

## ARTICLE

# Hydrogen-bonded Intramolecular Charge Transfer Excited State of Dimethylaminobenzophenone using Time Dependent Density Functional Theory

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Density functional theory and time-dependent density-functional theory have been used to investigate the photophysical properties and relaxation dynamics of dimethylaminobenzophenone (DMABP) and its hydrogen-bonded DMABP-MeOH dimer. It is found that, in non-polar aprotic solvent, the transitions from  $S_0$  to  $S_1$  and  $S_2$  states of DMABP have both  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  characters, with the locally excited feature mainly located on the C=O group and the partial CT one characterized by electron transfer mainly from the dimethylaminophenyl group to the C=O group. But when the intermolecular hydrogen bond  $C=O \cdots H-O$  is formed, the highly polar intramolecular charge transfer character switches over to the first excited state of DMABP-MeOH dimer and the energy difference between the two low-lying electronically excited states increases. To gain insight into the relaxation dynamics of DMABP and DMABP-MeOH dimer in the excited state, the potential energy curves for conformational relaxation are calculated. The formation of twisted intramolecular charge transfer state via diffusive twisting motion of the dimethylamino/dimethylaminophenyl groups is found to be the major relaxation process. In addition, the decay of the  $S_1$  state of DMABP-MeOH dimer to the ground state, through nonradiative intermolecular hydrogen bond stretching vibrations, is facilitated by the formation of the hydrogen bond between DMABP and alcohols.

**Key words:** Hydrogen-bond, Intramolecular charge transfer, Relaxation dynamic, Twisting dynamic

## I. INTRODUCTION

The photophysical and photochemical properties of the excited state of benzophenone and its numerous kinds of derivatives have been investigated by the ultrafast dynamics, surface-enhanced Raman scattering (SERS), and Raman spectroscopy [1–3]. The substituent of the aromatic rings influences the relative position of two kinds of excited states, namely,  $n\pi^*$  and  $\pi\pi^*$  states, on the energy scale in both the singlet and the triplet manifolds. The properties of the excited singlet and triplet states of the hydroxy- and amino-substituted benzophenone derivatives have been studied using time-resolved fluorescence and absorption spectroscopic techniques, and the different fluorescence characteristics in the two derivatives were ob-

served [1]. Benzophenone and its hydroxyl substituted derivatives were found almost nonfluorescent, while the amino-substituted derivatives were only weakly fluorescent. Recently, the ultrafast relaxation dynamic of the excited states of dimethylaminobenzophenone (DMABP), and Michler's ketone (MK) were studied employing the femtosecond transient absorption spectrometer [1]. The remarkable red-shift of both absorption and fluorescence maxima observed in DMABP and MK in more polar solvents indicates a strong intramolecular charge-transfer (ICT) feature of the  $S_1$  state. Like other amino-substituted benzophenone derivatives, such as p-aminobenzophenone (PABP), the fluorescence of DMABP and MK are weak but these systems show a feature of "dual fluorescence".

The phenomenon of dual fluorescence in compounds such as 4-(N,N-dimethylamino)benzotrile (DMABN), first discovered by Lippert *et al.* [4], is an example of a more general process involving photoadiabatic reaction in the excited states. Since then, the dual-fluorescence feature was observed in a large variety of compounds such as non-substituted linear polyenes

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and in donor-acceptor systems, structurally similar to DMABN [5–7]. The implicit assumption of this model is a twisting motion of the donor group to a plane perpendicular to the acceptor group that takes the initially generated locally excited (LE) state to another minimum on the excited state potential energy surface (PES) [8]. Moreover, various models were proposed to explain the mechanism of the dual fluorescence, such as the twisted intramolecular charge transfer (TICT) [9], planar ICT (PICT) [10], and so on. Among them, the TICT model is supported by a large amount of experimental data [11], and its validity is also confirmed by numerous theoretical studies [7]. Dual-fluorescence strongly depends on the energy gap between the first two excited states ( $n\pi^*$  and  $\pi\pi^*$ ), which is significantly influenced by the substituted donor strength and the solvent polarity. For instance, in DMABN comparatively strong donor substituted by the amino group modifies the excited states ( $S_1$  and  $S_2$ ) by tuning their energy level and shows a dual emission, whereas a relatively weak donor primary amino group in 4-aminobenzonitrile (ABN) cannot tune the excited state energy level and is thus unable to show dual-fluorescence even in highly polar solvent [12].

