PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

Hydrogen Bonding Tunes the Early Stage of Hydrogen-Atom Abstracting Reaction

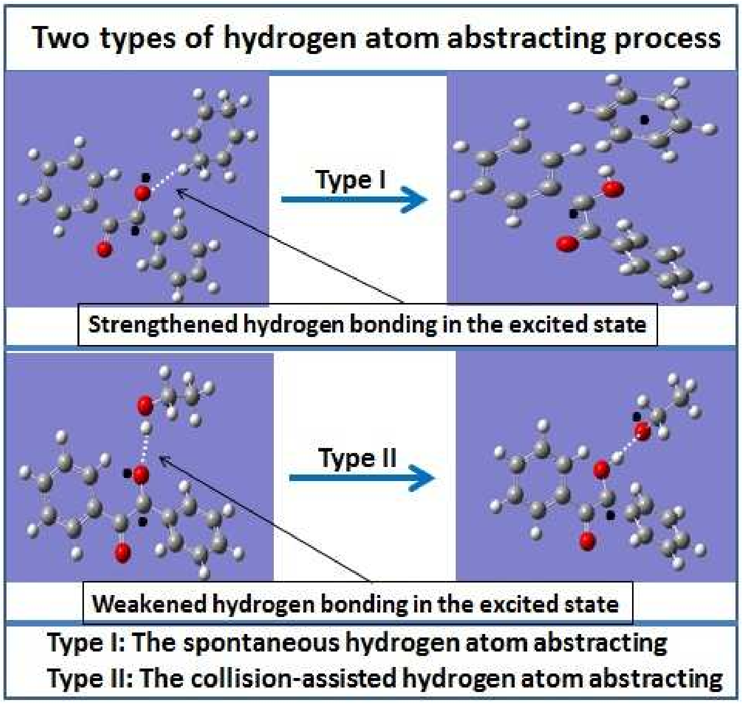
Yang Yang, Lei Liu, Junsheng Chen, and Keli Han[*]

State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, Dalian 116023, China

Corresponding Author(s)' e-mail address: klhan@dicp.ac.cn

Abstract: The spontaneous and collision-assisted hydrogen-atom abstracting reaction (HA) dynamics of triplet benzil are investigated through the combination of the transient absorption spectroscopy with TD-DFT calculations. HA dynamics exhibit remarkable dependence on the hydrogen donor properties. The effects of the triplet-state hydrogen bonding on the reaction dynamics are illustrated. In particular, it is experimentally observed that the strengthened triplet-state hydrogen bonding could accelerate the HA, whereas the weakened triplet-state hydrogen bonding would postpone the HA. The triplet-state hydrogen bonding has great influences on the early stage of HA reaction, while the bond dissociation energy of the hydrogen donors determines the subsequent reaction pathways. The protic solvents could sustain longer lifetime of the excited-state intermediate formed after HA than the non-protic solvents by 10 μs. This investigation provides the insights into the HA dynamics and one piece of guidance to improve the product efficiency of photochemical reactions.

TOC GRAPHICS



Key words: hydrogen-atom abstracting reaction dynamics, transient absorption spectroscopy, TD-DFT calculations, excited-state hydrogen bonding.

1. Introduction

Hydrogen atom abstracting reaction (HA), Equation (1), is one of the fundamental processes occurring in chemistry.

$$X^{\bullet}+H\text{-}Y\rightarrow X\text{-}H+Y^{\bullet} \qquad (1)$$

Due to its fundamental and pioneering roles in photochemical synthesis of plasmonic metamaterials,[1] bio-catalysis of transition-metal based enzyme,[2] as well as photosensitized damage to DNA,[3,4] HA is currently attracting wider research interests.[5-9] More specific investigations toward HA dynamics are imminently indispensable. The dynamical studies on HA would not only reveal its nature step by step, but also may provide strategies to optimize HA.

According to the hydrogen donor properties, the light-triggered HA can be classified into three types, including the electron transfer-initiated HA for tertiary amines, the charge transfer-initiated HA for the alkylbenzenes, as well as pure HA for the alkanes or alcohols.[10-13] The types of photo-induced electronic transitions (n,π* or π,π*), geometry of the triplet acceptors, bond dissociation energy of the donors, the redox potential of triplet acceptors, as well as the solvent environments have great influences on the light-triggered HA. After the hydrogen-atom abstraction, new reactive intermediate will be formed. The effect of the hydrogen donor properties on the lifetime of the new reactive intermediate is scarcely studied. For example, through using 1,4-cyclohexadiene (CHD) as the hydrogen donor, Scaiano et al. found the triplet benzophenone was able to abstract the H-atom to form ketyl radical, which could reduce the coexisting Ag^+ to generate Ag^0 nanoparticles.[1] By contrast, the H-atom on the hydroxyl of ethanol can also be abstracted by the triplet benzil to form the ben-eth biradical, which can be applied to the morphology-controlled synthesis of Ag nanomaterials.[14] The lifetime of the beneth biradical is globally fitted to be as long as 375.83±93.70 μs. Obviously, hydrogen donor is one significant factor in HA. The influence of hydrogen donor properties on the lifetime of the newly formed intermediate after HA remains unclear.

In addition, because of its fundamental importance in many branches of sciences, hydrogen bonding is of intense research interests.[15,16] Especially, it has been extensively demonstrated by our group that the hydrogen bonding interaction in the electronic excited state can be significantly strengthened or weakened upon photoexcitation of the hydrogen-bonded complexes,[17,18] and the excited-state hydrogen bonding dynamics will play a very vital role on the photophysical processes and photochemical reactions, such as the absorption and fluorescence spectral red-shift or blue-shift,[15] internal conversion,[19] intersystem crossing,[20,21] intramolecular charge transfer,[22] photoinduced electron transfer,[23,24] excited-state proton transfer,[25] metal-ligand charge transfer[26] and so on[27-29]. The singlet-state hydrogen bonding is demonstrated to be capable of tuning the photochemical reactions. Yet the effect of the triplet-state hydrogen bonding on the HA dynamics is scarcely explored. Understanding this effect might provide guidance to optimize the HA.

In this letter, we employ the combination of nanosecond transient absorption spectroscopy with TD-DFT calculations to focus on the HA dynamics of triplet benzil. The effect of triplet-state hydrogen bonding on the HA dynamics, energy relaxing, as well as lifetime of reactive intermediate are directly observed. The discussions based on the TD-DFT computational calculations are given to explain the experimental results. One piece of advice for optimizing photochemical reaction efficiency is deduced on the basis of our work.

