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Effects of single Water Molecule on Proton Transfer Reaction in Uracil Dimer Cation

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Abstract: Ionizing radiation to DNA induces sometimes the DNA damage. In this report, the ionization dynamics of uracil dimer (U_2) and its water complex (U_2 -H₂O) have been investigated by means of direct ab-initio molecular dynamics (AIMD) method in order to elucidate the effects of single water molecule on the reaction rate of proton transfer (PT) in DNA model base pair. The (U_2) dimer is widely used as a simplified mimetic model of Watson-Crick base pair. The static ab-initio calculation showed that two conformers exist as neutral complex of (U_2 -H₂O). The direct AIMD calculation of ionization process of (U_2 -H₂O) showed that the rate of PT is affected even by a single water molecule, while it was dependent on the position of H₂O around (U_2). The interaction of water molecule with (U_2) affected the potential energy curve for PT. Especially, the activation barrier along the PT coordinate was significantly changed by the interaction with one H₂O molecule. The effects of one H₂O molecule on the PT process were discussed on the basis of theoretical results.

Keywords: DNA damage; hydration effect; ionization; potential energy curve; barrier height

1. Introduction

High energy irradiation to the hydrogen bonded system is important in relevant with the initial process of DNA damage.¹⁻⁵ If DNA base pair is ionized by the irradiation, a proton is transferred into the neighbored base along the hydrogen bond, while a defect is formed in the damaged DNA. The defect leads to replication and transcriptional errors in DNA.

Excited states of DNA base pair and DNA model cluster have been considerable interest from experiments and theoretical calculations. 2-Aminopyridine dimer (AP)₂ is widely used as a simplified mimetic model of Watson-Crick base pair.⁶⁻¹⁰ Schultz et al. carried out femtosecond time-resolved mass spectroscopy of 2-aminopyridine monomer, dimer and clusters and showed that an excited-state lifetime of hydrogen-bonded dimer is significantly shorter than that of the monomer.⁶ Also, they suggested that the proton transfer is efficiently occurred as an energy migration process at the excited state of (AP)₂.

Uracil dimer (U)₂ is also used as a mimic model of base pair. Golan et al. investigated experimentally photo-ionization processes of uracil dimer using tunable vacuum ultraviolet synchrotron radiation technique.¹⁰ They showed uracil dimer cation leads to the proton transferred product after the ionization. They also measured the photo-ionization of methyl-uracil dimer (m-U)₂ having a pi-stacking structure. It was found that the proton transfer occurred in pi-stacked dimer.

As well as the excited states of (U)₂, the ionized states, (U)₂⁺, are important in the initial process of DNA damage. However, the investigation of (U)₂⁺ is limited, although the mechanism of proton transfer on the potential energy surface of ionized state of (U)₂ is strongly correlated with the DNA damage. In particular, the rate of proton transfer

and a lifetime of the ionized state play an important role in ability of self-defense of DNA.

In our previous work,¹¹ the reaction dynamics following the ionization of (AP)₂ was investigated by means of direct ab-initio molecular dynamics (AIMD) method to shed light on the mechanism of DNA self-defense against for cosmic ray (ionization). It was found that the reaction process is composed of three steps after the vertical ionization of (AP)₂: the approaching of dimer, proton transfer and energy relaxation processes.

In the present study, the effects of one water molecule on the proton transfer process in the (U)₂⁺ radical cation were investigated by means of direct ab-initio molecular dynamics (AIMD) method. Especially, we focus our attention on the effects of one water molecule on the rate of proton transfer in (U)₂⁺. The electronic states of DNA base pair are usually affected by the existence of water molecules.¹²

Some theoretical works for the effects of water molecules on the ionized states of DNA base pair have been carried out by several authors.¹³⁻¹⁸ Motegi and Takayanagi studied the micro hydration effects on the transformation from the dipole-bound to valence-bound anions of uracil and its vertical detachment energy.¹⁹ Thus, the static properties of DNA-H₂O base pair and base-H₂O complexes have been gradually accumulated from theoretical points of view. However, the dynamical property for DNA-H₂O system after the ionization is still not clearly understood. In the present work, we focus our attention on the effects of H₂O on the proton transfer dynamics in (U)₂⁺ to shed light on the dynamical features of ionized DNA-H₂O system.

2. Method of calculation

Ab-initio and density functional (DFT) calculations were carried out using Gaussian 09.²⁰ All geometry optimizations of (U)₂ dimer and water complexes (U)₂-H₂O were carried out at the MP2/6-311++G(d,p) and CAM-B3LYP/6-311++G(d,p) levels of theory. To confirm the stability of the molecules at all stationary points, the harmonic vibrational frequencies were calculated at the CAM-B3LYP/6-311++G(d,p) level of theory. We confirmed that all vibrational frequencies obtained are positive, indicating that all stationary points were located at the local minima on the ground state potential energy surface.

In the direct ab-initio molecular dynamics (AIMD) calculation, first, the structures of (U)₂ and (U)₂-H₂O were determined at the MP2/6-311++G(d,p) level. Using the optimized geometries, direct AIMD calculations were performed at the CAM-B3LYP/6-311G(d,p) level. Trajectories for the radical cation systems (U)₂⁺ and (U)₂-H₂O⁺ were then propagated from the vertical ionization point using the optimized structures of the neutral systems. Born-Oppenheimer approximation was used. The calculated values of $\langle S^2 \rangle$ were less than 0.765 at all trajectory points.

The equations of motion were numerically solved by the velocity Verlet algorithm method. No symmetry restriction was applied to the calculation of the energy gradients. The time step size was chosen to be 0.10 fs, and a total of 5,000-10,000 steps were calculated for each dynamics calculation. The trajectory calculations were performed under condition of constant total energy. The drift of the total energy was confirmed to be less than 0.01 kcal/mol throughout all trajectories. The trajectories for the cation system were run from the geometries of parent neutral systems on the assumption of vertical ionization. The electronic state of the system was monitored during the

simulation. We confirmed carefully that the electronic state is kept during the reaction. More details of the direct AIMD calculations are described elsewhere.²¹⁻²⁴

In addition to the trajectories from the equilibrium points, we generated geometries around the equilibrium points randomly and selected six geometries with the energy difference lower than 1.0 kcal/mol from the equilibrium point of (U)₂-H₂O (Frack-Condon (FC) sampling).

To check the effects of level of theory on the reaction rate of proton transfer in (U)₂⁺, five sets of method were examined as follows:

A: [CAM-B3LYP/6-311G(d,p): CAM-B3LYP/6-311G(d,p)]

B: [CAM-B3LYP/6-311G(d,p): CAM-B3LYP/6-311++G(d,p)]

C: [CAM-B3LYP/6-311G(d,p): CAM-B3LYP/6-311G(d,p)]

D: [CAM-B3LYP/6-311++G(d,p): MP2/6-311++G(d,p)]

E: [CAM-B3LYP/6-311++G(2d,2p): MP2/6-311++G(d,p)],

where [X:Y] means the AIMD calculation was carried out at the X level from the optimized structure obtained at the Y level. Note that all levels of theory gave the similar results as will be shown in section 3E.

2. Results

A. Structures of (U)₂ and (U)₂-H₂O

The structures and geometrical parameters of (U)₂ are given in Figure 1. Two hydrogen bonds connected the uracil monomers (U and U'), where U and U' mean uracil molecules play as proton donor and acceptor after the ionization, respectively. Circle drawn by dot curve means the proton transferred from U⁺ to U' after the ionization. The parameters R₁ and R₂ indicate the distances of hydrogen bond (H1-O1) and the N-H bond (N1-O1), respectively. The N1-O1 distance is expressed by R.

Figure 2 showed the optimized structures of the (U)₂ dimer and (U)₂-H₂O complexes obtained at the MP2/6-311++G(d,p) level. In (U)₂, the amino group of U orients to the C=O oxygen atom of ring of U' by a hydrogen bond. The distance of hydrogen bond of (U)₂ (H1-O1) was calculated to be R₁=1.784 Å, while the N1-H1 and N1-1 distances were R₂=1.030 Å and R=2.812 Å, respectively.

