ARTICLE

Absorption Spectra and Photoreactivity of p-Aminobenzophenone by Time-dependent Density Functional Theory

Xue-mei Cheng, Yao Huang, Jian-yi Ma, Xiang-yuan Li[*]

College of Chemical Engineering, Sichuan University, Chengdu 610065, China

The absorption spectral properties of para-aminobenzophenone (p-ABP) were investigated in gas phase and in solution by time-dependent density functional theory. Calculations suggest that the singlet states vary greatly with the solvent polarities. In various polar solvents, including acetonitrile, methanol, ethanol, dimethyl sulfoxide, and dimethyl formamide, the excited S_1 states with charge transfer character result from $\pi \rightarrow \pi^*$ transitions. However, in nonpolar solvents, cyclohexane, and benzene, the S_1 states are the result of $n \rightarrow \pi^*$ transitions related to local excitation in the carbonyl group. The excited T_1 states were calculated to have $\pi\pi^*$ character in various solvents. From the variation of the calculated excited states, the band due to $\pi \rightarrow \pi^*$ transition undergoes a redshift with an increase in solvent polarity, while the band due to $n \rightarrow \pi^*$ transition undergoes a blueshift with an increase in solvent polarity. In addition, the triplet yields and the photoreactivities of p-ABP in various solvents are discussed.

Key words: TDDFT, p-Aminobenzophenone, Photoreactivity, Excited state

I. INTRODUCTION

Photoexcitation of ground-state species leads to the formation of excited states. Some excited molecules can abstract hydrogen atoms from the neighboring molecules [1,2]. In the past century hydrogen-abstraction reactions from photoexcited molecules have been studied intensively by theoretical and experimental methods [3-8]. The rate, efficiency and mechanism of this reaction have been shown to depend to a great extent on the electronic configuration of the lowest triplet excited state [2,3,6]. The photoreduction of benzophenone (BP) is a typical photoreaction [5]. It has been shown that the S_1 and T_1 states of BP have $n\pi^*$ character in almost all kinds of solvents, including nonpolar and polar, as well as hydrogen-bonding ones [9]. The $n \rightarrow \pi^*$ transition can lead to a decrease in the charge density of the oxygen atom of the carbonyl group and sequentially induces the formation of a radical. Such a radical can abstract hydrogen atoms in a photoreduction reaction. However, owing to the existence of electron-donating groups, such as OH, OCH_3, $N(CH_3)_2$, and NH_2 substitutes on the aromatic rings of BP, the reactivities of these derivatives towards hydrogen abstraction reactions change greatly [9-15]. For example, one of the amino-substituted products of BP, para-aminobenzophenone (p-ABP), can hardly ever abstract hydrogen atoms in any kind of solvent [10,16]. Such a low photoreactivity of p-ABP is perhaps related to the $\pi\pi^*$ character of the T_1 state [9,12,16,17].

Time-dependent density functional theory (TDDFT)

extends the basic ideas of ground-state DFT towards the treatment of excited states or other time-dependent phenomena [18-22]. In recent years, it has been used more and more in computational chemistry. A mass of data have verified that TDDFT is a valid method for electronic excitations both in gas [23,24] and in solution [25]. The Onsager model [26] and the polarizable continuum model (PCM) [27,28] are generally applied to TDDFT for electronic excitations in solution. In this work, we adopt the integral equation formalism polarizable continuum model (IEFPCM) [29-31] for the calculation of the excited states in solution.

Photophysical and photochemical properties of p-ABP have been studied for several decades in experiment [10,13,16,32,33]. Ghoneim et $al.$ predicted that the transferred charge is about 0.8 from the amino-substituted aromatic ring to the carbonyl acceptor group in a "charge transfer" (CT) state of p-ABP [16]. They also observed that p-ABP exhibits a high triplet yield but a low reaction yield towards hydrogen abstraction reactions, which has continued to be hard to understand for many years. However, theoretical methods have been rarely adopted for this system, and the high triplet yield but low photoreduction reactivity of p-ABP has not been explained in detail. Hence, in this work, TDDFT is used to investigate the photophysical and photochemical properties of p-ABP. Firstly, the singlet states of p-ABP were calculated in various organic solvents and a comparison was made with experimental observations [10]. Since the photoreduction reactivity of p-ABP greatly depends on the electronic configuration of its lowest triplet state, a further investigation of the excited triplet states was performed. Based on the calculated results, the triplet yield and the low photoreactivity of p-ABP in different solvents are discussed.

