# Modeling Solvent Effects on Electronic Excited States

Albert DeFusco,[†] Noriyuki Minezawa,[†] Lyudmila V. Slipchenko,[‡] Federico Zahariev,[†] and Mark S. Gordon*[,†]

[†]Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011, United States
[‡]Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, United States

ABSTRACT: The effects of solvents on electronic spectra can be treated efficiently by combining an accurate quantum mechanical (QM) method for the solute with an efficient and accurate method for the solvent molecules. One of the most sophisticated approaches for treating solvent effects is the effective fragment potential (EFP) method. The EFP method has been interfaced with several QM methods, including configuration interaction, time-dependent density functional theory, multiconfigurational methods, and equations-of-motion coupled cluster methods. These combined QM−EFP methods provide a range of efficient and accurate methods for studying the impact of solvents on electronic excited states. An energy decomposition analysis in terms of physically meaningful components is presented in order to analyze these solvent effects. Several factors that must be considered when one investigates solvent effects on electronic spectra are discussed, and several examples are presented.

$$\mathcal{H}|\Psi\rangle = \left(\mathcal{H}_{QM} + \hat{V}^{EFP}\right)|\Psi\rangle$$
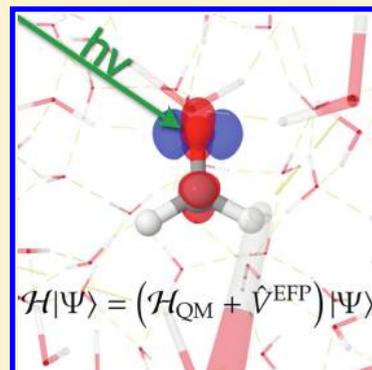
While multiple absorption and emission spectroscopic experimental studies provide valuable information on the magnitude and dynamics of solute−solvent coupling, calculations on electronic excited states in the condensed phase remain a major challenge to the theoretical chemistry community.[1] The increased number of nuclear and electronic degrees of freedom relative to the gas phase makes accurate fully ab initio calculations on a condensed-phase system unfeasible long before the system can approach the bulk. One general approach to this type of problem is to separate a system into two parts, such that one (active, usually solute) part is treated by quantum mechanical (QM) techniques and the other (usually larger, solvent) part is calculated using classical (molecular) mechanics (MM).[2] The Hamiltonian of the system then consists of three terms

$$\hat{H} = \hat{H}_{QM} + \hat{H}_{MM} + \hat{H}_{QM/MM} \tag{1}$$

In eq 1, $H_{QM/MM}$ is a coupling term between the two levels of theory. Separation of the QM and MM subsystems, in principle, allows one to use any level of theory in both the QM and MM parts.

> Combined QM−EFP methods provide a range of efficient and accurate methods for studying the impact of solvents on electronic excited states.

There have been an increasing number of studies devoted to a description of electronic spectroscopy in the condensed phase.[3−14] An alternative to the QM/MM approach is to study the electronic excited states of solutes with dielectric continuum methods.[3−5,9,11,12,15] While continuum models are computationally inexpensive, they cannot describe explicit solvent−solute interactions such as hydrogen bonding. Another promising approach for studying condensed-phase electronic spectroscopy in large molecular systems is to use a fragment-based technique, such as the fragment molecular orbital method (FMO).[16−20] The FMO and related methods have the advantage of being close to fully "ab initio", but these methods are still sufficiently computationally demanding that (for example) performing molecular dynamics simulations on excited states in solution is still not feasible.

If one is to perform QM/MM calculations to accurately capture solvent effects on electronic excited states, it is essential that the MM part can capture the polarization (induction) interaction between solute and solvent because the polarization can change dramatically upon electronic excitation. Polarizable QM/MM models for electronic excited states have been developed in several groups,[14,21−25] starting with the pioneering work of Warshel and co-workers, who developed a Langevin dipole solvent model.[26,27]

Traditionally, the MM component of a QM/MM calculation is included through highly parametrized force fields. A major drawback of such an approach is the dependence on fitted parameters for a chosen force field, such that different parametrizations may be optimal for different problems; therefore, the best parameters are often not well-defined. There is also a concern regarding the absence of short-range repulsion and dispersion, and often polarization coupling in the QM/MM term, although these issues have not been well studied.[1]