Most importantly, the phenomenal success of density functional theory (DFT) motivated us to employ this method for the examination of the small energy gap between the lower excited states ( $S_1$  and  $S_2$ ) of DMABP [9, 13–15]. In particular, the accuracy achieved for the ground state and the excited state calculation using TDDFT is good enough to aid in assigning experimental spectra for these systems.

On the other hand, the influences of the excited-state hydrogen bonding have been proven to play an important role in the excited state relaxation processes and strongly affects the various photophysical processes. And the combination of various spectroscopic experiments with theoretical calculations has led to tremendous progress in excited-state hydrogen-bonding research [16–18]. For example, Zhao *et al.* firstly demonstrated that the intermolecular hydrogen bond in the electronic excited state was greatly strengthened for coumarin chromophores and weakened for thiocarbonyl chromophores. As a conclusion, the intermolecular hydrogen-bond strengthening and weakening correspond to red-shifts and blue-shifts in the electronic spectra, respectively, was clarified [16]. The intermolecular hydrogen bonding was also found to facilitate the solute-solvent photoinduced electron transfer (PET), internal conversion (IC), intersystem crossing (ISC), metal-ligand charge transfer (MLCT), and so on [17, 18].

In this work, we try to address the relaxation dynamics of DMABP (molecular structure is shown in Fig.1) by characterizing its excited-state properties in alcohols using the TDDFT method. We pay attention to the conformational change of DMABP induced by the H-bonding between the solute and the alcohols, includ-

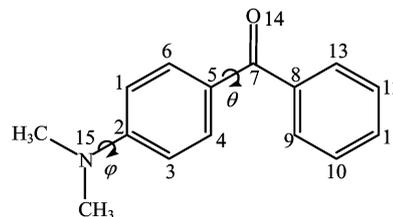


FIG. 1 Chemical Structure of the DMABP compound.

ing the dynamics process in the protic solvents, and we choose methanol as an example of protic solvent.

## II. THEORETICAL METHODS

All the electronic structure calculations were carried out using the TURBOMOLE program suite [19–22]. The geometry optimizations of the isolated monomers and the hydrogen-bonded solute-solvent complexes considered here for the ground state were performed, using DFT with Becke's three-parameter hybrid exchange function with Lee-Yang-Parr gradient-corrected correlation functional (B3-LYP functional) [20]. The triple- $\zeta$  valence quality with one set of polarization functions (def-TZVP) was chosen as basis sets throughout [21]. The potential energy curves were calculated using time-dependent density functional theory (TD-DFT) with B3-LYP hybrid functions and the def-TZVP basis set, fine quadrature grids 4 were also employed [22]. The convergence thresholds for the ground-state optimization were reset to be  $10^{-8}$  (default settings of  $10^{-6}$ ). Absorption energy obtained from TDDFT calculation is the vertical excitation energy without zero point correction [8, 13, 23]. For the construction of the energy curves, the geometry is kept frozen to that optimized for the ground state at any point and for any electronic state; the only changing parameter is the twisting angle which vary from  $0^\circ$  to  $180^\circ$  in steps of  $10^\circ$ .

## III. RESULTS AND DISCUSSION

### A. Ground state structures and MOs

To investigate the intermolecular hydrogen bonding interactions between DMABP and the protic methanol (MeOH) molecules, 1:1 hydrogen bonding complex has been used, and the bulk effect of the outer solvation shells is not considered, since there is only one alcoholic molecule participated in forming hydrogen bonding. This model has been widely used in previous works [7, 16, 17], and obtained good agreements with experiments results. In this work, only the intermolecular hydrogen bond  $C=O \cdots H-O$  between DMABP and MeOH is considered in the hydrogen-bonded DMABP-MeOH dimer. It is noted that the intermolecular hy-

TABLE I Selected electronic excitation energies and corresponding oscillator strengths  $f$ , main configurations and CI coefficients of the low-lying electronically excited states of the hydrogen-bonded DMABP dimer as well as the isolated DMABP.

