Supporting Information

Sugar Radical Formation by a Proton Coupled Hole Transfer in 2'-Deoxyguanosine Radical Cation (2'-dG$^{\bullet+}$): A Theoretical Treatment

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Complete List of Supporting Information

Video clips showing the proton transfer reaction from $C_{5'}$ to N_7 of guanine in the presence of water molecules (PT.avi) and rotational and stretching transition states (TS1.avi and TS2.avi) are provided. These can be played using windows media player. These clips were generated from an optimization of the structure after the transition state. This is not a molecular dynamics calculation. All steps are essentially downhill energetically. During optimization, the proton completely transfers from $C_{5'}$ to N_7 of guanine and the each step of the proton transfer during geometry optimization was saved as a jpeg image using JMOL program. Of the many optimization steps we chose 130 jpeg images (slides) to show the stepwise proton transfer in the form of a movie.

Scheme 1- Formation of neutral $C_{5'}^{\bullet}$ sugar radical ($C_{5'}^{\bullet}$ through proton coupled electron transfer (PCET) mechanism in 2'-deoxyguanosine radical cation (dG$^{\bullet+}$). The proton transfers from $C_{5'}$ to N_7 of guanine through waters results in electron transfer from $C_{5'}$ to guanine yielding the product, (dG($^{\bullet}C_{5'}$, N_7-H^+) + 7 H_2O).

Figure S1- B3LYP/6-31G* calculated potential energy surface (PES) of proton transfer from $C_{5'}$ to N_7 of guanine in dG$^{\bullet+}$ + 7 H_2O. The zero point energy corrected ΔE^a at 0 K and $C_{5'}$-H bond distances are given in kcal/mol and angstroms (Å), respectively. For atom numbering, see scheme 1.

Figure S2- B3LYP/6-31G* calculated spin density distribution during proton transfer from $C_{5'}$ to N_7 site of guanine in dG$^{\bullet+}$ + 7 H_2O. The stretching of $C_{5'}$-H bond from its equilibrium bond length (1.099) to 1.23 Å transfers hole from guanine to $C_{5'}$ site or transfers electron from $C_{5'}$ site to guanine.

Figure S3- B3LYP/6-31G* Optimized structure of one electron oxidized 2'-Deoxyguanosine radical cation (dG$^{\bullet+}$) in the presence of seven water molecules.

Figure S4- B3LYP/6-31G* optimized transition state (TS) structure of proton (H^+) transfer from $C_{5'}$ to water. The presence of a negative frequency -432 cm^{-1} ensures the occurrence of the TS.

Figure S5- B3LYP/6-31G* optimized structure of $dG^{\bullet+}$ + 7 H_2O at $C_{5'}$-H bond distance corresponding to 1.35 Å. During optimization the $C_{5'}$-H bond was constrained at 1.35 Å. The pink circle shows the position of the proton.

Figure S6- B3LYP/6-31G* optimized structure of $dG^{\bullet+}$ + 7 H_2O at $C_{5'}$-H bond distance corresponding to 1.5 Å. During optimization the $C_{5'}$-H bond was constrained at 1.5 Å. The pink circle shows the formation of hydronium ion (H_3O^+).

Figure S7- B3LYP/6-31G* optimized structure of $dG^{\bullet+}$ + 7 H_2O at $C_{5'}$-H bond distance corresponding to 1.7 Å. During optimization the $C_{5'}$-H bond was constrained at 1.7 Å. The pink circle shows the formation of the hydronium ion (H_3O^+) stabilized by three water molecules.

Figure S8- B3LYP/6-31G* optimized structure of N_7 protonated dG(H^+) + 7 H_2O. The proton completely transfers from $C_{5'}$ to N_7 of guanine shown by pink circle.

Figure S9- BHandHLYP/6-31G*//B3LYP/6-31G* calculated spin density distribution during proton transfer from $C_{5'}$ to N_7 site of guanine in $dG^{\bullet+}$ + 7 H_2O. The stretching of $C_{5'}$-H bond from its equilibrium bond length (1.099) to 1.23 Å subsequently transfers hole from guanine to $C_{5'}$ site or transfers electron from $C_{5'}$ site to guanine.

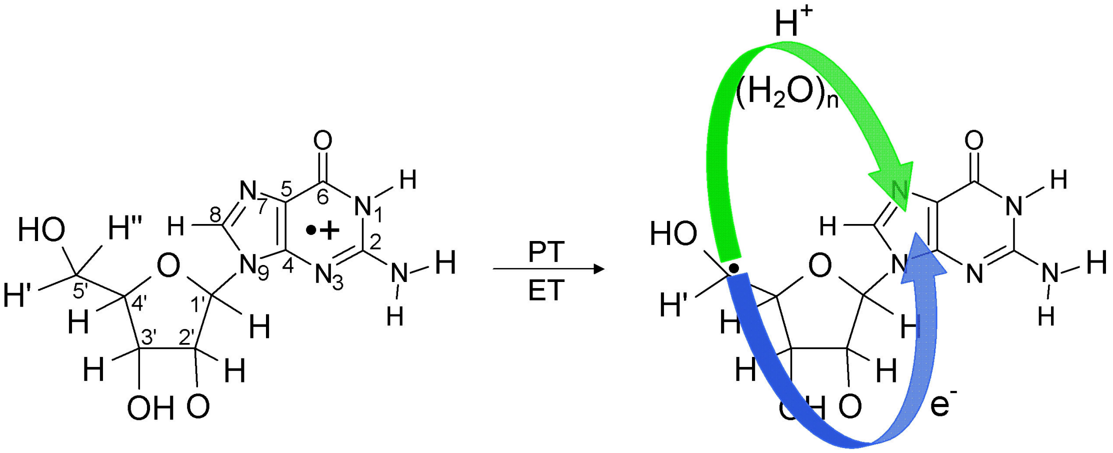
Figure S10- The B3LYP/6-31G* calculated vibrational frequency (cm^{-1}) of $dG^{\bullet+}$ + 7 H_2O complex.

Figure S11- The B3LYP/6-31G* calculated vibrational frequency (cm^{-1}) of TS of deptotonation of $C_{5'}$ site occurs at $C_{5'}$-H distance of 1.229 Å, see Figure S4.

Figure S12- The B3LYP/6-31G* calculated vibrational frequency (cm^{-1}) of deptotonation of $C_{5'}$ site occurs at $C_{5'}$-H distance of 1.35 Å, see Figure S5.

Figure S13- The B3LYP/6-31G* calculated vibrational frequency (cm^{-1}) of dG($^{\bullet}C_{5'}$, N_7-H^+) + 7 H_2O (product), see Figure S8.

Figure S14- B3LYP/6-31G* calculated spin density distribution at C5'-H bond distance of 4 Å without waters. In the calculation, the surrounding waters were removed from the optimized TS structure and single point B3LYP/6-31G* calculation was done by increasing the C5'-H bond distance at 4 Å. Spin density is localized on the detaching hydrogen atom. The spin contour level is 0.002.



Scheme 1- Formation of neutral $C_{5'}^{\bullet}$ sugar radical ($C_{5'}^{\bullet}$ through proton coupled electron transfer (PCET) mechanism in 2'-deoxyguanosine radical cation ($dG^{\bullet+}$). The proton transfers from $C_{5'}$ to N_7 of guanine through waters results in electron transfer from $C_{5'}$ to guanine yielding the product, ($dG(^{\bullet}C_{5'}, N_7\text{-}H^+) + 7\ H_2O$).