2. Experimental and computational methods

As one of the classical and paradigmatic aromatic carbonyl compounds, benzil possesses rich physical chemistry, which is worth giving the experimental and theoretical investigations. For most organic molecules without heavy elements, the intersystem crossing (ISC) from singlet state to triplet state is always forbidden. But for aromatic carbonyl compounds, Fang et al. have demonstrated one conical intersection point between S_1, T_2 and T_1 potential energy surfaces, which makes the $S_1 \rightarrow T_2$ intersystem crossing (ISC) and $T_2 \rightarrow T_1$ internal conversion (IC) take place on the time scale of picoseconds with high efficiency.[27] Hence, the transient absorption on the microseconds represents the decay of triplet states. CHD is one typical hydrogen donor, whereas ethanol could also work as hydrogen donor with obvious hydrogen bonding effect. The light triggered HA processes at room temperature (22 °C) were detected through using home-made nanosecond transient absorption spectroscopy, the excitation source of which is a nanosecond laser system with the output of 1−40 mJ@355 nm. Full width at half maximum of the laser pulse is about 10 ns. The apparatus response function length of our home-made nanosecond transient absorption spectroscopy is measured to be within 100 ns. The detailed information can be found in figure S2 in page 3 of the supporting information. Each spectrum was the average result of multiple measurements (10 times) and analyzed through the global curve fittings to obtain the lifetimes of the photochemically induced reactive intermediates. The sample solutions were deaerated through nitrogen bubbling for 30 min. Once this procedure was complete, the required volume of pure CHD was added with a microliter spring. Then the sample was sealed with parafilms and stirred (vortex) for ten seconds. All of the mentioned solutions in this manuscript are deaerated.

All calculations have been performed with Gaussian 09 suit of program using the density functional theory (DFT) and time-dependent density functional theory (TDDFT) with the 6-31++ G(d, p) basis set. The optimized geometries of benzil in the ground and triplet states were obtained through using RB3LYP and UB3LYP hybrid functional, respectively. The potential energy curves of benzil in the excited state (the Franck-Condon curves) were predicted by adding the TDDFT/6-31++G(d, p) vertical excitation energies to the corresponding ground state energy curve. The proton transfer process at T_1 state was scanned at DFT/UB3LYP/6-31++G(d,p) level of theory by performing a series of constrained optimizations on distance between the hydrogen atom of donors and the oxygen atom of benzil while other atoms were relaxed. To be exact, we set the distance between the hydrogen atom of donors and the oxygen atom of benzil first, and calculate the energy of the complex after doing the geometry optimization in the triplet state with other atoms relaxed. Then we change the distance and do the cycles until the proton transfer process is finished. This calculation method is also recognized as relaxed scan in Gaussian 09. All the energy calculation and geometry optimization are done in the triplet state. The optimized geometries and corresponding coordinates of hydrogen atom abstracting are given in page 4 of the supporting information. The DFT/TDDFT method has been confirmed to successfully describe the ground and excited states of many important hydrogen-bonded systems[14-22]. In addition, to get more accurate simulations, we took solvent corrections into the calculations by employing conductor polarized continuum model (CPCM). The bond dissociation energies are calculated at DFT/B3LYP/611++G(d,p) theory level with BSSE correction.

3. Results and discussions

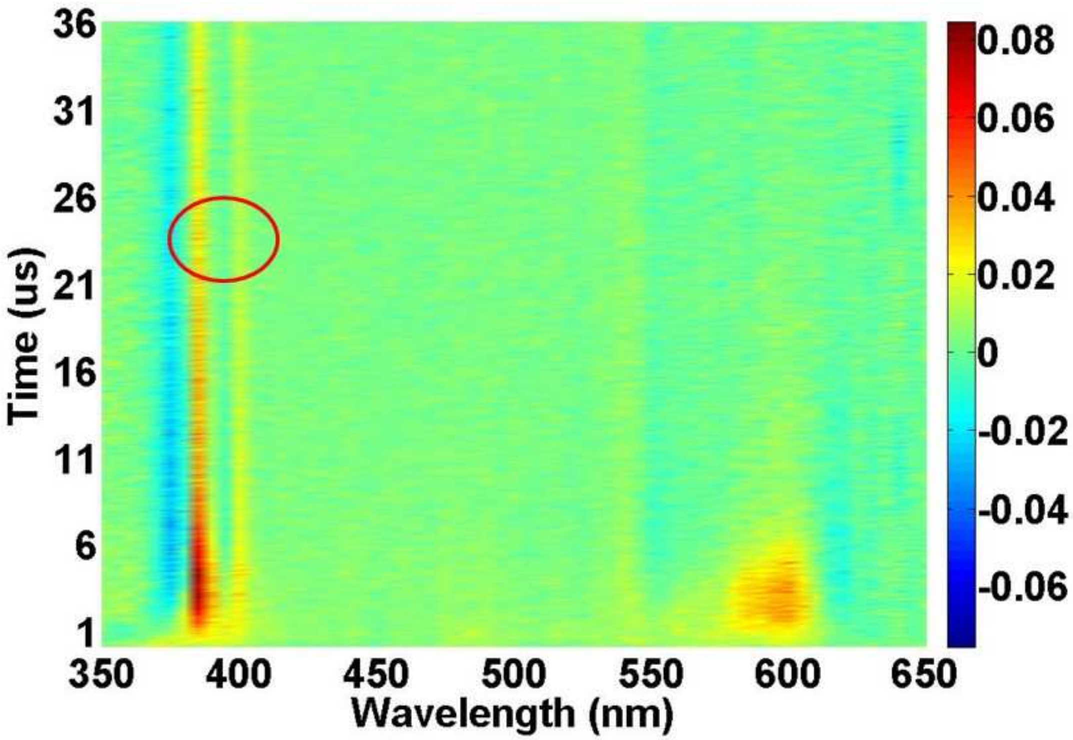


Figure 1. Transient absorption spectrum of 4 mM benzil and 10 mM CHD in acetonitrile excited by 13 mJ@355 nm at 0 μs. One red cycle is added to guide eyes.

Figure 1 shows the transient absorption spectrum of 4 mM benzil and 10 mM 1,4-cyclohexadiene (CHD) in acetonitrile excited by 13 mJ@355 nm at 0 μs. CHD is the hydrogen donor, the H-atom of which can form one weak hydrogen bonding with the oxygen-atom on carbonyl group of benzil. Since the two photon threshold of benzil in our condition is about 18 mJ, the light irradiation of benzil with pulse energy under 18 mJ only promotes the $S_0 \rightarrow S_1$ transition.[14] The absorption spectrum of benzil in acetonitrile and calculated electronic transition energies with corresponding oscillator strength of the low-lying singlet excited states in the page 14 of the supporting information can confirm the electronic transitions from S_0 to S_1 caused by the single photon excitation of 355 nm laser pulses. A series of absorption peaks existed on the time scale of several microseconds can be attributed to the triplet-triplet absorption (TTA). When these absorption peaks are compared with the situations in transient absorption spectrum of 4 mM benzil in acetonitrile without adding any CHD,[14] it is rather interesting to observe that the absorption peak around 370 nm lasts for longer time, indicating the generation of one new intermediate.