───────

[*]Author to whom correspondence should be addressed. E-mail: xyli@scu.edu.cn

273

II. COMPUTATIONAL METHODS

All the calculations in this work were carried out using the Gaussion03 package [34]. The geometry of *p*-ABP was optimized using B3LYP function [35] with the 6-31+G* basis sets in gas phase. Frequency analysis was performed to confirm the stability of the optimized geometry. The absorption spectra of *p*-ABP were calculated both in gas phase and in solution at the TD-B3LYP/6-311+G** level. Ground state geometry was used for all the calculations of the excited states. Hence, the theoretical excited energies are just the vertical transition energies without the zero-point energy correction and they are regarded to correspond to the band maxima in experimental spectra. In this work, five singlet states and three triplet states in each solvent and in vacuum were calculated, and these excited states are denoted as S_1, S_2, S_3, S_4, S_5 and T_1, T_2, T_3. The one-particle density matrix was used to calculate the dipole moments of excited states (key word: RhoCI). As expected, this method typically resulted in an overestimation of the dipole moment [15]. However, it is reasonable in the qualitative discussions.

III. RESULTS AND DISCUSSION

A. Ground-state properties and gas phase absorption of *p*-ABP

The model molecule *p*-ABP (Fig.1) was optimized by B3LYP/6-31+G*. Optimization indicated that this molecule is non-planar. The dihedral angle ∠5-6-7-14 was predicted to be 25.5° and the ∠9-8-7-14 was 32.3°. The dipole moment of the ground state was calculated to be about 4.54 D. The total energy for the system was estimated to be −632.01496 a.u..
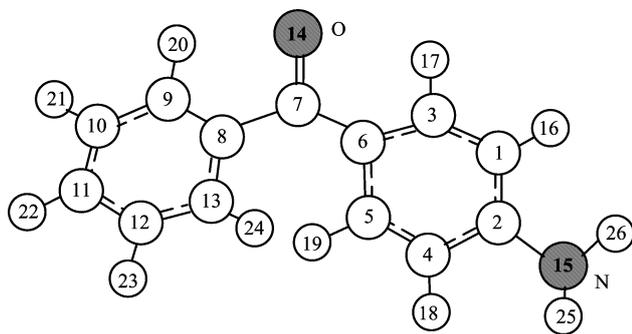

FIG. 1 The model molecule *p*-ABP.

The calculated results with TDDFT for absorption in gas phase are collected in Table I, including the lowest five singlet states and three triplet states, along with their excitation energies and oscillator strengths. The S_2 state from HOMO→LUMO transition with a large dipole moment (18.38 D) is assigned to be the most

TABLE I Vertical excitation energies of low-lying excited states of *p*-ABP in gas phase

State	ΔE^a	f^b	$\mu_e{}^c$	Dominant transition[d]
S_1	3.62	0.008	2.84	HOMO-1→LUMO (0.58)
S_2	3.99	0.302	18.38	HOMO→LUMO (0.60)
S_3	4.55	0.006	8.83	HOMO→LUMO+1(0.45)
S_4	4.67	0.014	9.29	HOMO-2→LUMO (0.51)
S_5	4.88	0.141	8.97	HOMO-3→LUMO (0.50)
T_1	2.87		8.21	HOMO→LUMO (0.65)
T_2	3.19		3.91	HOMO-1→LUMO (0.64)
T_3	3.53		3.60	HOMO-3→LUMO (0.57)

[a] Relative energy (in eV) of the excited state with ground state S_0 being taken as zero. The total energy of the ground state is −632.01496 a.u., and the dipole moment is 4.54 D. The calculations are performed at the level of TD-B3LYP/6-31+G**.
[b] Oscillator strengths.
[c] Dipole moment (in Debye).
[d] The largest coefficient in CI expansion.