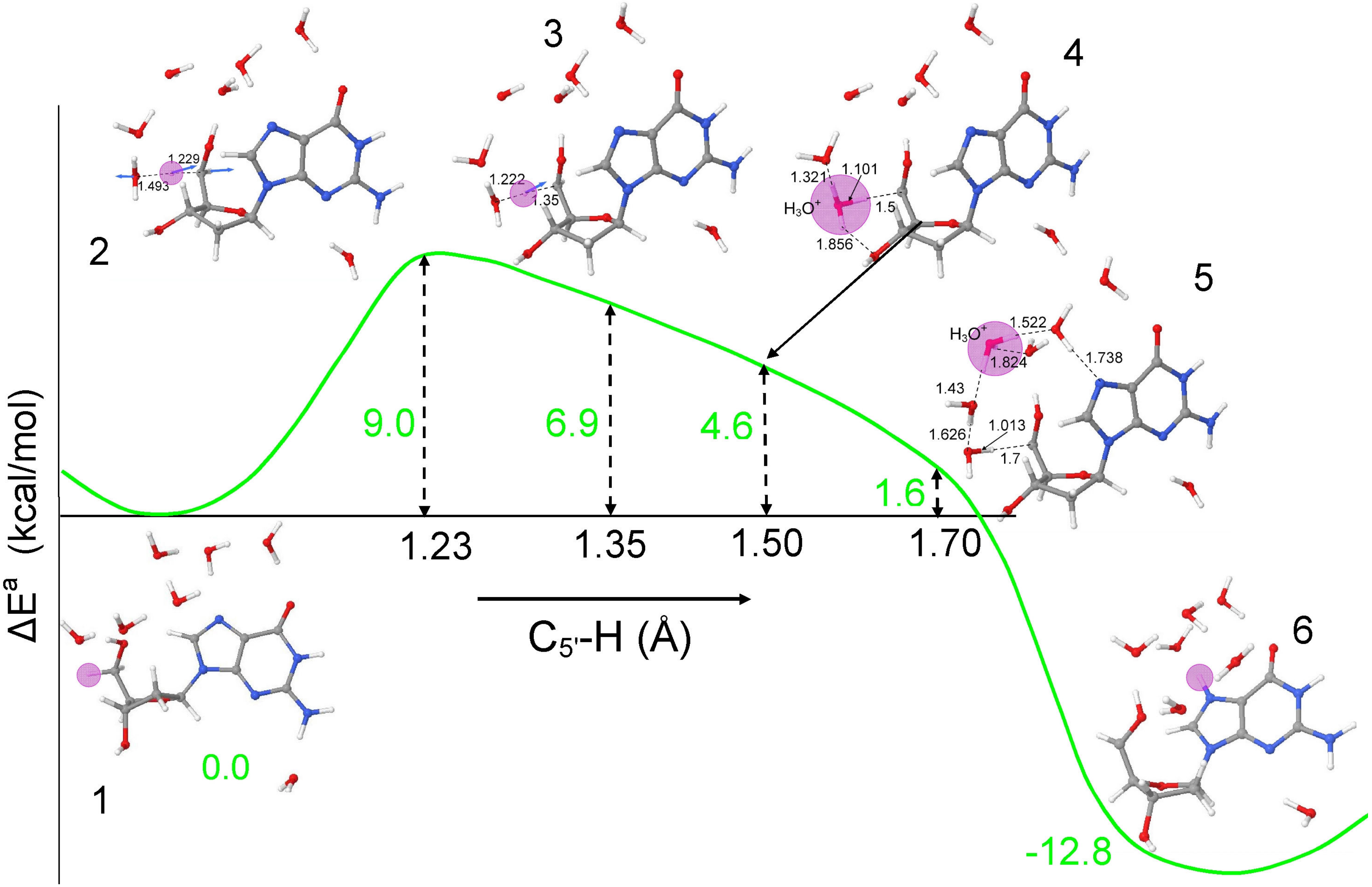


Figure S1- B3LYP/6-31G* calculated potential energy surface (PES) of proton transfer from $C_{5'}$ to N_7 of guanine in $dG^{\bullet+}$ + 7 H_2O. The zero point energy corrected ΔE^a at 0 K and $C_{5'}$-H bond distances are given in kcal/mol and angstroms (Å), respectively. For atom numbering, see scheme 1.

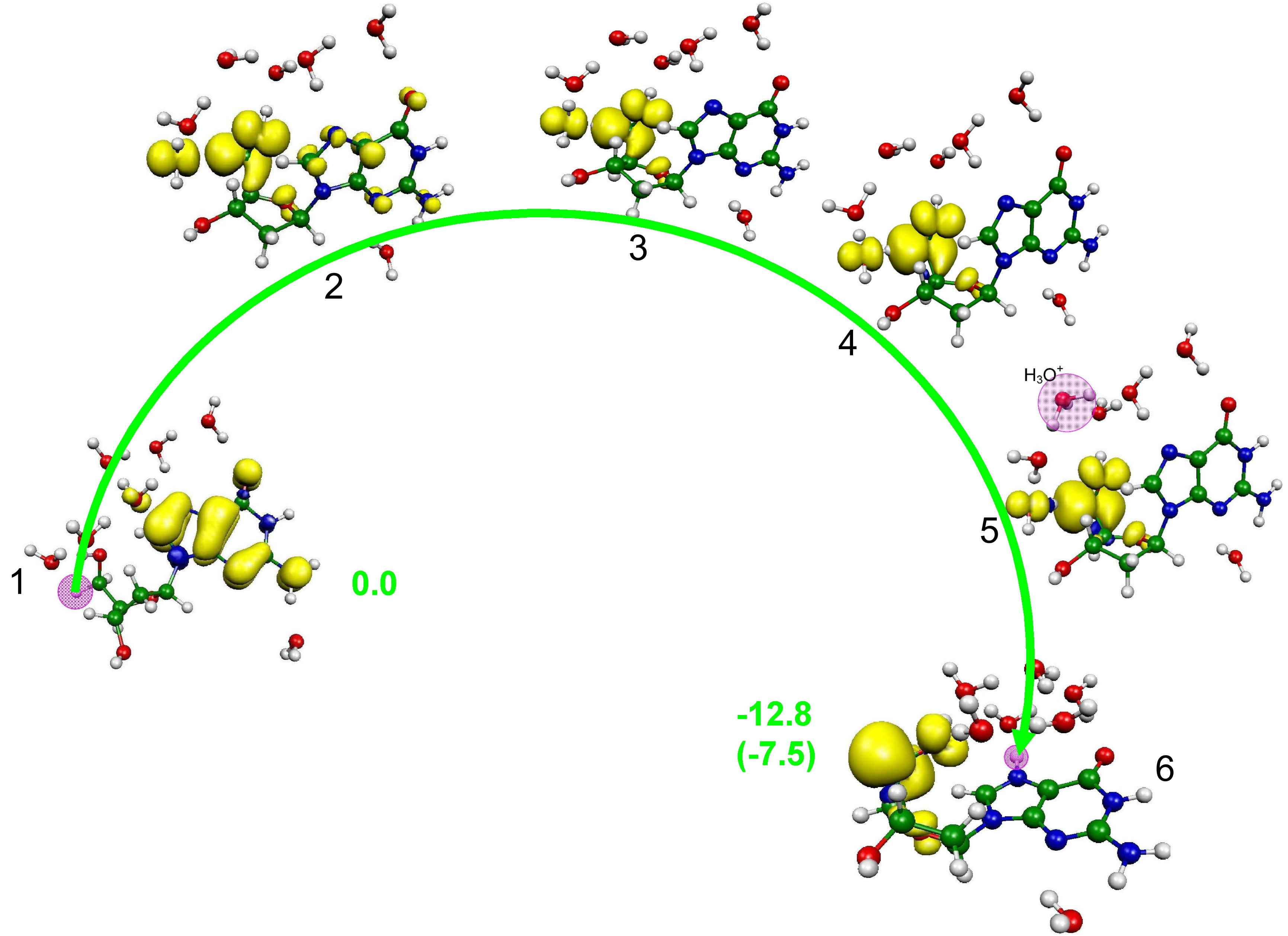


Figure S2- B3LYP/6-31G* calculated spin density distribution during proton transfer from $C_{5'}$ on the deoxyribose group to N_7 site of guanine in $dG^{\bullet+}$ + 7 H_2O. The stretching of the $C_{5'}$-H bond from its equilibrium bond length (1.099) to 1.23 Å results in the transfer of the hole from guanine to $C_{5'}$ site or transfers electron from $C_{5'}$ site to guanine.

