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Dipole-Bound Anions of Adenine−Water Clusters. Ab Initio Study

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An interesting configuration landscape has been predicted for dipole-bound (DB) anions of [adenine−(water)$_N$] complexes for $N = 1$, 2, and 3 using ab initio calculations. In these systems, the excess electron is bonded through the interaction with the dipole moment of the cluster. Since the DB electron affinities of adenine and water are practically zero, only if the water(s) dipole(s) aligns with the adenine dipole, the adenine ability to dipole-attach an excess electron can be sufficiently amplified to enable detection. This effect is investigated with the calculations.

1. Introduction

The interaction of adenine in a water environment with excess electrons is an important effect with numerous biological consequences. Excess electrons or hydrated electrons may appear in the cell environment due to secondary reactions following the interaction of high-frequency radiation with the cell. This may cause damage to the cell material, particularly to DNA, through attachment and the chemical reactions that follow. The excess electron is an extremely potent chemical agent. When it covalently binds to a molecule, it can considerably alter the molecular structure. A dipole-bound attachment, which places the excess electron outside the molecular frame, usually affects the intra-molecular structural parameters less than a valence attachment. However, the structural effect of a dipole-bound electron on molecular clusters, including hydrogen-bonded clusters, can be much more significant. For example, our recent theoretical-experimental studies on the indole-water clusters have revealed that the thermodynamic equilibria of some of these clusters are affected by dipole-bound electron attachment.[1]

In the present work we use ab initio calculations to examine the configurational topology of the dipole-bound anions of adenine−(water)$_N$ clusters for $N = 1$, 2, and 3. The goal of the study is to determine whether the interaction of the clusters with an excess electron can result in a change of their thermodynamical stability and their geometrical configurations. Since in the dipole-bound state, the excess electron has a long-range interaction with the system, this state can be considered as the first stage in the formation of a stable anion. In the next stage the electron may transfer to a valence state, if the valence state is more stable than the dipole-bound state, or remain attached through interaction with system's dipole, if the valence anion cannot be formed.

The major N_9H tautomeric form of adenine has three proton acceptor sites at N_1, N_3, and N_7, and three hydrogens connected to nitrogen atoms (one at N_9 and two at the amino group), which can be donated to hydrogen bonds. Because of this diversity, adenine can form a multiple of cluster structures with one, two and three water molecules. Protonation studies of adenine in the solid state showed evidence of the largest protonation strength at N_1.[2] This result is consistent with recent DFT calculations of Russo and co-workers,[3] who estimated the proton affinity at this site to be 945.3 kJ/mol. Smets' et al. MP2/6-311G** calculations on 9 -methyl-adenine yielded the proton affinities at the N_1, N_3, and N_7 sites of 961.3, 951.6, and 933.7 kJ/mol, respectively.

In the most recent unpublished studies, IR matrix-isolation spectroscopy was combined with ab initio and DFT calculations on adenine complexes with a single water molecule.[5] The calculations indicated that the most stable complexes are the ones where the water molecule is connected to adenine through two hydrogen bonds forming closed structures, which can be described as $N_3\cdots H-O(H)\cdots H-N_9$, $N_7\cdots H-O(H)\cdots H-NH$, and $N_1\cdots H-O(H)\cdots H-NH$. In each of them water acts as a proton donor and as a proton acceptor. The analysis of the IR experimental spectrum and the assignment of the bands assisted by the theoretically predicted IR frequencies and intensities performed in that work showed that all three complexes are present in the matrix. All three may also be present in the gas phase in non-negligible amounts, if the temperature of the experiment is sufficiently high.

Since both adenine and water are systems with non-zero dipoles, some of their complexes may have sufficient dipole moments to form dipole-bound anions. Also the question arises whether there are high-dipole complexes of adenine with one or more water molecules that are not stable as neutral species but become stable due to the interaction with an excess electron. This possibility is investigated in the present work.

