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Ionization Energy Thresholds of Microhydrated Adenine and Its Tautomers

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In the present work the vertical and adiabatic ionization energy thresholds (IET) of adenine, and its amino and imino tautomers complexed with 1−3 water molecules are presented. The vertical and adiabatic IETs have been calculated at the B3LYP and P3 levels of theory, using the standard 6-31++G(d,p) basis set. The results show that there is hardly any effect of microhydration on the vertical ΔIET of adenine, which is at odds with the experimental values determined by Kim et al. (*J. Phys. Chem.* **1996**, *100*, 7933). In an attempt to assign the experimental ΔIET values, calculations have been performed on the microhydrated amino and imino tautomers of adenine. Vertical ΔIET calculations and adiabatic ΔIET calculations on adenine N7H tautomers complexed with water are in better agreement with the experimental results than are calculations involving the canonical (N9H) form of adenine.

Introduction

An important experimental study by Kim et al.[1] reported the first determination of ionization energy thresholds (IET's) of microhydrated thymine and adenine in a cluster beam experiment in 1996. In the experimental work a single water molecule was seen to reduce the IET of adenine by 0.5 eV. Additional waters decrease the IET in 0.15 and 0.1 eV steps. The relative accuracy in these measurements is said to be ±0.05 eV.

In a recent article the ionization energy threshold calculations of microhydrated thymine were reported.[2] Calculations showed a small effect of microhydration on the IET's of thymine. The first water molecule was seen to decrease the IET by about 0.1 eV, while the second and third water molecules caused a further decrease of less than 0.1 eV each. These changes in IET calculated for the canonical form of thymine with 1−3 waters of hydration are smaller than the experimental values determined by Kim et al.[1]

A recent experimental study by Belau et al. reports the ΔIET's for all four of the microhydrated DNA bases.[3] In this work the appearance energy for thymine is reported to be 8.90 eV, which is close to the adiabatic ionization energy of 8.9178 eV reported by Choi et al. using VUV spectroscopy.[4] This agreement led the authors to conclude that their experimental results represent adiabatic appearance energies instead of vertical appearance energies.

It was therefore decided to calculate the adiabatic ionization energies of microhydrated thymine. The results showed that the changes in experimental ionization energies determined by Kim et al.[1] for microhydrated thymine were in good agreement with the calculated adiabatic ionization energies.[5] We believe that the reliability of the applied theoretical level for this investigation of the ionization energies has been established by this study.

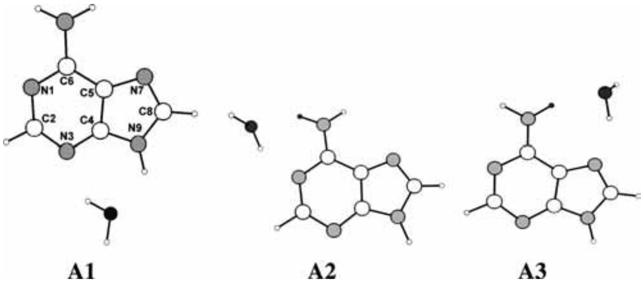

Figure 1. Structures of the three adenine monohydrates.

The aim of the present study is to perform a similar analysis on hydrated adenine and then to consider whether there is a set of microhydrated adenine structures that could explain the experimental results.

Review of the Literature on Adenine + *n*(H_2O) Structures. A study by Chandra et al. describes three adenine monohydrates.[6] A paper by Jalbout and Adamowicz shows the positions of several adenine monohydrates and dihydrates.[7] A paper by Kim shows structures of various adenine + $(H_2O)_n$ with $n = 1$ to 4 structures (Figures 2 and 3), including some interesting nonplanar structures.[8] All of these papers are helpful in finding the positions of waters around adenine. The numbering scheme used for the placements of the waters is as shown in Figure 1. Position 1 denotes a water molecule in the N3 N9 region, position 2 denotes a water near N1, and position 3 denotes a water between C6−N6 and N7.

A recent paper by Hanus et al. calculates 13 amino and imino tautomers of adenine in the gas phase, in a microhydrated environment ($n H_2O$, $n = 1, 2$), and in a water environment (C-

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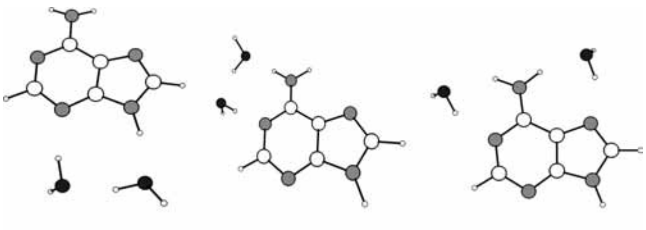
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Figure 2. Structures of three adenine dihydrates.

