Research paper

Photoinduced charge-transfer electronic excitation of tetracyanoethylene/tetramethylethylene complex in dichloromethane

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ABSTRACT

Based on the previous work on nonequilibrium solvation model by the authors, Intermolecular charge-transfer electronic excitation of tetracyanoethylene (TCE)/tetramethylethylene (TME) π-stacked complex in dichloromethane (DCM) has been investigated. For weak interaction correction, dispersion corrected functional DFT-D3 is adopted for geometry optimization. In order to identify the excitation metric, dipole moment components of each Cartesian direction, atomic charge, charge separation and Δr index are analyzed for TCE/TME complex. Calculation shows that the calculated excitation energy is dependent on the functional choice, when conjuncted with suitable time-dependent density functional, the modified nonequilibrium expression gives satisfied results for intermolecular charge-transfer electronic excitation.

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1. Introduction

Quantitative description of the electronic excited state has attracted huge amounts of interests both in the theoretical and experimental aspects because of its significant role in the fields from spectroscopy to organic photovoltaics and photosynthesis [1–4]. Time-dependent density functional theory (TD-DFT) [5], as a tool for simulating electronic excited states, achieved great successes in the last decades due to its remarkable accuracy and reasonable computational cost. According to the extent of excitation delocalization, the overall field of electronic excitation can be classified into three different groups: local electronic excitation, charge-transfer excitation and Rydberg excitation [6]. Recently, based on the orbital centroids and the hole-electron separation upon the electronic excitation, a new index $\Delta r = \frac{\sum_{ia} K_{ia}^2 (|\langle a|\mathbf{r}|a\rangle - \langle i|\mathbf{r}|i\rangle|)}{\sum_{ia} K_{ia}^2}$ is designed by Guido et al. to quantitatively distinguish between short- ($\Delta r \leqslant 10.5$ Å) and long-range ($\Delta r \geqslant 2.0$ Å) excitations in the framework of TD-DFT calculation [7]. Le Bahers et al. also proposed the D_{CT} index based on the barycenters of spatial regions [8].

Since many chemical reactions occur in condensed phases, especially in solvents, modeling the complicated chemical phenomena in solutions becomes essential for computational chemistry [9]. Among multifarious solvation models, the explicit one is usually impractical based on whole quantum-mechanical context

[10], thus continuum solvation model gains great popularity, in which the medium is characterized by its dielectric permittivity and averaged electronic charge density. Polarizable Continuum Model (PCM) [11] and Conductor-like Screening Model (COSMO) [12] are two main approaches in the family of CSM. Nowadays, COSMO is widely used in chemical engineering for real solvents and the integral equation formalism (IEF) version of PCM is preferential in many research papers [13]. Although some deficiency of PCM has been pointed out [14], PCM/TD-DFT is still the primary protocol to investigate excited states in solvents [15].

Generally, the dynamic picture of the solute-solvent interaction are presented in the process after ultrafast external perturbation like photoinduced electronic excitation and electron transfer, thus the nonequilibrium description in polar solvent deserves a close scrutiny [16]. Within the Born-Oppenheimer limit, the response process can be assumed to involve two components, one component is related to the rearrangements of the solvent nuclei and the other to the electronic polarization effects. Coupled with PCM theory, nonequilibrium solvation model is implemented [17] and get enriched in subsequent researches [18]. In our group, we noticed the theoretical defects in the traditional charging-process scheme to obtain the nonequilibrium solvation energy expression [19] and we presented one alternative modified formula based on the constrained equilibrium method. Details of our modified nonequilibrium polarization model are available in the review work [20].

In the present work, we broaden the application of our modified nonequilibrium solvation model to the intermolecular charge-transfer excitation of π-stacked complex. Grimme's D3 dispersion

correction [21] is employed to obtain the reasonable optimized structure. Δr index mentioned above is calculated to identify the charge-transfer metric. The influence of functional choice on the vertical excitation energy value is also investigated. The remain of this article is organized as follows: In Section 2, we present the outline of our modified nonequilibrium solvation model. In Section 3, computational details are summarized. Computational results of optimized geometrical structure, excitation metric and vertical excitation energy value are discussed in Section 4. Finally, conclusions are delineated in Section 5.

2. Theoretical method

The electronic excitation in solvent can be modeled as a ultra-fast vertical process according to Franck-Condon principle [22], as depicted in Fig. 1. Both the absorption and emission start from equilibrated nuclear arrangements but end at the nonequilibrium ones. Nonequilibrium here refers to the fast component of solvation response with the new solute electronic distribution after vertical excitation or de-excitation while the slow one keeps fixed. Solvent shift in absorption process, which is the difference between the vertical excitation energy in gas phase and in solvent, is given by

$$\Delta(h\nu_{ab}) = F_{2,sol}^{non} - F_{1,sol}^{eq} \tag{1}$$

For evaluating nonequilibrium polarization, Marcus presented the reversible electric work scheme [19]. While as what we explicated previously [20,23], it is unreasonable to directly apply the classical thermodynamics theory to the nonequilibrium polarization of the dielectric medium. Here, we draw the picture from constrained-equilibrium state method to deal with the nonequilibrium polarization within the framework of classical thermodynamics by several steps. The essence of constrained-equilibrium state method can refer to literatures [20,23] and is sketched as Fig. 2.