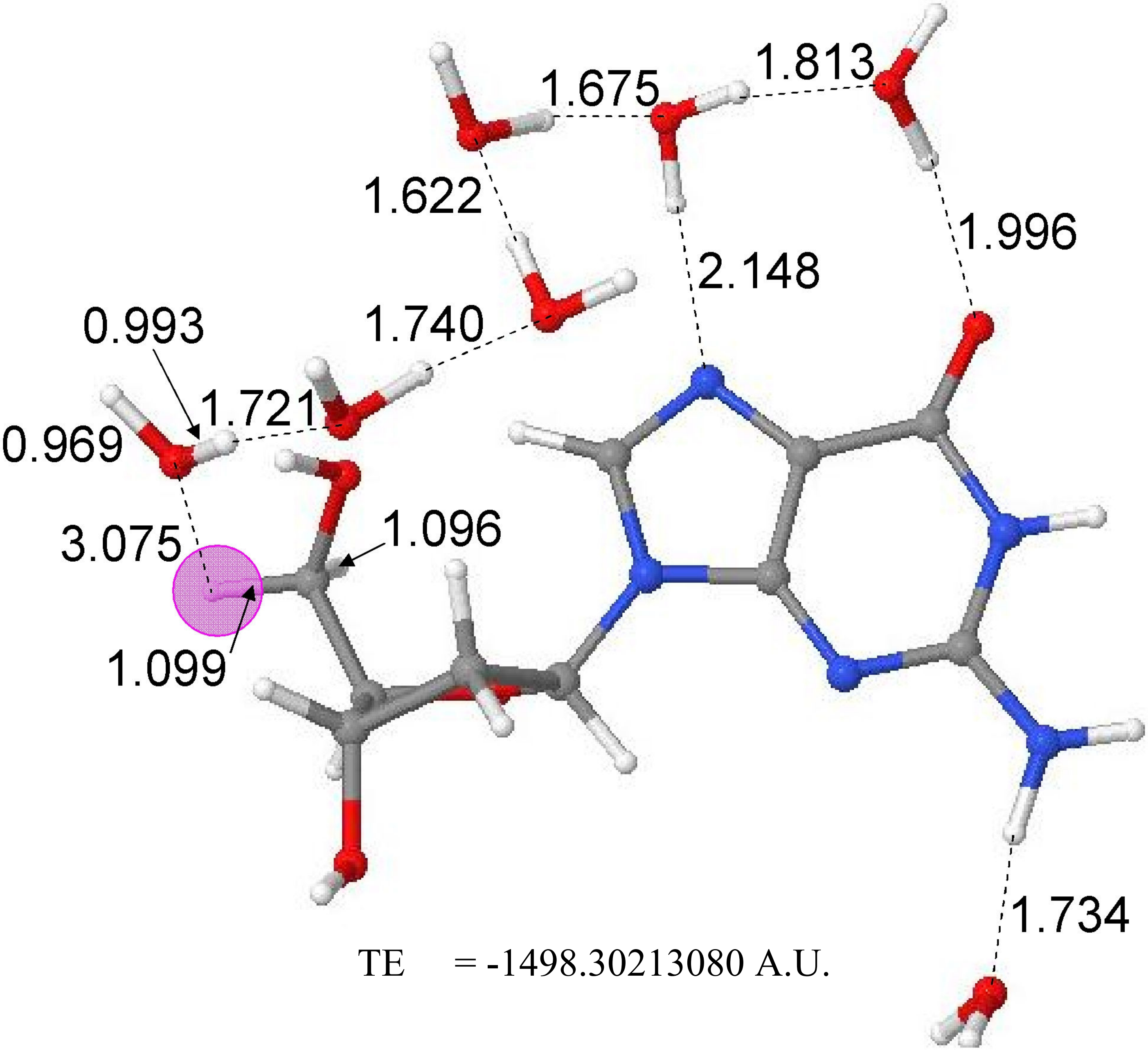


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Figure S3- B3LYP/6-31G* Optimized structure of one electron oxidized 2'-Deoxyguanosine radical cation ($dG^{\bullet+}$) in the presence of seven water molecules.

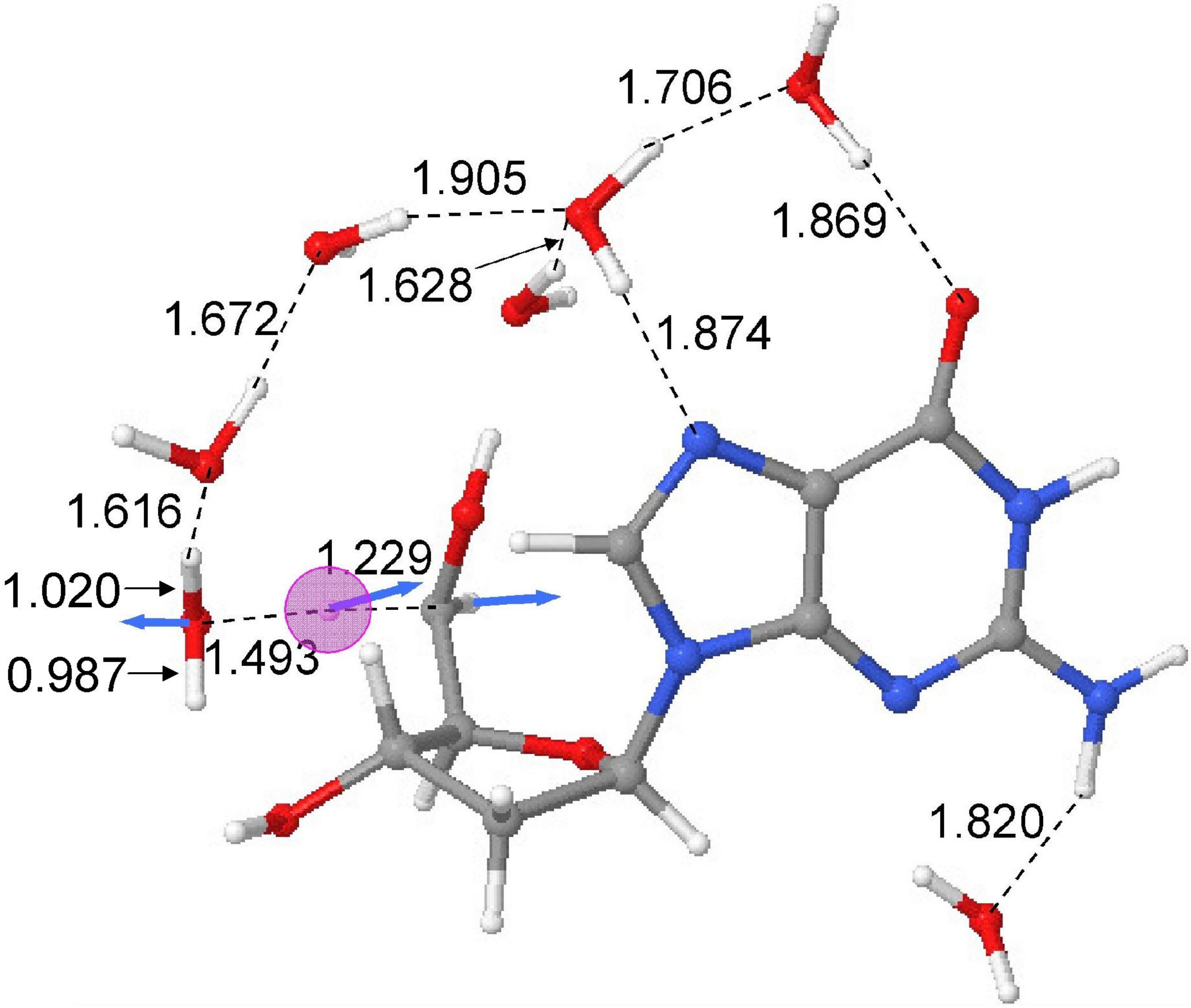

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Figure S4- B3LYP/6-31G* optimized transition state (TS) structure of proton (H^+) transfer from $C_{5'}$ to water. The presence of a negative frequency -432 cm^{-1} ensures the occurrence of the TS.

