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Search for Stable Anions of Uracil−Water Clusters. Ab Initio Theoretical Studies

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In this work we investigate the ability of the uracil·water complex to form stable anionic systems. As the experimental evidence and theoretical calculations have indicated, the isolated uracil molecule can only attach an excess electron into a diffuse dipole-bound state, while some recent experiments suggest that the uracil·water complex can form a more stable valence-type anion. In this work we demonstrate that it is possible to converge ab initio calculations of uracil·$(H_2O)_3^-$ to an equilibrium structure that is significantly different from the structure of the neutral cluster and that has a positive and remarkably significant vertical ionization potential. Apart from the valence anion, the uracil·$(H_2O)_3$ complex can form a stable dipole−bound anion, but as the present calculations indicate the electron affinity, which corresponds to this attachment, is very small (13 meV). The structure of the dipole-bound anion is virtually identical with the structure of the neutral complex.

1. Introduction

Following the theoretical ab initio calculations of our group[1−4] on the electron affinities of the nucleic acid bases uracil, thymine, adenine, and guanine, the very recent experiments by Schermann and co-workers at the University of Northern Paris, France, and by Bowen and co-workers at Johns Hopkins University[5,6] confirmed that the positive, but very small, electron affinities of these systems in the gas phase are due to dipole−electron attachment. The formation of stable anions of the DNA bases is, as currently believed, a crucial step in a cascade of events that result from irradiation of the biological material by high-energy radiation.[7] Also the affinity of the nucleic acid bases toward electrons is a phenomenon closely related to DNA conductivity properties, a topic vigorously debated in recent years.[8] Although dipole−bound anions are interesting species, their significance for the biological reactions that occur in the condensed phase probably only rests in their roles as precursors for “valence” electron attachment. We have used the term “valence” attachment to describe a process where the excess electron becomes localized near the atomic centers of the molecule and not, as it is in the case of dipole-bound anions, mostly outside the molecular frame. Over the past few years there have been attempts to theoretically describe stable valence states of an excess electron in nucleic acid bases and their complexes,[9,10] but no rigorous results have been presented that explicitly show that valence anionic states can exist for these systems. Also, in the gas-phase experiments performed by Bowen’s and Schermann’s groups, no valence anions of isolated nucleic acid bases were detected. The evidence of valence anions of uracil (U) and thymine (T), which were observed by the latter group and initially assigned to valence attachment, turned out to correspond to the $(U-H)^-$ and $(T-H)^-$ species after more precise mass calibration was performed. Therefore, it seems that a consensus on both the theoretical and experimental sides has been reached that isolated molecules of the nucleic acid bases form only dipole−bound states with excess electrons. The situation is quite different when the nucleic acid molecule forms a complex with water. Desfrançois et al.,[6] in their recent paper on electron attachment to isolated nucleic acid bases, report an experiment in which they produced anions of uracil−water clusters in charge-exchange collisions with laser-excited Rydberg atoms. These clusters had different water content, but the most significant population corresponded to clusters with few water molecules (U·(H_2O), U·$(H_2O)_2$, U·$(H_2O)_3$ and U·$(H_2O)_4$). Based on the Rydberg number (n) dependences of these anion creation rate constants, they concluded that excess electrons are covalently bonded to the anions. This is in agreement with the speculation by Sevilla et al.[10] about the stabilizing influence of the hydration on the electron attachment to nucleic acid bases. The covalent character of the electron attachment to nucleic acid bases has also been confirmed in experiments performed by Bowen and co-workers.[5] The stabilization of the electron attachment due to a polar solvent is an interesting phenomenon which can be investigated and described through ab initio calculations. The answer, which theory is expected to provide, concerns the physical principle behind the significant change of the electron affinity of a nucleic acid base molecule when it becomes involved in a complex with water. Both the isolated base molecule and the complex molecule in the ground electronic state are closed shell species and the formation of the anion must involve placing the excess electron into an “unoccupied” orbital of the neutral system. For most closed shell systems this is an endothermic process. One of the exceptions is electron attachment to the field of the dipole moment of the molecule. One other possible exception could be a situation when the structure of the system changes upon the attachment of the excess electron to create domains with positive potential which can bind the electron into a stationary state. It is a well-known fact that for covalently bonded atoms, which possess positive electron affinities as isolated species, if the bond is stretched far enough, the electron affinity of the molecule, calculated in the Born−Oppenheimer approximation, becomes positive. If the energy of the electron attachment is sufficiently large to compensate for the energy loss due to the bond stretching, the anion becomes a stable system. However, bond energy is usually much larger than the electron affinity, and the above-described scenario is rather unlikely unless the bond is considerably weaker. A similar mechanism can also result in electron attachment to a molecular complex, particularly to complexes with hydrogen bonds. Stretching or rupturing of these bonds, which are much weaker than typical covalent bonds, may create electron-deficient areas where the excess electron can attach and form a stationary state. If this happens, the molecular