It was shown[6] that binding a low-energy electron to the dipole field of a polar system is strongly dependent upon the value of its dipole moment, but it also depends on other factors such as the system size, its polarizability, etc. The binding energy of the dipole-bound electron is a rapidly varying function of the magnitude of the dipole moment and it is greater than zero only if the dipole moment exceeds the threshold value of about 2-−2.5 D.[7] Rydberg Electron Transfer (RET) spectroscopy,[8] which is based on transferring electrons from highly excited atoms into diffuse orbitals of polar systems, provides a useful method to study dipole-bound anions. The method allows discrimination between different geometrical configurations of the system, if their dipole moments differ. The other method which has been used to study anions of nucleic acid bases and their complexes is photoelectron spectroscopy (PS). This method was applied by Bowen and co-workers in a landmark study of the transformation of the uracil anion from a dipole-bound state to a covalent state upon solvation.[9] The present ab initio work may

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provide useful insight for the interpretation of analogous RET and PS experiments on adenine-water complexes.

2. Computational Method

First, the configurational landscape of the adenine−(water)$_N$ (A−W$_N$) neutral clusters was explored using the Hartree-−Fock method (HF) and the standard 6-31++G**(6d) basis set. Next, for complexes with dipole moments exceeding 3 D, dipole-bound anions were investigated in the calculations. The anion geometries were first optimized using the spin-unrestricted HF method (UHF). The standard 6-31++G**(5d) basis used in these calculations was augmented with six very diffuse Gaussian sp- -shells with the exponents equal to 0.01, 0.002, 0.0004, 0.00008, 0.000016, and 0.0000032, respecively. The additional diffuse Gaussians were centered on the peripheral hydrogen atom of either adenine or water, which is located closest to the positive direction of the dipole moment vector of the complex. The 6-31++G**(5d) basis augmented with six diffuse shells will be denoted as 6-31++G**(5d)X in further discussion. In our previous studies we have determined that this set of additional orbitals is sufficient to describe the ground states of the dipole-bound excess electron in systems with dipole moments similar to the dipole moments of the complexes considered in the present work. The use of the UHF method for anionic complexes did not introduce any noticeable spin-contamination because the dipole-bound electrons are located outside the molecular frame. Their exchange interaction with the core electrons, which would induce the contamination, is very small due to negligible overlap. For the A−W$_2$ complex, in addition to dipole-bound anions resulting from electron attachment to complexes which are stable as the neutral species, we also explored the possibility of formation of dipole-bound anionic complexes dissimilar from the neutral systems. For A−W$_3$ only the configuration with a complete first hydration sphere was considered.

Following the anion geometry optimizations, the obtained structures were used to initialize the geometry optimizations of the neutral complexes. These optimizations were performed with the spin-restricted HF method (RHF) and the 6-31++G**(5d)X basis set to generate the reference geometries of the neutral complexes for calculations of the adiabatic electron affinities (AEA). For both anion and neutral systems at their respective equilibrium HF/6-31++G**(5d)X geometries, we calculated the HF harmonic vibrational frequencies and the zero-point vibrational energies (ZPE). We also performed MP2/6-31++G**(5d)X energy calculations for all the systems. On the basis of these energies, the AEA's were calculated as the difference of the MP2+ZPE energies of the anions and the corresponding neutrals.

All the calculations presented in this work have been performed with the GAUSSIAN94 program package.[10]

3. Results and Discussion

3.1. Adenine−(Water)$_1$ Complex. In the first series of calculations we considered the adenine complexes with a single water molecule. As in the previous work,[5] we found three structures where a water molecule is connected to adenine through two hydrogen bonds. The structures are N$_7$···H−O(H)···H−NH, denoted here as **A**; N$_3$···H−O(H)···H−N$_9$, denoted as **B**; and N$_1$···H−O(H)···H−NH, denoted as **C**. The geometries of the complexes are shown in Figure 1. The total and relative energies and the dipole moments obtained in the calculations are presented in Table 1. The total MP2/6-31++G**(6d) energies of all three complexes are within a 1.8 kcal/mol range, with complex **B** being the most stable and complex **C** only 0.8 kcal/mol above it.

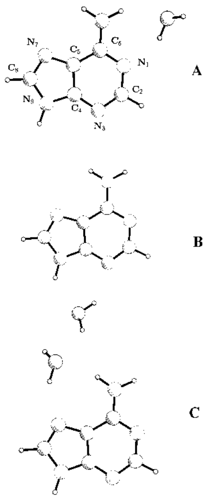

Figure 1. HF/6-31++G** equilibrium structures of three adenine−-(water)$_1$ complexes.