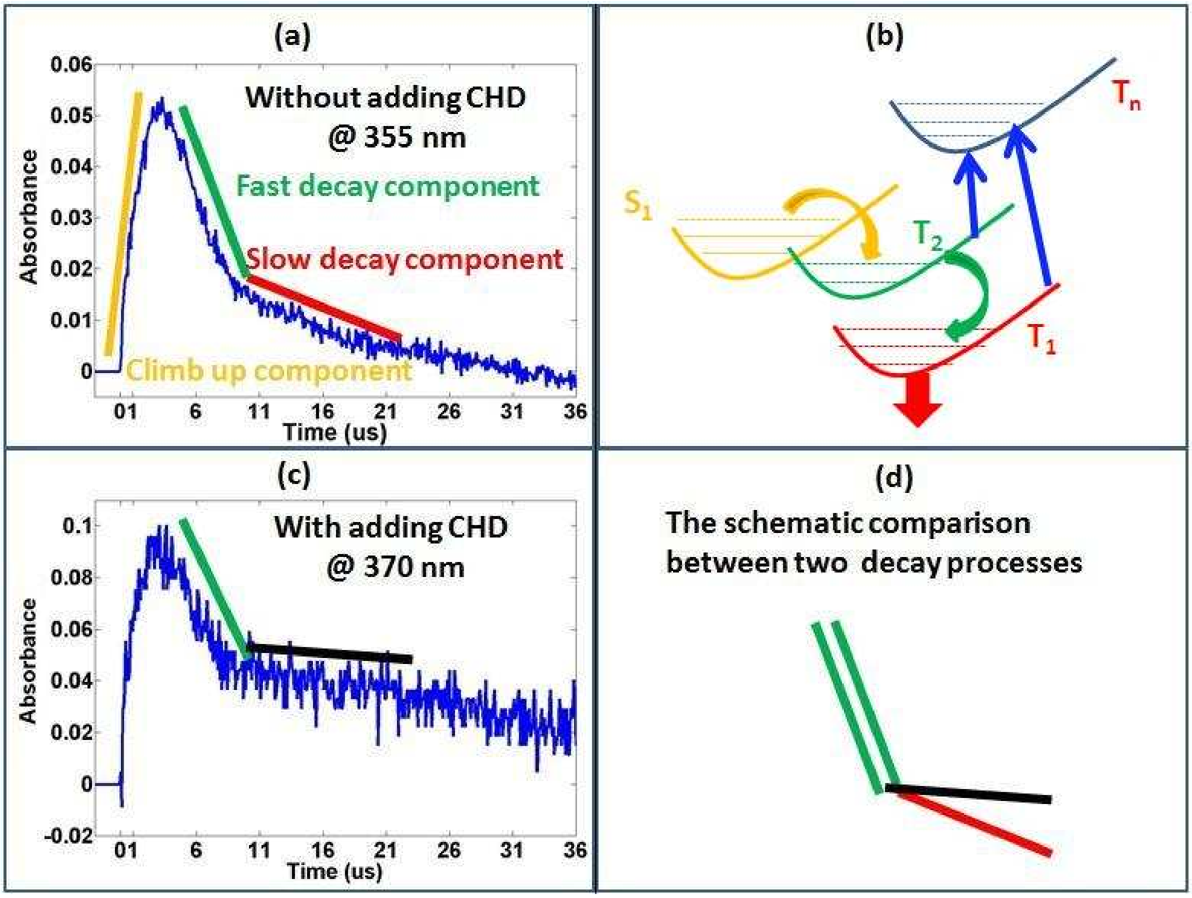


Figure 2. (a) Transient absorbance of 4 mM benzil in acetonitrile around 355 nm excited by 7 mJ@355 nm. (b) The intersystem crossing and internal conversion of excited-state benzil. (c) Transient absorbance of 4 mM benzil and 10 mM CHD in acetonitrile around 370 nm excited by 13 mJ@355 nm. (d) The schematic comparison between two slow decay processes.

To clarify the generation dynamics of the new intermediate, it is necessary to illustrate the photophysical properties of excited-state benzil first. Figure 2a shows the transient absorbance of 4 mM benzil in acetonitrile around 355 nm. The dynamical curve mainly consists of three parts, including climb-up component, fast decay component, as well as slow decay component. The excited-state benzil has been theoretically proved to possess the following two characteristics: i) Two intersections between S_1 and T_2 potential energy surfaces, ii) The relatively small energy gap between the T_2 and T_1 energy surfaces.[14,30,31] According to these predictions, the $S_1 \rightarrow T_2$ intersystem crossing (ISC) and $T_2 \rightarrow T_1$ internal conversion (IC) take place on the time scale of picoseconds with high efficiency. We argue the yellow climb-up could be attributed to the linear combination of transient absorption and delayed fluorescence. In other words, the yellow climb-up is caused by the overlap between the transient absorption and delayed fluorescence. In 2011, B. Bhattacharya et al. found that the excited-state benzil could emit photons from the first (S_1) as well as the second excited singlet (S_2) states depending on the excitation wavelength.[31] The emission band peaking at around 360 nm has been assigned to originate from the S_2 state. The lifetimes of S_1 and S_2 are measured to be about 2 ns. In 1978, by using the laser time-resolved spectroscopy, Fang et al. found that the delayed emissions of benzil consist of thermal ($T_1 \rightarrow S_1$) and P-type ($T_n+T_n \rightarrow S_n+S_0$) delayed fluorescences.[32] The emission wavelength caused by $T_1 \rightarrow S_1$ should be longer than 379.2 nm (This value is obtained by both of the experimental absorption spectra measurement and theoretical calculations, shown in page 14 of the supporting information). If the excitation wavelength is longer than 341 nm, the emission band peaking at around 360 nm should be caused by $T_n+T_n \rightarrow S_2+S_0$. Since ($T_n+T_n \rightarrow S_2+S_0$) is caused by the collision between two molecule, the decay rate of its emission should be two times faster than that of triplet molecules. Once the concentration of triplet molecules gets lower, the ($T_n+T_n \rightarrow$

S_2+S_0) process eliminates rapidly. Based on the above considerations, the yellow climb-up signal could be explained as follows: the low lying triplet benzil has strong transient absorption at 355 nm, while the delayed fluorescence at this wavelength dramatically decreases the transient absorption value, leaving one small transient absorption value at the early time stage. As the delayed fluorescence decays rapidly, the transient absorption value gradually increases to higher values, appearing as the yellow climb-up variation tendency. Then the decay of triplet state will dominate the subsequent dynamics. Due to the small energy gap between the T_2 and T_1 energy surface, the $T_1 \rightarrow T_n$ and $T_2 \rightarrow T_n$ absorption peaks always overlap, resulting in double exponential decay process. Therefore, the fast and slow decay components in Figure 2a reflect the decay processes of the T_2 and T_1, respectively. Figure 2b shows the transition pathways between different electronic states. Figure 2c exhibits the transient absorption curve of 4 mM benzil and 10 mM CHD in acetonitrile around 370 nm excited by 13 mJ@355 nm. The climb-up and fast decay component remains nearly unchanged, but the slow component dramatically changed. Namely, the decay rate of the slow decay component becomes smaller. In order to emphasize the difference between the two slow decay processes in Figure 2a and 2c, we make one direct and schematic comparison, as shown by Figure 2d. It is noticed that all the straight lines with the same color in Figure 2 are parallel with each other. The red and black lines represent the slow decay process in Figure 2a and 2c, respectively. The decay rates of the two green lines are almost the same, whereas the decay rate of the black curve is obviously smaller than that of the red curve, both of which suggest that one chemical reaction happens on the T_1 benzil rather than the T_2 benzil.

