Photo-induced Water Oxidation at the Aqueous GaN $(10\bar{1}0)$ Interface: Deprotonation Kinetics of the First Proton-Coupled Electron-Transfer Step

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ABSTRACT

Photoelectrochemical water splitting plays a key role in a promising path to the carbon-neutral generation of solar fuels. Wurzite GaN and its alloys (*e.g.*, GaN/ZnO and InGaN) are demonstrated photocatalysts for water oxidation, and they can drive the overall water splitting reaction when coupled with co-catalysts for proton reduction. In the present work, we investigate the water oxidation mechanism on the prototypical GaN $(10\bar{1}0)$ surface using a combined ab initio molecular dynamics and molecular cluster model approach taking into account the role of water dissociation and hydrogen bonding within the first solvation shell of the hydroxylated surface. The investigation of free-energy changes for the four proton-coupled electron-transfer (PCET) steps of the water oxidation mechanism shows that the first PCET step for the conversion of –Ga-OH to –Ga-$O^{\bullet-}$ requires the highest energy input. We further examine the sequential PCETs, with the proton transfer (PT) following the electron transfer (ET), and find that photo-generated holes localize on surface –NH sites, and the calculated free-energy changes indicate that PCET through –NH sites is thermodynamically more favorable than –OH sites. However, proton transfer from –OH sites with subsequent localization of holes on oxygen atoms is kinetically favored owing to hydrogen bonding interactions at the GaN $(10\bar{1}0)$–water interface. We find that the deprotonation of surface –OH sites is the limiting factor for the generation of reactive oxyl radical ion intermediates and consequently for water oxidation.

INTRODUCTION

Water splitting powered by sunlight provides a carbon-neutral framework for the generation of solar fuels.[1-3] The design and synthesis of more efficient solar water splitting systems require a deeper understanding of the key process of the catalytic oxidation of water to molecular oxygen,[4] which involves the transfer of four protons and four electrons with concomitant O-O bond formation (eq. 1):

$$2\ H_2O_{(liq)} \rightarrow O_{2(g)} + 4\ H^+ + 4\ e- \qquad (1)$$

Domen and co-workers synthesized wurtzite GaN/ZnO alloys as photocatalyts for water oxidation, which, when coupled with proton reduction co-catalysts, split H_2O into O_2 and H_2.[5-7] The holes generated by absorption of light migrate to the GaN/ZnO nanoparticle surface where oxidation of water to molecular oxygen occurs ($2H_2O + 4h^+ \rightarrow O_2 + 4H^+$), whereas the electrons are consumed on the co-catalyst surface for the proton reduction reaction ($4H^+ + 4e^- \rightarrow 2H_2$).[7] The net outcome is the use of four electron-hole pairs generated by incident photons to split two H_2O into O_2 and two H_2. Since GaN/ZnO alloys have narrower band gaps than either GaN or ZnO, and have significant visible light absorption,[8-11] they could be employed as photoanodes in photoelectrochemical cells for solar water splitting.[5,6,12] Additionally, successful water splitting has also been demonstrated using GaN[13,14] and InGaN alloys.[15] Therefore, it is crucial to understand the fundamental features of water oxidation on the prototype GaN surface.

In earlier work, Shen et al.[16] studied the water oxidation mechanism on the GaN $(10\bar{1}0)$ surface using cluster models generated from snapshots of ab initio molecular dynamics (AIMD)

simulations of the GaN $(10\bar{1}0)$–water interface.[17] The proposed mechanism consists of four proton-coupled electron-transfer (PCET) steps resembling those proposed earlier by Norskov et al. for other materials.[18,19] The highest energy requirement was found to be associated with the first PCET step leading to the generation of the reactive oxyl radical ion intermediate from a surface-bound hydroxide ion ($*OH^- \rightarrow *O^{\bullet -} + e^- + H^+$). Recently Akimov et al.[20] investigated the evolution of a photogenerated hole and the following proton-transfer step at the GaN $(10\bar{1}0)$–water interface by combining non-adiabatic molecular dynamics and time-dependent density functional theory (TDDFT) methods, and found that the hole localizes on the surface nitrogen atoms and promotes proton transfer from –NH groups to either surface –OH or bulk H_2O molecules.[20] This observation is quite interesting and presents a puzzle because the splitting of water and formation of an O-O bond require the hole to be localized on an oxygen atom.[16]

Turning to GaN/ZnO alloys, Kharche et al.[21] recently studied the structure of aqueous interfaces of the non-polar $(10\bar{1}0)$ and $(1\bar{2}10)$ wurtzite facets of the 1:1 GaN/ZnO alloy using AIMD simulations. This study found that, similar to the GaN $(10\bar{1}0)$ surface, water also dissociates spontaneously on the $(10\bar{1}0)$ and $(1\bar{2}10)$ surfaces of the GaN/ZnO alloy. The degree of water dissociation, however, is dependent on the surface composition. That work also reports similar hydrogen bonding patterns of the surface-adsorbed protons and hydroxide ions with the bulk water layer at the aqueous interfaces of GaN and GaN/ZnO alloys[21], which suggests that the water oxidation mechanism on the GaN/ZnO alloy surfaces should closely resemble that on the GaN surface.

In the present work, we employ AIMD simulations to investigate the atomic structure of the GaN $(10\bar{1}0)$–water interface and use snapshots from these simulations to investigate the water oxidation mechanism following PCET steps using molecular cluster models. In addition to the coupled PCETs, we also investigate sequential electron-transfer (ET) followed by proton-transfer (PT) steps. We find that photo-generated holes localize on surface –NH sites, confirming the result from ref. 20 and ref. 21 that the top of the valence band at the GaN $(10\bar{1}0)$-aqueous interface consists of N(2p) states, and furthermore that the PCET through –NH sites is thermodynamically more favorable than –OH sites. However, when we investigate the pathway for proton transfer, we find that proton transfer from –OH sites and subsequent localization of holes on oxygen atoms occur at a faster rate, compared to the –NH sites, because of hydrogen bonding interactions at the GaN $(10\bar{1}0)$–water interface. This provides an explanation for how the holes localize on oxygen atoms to promote water oxidation catalysis. Our calculations show that the deprotonation of surface –OH sites is the limiting step for the generation of reactive oxyl radical ion intermediates, which are required for the critical step of O-O bond formation through nucleophilic attack by water molecules.

COMPUTATIONAL METHODS

Ab initio Molecular Dynamics. The GaN-water interface is simulated using a repeated supercell in which a 12-layer slab of $(10\bar{1}0)$ oriented wurtzite GaN with a 3×2 lateral cell alternates with a water filled region containing 81 water molecules (Figure 1a-b). The MD trajectory for this supercell was simulated in our earlier study.[22] The simulation protocol[21,22] is summarized here for completeness. In brief, DFT calculations are carried out using the projector augmented wave (PAW) method[23] as implemented in VASP.[24,25] Based on prior experience,[8] the

semicore 3*d* levels for Ga are explicitly treated, and the DFT+*U* method within the Dudarev formulation[26] is employed with U_{Ga} = 3.9 eV for the 3*d* orbitals. The Brillouin zone is sampled only at the Γ-point, which is sufficient for the large supercells involved in this study. The Born-Oppenheimer MD simulations are performed using a Nose-Hoover thermostat and a Verlet integrator with a time step of 0.5 fs. The functional optB88-vdW,[27,28] including long-range van der Waals interactions, together with a slightly elevated temperature (T = 350 K), gives an accurate O-O pair distribution function and diffusivity.[21,22] Converged results require a cutoff energy of 600 eV. The MD simulation is run for 16 ps and structural analysis is performed for a 6 ps equilibrated window.

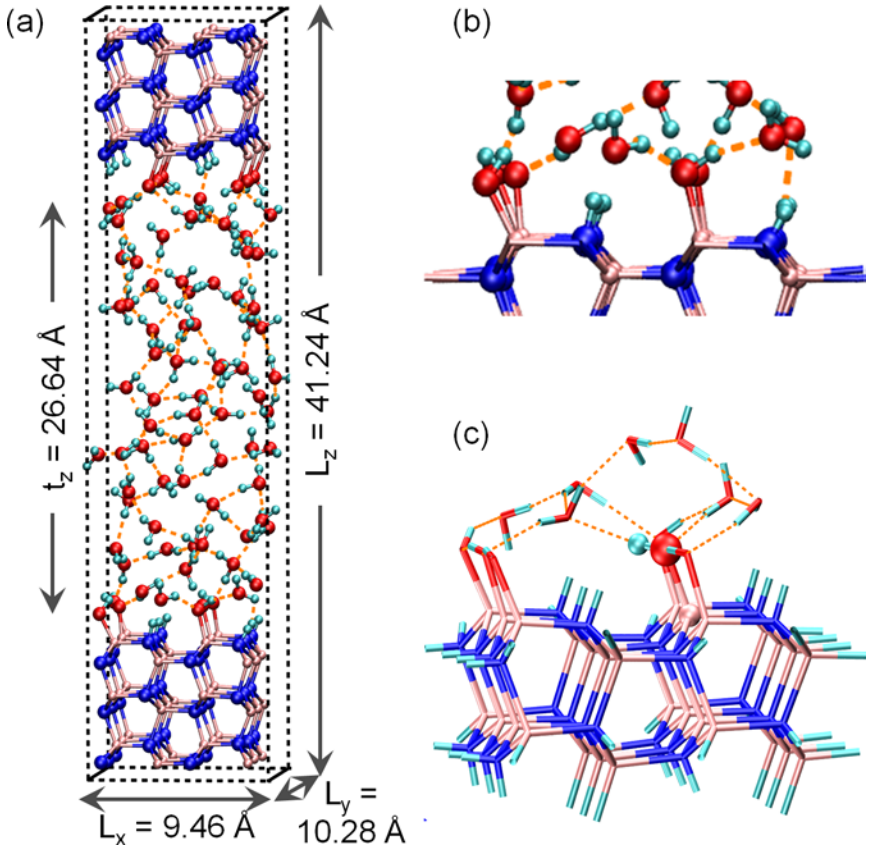


Figure 1. Atomistic schematics of (a) a snapshot from the equilibrated portion of the MD simulation illustrating the unit cell, (b) magnified view of the aqueous interface illustrating interface hydrogen bonds, and (c) the cluster model highlighting the reactive –Ga-OH site in the ball-and-stick representation. The hydrogen bond network is depicted by the dashed orange lines.

Molecular Cluster Model. The GaN $(10\bar{1}0)$ surface model was built from a representative structure obtained from ab initio molecular dynamics simulations, as detailed in the previous section. The 3×2 GaN $(10\bar{1}0)$ surface model contains 28 Ga and 28 N atoms, twelve of which form –Ga-OH and –NH surface species upon dissociation of 6 H_2O molecules (Figure 1c). In addition to that, 7 H_2O molecules are included in the model to preserve the H-bonding interactions and first-shell solvation effects. The dangling bonds formed at terminal positions of the model were passivated with H atoms to complete the coordination number of Ga and N atoms. The details of the comparison of the present cluster model with previous models in Ref. 16 are presented in the Supporting Information.

All geometries were fully optimized at the M11-L level of density functional theory[29, 30] with the SMD aqueous continuum solvation model[31] surrounding the entire cluster using the Stuttgart ECP28MWB contracted pseudopotential basis set on Ga[32, 33] and the 6-31G(d) 5d basis set[34] on all other atoms. Non-analytical integrals were evaluated using the *integral=grid=ultrafine* option as implemented in the Gaussian 09 software package.[35] The nature of all stationary points was verified by analytic computation of vibrational frequencies, which were also used for the computation of zero-point vibrational energies, molecular partition functions, and for determining the reactants and products associated with each transition-state structure (by

following the normal modes associated with imaginary frequencies). The transition state structures were optimized using "opt=(ts,noeigentest)" keyword starting with guess structures and final optimized transition state structures were verified to be associated with a single imaginary frequency. Partition functions were used in the computation of 298 K thermal contributions to the free energy employing the usual ideal-gas, rigid-rotator, harmonic oscillator approximation.[36] Free-energy contributions were added to single-point M11-L electronic energies computed at the optimized geometries obtained with the above-mentioned 6-31G(d) basis set using the SDD basis set on Ga and the 6-311+G(2df,p) 5d, 7f basis set on all other atoms to arrive at final, composite free energies.

As mentioned above, solvation effects associated with bulk water as solvent were accounted for using the SMD aqueous continuum solvation model.[31] A 1 M standard state was used for all species in solution; thus, an adjustment for the 1 atm to 1 M standard-state concentration change of RT ln(24.5), or 1.89 kcal/mol, was added to the computed free energies. In the case of water, the 1 atm gas-phase free energy is adjusted by the sum of a 1 atm to 1 M (1.89 kcal/mol) and 1 M to 55.6 M (2.38 kcal/mol) standard-state concentration change, 4.27 kcal/mol in total, and the experimental 1 M to 1 M self-solvation free energy, –6.32 kcal/mol, yielding an overall correction of –2.05 kcal/mol to the gas-phase free energy. The 1 M to 1 M solvation free energy of the proton was taken from experiment as –265.9 kcal/mol.[37-40] The free energy changes are reported at pH 4.0 as representative of the range of experimental conditions[5, 6] and denoted as $\Delta G^{*\prime}$ which includes a correction of –5.46 kcal/mol (–4RT ln(10)) for the free energy of the solvated proton.

Standard reduction potentials were calculated for various possible redox couples to assess the energetic accessibility of different intermediates at various oxidation states. For a redox reaction of the form

$$\mathrm{Ox}_{(aq)} + ne^{-}_{(g)} \rightarrow \mathrm{Red}_{(aq)} \tag{2}$$

where Ox and Red denote the oxidized and reduced states of the redox couple, respectively, and *n* is the number of electrons involved in redox reaction, the reduction potential $E_{Ox|Red}$ relative to NHE was computed as

$$E_{Ox|Red} = -\frac{\Delta G^{*}_{Ox|Red} - \Delta G^{o}_{NHE}}{nF} = -\frac{\Delta G^{*}_{Ox|Red}}{nF} + \frac{\Delta G^{*}_{NHE}}{F} \tag{3}$$

where $\Delta G^{*}_{Ox|Red}$ is the free-energy change associated with eq. 2 (using Boltzmann statistics for the electron), ΔG^{*}_{NHE} is the free-energy change associated with

$$H^{+}{}_{(aq)} + e^{-}_{(g)} \rightarrow \frac{1}{2}H_{2(aq)} \tag{4}$$

which is –4.28 eV with Boltzmann statistics for the electron,[39, 41, 42] and *F* is the Faraday constant.

To investigate the choice of density functional on reaction energetics, we performed single-point calculations at the B3LYP[43] level of theory using M11-L optimized structures of cluster models. Free-energy contributions from M11-L calculations were added to single-point B3LYP electronic energies computed with the SDD basis set on Ga and the 6-311+G(2df,p) 5d, 7f basis set on all other atoms to arrive at final free energies. The comparison of computed potentials for PCET steps of the proposed water oxidation mechanism indicate close agreement between M11-L and B3LYP for all the steps (Scheme S2 and Table S1). In addition to the above, we performed single-point B3LYP electronic energies computed with the SDD basis set on Ga and the 6-

311G(d,p) 5d, 7f basis set on all other atoms to compare with potentials computed by Shen et al[16] in an earlier work (Table S2).

RESULTS and DISCUSSION

Atomic Structure of the GaN $(10\bar{1}0)$–Water Interface. Ab initio MD simulations allow us to characterize the atomic structure of the aqueous interface of the $(10\bar{1}0)$ surface of GaN in the resting (or ‘‘dark’’) state. In agreement with earlier studies, [16, 21, 22, 44] all adsorbed water molecules on the GaN surface are found to dissociate spontaneously into protons (H^+) and hydroxide ions (OH^-) during the MD run. Surface N atoms accept protons from the dissociated water molecules forming –NH species while the corresponding hydroxide ions bond with surface Ga atoms forming –Ga-OH species. Thus, under ambient conditions the aqueous GaN $(10\bar{1}0)$ interface is fully hydroxylated (Figure 1a-b).