In part, to overcome these drawbacks, the effective fragment potential (EFP) method[28,29] has been developed to represent the solvent. In the EFP method, each solvent molecule is represented by an effective fragment (EF) whose parameter set is determined from a preparatory ab initio calculation. There are two EFP versions. The original EFP1 was developed specifically for water, while the more general EFP2 version is applicable to any molecule. The uniqueness of the EFP method is that all EFP parameters are derived from first principles, that is, the method is free of empirical parameter fitting. The EFP interaction energy is a sum of electrostatic (or Coulomb), polarization (or induction), dispersion, exchange−repulsion, and charge-transfer terms. Importantly, the polarization term is iterated to self-consistency. It is the iterative convergence of the polarization that accounts for many body effects. The EFP fragments can interact with each other and with QM components. It has been shown that EFP reproduces structures and binding energies in both hydrogen- and π-bonded systems with an accuracy that is similar to or, in some cases, even better than that of the second-order Moller−Plesset perturbation theory, MP2.[30−32] Moreover, in order to improve the accuracy and extend the applicability of the EFP method to strongly interacting species (e.g., polar or ionic fragments), ab-initio-derived short-range screening functions for the electrostatic, polarization, and dispersion terms have been introduced.[30,33] Briefly, EFP is a polarizable model potential that employs distributed multipoles and polarizability tensors obtained from ab initio calculations without fitting to any empirically determined parameters. The distributed approach ensures high accuracy for molecules of arbitrary sizes and shapes. As will be discussed in detail below, all QM−EFP schemes possess polarizable embedding. These properties differentiate EFP from many other polarizable potentials and QM/MM schemes that have been reported in the literature.[14,21−25]

The EFP1 water potential has been interfaced with several QM methods that are used to study electronic excited states, including configuration interaction with single excitations (CIS), time-dependent density functional theory (TDDFT), multiconfiguration self-consistent field (MCSCF), multireference CI (MRCI), and multireference perturbation theory (MRPT) methods to model absorption spectra of chromophores in water.[34−36] The EFP2 model has been interfaced with the equation-of-motion coupled cluster with single and double excitations (EOM-CCSD) method, and both EFP1 and EFP2 have been interfaced with configuration interaction singles with perturbative doubles (CIS(D)) methods.[37,38] Several variants of the combined QM−EFP methods are available in both the GAMESS[57,58] and Q-Chem[63] electronic structure programs.

The Coulomb, polarization and EFP1 exchange-repulsion contributions add one-electron integral terms to the QM Hamiltonian. The Coulomb contribution $\hat{V}^{coul}$ to the QM Hamiltonian consists of four terms, originating from the electrostatic potential of the corresponding multipoles (charges, dipoles, quadrupoles, octopoles). The polarization interaction $\hat{V}^{pol}$ in the one-electron part of the Hamiltonian consists of the potential due to induced dipoles of the effective fragments. Detailed expressions for the Coulomb and polarization contributions to the Hamiltonian are given in refs 28 and 39. The EFP2-QM exchange−repulsion[40] adds both one- and two-electron terms to the QM Hamiltonian.

The excitation energies in CI methods are found from diagonalization of the Hamiltonian in a chosen subspace of excited configurations. For example, CIS is defined by restricting the subspace to all single excitations from the reference determinant. Higher orders of CI and multireference CI (MRCI, based on a MCSCF reference) work in an analogous manner. In multireference, multistate perturbation theory (sometimes called multiconfiguration quasi-degenerate perturbation theory, MCQDPT), multiple states are included in a perturbative treatment of the MCSCF reference wave function.[41]

In the EOM-CC techniques, the electronic states are found from diagonalization of the so-called similarity-transformed Hamiltonian $\overline{H} \equiv e^{-T}\hat{H}e^{T}$, in which the cluster amplitudes T are found from the preceding coupled cluster calculation. Both the T cluster operator and the excitation operator R that defines the subspace of possible excitations in EOM-CC are usually truncated in order to make computations feasible. For example, truncation at the second level (all single and double excitations are included) gives the EOM-CCSD method.[42−44]

Density functional theory (DFT) has, in many areas of chemistry, such as inorganic, organic, and organometallic, become a defacto standard as a computational method for medium to large molecular systems in both ground and excited electronic states because of its reasonable accuracy at the expense of moderate scaling of the computational cost with an increasing molecular size. Following the success of DFT in computing the ground-state properties of molecules, TDDFT in its linear response regime has recently been enjoying a surge in popularity for its ability to reasonably estimate the excited-state properties of molecules as well.

