Effect of Hydration on the Lowest Singlet $\pi\pi$* Excited-State Geometry of Guanine: A Theoretical Study

M. K. Shukla and Jerzy Leszczynski*

Computational Centre for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, Jackson, Mississippi 39217

An ab-initio computational study was performed to investigate the effect of explicit hydration on the ground and lowest singlet $\pi\pi$* excited-state geometry and on the selected stretching vibrational frequencies corresponding to the different NH sites of the guanine acting as hydrogen-bond donors. The studied systems consisted of guanine interacting with one, three, five, six, and seven water molecules. Ground-state geometries were optimized at the HF level, while excited-state geometries were optimized at the CIS level. The 6-311G-(d,p) basis set was used in all calculations. The nature of potential energy surfaces was ascertained via the harmonic vibrational frequency analysis; all structures were found minima at the respective potential energy surfaces. The changes in the geometry and the stretching vibrational frequencies of hydrogen-bond-donating sites of the guanine in the ground and excited state consequent to the hydration are discussed. It was found that the first solvation shell of the guanine can accommodate up to six water molecules. The addition of the another water molecule distorts the hydrogen-bonding network by displacing other neighboring water molecules away from the guanine plane.

1. Introduction

Hydrogen bonding is ubiquitous. Depending upon hydrogen-bond energies, hydrogen bonds may be classified as strong, moderate, and weak.[1] There are other types of hydrogen bonds known as a blue-shifted hydrogen bond[2] and the dihydrogen bond.[3] Water plays an important role in the structure and function of nucleic acids. Theoretically, water molecules were found to increase the stacking interaction in base pairs.[4] Further, hydrations were also found to increase the stability of some minor tautomers of the DNA bases in the ground state.[5] The genetic information of any living system is encoded in the form of specific patterns of hydrogen bonds formed between purine and pyrimidine bases in DNA; the bases are in their normal tautomeric forms. Any change in hydrogen-bonding patterns due to the external or internal environments may be harmful if left unrepaired. We are all exposed to different kinds of irradiation and few are very dangerous. DNA (and its constituent bases) absorbs the UV radiation very efficiently, but the quantum efficiency of the emission of the absorbed radiation is very poor. Thus, most parts of the absorbed radiation are released in the form of ultrafast nonradiative processes. Recently, several experimental and theoretical investigations were performed to determine the possible mechanism of nonradiative processes in nucleic acid bases.[6] Such a deactivation mechanism includes the vibronic coupling of the electronic singlet $\pi\pi$* and $n\pi$* states and that between the lowest singlet excited state and the ground state.[6] Recently, another possible mechanism has also been suggested in which the lower-lying $\pi\sigma$* Rydberg state in the nucleic acid base adenine causes predissociation of the lowest singlet $\pi\pi$* excited electronic state to the ground-state potential energy surface.[6e,f] This conical intersection takes place along the stretching of the N9H bond. Unfortunately, the exact mechanism is still not known. But, it is clear that the time scales for the nonradiative processes in nucleic acid bases are in the order of subpicoseconds.[6,7]

Theoretical calculations suggest that guanine in the gas phase has a nonplanar geometrical structure in the lowest singlet $\pi\pi$* excited state.[8] Quantitative information regarding the excited-state geometry of guanine is not available experimentally; however, for other bases, excited-state geometries have been indicated to be nonplanar.[9] It is well-known that in-vivo DNA is heavily hydrated. Water molecules play an important role in the formation of the three-dimensional structure of DNA.[10] Chahinian et al.[11] have performed Overhauser spectroscopic studies on the hydration of uracil and found that the first solvation shell contains three water molecules. These authors have suggested that water molecules interacting with uracil form a cyclic trihydrated complex in which each of the water molecules is bonded between the NH and C=O groups. However, the theoretical investigation on the solvation of uracil (and thymine) with three water molecules predicted a different arrangement of hydration structure; one water molecule is bonded between the N1H and C2O groups, while two water molecules are bonded between the N3H and C4O groups.[12] Korter et al.[13] have performed an experimental investigation on the interaction of a water molecule with the N−H site of indole in the ground and the lowest singlet excited states. They have found that consequent to the electronic excitation, the position and orientation of the water molecule was changed with respect to the ground state.

The information about the excited-state geometry of guanine under a heavily hydrated environment is not known. In this paper, we present the results of the systematic study of the excited-state geometry of guanine under hydration with several water molecules in the first solvation shell. We have found that a minimum of six water molecules is necessary in the first solvation shell of the guanine. The excited-state geometry of the guanine was revealed to be nonplanar, irrespective of the number of water molecules used in the hydration. However, the mode of the structural nonplanarity of the guanine was revealed to be different for complexes where five or more water molecules were used in the hydration. The vibrational frequen-

* Corresponding author. E-mail: jerzy@ccmsi.us.