The strong perturbation in the structure of water, induced by the water dissociation resulting from the acid-base chemistry at the solvated GaN surface, extends up to 3 Å distance from the surface. The water layer beyond 3 Å distance from the surface exhibits a bulk-like hydrogen bond network and oxygen-oxygen radial distribution function.[22] In the bulk water region, the average density is 1.08 g/cm^3, slightly larger than the ambient density of water (1.00 g/cm^3). The interfacial water layer up to 3 Å distance from the surface includes surface adsorbed protons and hydroxide ions as well as the first solvation shell of the hydroxylated surface (Figure 1b). These species are explicitly included in our cluster model (Figure 1c).

The hydroxylated surface interacts with the water layer via a hydrogen bond network, indicated by the dashed orange lines in Figure 1a-b. An adsorbed hydroxide ion can form at most one donor and two acceptor hydrogen bonds, while an adsorbed proton can at most be involved in

only one donor hydrogen bond. The number of hydrogen bonds of each kind depends on how they are defined. Here, two species are considered to be hydrogen bonded when the distance between donor (D) and acceptor (A) atoms, $d_{D\text{-}A}$, is smaller than 3 Å and the DHA angle is greater than 140°. Quantitative analysis of the equilibrated portion of the MD trajectory over long periods (ca. 6 ps) indicates that substantially more hydrogen bonds are formed by the –Ga-OH species compared to the –NH species (Figure 2). Similar quantitative results for $d_{D\text{-}A}$ = 3.25 Å and 3.5 Å are included in Figure S1 in the Supporting Information. The fewer donor hydrogen bonds involving the –NH species with smaller $d_{D\text{-}A}$ indicates that these hydrogen bonds are relatively weaker compared to those involving the –Ga-OH species, where the number of donor hydrogen bonds is virtually independent of $d_{D\text{-}A}$. The different strength of –Ga-OH vs. –NH donor hydrogen bonds has important implications for the water oxidation mechanism as discussed in the following sections.

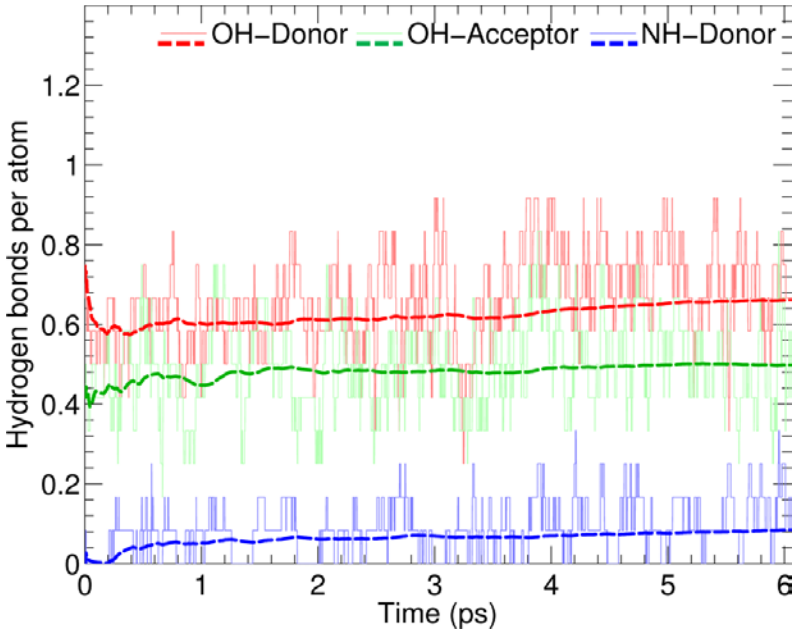


Figure 2. Time dependence of the number of hydrogen bonds between the hydroxylated GaN surface and the bulk water layer from the equilibrated portion of the MD simulation. Instantaneous and time-averaged traces are depicted by thin continuous and thick dashed lines, respectively.

Water Oxidation via Proton-Coupled Electron-Transfer (PCET) Steps. In the cluster model study of water oxidation at the GaN $(10\bar{1}0)$ surface by Shen et al.,[16] which employed smaller clusters than the one considered in the present work, several (4 or 6, depending on the model) explicit water molecules formed a hydrogen bonded layer over the dissociated water on the surface. Two of these water molecules were consumed in the water oxidation cycle, leaving a cluster with two fewer water molecules than it originally had. In order to return this final state to the initial state to complete a catalytic cycle, the two water molecules had to be replaced, and the free energy associated with this process was assessed equally to that of the two steps in which a water molecule was consumed. In the present work, a water molecule is added to the cluster model system before optimizing the geometry in the steps that consume water molecules. This is clear in Table 1, which presents the calculated data for the cluster model employed in the present work, by the definition of the "system" (the current state of the active catalyst) and a "reservoir" that initially contains two water molecules and to which is added every species removed from the previous states of the system. As appropriate for a catalytic process, the catalyst ("system") returns to its initial state at the end of the cycle, and the net reaction occurs in the reservoir.

Table 1. System and reservoir species for the various steps of the water oxidation catalytic cycle. Associated free energies (G*') in units of Hartree and free energy changes (ΔG*') in units

of eV from cluster model calculations are reported at pH 4.0.						
System	Reservoir	$G^{*\prime}_{sys}$ (Ha)[a]	$G^{*\prime}_{res}$ (Ha)[a]	$G^{*\prime}_{tot}$ (Ha)[a]	Rel. $\Delta G^{*\prime}$ (eV)[b]	Rel. $\Delta G^{*\prime}$ (eV vs NHE)[c]
–Ga-OH	$2H_2O_{(liq)}$	-2611.9859	-152.8648	-2764.8507	0.00	0.00
–Ga-$O^{\bullet-}$	$2H_2O_{(liq)}$), H^+, e^-	-2611.3073	-153.3042	-2764.6114	6.51	2.23
–Ga-OOH	$H_2O_{(liq)}$, $2H^+$, $2e^-$	-2687.1083	-77.3112	-2764.4195	5.22	0.94
–Ga-$OO^{\bullet-}$	$H_2O_{(liq)}$, $3H^+$, $3e^-$	-2686.4785	-77.7506	-2764.2291	5.18	0.90
–Ga-OH	$O_{2(g)}$, $4H^+$, $4e^-$	-2611.9859	-152.0805	-2764.0664	4.43	0.15
Net sys rxn: –Ga-OH^-→ –Ga-OH^-	Net res rxn: $2H_2O_{(liq)} \rightarrow O_{2(g)} + 4H^+ + 4e^-$				21.34	1.06

a) Absolute free energies relative to zero on the vacuum reference potential scale

b) Relative values of absolute free energies relative to zero on the vacuum reference potential scale

c) Relative values of absolute free energies relative zero on the normal hydrogen electrode scale

Using the cluster model approach (see computational methods for details), the obtained free-energy changes for the four PCET steps of water oxidation at the GaN $(10\bar{1}0)$ surface at pH 4.0 are 2.23, 0.94, 0.90 and 0.15 eV, respectively, at the M11-L level of theory (Table 1). The single-point calculations using the B3LYP functional on M11-L optimized structures also yielded similar free-energy changes for the PCET steps differing only by about 0.10 eV (Table S1). Comparison with the previous results by Shen et al.,[16] indicates agreement within 0.15 eV for the PCET steps using the same basis set for H, O and N atoms (Table S2). Moreover, the computed standard water oxidation potential is 1.06 V vs. NHE at pH 4.0 in good agreement with the experimental potential of 0.99 V vs. NHE at pH 4.0. The calculated $\Delta G^{*\prime}$ for the present cluster

(2.23 eV) model shows that the first PCET step is the rate limiting step, which determines the thermodynamic overpotential required to make all PCET steps downhill (see next section).

Water Oxidation Mechanism via Decoupled PCET Steps. Now we turn our attention to examining the mechanism of water oxidation via decoupled PCET steps at the aqueous GaN $(10\bar{1}0)$ interface via cluster models. We started the investigation with the first oxidation step, which occurs with an associated free-energy change of 1.30 eV. The hole generated by this oxidation delocalizes onto N atoms in the resulting positively charged system as displayed by unpaired spin density plots (Figure 3). This finding is consistent with the top of the GaN valence band being composed of N(2p) states in the periodic DFT calculations at the PBE level of theory,[8] but is surprising in the sense that the proposed water oxidation mechanisms for several molecular and heterogeneous catalysts involve hole localization on oxygen atoms to generate reactive species for the critical step of O-O bond formation.

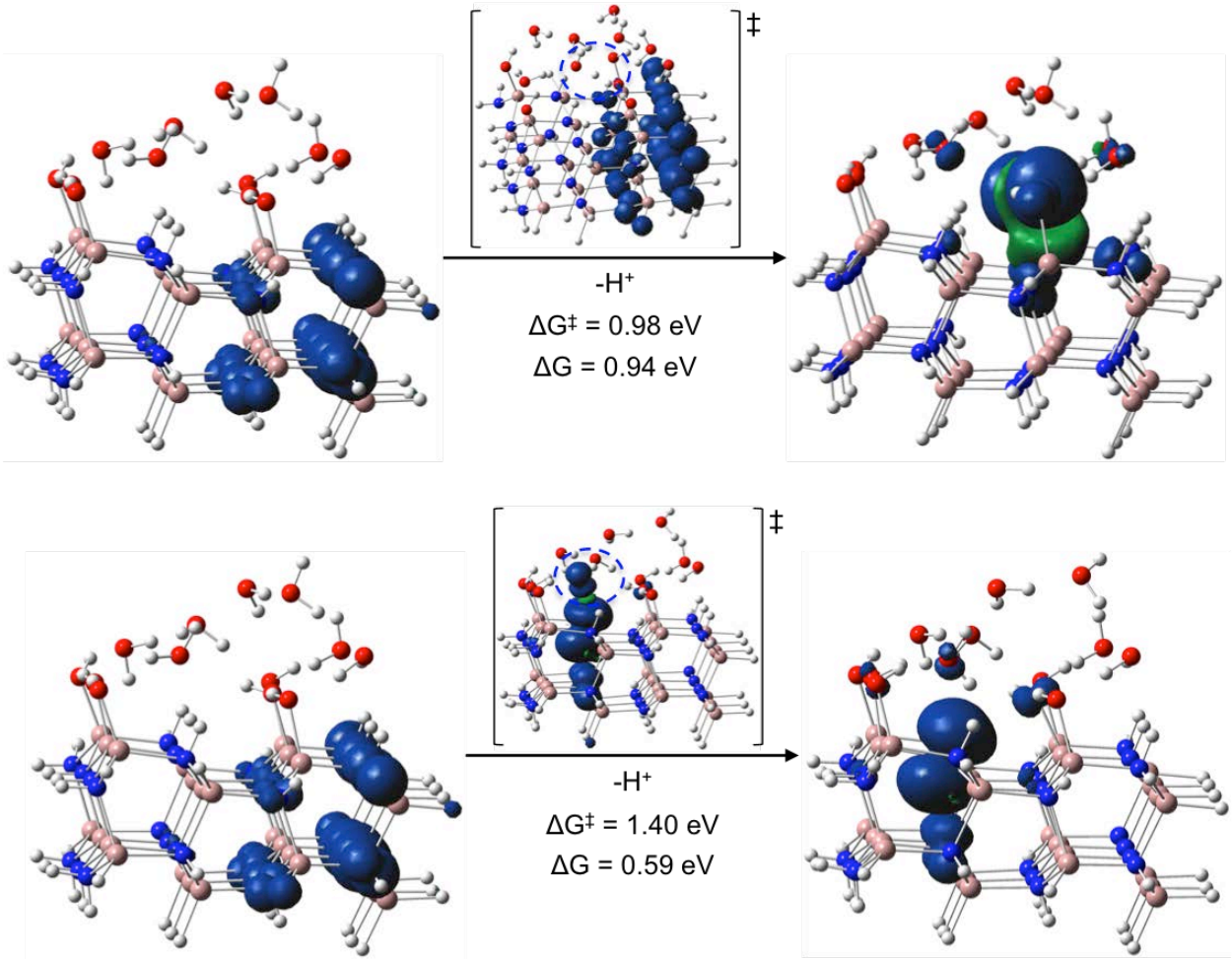
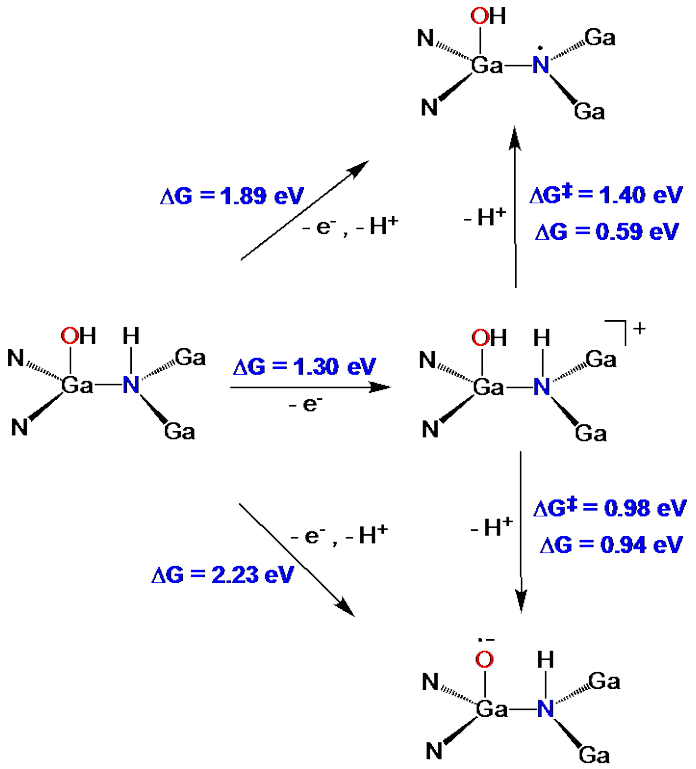


Figure 3. Atomistic models and unpaired spin densities for one-electron oxidized cluster model along with transition state and product structures associated with deprotonation through an –Ga-OH (top) and –NH (bottom) site.

Following this observation, we examined possible subsequent deprotonation steps from either an –NH site or a –Ga-OH site of the oxidized cluster. The calculated free-energy changes indicate that deprotonation from an –NH site is favored over a –Ga-OH site by 0.35 eV (0.59 eV vs. 0.94 eV). In contrast, the located transition-state (TS) structures for the deprotonation events exhibit free energy of activation ($\Delta G^{\ddagger}$) values of 1.40 eV and 0.98 eV for –NH and –GaOH sites, respectively (Figure 3, Scheme 1). We also performed single-point calculations at the B3LYP

Scheme 1. Energetics of proton coupled electron transfer from –NH and –Ga-OH sites.

level of theory for the first PCET step and found very good agreement with the M11-L results (Scheme S2).