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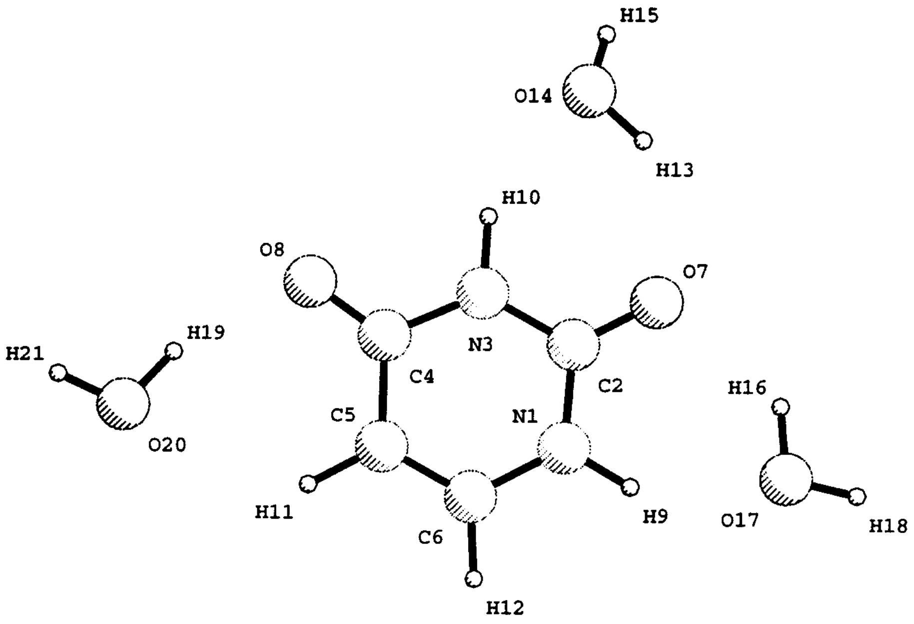
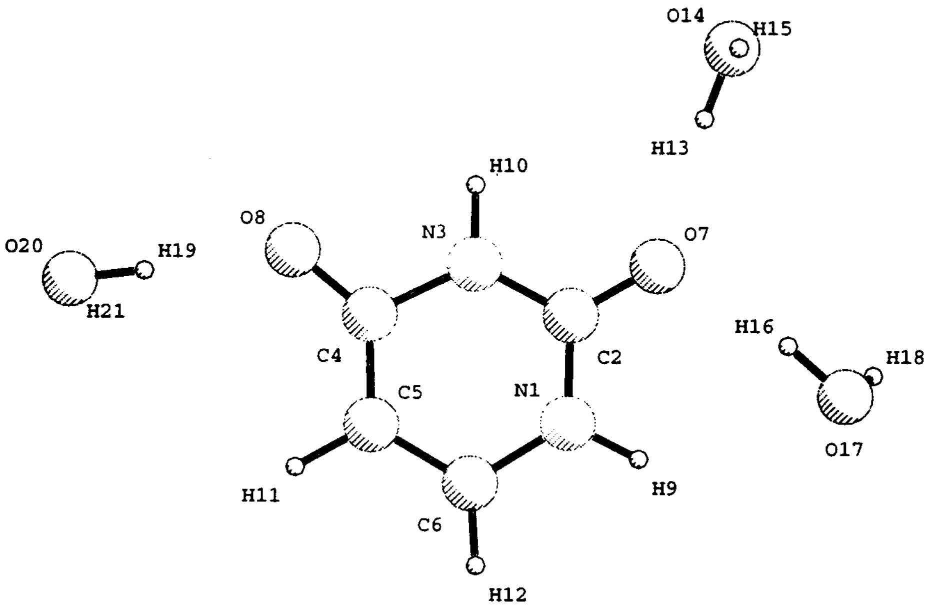