TABLE 1: Some Selected Dihedral Angles and Amino Group Angles of Guanine in the Isolated and Different Hydrated Forms in the Ground and Lowest Singlet $\pi\pi^*$ Excited State Obtained at the HF/6-311G(d,p) and CIS/6-311G(d,p) Levels, Respectively

parameters	G S_0	G S_1	G + 1W S_0	G + 1W S_1	G + 3W S_0	G + 3W S_1	G + 5W S_0	G + 5W S_1	G + 6W S_0	G + 6W S_1
H21N2C2	117.9	115.3	119.2	117.1	118.8	116.7	119.7	119.2	119.6	119.2
H22N2C2	113.8	112.7	115.2	114.3	115.7	114.4	120.1	120.4	120.4	120.4
H21N2H22	115.0	111.4	116.7	113.8	116.3	113.3	120.0	119.8	119.9	119.9
360-ΣHNH	13.3	20.6	8.9	14.8	9.2	15.6	0.2	0.6	0.1	0.5
C6N1C2N3	−0.6	64.0	−0.9	−64.7	0.2	−64.8	1.3	38.1	1.3	43.0
N1C2N3C4	0.8	−44.2	0.8	39.2	0.8	42.4	0.6	−1.7	0.9	−6.5
C2N3C4C5	−1.0	2.4	−0.6	2.0	−1.2	0.0	−1.6	−32.2	−2.1	−29.0
N3C4C5C6	−0.9	18.5	0.4	−18.1	0.5	−18.8	0.8	32.2	1.2	29.7
N1C6C5C4	−0.4	0.6	−0.3	−7.3	0.5	−3.3	1.0	2.6	1.0	5.4
N2C2N3C4	−177.2	161.4	−177.5	−159.7	−177.5	−160.5	−179.2	−177.3	−179.1	179.7
H21N2C2N1	30.4	−42.3	22.1	31.0	23.3	34.8	6.4	10.2	5.4	10.6
H22N2C2N1	169.4	−171.8	168.4	167.9	169.0	170.4	−178.6	−178.7	−176.5	−177.4

cies corresponding to the stretching vibrations of different hydrogen-bond-donating groups of the guanine were found to exhibit significant shift under electronic excitation and under hydration.

2. Computational Details

Ground-state geometries of the guanine and all studied complexes were optimized at the HF level. Different hydrated complexes were obtained by adding one, three, five, six, and seven water molecules in the first solvation shell. The geometries of the isolated and hydrated guanine in the lowest singlet $\pi\pi^*$ excited state were optimized at the CIS level.[14] The 6-311G-(d,p) basis set was used in all calculations. The harmonic vibrational frequencies were computed to ascertain the nature of potential energy surfaces. All geometries were found minimum at the respective potential energy surface. The calculations were performed using the Gaussian 03 program.[15] The molecular orbitals were visualized using the Molekel program.[16]

3. Results and Discussion

3.1. Geometries. The ground and the lowest singlet $\pi\pi^*$ excited-state optimized geometries of the isolated form of the guanine are shown in Figure 1. The atomic numbering scheme of guanine is also shown in the same figure. Selected dihedral
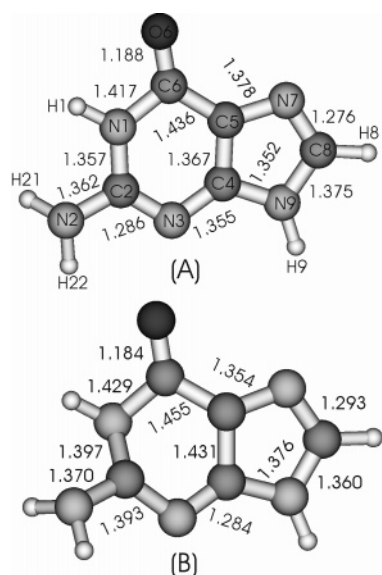

Figure 1. Ground and lowest singlet $\pi\pi^*$ excited-state structure of guanine: (a) atomic numbering schemes and ground-state bond distances; (b) excited-state structure and bond distances. Distances are in Å.

angles of the guanine and hydrated complexes in the ground and excited states demonstrating the nonplanarity of the guanine moiety are shown in Table 1. The amino group angles and dihedral angles are also shown in the same table. We will describe each case separately.

It should be noted that we have not included the complexes of guanine with two and four water molecules in our study. It has been shown theoretically that the first water molecule binds between the N1H and CO sites of the guanine.[5e] The bonding of the first water molecule with other proton acceptor/donor sites of guanine yields relatively less stable complexes. The addition of the second water molecule to the monohydrated complex of guanine yields the structure where both water molecules are bonded between the N1H and CO sites.[5e] Since one of the objectives of the present investigation is to complete the first solvation shell of the guanine, our attention was devoted to the complexes, where water molecules were bonded between different hydrogen-bond-donating and -accepting sites of the molecule. Therefore, the two and four water molecules were not included in the present investigation.