Closer inspection of the TS structures reveals that the –NH deprotonation proceeds via proton transfer to a neighboring H_2O molecule above the –NH site resulting in the generation of an H_3O^+ intermediate (Figure 4a), whereas the –Ga-OH deprotonation involves proton transfer to a neighboring –Ga-OH site assisted by a H_2O molecule (Figure 4b). This difference essentially stems from the difference between the hydrogen bonding network involving –NH and –Ga-OH sites as observed during the AIMD simulations in which –Ga-OH sites are always associated with water molecules as hydrogen bonding partners whereas –NH sites do not strongly interact with H_2O molecules. As a result, H_2O molecules are aligned in a favorable way to accept a proton from –Ga-OH (Figure 4b) whereas deprotonation from –NH involves disturbing those favorable interactions and bringing a single water molecule into close contact with a –NH site

(Figure 4a). Therefore, we propose that although deprotonation from an –NH site is favored thermodynamically, the positions and hydrogen bonding interactions of water molecules render –Ga-OH sites more favorable kinetically towards deprotonation following the oxidation step. The spin density data indicate that upon deprotonation, the hole localizes on the oxygen atom of –Ga-O resulting in an oxyl radical ion species, –Ga-$O^{\bullet-}$ (Figure 3). Similar hole dynamics upon changes in the hydrogen bonding pattern and deprotonation were also shown for anatase TiO_2.[45] The calculated $\Delta G^{*'}$ for the first coupled-electron and proton-transfer step is 2.23 eV at pH 4.0 (Table 1), and constitutes the step with the highest energy requirement for the proposed water oxidation mechanism as shown Scheme 2 in which the free energy changes associated with sequential PCETs, with the proton transfer (PT) following the electron transfer (ET), are presented for the overall water oxidation mechanism. Therefore, the deprotonation of surface –Ga-OH sites in the first oxidation step will be the limiting factor for the generation of reactive –Ga-$O^{\bullet-}$ intermediates and consequently for overall water oxidation cycle.

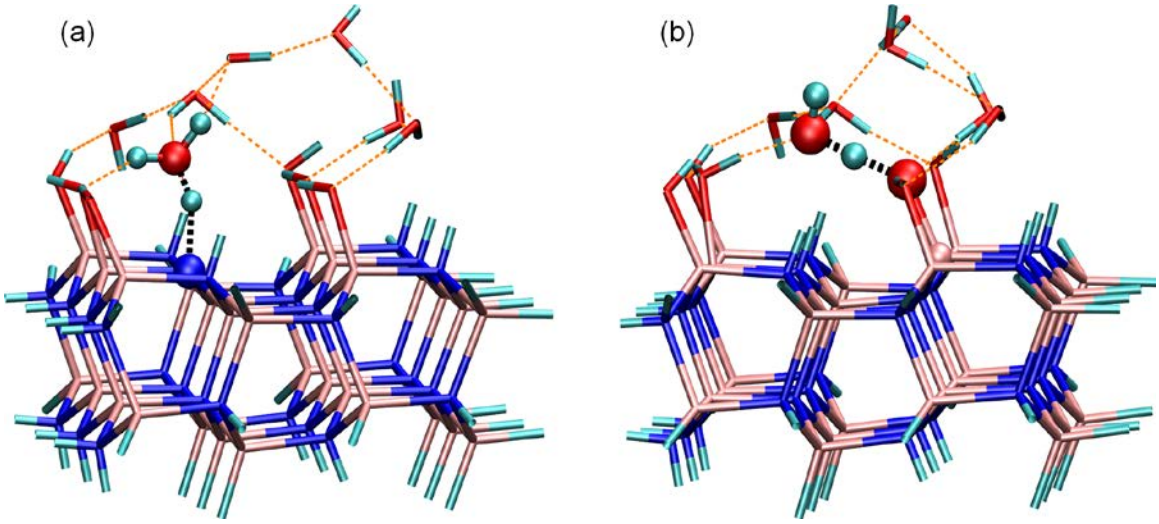
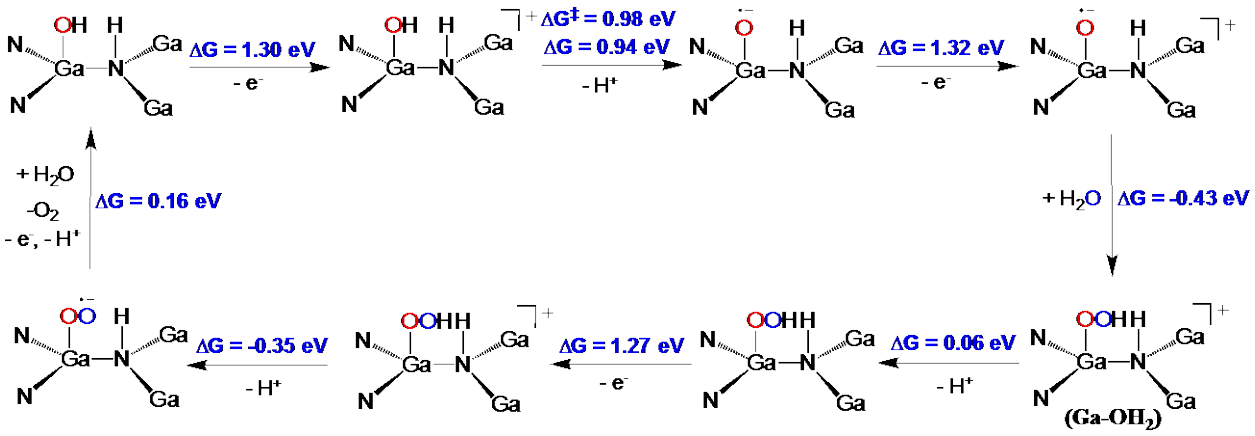


Figure 4. Transition state structures for deprotonation from (a) a –NH site and (b) an –Ga-OH site. Proton transfer pathways are depicted by the thick black dashed lines.

Scheme 2. Proposed water oxidation mechanism at pH 4.0 using molecular cluster models. (Ga-OH_2) refers to the protonation of a neighboring –Ga-OH site.



The second oxidation step requires 1.32 eV and results in a delocalized hole on N atoms similar to the first oxidation step, but now with a reactive –Ga-$O^{\bullet-}$ intermediate also on the surface so that a total of two oxidizing equivalents is stored in the cluster. The subsequent addition of a water molecule to generate an O-O bond is downhill by 0.43 eV. This nucleophilic addition of the H_2O molecule results in the formation of a –Ga-OOH hydroperoxide intermediate and involves a proton transfer to a nearby –Ga-OH site to form a transient –Ga-OH_2, from which a proton could be transferred to the bulk solution. Sequential oxidation ($\Delta G^{*\prime}$ = 1.27 eV) and deprotonation ($\Delta G^{*\prime}$ = -0.35 eV) of –Ga-OOH leads to a –Ga-$OO^{\bullet-}$ superoxide intermediate

which, upon an additional oxidation evolves molecular oxygen and regenerates the initial –Ga-OH species by the addition and dissociation of another water molecule.

CONCLUSION

We studied the GaN $(10\bar{1}0)$–water interface with AIMD simulations and examined the water oxidation mechanism following PCET steps by performing DFT calculations on cluster models. The calculated free energies for the four PCET steps of the oxygen evolution reaction indicate that the first PCET step for the conversion of –Ga-OH to –Ga-$O^{\bullet-}$ is associated with the highest energy requirement. Investigation of electron-transfer (ET) and proton-transfer (PT) steps separately for the first PCET reveals that deprotonation is rate limiting, and that the hole localizes on an oxygen atom to generate a reactive oxyl radical ion intermediate upon deprotonation. Our calculations show that although deprotonation from –NH sites is thermodynamically more favorable upon photo-generated hole creation, the hydrogen bonding network at the GaN $(10\bar{1}0)$–water interface renders deprotonation from an –OH site to be kinetically preferred. Therefore, the oxygen evolution activity will be enhanced by increasing the rate of deprotonation from –OH sites while limiting the –NH deprotonation especially for the case of GaN/ZnO alloys for which removal of a proton from –NH sites may not be as disfavored kinetically as for GaN. Furthermore, the present work displays the strength of the coupled approach of using periodic ab initio molecular dynamics and cluster models for the investigation of the mechanism of electrocatalytic reactions on surfaces of semiconductors.

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Supporting Information. Schemes S1-S3, Figures S1-S4, Tables S1 and S2, and Cartesian coordinates of optimized structures from cluster models. This material is available free of charge via the Internet as http://pubs.acs.org.

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Supporting Information

Photoinduced Water Oxidation at the Aqueous GaN $(10\bar{1}0)$ Interface: Deprotonation Kinetics of the First Proton-Coupled Electron-Transfer Step

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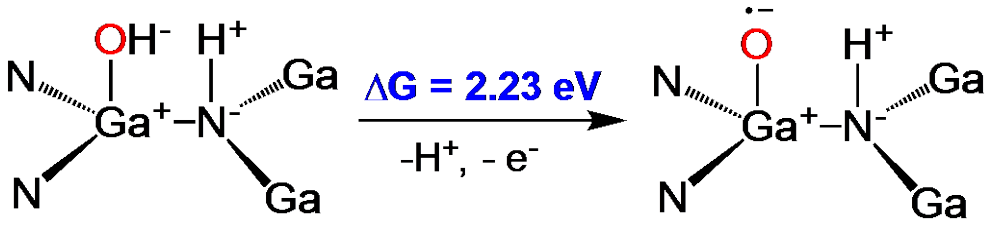
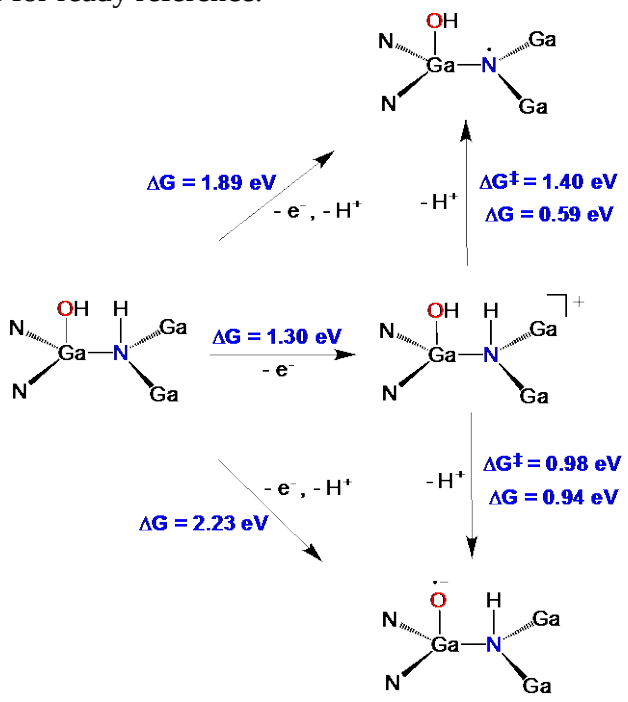
Bonding in tetrahedral Wurtzite GaN. The bonding in bulk Wurtzite GaN is best described as follows. Each group III Ga atom (s^2p) accepts an electron from a group V N atom (s^2p^3) so that both the resulting Ga^- and N^+ species take on group IV (s^2p^2), carbon-like character. These Ga^- and N^+ species then form sp^3 hybrid orbitals which make a tetrahedral network of covalent bonds in which each Ga^- ion is bonded to four N^+ ions, and each N^+ ion is bonded to four Ga^- ions. The electron pair in each of these covalent bonds is polarized toward the N^+ ion to compensate for the initial charge transfer. This motif describes the Wurtzite structure of bulk GaN, but not the non-polar (10-10) surface. At the surface, there is a dangling bond (singly occupied sp^3 orbital) on every surface atom exposed to either vacuum or an aqueous interface. This is not a stable configuration, so the surface reconstructs by the transfer of the electrons in Ga dangling bonds to the corresponding dangling bonds on N atoms, resulting in an overall neutral surface composed of an equal number of Ga^+ and N^- ions. The vacant orbital on the Ga^+ ions give it Lewis acid properties, and the doubly occupied (lone pair) on the N^- ions imparts both Lewis and Brønsted base properties to them. The dissociation of a water molecule to OH^- and H^+ with essentially no energy barrier (reported as 1 meV in Shen, X.; Allen, P. B.; Hybertsen, M. S.; Muckerman, J. T. *J. Phys. Chem. C* **2009**, *113*, 3365-3368) is consistent with the long-range stabilization of the stretching of the H—OH bond imparted by the ionic character of the surface. A lone pair on the dissociated OH^- ion occupies the vacant orbital on a Ga^+ site, and the H^+ attaches to the lone pair of a N^- site.



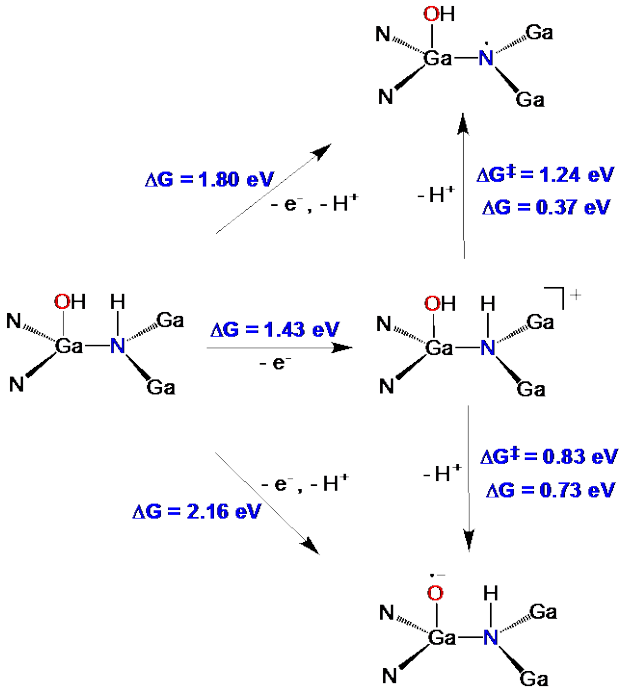
Molecular Cluster Model. The GaN $(10\bar{1}0)$ surface model was built from a representative structure obtained from ab initio molecular dynamics simulations, as detailed in the main text. The 3×2 GaN $(10\bar{1}0)$ surface model contains 28 Ga and 28 N atoms, twelve of which form –Ga-OH and –NH surface species upon the dissociation of 6 H_2O molecules. In addition to that, 7 H_2O molecules are included in the model to preserve the H-bonding interactions and first-shell solvation effects. The dangling bonds formed at terminal positions of the model were passivated with H atoms to complete the coordination number of Ga and N atoms. The two previous cluster models in Ref. 16 contain either (i) 15 Ga and 15 N atoms with 2 dissociated H_2O molecules and 4 additional explicit H_2O molecules or (ii) 21 Ga and 21 N atoms with 3 dissociated H_2O molecules and 4 additional explicit H_2O molecules. The present model is not only larger than previous models but details of the passivation of dangling bonds on Ga and N in the "interior" of the GaN semiconductor by hydrogen atoms have been improved. In the previous models, the presence of the polarizable continuum solvation model was essential to prevent (through stabilization of charge separation) a hydridic Ga–H hydrogen from reacting with a nearby acidic N–H hydrogen in certain regions where they were close enough to interact. In the present model, additional "bulk" GaN was added to an initial version of the present model to avoid such close interactions. Furthermore, the present model provides improvements in treating the hydrogen bonding interactions between

dissociated water molecules and first shell water molecules resulting in more compatible structures with AIMD simulations (*e.g.*, no strong H-bonding interactions with –NH sites).