From the excited equilibrium state to the constrained equilibrium state, the external constraining charge ρ_{ex} is slowly added. In this process, the solvent polarization keeps equilibrium with the solute charge plus external charge. Therefore the solvation free energy of the constrained equilibrium state can be evaluated by the reversible work here, i.e. [20,24]
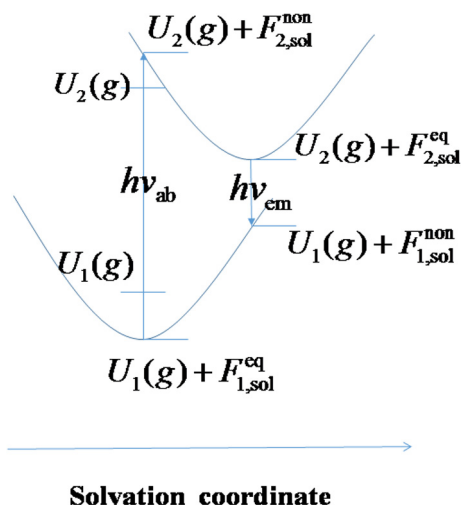

Fig. 1. Pictorial description of vertical transition in solvent. $U_i(g)$ denotes the energy of solute in vacuum, $F_{i,sol}^m$ means the solvation free energy, in which the superscript i ($i = 1, 2$) respectively means the ground and excited state, subscript m ($m = eq$ or non) indicates the equilibrium state or nonequilibrium state respectively.
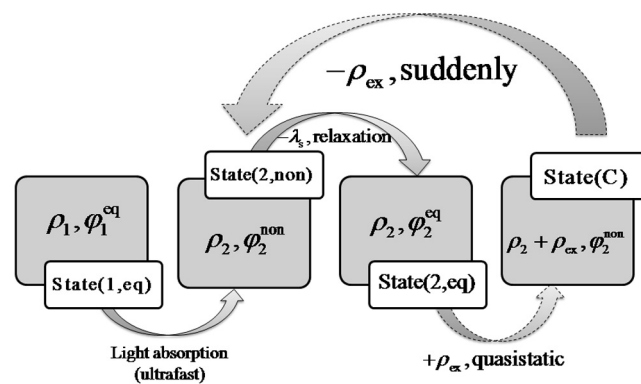

Fig. 2. Schematic illustration of constrained-equilibrium state method. ρ and φ stand for the solute charge distribution and polarization potential respectively; 1 indicates the initial state while 2 the final one of the solute; 'eq' and 'non' represent respectively the equilibrium and nonequilibrium state; State(C) denotes the constrained equilibrium state; ρ_{ex} is the external constraining charge.

$$F^c = \frac{1}{2}\int_V (\rho_2 + \rho_{ex})\varphi_2^{non}dV \tag{2}$$

The real nonequilibrium excited state is available after removing the external constraining charge suddenly from the constrained equilibrium state. The work in this fast process reads [20]

$$W_{C\to N} = -\int_V dV \int_{\rho_{ex}+\rho_2}^{\rho_2} \varphi^{non}d\rho = -\int_V \rho_{ex}\varphi_2^{non}dV \tag{3}$$

Since the polarization is identical between the constrained equilibrium state and nonequilibrium excited one, entropy is regarded to keep fixed. We can obtain the nonequilibrium solvation free energy as [20,24]

$$F_2^{non} = F^c + W_{C\to N} = \frac{1}{2}\int_V (\rho_2 + \rho_{ex})\varphi_2^{non}dV - \int_V \rho_{ex}\varphi_2^{non}dV \tag{4}$$

and the solvent reorganization energy is given by [20]

$$\lambda_s = F_2^{non} - F_2^{eq} = -\frac{1}{2}\int_V \rho_{ex}(\varphi_2^{non} - \varphi_2^{eq})dV$$

$$= \frac{1}{2}\int_V \rho_{ex}(\Delta\varphi_s - \Delta\varphi_{op})dV \tag{5}$$

Here $\Delta\varphi_s$ and $\Delta\varphi_{op}$ is respectively the polarization potential produced by $\Delta\rho = \rho_2 - \rho_1$ in medium of ε_s and ε_{op}. ε_{op} and ε_s denote respectively the optical and statics dielectric constant, and $\varepsilon_{op} = n^2$ with n being the solvent refractive index.

Based on our previous derivation [20], Eq. (5) can be refashioned as

$$\lambda_s = \frac{1}{2}\int_S \Phi_{ex}(\Delta\sigma^{eq} - \Delta\sigma^{op})dS = \frac{1}{2}\frac{\varepsilon_s - \varepsilon_{op}}{\varepsilon_s - 1}\int_S \Delta\Phi^{op}(\Delta\sigma^{eq} - \Delta\sigma^{op})dS \tag{6}$$

where $\Delta\Phi^{op}$ and $\Delta\sigma^{op}$ is respectively the total electric potential and the surface polarization charge density produced by $\Delta\rho = \rho_2 - \rho_1$ in medium of ε_{op}, $\Delta\sigma^{eq}$ is the surface polarization charge density produced by $\Delta\rho$ in medium of ε_s. And,

$$\Delta(h\nu_{ab}) = \frac{1}{2}\frac{\varepsilon_{op} - \varepsilon_s}{\varepsilon_s - 1}\int_S \Delta\Phi^{op}(\Delta\sigma^{op} - \Delta\sigma^{eq})dS$$

$$+ \frac{1}{2}\int_V (\rho_2\varphi_2^{eq} - \rho_1\varphi_1^{eq})dV \tag{7}$$

Here, we adopt the Onsager model, [25] in which the reaction field is computed as a truncated multipolar expansion and added as a perturbation term to the one-electron Hamiltonian [26]. Using the definition of $\Phi_i^{op}, \sigma_i^{op}$ and σ_i^{eq}, i.e.,