	Electronic transition	Calculated				Experimental [1]
		$\Delta E^a$ /eV	$f^b$	Composition <sup>c</sup>	CI <sup>d</sup>	
DMABP	S <sub>1</sub>	3.63 (342 nm)	0.107	H→L	45.7	325 nm
				H-1→L	44.3	
	S <sub>2</sub>	3.77 (329 nm)	0.236	H→L	50.8	
				H-1→L	44.0	
DMABP-MeOH	S <sub>1</sub>	3.60 (344 nm)	0.331	H→L	90.5	355 nm
	S <sub>2</sub>	3.80 (326 nm)	0.060	H-2→L	66.1	

<sup>a</sup> Only selected low-lying excited states were considered. The numbers in parentheses are the excitation energies at wavelength.

<sup>b</sup> Oscillator strength.

<sup>c</sup> H stands for HOMO and L stands for LUMO. Only the main configurations are presented.

<sup>d</sup> CI coefficients are in absolute values.

drogen bond N···H–O may also be formed between the amino group of DMABP and the hydroxyl group of MeOH and influence the formation of the TICT state. However, after the intramolecular charge transfer from the amino group moiety to the C=O group moiety in the electronically excited state, the amino group will be positively charged and slightly influenced by the intermolecular hydrogen bond N···H–O [7]. The optimized structures of isolated DMABP and DMABP-MeOH complex in ground state and their MOs are shown in Fig.2.

From the calculated values of the geometrical parameters, we note that the optimized geometries are nonplanar: the dihedral angle between the phenyl plane of the dimethylaminophenyl moiety and the carbonyl group of the DMABP-MeOH complex becomes about 21° with the two halves of the molecule having initial dihedral angle of about 53° (Fig.2(b)), while for the isolated DMABP molecule it is about 22° and 54° (Fig.2(a)), respectively, which is close to those reported previously by Duan *et al.* [8]. The nitrogen atom and two carbon atoms of the dimethylamino group are lying on the same plane of the phenyl ring to which the dimethylamino group is attached.

## B. Electronic spectra

Experimental absorption spectra and the calculated electronic transition energies as well as oscillator strengths of isolated DMABP molecule and hydrogen-bonded DMABP-MeOH complex are reported in Table I. Similar to the previous report by Duan *et al.* [8], the analysis of the electronic transition and the frontier molecular orbitals shows that the S<sub>1</sub> and S<sub>2</sub> states of DMABP are mainly composed of n→π\* (HOMO-1 to LUMO) and π→π\* (HOMO to LUMO) nature of transition, as can be seen from Table I and Fig.2(a). In addition, the comparative magni-

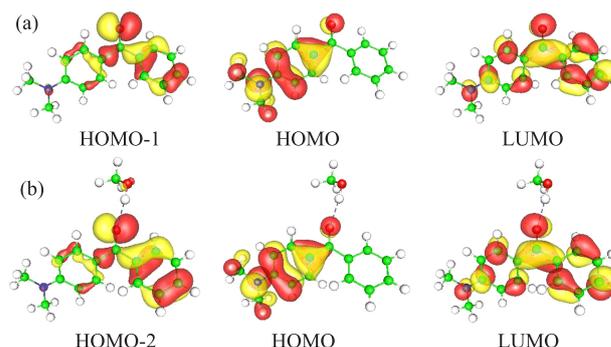


FIG. 2 Optimized geometric structures and frontier molecular orbitals (MOs) of the isolated DMABP and hydrogen-bonded DMABP-MeOH dimer.

tude of the HOMO→LUMO and the HOMO-1→LUMO transition contributes to the S<sub>1</sub> and S<sub>2</sub> state, respectively. Thus, in the case of the gas-phase absorption of DMABP (in vacuum), the S<sub>1</sub> and S<sub>2</sub> states of DMABP have both n→π\* and π→π\* characters, with the LE feature mainly located on the C=O group and the partial CT one characterized by electron transfer mainly from the dimethylaminophenyl group to the C=O group [1]. The energy difference between the two states has been calculated to be about 0.14 eV for DMABP, at the B3LYP/def-TZVP level (see Table I). The small energy gap between these two interacting states is an essential prerequisite for the ICT process, which includes the part of charge transfer inferred by n→π\* transition at the primary conformation, owing to the overlap of the orbitals.