To obtain the hydration structures of (U)₂, several initial conformations of H₂O around (U)₂ were generated, and the geometry optimizations were carried out for the (U)₂-H₂O complexes. Two independent structures of (U)₂-H₂O were obtained at the MP2/6-311++G(d,p) level. One is NH form where H₂O orients to the proton of NH group of U: this form is denoted by (U)₂-H₂O(NH). The second one is CO form where H₂O orients to the C=O carbonyl site of (U)₂, which is denoted by (U)₂-H₂O(CO).

In the NH form, the hydrogen bond between U and U' was close to that of free (U)₂ (R₁=1.781 Å and R₂=1.030, and R=2.809 Å vs. R₁=1.784 Å, R₃=1.030 Å, and R=2.812 Å). In the CO form, the distances of hydrogen bond were calculated to be R₁=1.777 Å and R₂=1.030 Å. The intermolecular distance was R=2.806 Å. The water molecule orients the C=O carbonyl of U with the bond distance of 1.951 Å, and the C-H

hydrogen atom with the distance of 2.382 Å (O-H bond). The binding energies of H₂O to (U)₂ were 8.8 kcal/mol (NH form) and 7.6 kcal/mol (CO form) at the MP2/6-311++G(d,p) level.

B. Ionization of (U)₂

Snapshots

Snapshots of (U)₂⁺ after the ionization of neutral (U)₂ are illustrated in Figure 3. At time zero, the initial structure of dimer cation (U)₂⁺ corresponds to the parent neutral dimer (U)₂ optimized at the MP2/6-311++G(d,p) level. The distances of N-H bond (R₂) and hydrogen bond (R₁) were 1.030 Å and 1.783 Å, respectively. The intermolecular distance was R=2.811 Å at time zero. After the ionization, U⁺ and U' approached gradually each other, and the intermolecular distance (R) was changed from 2.811 Å (point **a**) to 2.768 Å (point **b**, 33 fs). The position of proton was R₁=1.680 Å and R₂=1.084 Å at 33 fs, indicating that the distance of proton from nitrogen atom (R₂) is hardly changed at 33 fs (point **b**). The U⁺ and U molecules further approached gradually, and the proton was transferred rapidly from N1 to O1 atoms of U' at 80 fs. At 120 fs, the proton transfer was completed, while a new O-H bond (O1-H1) was formed. The transferred proton did not return to the initial position (292 fs and point **d**).

Potential energy

Time evolution of potential energy of (U)₂⁺ is given in Figure 4. Zero level of potential energy corresponds to the total energy of (U)₂⁺ at the vertical ionization point of (U)₂ with the optimized geometry. Time profile of potential energy can be classified to three regions: (1) approaching of U⁺ to U' (point **a** → **b**), (2) proton transfer (points **b**

→ **c**) and (3) energy relaxation processes (point **c** → **d**).

First, the potential energy rapidly decreased from zero to -2.2 kcal/mol (time = 0.0-5.0 fs) due to the internal structural relaxation of U^+ . Next, the potential energy decreases gradually from -2.2 to -6.0 kcal/mol (time 5-60 fs). This energy lowering was caused by the approaching process of U^+ to U' . The potential energy was rapidly stabilized at around 80 fs (-6.0 to -10.0 kcal/mol) due to the proton transfer from U^+ to U' . After the proton transfer, the potential energy vibrated strongly as a function of time. The excess energy generated by the reaction (reaction energy) was gradually relaxed into the internal vibrational modes of dimer cation (energy relaxation process).

Time evolution of intermolecular distance (R) and bond distances of N-H (R_1) and O-H (R_2) are plotted in Figure 4 (lower). The intermolecular distance between U^+ and U' (R) decreased with increasing time, and it was first minimized at 80.5 fs (point **c**). At this point, the proton was transferred from U^+ to U' . The change of R_1 was faster than that of R , indicating that the proton is more rapidly transferred than the approaching of U^+ to U' . After the PT process, a new O-H bond was formed (See, time dependence of R_1). The intermolecular distance was significantly shortened from $R=2.811$ Å (time zero) to 2.400 Å (120 fs), which is 0.41 Å shorter than that of time zero. The proton transfer was completed at 150 fs. It should be noted that the proton transfer takes place at 80 fs in $(U)_2^+$. After the proton transfer, the potential energy curve vibrated strongly in the range (-10)-(-4) kcal/mol. This is due to the fact that the excess energy is changed to the internal energy of $(U)_2^+$.

C. Ionization dynamics of $(U)_2-H_2O(NH)$

Snapshots

Snapshots of $(U)_2^+-H_2O(NH)$ after the ionization of $(U)_2-H_2O(NH)$ are illustrated in Figure 5. The distances between U^+ and U' were $R_1=1.781 \text{ \AA}$ and $R_2=1.030 \text{ \AA}$. H_2O was located in $r_1=1.976$ and $r_2=2.007 \text{ \AA}$ at time zero. After the ionization, the H_2O molecule approached gradually to the NH proton of U^+ due to Coulomb attractive interaction between NH^+ and $O^{\delta-}$ of H_2O . At 20 fs, the distances of H_2O were $r_1=1.854$ and $r_2=2.331 \text{ \AA}$. Also, U^+ approached gradually to U' . At 49 fs (point c), the proton passed near transition state (TS): $R_1=1.396 \text{ \AA}$ and $R_2=1.157 \text{ \AA}$. Immediately, the proton transfer was completed at 64 fs (point d): $R_1=0.995 \text{ \AA}$ and $R_2=1.517 \text{ \AA}$. After the proton transfer, the H_2O molecule was strongly bound to the NH proton of U . Also, U approached to $U'(H^+)$ because U' has a positive charge (H^+) after the proton transfer.

Potential energy

Time evolution of potential energy for the NH form is given in Figure 6. After the ionization, the potential energy decreased to -8.0 kcal/mol (point a $\rightarrow$ b) due to the re-orientation of H_2O around NH^+ in addition to both structural relaxation of U^+ and approaching to U . The proton transfer occurred from 49 to 64 fs (point c $\rightarrow$ d). Time profiles of bond distances showed that the R_1 and R_2 distances are crossed at 55 fs. The structure of $(U)_2^+-H_2O$ was close to the transition state for the PT process. The proton transfer takes place at 64 fs. It should be noted that the reaction time of PT in the NH form is significantly faster than that of $(U)_2$ (64 vs. 80 fs).

D. Ionization dynamics of $(U)_2-H_2O(CO)$

Snapshots

Snapshots of $(U)_2^+-H_2O(CO)$ are illustrated in Figure 7. At time zero, the proton and

oxygen atom of H₂O molecule oriented to the oxygen atom of C=O carbonyl and the C-H atom of U⁺, respectively. The distance of hydrogen bond between U⁺ and H₂O was 1.951 Å as the O-H distance (r₁). The distances between U⁺ and U' were R₁=1.777 Å and R₂=1.030 Å. The intermolecular distance between U⁺ and U' were R=2.806 Å at time zero.

After the ionization, the H₂O molecule leaved from the C=O carbonyl, and it approached gradually to the CH group of U⁺ due to Coulomb repulsive interaction between C=O⁺ and H^{δ+} of H₂O. The attractive interaction was formed between the oxygen atom of H₂O and the C-H proton of U⁺. At 52 fs (point b), the intermolecular distance between U⁺ and U' was R=2.582 Å, which was shorter than that at time zero (R=2.806 Å). Around 100 fs, the proton was transferred from U⁺ to U': R₁=1.053 Å, R₂=1.384 Å, and R=2.430 Å. However, the proton returned from U' to U at 160 fs. This feature was significantly different from those of (U)₂⁺ and (U)₂-H₂O(NH). Thus, H₂O attached to the CO carbonyl suppressed the proton transfer reaction.