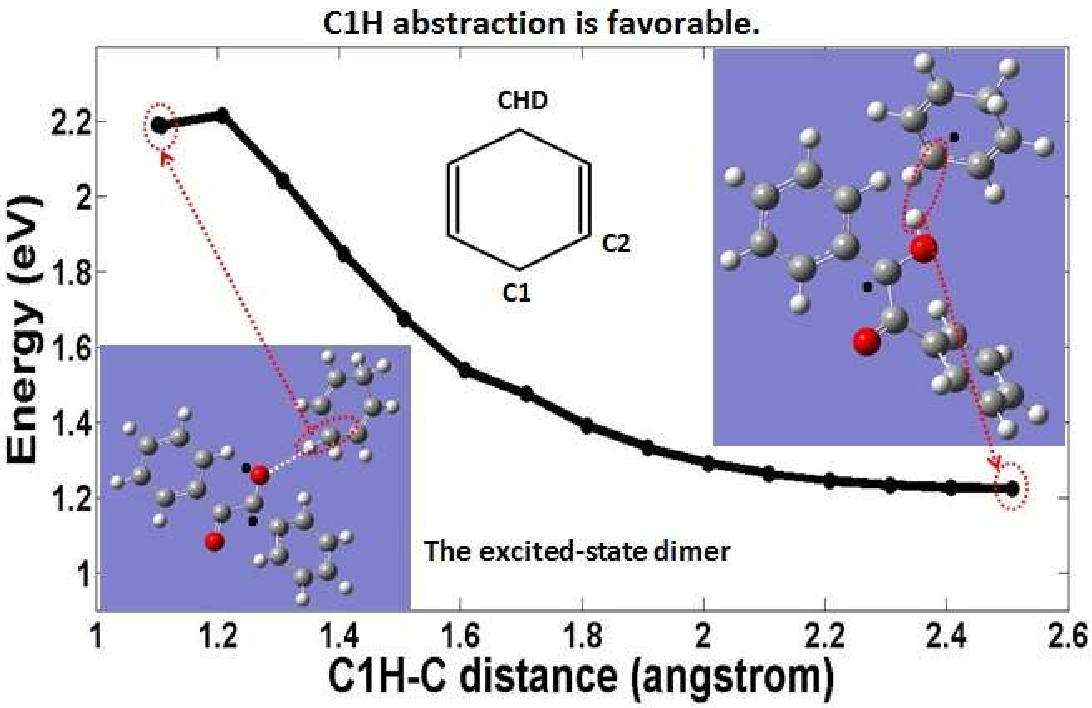


Figure 3. The excited-state energy variation of the T_1 dimer with the C1H-C distance

The calculations indicate that the HA happens. There are two types of H-atoms on CHD. As marked in Figure 3, they are named as C1H and C2H, respectively. We scan the excited-state energy of the T_1 dimer with the increased C1H-C distance. As can be seen in Figure 3, the total energy of the dimer gets smaller. There exists no potential barrier. Hence, the abstraction of C1H by T_1 benzil is spontaneous to take place on an ultrafast time scale. Then the benzil radical anion (named as benzil radical) is formed and shown by the right insets of Figure 3. We define this type of H-atom abstracting process as the spontaneous HA. Whereas the abstraction of C2H by T_1 benzil is forbidden, since the total energy of the dimer becomes bigger with a closer distance between the C2H and T_1 benzil, as shown in the figure S1 of the supporting information. One photochemical process with gradually increased energy is generally not preferred, while nearly all the chemicals with lower energy tend to be more stable. And the slow component of transient absorption around 370 nm in Figure 2c is caused by benzil radical.

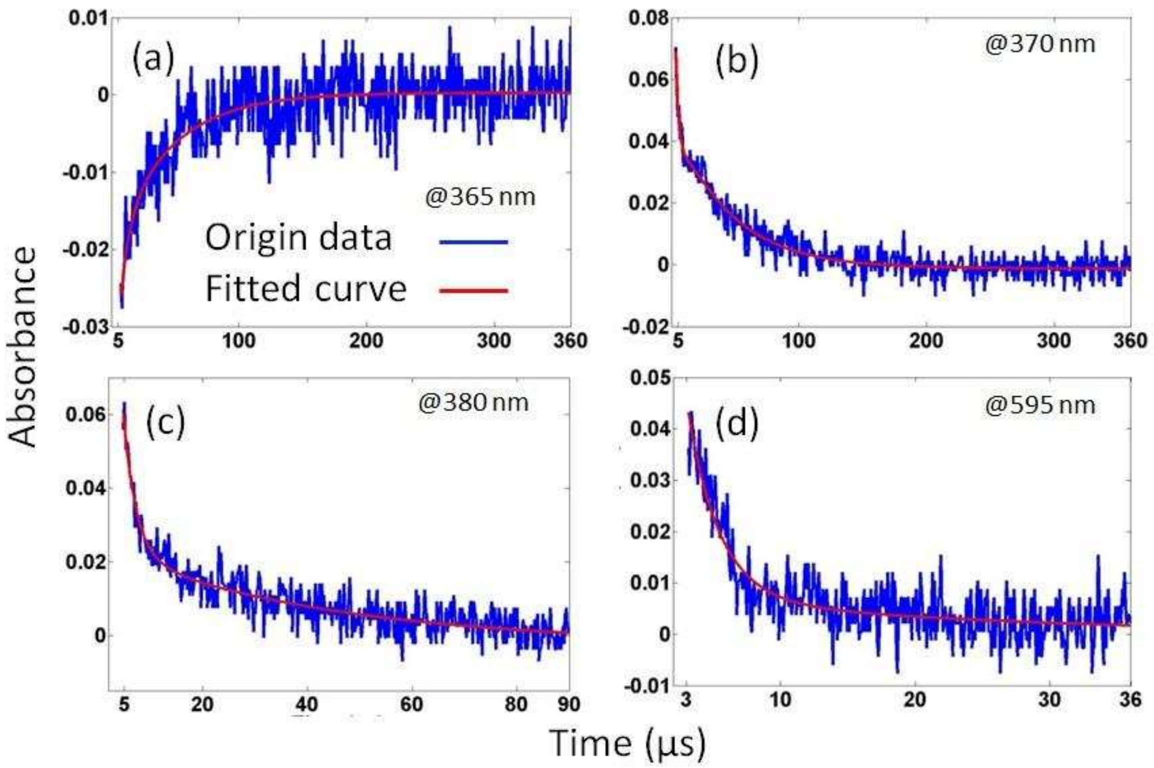


Figure 4. Transient absorbance and their global fittings of 4 mM benzil and 10 mM CHD in acetonitrile excited by 13 mJ@355 nm at different wavelengths: (a) 365 nm, (b) 370 nm, (c) 380 nm and (d) 595 nm.