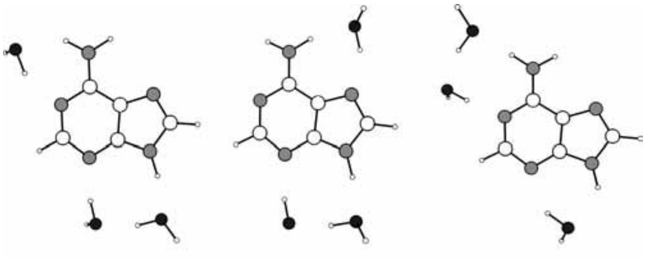
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Figure 3. Structures of three adenine trihydrates.

PCM).[9] Finally, a paper by Gu and Leszczynski reports the energetics of water assisted proton transfer in creating various tautomers in adenine.[10]

Computational Methods

The procedure followed herein is to take the best geometries available in the literature for adenine with various waters of hydration as input parameters and to reoptimize the structures at both the B3LYP/6-31++G(d,p) and P3/6-31++G(d,p) levels. Calculations to obtain vertical and adiabatic ionization energies were performed at the B3LYP level of theory. To obtain vertical ionization energies investigations were also carried out with electron propagator techniques in the partial third order (P3) approximation levels of theory, using the standard 6-31++G(d,p) basis set.[11] B3LYP frequency calculations were performed with the same basis set to verify stationary points. Calculations were performed on the Gaussian 98 suite of programs.[12]

The present work considers vertical and adiabatic ionization energies for the adenine−water complexes. The vertical ionization energies calculated herein are evaluated as the difference in total energy between the cation radical and the neutral base in the geometry of the neutral species (optimizations of the neutral molecule using the 6-31++G(d,p) basis set followed by a single-point calculation on the cation). The adiabatic ionization energy calculations involve an optimization of the cation geometry. These calculations were only performed at the B3LYP level of theory since the P3 method is currently not configured to calculate adiabatic ionization energies. The zero-point energy correction was not applied in these calculations.

The present study involves the calculation of the energies of a number of adenine tautomers. While the B3LYP/6-31++G(d,p) level has been applied successfully to calculate IET's, there are concerns about the use of DFT to obtain reliable energy values. For example, Forgarasi has examined the stability of the imino-oxo and the amino-hydroxy form of cytosine.[13] By performing electronic energies calculated at CCSD(T)/cc-pVTZ, he has shown that the amino-oxo form of cytosine is far overestimated by DFT calculation. Similarly Kwiatkowski and Leszczynski have warned that DFT may not be the best choice for calculating the relative energies of the nucleotide bases.[14] For this reason many of the DFT calculations presented here have been repeated by optimizing the structures at the MP2/6-31++G(d,p) level, followed by partial third order (P3) approximation levels of theory with the same basis set. Using these techniques, Dolgounitcheva et al.[15] report a IET for adenine as 8.49 eV, in excellent agreement with the experimental value of 8.48 eV.[16] Finally, Guerra et al. have done BP86/TZ2P calculations on the ionization energies of 12 adenine tautomers.[17] The vertical ionization of adenine is reported to be 8.27 eV, which is about 0.2 eV lower than the experimental value.

TABLE 1: B3LYP Energies for Adenine + nH$_2$O Structures

A + nH$_2$O	E(B3LYP) (hartrees)	vert. IET (eV)	dipole moments
adenine	−467.3533385	8.26	2.45
A1	−543.8051802	8.29	1.06
A2	−543.8031376	8.29	3.03
A3	−543.8048763	8.20	3.84
A11	−620.2609951	8.28	0.41
A13	−620.2573656	8.24	2.10
A12	−620.2546356	8.31	2.74
A22	−620.2556143	8.25	2.91
A113	−696.7134008	8.23	2.08
A112	−696.7103239	8.30	1.99
A123	−696.7058048	8.27	4.70
A122	−696.7070730	8.27	2.15
A322	−696.7053131	8.20	4.55

Results and Analysis

a. Adenine + (H$_2$O)$_n$. An analysis of the influence of waters of hydration on the IET of adenine has been undertaken and is presented in Table 1. At the B3LYP level of theory the calculated value of the IET of adenine, 8.26 eV, is smaller than the experimental value of 8.48 eV.[16] Previously Improta et al. noted that IET's calculated for the DNA bases by density functional theory are underestimated by ca. 0.3 eV.[18] In a previous study we showed that MP2 calculations of IET's on the DNA bases have problems with spin contamination that arises in the computation of the energy of the cation, which can be partially corrected by using projected MP2 (PMP2) energies.[19,20] Also, as mentioned above, more accurate vertical IET calculations can be obtained by optimizing the structures at the MP2 level, followed by partial third order (P3) approximation calculations. The dipole moments for neutral adenine and for the microhydrated adenine structures are also given in Table 1.