TABLE 1: Total (in hartree) and Relative (in kcal/mol) Energies of Three Adenine Complexes with a Water Molecule (denoted as *A*, *B*, and *C*) Calculated with 6-31++G(6d) Basis Set**

	A	*B*	*C*
HF	−540.593 079	−540.595 717	−540.594 044
MP2	−542.267 043	−542.269 961	−542.268 744
ΔMP2	1.8	0.0	0.8
dipole[a]	2.9	1.2	4.0

[a] Dipole moments in debye.

TABLE 2: Adiabatic Electron Affinity (AEA) Calculations for the Adenine−Water C Complex[a]

	anion	neutral	AEA
HF	−540.593 182	−540.592 986	5
MP2	−542.247 588	−542.247 070	14
ZPE	0.148 082	0.148 159	
MP2+ZPE	−542.099 506	−542.098 911	16

[a] Total energies in hartrees and AEA in meV. Calculations performed with the 6-31++G**(5d) basis set. Standard 6-31++G**(5d) basis set augmented with six sp-shells with exponents 0.01, 0.002, 0.000 4, 0.000 08, 0.000 016, and 0.000 003 2 and a p-orbital with exponent 0.036 centered at the hydrogen atom located closest to the positive pole of the molecular dipole.

Only complex **C** has a sufficient dipole moment to bind an excess electron in a dipole-bound state. In the next series of calculations the dipole-bound electron affinity of **C** was determined according to the procedure described above. The results are shown in Table 2. As one notices, including electron correlation at the MP2 level leads to a significant increase of the AEA from 5 to 14 meV. This result increases to 16 meV after including the ZPE correction. On the basis of our previous calculations on dipole-bound anions of molecular complexes smaller than A−(W)$_N$ clusters, where we used more complete basis sets and higher levels of theory, one may anticipate a possible increase of this result by as much as 30%. The dipole-bound character of the excess electron in the anion of **C** is examined in Figure 2, where the orbital occupied by the electron is shown. Typical of dipole-bound anions, the orbital has ó - -character and is located outside the molecular frame of the complex. Its diffuse character and its shape confirms that the calculations describe a dipole-bound anion.

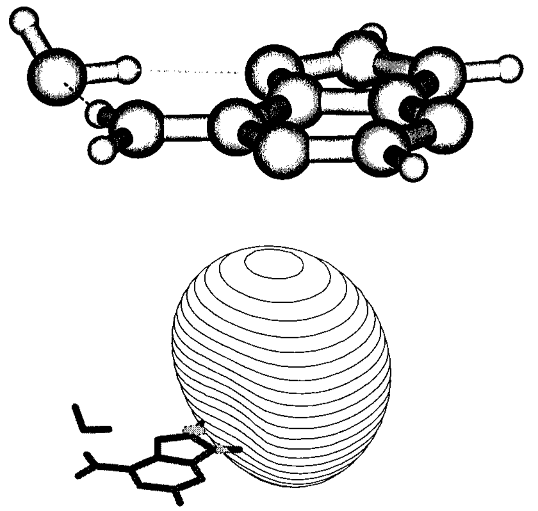

Figure 2. The orbital occupied by the excess electron in the dipole-bound anion of adenine−-(water)$_1$, complex **C**.

3.2. Adenine−(Water)$_2$ Complexes. The number of possible structures for the A−(W)$_2$ system is much greater than for the adenine complex with a single water molecule. In the search for minima on the A−(W)$_2$ potential energy surface, we first looked for structures with the highest number of hydrogen bonds formed either between the two water molecules and the adenine molecule or in configurations where two H- -bonded waters bridge two H--bonding sites of adenine. This first search resulted in six configurations denoted as **I**− **VI** and shown in Figure 3. In addition to these six structures, we also explored the possibility of the formation of complexes with fewer H--bonds, but possessing high dipole moments, which can strongly interact with an excess electron and acquire additional stabilization due to this interaction. In this second search four additional A−(W)$_2$ minima were found corresponding to configurations denoted as **VII**− **X** in Figure 3. In Table 3 we summarize the total (HF and MP2) and relative (MP2) energies of the identified complexes. The table also provides their dipole moments.