Potential energy

Time evolution of potential energy for (U)₂⁺-H₂O(CO) is given in Figure 8. The potential energy decreased gradually to -8.2 kcal/mol at 52 fs. Time evolution of R₁ indicated that the movement of proton accelerates at 90 fs, and the proton transfer occurred from 98-102 fs. The R₁ and R₂ distances were crossed at 96 fs, where the intermolecular distance was minimized (2.45 Å). The result indicates that the proton transfer takes place at the nearest intermolecular distance. This feature was the same as that of (U)₂. The proton transfer was completed at 108 fs. However, the proton returned from U' to U at 150 fs. The large H₂O movement was found at 300-400 fs. This feature

is a specific point observed in the water-(U)₂ system.

E. Summary of the direct AIMD calculations

The reaction rates of the proton transfer (PT) are calculated from the optimized geometries were 64 fs (non-H₂O), 80 fs (NH site), and 108 fs (CO site), indicating that the H₂O molecule in the NH site accelerates the rate of PT, whereas H₂O in the CO site suppresses. To confirm these specific features, the direct AIMD calculations were further carried out from the geometries in the FC region. Six points were selected. The results are given in Figure 9. The PT rates in (U)₂ without H₂O were distributed in the range 80-88 fs, while the average was calculated to be 81.9 fs. The average values of PT rates in NH and CO forms were 63.4 and 106.8 fs, respectively. These results suggests that the PT rates were expressed by $v(\text{NH}) > v(\text{non-H}_2\text{O}) > v(\text{CO})$.

To elucidate the method dependency on the reaction rate, five sets of methods were examined in the direct AIMD calculations. The results are given in Figure 10. It was clearly shown that the tendency of reaction rates is the same as those in Figure 9.

4. Discussion

The present calculations showed that the reaction rate of proton transfer (PT) is strongly affected even by a single water molecule. Also, the PT rate was strongly dependent on the position of H₂O around (U)₂. The water molecule in the NH site accelerated the PT rate in (U)₂⁺, whereas H₂O in the CO site was suppressed.

To elucidate these specific features shown in the effects of one H₂O molecule, the effects of the ionization on the atomic charges of (U)₂ were analyzed in detail. The potential energy curves for the proton transfer from U⁺ to U' were calculated along the

reaction coordinate, and the results are plotted in Figure 11. The geometries of $(U)_2^+$ and $(U)_2^+ \cdot H_2O$ except for the transferred proton were fixed to those of optimized structures calculated at the MP2/6-311++G(d,p) level, and the proton was only varied in the calculations. The calculations were carried out. The activation energies for PT in $(U)_2^+$, NH, and CO forms were 8.5, 6.5, and 8.6 kcal/mol, respectively. The barrier height in the NH form was significantly lower than those of non- H_2O and the CO form. This feature is the origin of fast PT in the NH form.

In the present study, several approximations were employed in the calculations. First, thermal and zero point energies (ZPEs) were neglected in the dynamics calculations because the effects of single water molecule on the reaction dynamics are purely interested in this work. In actual system, however, the DNA base pair exists under thermal energy and ZPEs. To simulate the actual system, the inclusion of these effects would be needed as a future work. Hence, it should be noted that the present model is limited in case of zero kelvin.

Next, the CAM-B3LYP functional was used in the direct AIMD calculation because this level is limited in our computer facility. To check the energetics of the functional, the energy diagram was calculated and was compared with that of the MP2 calculations. The result is given in Figure 12. Both calculations gave the same dimerization energy (18.6 kcal/mol): $U + U \rightarrow (U)_2$. The vertical ionization energies (I_p) were calculated to be 9.69 eV (MP2) and 9.36 eV (CAM-B3LYP). The reaction energy calculated by the CAM-B3LYP functional was 12.4 kcal/mol, which is in reasonable agreement with the MP2 calculation (14.5 kcal/mol). These results suggest that the CAM-B3LYP functional would give a reasonable energetics for the reaction of uracil dimer system. Despite several approximations employed here, it has been shown that a theoretical

characterization of PT dynamics enable us to obtained valuable information on the effects of single water molecule on the reaction mechanism of uracil dimer cation.

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Figure captions

Figure 1 (Color online). Structure and geometrical parameters of uracil dimer $(U)_2$. U and U' means proton donor and acceptor U molecules, respectively.

Figure 2 (Color online). Optimized structures of uracil dimer $(U)_2$ and uracil dimer-water complexes $(U)_2\text{-H}_2\text{O}$ with NH and CO forms. The calculations were carried out at the MP2/6-311++G(d,p) level. Bond lengths are in Å.

Figure 3 (Color online). Snapshots of $(U)_2^+$ following the ionization of neutral uracil dimer $(U)_2$ calculated by direct AIMD calculation. Distances are in Å.

Figure 4 (Color online). Time evolution of potential energy and bond distances of uracil dimer cation $(U)_2^+$ obtained by direct AIMD calculation.

Figure 5 (Color online). Snapshots of $(U)_2^+\text{-H}_2\text{O}(\text{NH})$ following the ionization calculated by direct AIMD calculation. Distances are in Å.

Figure 6 (Color online). Time evolution of potential energy and bond distances of hydrated uracil dimer cation $(U)_2^+\text{-H}_2\text{O}(\text{NH})$ obtained by direct AIMD calculation.

Figure 7 (Color online). Snapshots of $(U)_2^+\text{-H}_2\text{O}(\text{CO})$ following the ionization calculated by direct AIMD calculation. Distances are in Å.

Figure 8 (Color online). Time evolution of potential energy and bond distances of hydrated uracil dimer cation $(U)_2^+ \cdot H_2O(CO)$ obtained by direct AIMD calculation.

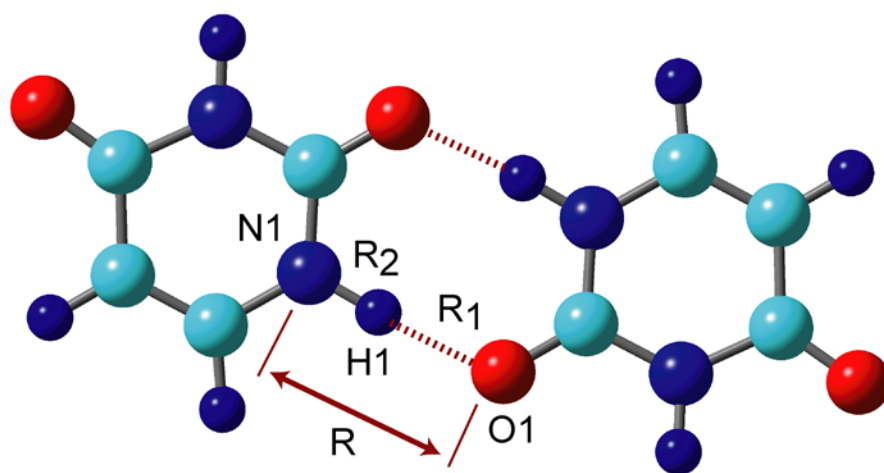
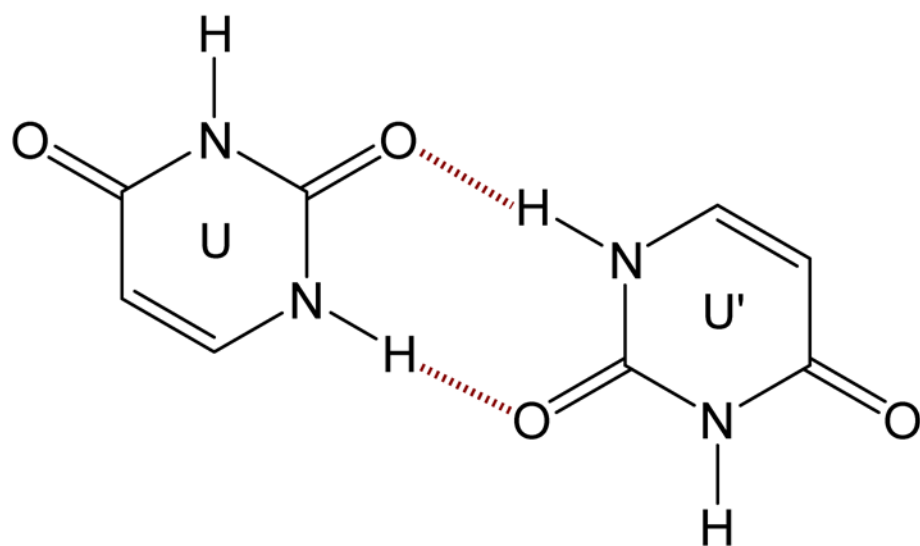
Figure 9 (Color online). Reaction rates of proton transfer in ionized uracil dimer and hydrated uracil dimer obtained by direct AIMD calculation.