When one employs TDDFT in the frequency domain to study excited electronic states, a linear response approach is typically followed, in which one solves the equations

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} \tag{2}$$

In eq 2, ω is the transition energy, $\mathbf{X}$, $\mathbf{Y}$ comprise transition vectors, and the matrices $\mathbf{A}$ and $\mathbf{B}$ depend on the Kohn−Sham (KS) orbital energy differences, the exchange−correlation energy, and the electron density. A key ingredient in the TDDFT linear response equation is the exchange−correlation kernel $f^{xc}(r,r')$, which is a functional derivative of the exchange−correlation potential with respect to the density. Due to the fact that only the polarization component of the EFP1 effective fragment potential has such a nonzero functional derivative, the EFP1 correction to the linear response TDDFT matrix equation is given by the following replacement[34]

$$f^{xc}(r,r') \rightarrow f^{xc}(r,r') + f^{pol}(r,r') \tag{3}$$

The same replacement in the nonlinear response equations of TDDFT introduces the EFP1 solvent effects into the computation of, for example, (hyper-)polarizabilities, two-photon cross sections, and nonlinear optical properties.

The Hamiltonian involved in the CI, MRCI, MCQDPT, or EOM-CC procedures is modified by the EFP terms, as shown in eq 4

$$\hat{H} = \hat{H}_0 + \langle p|\hat{V}^{coul} + \hat{V}^{pol} + \hat{V}^{exrep}|q\rangle \tag{4}$$

For EFP2, one can also add a dispersion interaction term. In the DFT formulation, the KS orbitals are also appropriately modified due to the modification of the Hamiltonian by the presence of the EFP solvent molecules.
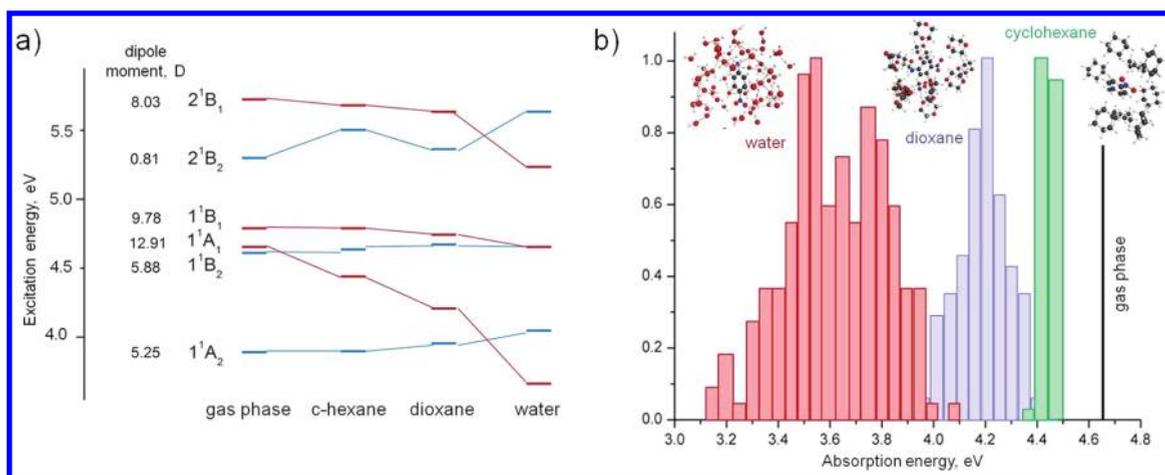
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Figure 1. Electronic spectroscopy of *para*-nitroaniline with CIS(D)/EFP. (a) Excitation energies of the singlet electronic states of *p*NA in cyclohexane, 1,4-dioxane, and water compared to the gas-phase energies. The electronic states possessing the dipole moment lower than the ground-state dipole moment (7.7 D) are blue-shifted in polar solvents; the states with larger dipole moments are red-shifted (stabilized) in polar solvents. (b) Simulated absorption spectra of the 1^1A_1 charge-transfer state in water (red), 1,4-dioxane (blue), and cyclohexane (green).