3.1.1. Guanine. Ground-state geometry of the guanine was revealed to be planar except the amino group, which was found to be pyramidal due to the partial sp³ hybridization of the amino nitrogen. This is in agreement with numerous theoretical calculations on the guanine at different levels of the theory.[5a,f] The difference between the summation of all amino angles and 360 degrees is a measure of the pyramidalization of the amino group. At the HF/6-311G(d,p) level of the theory, the amino group pyramidalization of the guanine was revealed to be 13.3 degrees. The dihedral angles of amino hydrogens with respect to the N2C2N1 are 30.4 and 169.4 degrees, respectively (Table 1), at the HF/6-311G(d,p) level. It should be noted that earlier investigations have suggested that the ring geometries of nucleic acid bases are flexible and the predicted values of amino group dihedral angles are basis set- and method-dependent.[5a,17] The electronic excitation to the lowest singlet $\pi\pi^*$ excited state (S1-($\pi\pi^*$)) at the CIS/6-311G(d,p) level is dominated by the configuration HOMO (H) → LUMO (L). Geometry of the guanine in the S1($\pi\pi^*$) state is highly nonplanar, and such nonplanarity is mainly localized at the C6N1C2N3 fragment of the six-membered ring (Table 1, Figure 1B). The amino group pyramidalization is also increased in the excited state, which is evident from the increased value of dihedral angles associated with the amino hydrogens and decrease in the planarity of the amino group (Table 1).

3.1.2. Guanine + 1 Water Molecule. In the singly hydrated complex of the guanine, the water molecule was bonded between the N1H and carbonyl sites acting as a hydrogen-bond donor and acceptor, respectively (Figure 2). The selected sites for the hydration are important in view of the keto−enol tautomerism
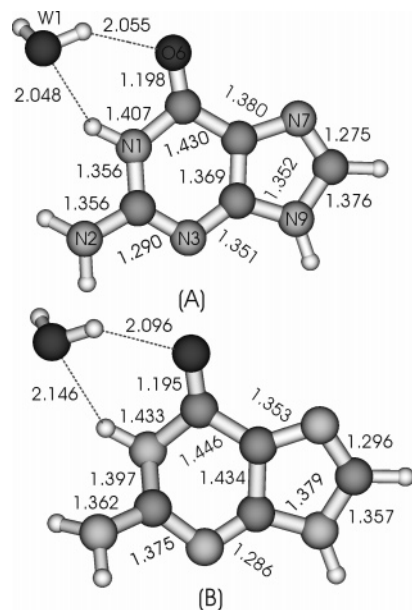
ππ* Excited-State Geometry of Guanine

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Figure 2. Ground and lowest singlet ππ* excited-state structures of the monohydrated guanine: (a) ground-state structure and bond distances; (b) excited-state structure and bond distances. Distances are in Å.

of the guanine. It has been shown theoretically that the presence of a water molecule between the N1H and carbonyl group sites reduces the barrier height corresponding to the proton transfer from the keto to the enol form significantly.[5a,b] It should be noted that the studied monohydrated complex was found to be the most stable among different monohydrated complexes of the guanine at the RI-MP2/TZVPP and MD/Q levels.[5e]

The ground-state ring geometrical parameters of the monohydrated guanine are generally similar to that of the isolated guanine. However, the amino group planarity is slightly increased in the ground state as a result of the hydration. Thus, while in the isolated guanine the amino group is about 13.3 degrees nonplanar in the ground state, the corresponding nonplanarity for the hydrated guanine is only 8.9 degrees (Table 1). It is interesting that although the water molecule is not directly bonded to the amino group, it indirectly induces planarity in the amino group of the guanine. It appears that the water molecule bonded at the N1H site decreases the stearic repulsion between the amino hydrogen (H21, Figure 1A) and the hydrogen attached to the N1 site and thus reduces the nonplanarity in the amino group. This explanation is also supported by the fact that the dihedral angle H21N2C2N1 associated with the H21 amino hydrogen is 30.4 degrees for the isolated guanine and 22.1 degrees for the monohydrated guanine in the ground state. The dihedral angle H22N2C2N1 associated with the other amino hydrogen does not show significant change under the hydration (Table 1). The electronic excitation to the lowest singlet ππ* excited state of the monohydrated guanine is also dominated by the H → L configuration. The geometrical deformation in the monohydrated complex of the guanine in the lowest singlet ππ* excited state is similar to that of the isolated guanine (Figures 1B, 2B). The most prominent change is found in the N1C6C5C4 dihedral angle which is changed from 0.6 to 7.3 degrees in going from the isolated to the hydrated guanine in the excited state. Further, the amino group in the excited state was also revealed to be more planar than that in the isolated guanine (Table 1).