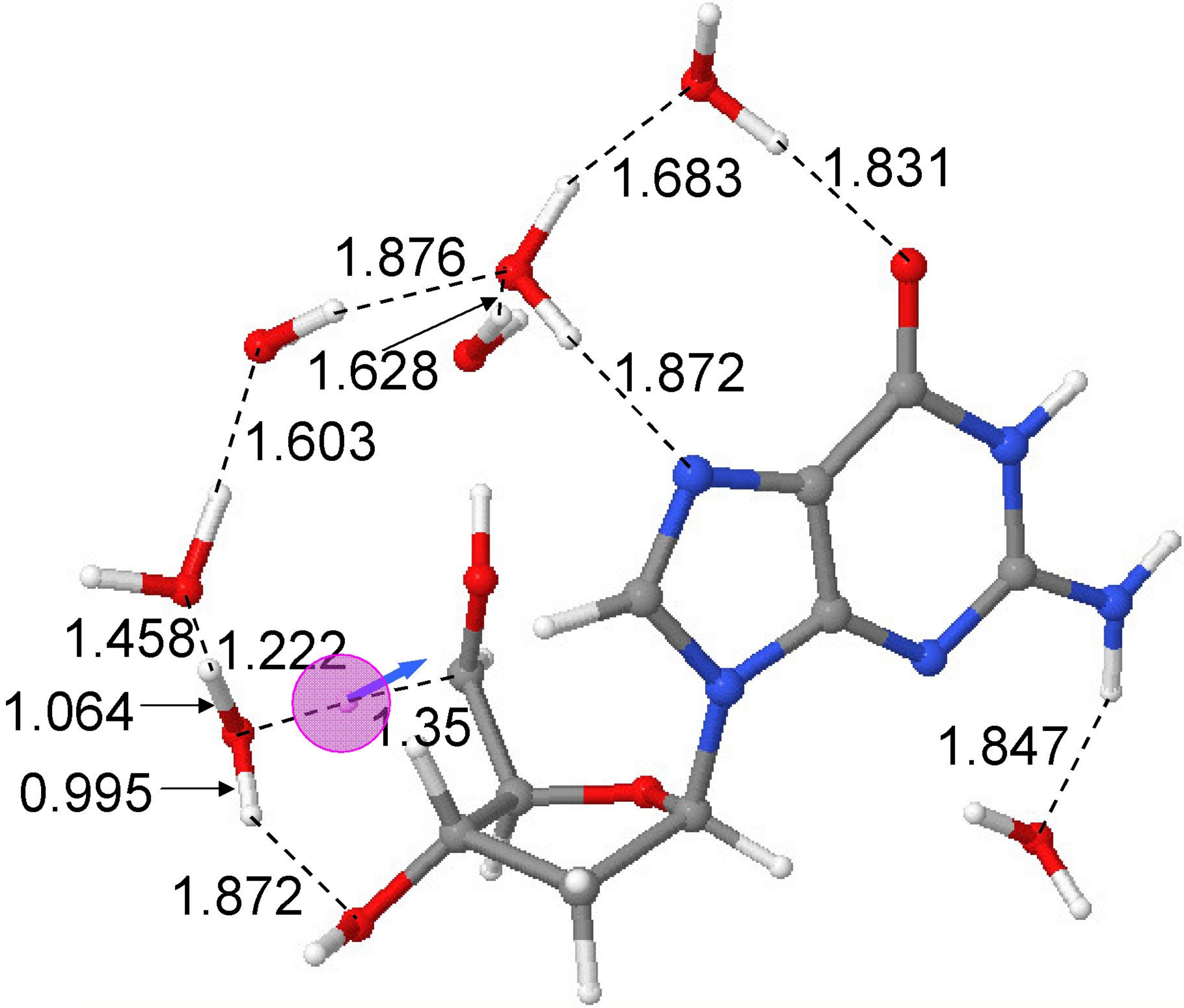

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Figure S5- B3LYP/6-31G* optimized structure of $dG^{\bullet+}$ + 7 H_2O at $C_{5'}$-$H_{5'}$ bond distance corresponding to 1.35 Å. During optimization the $C_{5'}$-$H_{5'}$ bond was constrained at 1.35 Å. The pink circle shows the position of the proton.

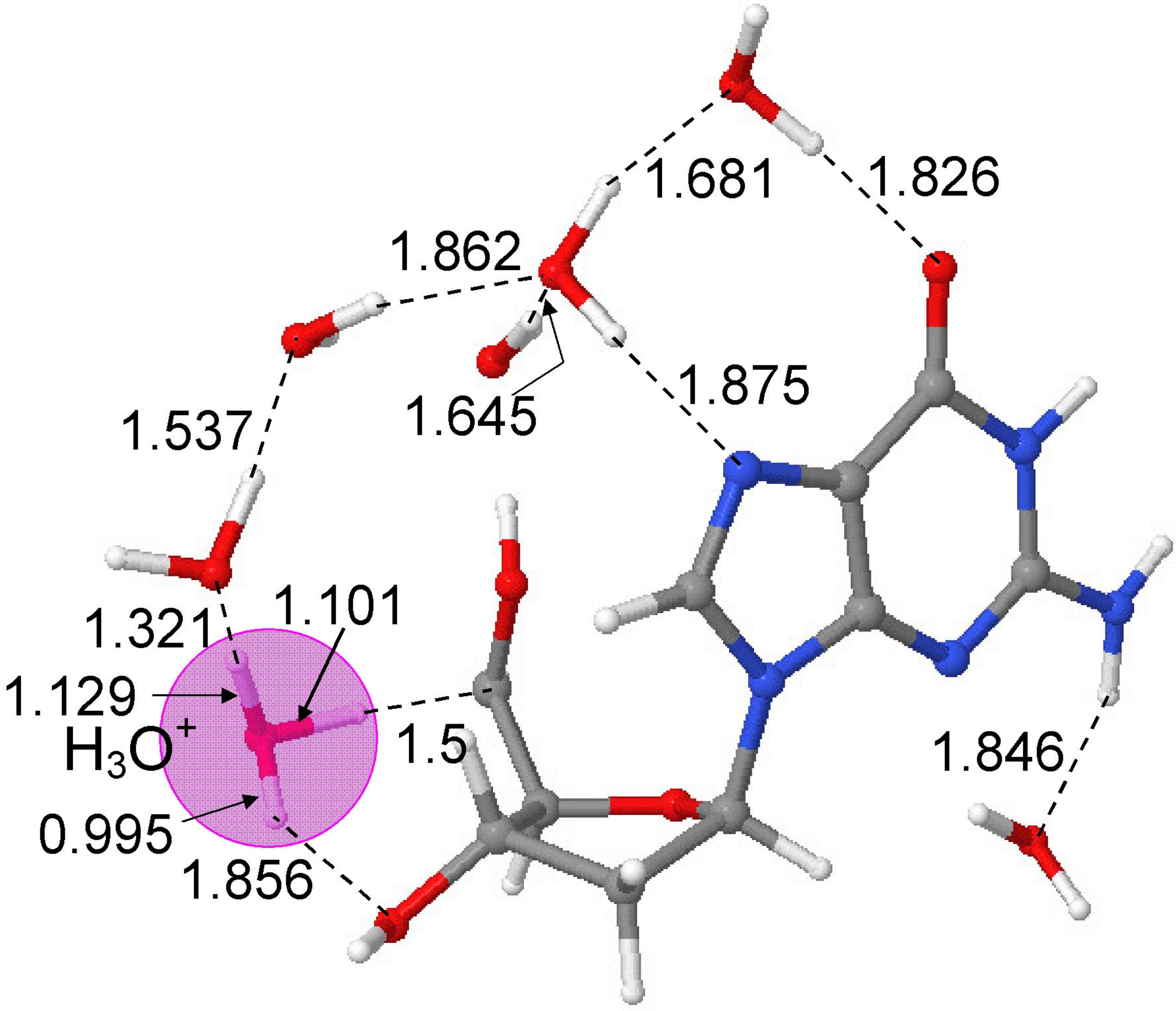

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Figure S6- B3LYP/6-31G* optimized structure of $dG^{\bullet +}$ + 7 H_2O at $C_{5'}$-$H_{5'}$ bond distance corresponding to 1.5 Å. During optimization the $C_{5'}$-$H_{5'}$ bond was constrained at 1.5 Å. The pink circle shows the formation of hydronium ion (H_3O^+).