intense absorption observed in experiment due to the largest oscillator strength among the given five singlet states. The S_1 state is mainly contributed by the electron transition from HOMO-1 to LUMO. The HOMO-1 is an *n*-type orbital mainly located on the oxygen atom of the carbonyl group, while the HOMO and the LUMO are π-type orbitals mainly located on the aminobenzene moiety and the carbonyl group, respectively (Fig.2). Hence, S_1 is a locally excited (LE) state from *n*→π* excitation, and S_2 is a charge transfer (CT) state from π→π* excitation. The energy gap between the two states is about 0.37 eV. The S_3 state can be attributed to the transition from HOMO to LUMO+1, with some contributions from the HOMO-4→LUMO and HOMO-2→LUMO transitions. The S_4 and S_5 states relate to HOMO-2→LUMO and HOMO-3→LUMO transitions respectively. It is possible to observe the S_5 state with large oscillator strength in the experimental spectrum. S_3, S_4, and S_5 are assigned as ππ* states (Fig.2). The *n*→π* transition generally leads to a decrease in molecular dipole moment since this transition reduces the charge density of the oxygen atom in the carbonyl group and enhances the charge density of the carbon atom of the carbonyl group, while the π→π* transition leads to an increase in molecular dipole moment. The calculated results indicate that the dipole moment of the S_1 state decreases but those of other singlet states increase with respect to the ground state. According to the changes of the dipole moments, the S_1 can still be attributed to an *n*→π* transition, and the other states to π→π* transitions.

Calculations show that the T_1 state is related to the HOMO→LUMO transition with a dipole moment of 8.21 D, while the T_2 state results from the HOMO-1→LUMO transition with dipole moment of 3.91 D.
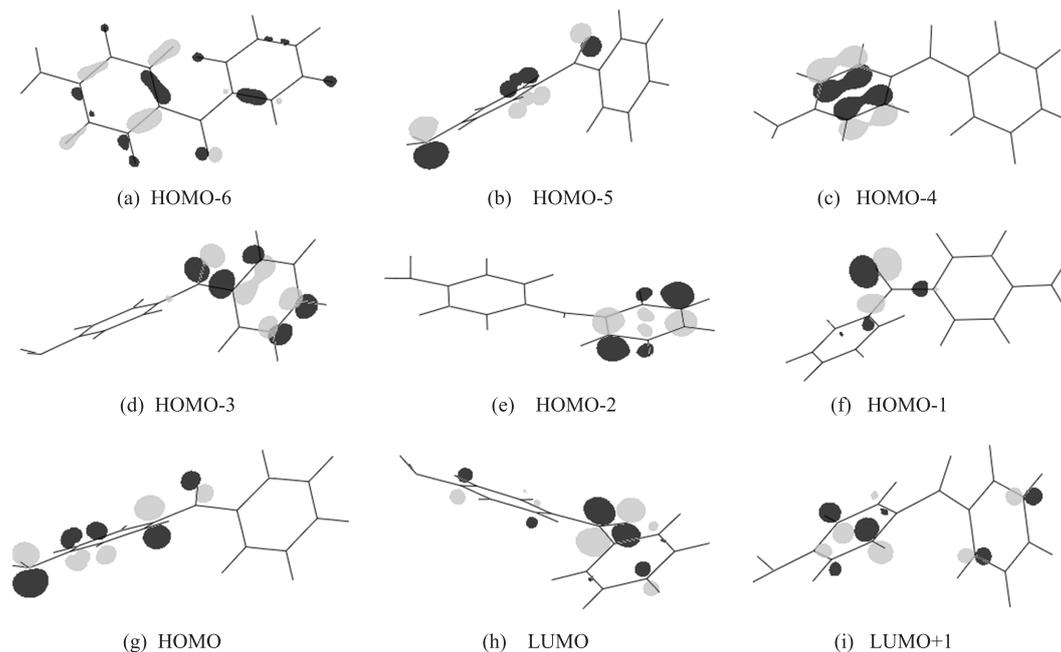
(a) HOMO-6	(b) HOMO-5	(c) HOMO-4
(d) HOMO-3	(e) HOMO-2	(f) HOMO-1
(g) HOMO	(h) LUMO	(i) LUMO+1

FIG. 2 Frontier orbitals involved in the low-lying transitions of p-ABP.