Figure 4 exhibits the dynamical curves and their global fitting results of 4 mM benzil and 10 mM CHD in acetonitrile excited by 13 mJ@355 nm at different wavelengths. The R^2 for this fitting is 0.85. In this case, the lifetimes of T_1 and T_2 benzil are estimated as 7.23 ± 4.68 μs and 2.31 ± 0.31 μs, respectively. The lifetime of benzil radical is 44.27 ± 2.64 μs. The transient absorption and emission signals in Figure 3a and 3b decay with similar dynamical characteristics. Namely, they decay with similar rate and return to zero at nearly the same time point. The dynamical curves at 365 nm and 370 nm are attributed to the transient emission and absorption of benzil radical. It should be noticed that the transient emission and absorption with similar dynamical characteristics always appear as one pair. Moreover, one emission wavelength is smaller than the other absorption wavelength. The transient absorption can be attributed to the electronic transition from lower triplet state to higher triplet state, while the transient emission is caused by the electronic transition from lower triplet state to the ground state. In this study, the wavelength of the paired emission is always shorter than that of the paired absorption. Whatever the transient absorption or emission, reflects the dynamical properties of the same lower triplet state. Therefore, the time-resolved variation tendency of the transient absorption and emission in one pair remains very similar. Because the lifetime of the benzil radical is on the order of several ten microseconds, we argue that it is still in the triplet state and the excited energy mainly relaxes via photon emission. The H-atom abstracting process does not change the electron spin of the excited-state acceptors.

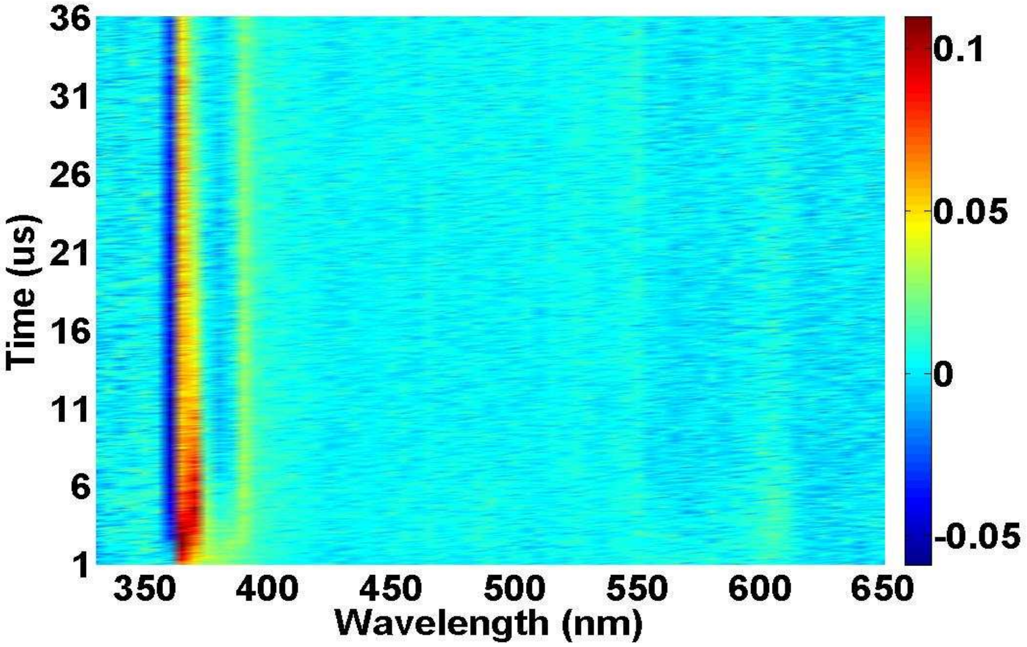


Figure 5. Transient absorption spectrum of 4 mM benzil and 10 mM CHD in ethanol excited by 13 mJ@355 nm at 0 µs.

Different from acetonitrile, ethanol is not only the hydrogen donor but also act as solvents with hydrogen bonding effects. It has been demonstrated that the T_1 benzil could abstract the H-atom on the hydroxyl of the ethanol to form the ben-eth biradical, which has a transient absorption peak at 405 nm.[14] In the previous work reported in ref. 14, the ethanol acts as both of the solvent and the hydrogen donor and there are no other hydrogen donors. This type of HA is recognized as collision-assisted HA. It shows unique features. After the laser pulse excitation, the triplet benzil abstracts the H-atom from ethanol. The newly formed intermediate with a transient absorption around 405 nm is named as ben-eth biradical. Its transient absorption value gets larger gradually before 26 us, showing a rather slow generation process. The calculations show that the triplet benzil needs to overcome one 0.7 eV potential barrier to abstract the H-atom. Such potential barrier is compensated by the solvent collision. Overcoming the potential barrier through the solvent collision makes this type of HA a slow process. And then ben-eth biradical decays with a rather slow rate. The lifetime of the ben-eth biradical is globally fitted as 375.83 ± 93.70 μs, which seems much longer than that of most radicals. The existence of hydrogen bonding lowers the energy of ben-eth biradical, which dramatically prolongs its lifetime. In this study, we added excessive dosage of CHD into the deaerated ethanol, resulting in the coexistence of CHD and ethanol. Figure 5 shows the transient absorption spectrum of 4 mM benzil and 10 mM CHD in ethanol excited by 13 mJ@355 nm. As can be seen clearly, the transient absorption peak of the ben-eth biradical at 405 nm does not appear at all, which does not suggest the generation of ben-eth biradical. The transient absorption spectrum looks identical with that in Figure 1. All experimental results prove that the triplet benzil is more prone to abstract the C1H of CHD to form benzil radical rather than the H-atom on the hydroxyl of ethanol in our condition.