Figure 10 (Color online). Effects of level of theory on reaction rates of proton transfer in $(U)_2^+$ and $(U)_2^+ \cdot H_2O$ following the ionization. A: [CAM-B3LYP/6-311G(d,p): CAM-B3LYP/6-311G(d,p)], B: [CAM-B3LYP/6-311G(d,p): CAM-B3LYP/6-311++G(d,p)], C: [CAM-B3LYP/6-311G(d,p): CAM-B3LYP/6-311G(d,p)], D: [CAM-B3LYP/6-311++G(d,p): MP2/6-311++G(d,p)], E: [CAM-B3LYP/6-311++G(2d,2p): MP2/6-311++G(d,p)],

Figure 11 (Color online). Potential energy curves for proton transfer in $(U)_2^+$ and $(U)_2^+ \cdot H_2O$ plotted as a function of R_2 .

Figure 12 (Color online). Energy diagram of dimerization of uracil molecule, ionization of uracil dimer (ionization potential (I_p) in eV), and proton transfer (PT) reaction energy in uracil dimer cation. Values (in kcal/mol) were calculated at the MP2/6-311++G(d,p) and CAM-B3LYP/6-311++G(d,p) levels of theory.

Figure 1.



Uracil dimer (U)₂

Figure 2.

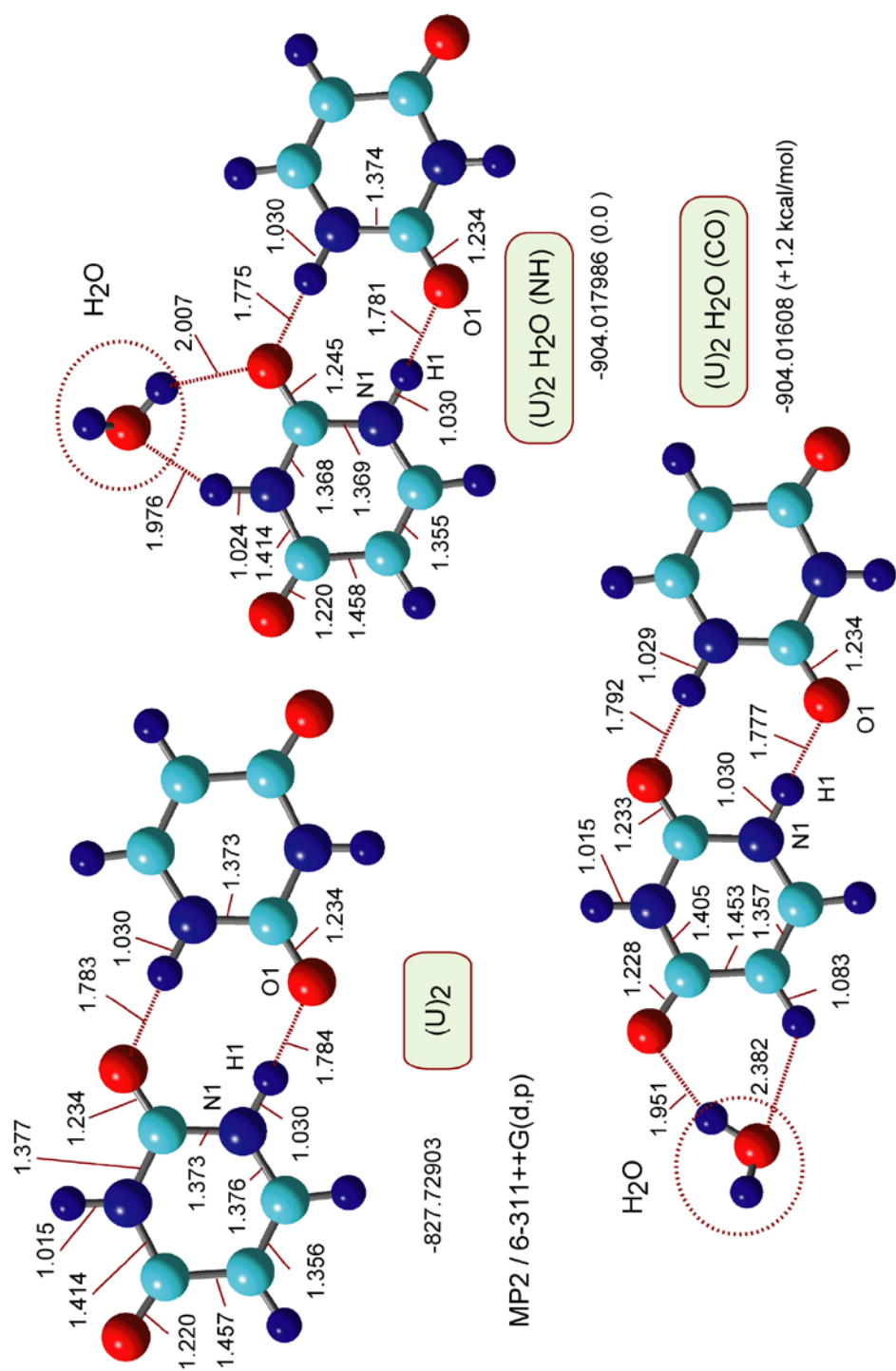


Figure 3.

