



Intermolecular-charge-transfer-induced fluorescence quenching in protic solvent



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ARTICLE INFO

Article history:

Received 13 January 2016

Received in revised form

6 June 2016

Accepted 6 June 2016

Available online 8 June 2016

Keywords:

Intermolecular charge transfer

Relaxed scans

Conical intersection

Saddle point

ABSTRACT

The fluorescence quenching of fluorenone in protic solvent has been extensively investigated, and the intermolecular hydrogen bond was found to play a crucial role. Unfortunately, the mechanism at atomic level is still not clear. In the present work, we theoretically put forward the charge transfer along the hydrogen bond in the excited states. The vertical excitation energies of the fluorenone-methanol complex as well as the potential energy profiles and surfaces of the vertical excited states and charge transfer states were calculated by using the ab initio electronic-structure methods. The photochemical reactions occurring in the diverse charge transfer states were compared and their decisiveness to the fluorescence quenching was discussed in the paper.

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1. Introduction

The fluorescence quenching phenomenon has always been a research hotspot. Since it can be used for fluorescence probing and has wide range of applications on the fluorescent sensor, constituent determination, protein analysis, etc. [1–5]. As the extensive use of protic solvent in photochemical reaction and its applications in the studies of solvent effect, it has great significance on the investigation of the quenching in protic solvent [6–8]. In protic solvent, in addition to the influence of molecular polarity, the quenching process is greatly impacted by the hydrogen bond which is formed between the solute and solvent [9–12]. It is generally recognized that the photo-induced reactions occurring in the excited states result in the charge transfer process between the H-atom donor and acceptor which are assembled by the hydrogen bond [13–15]. To be more specific, the change of the charge distribution of the molecule following the excitation is effected by the presence of the hydrogen bond, and for this reason, it may generate new electronic charge transfer states [16–18]. According to the reaction path of the transfer process, there may be various degrees of charge transfer, e.g., delocalized electron transfer through the

hydrogen bond [19,20], reversible proton movement between the solute and solvent [21,22], or electron-driven proton-transfer reaction leading to reversible or irreversible H-atom transfer [23,24]. Compared with the numerous experimental results, however, there are few theoretical investigations on the effects of the charge transfer process on the fluorescence quenching, and the mechanism of the quenching process is still unclear.

The photochemical reaction of the fluorenone-methanol complex in the excited states is an example of the intermolecular hydrogen bond participating fluorescence quenching process in protic solvent. The carbonyl group of the fluorenone molecule and the hydroxyl group of the methanol molecule would form the hydrogen bond in solution. The fluorescence of fluorenone is sensitive, and it responds specifically to both the solvent polarity and the hydrogen bond. In aprotic solvent, the fluorescent state is mainly decayed to the lowest triplet state by the intersystem crossing, and the fluorescence becomes extremely weak when the polarity of the solvent decreases [25–28]. In contrast, the fluorescence is weak in protic solvent despite the polarity of the solvent, and the quenching process shows the polarity-independent character [29,30].

In our work, the charge transfer process along the hydrogen bond which takes place following the excitation of the fluorenone molecule was theoretically investigated using the ab initio electronic-structure methods. The vertical excitation energies of the fluorenone-methanol complex and fluorenone molecule were

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calculated to find the effects of the hydrogen bond on the vertical excitation process. We investigated the charge transfer process by constructing the potential energy (PE) profiles of both the vertical excited states and charge transfer (CT) states as well as the two-dimensional PE surfaces of the CT states. Since the internal conversion (IC) and the intersystem crossing (ISC) are the dominant relaxation processes in the non-radiative transition, based on our computational results, we put emphasis on the discussion of the effects of the charge transfer process on the IC and ISC which eventually induce the fluorescence quenching.

2. Computational methods

In the present study, the second-order Møller-Plesset (MP2) method was used to optimize the ground state geometry of the fluorenone-methanol complex as well as to calculate the potential energy of the ground state. While the second-order algebraic-diagrammatic construction (ADC(2)) method which is a single-reference Green's function method [31] and has been proved to be reliable in the calculation of the energy crossing [32,33] was used to optimize the geometries of the CT states as well as to calculate the vertical excitation energies and the potential energies of the CT states.

We constructed the PE profiles of the vertical excited states and CT states by using the relaxed scans. That is, in the optimizing of the geometries, the reaction coordinate R_{OH} (the bond length of the hydroxyl group of the methanol molecule) was treated as a fixed value and other internal coordinates of the fluorenone-methanol complex were relaxed. Similarly, the PE surfaces of the different CT states were constructed by using the two-dimensional relaxed scans. Again, the reaction coordinate R_{OH} and R_{OO} (the distance between the O-atom of methanol and the O-atom of fluorenone) were treated as fixed values, while other internal coordinates were relaxed. All of the calculations were constrained to C_s symmetry, *i.e.* the methanol molecule is constrained to be co-plane with the fluorenone molecule. The zero-point of the potential energies for all of the excited states and corresponding S_0 states was chosen as the energy of the S_0 state calculated in the ground state geometry with C_s symmetry.