Upon examining the results one sees that the lowest energy configuration (**IV**) has almost zero dipole moment and cannot form a dipole-bound state. There are, however, five configurations whose dipole moment is sufficiently large to support an excess electron in a bound state (complexes **III**, **V**, **VI**, **VII**, and **VII**). For all these five configurations we calculated the dipole-bound electron affinities and the results are summarized in Table 4. In addition we found a configuration (denoted **D** in Table 4), which does not have a neutral counterpart. In this configuration the alignment of the dipole moments of adenine

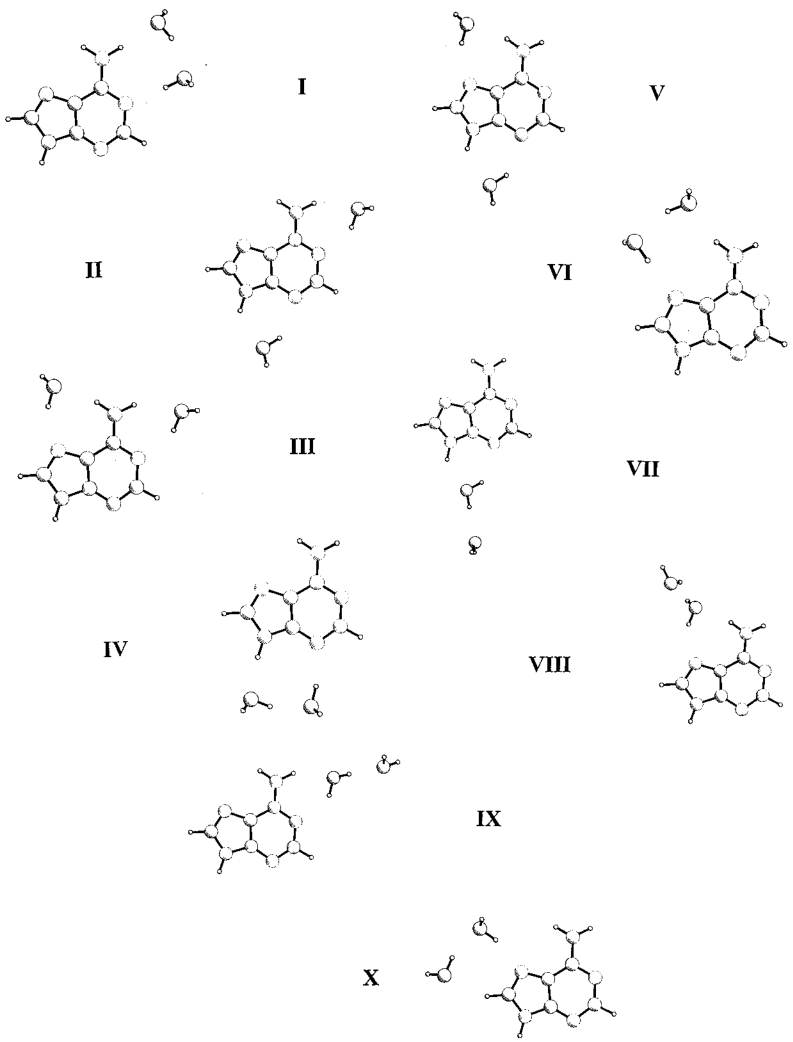

Figure 3. HF/6-31++G** equilibrium structures of 10 adenine−(water)$_2$ complexes. Structures **I**−**VI** involve water dimers bridging two H--bonding sites of adenine, structures **VII**−**IX** in which one of the waters is H -bonded to one of the three double H -bonding sites of adenine and the other water is H-bonded to the first water but not H -bonded to adenine, and structure **X**, where a water dimer bridges N_7 and the hydrogen atom attached to C_8.