Hence, the T_1 state is of $\pi\pi^*$ character while T_2 state is of $n\pi^*$. Although such triplet states are hard to observe in experiment because of the spin forbiddance, the calculated results are still useful in discussing the electronic configurations of the triplet states.

B. Absorption spectra of p-ABP in solution

Since steady-state absorption spectra of p-ABP were detected in various solvents in experiment [10], we can use the continuous medium theory to perform calculations for the low-lying excited states in these solvents. Vertical excitation energies, oscillator strengths and dipole moments of the first three singlet and triplet excited states of p-ABP in these solutions are listed in Table II. Comparing Table I with Table II, we note that the solvent effects produce apparent redshifts on the $\pi\pi^*$ absorption bands but blueshifts on the $n\pi^*$ bands, while producing little influence on the oscillator strengths. In cyclohexane, the transition energy of the excited S_1 state with $n\pi^*$ character was calculated to be 3.65 eV, hence S_1 relates to the long tail band around 350 nm (3.54 eV) [10] in the low energy area in the experimental spectrum, while the excited S_2 state of $\pi\pi^*$ character with the transition energy 3.84 eV is related to the intense and wide band with a maxima at 303 nm [10] (4.09 eV). In benzene, the excited S_2 state with transition energy 3.82 eV is related to the $\pi\pi^*$ band maximized at 318 nm [10] (3.90 eV). In polar solvents, including acetonitrile, methanol and dimethyl sulphoxide (DMSO), the transition energy of the S_1 state was calculated to be 3.63, 3.63, and 3.61 eV respectively.

These values are assigned to the spectral maxima at 320 (3.87 eV), 332 (3.73 eV), and 335 nm (3.70 eV) [10] in experiment respectively. Both the experimental spectra and the TDDFT calculations verify that the band due to the $n\rightarrow\pi^*$ transition undergoes a blueshift in a more polar solvent, whereas the high-density $\pi\pi^*$ band suffers a redshift with the increase of solvent polarity. However, we also note some discrepancies between the calculated and experimental results. Firstly, the calculations show very limited redshift (about 0.02 eV) from cyclohexane to benzene, but the experimental spectrum shifts 15 nm (nearly 0.19 eV) towards long wave from cyclohexane to benzene. As a conjugated system, the benzene molecule is easily polarized by inducement. However, this has not been considered in the continuum medium model [27,28,36]. In particular, the PCM method brings a departure for the shift in benzene. Secondly, TDDFT calculations ignore hydrogen-bond interaction in methanol and hence provide the same transition energy towards methanol and acetonitrile. Thirdly, the transition energy of the charge transfer state by TDDFT in each solvent is generally smaller when compared with the corresponding experimental spectrum, though the deviation is not too large.

Similarly, the triplet $\pi\pi^*$ state undergoes redshift and the triplet $n\pi^*$ state undergoes blueshift with the increase in solvent polarity. Here, it is noticeable that the ordering of the electronic configuration character for each excited state is preserved in various solutions. Ghoneim et $al.$ [16] investigated quantum yields of photoreduction and triplet yields of p-ABP in various solvents and found that the triplet yield of p-ABP is 0.82 in

TABLE II Vertical excitation energies of low-lying excited states of *p*-ABP in different solvents[a]

