d*) set (even tempered exponents starting at 0.015 with a scaling factor of 5) centered at the center of mass of the molecule. All calculations were performed at the Pittsburgh Center for Molecular and Materials Simulations with the GAUSSIAN package of programs.[16]

III. ELECTRON ACCEPTOR PROPERTIES OF FRUCTOSE

Before discussing electron attachment to different fructose isomers, let us briefly review these isomers and their properties. As most sugars, fructose can exist as an acyclic, chain isomer with a carbonyl group at C2, and it can form

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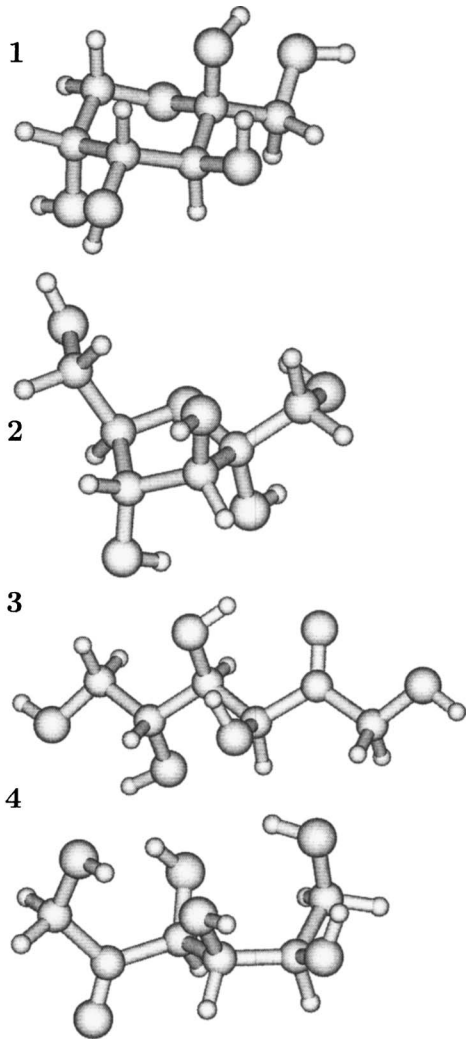

FIG. 1. Geometrical structures of neutral fructose isomers: 1, pyranose form; 2, furanose form; 3 and 4, conformers of the open-chain form. Hydrogen, carbon, and oxygen atoms are represented by small, intermediate, and large spheres, respectively. The geometries have been optimized using the MP2 method and the 6-31G* basis set.

intramolecular hemiketals with six-membered rings (pyranose form) and five-membered rings (furanose form). Each of these isomers will have many different conformers, and representative examples for each isomer are shown in Fig. 1. In solution there is a dynamic equilibrium between the different isomers with the pyranose isomer dominating, the furanose isomer being abundant, and only small ($<1\%$) amounts of the chain isomer, even though the dynamic equilibrium between the different ring isomers proceeds through the chain isomer.[17–19] In the gas phase, the isomer populations will be different. First, free energy of the isomers has no contribution from the solvent interaction. Second, formation and cleavage of the hemiketals are catalyzed by water, and in the gas phase the barrier for this reaction will be much higher, such that one may expect no appreciable isomer conversion on the experimental time scale. Experimental evidence[17,19] suggests that under different source conditions the pyranose isomer dominates the gas phase populations, and this is consistent with both the kinetic argument (the solids and solutions used as sources are dominated by the pyranose form) as well as the energetic argument: At the G3(MP2) level the pyranose form is the most stable isomer, energy- and free-energy-wise (see Table I and c.f. Ref. 19). Thus, in the DEA experiments the dominating isomer is expected to be the pyranose ring, even though small amounts of the other isomers cannot be excluded.

DEA at low energies is usually rationalized within two mechanisms. The most common DEA mechanism proceeds through an intermediate resonance state, i.e., the excess electron directly occupies an antibonding orbital, forming an electronically metastable state. This mechanism has been studied for decades; however, owing to the non-square-integrable wave function of the metastable state, theoretical description of the dissociation process is computationally demanding, and applications to larger molecules are rare (see, e.g., Ref. 9 and 20). Recently, more approximate approaches have been applied to a series of biomolecules;[21–25] yet, it has been argued that the mechanisms extracted from some of these approaches are invalid.[26,27] For fructose, the resonance mechanism cannot explain the observed threshold peaks,[7] since the pyranose isomer is a saturated closed-shell molecule with its lowest virtual valence orbitals well above 5 eV. Resonance attachment could occur to the π^* orbital of open-chain isomer, but this resonance should still be well above threshold.