On the other hand, the S<sub>1</sub> and S<sub>2</sub> states of the hydrogen-bonded DMABP-MeOH complex behave differently as compared to the isolated DMABP molecule. Experimentally, the steady-state absorption spectrum of DMABP in the methanol solvent exhibits an intense absorption band with maximum at 355 nm (3.50 eV),

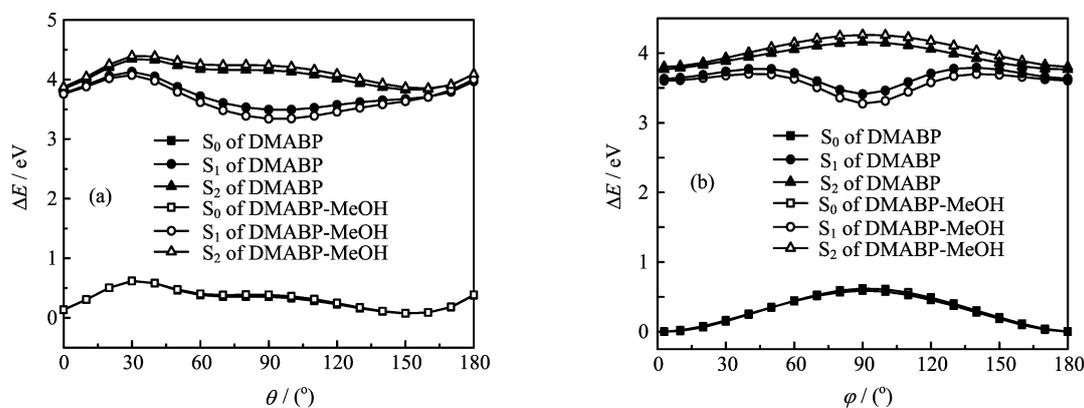


FIG. 3 Ground and low-lying singlet excited-state potential curves (energy relative to the minimum of the ground state) as a function of the twisting angle of (a)  $\theta$ -dimethylaminophenyl group and (b)  $\varphi$ -dimethylamino group.

which is assigned to a  $\pi \rightarrow \pi^*$  transition [24, 25]. Our calculations of DMABP-MeOH complex indicate that this maximum absorption band observed in the experiment corresponds to the S<sub>1</sub> state (electric transition energy  $\sim 3.60$  eV), which has the larger oscillator strength and is characterized by charge transfer, mainly comes from the HOMO  $\rightarrow$  LUMO transition. The good agreement between the calculated absorption spectral features and the spectral results recorded in experiments confirms that the intermolecular hydrogen bonding C=O  $\cdots$  H-O interaction between DMABP and methanol in the first solvation shell is formed and plays a dominant role in the steady-state and dynamic spectral properties. While for S<sub>2</sub> state, which is of LE feature, comes from the HOMO-2  $\rightarrow$  LUMO transition with a relatively small contributions from other transitions (HOMO  $\rightarrow$  LUMO and so on). As the energy difference between these two states increases to 0.2 eV when the hydrogen-bond C=O  $\cdots$  H-O is formed, the conclusion of the excited-state hydrogen bonding being strengthened can be gotten.

Furthermore, from the calculated oscillator strengths in vacuum, the first singlet excited state is weakly allowed transition, and the relatively intensive transition corresponds to the second excited state. In methanol solution, the case is inverted, namely, the first excited state becomes the most intensive transition. This indicates a transformation from the forbidden  $n \rightarrow \pi^*$  transition to the allowed  $\pi \rightarrow \pi^*$  transition for the S<sub>1</sub> state on going from gas phase to solution.

