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A DFT/TDDFT study of hydrogen bonding interactions between resorufin anion and water molecules in the excited state

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ABSTRACT

In order to explore the hydrogen bonding interactions between resorufin anion (denoted as Res^- in this paper) and water molecules, we have calculated the geometric structures as well as the total energies of the various hydrogen-bonded Res^-–water complexes composed based on the atomic charges obtained from the NBO analysis. We found that there are four sites (O_{1-3}, N_1) within the Res^- molecule through which intermolecular hydrogen bonds can be formed with water molecule. Furthermore, by comparing the hydrogen bond lengths and the relative energies of the four singly hydrogen-bonded complexes Res^-–H_2O, we found that hydrogen bonds formed at the two carbonyl oxygen atoms (O_2 and O_3) are stronger than those formed at heteroatom O_1 and N_1 which can be reasonably predicted by the highest negative charge localized on the two former atoms. Moreover, as the number of the water molecules hydrogen-bonded to the Res^- increases, the hydrogen-bonded complex Res^-–water becomes more stable although the strength of each hydrogen bond decreases. In addition, the electronic spectra of the various hydrogen-bonded Res^-–water complexes as well as the Res^- monomer are also calculated. We found that, compared with that of the Res^- monomer, the excitation spectra of the hydrogen-bonded Res^-–water complexes are mostly blue-shifted in the S_2 and S_3 states while they are all red-shifted in the higher excited states, especially in states S_{10}, S_{11} and S_{12}. According to the relationship between electronic spectral shifts and electronic excited-state hydrogen-bonding dynamics first clarified by Zhao and coworkers [51], we demonstrate that, for all the hydrogen-bonded Res^-–water complexes, most of the hydrogen bonds are weakened in the S_2 and S_3 states while they are all strengthened in excited states S_{10}, S_{11} and S_{12}.

1. Introduction

Hydrogen bonding, as a site-specific interaction between hydrogen donor and acceptor molecules, is an important type of solute–solvent interaction which has been recognized to play a fundamental role in molecular and supramolecular photochemistry [1–25]. The hydrogen bonds in the hydration shells of ions, photobiological reactions and interactions between DNA and drugs have been investigated by Hynes et al. [6,8,17,19,22] while Mataga and co-workers have contributed to the recognition of the role of hydrogen bonds in photochemistry and photobiology [1,3,5,16]. Hydrogen bonding in the ground state has been extensively studied by many different experimental and theoretical methods [26–36]. Furthermore, Sobolewski et al. have reported theoretical results on intramolecular hydrogen bonds in excited states and their role in the phenomenon of excited-state intramolecular proton transfer (ESIPT) [37–42]. Moreover, Fukuzumi et al. have contributed work about the effects of hydrogen bonding on photoinduced electron transfer (PET) in complex systems [43–47]. In addition, Zhao and coworkers have first demonstrated that the molecular photochemistry in solution can be significantly tuned by hydrogen bonding interactions in electronically excited states [48–51]. Especially, in their studies on the effects of intermolecular hydrogen bonding on tuning the photochemistry of two representative thiocarbonyl chromophores, thiocoumarin (TC) and 4H-1-benzopyrane-4-thione (BPT), they found that, due to the concerted intermolecular hydrogen bond strengthening and weakening, the S_2 fluorescence via the direct $S_2 \rightarrow S_0$ pathway which dominates the deactivation process of the S_2 state of the two thiocarbonyl chromphores is strongly quenched in polar protic methanol solvent and replaced by the T_1 phosphorescence via the $S_2 \rightarrow S_1 \rightarrow T_1 \rightarrow S_0$ decay channel [51]. Furthermore, the relationship between electronic spectral shifts and the electronic excited-state hydrogen-bonding dynamics has also been clarified for the first time. They confirmed that hydrogen bond strengthening can lower the excitation energy of a related excited state and therefore induce an electronic spectral red-shift while hydrogen bond weakening can heighten the excitation energy of a related

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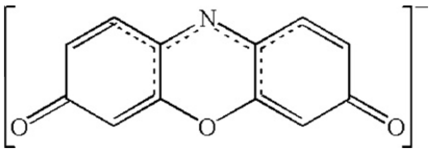
excited state and induce an electronic spectral blue-shift [51]. Therefore, it provides us another reliable tool to investigate the excited-state hydrogen bonding dynamics by monitoring the electronic spectral shifts of different excited states.

Resorufin, as an important chromophore molecule, has been widely studied both experimentally and theoretically [52–58]. The rotational relaxation of the negatively charged resorufin (Res$^-$, see in Scheme 1) in ethanol is observed to be slower than that of the positively charged solutes and has been explained by the hydrogen bond donating character of the alcohol solvents and solvent association with the solute [52,57]. Furthermore, subtle state-dependent reorientation characteristics of resorufin in a series of butanols have also been revealed in experiments which can be interpreted in terms of excitation-dependent changes in Lewis basicity at the heteroatom sites and provides evidence for strong solvent interaction at the end groups. At the same time, semiempirical MNDO molecular orbital calculations indicate that the π-electron density at the ring-bound nitrogen increases significantly upon excitation [53]. Moreover, in the studies of the Non-photochemical hole burning (NPHB) of resorufin in ethanol solvents, a model of photoinduced concerted rearrangement of intermolecular hydrogen bonds between two ethanol molecules and a resorufin molecule was proposed by Kokai and coworkers [54]. Otherwise, a spectroscopically identified species which can only be detected at temperature lower than 190 K has been discovered to result from the interaction of the resorufin probe with protic solvent alcohols. The resemblance of such a species to the neutral form of resorufin indicates the involvement of a strong hydrogen bond between the solvent and the alkoxide ion of resorufin which means that a hydrogen-bonded Res$^-$–alcohol complex may be formed and thermally equilibrated with the ionic form of resorufin [55]. In the studies of the reorientation dynamics of solvent molecules, resorufin has been used as a probe molecule and shown some interesting chemistry and photochemistry properties in protic solvents which strongly depends on the temperature, viscosity and structure of the solvent, such as the equilibrium of the two forms in which resorufin is present which can be interchanged photochemically [56].