The first observation of the results in Table 1 is that the IET of adenine is hardly influenced by hydration with 1−3 waters. These results are therefore at odds with the experimental IET's of microhydrated adenine reported by Kim et al.[1] Therefore it is necessary to look at the actual experimental results reported by Kim et al.[1] In their cluster beam experiments, the vertical ionization energy of unhydrated adenine was not actually measured.[21] The experimental values had to be scaled to match experimental IET's reported by Hush and Cheung.[22] For the changes in IET's reported for hydrated adenine one cannot rule out the possibility that those measurements involve the vertical IET of tautomers of adenine complexed to a water molecule due to the relatively high water pressure and temperatures used in these experiments.

b. Adenine Tautomers. The next step is to systematically examine the tautomers of adenine in the gas phase and in a microhydrated environment. Table 2 shows first the calculated IET's of the amino tautomers of adenine. One notes that the

TABLE 2: B3LYP Energies for Adenine Amino Tautomers

A + nH$_2$O	E(B3LYP) (hartrees)	vert. IET (eV)	dipole moments
adenine	−467.3533385	8.26	2.46
N1H	−467.3233903	8.36	8.69
N3H	−467.3403823	8.22	4.19
N7H	−467.3400569	8.63	7.01
N1N7Imc	−467.3267641	8.04	3.54
N1N7Imt	−467.3263710	8.07	3.13
N1N9Imc	−467.3337938	7.88	3.93
N1N9Imt	−467.3228967	7.87	3.74
N3N7Imc	−467.3138894	7.95	4.87
N3N7Imt	−467.3258410	7.88	2.90
N3N9Imc	−467.3024190	7.81	10.1
N3N9Imt	−467.3027379	7.75	9.59
N7N9Imc	−467.2983850	7.21	8.62
N7N9Imt	−467.2821136	7.23	11.30

most stable entry in Table 2 is the canonical form (N9H) of adenine, followed by the N3H and N7H amino tautomers which are ca. 7 kcal/mol higher in energy than the canonical form of adenine.

The next entries in Table 2 are for the imino tautomers of adenine. The notation is to list the rotomers of the N6−H's as being cis (c) or trans (t) to N1. Since Kim et al.[1] were looking at hydrated adenines, the importance of this table is more for establishing a baseline of the energetics of the various tautomers in the vacuum state, and to have an idea of their dipole moments. As pointed out in the article by Hanus et al.,[9] while the canonical form of adenine has a small dipole moment, some of the tautomers of adenine have dipole moment as large as 10 debyes.

There is broad agreement from experimental and theoretical work that two isomers of adenine coexist at significant concentration in the gas phase: the 9H-amino and the 7H-amino forms.[23,24] Therefore, as a first step, calculations were performed on the N3H and N7H-amino tautomers of adenine at various hydrations levels (nH$_2$O, $n = 1, 3$). A new addition to the table here is to include electron propagator calculations in the partial third order (P3) approximation levels of theory, using the same 6-31++G(d,p) basis set. This offers a convenient way of comparing hybrid Hartree−Fock DFT calculations with calculations performed with second-order Møller−Plesset perturbational theory. The results are presented in Table 3.

The first thing to observe in Table 3 is the list of monohydrated N3H amino tautomers of adenine. Here one notes hardly any change in the IET as compared to the N3H tautomer of adenine. So no further calculations are reported for this tautomer.

The next entries in Table 3 are for the N7H adenine tautomers. One sees some spread in IET's for the various hydrated adenine derivatives. The entries in Table 3 with waters in the 3 position have rather small IET's. The difference in IET's of N7H and N7H3 is 0.50 eV, which is the stabilization energy reported by Kim et al.[1] The difference in IET's between N7H3 and N7H33 is 0.12 eV, close to what Kim et al.[1] report (0.10 eV). These two structures are shown in Figure 4.