3.1.3. Guanine + 3 Water Molecules. The structure of the trihydrated guanine was obtained by attaching one water
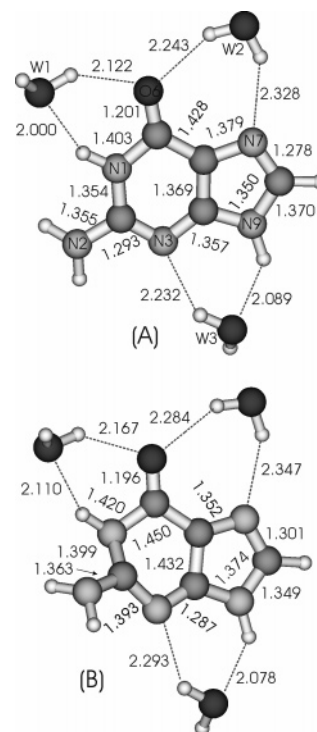

Figure 3. Ground and lowest singlet ππ* excited-state structures of the trihydrated guanine: (a) ground-state structure and bond distances; (b) excited-state structure and bond distances. Distances are in Å.

molecule between the N7 and carbonyl sites where water acts as a dihydrogen bond donor and another water molecule between the N9H and N3 sites of the monohydrated guanine (Figure 3). The ground-state nonplanarity of the amino group of the trihydrated guanine is similar to that in the monohydrated guanine. Further, water molecules are bonded in the plane of the guanine, except for those hydrogens on the water molecules that are not involved in the hydrogen bonds and are out of the molecular plane. The electronic excitation to the lowest singlet ππ* excited state is dominated by the H → L configuration. The excited-state geometry is appreciably nonplanar, and the nonplanarity is localized in the six-membered ring (Figure 3B). The geometrical deformation of the guanine in the trihydrated complex is similar to that in the monohydrated and isolated guanine in the excited state. The largest change is revealed in the N1C6C5C4 dihedral angle which is decreased by 4.0 degrees in magnitude in the excited state of the trihydrated guanine as compared to same state of the monohydrated guanine (Table 1). The amino group pyramidalization of guanine in the trihydrated complex is similar to that in the monohydrated guanine in the excited state. The predicted similarity in the amino group pyramidalization of the guanine in the mono- and trihydrated complex in the ground and excited state is understandable, since the amino group in both complexes is not involved in the direct interaction with water molecules. Further, the strength of hydration in the trihydrated complex of guanine is decreased in the lowest singlet excited state as compared to that in the ground state. This point is evident from the hydrogen-bond lengths depicted in Figure 3, which shows that hydrogen-bond distances are increased in going from the ground state to the excited state except for the H(W3)···N9H, which is slightly decreased.

3.1.4. Guanine + 5 Water Molecules. In the pentahydrated complex of the guanine, one water molecule was placed between the N1H site and amino group and another water molecule was placed between the amino group and the W3 water bonded between the N9H and N3 sites of the trihydrated complex of
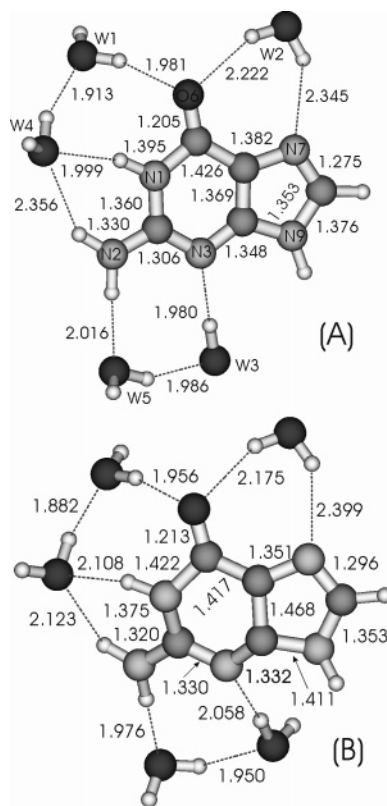
Figure 4. Ground and lowest singlet $\pi\pi^*$ excited-state structures of the pentahydrated guanine: (a) ground-state structure and bond distances; (b) excited-state structure and bond distances. Distances are in Å.