Neutral



Anion

Figure 1. Structures of uracil•(water)$_3$ and uracil•(water)$_3^-$ obtained in this work.

structure of the anion will be considerably different from the structure of the neutral complex, particularly in terms of lengths and numbers of hydrogen bonds. In the present work we performed ab initio calculations to test the above hypothesis and to determine if the uracil complex with three water molecules (U•(H$_2$O)$_3$) can form a stable valence anion. We selected the complex with three waters, since this is one of the species that gave a strong signal in the experiment performed in Schermann's laboratory (the strongest signal corresponded to the U(H$_2$O)$_2^-$ anion).

In the complex of uracil with three water molecules, the water oxygens form H-bonds with three uracil hydrogens (see Figure

1), and one of the hydrogens in each water molecule forms an H-bond with uracil oxygens. With three waters in the complex, only one oxygen H-bonding site at O_8 in the uracil molecule remains open to an H-bond. However, if an H-bond is formed at this site with the fourth water molecule, the oxygen atom in water would form an H-bond with H_{10} of uracil, which is already involved in an H-bond with one of the three water molecules. Since formation of two H-bonds by a single hydrogen atom is not possible, the fourth water would form only a single H-bond with uracil which would be significantly weaker than the double hydrogen bonds connecting each of the other three waters to the uracil molecule. Therefore, the hydration shell consisting of three water molecules should be considered as the complete first hydration shell for uracil. This is the other reason the $U\cdot(H_2O)_3$ complex was selected for this study.

In addition to the search for the valence anionic state, we have also performed calculations to determine whether the complex will attach the excess electron to the dipole field. We present results of calculations where we calculated the dipole-bound electron affinity of the $U\cdot(H_2O)_3$ complex.

2. Method of Calculation and Numerical Results

One can distinguish several different interaction effects that contribute to the bonding effect of the excess electron to a molecule. These are, in principle, the same effects that are present in the interaction of two molecular systems and include electrostatic, polarization, exchange, and dispersion contributions. In valence electron attachment, the dispersion may play a significant role, and it can be accounted for only if a correlated electronic structure method is used in the calculations. Even if the excess electron is bonded through dipole−electron interaction, the electron correlation contribution can be large[1−4] and may result not only from the dispersion interaction of the extra electron with the electrons of the core but also from the well-known and frequently significant correlation contribution to the molecular dipole moment. The following calculations have been performed.

(1) In the first step of the present calculation we performed a search for a stable valence anion of the $U\cdot(H_2O)_3$ system. In this search we optimized the structure of the anion at the UHF/6-31+G* level starting with the geometry of the complex with all three water molecules separated by a considerable distance from the uracil molecule, but positioned at the same directions and orientations as in the fully optimized neutral $U\cdot(H_2O)_3$ cluster. Starting the anion geometry optimization from this point, rather than from the optimal geometry of the neutral cluster, made the search more open to the possibility that the hydrogen-bonding structure of the anion is considerably different from the structure of the neutral complex. As mentioned in the Introduction, we anticipated that this is the case for the $U\cdot(H_2O)_3^-$ system.

Although the $U\cdot(H_2O)_3$ cluster and its anion are complex systems, the lowest energy structures are rather easy to predict. They most likely correspond to each water molecule being connected to the uracil molecule through hydrogen bonds engaging water hydrogens and uracil oxygens. Therefore, in this case the problem of multiple minima should not be as severe as in some other water complexes. By initiating the geometry optimization of the anionic cluster from the structure mentioned above, we very likely converged the calculation to the global minimum of this system.

The geometry optimization for the anion converged to the equilibrium geometry that is shown in Figure 1.[12] The corresponding energy values calculated for the anionic system and the neutral system at the MP2/6-31+G* level of theory (MP2 denotes the second-order Møller−Plesset perturbation theory; 6-31+G* denotes a standard basis set implemented in the GAUSSIAN94 program) at this geometry are presented in Table 1.