TABLE 3: Total (in hartree) and Relative (in kcal/mol) Energies of Adenine Complexes with Two Water Molecules[a]

	HF	MP2	ΔMP2	dipole
I	−616.638 198	−618.518 271	3.8	2.7
II	−616.638 547	−618.518 879	3.4	2.3
III	−616.636 385	−618.517 073	4.5	4.4
IV	−616.643 339	−618.524 305	0.0	0.6
V	−616.640 166	−618.521 287	1.9	3.1
VI	−616.636 983	−618.517 150	4.5	3.8
VII	−616.634 887	−618.512 533	7.4	4.3
VIII	−616.632 679	−618.510 789	8.5	5.1
IX	−616.631 328	−618.508 593	15.5	2.1
X	−616.634 801	−618.513 748	6.6	1.6

[a] Structures of the complexes optimized at the HF level. The 6-31++G**(6d) basis set was used in the calculations. Dipole moments in debye.

and two waters is stabilized by the interaction with the excess electron. When the electron is removed, geometry optimization for this configuration converges to one of the configurations already identified for the neutral complex, which is dissimilar from the configuration of the anion. Upon examining the results in Table 4, one sees that the predicted values of dipole-bound AEA vary widely between the different A−(W)$_2$ complexes from values as small as 0.1 meV to as large as 90 meV. The pictures of the orbitals occupied by the excess electron in the six dipole-bound A−(W)$_2$ anions presented in Figure 4 show distinct patterns of electrons attached to the dipole field of the complex. In some of the anions the excess electron is located closer to the water molecules, and in the others it is located by adenine.

3.3. Adenine−(Water)$_3$ Complex. For this complex we examined only one structure, which corresponds to a complete first hydration sphere around the adenine molecule. This structure should be the lowest-energy configuration. Unlike in A−(W)$_1$ and in A−(W)$_2$ systems, where the lowest-energy configurations did not have sufficient dipole moments to dipole-bind an excess electron, the dipole moment of A−(W)$_3$ of 3.75 D (the HF result) is large enough to form a dipole-bound state. However, the large size of the complex, which is one of the factors affecting the dipole-bound electron affinity, reduces its binding to the excess electron. Thus, the AEA calculated for this system is only 3 meV (MP2+ZPE result, see Table 5). The orbital occupied by the excess electron in A−(W)$_3$ has an interesting shape (see Figure 5). Its long distance behavior is typical for a dipole-bound state. However, in the region close to the complex, the orbital shows that an excess electron is locally attracted to two positive sites of the complex, one at the water molecule attached at N3 to adenine and the other at the five-member ring of adenine. This pattern indicates that the dipole-bound electron attachment to a molecule or a complex can only in the first approximation be viewed as the dipole-electron electrostatic interaction. When the excess electron approaches closer to the system, it is affected by the local charges, dipoles and higher multipoles, which complicate the attachment effect and may contribute to the electron affinity.

4. Conclusions

The ability of adenine−water complexes to form dipole-bound states with excess electrons was investigated with the use of ab initio calculations. It was determined that the lowest energy configurations of the A−(W)$_1$ and A−(W)$_2$ complexes have insufficient dipole moments to form dipole-bound states. However, A−(W)$_3$ can form a very weakly bound anion. In this case the three water molecules H- -bonded to the adenine molecule complete its first hydration sphere. The study shows that hydration of adenine changes its long-range interaction with excess electrons, due to either reduction or enhancement of the dipole moment. We identified one A−(W)$_1$ and six A−(W)$_2$ complexes that form dipole-bound states with the excess electrons. However, these complexes are not the lowest-energy configurations.

In a recent study Periquet et al.[11] experimentally determined the thresholds for the formation of stable valence hydrated anions of some nucleic acid bases including adenine. Valence anions are different species than dipole-bound anions due to localization of the excess electron within the molecular frame in the former, and mostly outside in the latter. According to this study, the number of water molecules that is sufficient to observe a stable adenine valence anion is two. Thus, the A−(W)$_1$ anion described in this study is probably the only stable dipole-bound anion of hydrated adenine which can be formed in the

TABLE 4: Total (in hartree) and Relative (in kcal/mol) Energies and Zero-Point Vibrational Energies (ZPE) of Adenine Complexes with Two Water Molecules and Their Anions[a]