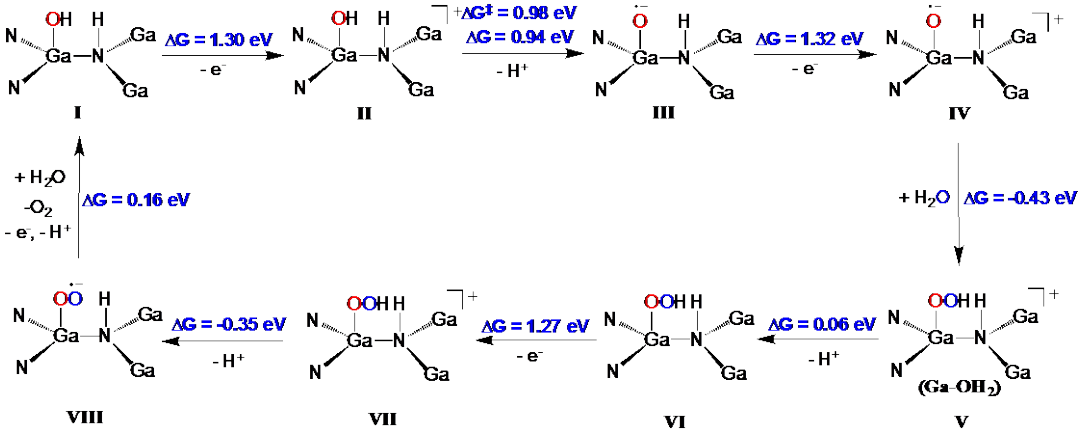
Scheme S1. Energetics of proton-coupled electron-transfer from –NH and –Ga-OH sites at the M11-L level of theory This scheme, which is the same as Scheme 1 in the main text, is repeated here for ready reference.



Scheme S2. Energetics of proton-coupled electron-transfer from –NH and –Ga-OH sites obtained via B3LYP single-point calculations on M11-L optimized structures.



Scheme S3. Proposed water oxidation mechanism at pH 4.0 using molecular cluster models. (Ga-OH_2) refers to protonation of a neighboring –Ga-OH site. This scheme, which is the same as Scheme 2 in the main text, is repeated here for ready reference.



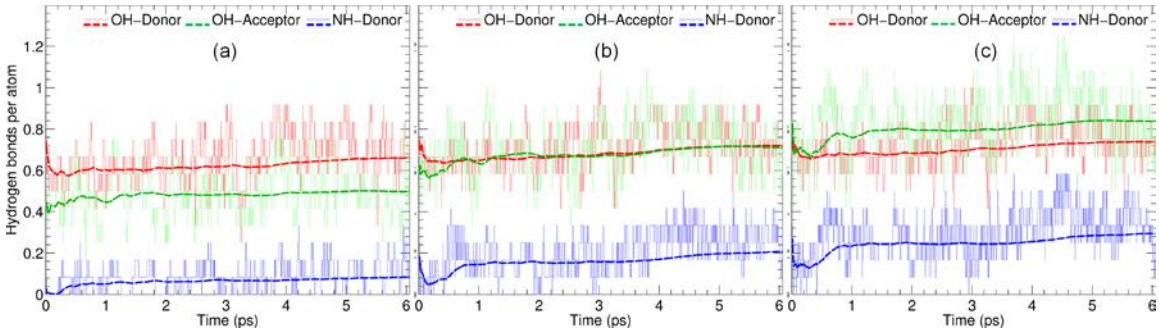


Figure S1. Time dependence of the number of hydrogen bonds between the hydroxylated GaN surface and the bulk water layer from the equilibrated portion of the MD simulation. The data in (a), (b) and (c) are obtained using the donor-acceptor distance cutoff of 3.0 Å, 3.25 Å, and 3.5 Å, respectively. Panel (a) is the same as Figure 2 in the main text. Instantaneous and time-averaged traces are depicted by thin continuous and thick dashed lines, respectively.

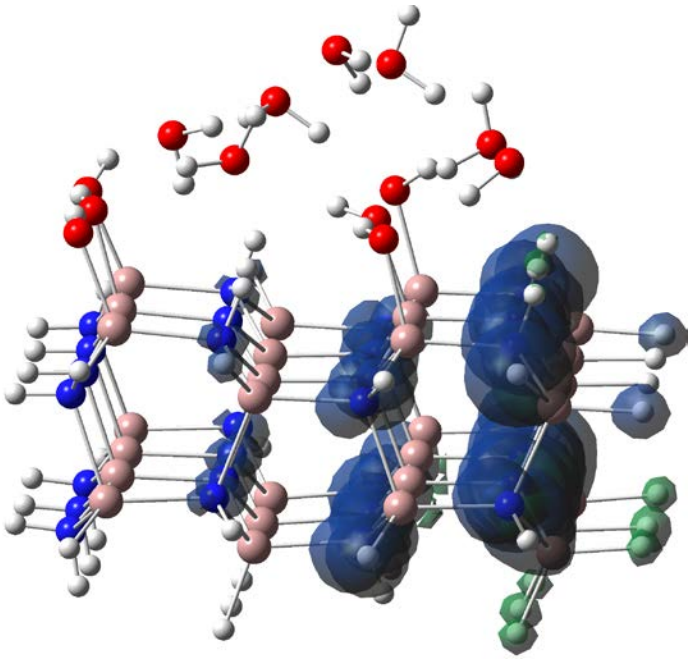


Figure S2. Unpaired spin density plot for **II** (doublet) in Scheme S3.

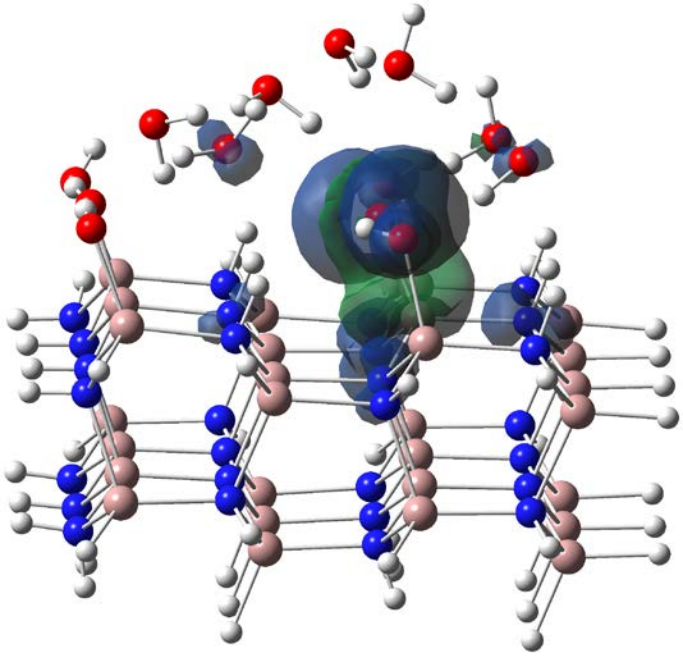


Figure S3. Unpaired spin density plot for **III** (doublet) in Scheme S3

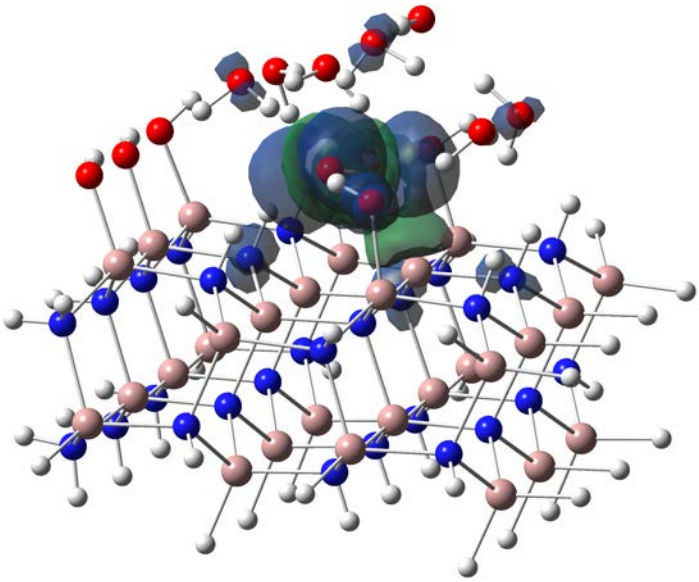


Figure S4. Unpaired spin density plot for **VIII** (doublet) in Scheme S3.

Table S1. Comparison of different density functionals for free-energy changes of PCET steps of proposed water oxidation mechanism at the aqueous GaN $(10\bar{1}0)$ interface via cluster models. Associated free-energy changes (ΔG*') in units of eV from cluster model calculations are reported at pH 4.0.(see computational methods for details).		
	ΔG*' (eV vs NHE)	
	M11-L	**B3LYP**
–Ga-OH → –Ga-O$^{\bullet-}$ + H$^+$ + e^-	2.23	2.16
–Ga-O$^{\bullet-}$ + H_2O → –Ga-OOH + H$^+$ + e^-	0.96	0.83
–Ga-OOH → –Ga-OO$^{\bullet-}$ + H$^+$ + e^-	0.91	0.78
–Ga-OO$^{\bullet-}$ + H_2O → –Ga-OH + O_2 + H$^+$ + e^-	0.16	0.01

Table S2. Comparison of computed free-energy changes of PCET steps of proposed water oxidation mechanism at the aqueous GaN $(10\bar{1}0)$ interface at the B3LYP level of theory via cluster models of the present work and by Shen et al. (Ref 16). Associated free-energy changes (ΔG*') in units of eV from cluster model calculations are reported at pH 4.0.(see computational methods for details).		
	ΔG*' (eV vs NHE)	
	This work (SDD/6-311G(d,p)	**Ref 16 SBKJC/6-311G(d,p)**
–Ga-OH → –Ga-O$^{\bullet-}$ + H$^+$ + e^-	2.18	2.32
–Ga-O$^{\bullet-}$ + H_2O → –Ga-OOH + H$^+$ + e^-	0.60	0.75
–Ga-OOH → –Ga-OO$^{\bullet-}$ + H$^+$ + e^-	0.87	0.77
–Ga-OO$^{\bullet-}$ + H_2O → –Ga-OH + O_2 + H$^+$ + e^-	-0.20	-0.35

Geometry (Atomic Numbers Followed by the Cartesian Coordinates in Å) and Energy of Optimized Structures from Cluster Models

I (restricted singlet) in Scheme S3

E = -2611.28912555 a.u.

1	-3.486452	-1.149199	2.070792
1	-0.588025	-0.028948	3.320027
1	-0.284003	-1.649689	2.140460
1	-1.300474	-1.598973	4.782576
1	-1.251875	-2.791926	3.775718
1	1.315374	-5.107707	3.233345
1	-4.589929	-3.829066	3.202963
1	2.893775	-2.122888	2.376269
1	-1.825453	-4.637696	3.026957
1	-6.202903	-2.195911	2.528629
1	-5.416023	-1.862086	3.778168
1	-2.600984	1.800215	3.771582
1	-3.874739	-0.086709	4.074568
1	-3.357499	-1.469168	4.373266
1	1.269845	0.721360	7.306908
1	1.600102	1.264077	5.931258
1	2.121302	0.101999	3.461049
1	-0.482881	1.885120	4.184242
1	-0.810319	2.442208	5.563640
1	1.312628	2.835547	4.582961
1	2.510755	1.935342	4.261343
1	-0.457488	0.112964	6.084534
1	-1.812763	0.328568	5.427336
1	3.775570	3.113349	2.737608
1	-2.616886	4.113448	2.512119
1	0.563022	3.584723	2.602146
1	-3.810323	6.528883	0.754314
1	6.402174	2.978283	-1.316077
1	6.796244	2.520694	1.832483
1	2.549266	5.500065	1.019454
1	-0.592920	5.999990	0.910700
1	-5.361046	1.976352	0.873136
1	-6.495664	-0.786711	0.924500
1	-5.668674	-0.445712	-2.153402
1	-5.917370	2.101165	-2.288921
1	-5.542092	-4.733136	-0.179031
1	0.823771	-5.661419	0.175683
1	5.791766	-5.305939	-2.083746
1	4.936041	-5.259151	1.041362

1	5.955032	-2.785272	1.529132
1	5.777006	0.203973	1.353289
1	6.591761	0.034805	-1.746933
1	5.555261	-2.305084	-1.618953
1	-3.281337	-0.887032	-4.189036
1	-2.838674	1.909836	-3.222965
1	0.035195	-1.444620	-4.060277
1	0.417586	1.378876	-3.116931
1	3.364132	-2.022040	-3.875683
1	3.718873	0.808800	-2.963646
1	-6.796104	-3.205165	-2.767485
1	-6.277717	-3.436985	0.442423
1	-2.419027	-5.144429	-0.027924
1	-5.584597	4.504774	1.400329
1	5.799353	4.989760	1.078751
1	-4.840265	4.829030	-1.719140
1	3.873675	-6.267743	0.357918
1	4.129075	3.297066	-3.476257
1	4.391306	5.383132	-1.690285
1	0.835150	3.807726	-3.619589
1	1.111042	5.906324	-1.861865
1	-2.437590	4.383715	-3.711588
1	-2.147334	6.451775	-1.907945
1	-3.936858	-4.804765	-2.662625
1	-3.708067	-3.575475	-3.690759
1	-0.398810	-4.060660	-3.549802
1	-0.668594	-5.318433	-2.560488
1	2.860163	-4.675715	-3.331241
1	2.573356	-5.891819	-2.301488
7	-4.946001	-0.986857	-1.669210
7	-5.441390	-3.722982	-0.069206
7	1.499161	-1.983046	-1.474527
7	4.655735	-2.566806	-1.204217
7	2.930573	-2.442544	1.403364
7	-2.265838	-4.138393	0.079480
7	-1.755509	-1.448205	-1.622637
7	-3.521977	-1.427566	1.085768
7	-0.273267	-1.921385	1.153704
7	0.964223	-4.652266	0.272397
7	4.096915	-5.276577	0.460020
7	-4.590718	1.523063	0.374169
7	-4.110572	4.307153	-1.227831
7	0.321025	0.953937	-2.189788
7	3.587935	0.400836	-2.033697
7	4.944487	-0.005351	0.795485
7	-0.913182	3.816488	-1.181303

7	-2.649020	3.870777	1.518271
7	2.330030	3.295060	-1.066300
7	-2.940380	1.482328	-2.297954
7	-1.437817	1.044691	0.498254
7	1.799315	0.538654	0.597485
7	0.567027	3.303732	1.618120
7	5.510364	2.737928	-0.876797
7	3.807530	2.849106	1.749501
7	-3.792715	-3.794472	-2.697485
7	-0.498641	-4.311913	-2.565422
7	2.769773	-4.890535	-2.337545
8	-4.120526	-0.899411	4.557397
8	-1.580413	-1.884830	3.897734
8	2.270386	-5.153508	3.097560
8	-3.868246	-4.256470	2.718649
8	-0.873682	-4.477152	2.939252
8	-6.086675	-2.484697	3.439875
8	-3.217965	1.308120	3.213855
8	0.154563	0.586293	3.263607
8	1.286021	0.462071	6.380822
8	3.056634	0.357424	3.464017
8	-0.803386	2.696118	4.634523
8	2.220636	2.651821	4.858291
8	-1.374574	-0.216228	6.089156
31	-5.071897	-0.409671	0.267591
31	-5.475886	-2.870780	-1.942221
31	-3.212763	-0.476322	-2.627942
31	0.031242	-1.011734	-2.499833
31	3.274764	-1.557159	-2.330304
31	4.798254	-1.994997	0.736636
31	-3.809764	-3.374913	1.068654
31	-1.755951	-0.885340	0.283119
31	1.517465	-1.395683	0.421896
31	-2.085140	-3.351976	-1.744405
31	1.214771	-3.895990	-1.557540
31	-0.619578	-3.871404	1.169033
31	4.575397	-4.531753	-1.407037
31	2.579515	-4.374801	1.420818
31	-4.555279	2.385767	-1.469674
31	-4.179526	4.944862	0.699789
31	2.035663	1.368605	-1.212858
31	5.327797	0.767634	-1.056311
31	-0.881650	4.414124	0.711317
31	-1.240659	1.896456	-1.326946
31	-2.951494	1.925420	1.420564
31	0.241646	1.357629	1.501096

31	3.422360	0.917147	1.673113
31	2.351342	3.899343	0.827730
31	5.647514	3.368963	1.046623
31	4.091461	3.790599	-1.915379
31	0.862060	4.294013	-2.052381
31	-2.357455	4.846569	-2.143614

II (doublet) in Scheme S3

E = -2611.08759176 a.u.