TABLE 1: Vertical Electron Detachment Energy (VDE) and Adiabatic Electron Affinity (EA) Calculations of the Uracil·$(H_2O)_3$ Complex. Total energies in Hartrees; EA in eV

Anion	
UHF/6-31++G*//UHF/6-31++G*	−640.564 917 9
UMP2/6-31++G*//UHF/6-31++G*	−642.329 687 6
UHF/aug-cc-pvdz//UHF/6-31++G*	−640.683 850 4
UMP2/aug-cc-pvdz//UHF/6-31++G*	−642.632 056 5
Neutral (at UHF/6-31++G* Geometry of the Anion)	
UHF/6-31++G*	−640.524 212 6
UMP2/6-31++G*	−642.275 230 4
RHF/6-31++G*	−640.520 989 8
MP2/6-31++G*	−642.297 017 0
RHF/aug-cc-pvdz	−640.692 623 3
MP2/aug-cc-pvdz	−642.627 897 6
Vertical VDE	
UHF/6-31++G*	1.11
UMP2/6-31++G*	1.48
RHF/6-31++G*	1.20
MP2/6-31++G*	0.89
Neutral (at RHF/6-31++G* Geometry of the Neutral[a])	
RHF/6-31++G*	−640.573 577 8
MP2/6-31++G*	−642.332 421 8
Adiabatic EA	
HF/6-31++G*	−0.24
MP2/6-31++G*	−0.07
HF/aug-cc-pvdz	−0.24
MP2/aug-cc-pvdz	−0.11

[a] RHF and UHF optimization of the neutral cluster converged to the same result.

(2) The calculations for the neutral system have been done with both RHF and UHF reference wave functions to determine whether some spin polarization may take place at the geometry that is not the equilibrium point for the neutral cluster. The UHF calculation was initiated with the guess for the wave function taken from the anion UHF calculation. The RHF and UHF calculations converged to slightly different energies, with the UHF value, being lower than the RHF result, as expected. Also, the corresponding MP2 and UMP2 energies differ slightly, leading to somewhat different results for the vertical electron detachment energy, which are also shown in Table 1. We consider the UHF and UMP2 electron detachment energy to be more correct than the RHF and MP2 results, since the anion calculations were also done at the UHF level.

However, since the present calculations have not been extended to higher orders of the perturbation theory due to our limited computational resources, the results obtained here should be considered as semiquantitative. Although the MP2 level of theory accounts for the majority of the important interaction effects including the dispersion contribution, there is still a question whether the perturbation series converges sufficiently fast so that the MP2 results for the systems studies in this work are reliable. It would be difficult to answer this question without performing calculations of higher order perturbation correlation corrections. However, a good symptom of divergency problems in MP calculations is a larger value of the norm of the first-order correction to the wave function. In none of the calculations in this work have we observed this norm to be unusually large. However, without higher order calculations we still recommend considering our results as the first approximation, which we hope to refine once more computational resources become available.

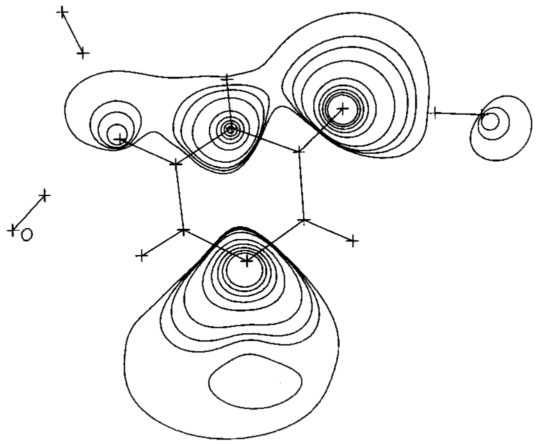


Figure 2. Orbital occupied by the excess electron in the valence uracil•(water)$_3^-$ anion ploted with the following contour levels: 0.11, 0.09, 0.07, 0.05, 0.03, 0.01, 0.005, 0.003, and 0.001.

The most interesting result at this point is that, at both MP2 and UMP2 levels of theory, the values of the vertical electron detachment energy are positive and close to 1 eV.