the guanine. The optimized geometry of the pentahydrated guanine shows that the W3 water molecule, which was bonded between the N9H and N3 sites in the trihydrated guanine, is shifted from the N9H site and is hydrogen-bonded between the N3 site and the W5 water molecule due to the stronger water–water interaction (Figure 4). Further, the W1 water molecule, which was hydrogen-bonded between the C6O and N1H sites in the trihydrated complex, is bonded between the C6O site and the W4 water molecule in the pentahydrated guanine complex. The W4 water molecule in the pentahydrated guanine being bonded between the N1H site and the amino group acts as a biproton acceptor (Figure 4). The geometry of the guanine including that of the amino group is generally planar in the pentahydrated complex. Further, W2, W4, and W5 water molecules, which are hydrogen-bonded between the N7 and carbonyl group, the N1H and amino group, and between the amino group and W3 water molecule respectively, are situated in the molecular plane of the guanine (Figure 4). However, W1 and W3 water molecules are slightly out-of-the-plane mode and are at the same side relative to the guanine plane. It should be noted that those hydrogens of water molecules which are not involved in hydrogen bonding are out of the molecular plane. The electronic excitation to the lowest singlet $\pi\pi^*$ excited state is dominated by the H → L configuration. The excited-state geometry is appreciably nonplanar. In the excited state, the N1C2N3C4 part of the guanine is folded along the N1C4 direction, and the N1C6 atoms are approximately in plane with the plane of the five-membered ring. Although the nonplanarity is localized in the six-membered ring, it appears appreciably different than that in the isolated and mono- and trihydrated forms of the guanine (Figure 4B, Table 1). For example, the dihedral angles C6N1C2N3 and N1C2N3C4 are decreased from 64.0 and 44.2 degrees to 38.1 and 1.7 degrees, respectively, in
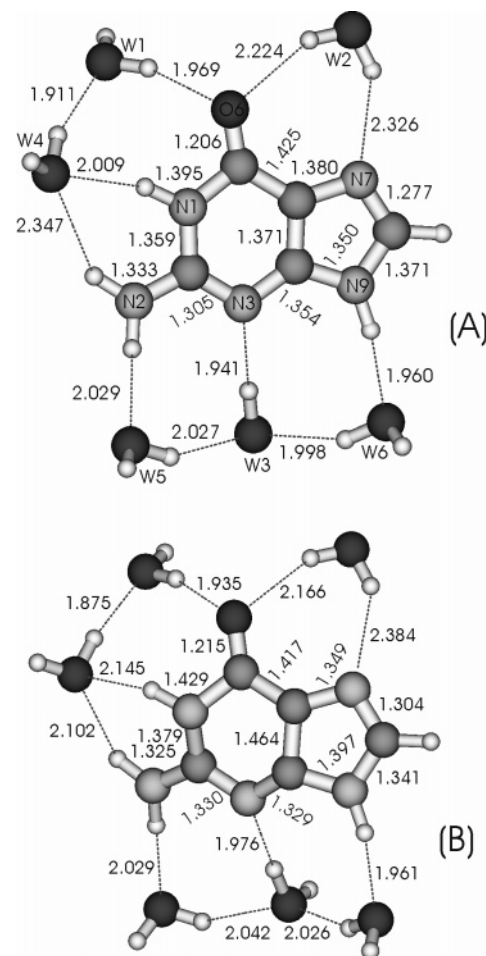

Figure 5. Ground and lowest singlet $\pi\pi^*$ excited-state structures of the hexahydrated guanine: (a) ground-state structure and bond distances; (b) excited-state structure and bond distances. Distances are in Å.

going from the isolated to the pentahydrated guanine in the excited state. Further, the C2N3C4C5 and N3C4C5C6 dihedral angles are changed by 34.6 and 13.7 degrees, respectively, in going from the isolated to the pentahydrated guanine in the excited state. The amino group of the guanine in the excited state of the pentahydrated guanine is also almost planar in the excited state. This is evident from the amino angles shown in Table 1. Thus, water molecules directly hydrogen-bonded with amino hydrogens induce planarity both in the ground and the excited states. The analysis of hydrogen-bond distances in the ground and excited state of the pentahydrated guanine shown in Figure 4 suggests that hydrogen-bond distances associated with the interaction of water molecules with N7, N3, and N1H sites are increased while other hydrogen-bond distances are decreased in the excited state as compared to that in the ground state. Thus, the hydrogen bonding associated with N7, N3, and N1H sites would be weaker in the excited state, while hydrogen bonding associated with the carbonyl group and amino hydrogens would become stronger than in the ground state. Further, the intermolecular hydrogen bonds between water molecules are also stronger in the excited state than in the ground state of the pentahydrated guanine.