1	-3.505243	-1.106828	2.066917
1	-0.578111	-0.063359	3.344170
1	-0.308568	-1.672809	2.143778
1	-1.314152	-1.613457	4.792000
1	-1.277437	-2.802494	3.780521
1	1.265904	-5.137218	3.224969
1	-4.632394	-3.775150	3.199102
1	2.871683	-2.171317	2.376555
1	-1.906489	-4.616994	3.012175
1	-6.227821	-2.118826	2.523304
1	-5.435066	-1.805562	3.774480
1	-2.578014	1.821014	3.777471
1	-3.867134	-0.057715	4.078321
1	-3.365119	-1.448363	4.366813
1	1.267215	0.667459	7.327292
1	1.611283	1.222285	5.960074
1	2.123480	0.059041	3.486191
1	-0.463656	1.863986	4.201531
1	-0.803355	2.439797	5.569808
1	1.330578	2.798017	4.623012
1	2.522459	1.893350	4.290915
1	-0.463075	0.098368	6.093166
1	-1.811073	0.323833	5.423576
1	3.775893	3.068715	2.760180
1	-2.533988	4.132531	2.533147
1	0.593870	3.542047	2.641709
1	-3.671080	6.598262	0.765008
1	6.361955	2.972138	-1.317309
1	6.767157	2.457263	1.829340
1	2.583815	5.476297	1.022044
1	-0.485909	6.003113	0.910528
1	-5.322885	2.069613	0.860487
1	-6.503074	-0.676068	0.926358
1	-5.665946	-0.358916	-2.159631

1	-5.850066	2.243245	-2.310952
1	-5.610615	-4.655383	-0.190729
1	0.764937	-5.681759	0.166270
1	5.741214	-5.346046	-2.101591
1	4.878690	-5.318942	1.024276
1	5.934991	-2.825414	1.526780
1	5.767916	0.159298	1.352615
1	6.588118	0.029706	-1.750749
1	5.525999	-2.352022	-1.625131
1	-3.283145	-0.828807	-4.195772
1	-2.781690	1.946757	-3.223626
1	0.020854	-1.454926	-4.067645
1	0.440016	1.363211	-3.113323
1	3.334932	-2.035854	-3.883895
1	3.705339	0.783154	-2.958974
1	-6.842772	-3.093369	-2.772825
1	-6.327001	-3.350186	0.434848
1	-2.501559	-5.115100	-0.036659
1	-5.470665	4.577752	1.393727
1	5.815784	4.960593	1.096007
1	-4.679393	4.927934	-1.717219
1	3.807381	-6.311193	0.331669
1	4.093871	3.260272	-3.476948
1	4.370809	5.368661	-1.679642
1	0.881450	3.744186	-3.636634
1	1.187447	5.893233	-1.905466
1	-2.293889	4.409118	-3.711219
1	-1.971954	6.488411	-1.887262
1	-4.012207	-4.744640	-2.681831
1	-3.760153	-3.512468	-3.700855
1	-0.448219	-4.051174	-3.559847
1	-0.732966	-5.311087	-2.578372
1	2.809249	-4.695338	-3.344106
1	2.519759	-5.916988	-2.321869
7	-4.953623	-0.911376	-1.672456
7	-5.494640	-3.647189	-0.077163
7	1.475354	-2.007405	-1.474715
7	4.625062	-2.606213	-1.208416
7	2.907812	-2.484385	1.401403
7	-2.325761	-4.112351	0.069196
7	-1.772660	-1.433362	-1.626955
7	-3.545107	-1.380325	1.080650
7	-0.298649	-1.939052	1.155476
7	0.909742	-4.673111	0.263751
7	4.040213	-5.322979	0.441612
7	-4.561287	1.599646	0.362985

7	-3.984163	4.371311	-1.211063
7	0.334804	0.933473	-2.189253
7	3.583826	0.369248	-2.030132
7	4.935440	-0.047142	0.793057
7	-0.830013	3.795984	-1.145288
7	-2.578795	3.892354	1.538734
7	2.328892	3.248631	-1.027887
7	-2.903176	1.522494	-2.299295
7	-1.426210	1.044680	0.504339
7	1.796871	0.500041	0.608913
7	0.599784	3.267741	1.654876
7	5.485107	2.707512	-0.858512
7	3.815430	2.799612	1.773021
7	-3.848077	-3.737038	-2.709012
7	-0.551920	-4.306341	-2.576710
7	2.718724	-4.915900	-2.351558
8	-4.120427	-0.870309	4.556374
8	-1.587449	-1.889002	3.901719
8	2.220110	-5.188962	3.087182
8	-3.914959	-4.205129	2.710862
8	-0.947877	-4.500463	2.923910
8	-6.115964	-2.414899	3.432658
8	-3.200779	1.337659	3.218168
8	0.161175	0.555641	3.281545
8	1.285413	0.418919	6.398275
8	3.059228	0.313300	3.480519
8	-0.769072	2.686932	4.639369
8	2.241102	2.611787	4.888861
8	-1.383707	-0.220675	6.092718
31	-5.076125	-0.333934	0.262045
31	-5.516981	-2.789660	-1.946980
31	-3.214010	-0.441570	-2.631830
31	0.017717	-1.036073	-2.507550
31	3.251591	-1.597284	-2.333932
31	4.775726	-2.044828	0.732885
31	-3.860329	-3.327247	1.060485
31	-1.768997	-0.888911	0.283446
31	1.496046	-1.438426	0.427204
31	-2.132944	-3.337739	-1.755834
31	1.166824	-3.922294	-1.567257
31	-0.673004	-3.889865	1.161106
31	4.527598	-4.574034	-1.419701
31	2.532162	-4.416115	1.410192
31	-4.492006	2.464547	-1.472400
31	-4.061398	5.026468	0.706587
31	2.034904	1.317067	-1.195064

31	5.316961	0.732020	-1.049508
31	-0.806806	4.430316	0.738734
31	-1.205112	1.878958	-1.313980
31	-2.927383	1.948171	1.431090
31	0.245864	1.319231	1.525673
31	3.419306	0.861836	1.692569
31	2.375061	3.884386	0.855207
31	5.642131	3.349548	1.054159
31	4.098894	3.789413	-1.941112
31	0.919805	4.303954	-2.113066
31	-2.239475	4.912220	-2.168186

II-TS (doublet) in Scheme S3

E = -2611.04947898 a.u.

1	-3.363742	-1.375446	2.091345
1	-0.054076	-0.739764	3.691610
1	-0.140762	-1.610483	2.072378
1	0.177105	-1.662766	5.007289
1	-0.537759	-3.342058	3.523297
1	2.350941	-4.476235	3.649885
1	-3.989039	-3.994163	3.359386
1	3.034437	-1.885810	2.304427
1	-1.736235	-4.286001	3.120106
1	-5.524058	-2.320281	3.072188
1	-4.416302	-2.083200	4.083036
1	-2.743747	1.631096	3.759352
1	-2.969799	-0.391068	3.955837
1	-1.947445	-1.501295	4.294650
1	1.449998	0.000773	7.147840
1	1.399117	0.805984	5.865974
1	1.994455	0.237578	3.375546
1	-0.655609	1.626381	4.096587
1	-1.316655	1.871384	5.442596
1	0.950008	2.570763	4.778732
1	2.261088	1.918137	4.338481
1	-0.665690	0.137113	6.430966
1	-2.062845	-0.168851	5.907511
1	3.486462	3.303850	2.762867
1	-2.875866	3.915624	2.535837
1	0.315106	3.540343	2.644351
1	-4.222147	6.293795	0.768024
1	6.062442	3.469677	-1.322023
1	6.536329	2.978565	1.813911

1	2.143035	5.628446	1.036279
1	-0.955477	5.934895	0.930904
1	-5.491212	1.641422	0.893482
1	-6.393894	-1.225861	1.062641
1	-5.671480	-0.824908	-2.092264
1	-6.060130	1.766293	-2.283451
1	-5.224256	-5.095957	-0.092470
1	1.183568	-5.596288	0.204777
1	6.113331	-4.859083	-2.203280
1	5.285248	-4.921308	0.935867
1	6.129230	-2.386528	1.436503
1	5.734387	0.606825	1.294663
1	6.510806	0.569943	-1.824644
1	5.657551	-1.898446	-1.713708
1	-3.314163	-1.093218	-4.181600
1	-2.977123	1.719782	-3.213652
1	0.067182	-1.438370	-4.104045
1	0.265216	1.396254	-3.128556
1	3.438136	-1.746582	-3.952261
1	3.580197	1.083991	-3.000336
1	-6.630236	-3.669065	-2.647455
1	-6.017408	-3.837858	0.541737
1	-2.053906	-5.298501	-0.013303
1	-5.831519	4.127818	1.420461
1	5.343029	5.382482	1.102681
1	-5.103100	4.541477	-1.704233
1	4.279380	-5.980768	0.247653
1	3.781118	3.616169	-3.485551
1	3.903807	5.711049	-1.658387
1	0.529630	3.826703	-3.635401
1	0.682097	5.981946	-1.895956
1	-2.687332	4.209603	-3.699374
1	-2.531456	6.311163	-1.883136
1	-3.674024	-5.062153	-2.655660
1	-3.547818	-3.803895	-3.666762
1	-0.158911	-4.094029	-3.570101
1	-0.357946	-5.371984	-2.589884
1	3.104205	-4.496693	-3.380739
1	2.951730	-5.721473	-2.332665
7	-4.905225	-1.311186	-1.616277
7	-5.177989	-4.081547	0.013764
7	1.591667	-1.902650	-1.533062
7	4.786468	-2.226089	-1.285040
7	3.087625	-2.230031	1.339861
7	-1.974717	-4.282707	0.081555
7	-1.699047	-1.573994	-1.645349

7	-3.408518	-1.650993	1.105280
7	-0.151137	-1.912669	1.096818
7	1.273188	-4.579810	0.285988
7	4.442978	-4.979211	0.361385
7	-4.704659	1.228827	0.384046
7	-4.364916	4.041464	-1.199901
7	0.206429	0.956897	-2.204728
7	3.492809	0.656130	-2.073773
7	4.916704	0.331975	0.743239
7	-1.166938	3.728599	-1.139699
7	-2.901481	3.681921	1.539148
7	2.026877	3.430273	-1.041817
7	-3.060795	1.286148	-2.289389
7	-1.526814	0.936639	0.495423
7	1.740254	0.634901	0.556742
7	0.317651	3.272282	1.654109
7	5.206957	3.133660	-0.869734
7	3.555876	3.049135	1.773120
7	-3.592544	-4.044490	-2.675494
7	-0.249171	-4.356901	-2.587394
7	3.059348	-4.707338	-2.382747
8	-2.856132	-1.200955	4.496809
8	-0.192243	-1.752650	4.121560
8	2.868765	-5.026886	3.054432
8	-3.390198	-4.467583	2.761140
8	-0.748883	-4.185777	3.051270
8	-5.226754	-2.603009	3.943572
8	-3.368923	1.123618	3.218950
8	0.118600	0.482426	3.235756
8	1.165080	-0.063171	6.231089
8	2.960316	0.393061	3.392031
8	-1.068579	2.355148	4.636157
8	1.881757	2.487405	5.030054
8	-1.600319	0.365435	6.571846
31	-5.048575	-0.740532	0.319640
31	-5.313117	-3.232668	-1.868449
31	-3.229592	-0.694389	-2.621870
31	0.046742	-1.030137	-2.542263
31	3.322924	-1.329438	-2.399058
31	4.920060	-1.667100	0.659642
31	-3.560080	-3.610508	1.092280
31	-1.716313	-0.993822	0.256432
31	1.607581	-1.300751	0.352699
31	-1.896855	-3.499761	-1.769465
31	1.448210	-3.835074	-1.594906
31	-0.345119	-3.846514	1.090945

31	4.852794	-4.193296	-1.496312
31	2.910070	-4.179555	1.389006
31	-4.718009	2.095228	-1.451733
31	-4.471825	4.692884	0.716098
31	1.874887	1.483127	-1.221408
31	5.195860	1.158680	-1.097508
31	-1.165585	4.341883	0.751065
31	-1.386589	1.788939	-1.304227
31	-3.086011	1.714953	1.430894
31	0.134607	1.272390	1.574818
31	3.324206	1.089580	1.662225
31	2.033873	4.025306	0.856151
31	5.326773	3.762874	1.053230
31	3.746914	4.119213	-1.940226
31	0.538089	4.375327	-2.105261
31	-2.664735	4.715159	-2.154717

III (doublet) in Scheme S3

E = -2610.59972887 a.u.

1	-3.504441	-1.145273	2.063700
1	-0.317144	-1.633363	2.163978
1	-1.369116	-1.669819	4.739116
1	-1.310788	-2.916624	3.802465
1	1.282043	-5.118419	3.223352
1	-4.631528	-3.844308	3.159391
1	2.886869	-2.154143	2.387860
1	-1.867274	-4.700983	2.977598
1	-6.253840	-2.190966	2.475494
1	-5.478141	-1.871476	3.735238
1	-2.670004	1.798440	3.792481
1	-3.915596	-0.113655	4.062253
1	-3.451255	-1.513995	4.379395
1	1.254184	0.452283	7.217046
1	1.539372	1.137296	5.894786
1	2.255366	-0.171995	3.447746
1	-0.591354	1.831533	4.181777
1	-0.904687	2.381195	5.562392
1	1.201513	2.750859	4.606968
1	2.399285	1.858462	4.247057
1	-0.519371	0.028254	6.012803
1	-1.881792	0.251032	5.367628
1	3.787183	3.076571	2.772376
1	-2.592960	4.116197	2.538580

1	0.588922	3.574257	2.625974
1	-3.767154	6.546048	0.795446
1	6.428757	2.955361	-1.277041
1	6.809575	2.470467	1.868030
1	2.593515	5.488012	1.053903
1	-0.565413	6.006822	0.947703
1	-5.344364	2.006581	0.875947
1	-6.499824	-0.747505	0.911894
1	-5.661367	-0.391686	-2.164390
1	-5.892964	2.155645	-2.291025
1	-5.557978	-4.701748	-0.235902
1	0.789425	-5.656501	0.162132
1	5.765526	-5.326510	-2.089759
1	4.902636	-5.291726	1.033938
1	5.939664	-2.819147	1.539491
1	5.779554	0.170159	1.366908
1	6.605695	0.013237	-1.736400
1	5.546138	-2.327192	-1.610551
1	-3.265864	-0.843941	-4.189949
1	-2.816811	1.947096	-3.216319
1	0.044221	-1.426527	-4.051884
1	0.438013	1.393459	-3.108426
1	3.351049	-2.025509	-3.863777
1	3.736947	0.798702	-2.954408
1	-6.802951	-3.137623	-2.810971
1	-6.300309	-3.415774	0.397854
1	-2.439593	-5.121115	-0.056493
1	-5.557798	4.527732	1.420008
1	5.831226	4.952751	1.126690
1	-4.803142	4.871768	-1.693315
1	3.833411	-6.287772	0.343046
1	4.164734	3.293795	-3.445358
1	4.432794	5.371838	-1.649335
1	0.870172	3.829233	-3.590633
1	1.155052	5.914631	-1.815931
1	-2.401139	4.420763	-3.687254
1	-2.100745	6.479701	-1.873291
1	-3.953680	-4.757577	-2.695670
1	-3.710965	-3.526911	-3.718877
1	-0.406388	-4.020081	-3.567383
1	-0.689872	-5.287903	-2.595116
1	2.839569	-4.673026	-3.339732
1	2.542554	-5.890473	-2.314571
7	-4.945238	-0.942328	-1.681169
7	-5.460683	-3.692638	-0.113330
7	1.491749	-1.978563	-1.461804