For N7H adenine + 3H$_2$O calculations in Table 3, however, there is no arrangement of the three waters that lowers the IET an additional 0.1 eV. Therefore additional calculations were performed at the P3 level. Here the lowering of the IET's with each additional water of hydration is in slightly better agreement with the experimental data of Kim et al.[1] (Table 4). A challenging problem remains of finding an arrangement of 3H$_2$O's around an N7H adenine that is in better agreement with the experimental values.

TABLE 3: B3LYP Energies for Hydrated N3H and N7H Adenine Tautomers

A + nH$_2$O	E(B3LYP) (hartrees)	vert. IET DFT (eV)	vert. IET P3 (eV)	dipole moments
N3H	−467.3403823	8.22		4.19
N7H	−467.3400569	8.63	8.89	7.01
N3H1	−543.7955375	8.26		2.69
N3H2	−543.7879401	8.21		4.97
N3H3	−543.7965205	8.26		3.61
N7H1	−543.7859130	8.82	9.21	10.32
N7H2	−543.7899915	8.59	8.82	5.81
N7H3	−543.7893210	8.12	8.36	10.62
N7H11	−620.2349597	8.83		11.03
N7H12	−620.2354555	8.75		9.11
N7H13	−620.2364658	8.35		13.96
N7H22	−620.2423730	8.49		5.70
N7H23	−620.2399416	8.10		9.40
N7H33	−620.2357047	8.01	8.30	11.98
N7H122	−696.6889659	8.68		8.97
N7H123	−696.6866211	8.29		12.56
N7H133	−696.6832999	8.25		15.70
N7H223	−696.6913537	8.06		9.17
N7H233	−696.6868086	8.03		10.46
N7H333	−696.6874050	8.01	8.25	10.28

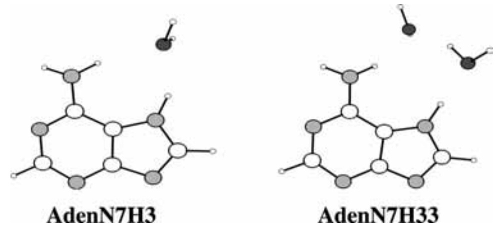
AdenN7H3 **AdenN7H33**

Figure 4. Two hydrated N7H adenine tautomers.

TABLE 4: B3LYP and P3 ΔIET's for Hydrated Adenine Tautomers

A + nH$_2$O	ΔIET (eV) exptl	calcd B3LYP	calcd MP2/P3
adenine	(8.26)	(8.63)	(8.40)
AN7H3	0.50	0.51	0.53
AN7H33	0.15	0.11	0.06
AN7H333	0.10	0.00	0.05

The calculated results discussed on the N7H adenine + nH$_2$O are summarized in Table 4. While the calculations at the B3LYP and MP2/P3 agree reasonably with the experimental results, the results obtained recently for microhydrated thymine prompted us to calculate adiabatic IET's of microhydrated adenine.

Here it is important to comment on the overall accuracy of the calculations presented. In Table 3 there is a commonly observed problem in comparing DFT calculations with MP2/P3 calculations. In general DFT calculations underestimate ionization energies of microhydrated structures slightly.[18] This is most likely due to problems the density functional theory has describing weakly bonded complexes.[25] For the present work, however, we are not interested in the absolute value of the ionization energy, but rather the ΔIET. In Table 4 it is gratifying to see that the ΔIET's computed by both methods are similar.

Next the various hydrated imino tautomers of adenine were examined. While the 9H-amino and the 7H-amino tautomers of adenine have both been observed in jet-cooled experiments, the same cannot be said for the imino tautomers of adenine. They are normally excluded from consideration since they are higher in energy than the N7H tautomers. For example, the N1N9Imc imino tautomer in Table 2 is 12.3 kcal/mol higher in energy than the canonical form of adenine.

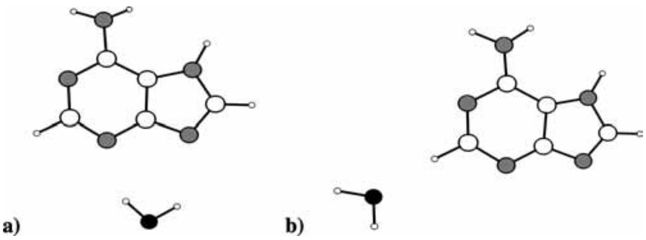

Figure 5. Optimization of (a) neutral AN7H1 and (b) AN7H1 cation.