3.1.5. Guanine + 6 Water Molecules. The hexahydrated guanine was obtained by adding a water molecule between the W3 water molecule acting as a hydrogen-bond acceptor and the N9H site acting as a hydrogen-bond donor of the pentahydrated guanine (Figure 5). In the ground state, the geometry of the guanine including the amino group is planar in the
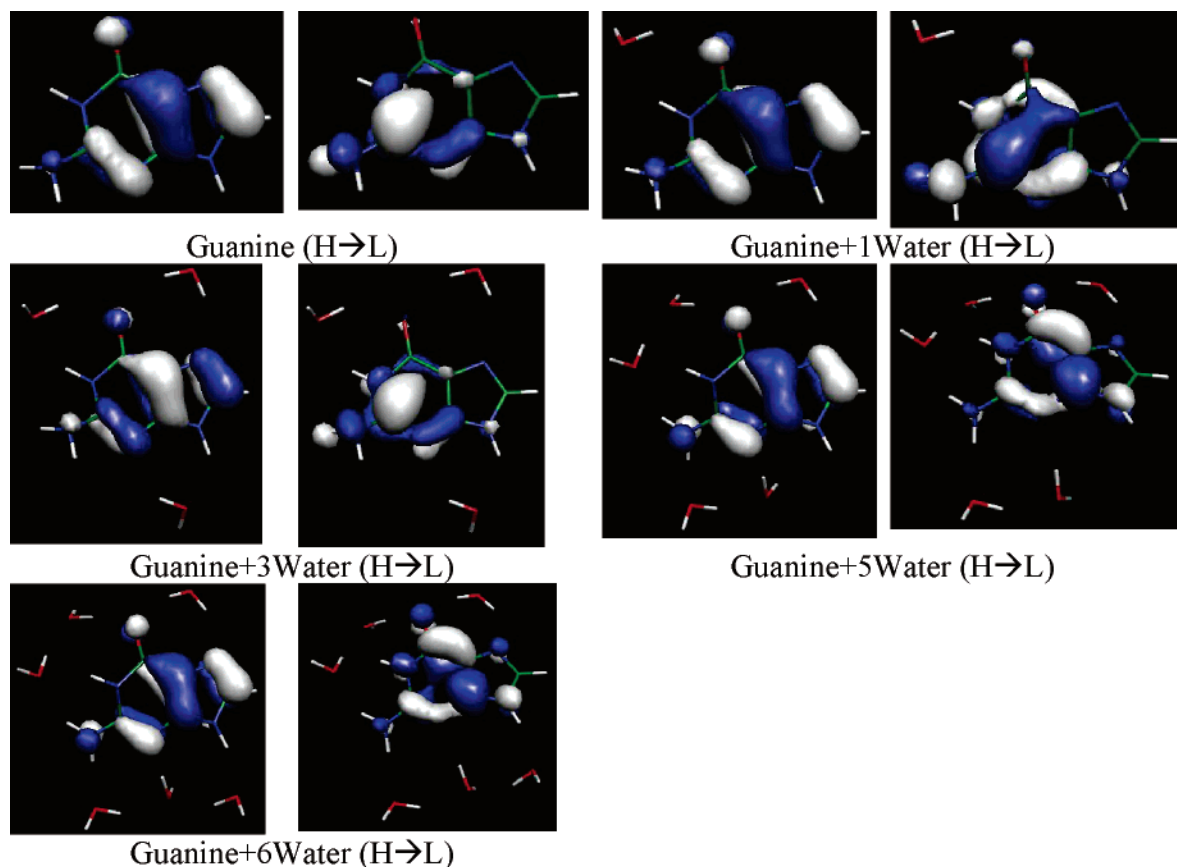
$\pi\pi*$ Excited-State Geometry of Guanine

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Figure 6. HOMO and LUMO orbitals of the guanine and different hydrated forms of guanine corresponding to the excited-state geometries.

hexahydrated complex. Further, all but W1 and W3 water molecules are located in the plane of the guanine. Similar to the pentahydrated complex, the W1 and W3 water molecules of the hexahydrated complex are slightly out-of-the-plane and are located in the same site relative to the guanine plane. The water hydrogens which are not involved in hydrogen bonding are also out-of-the-plane with respect to the guanine plane. The comparison of hydrogen-bond distances between the penta- and the hexahydrated guanine in the ground state suggests that the hydrogen-bond lengths corresponding to the interaction of water molecules with guanine sites are generally decreased in going from the penta- to hexahydrated guanine (Figures 4 and 5). In other words, the hydration structure is more stabilized by the addition of a water molecule to the pentahydrated guanine. The electronic excitation to the lowest singlet $\pi\pi*$ excited state is dominated by the H $\rightarrow$ L configuration. The excited-state geometry of the guanine in the hexahydrated complex is nonplanar except for the amino group, which is planar (Figure 5B). The computed data shown in Table 1 suggest that the geometrical distortion of the guanine in the hexahydrated form is similar to that in the pentahydrated form, discussed earlier. The change in the strength of different hydrogen bonds in going from the ground state to the excited state of the hexahydrated guanine is similar to that of the pentahydrated guanine, except for the intermolecular interaction between the W3 and W5 water molecules. It should be mentioned that in the pentahydrated guanine, the interaction between the W3 and W5 water molecules is increased in the excited state, but it is decreased for the hexahydrated guanine. The interaction between the W3 and W6 water molecules is also decreased in the excited state as compared to that in the ground state (Figure 5B).