7	4.644988	-2.585608	-1.197219
7	2.918549	-2.459891	1.410506
7	-2.286280	-4.115393	0.054620
7	-1.755121	-1.421935	-1.621311
7	-3.534526	-1.412439	1.075503
7	-0.288211	-1.916754	1.179116
7	0.937786	-4.648589	0.260556
7	4.064746	-5.299025	0.450600
7	-4.577525	1.551407	0.373249
7	-4.076827	4.342278	-1.205103
7	0.338331	0.969048	-2.181375
7	3.603397	0.393084	-2.023878
7	4.949582	-0.033246	0.803056
7	-0.884140	3.833125	-1.157100
7	-2.625119	3.876619	1.543986
7	2.359442	3.290967	-1.039856
7	-2.921743	1.517679	-2.292573
7	-1.425679	1.053866	0.506402
7	1.810226	0.530055	0.604444
7	0.590959	3.306669	1.638486
7	5.533846	2.715296	-0.843732
7	3.823740	2.821304	1.782035
7	-3.803067	-3.748045	-2.726794
7	-0.513528	-4.282484	-2.586680
7	2.746259	-4.890488	-2.346922
8	-4.195700	-0.914430	4.545373
8	-1.722922	-2.045983	3.918210
8	2.236777	-5.169715	3.087696
8	-3.912255	-4.270754	2.670881
8	-0.910046	-4.575917	2.891070
8	-6.140047	-2.495016	3.382077
8	-3.230129	1.276056	3.204325
8	0.083919	0.506531	3.221571
8	1.246142	0.290064	6.269081
8	3.065757	0.351463	3.476489
8	-0.863642	2.651186	4.638393
8	2.116710	2.567249	4.857989
8	-1.443568	-0.278706	6.041530
31	-5.072652	-0.377701	0.258883
31	-5.485695	-2.819291	-1.975203
31	-3.203704	-0.438600	-2.627087
31	0.035824	-0.995603	-2.490889
31	3.270973	-1.562701	-2.317255
31	4.789429	-2.022560	0.744534
31	-3.836034	-3.358639	1.038852
31	-1.758892	-0.877470	0.290626

31	1.506509	-1.404810	0.438166
31	-2.097884	-3.322472	-1.762412
31	1.195931	-3.889625	-1.564908
31	-0.645469	-3.866894	1.161072
31	4.552421	-4.548834	-1.411473
31	2.552536	-4.390795	1.412470
31	-4.533957	2.426310	-1.462599
31	-4.148896	4.965765	0.727190
31	2.057233	1.367951	-1.205564
31	5.344829	0.747234	-1.042695
31	-0.858762	4.424393	0.736970
31	-1.221629	1.917529	-1.322779
31	-2.941099	1.935153	1.431372
31	0.261091	1.369202	1.486114
31	3.433175	0.896242	1.677783
31	2.384202	3.890906	0.854884
31	5.670608	3.333587	1.085136
31	4.126308	3.782408	-1.883320
31	0.897589	4.306016	-2.021137
31	-2.320977	4.877719	-2.118027

IV (triplet) in Scheme S3

E = -2610.39760452 a.u.

1	-3.524920	-1.097895	2.059786
1	-0.342681	-1.652297	2.167485
1	-1.382562	-1.668467	4.741192
1	-1.346101	-2.914531	3.802960
1	1.232487	-5.160015	3.211737
1	-4.679477	-3.787374	3.158613
1	2.864881	-2.202666	2.387434
1	-1.949902	-4.675142	2.966882
1	-6.279240	-2.107994	2.473862
1	-5.498168	-1.811860	3.736098
1	-2.650380	1.819332	3.796287
1	-3.911377	-0.083572	4.067998
1	-3.458167	-1.489921	4.373525
1	1.263796	0.399606	7.237054
1	1.558567	1.095870	5.922957
1	2.252946	-0.222014	3.464766
1	-0.567287	1.816996	4.195488
1	-0.894164	2.392912	5.561499
1	1.227069	2.713558	4.648634
1	2.414554	1.813756	4.273581

1	-0.518657	0.018140	6.028799
1	-1.873507	0.259429	5.373891
1	3.787070	3.028916	2.795228
1	-2.510903	4.133896	2.559277
1	0.620850	3.529222	2.666918
1	-3.625895	6.616056	0.805802
1	6.387579	2.947569	-1.278567
1	6.783504	2.406658	1.862239
1	2.627747	5.461803	1.056139
1	-0.455873	6.008770	0.948640
1	-5.307030	2.101687	0.858453
1	-6.506655	-0.636224	0.913000
1	-5.659361	-0.304543	-2.172221
1	-5.819799	2.301409	-2.318219
1	-5.630433	-4.619886	-0.243189
1	0.724672	-5.675526	0.156159
1	5.712188	-5.368642	-2.109921
1	4.845593	-5.346649	1.016663
1	5.918383	-2.863070	1.534121
1	5.770978	0.122335	1.364846
1	6.602913	0.006555	-1.741199
1	5.514623	-2.375496	-1.618479
1	-3.268178	-0.786487	-4.197601
1	-2.756351	1.982677	-3.219982
1	0.026403	-1.438335	-4.059234
1	0.461877	1.374984	-3.106445
1	3.318296	-2.041742	-3.872955
1	3.723958	0.770438	-2.951171
1	-6.848600	-3.026386	-2.814930
1	-6.351716	-3.322203	0.391376
1	-2.523055	-5.090190	-0.059521
1	-5.443237	4.602724	1.410371
1	5.846193	4.921143	1.142343
1	-4.637513	4.972148	-1.692630
1	3.770739	-6.331532	0.319321
1	4.128932	3.252628	-3.446995
1	4.412839	5.354748	-1.641591
1	0.917816	3.765500	-3.608050
1	1.233430	5.901559	-1.859289
1	-2.251814	4.450199	-3.686373
1	-1.921625	6.517473	-1.847759
1	-4.029733	-4.698764	-2.712504
1	-3.762331	-3.465868	-3.726848
1	-0.460773	-4.024335	-3.572472
1	-0.758349	-5.286756	-2.598160
1	2.784891	-4.692485	-3.351498

1	2.486140	-5.916424	-2.334865
7	-4.953369	-0.865713	-1.685812
7	-5.515889	-3.612721	-0.118671
7	1.465793	-2.004396	-1.462128
7	4.612320	-2.626789	-1.202891
7	2.894821	-2.503056	1.408310
7	-2.348411	-4.087437	0.049056
7	-1.774396	-1.407685	-1.625382
7	-3.558360	-1.362656	1.070966
7	-0.314631	-1.930302	1.180873
7	0.880235	-4.668553	0.254904
7	4.008259	-5.344784	0.432291
7	-4.548360	1.629093	0.358883
7	-3.947187	4.407020	-1.189032
7	0.353662	0.946631	-2.182087
7	3.599760	0.358610	-2.021844
7	4.940599	-0.077419	0.799718
7	-0.798903	3.811971	-1.119906
7	-2.554730	3.898167	1.563721
7	2.358362	3.242025	-1.001321
7	-2.881080	1.557532	-2.296525
7	-1.414087	1.055329	0.511000
7	1.807772	0.490620	0.615113
7	0.624311	3.268742	1.676643
7	5.507790	2.682072	-0.825649
7	3.832050	2.769299	1.805734
7	-3.858647	-3.692203	-2.736248
7	-0.570275	-4.283315	-2.590986
7	2.692445	-4.916675	-2.359964
8	-4.195957	-0.884207	4.547576
8	-1.732500	-2.031381	3.912638
8	2.187047	-5.210605	3.076258
8	-3.965016	-4.217459	2.666347
8	-0.988398	-4.582978	2.881851
8	-6.171825	-2.420060	3.378381
8	-3.217286	1.306184	3.206390
8	0.091395	0.471853	3.240291
8	1.252393	0.249091	6.287192
8	3.062694	0.302787	3.489182
8	-0.815308	2.651896	4.636684
8	2.145764	2.526510	4.885330
8	-1.446889	-0.276735	6.050103
31	-5.076950	-0.300264	0.251514
31	-5.525836	-2.738040	-1.979075
31	-3.205585	-0.403908	-2.632175
31	0.019943	-1.021413	-2.498595

31	3.245291	-1.605126	-2.321847
31	4.765563	-2.074574	0.739304
31	-3.889338	-3.308163	1.034464
31	-1.773110	-0.878960	0.290416
31	1.484073	-1.447788	0.443242
31	-2.147324	-3.308792	-1.770088
31	1.145670	-3.916943	-1.572389
31	-0.700396	-3.880108	1.155784
31	4.502888	-4.592640	-1.425203
31	2.504092	-4.433218	1.402342
31	-4.465979	2.506108	-1.468621
31	-4.028504	5.048221	0.733507
31	2.057317	1.313706	-1.188633
31	5.334013	0.708552	-1.036924
31	-0.781902	4.439075	0.767092
31	-1.183616	1.899699	-1.310742
31	-2.918340	1.958665	1.439796
31	0.264618	1.330002	1.510139
31	3.430113	0.839068	1.695677
31	2.408239	3.872836	0.884319
31	5.665462	3.311544	1.092841
31	4.134003	3.778608	-1.910522
31	0.958175	4.316341	-2.081987
31	-2.198195	4.945949	-2.141570

V (restricted singlet) in Scheme S3

E = -2686.84566332 a.u.

1	-3.463127	-1.298915	2.064963
1	-0.266928	-1.637107	2.120424
1	-0.655409	-2.648826	5.489963
1	-0.747820	-3.879197	3.539203
1	1.560405	-5.160537	3.194590
1	-4.158867	-3.914162	3.255949
1	2.992129	-2.042306	2.325713
1	-1.959465	-4.614100	2.914044
1	-5.686927	-2.179560	2.947531
1	-4.645865	-1.951181	4.029113
1	-2.800410	1.771779	3.762085
1	-3.148945	-0.272269	3.956836
1	-2.367438	-1.557035	4.359277
1	1.943981	-0.190178	6.373090
1	1.609970	1.247255	5.987310
1	2.626684	-0.039204	3.523456

1	-0.689383	1.828422	4.086642
1	-1.228253	2.073268	5.459843
1	1.152835	2.677316	4.605863
1	2.469157	1.962408	4.238721
1	-0.719437	0.223954	6.341246
1	-2.134799	-0.030381	5.826111
1	3.731497	3.234076	2.671449
1	-2.757855	4.019914	2.516128
1	0.458913	3.575867	2.615289
1	-4.032359	6.417401	0.776214
1	6.267929	3.200726	-1.443153
1	6.731050	2.756154	1.717448
1	2.321873	5.580177	1.012135
1	-0.749251	5.964463	0.946467
1	-5.434082	1.809907	0.877377
1	-6.442002	-1.021441	1.007639
1	-5.693113	-0.597374	-2.137630
1	-6.019650	1.943044	-2.293269
1	-5.449059	-4.894098	-0.198298
1	0.974235	-5.637683	0.141493
1	5.917055	-5.118426	-2.193675
1	5.091810	-5.105433	0.943888
1	6.035970	-2.592851	1.439464
1	5.803998	0.382140	1.215405
1	6.535454	0.261976	-1.936239
1	5.585998	-2.123220	-1.722718
1	-3.312196	-0.966793	-4.197313
1	-2.939251	1.847518	-3.236580
1	0.053303	-1.422763	-4.076908
1	0.357506	1.405464	-3.114000
1	3.335421	-1.903435	-3.930095
1	3.586065	0.933728	-3.015349
1	-6.737444	-3.396672	-2.781556
1	-6.181133	-3.596863	0.430393
1	-2.259859	-5.217021	-0.113774
1	-5.728504	4.327279	1.430014
1	5.647088	5.189113	0.952962
1	-5.019727	4.702184	-1.699424
1	4.054193	-6.143745	0.268307
1	3.916054	3.433308	-3.533697
1	4.159418	5.522965	-1.744666
1	0.668224	3.833305	-3.622913
1	0.904900	5.941471	-1.868944
1	-2.600309	4.344465	-3.694901
1	-2.376081	6.404629	-1.869562
1	-3.827662	-4.894977	-2.723507

1	-3.658374	-3.648590	-3.742126
1	-0.283025	-4.043733	-3.617399
1	-0.543063	-5.315458	-2.643062
1	2.942521	-4.602977	-3.392830
1	2.711798	-5.813433	-2.342594
7	-4.951697	-1.123668	-1.665088
7	-5.352582	-3.883216	-0.093371
7	1.521528	-1.935371	-1.492131
7	4.704367	-2.418217	-1.292103
7	3.014499	-2.355516	1.349930
7	-2.145717	-4.206649	0.001754
7	-1.748072	-1.483126	-1.647019
7	-3.481359	-1.549594	1.071644
7	-0.241754	-1.938530	1.143675
7	1.089435	-4.625358	0.239638
7	4.247918	-5.146363	0.370419
7	-4.659075	1.382325	0.362688
7	-4.275248	4.195314	-1.214463
7	0.254983	0.974368	-2.190141
7	3.513362	0.518863	-2.081808
7	4.968006	0.155805	0.669129
7	-1.061184	3.800973	-1.172446
7	-2.778417	3.791452	1.518504
7	2.190466	3.363582	-1.078386
7	-3.024285	1.415863	-2.311919
7	-1.483886	1.008770	0.476573
7	1.789133	0.575743	0.622261
7	0.460745	3.294889	1.631004
7	5.400157	2.919331	-0.980929
7	3.740973	2.988197	1.677891
7	-3.718351	-3.879970	-2.749714
7	-0.395199	-4.305357	-2.636919
7	2.876809	-4.807115	-2.394866
8	-3.162543	-1.039311	4.568306
8	-0.794615	-2.516132	4.546618
8	2.510056	-5.099648	3.043565
8	-3.622199	-4.429000	2.633018
8	-0.966248	-4.576206	2.876148
8	-5.413240	-2.509573	3.810135
8	-3.374928	1.250040	3.186917
8	-0.349323	0.374616	3.104264
8	1.197905	0.407174	6.258760
8	3.398920	0.533421	3.444760
8	-0.916247	2.565030	4.680496
8	2.089065	2.625487	4.845826
8	-1.636728	0.500278	6.467540

31	-5.077935	-0.564738	0.277694
31	-5.424101	-3.018375	-1.966991
31	-3.243569	-0.546581	-2.639958
31	0.023373	-0.992250	-2.518021
31	3.271028	-1.447352	-2.382635
31	4.860697	-1.837528	0.641793
31	-3.718396	-3.496742	0.998252
31	-1.752722	-0.922429	0.262348
31	1.555306	-1.360224	0.404718
31	-2.013971	-3.389294	-1.827343
31	1.306737	-3.854535	-1.613885
31	-0.516061	-3.863702	1.044052
31	4.688016	-4.384606	-1.498305
31	2.723905	-4.295224	1.366354
31	-4.667226	2.263663	-1.472279
31	-4.349044	4.823014	0.716443
31	1.956708	1.433035	-1.218304
31	5.281510	0.946582	-1.183296
31	-1.027591	4.381624	0.725301
31	-1.337908	1.878405	-1.342462
31	-3.028239	1.841244	1.402348
31	0.201931	1.350910	1.472884
31	3.459917	1.044168	1.613089
31	2.218989	3.974384	0.812148
31	5.552740	3.565663	0.936387
31	3.914932	3.922097	-1.971706
31	0.689983	4.325525	-2.058476
31	-2.539138	4.797872	-2.124050
8	0.720670	-0.390379	3.679561
1	0.793916	0.000284	4.576154
1	-0.163567	-1.815143	4.302854

VI (restricted singlet) in Scheme S3

E = -2686.38903684 a.u.