(3) In the next step we performed structure optimization of the U•(H_2O)$_3$ neutral cluster starting with the optimal structure obtained for the anion. This optimization converged to the structure that is presented in Figure 2. Both UHF and RHF (with the 6-31+G* basis set) structure optimizations were performed, and both converge to the same equilibrium geometry. Upon comparing the structure of the anion in Figure 1 and the structure of the neutral complex, one sees some striking differences in the hydrogen bondings. While water molecules in the anion are connected by single hydrogen bonds to the uracil molecule, each water molecule has two hydrogen bonds toward uracil in the neutral cluster. In one of these two H-bonds water donates its hydrogen, and in the other an oxygen lone pair connects to a hydrogen in the uracil molecule. The difference in structures indicates that in order to accommodate the excess electron, the weaker hydrogen bonds open up and create regions within the complex with sufficiently high electron affinity to support a stationary bound state of the excess electron. In Figure 2 we show a contour plot of the HOMO of the anion. It is clear that an excess electron is localized at the uracil molecule, and this is a case of a valence attachment. At the bottom of Table 1 we show the results for the adiabatic electron affinity calculated at the HF and MP2 levels. In these calculations we used the 6-31++G* basis set, as well as the more extended aug-cc-pvdz set. At these levels of theory the values for the adiabatic electron affinity are negative. However, one can see that with the inclusion of the electron correlation effects the electron affinity decreases nearly 3-fold and becomes much less negative. It is quite possible that by using a method of higher order than MP2, which only captures the lowest order correlation contribution, one can get a positive electron affinity value. However, such calculations would exceed our current computational capabilities and could not be done. The picture of the electron attachment to U•(H_2O)$_3$ would not be complete without investigating a possibility of dipole−bound anionic states of the cluster.

It should be mentioned that in the dipole−bound anion of a system with structural complexity similar to the U•(H_2O)$_3$ cluster there may be additional factors contributing to the bonding effect apart from the dominating contribution resulting from the dipole−electron interaction. Some of these additional contributions may result from interactions of the excess electron with higher multipole moments of the cluster.

The calculations performed at the RHF/6-31++G* level indicate that the dipole moment of the U•(H_2O)$_3$ complex, determined to be around 4.73 D, far exceeds the practical threshold of 2.5 D, above which the molecule is expected to form stable dipole−bound states with an excess electron. Therefore, we performed calculations to determine the electron affinity of the complex corresponding to the electron attachment to the U•(H_2O)$_3$ dipole field. The computational procedure used in these calculations was similar to the one employed previously in calculations of the electron affinities of uracil, thymine, guanine, and adenine[1−4] and in calculations of electron affinities of some hydrogen-bonded complexes.[17−19] The use of very diffuse basis functions and the account of the electron correlation effects are essential in such calculations because the dipole−bound excess electron is usually significantly delocalized along the direction of the molecular dipole moment. The extent of the delocalization depends on the size and the orientation of the molecular dipole; these parameters are usually sensitive to the theoretical level used in the calculation and, in particular, to the degree the electron correlation effects are accounted for. All the calculations presented in this work were performed with the GAUSSIAN94 program package.[13] To determine the dipole−bound electron affinity of U•(H_2O)$_3$, the following calculations were performed.

(7) First we considered the neutral U•(H_2O)$_3$ cluster with the geometry optimized at the RHF/6-31++G* level. We augmented the standard 6-31+G* basis set with an additional set of four diffuse sp shells with exponents equal to α, 0.1 × α, 0.01 × α, and 0.001 × α, where α is a scaling factor. The additional set was selected on the basis of the analysis presented in refs 14−16, where numerical orbitals produced by the Hartree−Fock and MCSCF procedures for some dipole−bound diatomic polar systems were projected onto Slater-type atomic orbitals. The additional diffuse set was placed at the point whose coordinates were equal to the dipole moment coordinates, with the molecular principle rotational axis aligned with the axis of the coordinate system (standard orientation).

Although, as we noticed in our previous calculations of dipole−bound anions, the results are not very sensitive to the position of the diffuse orbitals, placing them at the positive end of the molecular dipole is most optimal since the molecular orbital, which the excess electron occupies, is expected to extend in this direction. The purpose of these calculations was to determine the optimal value of the scaling factor α, which was accomplished by minimization of the LUMO (the lowest unoccupied orbital) energy. This optimal value was determined to be 0.15, yielding the LUMO energy of 4 meV. The 6-31++G* basis augmented with the four diffuse sp shells is referred to as 6-31++G****X*** in the further discussion and in Table 2.

(2) In the next step we performed a UHF optimization of the U•(H_2O)$_3$ anion geometry with the 6-31++G****X*** basis, allowing the position of the diffuse set ***X*** to also be optimized concurrently with the atomic positions. We placed no restrictions on the coordinates of the ***X*** set, and although they were allowed to collapse on the atomic centers, this did not occur in the optimization process.