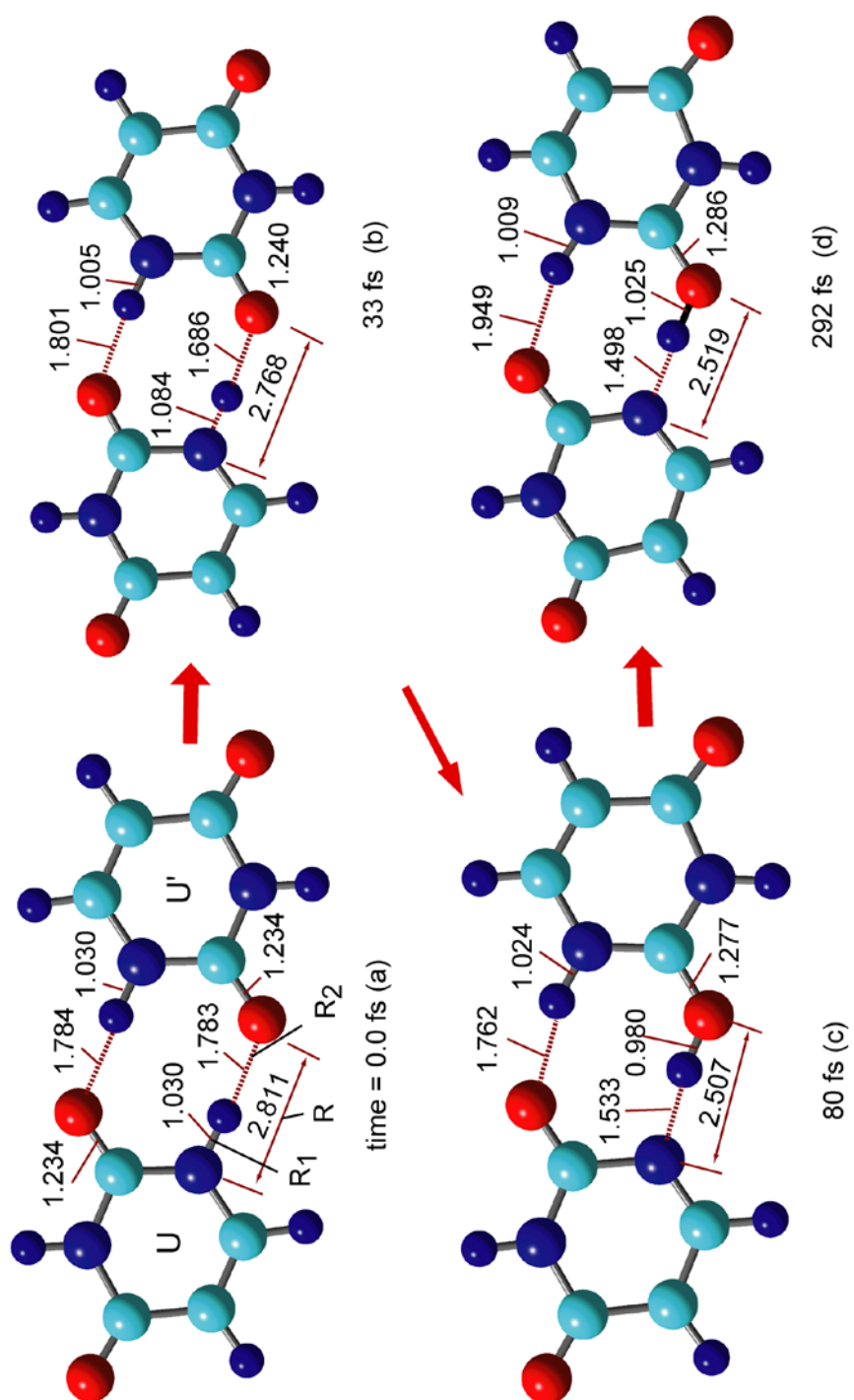


Figure 4.

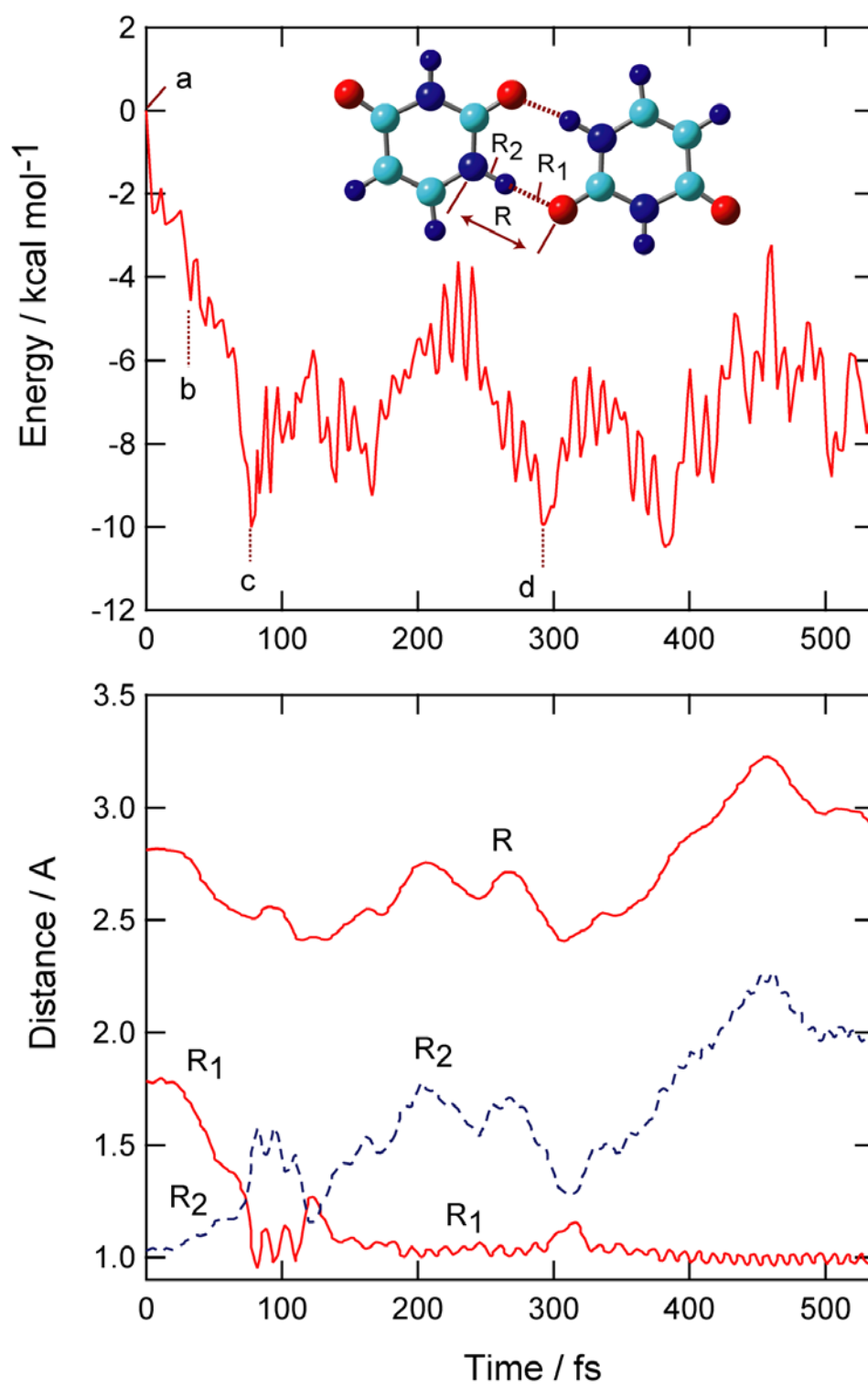


Figure 5.

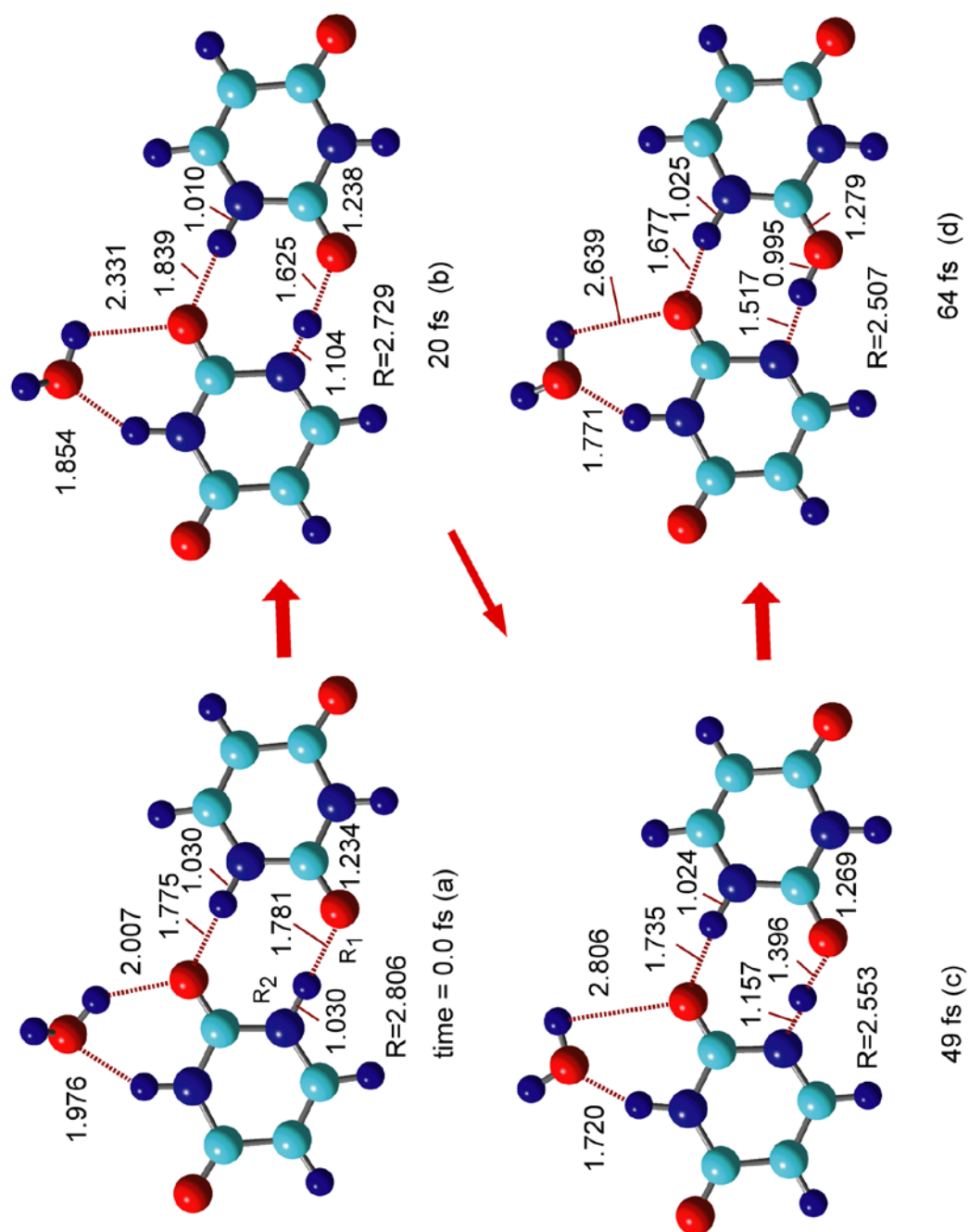


Figure 6.