The QM−EFP1 method for electronic excitations is usually performed by first carrying out a ground-state molecular dynamics (MD) simulation on the QM solute molecule in a solvent that is represented by EFP fragments. Upon the equilibration of the ground-state MD simulation, vertical excitations on selected snapshots are computed by the chosen QM−EFP method, and the results are averaged. This procedure models the solvent effect on the absorption spectrum of the solute. A complementary version could be developed for the emission. This would require analogous MD simulations on the excited state, followed by vertical emission calculations at many points.[45]

Equations 3 and 4 demonstrate that the molecular orbitals (or the KS orbitals in DFT), the density matrix, and, as a result, electronic excitations of a solute are affected by EFP fragments. This effect may be referred to as an "indirect" contribution of a solvent to the electronic states of a solute. The term indirect is used, because the effect of the EFP solvent is experienced via modification of the ground-state orbitals and density matrix.

Additionally, each electronic state of the solute can experience a direct response of the polarizable environment, such that the effective Hamiltonians of the different states differ by state-specific V^{pol} terms. Therefore, one can treat the polarizable environment fully self-consistently for each electronic state of interest (called the fully self-consistent method in ref 35), or one can decouple the solute and solvent and solve the CI, MCQDPT, EOM-CC, or TDDFT eigenvalue problem with a constant ("frozen") response of the polarizable environment corresponding to its reference state (e.g., ground state) value (called "method 1" in ref 35). The fully self-consistent approach results in a set of (nonorthogonal) electronic states with different effective Hamiltonians, unless a state-averaging procedure is used, as is often the case in multireference approaches. Method 1 preserves the orthogonality between the electronic states but neglects the interaction of the excited-state wave function or density with the polarizable environment. One can include this interaction perturbatively. In this case (called "method 2" in ref 35), the one-electron density of the excited state is calculated and used to repolarize the environment, that is, to obtain the EFP-induced dipoles and polarization energy corresponding to this density. This perturbative correction is called the "direct" polarization contribution to the electronic energy of the excited state.

It has been shown in recent papers (refs 34, 35, 41, 45, and 46) that the fully self-consistent approach (that is, fully iterating the polarizability in the presence of the excited-state density) is typically not important because method 1, as defined above, captures more than 90% of solvent-induced shifts in excitation energies and other properties. This is an important finding because for most QM methods, especially nonvariational ones like the MP2 and CC approaches, the fully self-consistent method can become very computationally expensive. Of course, there may be some molecular species for which method 1 is not adequate. In such cases, the perturbative method 2 may be a viable compromise approach,[35,37] especially because it preserves the orthogonality between the electronic states. Orthogonality, which is also preserved in the fully self-consistent approach when state averaging is used, is important for the calculation of the transition properties. In both the perturbative and state-averaged approaches, several electronic states can be found simultaneously, as is illustrated in recent CIS(D)/EFP and TDDFT/EFP studies of solvatochromic shifts of the electronic states of *para*-nitroaniline (*p*NA)[38,46] (see Figure 1).