3.1.6. Guanine + 7 Water Molecules. The geometry of the hydrated structure of the guanine with seven water molecules,

where the seventh water molecule was placed between the W1 and W2 water molecules of the hexahydrated guanine complex, was also optimized in the ground state. It was found that the addition of another water molecule to the hexahydrated guanine distorts the hydrogen-bonding network by forcing other neighboring water molecules away from the guanine plane. Therefore, it appears that the first solvation shell of guanine can accommodate six water molecules. The Cartesian coordinates of the optimized geometries of guanine and hydrated complexes in the ground and excited states are given in the form of Supporting Information.

3.2. Excited-State Electronic Configuration and Explanation of Nonplanarity. The electronic excitation of the guanine and different hydrated guanine to the lowest singlet $\pi\pi*$ excited state is mainly dominated by the H $\rightarrow$ L configuration. The nature of the HOMO and the LUMO for the guanine and hydrated guanine complexes corresponding to the respective optimized excited-state geometries is shown in Figure 6. It is evident that the nature of the HOMO is similar for both the isolated and hydrated guanine and corresponds to the π-type orbital. The LUMO, which is a $\pi*$-type, is localized mainly on the six-membered ring. It should be noted that the orbital contamination from the water molecule is not found for hydrated guanine complexes. In the hydration of the excited state, whose energy approaches the excitation energy of the solvents, one expects a rather large overlap between the virtual orbitals involved in the excitation process. Then one may expect a delocalization of the solute and solvent orbitals which would lead to the violation of simple ideas which regard the solvent molecule as separate entities. The examination of LUMOs for the isolated and hydrated guanine reveals that guanine, mono-, and trihydrated complexes have similar features which are different from those of the LUMOs of the penta- and hexahy-

TABLE 2: Some Stretching Vibrational Frequencies (cm^{-1}) of Guanine and Hydrated Guanine Complexes in the Ground and the Lowest Singlet $\pi\pi^*$ Excited State Obtained at the HF/6-311G(d,p) and CIS/6-311G(d,p) Levels, Respectively[a]

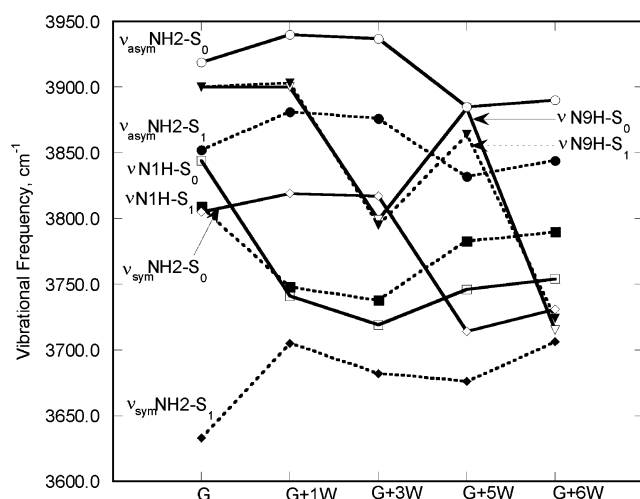| modes	G S$_0$	G S$_1$	G + 1W S$_0$	G + 1W S$_1$	G + 3W S$_0$	G + 3W S$_1$	G + 5W S$_0$	G + 5W S$_1$	G + 6W S$_0$	G + 6W S$_1$
νN1H	3844	3809	3741	3748	3719	3738	3746	3783	3754	3790
νN9H	3900	3900	3900	3903	3799	3795	3884	3864	3715	3724
ν_{asym}NH2	3919	3852	3940	3881	3937	3876	3885	3832	3890	3844
ν_{sym}NH2	3805	3633	3819	3705	3817	3682	3714	3676	3731	3706

[a] Uscaled values.

Figure 7. Variation of different stretching vibrational modes (unscaled values) of the guanine in the isolated and hydrated forms in the ground and lowest singlet $\pi\pi^*$ excited state.

drated complexes. The LUMOs for the penta- and hexahydrated guanine complexes exhibit again similar features (Figure 6). In the guanine, mono-, and trihydrated complexes, the π^*-orbital is mainly localized toward the N1C2N3 fragment; in the penta- and hexahydrated complexes, it is localized toward the C6C5C4 fragment of guanine. The difference in the localization of the LUMO for penta- and hexahydrated guanine as compared to those of the other complexes appears responsible for the distinct type of the structural deformation of guanine in the excited state, as discussed earlier (Table 1).