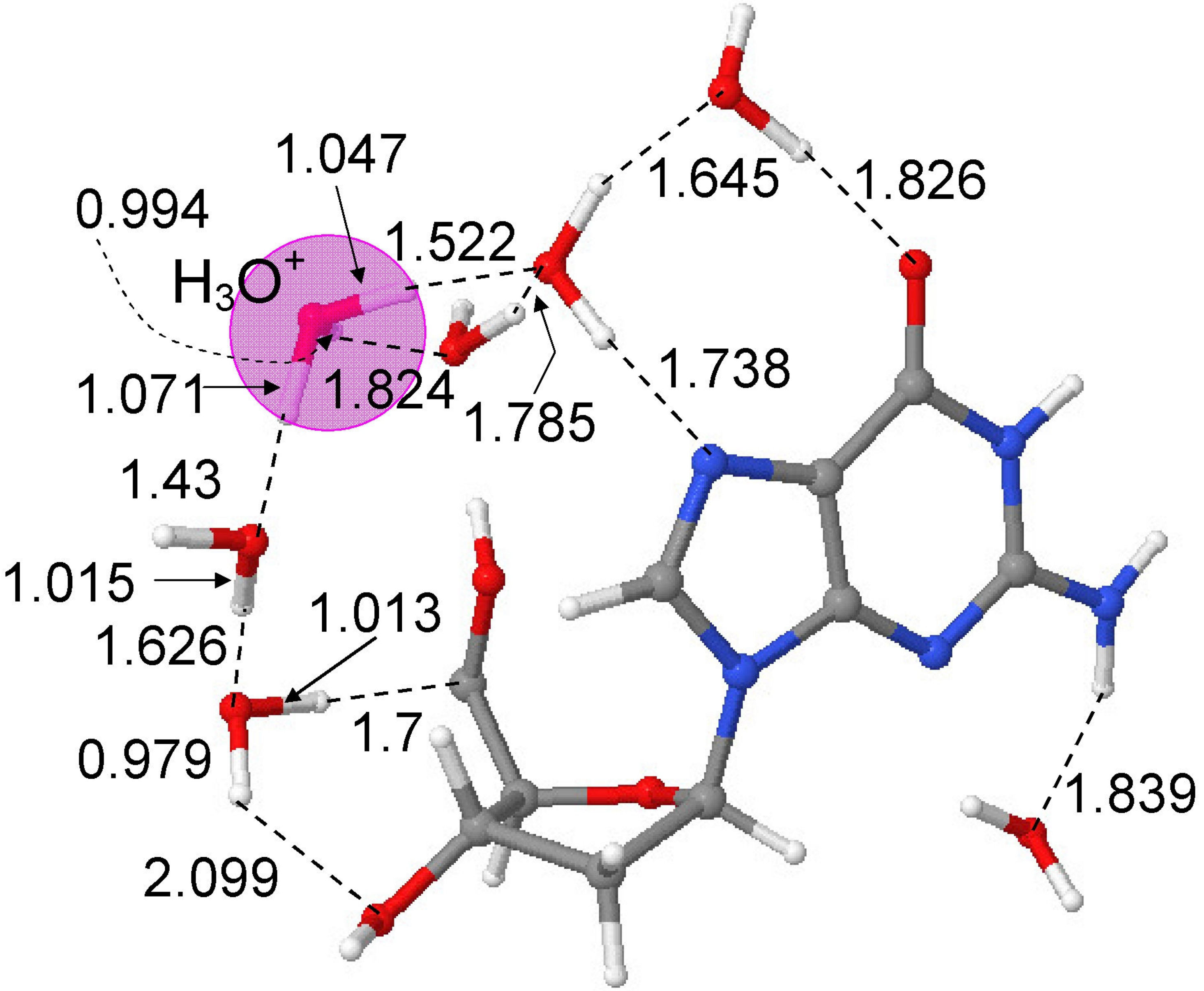

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Figure S7- B3LYP/6-31G* optimized structure of $dG^{\bullet+}$ + 7 H_2O at $C_{5'}$-$H_{5'}$ bond distance corresponding to 1.7 Å. During optimization the $C_{5'}$-$H_{5'}$ bond was constrained at 1.7 Å. The pink circle shows the formation of the hydronium ion (H_3O^+) stabilized by three water molecules.

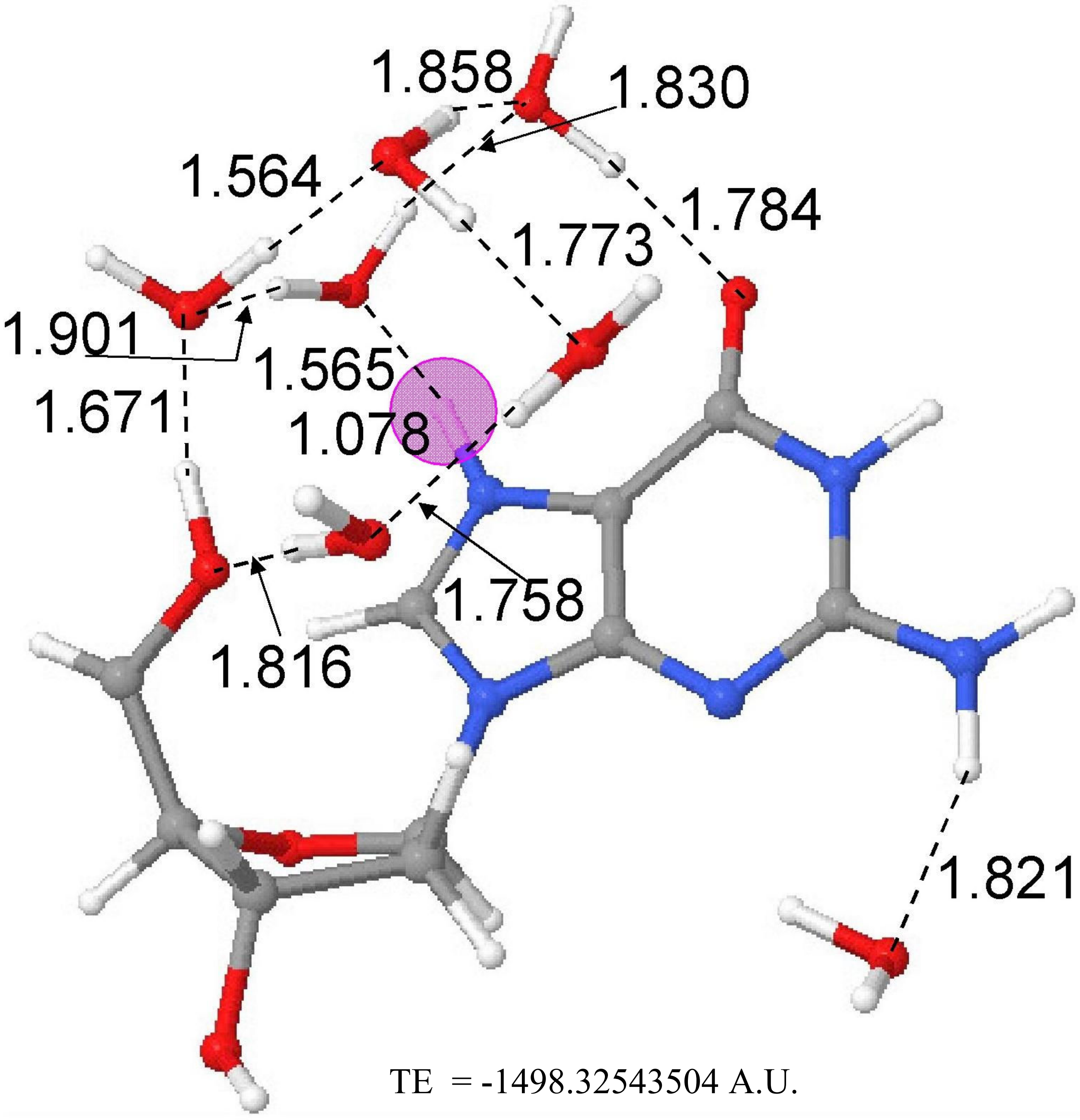

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Figure S8- B3LYP/6-31G* optimized structure of product (dG($^{\bullet}C_{5'}$, N_7-H^+) + 7 H_2O) protonated at N_7. The proton completely transfers from $C_{5'}$ to N_7 of guanine shown by pink circle.