Applications. Coupled Cluster Methods. The general interface between EOM-CCSD and EFP allows one to exploit the advantages of various EOM techniques,[47] such as spin−flip (SF),[47a−c] ionization potential (IP),[47d−g] or electron affinity (EA)[47h] variants. For example, the EOM-IP-CCSD/EFP method has been used for investigating vertical ionization energies (VIE) of thymine in an aqueous environment.[48] It is noteworthy that the convergence of the VIE with the number of hydration shells to the bulk value is slow and nonmonotonic; at least five hydration shells (resulting in a simulation box of at least 30 Å) are required (see Figure 2a). Surprisingly, the first solvation shell increases the VIE by ∼0.1 eV, while the overall decrease of the VIE due to solvation is 0.9 eV. The unexpected effect of the first hydration shell can be explained by interactions with individual water molecules (microhydrates); thus, it cannot be described by implicit solvent models. Another interesting observation is that the polarization terms, especially the direct polarization contribution, become even more important for
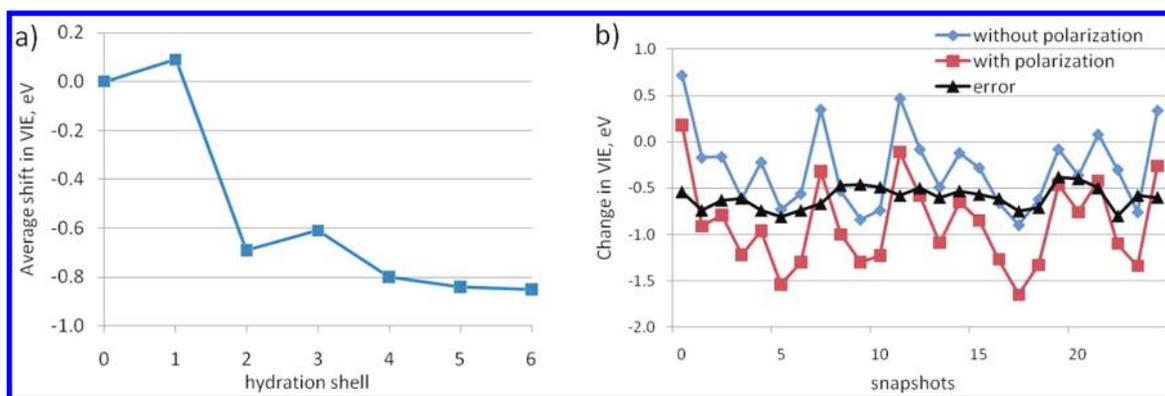
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Figure 2. Vertical ionization energy (VIE) of thymine in water by EOM-IP-CCSD/EFP. (a) Dependence of the average shift of the vertical ionization energy (VIE, eV) on the number of water shells around a thymine molecule. Five solvation shells are required for converged results. (b) Inclusion of polarization of the solvent is crucial for an accurate description of the shift of the VIE due to hydration.
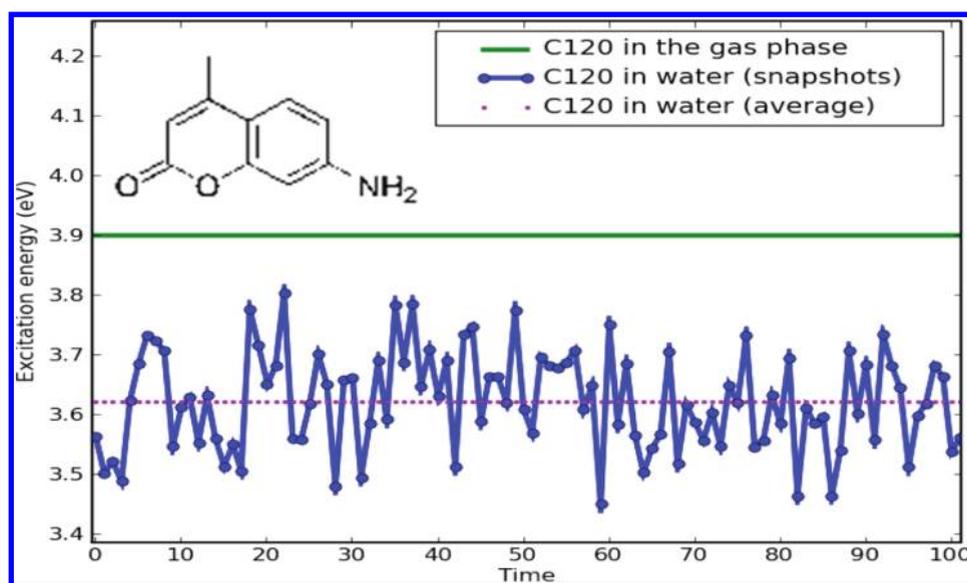

Figure 3. Water solvent shift on the coumarin C120 excitation by (TD)DFT/EFP1 MD simulations. (The chemical formula of coumarin C120 is depicted in the upper left corner.).

evaluating ionization energies than they are in the case of the excited states of neutral species (see Figure 2b). The relative importance of polarization is larger in the EOM-IP-CCSD method than that in the standard EOM-CCSD methods because the reference and target (ionized) states have different numbers of electrons and induce dramatically different responses of the polarizable environment.

Coumarin 120 Absorption Spectrum. To illustrate the combined (TD)DFT/EFP1 method[34] for electronic excitations, consider the coumarin (C120, 7-amino-4-methylbenzopyrone) molecule solvated in 100 water molecules (see Figure 3). First, the system was equilibrated for 10 ps by an *NVT* simulation at 300 K by DFT/EFP1 molecular dynamics. Next, 100 snapshots were chosen from the equilibrated trajectory separated in 10 fs intervals. Finally, vertical $\pi-\pi^*$ (S_0-S_1) electronic excitations of C120 in each of the snapshots were computed with TDDFT/EFP1. In both DFT and TDDFT computations, the B3LYP density functional[50] with the DH(d,p) basis set[51] was used. Excitations that exhibit significant charge-transfer character are sometimes poorly described by TDDFT. Because the C120

excitation is known to be of this type, a "lambda diagnostic"[52] was performed. The TDDFT (gas-phase) value is 0.72, and the average TDFT/EFP1 value is 0.66, assuring that the B3LYP/DH(d,p) combination is appropriate for the description of the C120 excitation. Lambda values that approach zero suggest that the functional will significantly underestimate excitation energies.