	energy						AEA		
structure	HF	MP2	ZPE	Δ(MP2+ZPE)	Dipole (HF)	LUMO/HOMO	HF	MP2	MP2+ZPE
A (**VIII**)									
neutral	−616.631326	−618.486487	0.173823	6.2	5.1	−0.00024	16	31	39
anion	−616.631902	−618.487617	0.173520	5.3		−0.00120			
B (**VI**)									
neutral	−616.635701	−618.492917	0.175072	3.0	3.8	−0.00010	4	14	18
anion	−616.635852	−618.493413	0.174903	2.6		−0.00024			
C (**III**)									
neutral	−616.635092	−618.492823	0.174870	2.9	4.4	−0.00024	10	26	27
anion	−616.635450	−618.493759	0.174802	2.3		−0.00054			
D									
neutral	−616.633540	−618.488227[b]	0.172861	4.5	4.3	−0.00042	29	79	90
anion	−616.634598	−618.491131	0.172457	2.5		−0.00402			
E (**VII**)									
neutral	−616.633540	−618.488231[b]	0.172869	4.5	4.3	−0.00042	18	50	47
anion	−616.634191	−618.490080	0.172982	3.5		−0.00106			
F (**V**)[c]									
neutral	−616.638892	−618.497206	0.174626	0	3.1	*d*	0.1	0.2	0.1
anion	−616.638897	−618.497215	0.174593	0		*d*			

[a] Dipole moments in debyes, LUMO/HOMO energies in hartree, and adiabatic electron affinities (AEA) in meV. Calculations performed with the 6-31++G**(5d) X basis set. [b] Calculations of the neutral systems started with anion structures **D** and **E** converged to the same structure. [c] Additional sp-shell with exponent 0.000 000 64 was added to the basis set. [d] Both LUMO and HOMO energies negative but greater than −0.000 01.

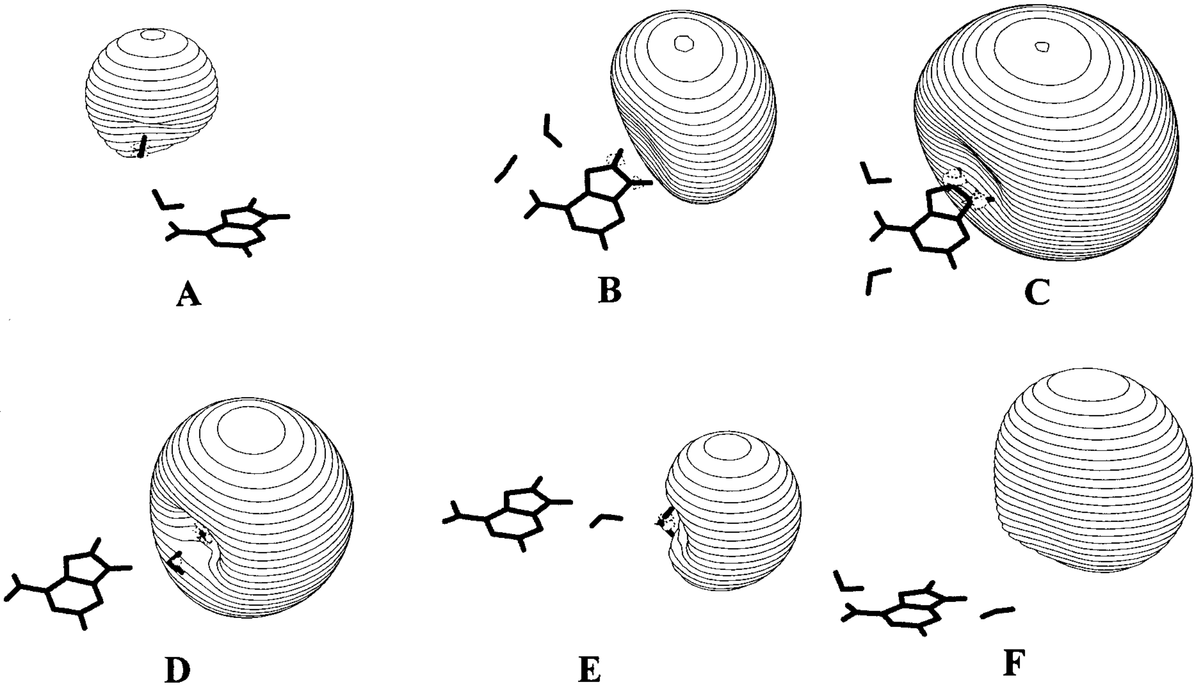

Figure 4. Orbitals occupied by excess electrons in dipole-bound anions of adenine−(water)$_2$ complexes.