3.3. Vibrational Frequencies. Computed vibrational frequencies (unscaled) corresponding to the stretching vibrational modes of the N9H (νN9H), N1H (νN1H), symmetric NH2 (ν_{sym}NH2), and asymmetric NH2 (ν_{asym}NH2) vibrations in the ground and lowest singlet $\pi\pi^*$ excited state of the guanine and different hydrated guanine complexes are presented in Table 2. The variations of vibrational frequencies with the hydration of guanine are shown in Figure 7. It is evident from this figure that the νN9H vibrational frequency of the guanine, mono-, and pentahydrated guanine are similar, while a substantial red-shift is revealed in the case of the tri- and hexahydrated complexes of guanine in the ground state. The predicted red-shift is more pronounced for the hexahydration than the trihydration. It should be noted that a water molecule is hydrogen-bonded with the N9H site in the case of tri- and hexahydrated guanine. Therefore, the predicted red-shift in vibrational frequency is in agreement with the experimental fact that the stretching frequency of the NH vibration is red-shifted in the hydrogen-bonding environment.[18] In the lowest singlet $\pi\pi^*$ excited state, a significant shift in the νN9H vibrational frequency in comparison to the corresponding ground-state value is not revealed for the guanine and hydrated guanine. The similarity between the ground- and

excited-state vibrational frequencies of the N9H vibration is related to the excited-state geometry of the five-membered ring of the guanine in the isolated and hydrated forms which was revealed to be planar.

The stretching vibrational frequency corresponding to the N1H vibration of the guanine in the ground state shows significant red-shift upon hydration. The maximum red-shift is revealed for the trihydrated complex. The larger red-shift of the νN1H vibration in the trihydrated complex as compared to the monohydrated complex is in accordance with the change of the hydrogen-bond length associated with the N1H site (Figures 2 and 3). It should be noted that this bond length is decreased from 2.048 to 2.000 Å in going from the mono- to trihydration. In other words, the strength of the hydrogen bond is increased in the trihydrated complex of the guanine. Although the corresponding hydrogen-bond length for the penta- and hexahydrated complex is similar to that in the trihydrated form and smaller than that in the monohydrated form, the νN1H vibrational frequency corresponding to the penta- and hexahydrated complex is slightly blue-shifted compared to the mono- and trihydrated forms. These results could be related to the fact that the corresponding bonded water molecule (W1 in the case of the mono- and trihydrated complexes and W4 in the penta- and hexahydrated complexes) acts only as a single hydrogen-bond acceptor in the mono- and trihydrated complexes, while it acts as a double hydrogen-bond acceptor, being bonded with both the N1H and amino group hydrogen sites, in the penta- and hexahydrated complexes. In the excited state, the νN1H frequency of the isolated guanine is red-shifted, and the predicted red-shift is related to the nonplanarity of the molecule in the excited state. Further, the νN1H frequency of the hydrated guanine in the excited state is slightly blue-shifted compared to the corresponding value in the ground state. The value of the blue shift is found to increase with the number of water molecules involved in the hydration. Data shown in Figures 2−5 suggest that the hydrogen-bond length associated with the N1H site is increased in going from the ground state to the excited state of different complexes. In other words, the strength of the hydrogen bond is weaker in the excited state, and therefore blue-shift is revealed in the excited state.

The ν_{asym}NH2 vibrational frequency of the isolated, mono-, and trihydrated guanine is found to have almost similar value while a slight red-shift is revealed in the penta- and hexahydrated guanine in the ground state. In the excited state, the ν_{asym}NH2 vibrational frequency of the guanine and different hydrated guanine is red-shifted compared to the ground-state frequencies. A similar situation was revealed for the ν_{sym}NH2 vibration of the guanine and hydrated guanine in the ground and excited states. However, the ν_{sym}NH2 vibration shows significant red-shift for the isolated guanine in the excited state. The predicted red-shift in the symmetric and asymmetric NH2-vibrational frequencies of the guanine in the isolated and hydrated complexes in the excited state is related to two factors: (i) hydration-induced amino group planarity, and (ii) the structural nonplanarity of the molecule in the excited state. Further, the predicted red-shift in the ν_{asym}NH2 and ν_{sym}NH2 vibration of penta- and hexahydrated guanine as compared to that in the isolated and mono- and trihydrated guanine is in agreement with the fact that in the penta- and hexahydrated form, the amino group is hydrogen-bonded with water molecules.

4. Conclusions

The present comprehensive investigation of hydration of guanine with 1−7 water molecules in the ground and the lowest

ππ* Excited-State Geometry of Guanine

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singlet ππ* excited state led to important conclusions. It is found that six water molecules are needed to accommodate the first solvation shell of the guanine. The excited-state geometry of guanine in the excited state was found to be nonplanar, irrespective of the number of water molecules used in the hydration. However, the structural deformation of the guanine in the excited state was different in the penta- and hexahydrated complexes as compared to that in the isolated and mono- and trihydrated complexes. The changes in the vibrational frequencies corresponding to the stretching vibrations of different hydrogen-bond-donating groups of guanine under hydration in the ground and excited states were generally found to be coherent with the change in the hydrogen-bond length with the increase in the number of water molecules in hydration and in going from the ground state to the excited state.

Supporting Information Available: Tables showing the Cartesian coordinates of guanine and the different hydrated guanine complexes in the ground state and the lowest singlet ππ* excited state. This material is available free of charge via the Internet at http://pubs.acs.org.

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