The averaged C120 excitation in water is compared with the gas-phase result in Figure 3. The vertical excitation of C120 in water (3.62 eV) is in excellent agreement with the experimental result (3.63 eV),[53] while the gas-phase excitation energy (3.90 eV) has similar agreement with other TDDFT calculations (3.94,[54] 4.00[55]).

Several factors affect the electronic excitations of coumarin C120. For example, there are several types of hydrogen bonds between specific atoms of C120 (amino nitrogen (type A), carbonyl oxygen (type B), amino hydrogen (type C)) and water influencing the excitations as well, as illustrated in Figure 4. While the effect of the solvent polarity can be successfully modeled by an implicit solvent method, the effect of hydrogen bonds on electronic spectra can only be captured accurately by an explicit
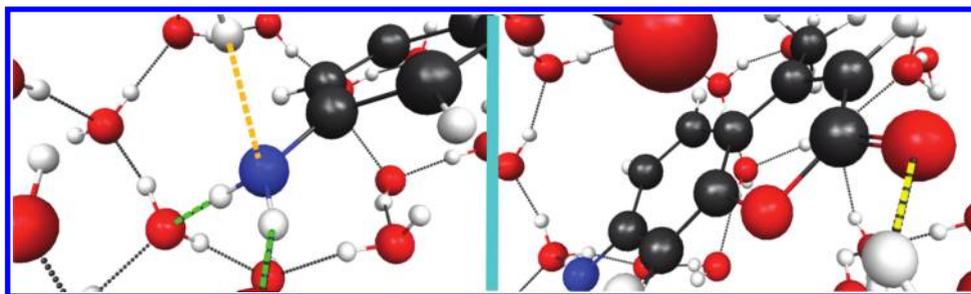
Figure 4. Fragments from two MD snapshots illustrating the hydrogen bonds between coumarin C120 and water. Type A is between the amino nitrogen of C120 and a water hydrogen (in gold on the left). Type B is between the carbonyl oxygen of C120 and a water hydrogen (in yellow on the right). Type C is between the amino hydrogen and a water oxygen (in green on the left).

solvent model like the EFP method. The calculations presented here confirm the observation from the literature[56] that hydrogen bonds of types B and C cause a red shift, while those of type A cause a blue shift.

Fluorescence Spectroscopy. Fluorescence spectroscopy is a useful experimental technique that provides valuable insight into the structure of molecules in electronically excited states. Generally, fluorescence spectroscopy is classified into two types, steady-state and time-resolved measurements. Because these fluorescence spectra are usually measured in the solution phase, it is important to take account of solvent effects to explain the spectral line shape. In steady-state fluorescence experiments, it is expected that the fluorescence is initiated from the excited-state minimum because the solvent molecules are already in equilibrium with the relaxed solute molecule. The solute—solvent interaction moves the peak position, and solvent fluctuations account for the inhomogeneous spectral width. The difference in emission energy observed in vacuum and solution, or the solvatochromic shift, reflects a solvent-induced change in the solute electronic structure. In the time-resolved measurements, the time-dependent fluorescence is often expressed in terms of the response function

$$S(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}$$

where $\nu(t)$ is the emission energy at time t. When the solute absorbs the light, the solvent molecules accommodate themselves to a new solute electronic distribution. During the reorganization process, the time-dependent fluorescence, $\nu(t)$, is observed because both the solute structure and the solute—solvent interaction change continuously. The response function is well-approximated as the sum of Gaussian and/or exponential functions whose time constants are characteristic of the solvent. Each time constant reflects a time scale of some relevant solvent motions such as libration, translation, and hydrogen-bond breaking and re-formation. As $t \rightarrow \infty$, the fluorescence peak approaches the value that would be observed in a steady-state experiment.