1	-3.454622	-1.288269	2.058090
1	-0.257752	-1.653978	2.117641
1	-0.754163	-3.294401	3.903258
1	1.519985	-5.134951	3.145558
1	-4.256399	-3.873832	3.254333
1	2.989862	-2.036528	2.330230
1	-1.666240	-4.807419	2.920714
1	-5.726422	-2.095410	2.869291
1	-4.709176	-1.902478	3.981076

1	-2.833307	1.748571	3.747726
1	-3.158817	-0.307199	3.939533
1	-2.410525	-1.617243	4.340475
1	1.851994	-0.212449	6.401293
1	1.540373	1.223667	5.987766
1	2.581144	-0.018637	3.534301
1	-0.720693	1.834472	4.078810
1	-1.284519	2.075939	5.442203
1	1.113662	2.673635	4.617523
1	2.431263	1.957496	4.256595
1	-0.792790	0.250252	6.360969
1	-2.187314	-0.033227	5.807864
1	3.690284	3.247156	2.693467
1	-2.789432	4.004525	2.502399
1	0.425892	3.577915	2.614766
1	-4.075239	6.392968	0.756412
1	6.257573	3.240490	-1.402559
1	6.704101	2.796540	1.759524
1	2.290920	5.592306	1.021066
1	-0.788183	5.961449	0.936354
1	-5.444520	1.783177	0.854718
1	-6.443428	-1.041257	0.972780
1	-5.680512	-0.642208	-2.154679
1	-6.019840	1.908853	-2.320962
1	-5.405585	-4.916514	-0.168963
1	1.028788	-5.629985	0.104705
1	5.957727	-5.067624	-2.188769
1	5.132555	-5.058754	0.947089
1	6.046210	-2.559515	1.451357
1	5.792083	0.411311	1.245990
1	6.546420	0.307852	-1.899358
1	5.604057	-2.081974	-1.704967
1	-3.289673	-0.992782	-4.202941
1	-2.936238	1.819357	-3.250321
1	0.061698	-1.414076	-4.081879
1	0.362424	1.409278	-3.115421
1	3.368476	-1.865983	-3.925873
1	3.600569	0.966483	-2.998915
1	-6.706844	-3.449731	-2.760064
1	-6.148123	-3.621513	0.448702
1	-2.250378	-5.228259	-0.094253
1	-5.759109	4.292501	1.402112
1	5.603925	5.220147	0.993552
1	-5.038029	4.671731	-1.723926
1	4.115341	-6.119127	0.273288
1	3.922850	3.463036	-3.511988

1	4.135368	5.549722	-1.718164
1	0.666641	3.841209	-3.621676
1	0.879753	5.946320	-1.863177
1	-2.610156	4.326331	-3.709664
1	-2.404115	6.389053	-1.886958
1	-3.785086	-4.926832	-2.711868
1	-3.621727	-3.676195	-3.726453
1	-0.277325	-4.050172	-3.607982
1	-0.503739	-5.320277	-2.623770
1	2.992233	-4.557369	-3.404957
1	2.757403	-5.779251	-2.369152
7	-4.935348	-1.157445	-1.676384
7	-5.315772	-3.904319	-0.070920
7	1.539578	-1.917817	-1.498944
7	4.721711	-2.383769	-1.280706
7	3.022099	-2.344233	1.353019
7	-2.126866	-4.218868	0.019494
7	-1.731221	-1.496545	-1.645752
7	-3.471518	-1.553262	1.068889
7	-0.233278	-1.952508	1.139572
7	1.130710	-4.616639	0.206060
7	4.290002	-5.118197	0.373420
7	-4.665839	1.360119	0.342085
7	-4.292682	4.169515	-1.235450
7	0.259296	0.976819	-2.192352
7	3.523787	0.546569	-2.068063
7	4.960848	0.182718	0.693551
7	-1.077032	3.793557	-1.180223
7	-2.805133	3.775820	1.504761
7	2.177547	3.375671	-1.068915
7	-3.022344	1.391976	-2.323820
7	-1.487200	1.000934	0.467321
7	1.781015	0.581236	0.624688
7	0.434491	3.299379	1.629723
7	5.387957	2.953557	-0.947309
7	3.710550	3.003374	1.699496
7	-3.683672	-3.911101	-2.735112
7	-0.368815	-4.308465	-2.624658
7	2.917756	-4.771693	-2.409871
8	-3.188903	-1.069462	4.554227
8	-0.892486	-2.563795	4.533178
8	2.476720	-5.097576	3.021518
8	-3.641577	-4.374122	2.696882
8	-0.705744	-4.732793	2.798408
8	-5.505797	-2.414107	3.751372
8	-3.400742	1.226352	3.166228

8	-0.368864	0.387400	3.100912
8	1.115849	0.394127	6.272338
8	3.363564	0.541608	3.458671
8	-0.958595	2.570406	4.669841
8	2.045663	2.611304	4.870385
8	-1.715878	0.522968	6.448544
31	-5.066333	-0.591589	0.261221
31	-5.391429	-3.062239	-1.949551
31	-3.226591	-0.576492	-2.642867
31	0.034280	-0.993165	-2.518821
31	3.286810	-1.419668	-2.375143
31	4.862080	-1.812151	0.657251
31	-3.677962	-3.510317	1.036420
31	-1.738301	-0.939945	0.266488
31	1.549005	-1.362192	0.407590
31	-1.985574	-3.409142	-1.791339
31	1.332750	-3.838609	-1.615564
31	-0.488589	-3.916573	1.111296
31	4.716667	-4.349587	-1.495729
31	2.738639	-4.288565	1.351328
31	-4.671855	2.233832	-1.493173
31	-4.378357	4.795340	0.695371
31	1.953340	1.442182	-1.209385
31	5.280860	0.979700	-1.153470
31	-1.055448	4.375626	0.717523
31	-1.342404	1.866790	-1.347953
31	-3.039238	1.821985	1.386550
31	0.188798	1.351162	1.470182
31	3.438669	1.056161	1.628485
31	2.191784	3.985422	0.822409
31	5.522225	3.595559	0.972816
31	3.903506	3.946770	-1.948309
31	0.675952	4.328286	-2.055065
31	-2.556193	4.780036	-2.138074
8	0.690283	-0.393215	3.674698
1	0.727009	-0.041391	4.588824
1	-0.270742	-1.881478	4.239475

VII (doublet) in Scheme S3

E = -2686.18713534 a.u.

1	-3.473805	-1.263968	2.046468
1	-0.275787	-1.678991	2.124710
1	-0.826967	-3.316157	3.894645

1	1.491696	-5.172147	3.138209
1	-4.299242	-3.844030	3.237096
1	2.980373	-2.072548	2.336584
1	-1.722703	-4.820188	2.901994
1	-5.751220	-2.048722	2.845337
1	-4.742645	-1.865188	3.966981
1	-2.819537	1.769120	3.741642
1	-3.184182	-0.281400	3.940177
1	-2.452738	-1.594943	4.354794
1	1.636162	-0.208128	6.593076
1	1.442346	1.188972	5.997583
1	2.581773	-0.060324	3.549305
1	-0.715340	1.816011	4.118880
1	-1.347445	2.106619	5.443576
1	1.139871	2.662246	4.624892
1	2.441025	1.906403	4.295207
1	-0.922909	0.328964	6.432111
1	-2.295220	0.028707	5.837446
1	3.680674	3.217721	2.721695
1	-2.739322	4.020580	2.507850
1	0.443884	3.551400	2.652164
1	-3.967059	6.452609	0.740207
1	6.205307	3.254507	-1.396286
1	6.675199	2.760701	1.754617
1	2.310179	5.580456	1.028360
1	-0.710387	5.968074	0.941009
1	-5.415133	1.848396	0.822790
1	-6.451868	-0.958799	0.948759
1	-5.668725	-0.584949	-2.179158
1	-5.958750	2.023532	-2.361452
1	-5.461101	-4.861674	-0.191573
1	0.995638	-5.647910	0.102149
1	5.934016	-5.089112	-2.196445
1	5.102736	-5.097742	0.940305
1	6.037818	-2.579337	1.455241
1	5.787843	0.386250	1.249776
1	6.542323	0.329672	-1.897081
1	5.589796	-2.109199	-1.704484
1	-3.268137	-0.947797	-4.219999
1	-2.871495	1.847332	-3.256959
1	0.066019	-1.421204	-4.086450
1	0.387872	1.399658	-3.106630
1	3.351892	-1.867233	-3.927108
1	3.581307	0.954994	-2.985312
1	-6.727357	-3.371802	-2.790897
1	-6.182945	-3.553828	0.423595

1	-2.302136	-5.214450	-0.105440
1	-5.673278	4.352555	1.364386
1	5.600049	5.214243	1.014191
1	-4.894061	4.750262	-1.748468
1	4.081724	-6.149353	0.259151
1	3.875003	3.436415	-3.509905
1	4.090331	5.548982	-1.705276
1	0.709756	3.794873	-3.635503
1	0.944122	5.945433	-1.890998
1	-2.468155	4.330567	-3.720446
1	-2.249819	6.417341	-1.886419
1	-3.824678	-4.892712	-2.726766
1	-3.640405	-3.644849	-3.740883
1	-0.298209	-4.048050	-3.614040
1	-0.537639	-5.319222	-2.634683
1	2.965121	-4.568891	-3.408543
1	2.730654	-5.796076	-2.379244
7	-4.931218	-1.107229	-1.696323
7	-5.354031	-3.851081	-0.093688
7	1.528702	-1.935240	-1.491548
7	4.706649	-2.407034	-1.278824
7	3.010883	-2.375287	1.357630
7	-2.163750	-4.207015	0.009896
7	-1.735431	-1.488925	-1.650201
7	-3.490013	-1.525614	1.056121
7	-0.251588	-1.969624	1.144228
7	1.099931	-4.634810	0.205203
7	4.260509	-5.149681	0.365304
7	-4.639760	1.413326	0.314548
7	-4.182736	4.216302	-1.240009
7	0.274145	0.960083	-2.188094
7	3.517948	0.528481	-2.056275
7	4.955747	0.159173	0.697589
7	-1.002899	3.773357	-1.143282
7	-2.759286	3.792323	1.509673
7	2.166301	3.336028	-1.023861
7	-2.981368	1.420962	-2.332234
7	-1.474676	0.997245	0.475942
7	1.778103	0.551036	0.649240
7	0.454788	3.271256	1.666785
7	5.351308	2.942970	-0.923979
7	3.711715	2.969352	1.728502
7	-3.709428	-3.878338	-2.749585
7	-0.394754	-4.308405	-2.631665
7	2.891718	-4.788324	-2.414377
8	-3.227467	-1.038538	4.559419

8	-0.961521	-2.580258	4.519152
8	2.448568	-5.129821	3.018017
8	-3.687886	-4.348843	2.679732
8	-0.760410	-4.752599	2.789427
8	-5.538176	-2.373840	3.726864
8	-3.396698	1.256398	3.160429
8	-0.360671	0.360574	3.137252
8	0.958162	0.380938	6.247730
8	3.362931	0.502464	3.476962
8	-0.988965	2.571456	4.667243
8	2.055921	2.555204	4.914456
8	-1.850142	0.599722	6.483998
31	-5.066095	-0.541059	0.239044
31	-5.410526	-3.010584	-1.972898
31	-3.214904	-0.555770	-2.656577
31	0.033928	-1.015783	-2.523532
31	3.275553	-1.448048	-2.371826
31	4.850157	-1.843819	0.659320
31	-3.715435	-3.484414	1.021246
31	-1.744923	-0.949263	0.266387
31	1.535642	-1.396856	0.421195
31	-2.008496	-3.403433	-1.800926
31	1.307899	-3.860010	-1.616119
31	-0.522074	-3.936162	1.107190
31	4.692813	-4.376999	-1.499709
31	2.713719	-4.321232	1.349866
31	-4.615644	2.289450	-1.512365
31	-4.284768	4.864534	0.678236
31	1.948142	1.394656	-1.178209
31	5.267635	0.964539	-1.141108
31	-0.998525	4.392548	0.746097
31	-1.307842	1.846644	-1.332392
31	-3.022384	1.835464	1.386164
31	0.190856	1.315814	1.511157
31	3.439279	1.015392	1.654048
31	2.202445	3.980383	0.858779
31	5.505482	3.597076	0.986639
31	3.899299	3.959951	-1.973518
31	0.722882	4.352248	-2.111767
31	-2.452539	4.833679	-2.177171
8	0.694414	-0.453082	3.672108
1	0.736207	-0.127752	4.597957
1	-0.314260	-1.917484	4.237362

VIII (doublet) in Scheme S3

E = -2685.74714759 a.u.

1	-3.441691	-1.310843	2.079547
1	-0.266311	-1.728875	2.128174
1	-0.582936	-3.308296	3.933114
1	1.524854	-5.128074	3.152129
1	-4.229004	-3.894312	3.276337
1	2.985502	-2.039257	2.340322
1	-1.645648	-4.782005	2.951632
1	-5.654136	-2.066340	2.953691
1	-4.593127	-1.936595	4.034819
1	-3.218616	1.753651	3.809705
1	-2.981714	-0.423803	3.962473
1	-2.211850	-1.709180	4.400564
1	1.194965	-0.344256	5.372183
1	1.482551	1.030946	5.899713
1	2.888767	-0.112591	3.639826
1	-1.240150	2.800251	3.719204
1	-1.227939	2.180420	5.104824
1	0.942998	2.597126	4.575889
1	2.296206	1.930710	4.219478
1	-0.592467	0.462544	6.199235
1	-1.978918	0.046154	5.696009
1	3.664847	3.278373	2.675289
1	-2.818376	4.002747	2.537716
1	0.478040	3.620277	2.595635
1	-4.098393	6.362115	0.803516
1	6.240034	3.250570	-1.416696
1	6.684789	2.808924	1.744435
1	2.281970	5.620565	0.971856
1	-0.862204	5.976778	0.956308
1	-5.439017	1.761123	0.887439
1	-6.430770	-1.061129	1.023694
1	-5.690866	-0.656453	-2.119605
1	-6.034528	1.882892	-2.291191
1	-5.416406	-4.930662	-0.140687
1	1.055065	-5.642020	0.094893
1	5.959691	-5.054219	-2.186271
1	5.136216	-5.049421	0.950962
1	6.042730	-2.540679	1.458991
1	5.779327	0.427953	1.245309
1	6.537054	0.316184	-1.897741
1	5.598016	-2.069082	-1.699362
1	-3.308254	-0.999233	-4.180102
1	-2.945600	1.809414	-3.217828

1	0.051991	-1.416105	-4.068358
1	0.330979	1.408387	-3.100860
1	3.354648	-1.869475	-3.916870
1	3.592967	0.965847	-3.005894
1	-6.714788	-3.466051	-2.733411
1	-6.145280	-3.626888	0.475292
1	-2.259853	-5.248251	-0.100266
1	-5.784771	4.254050	1.433765
1	5.593280	5.236433	0.973655
1	-5.068946	4.651695	-1.688190
1	4.119334	-6.110556	0.277511
1	3.911789	3.451152	-3.538168
1	4.115402	5.553835	-1.759852
1	0.601021	3.841350	-3.619866
1	0.837701	5.944768	-1.857676
1	-2.647611	4.308320	-3.684527
1	-2.439095	6.375774	-1.865222
1	-3.788569	-4.931093	-2.711402
1	-3.634522	-3.670459	-3.714696
1	-0.276727	-4.033908	-3.604487
1	-0.497442	-5.314171	-2.632333
1	2.994106	-4.549861	-3.401487
1	2.758916	-5.770353	-2.364007
7	-4.943443	-1.173070	-1.646289
7	-5.317761	-3.918913	-0.047062
7	1.534060	-1.912122	-1.483494
7	4.717148	-2.374011	-1.274243
7	3.018794	-2.336783	1.360255
7	-2.129654	-4.240574	0.020987
7	-1.737740	-1.504079	-1.630265
7	-3.463666	-1.572297	1.089728
7	-0.238026	-1.981683	1.138723
7	1.139131	-4.627854	0.203613
7	4.293642	-5.109530	0.377433
7	-4.663657	1.340942	0.367410
7	-4.319440	4.151688	-1.203828
7	0.241326	0.974796	-2.176829
7	3.514949	0.550791	-2.073093
7	4.948798	0.197034	0.692596
7	-1.105761	3.785817	-1.155500
7	-2.826380	3.751163	1.545365
7	2.161836	3.380828	-1.094891
7	-3.035904	1.378888	-2.293120
7	-1.477270	0.985524	0.508998
7	1.776620	0.596035	0.622956
7	0.435362	3.337791	1.613649