Solvent	State	ΔE/eV	f	μ_e/Debye	Dominant transition	$\Delta E_{\text{Exp.}}$[b]/eV	ϕ[c]
Cyclohexane	S_1	3.65	0.064	6.04	HOMO-1→LUMO (0.49)	3.54	
	S_2	3.84	0.348	15.49	HOMO→LUMO (0.54)	4.09	
	S_3	4.47	0.006	9.95	HOMO→LUMO+1(0.45)		
	T_1	2.84		10.90	HOMO→LUMO (0.68)		0.82
	T_2	3.22		3.46	HOMO-1→LUMO (0.66)		
	T_3	3.53		3.88	HOMO-4→LUMO (0.54)		
Benzene	S_1	3.65	0.089	7.20	HOMO-1→LUMO (0.46)		
	S_2	3.82	0.337	14.41	HOMO→LUMO (0.51)	3.90	
	S_3	4.47	0.006	10.11	HOMO→LUMO+1(0.44)		
	T_1	2.83		11.24	HOMO→LUMO (0.68)		0.67
	T_2	3.22		3.45	HOMO-1→LUMO (0.66)		
	T_3	3.53		3.93	HOMO-4→LUMO (0.57)		
Acetonitrile	S_1	3.63	0.340	19.07	HOMO→LUMO (0.64)	3.87	
	S_2	3.85	0.080	4.87	HOMO-1→LUMO (0.54)		
	S_3	4.41	0.003	12.24	HOMO-2→LUMO (0.45)		
	T_1	2.76		14.82	HOMO→LUMO (0.71)		
	T_2	3.30		4.38	HOMO-1→LUMO (0.64)		
	T_3	3.58		4.47	HOMO-4→LUMO (0.61)		
Methanol	S_1	3.63	0.335	18.99	HOMO→LUMO (0.63)	3.73	
	S_2	3.85	0.082	4.94	HOMO-1→LUMO (0.54)		
	S_3	4.41	0.003	12.23	HOMO-2→LUMO (0.45)		
	T_1	2.76		14.79	HOMO→LUMO (0.71)		
	T_2	3.30		4.37	HOMO-1→LUMO (0.64)		
	T_3	3.58		4.46	HOMO-4→LUMO (0.61)		
Ethanol	S_1	3.63	0.337	18.83	HOMO→LUMO (0.63)		
	S_2	3.84	0.086	4.98	HOMO-1→LUMO (0.54)		
	S_3	4.42	0.003	12.15	HOMO-2→LUMO (0.44)		
	T_1	2.77		14.67	HOMO→LUMO (0.70)		$<10^{-5}$
	T_2	3.30		4.30	HOMO-1→LUMO (0.64)		
	T_3	3.58		4.44	HOMO-4→LUMO (0.61)		
DMSO	S_1	3.61	0.369	19.30	HOMO→LUMO (0.64)	3.70	
	S_2	3.85	0.077	4.58	HOMO-1→LUMO (0.54)		
	S_3	4.41	0.003	12.24	HOMO-2→LUMO (0.45)		
	T_1	2.76		14.87	HOMO→LUMO (0.71)		
	T_2	3.30		4.41	HOMO-1→LUMO (0.64)		
	T_3	3.58		4.48	HOMO-4→LUMO (0.61)		
DMF	S_1	3.62	0.361	19.26	HOMO→LUMO (0.64)		
	S_2	3.85	0.077	4.64	HOMO-1→LUMO (0.54)		
	S_3	4.41	0.003	12.25	HOMO-2→LUMO (0.45)		
	T_1	2.76		14.86	HOMO→LUMO (0.71)		0.1
	T_2	3.30		4.42	HOMO-1→LUMO (0.64)		
	T_3	3.58		4.46	HOMO-4→LUMO (0.61)		

[a] See the footnotes of Table I for the definitions of symbols. The calculations are performed at the level of at the TD-B3LYP/6-31+G**.
[b] From Ref.[10].
[c] Triplet yields of *p*-ABP in solvents, from Ref.[16].