TABLE 5: Experimental Data on the IET's for Hydrated Thymine

$A + nH_2O$	exptl IET (eV) Kim et al.[1]	exptl IET (eV) Belau et al.[3]
adenine	8.45 ± 0.15	8.30 ± 0.05
$A + 1H_2O$	7.95 ± 0.05	8.20 ± 0.05
$A + 2H_2O$	7.80 ± 0.05	8.10 ± 0.10
$A + 3H_2O$	7.70 ± 0.05	

One can find a few calculated ΔIET's among the many combinations of the microhydrated imino tautomers of adenine that are similar to the experimental data of Kim et al.[1] For example, the ΔIET for AN3HN7HImc3 is calculated as 8.26 eV − 7.80 eV = 0.46 eV. However the agreement with the experimental data is not as good for the dihydrates or the trihydrates of the imino tautomers of adenine. Therefore further calculations involving the microhydration of the imino tautomers of adenine are not considered here. Since the imino tautomers are of interest to experimentalists and to those modeling point mutations in DNA, the details on the structures, energies, and ionization energies of the microhydrated imino tautomers of adenine are given in the Supporting Information.

c. Adiabatic Ionization Energies. Recently it has been shown that adiabatic ionization calculations on microhydrated thymine[5] seem to agree best with the experimental results of Kim et al.[1] New experimental work be Belau et al. reports single photon UV photoionization (VUV SPI) studies of the microhydrated DNA bases.[3] Table 5 shows the ΔIET values obtained for the microhydrated adenines in these two experiments.

The 8.30 eV IET of adenine reported by Belau et al.[3] is very close to the 8.26 eV adiabatic ionization potential reported by Orlov et al.[26] or the 8.20 eV value reported by Jochims et al.[27] *The authors therefore state that these new results represent adiabatic appearance energies*. This is different from the assumptions made in interpreting the original experiments of Kim et al.[1] where the appearance energies were scaled to the vertical ionization potentials reported by Hush and Cheung.[22] Differences in the two sets of experimental results were discussed previously.[5]

A new set of calculations have been performed to obtain adiabatic ΔIET's on microhydrated adenines. The optimization calculations on the cations can be very time-consuming. An example is shown in Figure 5 for the AN7H1 tautomer. The starting geometry for the cation has the water between N3 and N9 (as in the neutral structure Figure 5a). During the optimization of the cation the water wanders over a shallow potential energy surface for 80 iterations before converging to the structure shown in Figure 5b.

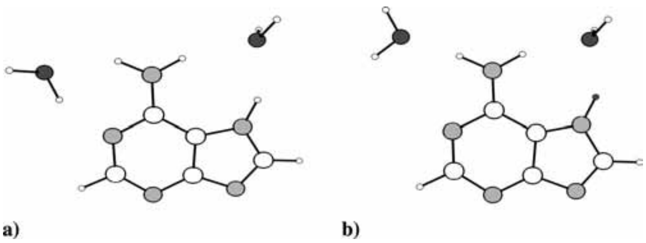

Figure 6. (a) Neutral AN7H23 and (b) cation of AN7H23.

TABLE 6: Calculated Adiabatic ΔIET's for Hydrated Adenines

$A + nH_2O$	*E*(B3LYP) cations (hartrees)	IET (eV) calcd B3LYP	ΔIET (eV) calcd B3LYP	ΔIET (eV) exper.
adenine	−467.1470976	(8.07)		
A1	−543.5163549	7.86	0.21	0.50
A2	−543.5140792	7.87	0.20	0.50
A3	−543.6235336	7.89	0.18	0.50
A11	−620.9694587	7.93	0.00	0.15
A22	−620.9655082	7.89	0.00	0.15
AN7H	−467.0350364	(8.30)		
AN7H1	−543.4816750	8.28	0.02	0.50
AN7H2	−543.4933879	8.07	0.23	0.50
AN7H3	−543.5021049	7.82	0.48	0.50
AN7H11	−619.9209002	8.55		
AN7H23	−619.9581907	7.67	0.15	0.15
AN7H233	−696.4112086	7.50	0.17	0.10
AN7H333	−696.4135657	7.45	0.22	0.10

Table 6 shows adiabatic ionization energies for various microhydrated adenines. The first entries involve the canonical form of adenine. One sees that the ΔIET's of the monohydrates are only about 0.20 eV, whereas the ΔIET observed by Kim et al.[1] was 0.50 eV. Furthermore, for the dehydrates there is no further decrease in the ionization energies. These results (column 4 of Table 6) then do not fit the experimental data (column 5 of Table 6) obtained by Kim et al.[1]