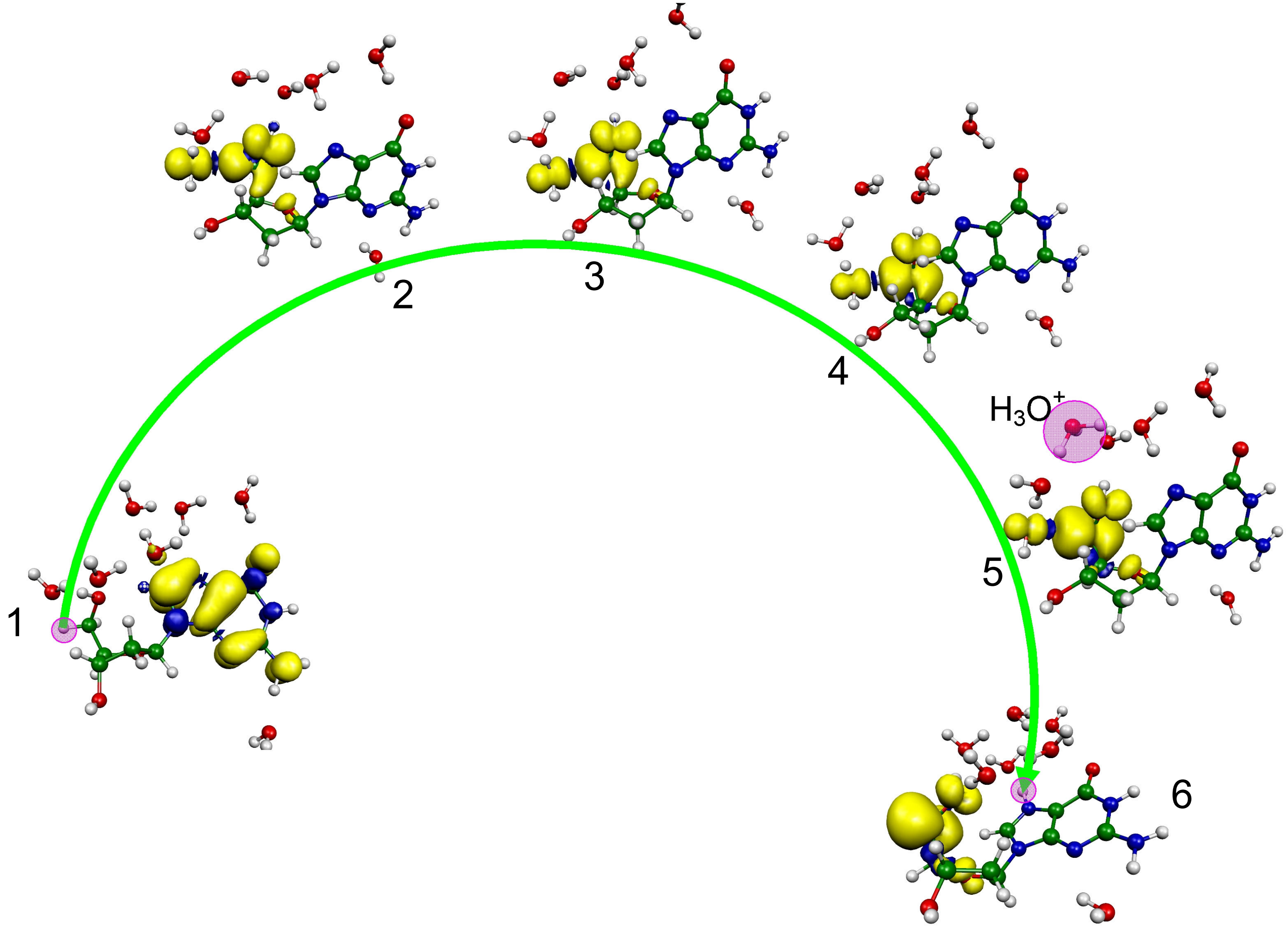


Figure S9- BHandHLYP/6-31G*//B3LYP/6-31G* calculated spin density distribution during proton transfer from $C_{5'}$ on the deoxyribose group to N_7 site of guanine in $dG^{\bullet+}$ + 7 H_2O. The stretching of the $C_{5'}$-H bond from its equilibrium bond length (1.099) to 1.23 Å results in the transfer of the hole from guanine to $C_{5'}$ site or transfers electron from $C_{5'}$ site to guanine.