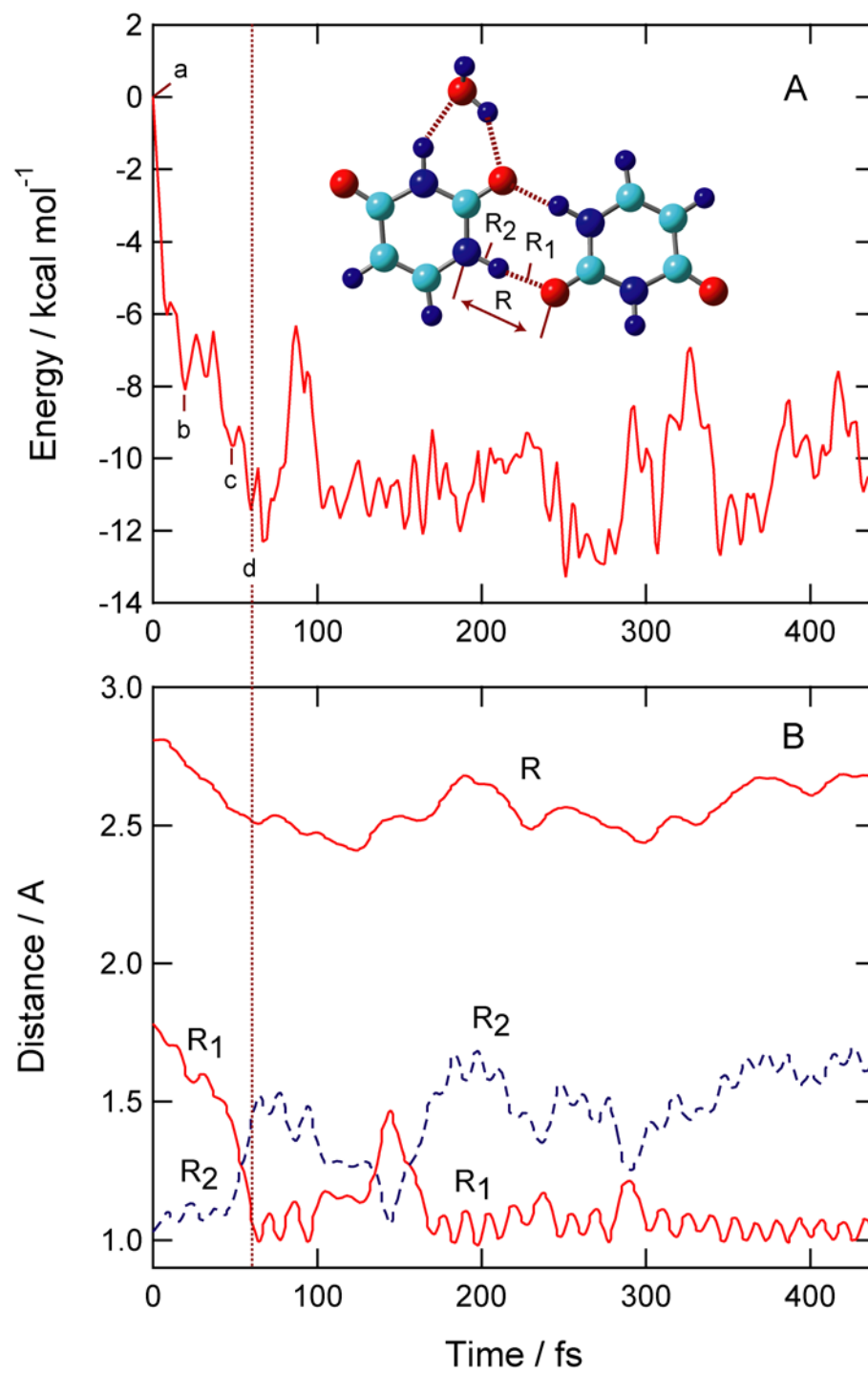


Figure 7.

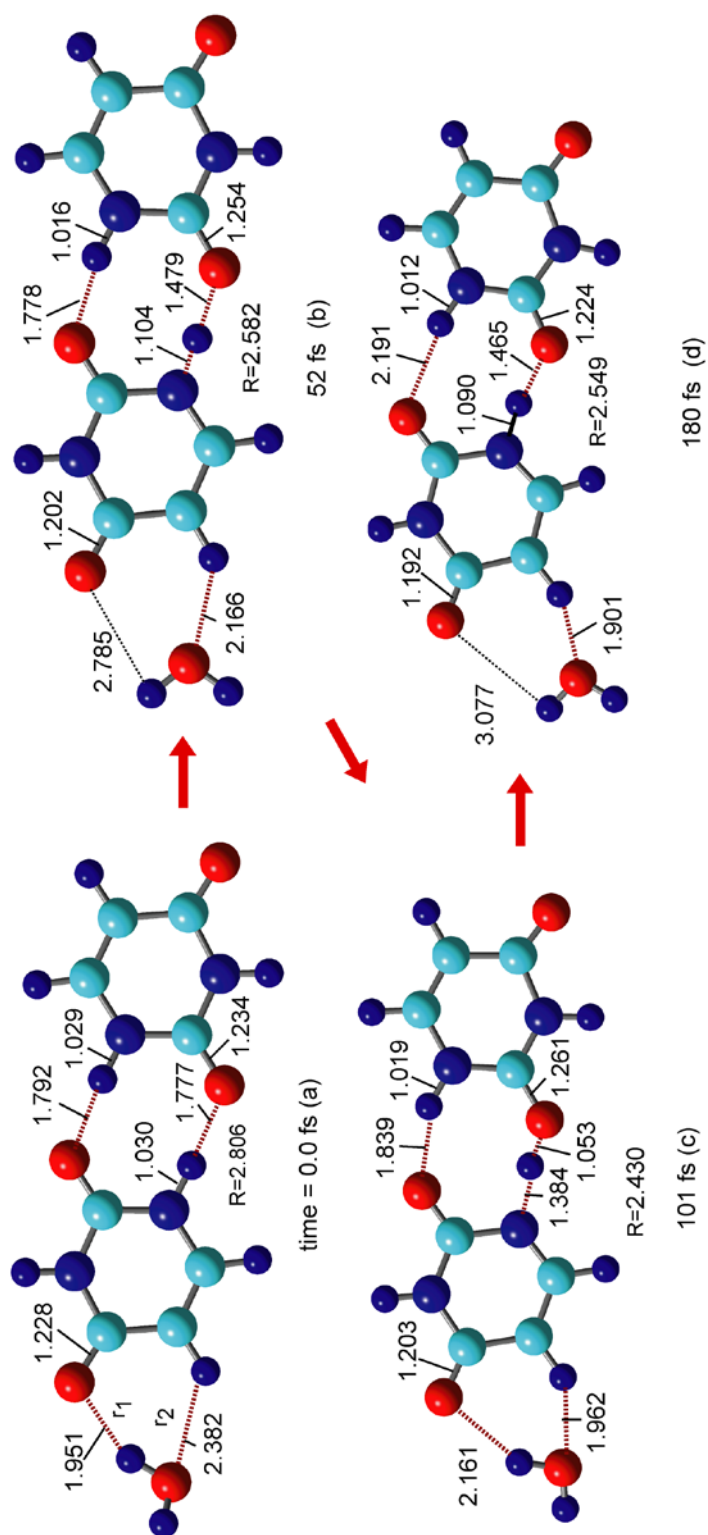


Figure 8.