### C. Twisting dynamics in vacuum and in methanol solvent

Experimental observations clearly indicate that: the low fluorescence quantum yields and the short excited-state lifetimes of DMABP in solutions are the direct indications of the nonradiative processes being dominant in the excited-state relaxation process of DMABP [1]. In alcohols, very short lifetimes of the S<sub>1</sub> state, strong dependence of the lifetimes on viscosity, as well as very

large nonradiative decay rates (in methanol the  $k_{\text{NR}}$  value is about  $\sim 200$  times larger than those in aprotic solvents) are indicative of the fact that very fast energy degradation via the intermolecular hydrogen bond stretching vibrations also play an important role in the deactivation process along with the intramolecular conformational relaxation processes [9]. Therefore, in this section, we will discuss the potential energy curve of conformational relaxation via molecular twisting: (i) twisting of only the dimethylamino group or (ii) twisting of the dimethylaminophenyl group with respect to the benzoyl group. The results for the ground state and the two lowest excited states along the twisting coordinate of both isolated DMABP and hydrogen-bonded DMABP-MeOH dimer are presented in Fig.3. As compared the potential energy curve of the selected excited states with those in vacuum, the presence of the methanol solvent significantly changes the energy gaps of these states, but the profile is insensitive to the intermolecular hydrogen bond interaction. In detail, as can be seen from Fig.3, either twisting the angle  $\varphi$  or  $\theta$  is found to facilitate stabilizing the S<sub>1</sub> state of DMABP-MeOH dimer, while the energy gap is enhanced between its S<sub>2</sub> state and the ground state. In addition, both the twisting-angle  $\varphi$  and  $\theta$  potential-energy curves of their S<sub>1</sub> states have energy gaps with the minimum energy at 90°, and the later one behaves obviously. The potential energy curves also imply a relatively weak barrier for twisting both the angle  $\varphi$  and  $\theta$  in the excited state. So after photoexcitation, DMABP and its DMABP-MeOH dimer can be initially excited to the conformation unrelaxed Franck-Condon state, and in succession the dimethylamino and dimethylaminophenyl groups wag along the N15-C2 and C5-C7 bond, respectively, until it gets a stable conformational geometry with the charge transfer from donor to acceptor.

Furthermore, in protic solvents, the configuration with the maximum dipole moment is preferentially stabilized, so that for strong dipolar stabilization and weak mesomeric interaction, the lowest excited state corre-

sponds to the twisted structure [26], with angles of the dimethylamino and dimethylaminophenyl groups both twisted. Under this configuration, the energy gap between the  $S_1$  state and the ground state of DMABP-MeOH dimer becomes minimal due to the intermolecular hydrogen bond interaction. Therefore, the non-radiative decay via the intermolecular hydrogen bond stretching vibrations dominates the deactivation process of this excited state along with the intramolecular conformational relaxation to the TICT state, which results in the low fluorescence quantum yields of DMABP in alcohols.

#### IV. CONCLUSION

We have studied the photophysics and the relaxation dynamics in the excited singlet states of DMABP and DMABP-MeOH dimer. In non-polar aprotic solvent (similar to vacuum), due to the energetic proximity of the  $S_1$  and  $S_2$  states, the two transitions have both  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  characters. But in the presence of intermolecular H-bonding, the highly polar ICT state switches over to the first excited state and the energy difference between the two states increases. This indicates a transformation from the forbidden  $n \rightarrow \pi^*$  transition to the allowed  $\pi \rightarrow \pi^*$  transition for the  $S_1$  state on going from gas phase to solution. Furthermore, by using twisting dynamics analysis theoretically, we could obtain the direct evidence for the configuration relaxation process of the excited state, where the twisting motion accompanied. And in alcoholic solvents, due to strong hydrogen-bonding interaction with the  $S_1$  state, nonradiative transition of the TICT state dominates the deactivation process via the intermolecular hydrogen bond stretching vibrations.

#### V. ACKNOWLEDGMENTS

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