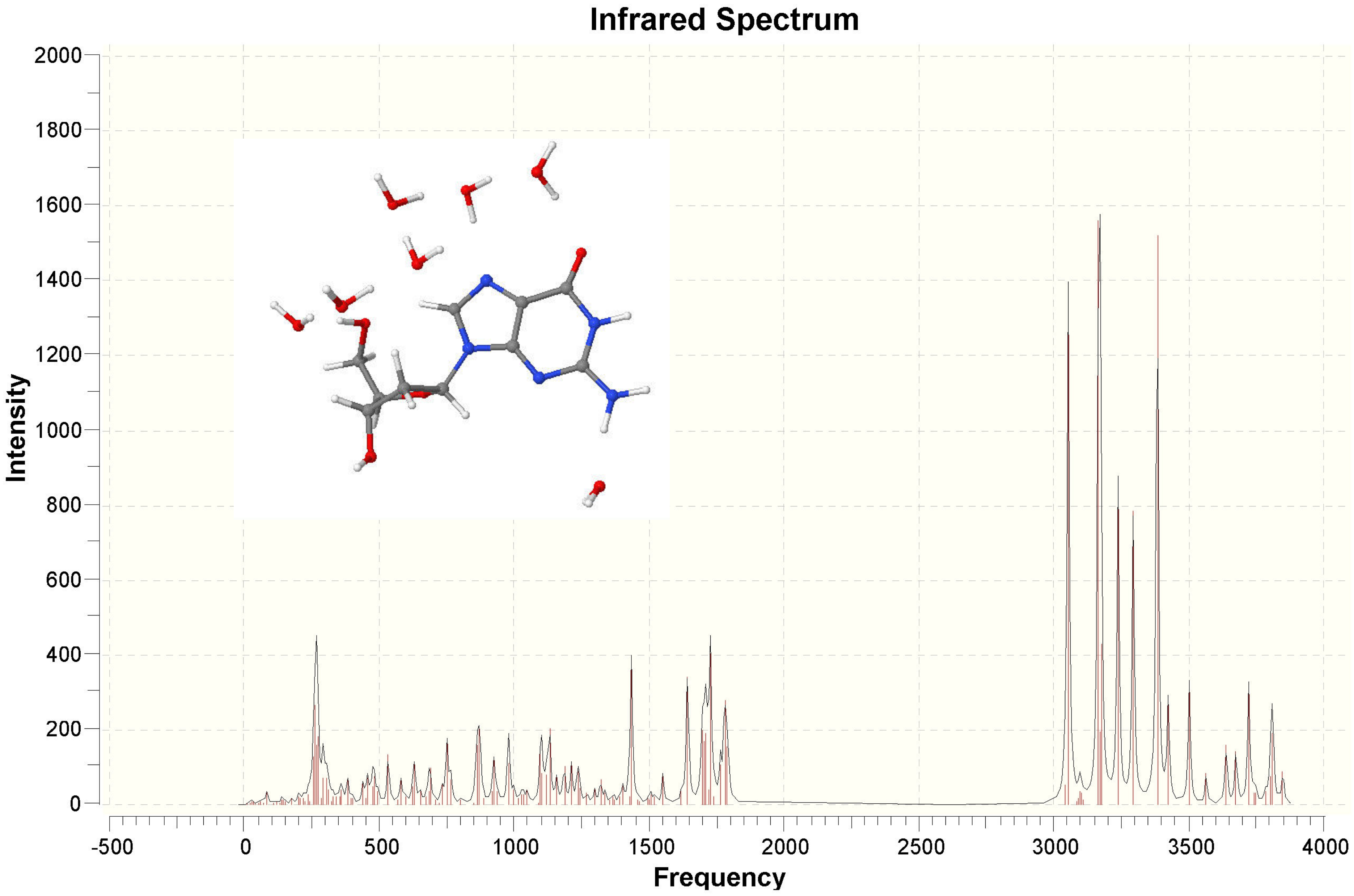
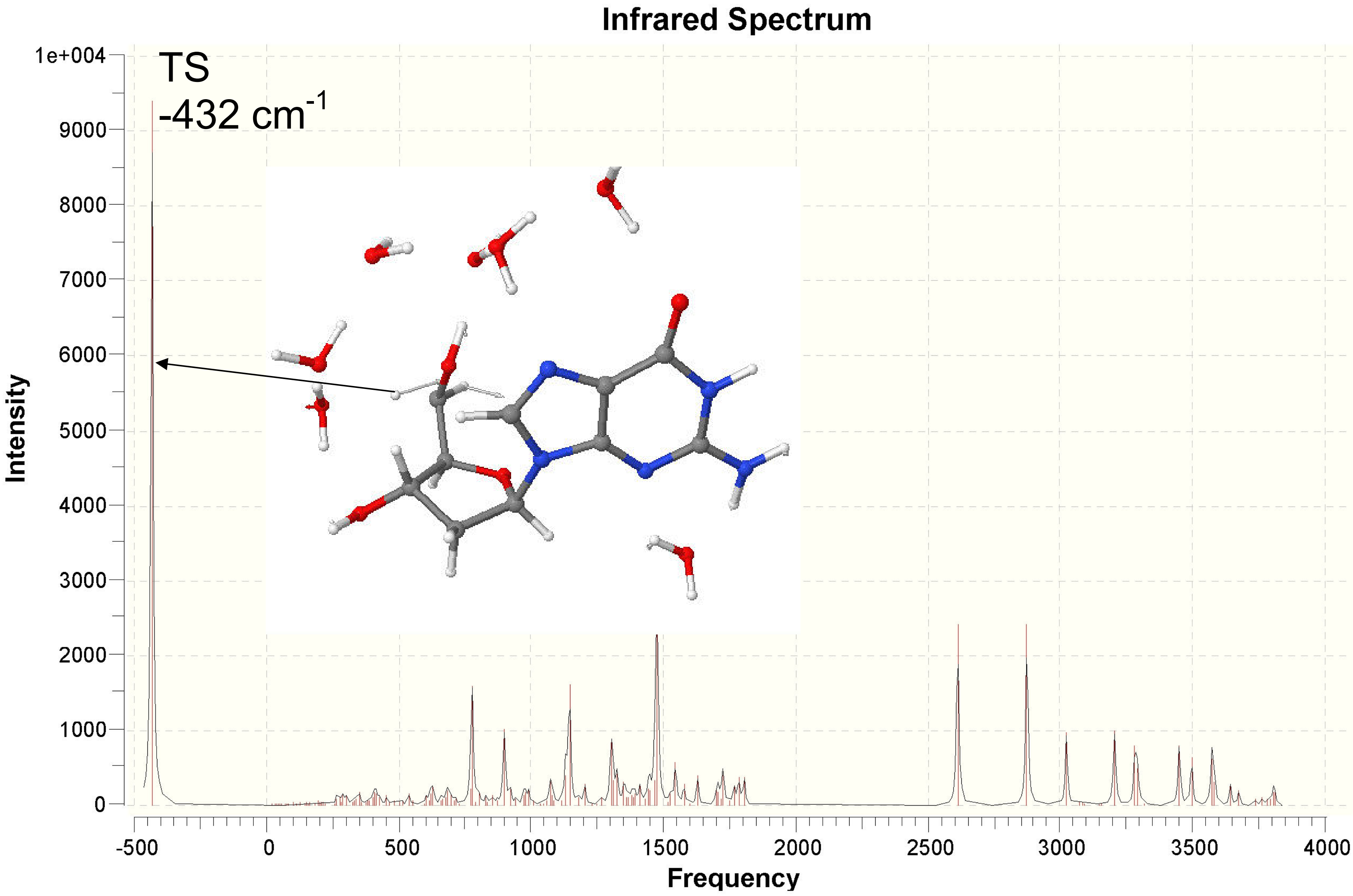


Figure S10- The B3LYP/6-31G* calculated vibrational frequency (cm^{-1}) of dG$^{\bullet+}$ + 7 H_2O complex (reactant).