7	5.369234	2.965225	-0.962504
7	3.691298	3.026997	1.683153
7	-3.690588	-3.914842	-2.725250
7	-0.368048	-4.301659	-2.623617
7	2.919167	-4.762793	-2.406180
8	-3.007513	-1.177000	4.586442
8	-0.668205	-2.608399	4.607490
8	2.481259	-5.089642	3.025426
8	-3.625036	-4.397212	2.709702
8	-0.686618	-4.731253	2.806327
8	-5.420301	-2.405191	3.824877
8	-3.315526	1.056500	3.153594
8	-0.039451	0.460464	3.261527
8	1.225643	0.143974	6.205102
8	3.446116	0.657531	3.490777
8	-0.974018	2.992151	4.623578
8	1.873896	2.549284	4.843557
8	-1.520908	0.753566	6.174318
31	-5.064764	-0.611265	0.292671
31	-5.398215	-3.077476	-1.925836
31	-3.240130	-0.587728	-2.619781
31	0.026450	-0.996389	-2.505566
31	3.278165	-1.416248	-2.367954
31	4.857171	-1.799143	0.662274
31	-3.673322	-3.531663	1.050605
31	-1.736443	-0.961103	0.282174
31	1.542747	-1.354577	0.427108
31	-1.990350	-3.417679	-1.785368
31	1.333419	-3.832670	-1.610713
31	-0.486662	-3.949128	1.103306
31	4.717855	-4.339615	-1.491460
31	2.740718	-4.282752	1.354185
31	-4.688665	2.215617	-1.463926
31	-4.409145	4.767592	0.728169
31	1.947167	1.446030	-1.218820
31	5.270148	0.989746	-1.156177
31	-1.088417	4.387701	0.735413
31	-1.358138	1.857337	-1.324276
31	-3.041992	1.801155	1.418548
31	0.204373	1.403295	1.445295
31	3.431487	1.076154	1.632302
31	2.193486	4.013734	0.783505
31	5.506477	3.612196	0.957144
31	3.887427	3.949300	-1.979970
31	0.639866	4.327427	-2.054427
31	-2.590230	4.767207	-2.115536

8	0.851103	-0.482934	3.413798
1	-0.065888	-1.913476	4.309284

-NH Deprotonation TS Structure (doublet) in Scheme S2

E = -2611.03270371 a.u.

1	-3.461759	-1.232393	2.090404
1	-1.060449	0.445673	3.296724
1	-0.669961	-1.856796	2.688153
1	-0.790775	-1.708818	4.401132
1	-0.859481	-3.164668	3.602068
1	1.495507	-5.102685	3.148307
1	-4.530476	-3.791019	3.247755
1	2.965277	-2.097167	2.370430
1	-1.175518	-5.159848	3.042778
1	-5.940051	-2.097308	2.736766
1	-5.153334	-1.850756	4.008822
1	-2.796845	1.734538	3.777539
1	-3.440673	-0.335447	4.155120
1	-3.071167	-1.798358	4.319525
1	0.218793	1.609202	7.164370
1	1.253080	1.570980	6.053082
1	2.308696	-0.116829	3.471276
1	-0.567102	2.192297	4.145587
1	-0.772704	2.909400	5.471922
1	1.321629	2.930483	4.509513
1	2.429042	1.885520	4.300797
1	-0.362820	-0.232184	5.994520
1	-1.803449	-0.740441	5.767187
1	3.600626	3.228889	2.753533
1	-2.747028	4.020150	2.518562
1	0.405988	3.633229	2.580497
1	-4.027005	6.405257	0.769875
1	6.252318	3.228663	-1.291382
1	6.646503	2.765814	1.864819
1	2.379353	5.594805	0.989911
1	-0.850529	5.998979	0.875851
1	-5.417274	1.822639	0.871408
1	-6.452017	-0.984885	0.960928
1	-5.652688	-0.618211	-2.139886
1	-5.982753	1.929689	-2.303128
1	-5.416904	-4.875486	-0.121698
1	1.023060	-5.660777	0.099207
1	5.978623	-5.065122	-2.167075

1	5.145297	-5.079757	0.973911
1	6.019062	-2.581312	1.529462
1	5.746845	0.389841	1.361477
1	6.576111	0.295346	-1.754541
1	5.624613	-2.088407	-1.630374
1	-3.218046	-1.012045	-4.159545
1	-2.902264	1.805957	-3.236706
1	0.062052	-1.452700	-4.047929
1	0.388856	1.374874	-3.111053
1	3.406704	-1.878548	-3.874525
1	3.657557	0.950093	-2.936568
1	-6.700570	-3.414054	-2.738070
1	-6.161723	-3.577134	0.483284
1	-2.284899	-5.241895	0.024595
1	-5.730263	4.306525	1.389977
1	5.557556	5.199977	1.098707
1	-4.984529	4.693720	-1.718241
1	4.142749	-6.147887	0.289452
1	3.986053	3.397007	-3.478206
1	4.145104	5.523686	-1.709123
1	0.706967	3.797284	-3.639229
1	0.889962	5.932011	-1.892733
1	-2.589706	4.289373	-3.731214
1	-2.357328	6.390362	-1.940765
1	-3.808920	-4.946507	-2.623563
1	-3.603874	-3.717349	-3.657645
1	-0.318926	-4.075543	-3.557753
1	-0.496794	-5.349387	-2.568464
1	3.025584	-4.553233	-3.389184
1	2.783272	-5.782568	-2.364085
7	-4.916809	-1.138993	-1.653096
7	-5.325951	-3.862648	-0.029874
7	1.555537	-1.933268	-1.470746
7	4.738433	-2.396611	-1.218983
7	2.999313	-2.380571	1.386041
7	-2.143365	-4.233002	0.123987
7	-1.713144	-1.528475	-1.607124
7	-3.473689	-1.516968	1.106737
7	-0.240420	-1.954920	1.180546
7	1.141647	-4.649696	0.202635
7	4.307060	-5.145796	0.394599
7	-4.641542	1.387379	0.364683
7	-4.245448	4.184078	-1.226657
7	0.279866	0.951769	-2.184379
7	3.556796	0.528055	-2.009030
7	4.927698	0.159505	0.791859

7	-1.056379	3.781928	-1.192686
7	-2.786391	3.771943	1.526020
7	2.182232	3.353173	-1.057609
7	-3.000442	1.387637	-2.307022
7	-1.472762	1.002597	0.469121
7	1.750782	0.579819	0.639268
7	0.436106	3.349876	1.597150
7	5.375589	2.935429	-0.852152
7	3.663024	2.963178	1.766550
7	-3.686849	-3.933452	-2.663442
7	-0.375852	-4.335739	-2.572153
7	2.941454	-4.774282	-2.396374
8	-3.596025	-1.105398	4.739459
8	-1.116937	-2.188779	3.582531
8	2.454627	-5.155303	3.019208
8	-3.816319	-4.268063	2.798122
8	-0.442791	-4.545515	2.928357
8	-5.872342	-2.398180	3.649570
8	-3.165867	1.083107	3.170117
8	-0.127908	0.708546	3.284377
8	0.758872	0.993685	6.660956
8	3.106093	0.424940	3.485128
8	-0.754038	3.074694	4.524215
8	2.169543	2.637857	4.869089
8	-0.889066	-1.042038	5.860711
31	-5.053403	-0.563006	0.279139
31	-5.390529	-3.044618	-1.912842
31	-3.205405	-0.585000	-2.600827
31	0.053627	-1.026987	-2.486386
31	3.312911	-1.436652	-2.322862
31	4.838897	-1.838288	0.724304
31	-3.701580	-3.473859	1.112901
31	-1.704090	-0.952740	0.331165
31	1.503825	-1.377928	0.473505
31	-1.990065	-3.451089	-1.717113
31	1.349575	-3.853674	-1.603267
31	-0.448995	-3.901769	1.118995
31	4.736196	-4.359922	-1.464485
31	2.743425	-4.334132	1.363906
31	-4.636567	2.252625	-1.474939
31	-4.342853	4.814372	0.702047
31	1.969063	1.409586	-1.179211
31	5.287226	0.959099	-1.046370
31	-1.049589	4.402795	0.693055
31	-1.305075	1.847198	-1.336183
31	-3.007967	1.818289	1.403528

31	0.179672	1.384167	1.518572
31	3.375973	1.016913	1.688297
31	2.199396	3.995082	0.818768
31	5.480245	3.578364	1.067669
31	3.935766	3.922351	-1.935920
31	0.712205	4.318954	-2.092505
31	-2.521898	4.786809	-2.179277

-N$^{\bullet-}$ Structure (doublet) in Scheme S2

E = -2610.61095071 a.u.

1	-3.507894	-1.135354	2.068881
1	-0.431895	-0.259966	3.192910
1	-1.271527	-1.584642	4.681731
1	-1.204601	-2.726697	3.625437
1	1.323508	-5.112206	3.246889
1	-4.590160	-3.821647	3.208417
1	2.909915	-2.119992	2.378916
1	-1.869514	-4.578580	3.035027
1	-6.211473	-2.178582	2.531781
1	-5.408898	-1.867013	3.777362
1	-2.591930	1.746469	3.781121
1	-3.868072	-0.106616	4.074200
1	-3.317756	-1.485691	4.320066
1	1.267519	0.637089	7.297145
1	1.595374	1.188166	5.924503
1	2.127302	0.082483	3.438822
1	-0.495763	1.735719	4.182922
1	-0.820203	2.331589	5.550307
1	1.276963	2.745466	4.585252
1	2.507337	1.890238	4.264866
1	-0.461643	0.027281	6.079550
1	-1.838164	0.241029	5.463695
1	3.792111	3.100708	2.747872
1	-2.604680	4.109449	2.536051
1	0.575838	3.561803	2.624247
1	-3.789980	6.537890	0.787789
1	6.407474	2.974293	-1.314692
1	6.809767	2.509132	1.831939
1	2.547164	5.487060	1.042597
1	-0.564288	5.987955	0.945311
1	-5.358557	1.994726	0.882243
1	-6.509830	-0.767245	0.922807
1	-5.680492	-0.423114	-2.155499

1	-5.911763	2.133205	-2.280866
1	-5.561621	-4.712677	-0.182799
1	0.853734	-5.687997	0.164385
1	5.772169	-5.318198	-2.089334
1	4.924715	-5.262447	1.038034
1	5.963336	-2.802255	1.517087
1	5.792024	0.194651	1.342193
1	6.593573	0.032739	-1.761586
1	5.552314	-2.317674	-1.629286
1	-3.294072	-0.861669	-4.192810
1	-2.834870	1.932054	-3.212831
1	0.029932	-1.441582	-4.054300
1	0.412643	1.385016	-3.111651
1	3.356270	-2.027879	-3.883589
1	3.722086	0.806741	-2.970856
1	-6.812690	-3.179744	-2.768093
1	-6.296541	-3.416319	0.439702
1	-2.483776	-5.146208	-0.051902
1	-5.570790	4.516341	1.425827
1	5.812901	4.980997	1.084434
1	-4.825870	4.853757	-1.692264
1	3.856240	-6.267513	0.358838
1	4.131105	3.308938	-3.467069
1	4.399605	5.384926	-1.669042
1	0.837637	3.816206	-3.601778
1	1.120986	5.910739	-1.839858
1	-2.424045	4.409011	-3.685962
1	-2.126155	6.466338	-1.870563
1	-3.957742	-4.784131	-2.670583
1	-3.725223	-3.551590	-3.694042
1	-0.407547	-4.038267	-3.546748
1	-0.684514	-5.303800	-2.568936
1	2.839341	-4.677334	-3.329004
1	2.552125	-5.891821	-2.297237
7	-4.958103	-0.964577	-1.671156
7	-5.459667	-3.702840	-0.070749
7	1.496621	-1.980883	-1.478619
7	4.652214	-2.572941	-1.211630
7	2.939709	-2.441789	1.406611
7	-2.298643	-4.146816	0.069301
7	-1.768503	-1.436266	-1.628450
7	-3.538910	-1.414132	1.084524
7	-0.277279	-1.988463	0.963265
7	0.960323	-4.675660	0.272939
7	4.083943	-5.277096	0.458940
7	-4.590656	1.538557	0.382001

7	-4.098363	4.326357	-1.203633
7	0.320504	0.959820	-2.184132
7	3.590080	0.399072	-2.040889
7	4.956826	-0.014324	0.788181
7	-0.903681	3.821361	-1.159237
7	-2.638032	3.872137	1.541019
7	2.337487	3.294520	-1.054450
7	-2.939080	1.500573	-2.289890
7	-1.437452	1.047876	0.509101
7	1.815850	0.540352	0.592266
7	0.576574	3.282205	1.639800
7	5.516535	2.733085	-0.874014
7	3.822214	2.840093	1.758771
7	-3.810345	-3.774170	-2.701582
7	-0.512993	-4.297549	-2.564975
7	2.750862	-4.891024	-2.334886
8	-4.084528	-0.935625	4.544009
8	-1.526489	-1.821475	3.774356
8	2.277385	-5.148129	3.104414
8	-3.872006	-4.245064	2.715886
8	-0.910645	-4.462609	2.940356
8	-6.094530	-2.474074	3.440781
8	-3.244681	1.305305	3.220910
8	0.183842	0.487282	3.226888
8	1.284165	0.382655	6.369712
8	3.067313	0.325245	3.453218
8	-0.810046	2.560038	4.614701
8	2.191019	2.595085	4.862220
8	-1.370789	-0.322788	6.088685
31	-5.087392	-0.388912	0.265699
31	-5.491147	-2.848427	-1.944019
31	-3.225786	-0.454423	-2.631138
31	0.023258	-1.003483	-2.496013
31	3.277005	-1.558692	-2.339616
31	4.810896	-2.003665	0.729032
31	-3.827747	-3.360860	1.066599
31	-1.783454	-0.865707	0.286049
31	1.550101	-1.382896	0.424134
31	-2.102247	-3.340034	-1.745957
31	1.199622	-3.892118	-1.551195
31	-0.644436	-3.932246	1.158549
31	4.560283	-4.538676	-1.410737
31	2.570894	-4.371598	1.424655
31	-4.550581	2.408910	-1.457342
31	-4.164769	4.955635	0.727107
31	2.041637	1.370993	-1.216957

31	5.332665	0.763546	-1.063731
31	-0.867608	4.406215	0.737546
31	-1.237608	1.904921	-1.316881
31	-2.951273	1.930126	1.436956
31	0.252103	1.338666	1.509657
31	3.439883	0.910398	1.674079
31	2.359213	3.886195	0.844492
31	5.660708	3.360582	1.050593
31	4.097964	3.794404	-1.903629
31	0.869860	4.299722	-2.033975
31	-2.343811	4.863913	-2.115763