The next entries in Table 6 are for the N7H adenine tautomers. Here one sees a ΔIET of 0.48 eV in going from AN7H to the AN7H3 monomer, a ΔIET of 0.15 eV in going from the AN7H3 monomer to the AN7H23 dimer, and a ΔIET of 0.17 eV in going from the AN7H23 dimer to the AN7H233 trimer. All of the ΔIET values agree well with the experimental results reported by Kim et al.[1]

The AN7H tautomers from Table 6 whose ΔIET's have the best agreement with experimental data are shown in the following figures. The geometry of neutral AN7H3 is shown in Figure 4. Optimization of the AN7H3 cation does not lead to much displacement of the water in position three, so this structure is not shown. The structure of the neutral AN7H23 is shown in Figure 6a. Upon optimization of the AN7H23 cation, there is a considerable displacement of the water in position two, as shown in Figure 6b. Basically the same displacement is observed upon formation of the AN7H233 cation.

It needs to be pointed out that many microhydrated structures of N7H adenine are not included in Table 6. For example, hydration in the one position (AN7H1) had no effect on the change in adiabatic ionization energy. The same was true for dehydrates and trihydrates with waters in position one.

Also it should be noted that there are problems with some of these calculations. One notes the high ionization energy associated with the AN7H11 entry in Table 6. This is caused by the calculation on the cation, which had an appreciable delocalization of spin density on the water that is nearest to the N9 of the adenine.

In the second column of Table 6 the energies of the optimized cations are given. It is gratifying to see that the entries that have the ΔIET's that agree best with the experimental data of Kim et al.[1] have the cations with the lowest energy.

One electron oxidation of adenine yields the adenine cation radical that is a strong acid (pK_a < 1).[28] This represents a strong driving force for deprotonation. For the N7H adenine tautomer: deprotonation will occur either at N7−H or at the NH_2 amino group. In the microhydrated states, deprotonation of the radical cation leads to formation of a hydronium ion and the neutral adenine radical.

For the AN7H3 neutral species the dominant vibration (3576.5 cm^{-1}) involves both N7−H and NH_2 stretching toward the lone water molecule. This transition shifts to 3451.2 cm^{-1} in the cation. For the AN7H23 dimer, the most intense vibration involves NH_2 stretching (3502.4 cm^{-1}) in the neutral molecule. This same mode is 3135.7 cm^{-1} in the cation. In the AN7H233 trimer, the most intense vibration involves N7−H stretching (3417.9 cm^{-1}), which shifts down to 3108.7 cm^{-1} in the cation. In the previous study on microhydrated thymine[5] these shifts were much more pronounced because deprotonation of the radical cation is confined to just a single N1−H vibration, whereas in adenine the vibration energy is shared by the three possible sites for deprotonation (N7−H and NH_2)

It should be noted in passing that even with all the different calculations performed herein there do not seem to be a set of calculations that would explain the new results of Belau et al.[3] There is a long discussion in our previous study on microhydrated thymine on the difficulties of comparing different types of experiments (electron impact versus photoionization), and on cases where electron impact ionization energies unexpectedly tend to agree with adiabatic rather than the vertical ionization energies.[5] We plan to address these issues in a forthcoming study.

Conclusions

The present study has shown that hydration of the canonical form of adenine (N9H amino form) does not lower the IET's sufficiently to explain the experimental data of Kim et al.[1] (see Table 1). Reliable calculations have been presented to show that hydrated N7H adenine tautomers are good candidates for explaining the experiments of Kim et al.[1] For completeness we have also included the microhydrated adenine imino tautomers. If future experiments are performed on microhydrated adenine, then one should be able to make use of the energetics and conformations of the various hydrated adenine tautomers presented here.

The adiabatic ionization calculations on microhydration of the canonical form of adenine do not fit the experimental results of Kim et al.[1] However, adiabatic ionization calculations on microhydration of the N7H tautomer of adenine do agree with the experimental results of Kim et al.[1] rather well. The suggestion that the adiabatic and not vertical IETs were measured by Kim et al. in the case of adenine is in line with our previous suggestions for the microhydrated thymine complexes.[5]

From the theoretical results presented, it appears that under the experimental conditions used by Kim et al.[1] it is more efficient to ionize the hydrated N7H adenine tautomers rather than the canonical N9H form. It appears as if in some cases ionization energies unexpectedly tend to agree with adiabatic rather than the vertical ionization energies. This leads to a number of questions that should be considered in future experimental studies.

Supporting Information Available: Energy values and dipole moments for the various adenine hydrated tautomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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