Although the experimentally observed fluorescence spectra contain a great deal of information, it is difficult to elucidate the origin of the spectral width and shift and to assign the time constant to some specific solvent motions. Therefore, computational methods that have been developed to interpret experimental spectra can be very useful. In order to reproduce both types of fluorescence experiments (time-dependent and steady-state) by theoretical methods, it is necessary to describe the probe molecules in electronically excited states. In addition, the
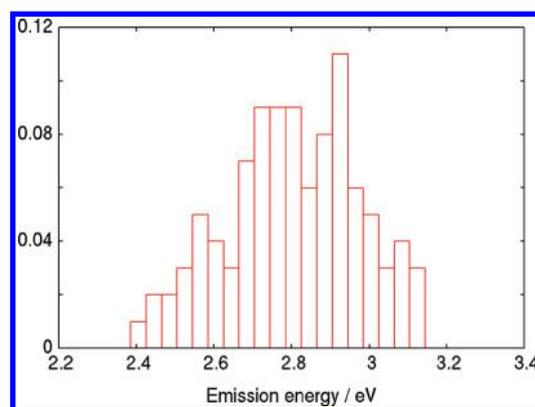

Figure 5. Simulated fluorescence spectrum for coumarin 120 in aqueous solution. Probability is plotted on the vertical axis.

solute—solvent relaxation involves the electronic and geometrical changes of the solute molecule. Therefore, a quantum mechanical description is necessary. A QM/MM MD simulation is a powerful tool that one can employ to monitor the relaxation of both the solute electronic structure and the solvent motions. However, most of the solutes employed in experiments are dye molecules whose size is too large for traditional wave-function-based methods. To perform an excited-state QM/MM MD simulation with moderate computational cost, the TDDFT/EFP1 energy[34] and gradient[45] have been implemented in the GAMESS program package.[57,58] The TDDFT/EFP1 excited-state MD simulation has been shown to be a promising approach in a recent study on the simulated emission spectrum of aqueous formaldehyde.[45] Because local solute—solvent structures such as hydrogen bonds play a vital role in solvent relaxation, it is highly desirable to use a reliable explicit solvent model such as EFP.

As a first step toward providing a quantitative description of solvation dynamics, a TDDFT/EFP1 excited-state equilibrium MD has been performed to examine the steady-state fluorescence spectrum of C120. The C120 was immersed in 100 EFP1 water molecules, and the whole system was treated as a cluster. The solute was excited to the S_1 state, and the system was equilibrated for 10 ps with TDDFT/EFP1. The *NVT* ensemble was adopted, and the temperature was set to be 300 K. The B3LYP density functional and the DH(d,p) basis set were employed. Figure 5 shows the distribution of emission energies taken from the 100 snapshots of a 5 ps trajectory. The average emission energy is computed to be 2.81 ± 0.17 eV. Using the computed average excitation energy of 3.62 eV, the Stokes shift is

estimated to be 0.81 eV. These values are in quantitative agreement with the experimental values of 2.82 and 0.81 eV, respectively.[59]

The application to the time-dependent fluorescence spectrum is straightforward. Initial configurations are generated by a ground-state MD simulation, and a nonequilibrium TDDFT/EFP1 MD is performed for the S_1 state using these snapshots. The method is promising in view of the modest computational cost despite the fact that many trajectories are required to obtain statistically converged results. Work on such simulations is in progress, and the results will be reported in due course.

Analysis of Excitation Energy Solvent Shifts. The total energy, E_{tot}, of a single geometry snapshot of an EFP-solvated molecule can be decomposed into five contributing terms.[41] Four intermolecular interactions arise from the QM−EFP Hamiltonian: the electrostatic (Coulomb), exchange−repulsion, fragment induction, and solute induction have been derived independently of the QM method employed. The intramolecular solute-only energy change, due to a change in the solute geometry in solution relative to the optimized gas-phase value, is called relaxation. Because EFP1 fragments have fixed internal geometries, they do not contribute to the relaxation energy. The QM−EFP energy analysis can be performed for any QM method that has been interfaced with the EFP method and that allows the computation of the density matrix in the presence of EFP molecules. For perturbation theories, this generally requires the availability of QM−EFP analytic gradients and first-order wave functions. The methods that are currently available with the QM−EFP energy analysis method, in the GAMESS package,[57,58] are HF, DFT, TDDFT, CI, MCSCF, MP2, CCSD, and EOM-CCSD. In the results shown below for vertical excitations of formaldehyde in solution, the solvent reorganization after excitation is not considered. Also, the contributions from the EFP−EFP electrostatic and remainder interactions are constant for vertical excitations because they do not depend on the solute density and are not considered here.