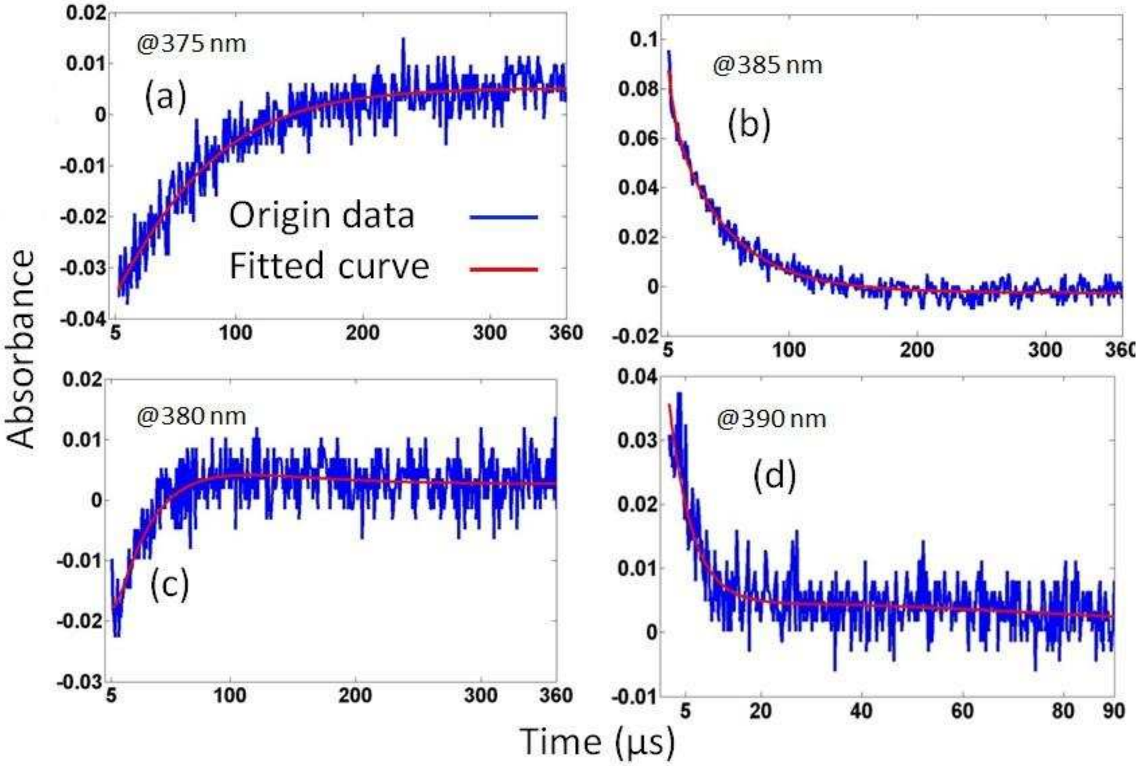


Figure 6. Transient absorbance and their global fittings of 4 mM benzil and 10 mM CHD in ethanol excited by 13 mJ@355 nm at different wavelengths: (a) 375 nm, (b) 385 nm, (c) 380 nm and (d) 390 nm.

Figure 6 exhibits the dynamical curves and their global fitting results of 4 mM benzil and 10 mM CHD in ethanol excited by 13 mJ@355 nm at different wavelengths. The R^2 for this fitting is 0.90. In this case, the lifetimes of T_1 and T_2 benzil are estimated as 37.00 ± 6.32 μs and 4.70 ± 0.62 μs, respectively. The lifetime of benzil radical is 55.99 ± 8.36 μs. The time-resolved variation tendencies of the transient absorption in Figure 6a and emission in Figure 6b are very similar. They could also be recognized as one pair. In ethanol, the excited-state energy of benzil radical still relaxes via photon emission.

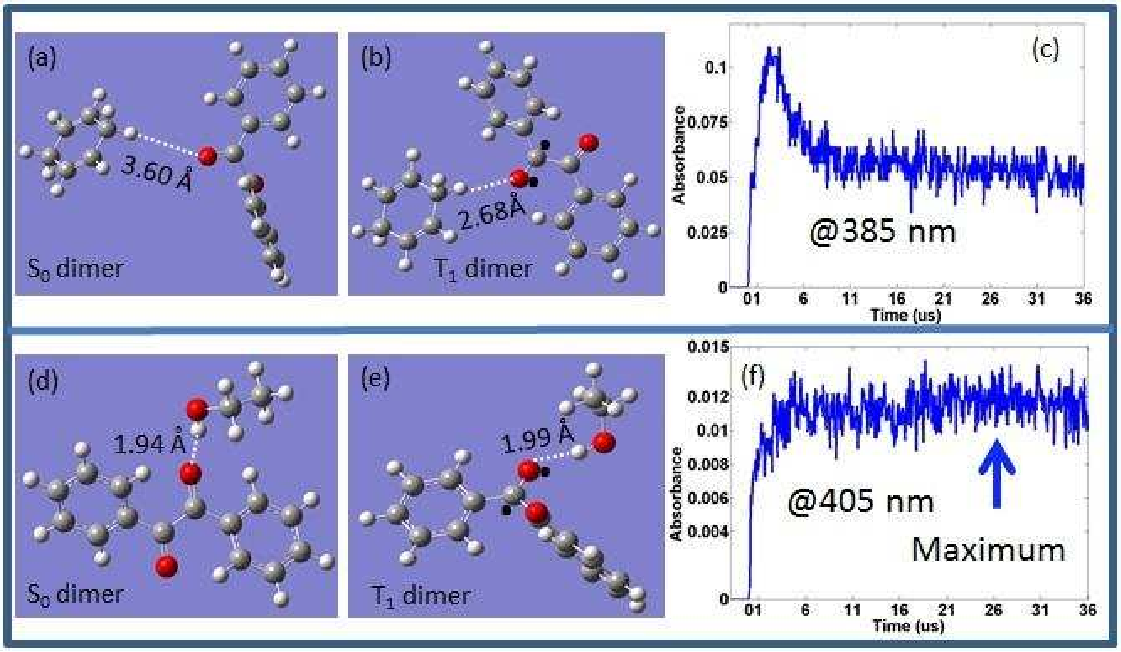


Figure 7. (a) and (d) The hydrogen bonding length in the S_0 dimer. (b) and (e) The hydrogen bonding length in the T_1 dimer. (c) The transient absorbance of 4 mM benzil and 10 mM CHD in ethanol around 385 nm. (f) The transient absorbance of 4 mM benzil in ethanol around 405 nm.