The optimal geometry that resulted from this optimization was virtually identical with the geometry of the neutral complex. To determine the adiabatic dipole−bound electron affinity, SCF and MP2 calculations were performed with the basis set 6-31++G****X*** for the anion and the neutral cluster. The electron affinity values were calculated as differences of the total energies. In calculations performed to determine very small energy effects, such as the electron affinity of the dipole-bound

TABLE 2: Dipole-Bound Adiabatic Electron Affinity Calculations of the Uracil·$(H_2O)_3$ Complex. Total Energies in Hartrees; EA and LUMO Energy in eV

Anion	
UHF/6-31++G****X***//UHF/6-31++G****X***[a]	−640.573 903 6
UMP2/6-31++G****X***//UHF/6-31++G****X***	−642.333 121 1
Neutral	
RHF/6-31++G****X***//RHF/6-31++G*	−640.573 650 1
UMP2/6-31++G****X***//RHF/6-31++G*	−642.332 649 3
dipole moment[D]/6-31++G*	4.73
-LUMO/6-31++G*	0.004
EA	
HF/6-31++G****X***	0.007
MP2/6-31++G****X***	0.013

[a] The basis set was augmented with the "***X***" orbital set, which contains four sp shells with exponents0.015, 0.0015, 0.000 15, and 0.000 015.

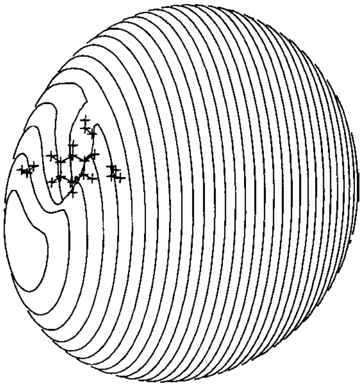


Figure 3. Orbital occupied by the excess electron in the dipole—bound uracil·(water)$_3^-$ anion plotted with the 0.001 contour surface.

electron, it is essential to maintain high precision at each computational step. These include sustaining high accuracy in calculating the atomic integrals, using tight convergence criteria in the SCF and post-SCF calculations, etc. Those aspects of the calculations were closely monitored and adjusted when needed.

(3) The RHF and MP2 results leading to determination of the electron affinity of the U·$(H_2O)_3$ cluster are presented in Table 2. At both levels of theory the dipole—bound cluster anion is predicted to be stable. The RHF and MP2 electron affinity values are very small: 7 and 13 meV, respectively. The electron attachment to the field arising from the molecular dipole moment leads to an orbital for the excess electron that is diffuse and localized along the dipole moment direction. In Figure 3 we present a contour plot of HOMOs from the SCF/6-31++G****X*** calculation for the anionic cluster. As anticipated, the state of the excess electron has a dipole—bound character. The maximum of the HOMO is located several bohrs away from the molecular frame of the dimer.

3. Conclusions

Motivated by the recent experimental findings that the uracil·water clusters can attach an excess electron much stronger than an isolated uracil molecule, which only forms dipole—bound anionic states, we have performed calculations to explain this phenomenon. The geometry optimization for the anion of the uracil complex with three water molecules converged to a structure at which, according to the calculations, the anion is stable with respect to a vertical electron detachment. When this structure was used to initiate the geometry optimization of the neutral complex, a significant geometry arrangement took place. In the converged structure of the neutral complex, each of the water molecules is connected through two hydrogen bonds to the uracil molecule. This is different from the anionic structure, where only a single hydrogen bond exists between each water molecule and uracil.

The present results seem to confirm our hypothesis that the valence electron attachment to the uracil—water complex is a result of the energy gain that occurs when weaker hydrogen bonds in the complex rupture and this creates electron-deficient areas where the excess electron can attach and form a stationary state. This rearrangement makes the structure of the valence anion considerably different from the structure of the neutral complex, particularly in terms of lengths and numbers of hydrogen bonds. The energy gain due to electron attachment is sufficient to compensate for the energy loss due to the H-bond stretching.

We also investigated dipole—bound attachment to the uracil·(water) cluster, which was determined to produce an anion with very small ionization potential. The results of these calculations are consistent with the available experimental observations.

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