Dunning's correlation-consistent split-valence double- ζ basis set with polarization functions (cc-pVDZ) [34] was employed on all atoms in the calculations. The MP2 and ADC(2) calculations were carried out with the TURBOMOLE program package [35], making use of the resolution-of-the-identity (RI) approximation [36] for the evaluation of the electron-repulsion integrals.

3. Results and discussion

3.1. Vertical excitation energies of the fluorenone-methanol complex and fluorenone molecule

The vertical excitation energies of the fluorenone-methanol complex calculated in this work were summarized in Table 1, including the vertical excitation energies of the fluorenone molecule for the purpose of comparison.

The four lowest excitation energies in both the singlet and triplet of the fluorenone-methanol complex and fluorenone were calculated, respectively. It can be seen from the excitation energies of the fluorenone molecule that the two excited states of $n\pi^*$ character are separately located at the lowest and the highest level, while the two excited states of $\pi\pi^*$ character are located between them in both the singlet and triplet. However, in the situation of the fluorenone-methanol complex, the two excited states of $n\pi^*$ character are blue-shifted (with the extent from 0.14 eV to 0.27 eV), while the two excited states of $\pi\pi^*$ character are red-shifted (with

Table 1

Vertical excitation energies (in eV) and the oscillator strengths (in parentheses) of the fluorenone-methanol complex and fluorenone molecule.

Fluorenone-methanol			
$1^1n\pi^*(A')$	$1^1\pi\pi^*(A')$	$2^1\pi\pi^*(A')$	$2^1n\pi^*(A')$
3.28(0.000)	3.54(0.009)	4.35(0.010)	5.36(0.000)
3.02(0.003) ^a	3.31(0.000) ^a	3.59(0.003) ^a	3.95(0.036) ^a
$1^3n\pi^*(A'')$	$1^3\pi\pi^*(A'')$	$2^3\pi\pi^*(A'')$	$2^3n\pi^*(A'')$
2.99	2.98	3.77	5.35
Fluorenone			
$1^1n\pi^*(A')$	$1^1\pi\pi^*(A')$	$2^1\pi\pi^*(A')$	$2^1n\pi^*(A')$
3.14(0.000)	3.71(0.010)	4.46(0.000)	5.09(0.000)
3.19(0.004) ^b	3.12(0.000) ^b	4.53(0.029) ^b	4.09(0.017) ^b
$1^3n\pi^*(A'')$	$1^3\pi\pi^*(A'')$	$2^3\pi\pi^*(A'')$	$2^3n\pi^*(A'')$
2.82	3.09	4.13	5.08

^a TDDFT-B3LYP/TZVP results from Ref. [37].

^b TDDFT-B3LYP/6-31G** results from Ref. [38].

the extent from 0.11 eV to 0.36 eV) in both the singlet and triplet. As a result, compared with the fluorenone molecule, the two lowest excited states in both the singlet and triplet of the fluorenone-methanol complex become closer. The difference between the two lowest excitation energies changes from 0.57 eV to 0.26 eV in the singlet and from 0.27 eV to -0.01 eV in the triplet. The shift of these energy levels is mainly induced by the hydrogen bond constructed between the fluorenone and methanol. As the lowest $n\pi^*$ and $\pi\pi^*$ states are strongly coupled in both the singlet and triplet, we focused on the investigation of the lowest $1^3n\pi^*$ and $1^3\pi\pi^*$ states in the following.

The electron distribution of the molecular orbitals correlated with the $1^1n\pi^*$ and $1^1\pi\pi^*$ states for the fluorenone-methanol complex is shown in Fig. 1. The $1^1n\pi^*$ state corresponds to the excitation from the $47a'$ (n) orbital to the $10a''$ (π^*) orbital. The excitation of the $1^1\pi\pi^*$ state, however, is from the mixture of the two highest π orbitals ($8a''$, $9a''$) to the mixture of the two lowest π^* orbitals ($10a''$, $11a''$).

3.2. Potential energy profiles of the vertical excited states and charge transfer states

The PE profiles of the vertical excited states and CT states as well as the corresponding S_0 states for the fluorenone-methanol complex are shown in Fig. 2. Being the most relevant to the charge transfer, the reaction coordinate R_{OH} was chosen as the bond length of the hydroxyl group of the methanol molecule which formed the hydrogen bond with the O-atom of fluorenone. The PE profiles are clearly separated to two parts by a dashed vertical line. The left part

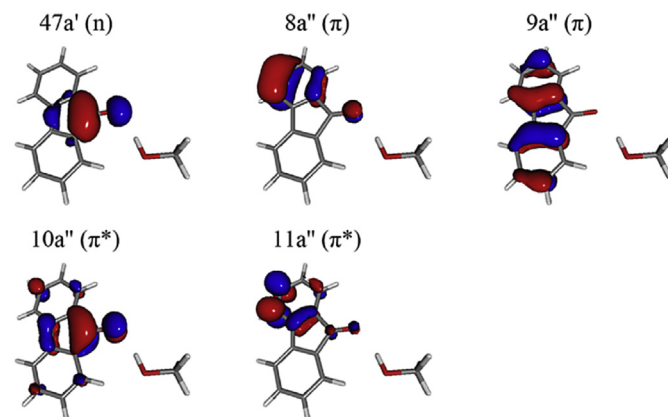


Fig. 1. The electron distribution of the relevant molecular orbitals.

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