TABLE 5: Dipole-bound Anion of Adenine Complex with Three Water Molecules[a]

	energy					AEA		
	HF	MP2	ZPE	dipole	LUMO/HOMO	HF	MP2	MP2+ZPE
neutral	−692.680 816	−694.742 961	0.201 374	3.75	−0.000 03	1	2	3
anion	−692.680 847	−694.743 025	0.201 311		−0.000 04			

[a] Total [in hartrees] and relative [in kcal/mol] energies and zero-point vibrational energies (ZPE) of the adenine complex with three water molecules. Dipole moment in debyes, LUMO/HOMO energies in hartrees, and adiabatic electron affinity (AEA) in meV. Calculations performed with the 6-31++G** (5d) basis set.

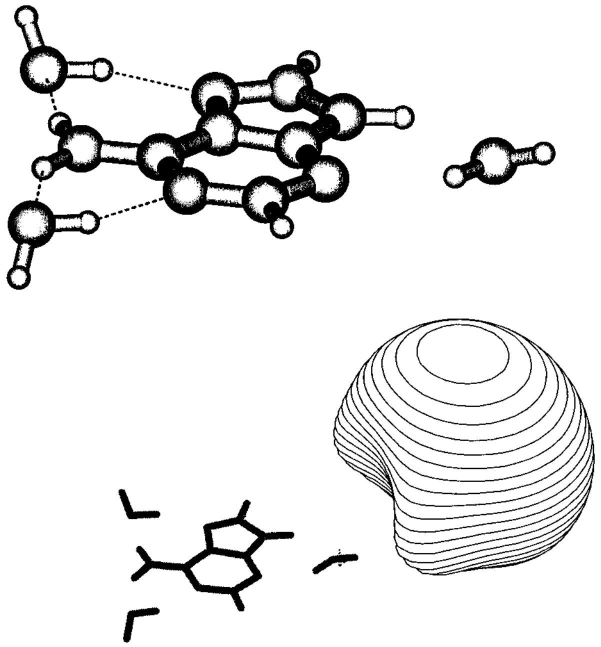

Figure 5. The structure of the dipole-bound anion of the adenine−(water)$_3$ complex, where all three double H-bonding sites of adenine form bonds with water molecules, and the orbital occupied by the excess electron in this system.

gas phase. For the A−(W)$_2$ system, the dipole-bound anions described here are intermediate species, which after formation will rearrange to form more stable valence anions. The same applies to the A−(W)$_3$ system. It is likely that the dipole-bound states are formed first when excess electrons come in contact with adenine hydrates, since the dipole-electron interaction has a longer range than dispersion and exchange interactions, which dominate the valence electron attachment. After the electron is trapped into a dipole-bound state, it can deexcite to a valence state. Usually a significant structural relaxation occurs with this deexcitation both in terms of inter- and intramolecular geometrical parameters.

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References and Notes

(1) Carles, S.; Desfrançois, C.; Schermann, J. P.; Smith, D. M. A.; Adamowicz, L. *J. Chem. Phys.* **2000**, *112*, 3726.

(2) Taylor, R.; Kennard, O. *J. Mol. Struct.* **1982**, *78*, 1.

(3) Russo, N.; Toscano, M.; Grand, A.; Jolibois, F. *J. Comput. Chem.* **1998**, *19*, 989.

(4) Smets, J.; Houben, L.; Schoone, K.; Maes, G.; Adamowicz, L. *Chem. Phys. Lett.* **1996**, *262*, 789.

(5) Houben, L. Ph.D. Thesis (G. Maes, advisor), University of Leuven, 2000.

(6) Shiöberg, D.; Luck, W. A. P. *J. Chem. Soc., Faraday Trans. 1* **1979**, 762.

(7) Frank, H. S.; Wen, W. Y. *Discuss. Faraday Soc.* **1957**, *133*, 24.

(8) Maes, G.; Graindourze, M.; Smets, J. *J. Mol. Struct.* **1991**, *248*, 89.

(9) Hendricks, J. H.; Lyapustina, S. A.; de Clercq, H. L.; Bowen, K. H. *J. Chem. Phys.* **1998**, *108*, 8.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peters-

son, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head- -Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision C.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

(11) Periquet, V.; Moreau, A.; Carles, S.; Schermann, J. P.; Desfrançois, C., J. El. *Spectrosc. Relat. Phenom*. **2000**, *106*, 141.