Recently, in the research of the rotational diffusion dynamics of resorufin in water and N-octyl-2-pyrrolidone (NOP) solvents, Blanchard and coworkers observed a broad absorption band from 400 to 500 nm in water which is not present in the NOP solvent [58]. Based on the properties of resorufin chromophore in alcohol solvents demonstrated above, we proposed that the absorption band from 400 to 500 nm in water may be originated from the hydrogen-bonded Res$^-$–water complex. In order to get a better understanding of the intermolecular hydrogen bonding between Res$^-$ and water molecules and its changes in different excited states, we are motivated to calculated the various hydrogen-bonded conformations formed by Res$^-$ and water molecules and their electronic excitation energies to different excited states. After complete optimizations of the hydrogen-bonded Res$^-$–water complexes, we found that four intermolecular hydrogen bonds can be formed between one Res$^-$ molecule and four water molecules in the ground state. Furthermore, by comparing the hydrogen bond lengths and the relative energies of the four singly hydrogen-bonded complexes Res$^-$–H_2O, we found that hydrogen bonds formed at the two carbonyl oxygen atoms (O_2 and O_3) are stronger than those formed at heteroatom O_1 and N_1. Moreover, upon photoexcitation to different excited states, two of the four intermolecular hydrogen bonds, labeled as HB-II and HB-III, change in quite similarly way while HB-I and HB-IV behaved rather differently. By comparing the electronic excitation spectra of the different hydrogen-bonded Res$^-$ complexes with that of the Res$^-$ monomer and based on the relationship between electronic spectral shifts and hydrogen bonding changes first clarified by Zhao and coworkers [51], we demonstrated that the strength of the intermolecular hydrogen bonds formed at different sites of the Res$^-$ molecule becomes strengthened or weakened in different excited states which can be visually illustrated by the increase or decrease of the electron density in the molecular orbitals (MOs) localized on the groups which are involved in the formation of the corresponding intermolecular hydrogen bonds.



Scheme 1. The schematic chemical structure of resorufin anion, denoted as Res$^-$ in this paper. For clarity, the hydrogen atoms are not shown.

2. Computational details

For all the different hydrogen-bonded Res$^-$–water complexes, calculations on the ground-state geometric structure optimizations and excitation energies as well as related frontier molecular orbitals for different excited states are performed using the density functional theory (DFT) method with the Becke's three-parameter hybrid exchange function with Lee–Yang–Parr gradient-corrected correlation functional (B3-LYP functional) [59–62] and 6-31G(d)/G(d, p) basis sets [59,60]. All calculations were carried out using Gaussian 03 program package [63].

3. Results and discussions

3.1. The chemical structure and atomic charges

The chemical structure of resorufin anion is shown in Scheme 1. From Scheme 1, we can see that the Res$^-$ has C2v symmetry which means that the two carbonyl oxygen atoms are equivalent. Therefore, the two atoms, labeled as O_2 and O_3, should bear the same fraction of negative charge, as shown in Fig. 1. In Fig. 1, we have presented the total atomic charges of Res$^-$ obtained from the NBO analysis by carrying out single-point calculation. It is noted that the two carbonyl oxygen atoms O_2 and O_3 have born the same

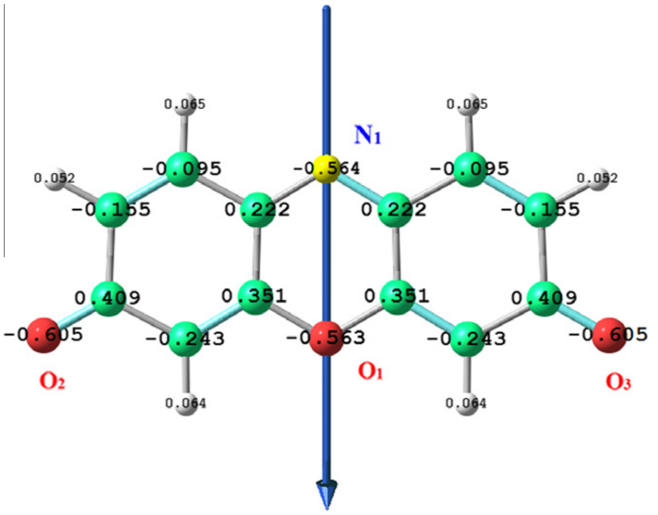


Fig. 1. The total atomic charges of the Res$^-$ obtained from the NBO analysis with the oxygen and nitrogen atoms labeled. The blue arrow denotes the dipole moment. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)