To emphasize the effect of hydrogen donor properties and triplet-state hydrogen bonding on the HA dynamics, we utilized T_1 benzil to abstract the C1H of CHD and the H-atom on the hydroxyl group of ethanol, respectively. Then we analyze the roles of the triplet-state hydrogen bonding in the HA dynamics. On one side, as can be seen in Figure 7a and 7b, the hydrogen bonding length in the S_0 benzil-CHD dimer is 3.60 Å, whereas in the T_1 state, it obviously deceases to be 2.68 Å. The strengthened hydrogen bonding in the T_1 dimer accelerates the HA. Figure 7c shows the transient absorbance of 4 mM benzil and 10 mM CHD in ethanol around 385 nm. The transient absorbance exhibits no increasing values, indicating that this HA happens faster than the apparatus resolution. In other words, this type of HA accompanied with the strengthened hydrogen bonding takes place faster than nanoseconds. On other side, as can be seen in Figure 7d and 7e, the hydrogen bonding length in the S_0 benzil-ethanol dimer is 1.94 Å, whereas in the T_1 state, it slightly increases to be 1.99 Å. The weakened hydrogen bonding in the T_1 dimer postpones the HA process. Moreover, the abstraction of H-atom on the hydroxyl group of ethanol by T_1 benzil needs to overcome one 0.7 eV potential barrier.[14] The 0.7 eV energy gap is compensated by the solvent collision. Both of the 0.7 eV potential barrier and weakened hydrogen bonding makes this HA a slow process. Actually, as can be seen in figure 7f, the transient absorption value continues to increase until 26 μs, proving experimentally this HA a rather slow process. We define this type of HA as collision-assisted HA. The transient absorption spectra and theoretical calculation suggest that the strengthened hydrogen bonding accelerates the HA, whereas the weakened one impedes the HA.

Figure 5 strongly indicates that the T_1 benzil prefers to abstract the H-atom from CHD rather than that from ethanol under identical conditions. To have better understanding of this phenomenon, we also need to consider the bond dissociation energies of the hydrogen donors. The bond dissociation energies are calculated as 98.2 Kcal/mol (4.26 eV) for C-H bond of CHD and 108 Kcal/mol (4.68 eV) for O-H bond of ethanol. Before the photon excitation, the hydrogen bonding length for the benzil-ethanol dimer is 1.94 Å, much shorter than 3.60 Å for the benzil-CHD dimer. After the photon excitation, although the triplet-state hydrogen bonding becomes 1.99 Å for the benzil-ethanol dimer, slightly shorter than 2.68 Å for the benzil-CHD dimer, the T_1 benzil is more prone to abstract the H-atom from CHD rather than ethanol. It is the bond dissociation energy that determines the subsequent reaction pathways. As the bond dissociation energy for C-H bond of CHD is smaller than that for O-H bond of ethanol by 10 Kcal/mol (0.43 eV), the T_1 benzil is more prone to abstract the H-atom from CHD. Hence, we argue that triplet-state hydrogen bonding mainly have great influences on the early stage of HA reaction, while the bond dissociation energies of the hydrogen donors determine the subsequent reaction dynamics.

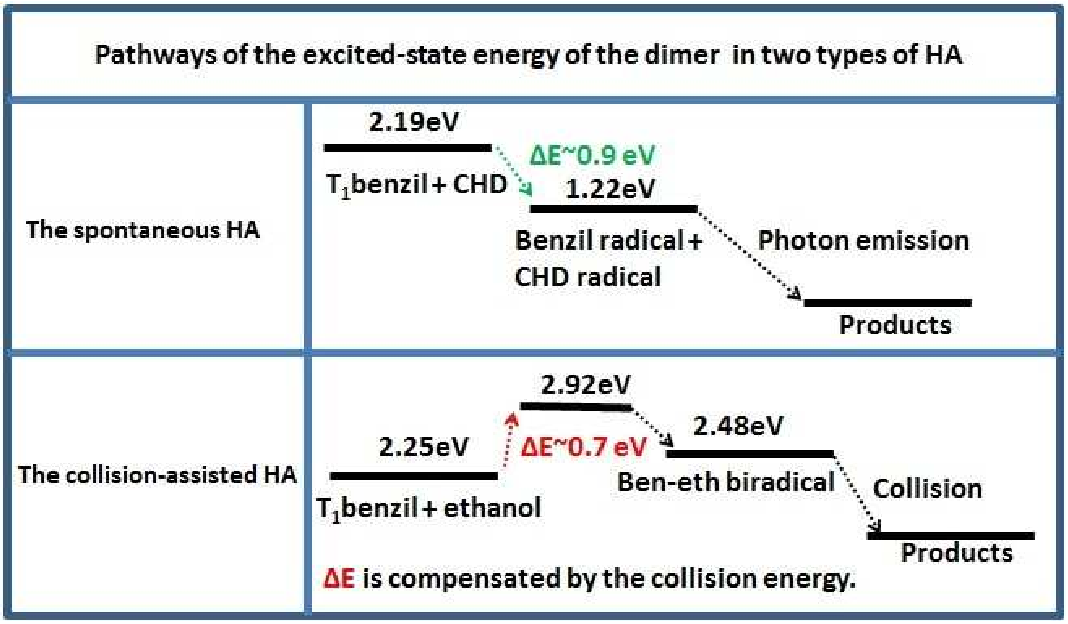


Figure 8. The pathways of the excited-state energy of the dimer in two types of HA

Two types of HA are summarized in Figure 8. After the photon excitation of the accepter-donor dimer in the spontaneous HA, the acceptor abstracts the H-atom from the donor within an ultrafast time scale, typically within nanoseconds. During this HA, the triplet-state energy of the dimer falls to lower level step by step. The newly formed intermediate is prone to deactivate through photon emission. By contrast, in the collision-assisted HA, the initial excitation energy is not high enough to make the collision-assisted HA happen smoothly. To make this HA happen, the triplet-state dimer needs to overcome one potential barrier through getting more energy from solvent collision. The collision-assisted HA happens on the time scale of microseconds, resulting in the formation of the new intermediate. This intermediate with lifetime on the order of several hundred microseconds tends to deactivate through the solvent collision without photon emission.

Table 1. The lifetimes of triplet-state intermediates in different solvents

Units: μs	Acetonitrile	Ethanol	Ethanol +CHD	Acetonitrile +CHD
T_2 benzil	1.95 ± 0.07[a]	9.17 ± 1.10[a]	4.70 ± 0.62	2.31 ± 0.31
T_1 benzil	8.94 ± 0.30[a]	48.61 ± 4.00[a]	37.00 ± 6.32	7.23 ± 4.68
Ben-eth biradical	○	375.83 ± 93.70[a]	○	○
benzil radical	○	○	55.99 ± 8.36	44.27 ± 2.64

[a] data reported in ref. 14.