At threshold there is the alternative doorway mechanism associated with initial capture in a vibrational Feshbach resonance.[28] The excess electron becomes trapped in a weakly bound, diffuse nonvalence state (dipole bound, quadrupole bound, or polarization bound[29,30]), and its energy is transferred into vibrational motion of the molecular target. In other words, the incoming electron has to couple with the nuclear motion of the fructose molecule and the energy transfer is a nonadiabatic process,[28] as opposed to Rydberg electron transfer, where this type of anion state can be populated directly. Provided the anion possesses also a stable valence state that can couple with the diffuse state, the valence state will be occupied, yielding a long-lived anion or initiating dissociation reactions depending on the electron affinity of the valence state and on the energetics of possible dissociation products. That is, the diffuse state provides a "doorway"[10–12,31,32] for the excess electron into an antibonding orbital.

To invoke a doorway mechanism for threshold attachment to fructose, we need to investigate three questions. First, does the pyranose isomer support a weakly bound, diffuse anion state? Second, does fructose possess a valence anion that is more stable than the neutral pyranose isomer, i.e., an anion with a positive electron affinity? Third, provided these two states exist, is the diffuse state an efficient doorway to the valence state? In the following we answer the first two questions, and briefly discuss the third one.

Regarding diffuse attachment states, note that the pyranose isomer has several conformers with dipole moments between 3 and 4 D. For example, the conformer shown in Fig. 1 (1) has a dipole moment of 3.2 D, and molecules with dipole moments in this order of magnitude typically support dipole-bound states.[29,30,33,34] Yet, even with a very flexible basis set (Sec. II) we did not find a dipole-bound orbital in

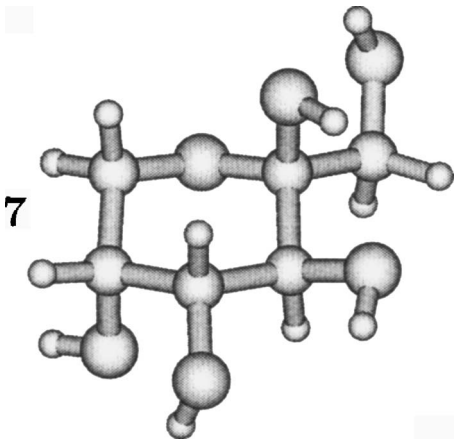

FIG. 2. Geometrical structures of a pyranose conformer of neutral fructose with a dipole moment of 4.05 D that supports a dipole-bound state. Hydrogen, carbon, and oxygen atoms are represented by small, intermediate, and large spheres, respectively. The geometry has been optimized using the MP2 method and the 6-31G* basis set.

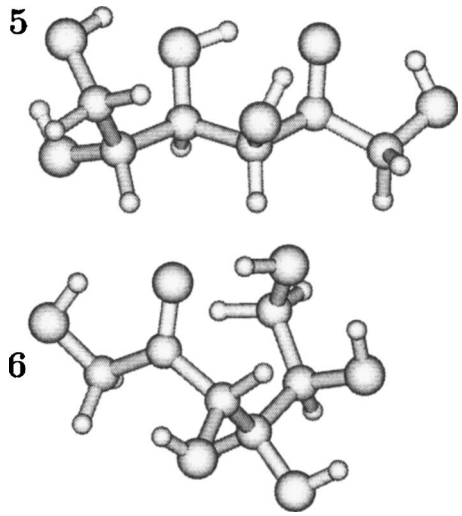

FIG. 3. Geometrical structures of two conformers of the fructose radical anion. Hydrogen, carbon, and oxygen atoms are represented by small, intermediate, and large spheres, respectively. The geometries have been optimized using the MP2 method and the 6-31+G* basis set.

Hartree-Fock calculations for 1, indicating that if 1 supports a dipole-bound state it will have a binding energy in the sub-meV range. This is quite unusual as molecules with dipole moments in excess of 2.5 D typically have dipole-bound states with binding energies of a few meV,[34] and may be due to an excluded volume effect of the methylene groups crowding the positive side of the dipole (see Ref. 35). Be this as it may, the conformer shown in Fig. 2 has a dipole moment of 4.05 D, and we find a dipole-bound state with a binding energy of 2.2 meV at the Hartree-Fock level and a binding energy of 4.8 meV taking into account electron correlation at the MP2 level. Taking correlation effects beyond second order into account is expected to yield even larger electron binding energies,[33] and we predict conformer 7 to possess a dipole-bound state with an electron binding energy of more than 5 meV. Thus, there are conformers of the pyranose isomer that possess weakly bound diffuse states with binding energies of a few meV suitable to support vibrational Feshbach resonances.