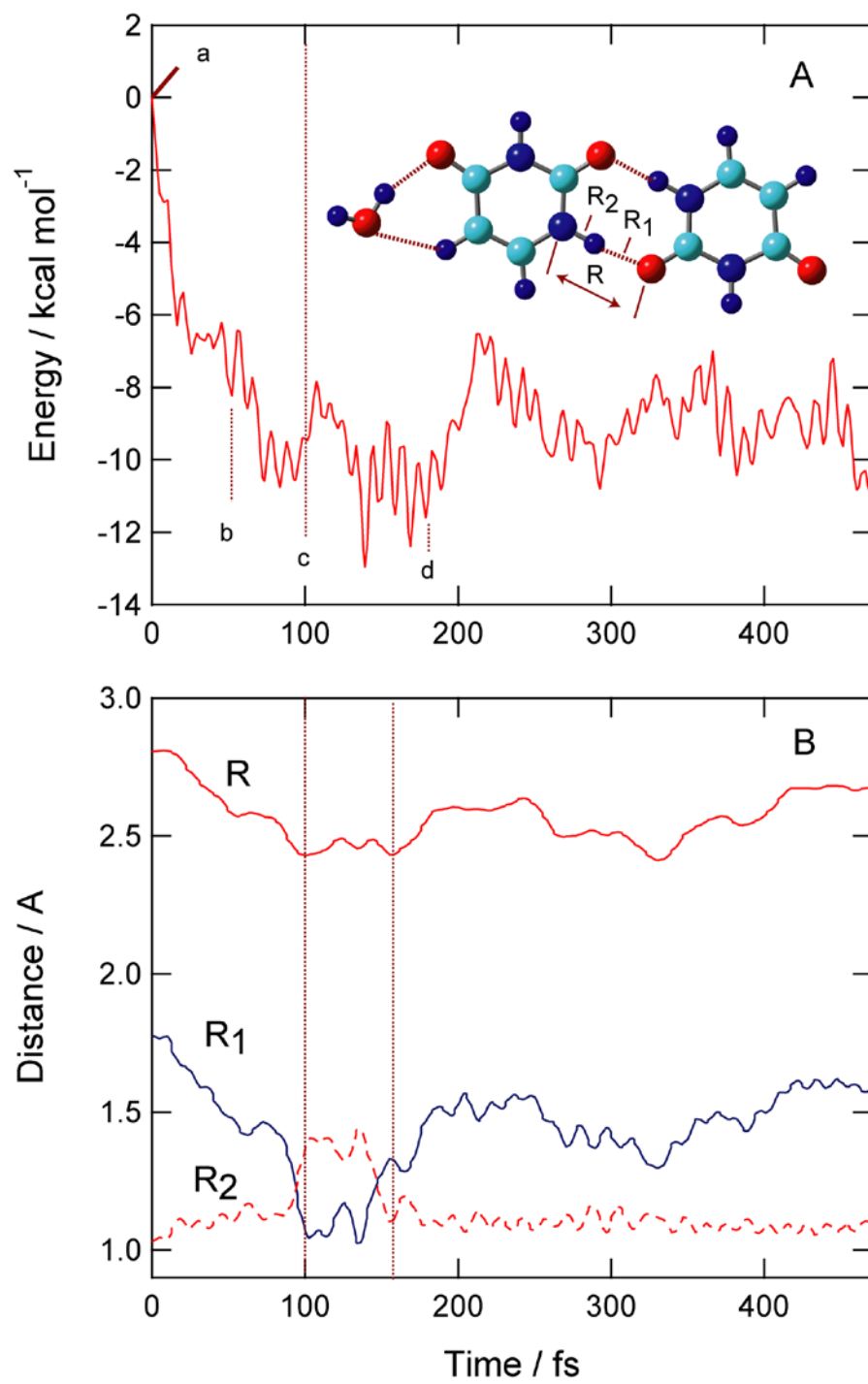


Figure 9.