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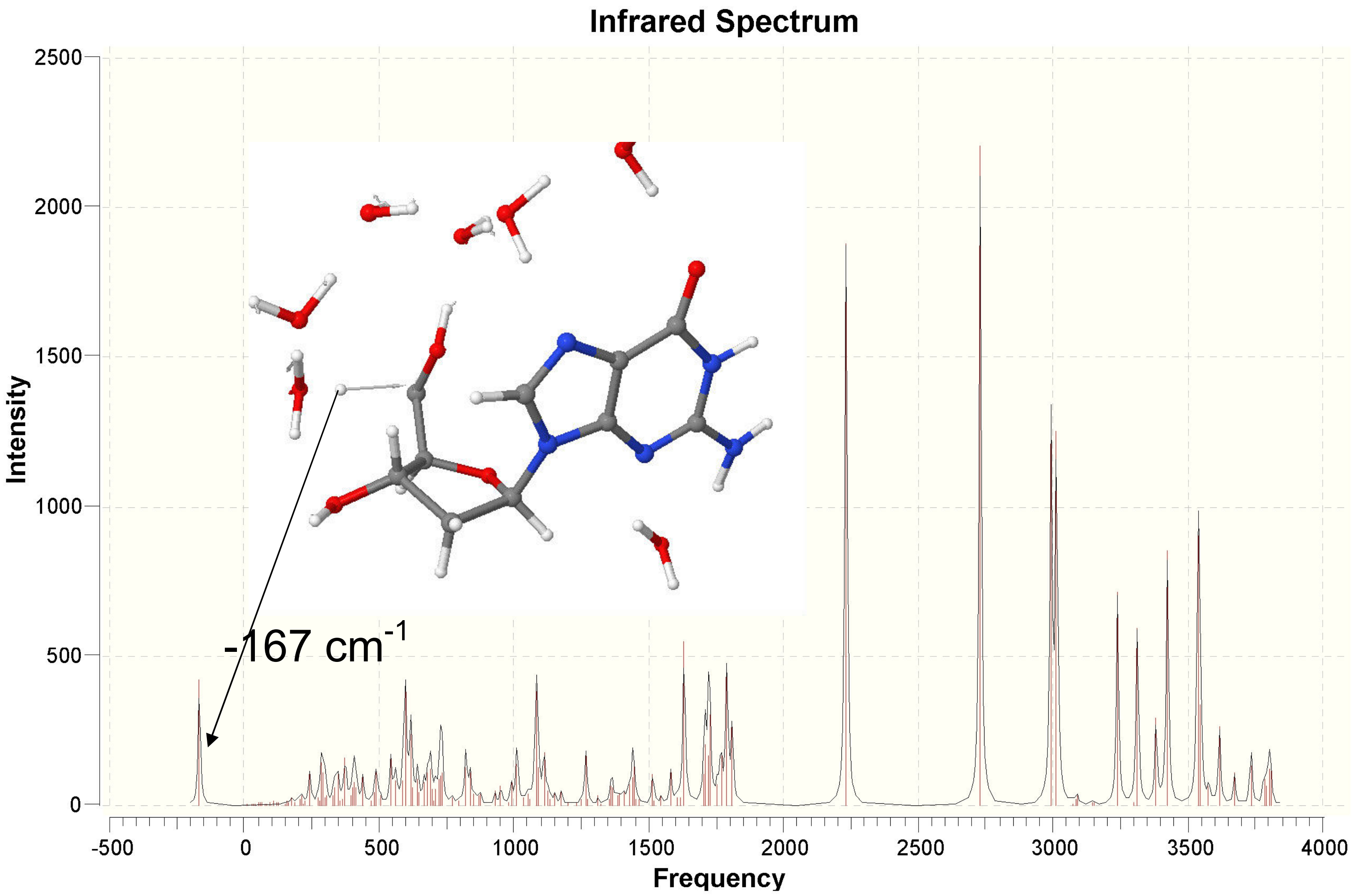
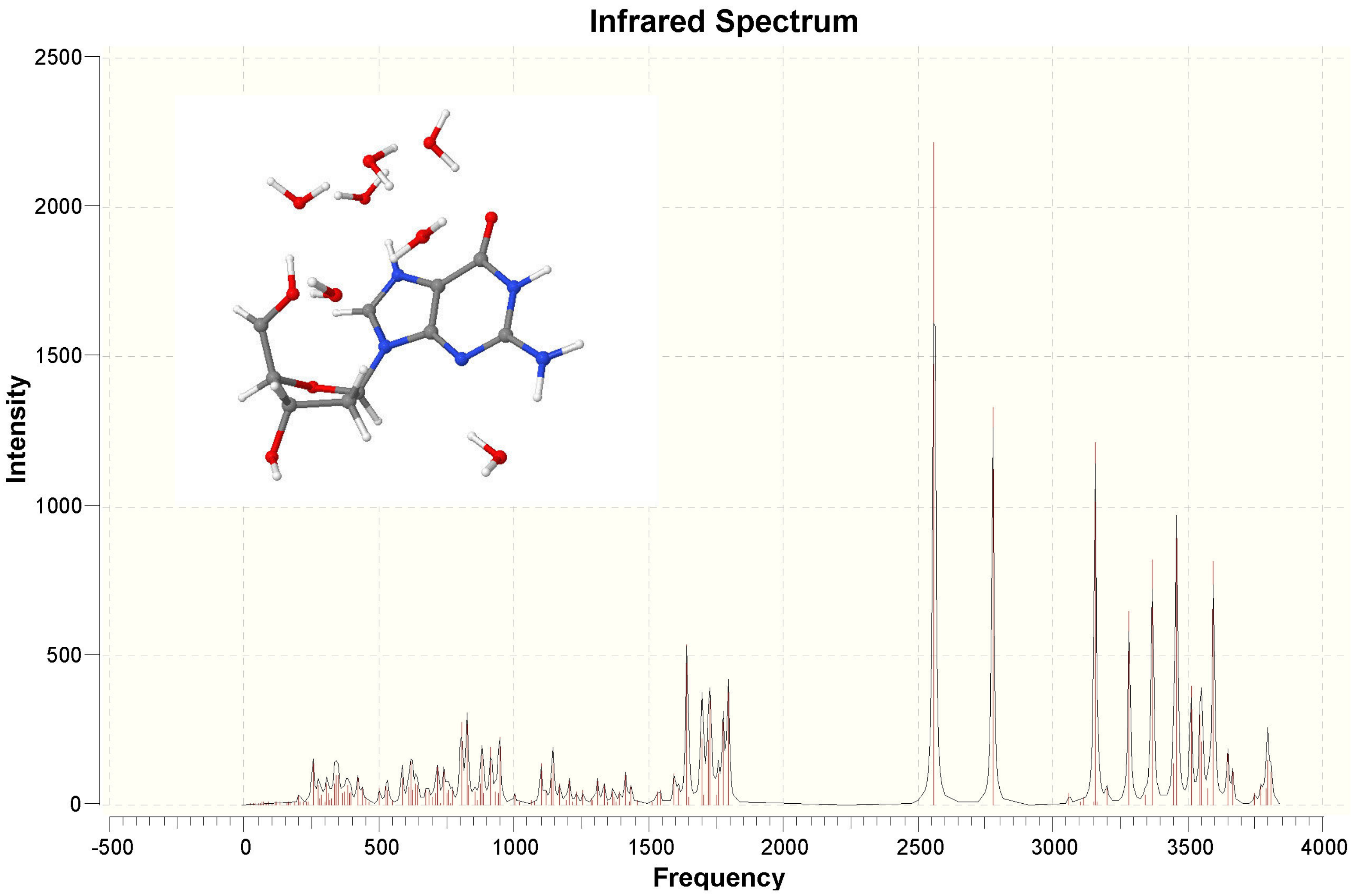


Figure S12- The B3LYP/6-31G* calculated vibrational frequency (cm^{-1}) of deptotonation of $C_{5'}$ site at $C_{5'}$-H distance of 1.35 Å, see Figure S5.



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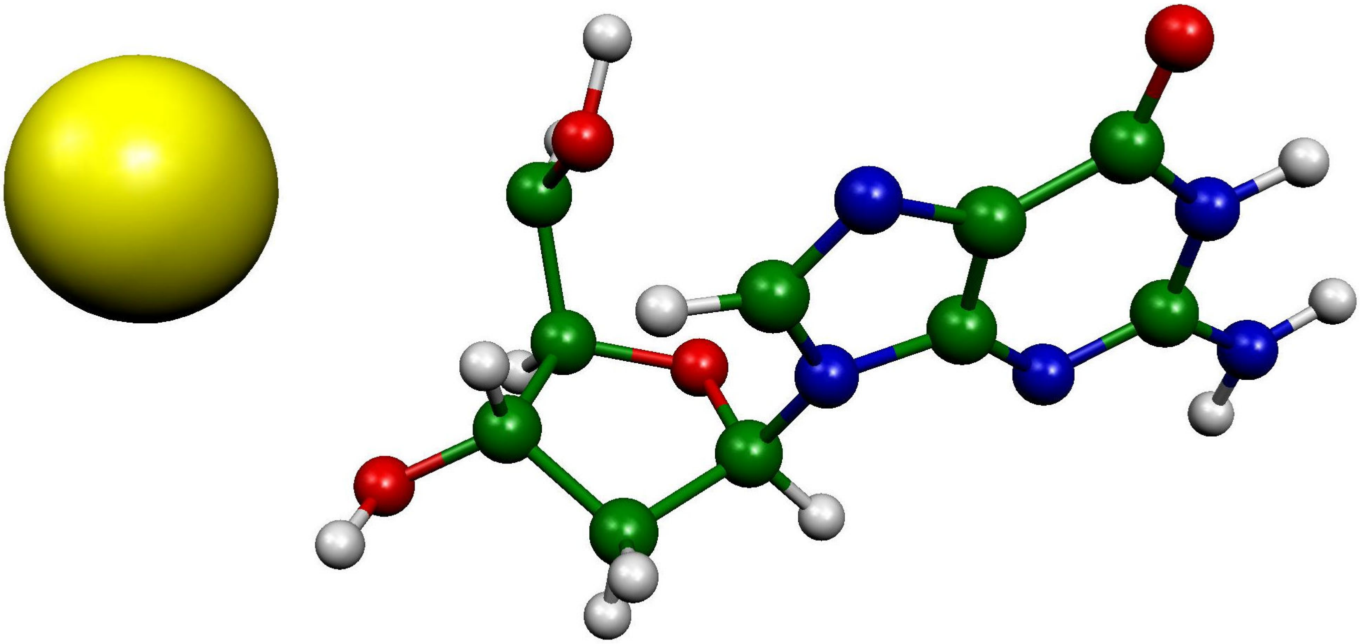

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