cyclohexane, 0.1 in Dimethyl Formamide (DMF), and $<10^{-5}$ in ethanol; and that the quantum yield of photoreduction of p-ABP is 0.21 in cyclohexane, and $<10^{-5}$ in both DMF and ethanol. Combined with the results calculated here, these experimental results can be well understood. It is well-known that the triplet manifold can be produced by the intersystem crossing from the singlet state when the energy gap between them is small. The selection rules (El Sayed's rules [37,38]) for intersystem crossing say that transition from the singlet $n\pi^*$ state to the triplet state $\pi\pi^*$ is allowed whereas the transition from the singlet $\pi\pi^*$ state to the triplet $\pi\pi^*$ state is forbidden. Since S_1 and T_1 in cyclohexane are calculated to be $n\pi^*$ and $\pi\pi^*$ respectively, according to the El Sayed's rules the transition from S_1 to T_1 is allowed and would show high triplet yield (0.82 from experiment [16]), but the transition in DMF is forbidden and would show low triplet yield (0.1 from experiment [16]). Through TDDFT calculations, we find that the energy gap between the triplet $\pi\pi^*$ and $n\pi^*$ states in nonpolar solvent is rather smaller than that in polar solvent, e.g. 0.39 eV in cylcohexane $vs.$ 0.54 eV in acetonitrile. Hence, the $n\pi^*$ triplet state of p-ABP in cyclohexane could show very weak reactivity toward photoreduction reactions. The analysis above shows that TDDFT results preferably verify some experimental findings [10,16]. However, TDDFT calculations in ethanol cannot explain its low triplet yield ($<10^{-5}$ from experiment [16]). Singh et $al.$ suggested that in methanol (polar and protic, just like ethanol) the S_1 state would quench immediately through proton transfer from the solvent or enjoy a very fast nonradiative relaxation by intermolecular hydrogen-bond stretching vibrations [10]. Such processes are not adequately considered in the present calculations for excited states, so considerable error is probably produced by TDDFT for the transition energy in polar and protic solvents.

IV. CONCLUSION

In this work, the geometry of p-ABP was optimized at the B3LYP/6-31+G* level. This molecule presents a non-planar conformation. The absorption spectra were investigated by TDDFT method that provides comparatively reasonable results for low-lying excitations of p-ABP both in gas phase and in solution. The gas-phase investigation shows that the S_2 state is characterized by charge transfer (CT) from the amino-substituted aromatic ring to the carbonyl acceptor group, while the S_1 state is characterized by local excitation mainly located on the carbonyl group. In solution, the CT band undergoes a redshift with the solvent polarity increasing, while the CT band undergoes a blueshift with the solvent polarity increasing. The CT band is predicted to be the most intense band observed in experimental spectra due to its high oscillator strength but the CT band

is possibly hard to be observed due to its low oscillator strength. According to spin-forbidden rules, the triplet states are hard to form from direct transition of $S_0{\rightarrow}T$, but through theoretical calculations we can obtain some approximate results. This work proves that the lowest triplet states have $\pi\pi^*$ character both in polar and nonpolar solvents and hence could hardly abstract hydrogen atoms in photoreduction reactions. However, the energy gap between the $\pi\pi^*$ and $n\pi^*$ states in cyclohexane is smaller than that in polar solvent. Thus, p-ABP would have partial $n\pi^*$ character in cyclohexane and hence could weakly abstract hydrogen atom from hydrogen donor substrates in this solvent. Combined with El Sayed's rules, some rational explanations for the variation of the triplet yield in different solvents are given in this work.

