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State-Specific Treatment of Solvent Effect on Excited States in Organic Photoredox Catalysis

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Abstract: Excited state behavior in organic photocatalysis is strongly influenced by solvent polarity. We benchmark solvation treatments for predicting charge-transfer (CT) and locally excited (LE) states by combining time-dependent density functional theory (TDDFT) with implicit and explicit solvation. Within implicit models, linear-response (LR) and four state-specific (SS) schemes (cLR, cLR^2, VEM, IBSF) are assessed, and explicit solvation is modeled using QM/MM with electrostatic embedding. Across representative systems, we examine solvent-dependent excited state energetics to compare the solvation models. For CT states, SS approaches consistently capture solvent-induced stabilization, whereas LR underestimates solvent relaxation and misrepresents solvent trends. Among SS methods, cLR and cLR^2 show nearly identical solvent dependence, and the additional transition density term in cLR^2 vanishes for triplets and becomes relevant only when the singlet state contains appreciable LE character. VEM produces similar solvent dependence, while IBSF tends to over-stabilize CT states in polar solvents. In explicit solvation, QM/MM reproduces the SS trends with small, systematic shifts in absolute energies. By contrast, LE states exhibit weak solvent sensitivity and are consistently described by all methods. Separately, results across density functionals highlight the importance of long-range corrected hybrids for describing CT states. These results provide practical guidelines for selecting solvation models and exchange correlation functionals to reliably capture solvent effects in organic photocatalysis, particularly in systems with pronounced CT states.

Key words: charge-transfer state, photoredox catalysis, state specific, solvent effect.

1. Introduction

Organic photocatalysis, including photoredox catalysis, has garnered increasing attention due to its high tunability and metal-free character [1,2]. Predictive insight into excited-state (ES) behavior is crucial for determining reaction pathways and controlling kinetics. In many organic photoredox systems, the excited states of the organic photocatalysts (OPC) and the catalyst-substrate complexes can display pronounced charge transfer (CT) or locally excited (LE) character. These excited-state features are highly sensitive to the polarity of the surrounding solvent, and their relative energy ordering may change across solvents, reshaping the accessible electron or energy transfer pathways and the associated kinetics [2-6]. Therefore, accurate theoretical prediction of excited-state energies in solution, particularly the adiabatic 0-0 transition energy (E0-0), defined as the energy gap between the relaxed excited and ground states, is crucial for identifying the reactive excited state and elucidating the underlying photochemical reactivity and kinetics.

From a theoretical perspective, accurate treatment of solvent effects on excited states remains challenging, as it requires simultaneous consideration of CT and LE states in a solvent environment [7]. The available theoretical solvation models are broadly divided into explicit models, which represent individual solvent molecules, and implicit models, in which the medium is approximated as a polarizable continuum. Among implicit schemes, the polarizable continuum model (PCM) provides an efficient route to estimate solvent effects at low computational cost [8,9]. In recent years, considerable effort has been devoted to developing density functional theory (DFT) protocols within the PCM for predicting the photophysical properties. A standard protocol is linear-response time-dependent DFT (LR-TDDFT), which captures the solvent response through the transition density between the ground and excited states. This approach, however, is generally effective only for molecules with relatively weak CT character. For excitations involving substantial density rearrangement, the LR scheme becomes insufficient because it does not account for the density-dependent relaxation of the solvent polarization [10-14]. This limitation is further demonstrated in this work. In contrast, within the state-specific (SS) framework [15-17], the solvent response is constructed directly from the excited-state electron density, enabling a more accurate description of solute solvent interactions, particularly for CT states.

As noted above, state-specific treatment of solvation effects can be directly treated at the quantum mechanical (QM) level, and various approximate SS models within the PCM have also been formulated for TDDFT [8,9,18]. Among these approaches, the corrected linear-response model (cLR) uses the excited-state density to perturbatively estimate the SS polarization of the solvent [15]. More recently, the cLR2 method has been proposed [2,19], which combines the cLR correction to SS polarization with the LR term that accounts for part of the dispersion contribution. Moreover, the vertical excitation method (VEM) performs a self-consistent reaction-field calculation in which the solvent polarization is iteratively updated based on the ES electron density [20], while the ground state (GS) density remains fixed. The scheme proposed by Improta, Barone, Scalmani, and Frisch (IBSF) is fully self-consistent, involving iterative updates of both the GS and ES electron densities to determine the solvent polarization [16,21]. In addition to TDDFT-based SS models, high-level wavefunction-based methods such as equation-of-motion coupled-cluster singles and doubles (EOM-CCSD), algebraic diagrammatic construction to second order ADC(2), and ΔSCF at the DFT level often provide more reliable results for CT states [22-25]. However, the associated computational cost generally restricts their applicability to model systems and benchmark studies. Quantum mechanics/molecular mechanics (QM/MM) schemes, in which the solvent is represented explicitly by a molecular mechanics (MM) force field [26-29], offer an alternative to treat solvent effects accurately. Within QM/MM, electrostatic embedding incorporates MM point charges directly into the QM Hamiltonian, allowing the QM electronic structure to respond to the classical environment. This affords a more faithful description of solvent effects, because the explicit inclusion of solvent molecules enables the sampling of the accessible configurational space and the evaluation of excited-state properties over multiple snapshots. In addition, QM/MM schemes enable explicit treatment of solute-solvent interactions, including hydrogen bonding and steric effects, that are often neglected by implicit solvation models. Such protocols have been widely applied. For example, De Vetta and co-workers used QM/MM to simulate the absorption spectra of various fluorophores [30].

In this work, we employ a range of TDDFT-based computational protocols, including linear-response and state-specific schemes (cLR, cLR2, VEM, and IBSF), as well as the explicit solvent QM/MM approach, to predict key photophysical properties in solution, including vertical absorption energies (Eabs), emission energies (Eem), and adiabatic 0-0 transition energies (E0-0). Specifically, we investigate the excited-state behavior of a representative OPC, and a donor-acceptor (D-A) complex formed by the OPC and the substrate molecule. The strengths and limitations of the different approaches are discussed by comparing results from implicit solvation models and explicit solvent QM/MM calculations performed at the same TDDFT level of theory. Our primary objectives are to identify reliable solvation protocols for excited states in organic photocatalysis and to extend the methodology to investigate intermolecular charge transfer complexes.

2. Theoretical and computational details

2.1. Solvent effects with implicit solvent.

In this work, solvent effects with Implicit Solvent were described by the PCM [8,31], and explicit solvent using a QM/MM framework, with details provided in the following subsection. Within PCM, the solvent response is typically partitioned into fast (electronic) and slow (nuclear or inertial) components. Upon vertical excitation, solvent nuclei cannot respond on the electronic time scale, so the medium remains at the initial solvent configuration. In this nonequilibrium (neq) condition, only the fast component of the solvent polarization is allowed to relax. This treatment is standard for vertical spectra: for vertical absorption, the slow component is frozen at the GS configuration, whereas for vertical emission it is frozen at the relaxed ES configuration. For adiabatic processes such as the 0-0 transition, the solvent should be treated in equilibrium (eq) with each electronic state, and both fast and slow components are fully relaxed with respect to the electron density of each state at its optimized geometry. The distinction between eq and neq solvation is particularly important for