The lifetimes of the triplet-state intermediates rely greatly on its solvents. As shown in Table 1, the lifetimes of T_2 and T_1 benzil in ethanol are longer than that in acetonitrile by approximate 10 μs. The lifetime of benzil radical in ethanol is still longer that than in acetonitrile by 10 μs. The lifetimes of the triplet-state intermediates in ethanol are obviously longer than that in acetonitrile. The triplet-state intermediates with longer lifetime may have more possibilities to interact with other chemicals. Thereby, if one utilizes photochemical methods in liquid to synthesize chemicals, the protic solvents might be better choice to improve the product efficiency than the non-protic solvents. In previous studies, the inside mechanism for the higher product efficiency of photoreactions in protic solvents is attributed to the enhanced efficiency of charge separation in photoinduced electron-transfer (PET) processes, which facilitate the generation of separated free radicals, resulting in higher reactivity and reaction rate.[33] In general, the undesired physical recombination processes intrinsically compete with the photochemical reactions. The reactive intermediates (free radicals or triplet molecule) with longer lifetime have more possibilities to trigger photochemical reactions rather than come back to the original molecule. In our studies, we found that the protic solvents could sustain longer lifetime of the reactive intermediates. By contrast with the enhanced efficiency of charge separation, our predicted higher efficiency of photoreactions in protic solvents is actually based on the longer lifetime of the reactive intermediates, which is different from the previous.

4. Conclusions

In summary, we have investigated the HA dynamics of triplet benzil through using the transient absorption spectroscopy and TD-DFT methods. Only T_1 benzil except other excited-states could abstract H-atom from the donors. Two types of HA, including the spontaneous and collision- assisted HA are clarified. The properties of the hydrogen donor determine the type of HA, energy relaxation as well as the lifetime of intermediate. It is found that the T_1 benzil is more prone to abstract the C1H of CHD than that of ethanol. The strengthened triplet-state hydrogen bonding could accelerate the HA, whereas the weakened triplet-state hydrogen bonding would postpone the HA. The photochemical reactions might have higher product efficiency in protic solvents than that in non-protic solvents.

Associated content

Supporting Information Available:

The excited-state energy variation of the dimer with O-H distance on the carbonyl of T_1 benzil are available free of charge via the Internet at http://pubs.acs.org.

Author information

Corresponding Author

klhan@dicp.ac.cn

Notes

The authors declare no competing financial interest.

Acknowledgments

We are grateful to the National Basic Research Program of China (2013CB834604) for their financial support.

Reference:

1 J. C. Scaiano, C. Aliage, S. Maguire and D. Wang, J. Phys. Chem. B, 2006, **110**, 12856-12859.

2 W. Lai, C. Li, H. Chen and S. Shaik, Angew. Chem. Int. Ed., 2012, **51**, 5556-5578.

3 M. L. T. Porro and M. M. Greenberg, J. Am. Chem. Soc., 2013, **135**, 16368-16371.

4 M. C. C. Cuquerella, V. Lhiaubet-vallet, J. Cadet and M. A. Miranda, Acc. Chem. Res., 2012, **45**, 1558-1570.

5 J. Zhang, D. C. Grills, K. Huang, E. Fujita and R. M. Bullock, J. Am. Chem. Soc., 2005, **127**, 15684-15685.

6 Sharon, H. S. Theory of Photon-Coupled Electron Transfer in Energy Conversion Processes. Acc. Chem. Res., 2009, **42**, 1881-1889.

7 M. T. Laren and M. S. Kyril, Acc. Chem. Res., 2002, **35**, 19-27.

8 B. C. Westlake, M. K. Brennaman, J. J. Concepcion, J. J. Paul, S. E. Bettis, S. D. Hampton, S. A. Miller, N. V. Lebedeva, M. D. E. Forbes, A. M. Moran, T.J. Meyer and J. M. Papanikolas, Proc. Natl. Acad. Sci., 2011, **108**, 8554-8558.

9 D. Andrea, S. C. Marina, N. K. Jyllian, L. Nicolai, I. S. Edward, J. Am. Chem. Soc., 2006, **128**, 4719-4733.

10 I. Andreu, F. Palumbo, F. Tilocca, I. M. Morera, F. Bosca, M. A. Miranda, Org. Lett., 2011, **13**, 4096-4099.

11 E. C. Lathioor and W. J. Leigh, Photochem. Phototobiol., 2006, **82**, 291-300.

12 W. J. Leigh, E. C. Lathioor and M. J. St. Pierre, J. Am. Chem. Soc., 1996, **118**, 12339-12348.

13 E. C. Lathioor, W. J. Leigh, M. J. St. Pierre, J. Am. Chem. Soc., 1999, **121**, 11984-11992.

14 Yang Y., L. Liu, H. Yin, D. Xu, G. Liu, X. Song and J. Liu, J. Phys. Chem. C, 2013, **117**, 11858-11865.

15 G. J. Zhao and K. L. Han, Acc. Chem. Res., 2012, **45**, 404-413.

16 K. L. Han and G. J. Zhao, Hydrogen Bonding and Transfer in the Excited State. John Wiley & Sons Ltd.: Chichester, U.K., 2011, Vol. I & II.

17 G. J. Zhao and K. L. Han, J. Phys. Chem. A, 2007, **111**, 2469-2474.

18 G. J. Zhao and K. L. Han, ChemPhysChem., 2008, **9**, 1842-1846.

19 G. J. Zhao and K. L. Han, J. Phys. Chem. A, 2007, **111**, 9218-9223.

20 K. L. Han and G. Z. He, J. Photochem. Photobiol. C: Photochem.Rev., 2007, **8**, 55-66.

21 G. J. Zhao and K. L. Han, J. Phys. Chem. A, 2009, **113**, 14329-14335.

22 G. J. Zhao and K. L. Han, Biophys. J., 2008, **94**, 38-46.

23 F. Yu, P. Li, G. Li, G. Zhao, T. Chu and K. Han, J. Am. Chem. Soc., 2011, **133**, 11030-11033.

24 G. J. Zhao, J. Y. Liu, L. C. Zhou and K. L. Han, J. Phys. Chem. B 2007, **111**, 8940-8945.

25 G. J. Zhao and K. L. Han, J. Chem. Phys., 2007, **127**, 024306.

26 G. J. Zhao, B. H. Northrop, K. L. Han and P. J. Stang, J. Phys. Chem. A, 2010, **114**, 9007-9013.

27 D. Yang, Y. Yang and Y. Liu, Commun. Comput. Chem., 2013, **1**, 205-215.

28 M. Zhang, B. Ren, Y. Wang and C. Zhao, Commun. Comput. Chem., 2013, **1**, 216-224.

29 Y. Liu and S. Lan, Commun. Comput. Chem., 2013, **1**, 235-243.

30 W. H. Fang, Acc. Chem. Res. 2008, 41, 452-457.

31 B. Bhattacharya, B. Jana, D. Bose and N. Chattopadhyay, J. Chem. Phys., 2011, 134, 044535.

32 T. S. Fang, R. E. Brown, C. L. Kwan and L. A. Singer, J. Chem. Phys., 1978, 82, 2489-2496.

33 A. Lewandowska, G. L. Hug, G. Hçrner, T. Pedzinski, P. Filipiak, and B. Marciniak, ChemPhysChem, 2010, 11, 2108 – 2117.