[1] G. J. Kavarnos, *Fundamentals of Photoinduced Electron Transfer*, New York: VCH Publishers, Inc., 2 (1993).
[2] P. J. Wagner and B. S. Park, Org. Photochem. **11**, 111 (1991).
[3] S. G. Cohen, A. Parola, and G. H. Parsons, Chem. Rev. **73**, 141 (1973).
[4] N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemezyk, and N. Schore, Acc. Chem. Res. **5**, 92 (1972).
[5] G. Ciamician and P. Silber, Berchte **33**, 2911 (1900).
[6] W. J. Leigh, E. C. Lathioor, and M. J. St. Pierre, J. Am. Chem. Soc. **118**, 12339 (1996).
[7] S. H. Mousavipour, M. A. Namdar-Ghanbari, and L. Sadeghian, J. Phys. Chem. A **107**, 3752 (2003).
[8] H. Zhang, Z. S. Li, J. Y. Liu, L. Sheng, and C. S. Sun, J. Mol. Stru. (Theochem) **674**, 23 (2004).
[9] (a) G. Porter and P. Suppan, Trans. Faraday Soc. **62**, 3375 (1996);
(b) G. Porter and P. Suppan, Trans. Faraday Soc. **61**, 1664 (1965).
[10] A. K. Singh, A. C. Bhasikuttan, D. K. Palit, and J. P. Mittal, J. Phys. Chem. A **104**, 7002 (2000).
[11] (a) S. G. Cohen, G. A. Davis, and W. D. K. Clark, J. Am. Chem. Soc. **94**, 869 (1972);
(b) S. V. Jovanovic, D. G. Morris, C. N. Pliva, and J. C. Scaiano, J. Photochem. Photobiol. A: Chem. **107**, 153 (1997).
[12] (a) P. J. Wager, A. E. Kemppainen, and H. N. Schott, J. Am. Chem. Soc. **95**, 5604 (1973);
(b) P. J. Wager, J. Am. Chem. Soc. **89**, 5898 (1967).
[13] A. C. Bhasikuttan, A. K. Singh, D. K. Palit, A. V. Sapre, and J. P. Mittal, J. Phys. Chem. A **102**, 3470 (1998).

[14] A. K. Singh, G. Ramakrishna, H. N. Ghosh, and D. K. Palit, J. Phys. Chem. A **108**, 2583 (2004).

[15] X. H. Duan, X. Y. Li, R. X. He, and X. M. Cheng, J. Chem. Phys. **122**, 084314 (2005).

[16] N. Ghoneim, A. Monbelli, D. Pilloud, and P. Suppan, J. Photochem. Photobiol. A: Chem. **94**, 145 (1996).

[17] P. Aspari, N. Ghoneim, E. Haselbach, M. vonRaumer, P. Suppan, and E. Vauthey, J. Chem. Soc., Faraday Trans. **92**, 1689 (1996).

[18] S. Hirata, S. Ivanov, I. Grabowski, and R. J. Bartlett, J. Chem. Phys. **116**, 6468 (2002).

[19] R. Bauernschmitt and R. Ahlrichs, Chem. Phys. Lett. **256**, 454 (1996).

[20] N. C. Handy and D. J. Tozer, J. Comput. Chem. **20**, 106 (1999).

[21] A. S. Zyubin and A. M. Mebel, J. Chem. Phys. **119**, 6581 (2003).

[22] X. H. Duan, Z. R. Li, X. Y. Li, and L. M. Li, J. Chem. Phys. **120**, 10025 (2004).

[23] C. Adamo and V. Barone, Chem. Phys. Lett. **330**, 152 (2000).

[24] C. Neiss, P. Saalfrank, M. Parac, and S. Grimme, J. Phys. Chem. A **107**, 140 (2003).

[25] M. Cossi and V. Barone, J. Chem. Phys. **115**, 4708 (2001).

[26] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

[27] J. Tomasi and M. Persico, Chem. Rev. **94**, 2027 (1994).

[28] S. Miertus, E. Scrocco, and J. Tomasi, Chem. Phys. **55**, 117 (1981).

[29] E. Cances, B. Mennucci, and J. Tomasi, J. Chem. Phys. **107**, 3032 (1997).

[30] B. Mennucci and J. Tomasi, J. Chem. Phys. **106**, 5151 (1997).

[31] D. M. Chipman, J. Chem. Phys. **112**, 5558 (2000).

[32] D. K. Palit, Res. Chem. Intermed. **31**, 205 (2005).

[33] K. Takahashi, K. Abe, S. Sawamura, and C. D. Jonah, Chem. Phys. Lett. **282**, 361 (1998).

[34] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussion* 03 B05, Pittsburgh: Gaussion Inc., (2003).

[35] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[36] L. Reynolds, J. A. Gardecki, S. J. V. Frankland, M. L. Horng, and M. Maroncelli, J. Phys. Chem. **100**, 10337 (1996).

[37] M. A. El Sayed, Acc. Chem. Res. **1**, 8 (1968).

[38] S. K. Lower and M. A. El Sayed, Chem. Rev. **66**, 199 (1966).