To address the second question we started from different conformers of the three fructose isomers (Fig. 1), added an electron to the lowest unoccupied valence orbital, and optimized the geometry. For both the pyranose and furanose isomers, this leads to cleavage of one of the OH bonds of two adjacent OH groups, yielding a H atom and an alcoholate anion stabilized by a OH bond donated by the neighboring OH group. These calculations can be understood as a very approximate simulation of resonance attachment at energies associated with σ^* orbitals, but since the attachment products are considerably higher in energy than neutral fructose, this channel is certainly closed at threshold. Thus, neither the pyranose nor the furanose isomer possesses a valence anion more stable than the respective neutrals.

In contrast, attaching an electron to the chain isomer leads, without major geometrical changes, to a stable radical anion. Two conformers of this anion are shown in Fig. 3. The negative charge resides essentially on the carbonyl oxygen, and is stabilized by intramolecular hydrogen bonds donated by two (6) or three (5) OH groups, while an unpaired electron resides on the carbonyl carbon. Thus, *cum grano salis*, the fructose anions 5 and 6 are distonic radical anions with CO groups described by the Lewis dot structure $R_2\dot{C}-\overline{\underline{O}}|$. This electronic structure is reflected in the geometrical parameters of the anions; upon electron attachment the C–O bond length increases from about 1.2 Å, typical for CO double bonds, to 1.32 Å for 5 and 1.33 Å for 6, half way between typical CO single and double bonds. Moreover, the carbonyl carbon changes from an almost perfectly planar to a slightly pyramidal configuration.

Both anion conformers 5 and 6 have substantial vertical detachment energies of 1.71 and 1.39 eV (MP2/aug-cc-pVDZ level), and both are more stable than the neutral pyranose isomer 1 [by 0.36 and 0.20 eV at the MP2/aug-cc-pVDZ level and by 0.31 and 0.18 eV at the G3(MP2) level]. Thus, both conformers have a positive electron affinity, and the chain isomer of fructose forms a stable valence anion that can be an intermediate in a DEA processes.

The remaining question is now whether the dipole-bound state of the pyranose anion is an efficient doorway into the valence state of the chain isomer. To answer this question, one needs to investigate the reaction path leading from the equilibrium structure of the dipole-bound state to that of the valence anion. In a diabatic picture the two states will cross, and the coupling can be estimated from the splitting of the two adiabatic states obtained from a calculation.[11] However, fructose represents a far more challenging example than all systems investigated so far,[11,12,32,36] since for fructose the reaction coordinate is far from obvious. The additional complexity stems from the association of the intramolecular electron transfer with the breaking of the hemiketal bond. The potential energy surface of neutral fructose exhibits a considerable barrier between the pyranose and the chain isomers, and the surfaces relevant for the doorway mechanism are the two anion states resulting from attachment to the neutral. Thus, the question of an efficient doorway is not only related to the coupling between these two states but also

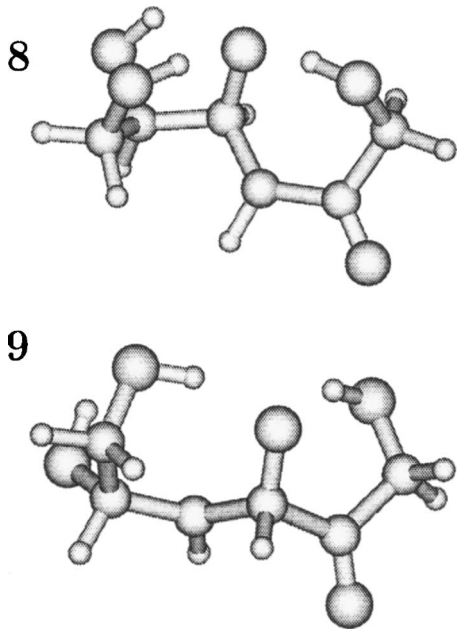

FIG. 4. Geometrical structures of two conformers of the (fructose-H_2O)$^-$ radical anion. Hydrogen, carbon, and oxygen atoms are represented by small, intermediate, and large spheres, respectively. The geometries have been optimized using the MP2 method and the 6-31G* basis set.