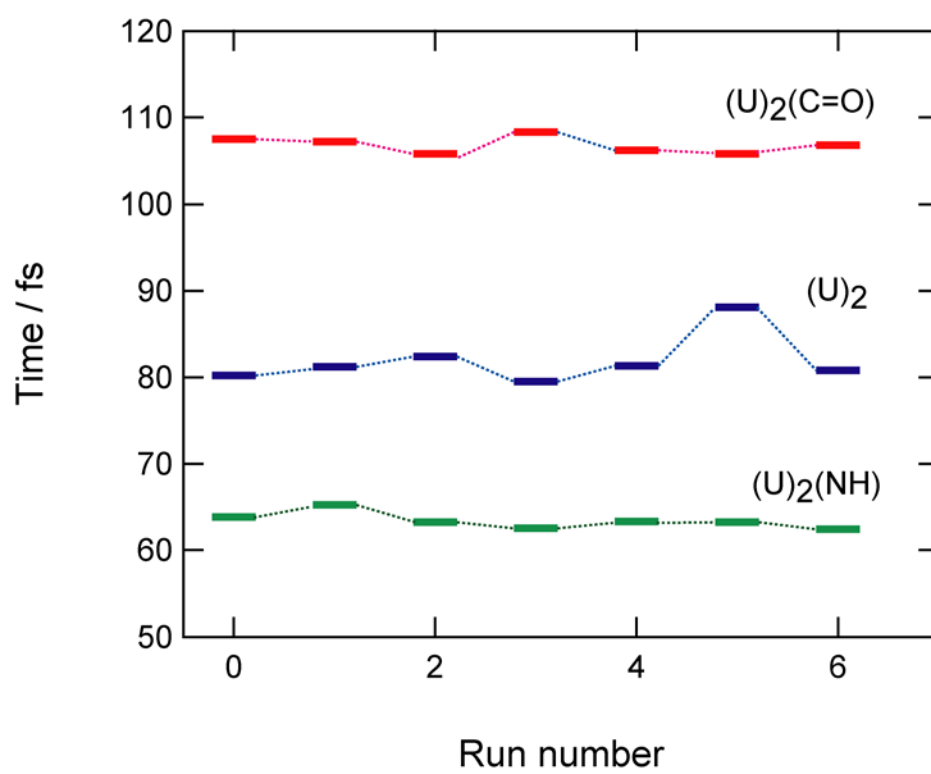


Figure 10

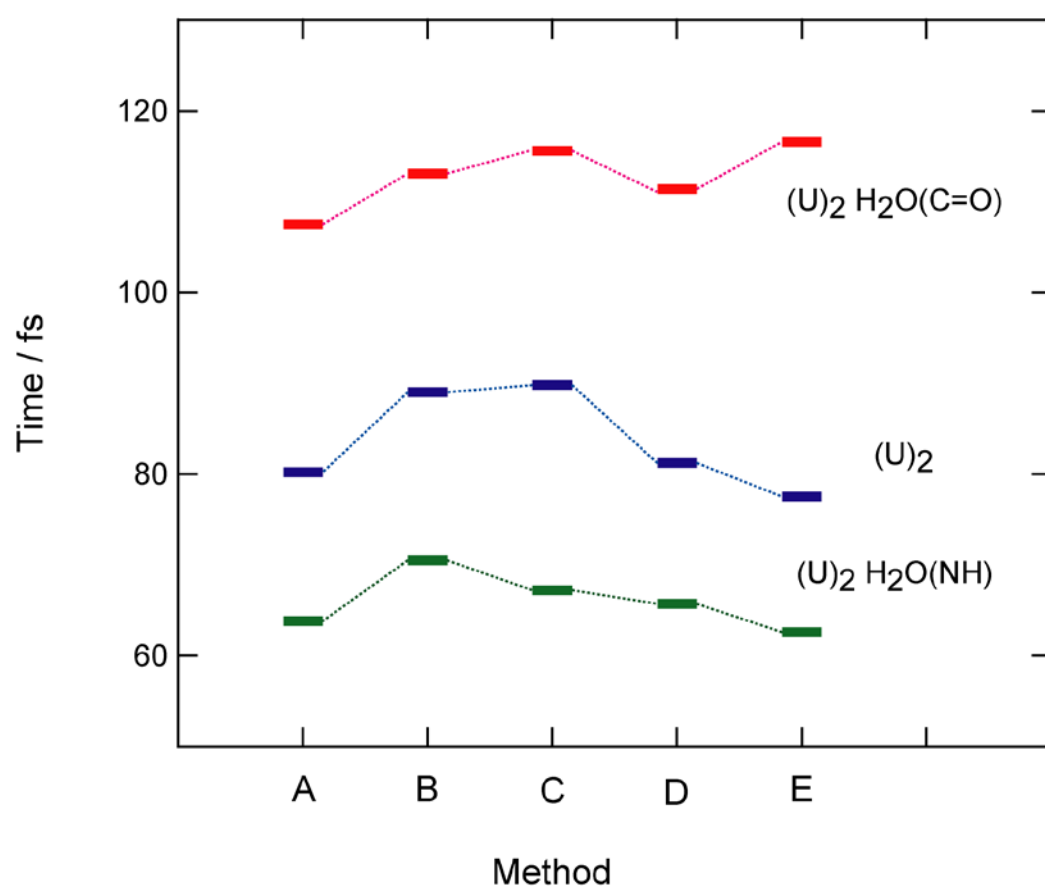


Figure 11

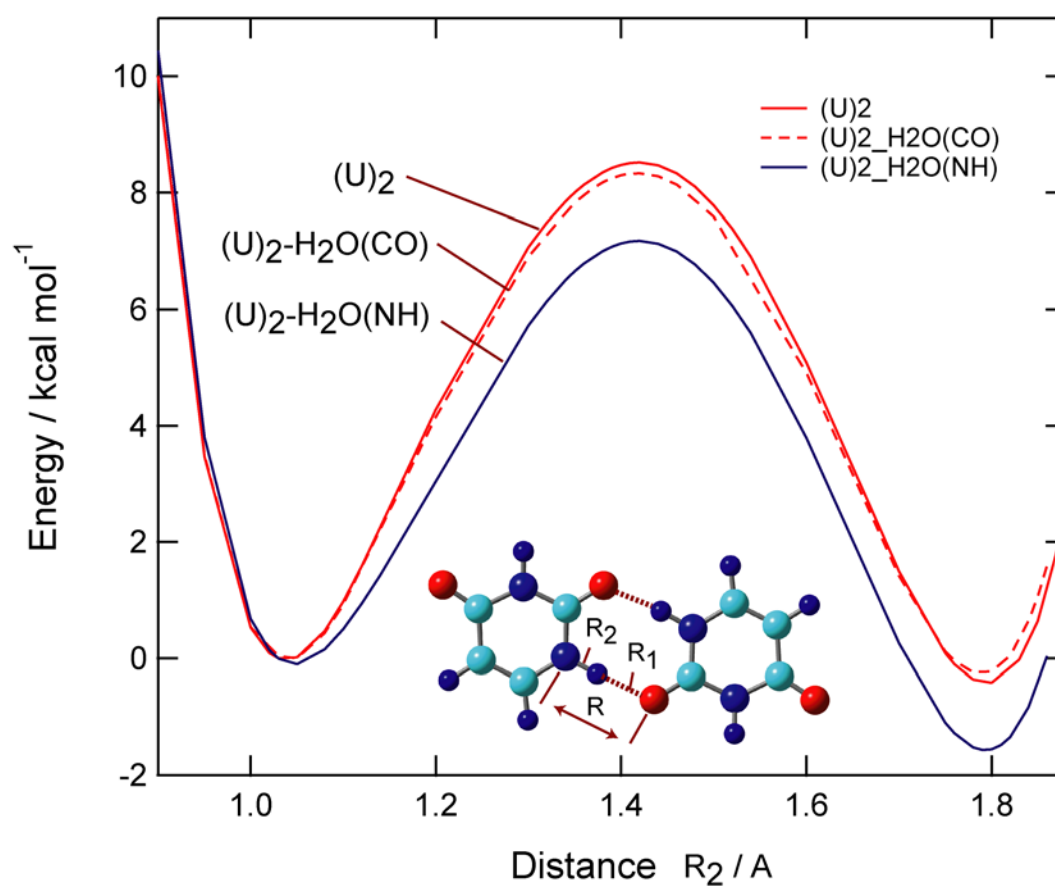
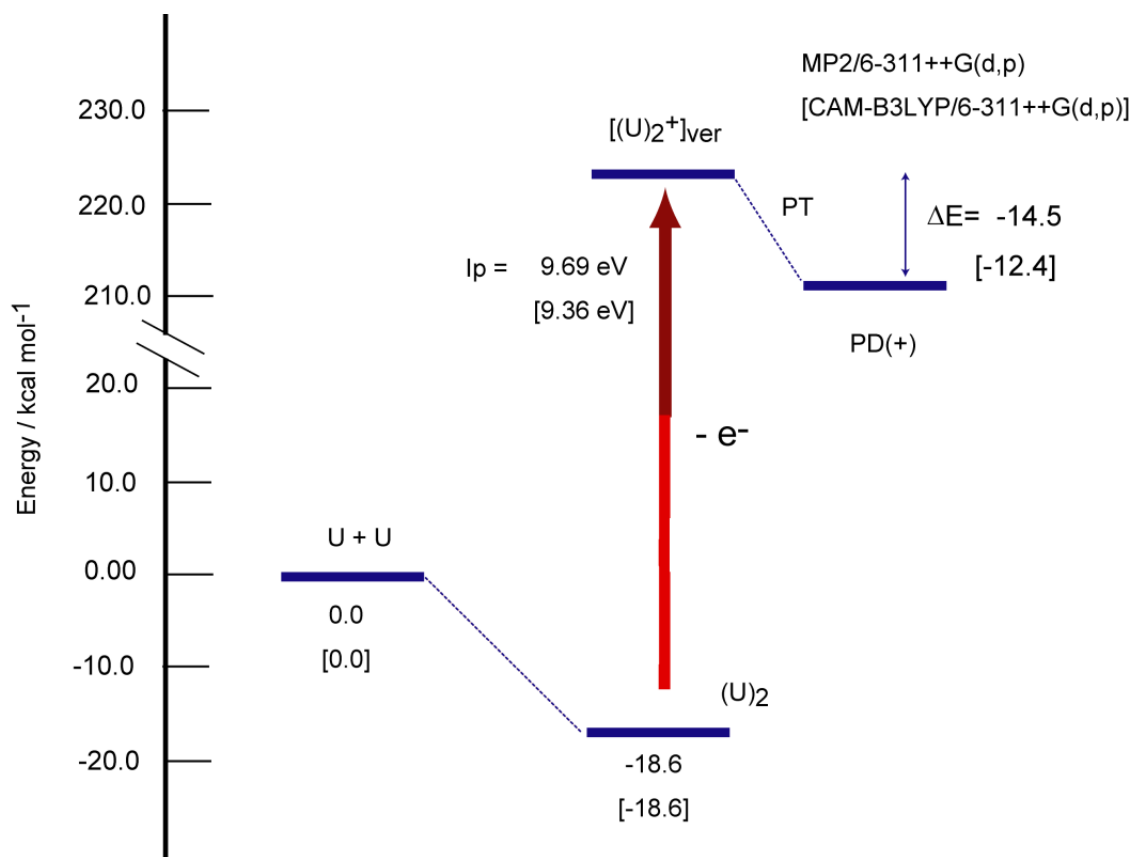


Figure 12.



Graphical Abstract