to the extent the bond-breaking barrier is lowered by the excess electron. Only if the coupling between the dipole-bound state and the valence state is strong, and if the presence of the excess electron decreases the barrier for breaking the hemiketal bond substantially, will the dipole-bound state of the pyranose isomer act as an efficient doorway to the valance anion of the chain isomer. At the moment we can only speculate on these two issues, but in all examples studied today[11,12,32,36] the coupling between the two anion states is in the order of a few tenths of an eV, indicating a rapid electron transfer in the intersection region. Moreover, there are many examples of electron-induced reactions proceeding efficiently where there are high barriers on the potential surface of the neutral (see, e.g., Ref. 37). Thus, we expect the doorway mechanism to be operative in electron attachment of 0 eV electrons to fructose.

Finally, let us briefly consider the observed (fructose-H_2O)$^-$ anion.[7] If our doorway conjecture is correct, a conformer of the chain anion 5 is the reactant for the water elimination. Elimination from adjacent OH groups should be most likely, and here we consider elimination from the two "activated" OH groups adjacent to the carbonyl radical anion group of 5. Several products including carbon centered anions are possible, but at the G3(MP2) level the by far most stable species are the distonic radical anions 8 and 9 (Fig. 4) with the negative charge on an O atom and a radical center at a C atom. In isomer 8 the radical center is resonance stabilized by the carbonyl group, and 8 is the most stable product of water elimination from the considered OH groups. The results in Table I show that water elimination from anion 5 is an uphill process; yet, 8 is energetically lower than the pyranose isomer 1, and consequently 8 can be produced by DEA at threshold, while 9 cannot. Provided arbitrary rearrangements of the remaining radical anion are considered, there

TABLE I. Relative energies E and free energies G of neutral fructose isomers, fructose anions, and dissociation products. The results have been obtained at the G3(MP2) level, where the energies are evaluated at 0 K and the free energies at 298 K. All values are in kJ/mol.

	E	G
1	0	0
2	11.9	9.4
3	41.1	30.7
4	28.8	23.0
5	−30.2	−38.2
6	−17.0	−24.0
8+H_2O	−19.0	−14.6
9+H_2O	15.2	20.7

are other products with even lower energies,[7] but 8 is the only energetically allowed product resulting from a simple elimination (without further rearrangement), making it a likely candidate for the experimentally observed species.

IV. CONCLUSIONS

Electron acceptor properties of three fructose isomers were studied using the MP2 and G3(MP2) *ab initio* methods with regard to a possible doorway mechanism for the attachment of zero-energy electrons. The pyranose form of fructose is expected to be the dominating isomer in the gas phase, and our calculations show that there are conformers of the pyranose isomer that possess dipole-bound states with electron binding energies of a few meV. These diffuse anion states can support vibrational Feshbach resonances, the first crucial ingredient of a doorway mechanism. However, neither the pyranose nor the furanose hemiketal isomers have valence anion states assessable at threshold. Only the chain isomer has a stable anion state with an electron affinity of a few tenths of an eV; the two conformers 5 and 6 we investigated have electron affinities of 0.3 and 0.2 eV. Thus, DEA at threshold can proceed by initial capture in a vibrational Feshbach resonance supported by the dipole-bound state of the pyranose isomer, followed by an essentially simultaneous opening of the hemiketal ring and transfer of the excess electron into the valence orbital of the chain isomer. We expect this mechanism to be efficient; yet, only a detailed investigation of the reaction path with an appropriate description of the two anionic states can answer this question definitely.

The doorway mechanism associated with opening of the hemiketal bond explains two experimental observations: first, the pronounced difference in DEA to furan and tetrahydrofuran on the one hand, and fructose and ribose on the other hand,[5,7] and second, that no threshold peak is found in electron attachment to thyminidine.[26] Experimental tests of the proposed mechanism include, in the first place, a high resolution study of the threshold region that can show whether the threshold peak has vibrational structure associated with the neutral pyranose isomer indicative of a vibrational Feshbach resonance. Second, if opening of the hemiketal is a prerequisite of water elimination, there should be no threshold peak in DEA to the methyl or ethyl glycoside of fructose or ribose. Third, the fragmentation process should be observable in a Rydberg electron transfer experiment.

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