The solute-only relaxation energy for a state s is computed as the difference between the energy of the isolated solute at the solvated geometry E_0^s using H_{QM} and the energy of the gas-phase optimized solute E_{gas}^s

$$E_{relax}^s = E_0^s - E_{gas}^s \qquad (5)$$

The first-order QM−EFP interactions, Coulomb and exchange−repulsion, are computed as expectation values over the isolated solute wave function Ψ_0^s for state s

$$E_{coul}^s = \langle \Psi_0^s | \hat{V}^{coul} | \Psi_0^s \rangle \qquad (6)$$

$$E_{exrep}^s = \langle \Psi_0^s | \hat{V}^{exrep} | \Psi_0^s \rangle \qquad (7)$$

The polarization energies for both the solute and solvent molecules are evaluated using the polarized wave function $\Psi_{solvated}^s$, called solvated for state s, computed with the full QM−EFP Hamiltonian H in eq 4. The solute polarization energy is computed as the difference between the expectation value of $H^{(1)} = H_{QM} + \hat{V}^{coul} + \hat{V}^{exrep}$ computed with Ψ_0^s and the expectation value of the same Hamiltonian computed with the polarized wave function $\Psi_{solvated}^s$ for state s

$$E_{pol(solute)}^s = \langle \Psi_{solvated}^s | H^{(1)} | \Psi_{solvated}^s \rangle - \langle \Psi_0^s | H^{(1)} | \Psi_0^s \rangle \qquad (8)$$
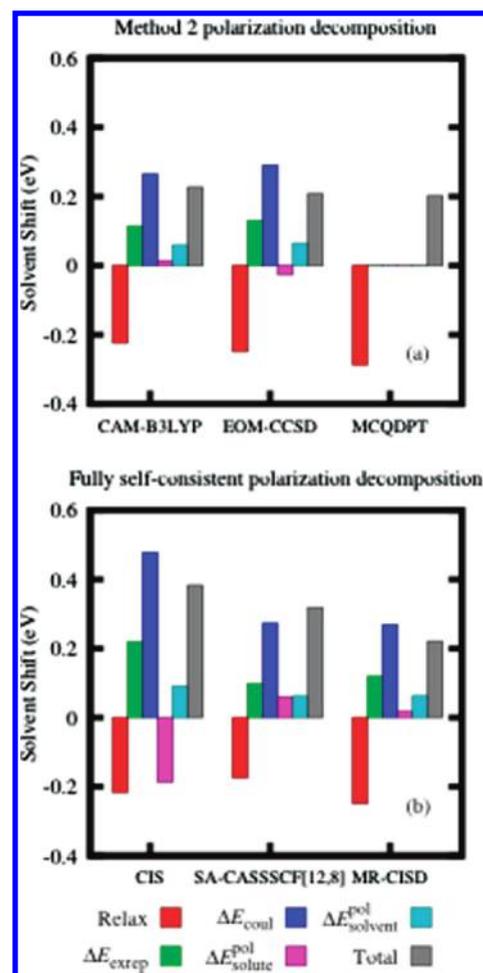

Figure 6. QM(cc-pVDZ) EFP method comparison of the solvent shift decomposition (eV) of the n−π^* formaldehyde excited state in 150 EFP1 water molecules. The MQDPT solvent shift (panel a) has been computed using the indirect polarization method; therefore, further decomposition is not possible.

For fully self-consistent QM−EFP methods (e.g., HF, DFT, CI, MCSCF), the solvent polarization energy is the expectation value of the solvent polarization interaction evaluated over the polarized wave function

$$E_{pol(solvent)}^s = \langle \Psi_{solvated}^s | \hat{V}^{pol} | \Psi_{solvated}^s \rangle \qquad (9)$$

For Method 2 polarization (MP2 and CC), a perturbative correction must be added to the polarization energy[35] to allow for direct polarization between solvent and solute molecules

$$E_{pol2(solvent)}^s = \langle \Psi_{solvated}^s | \hat{V}^{pol} | \Psi_{solvated}^s \rangle + \Delta E_{pol2} \qquad (10)$$

The QM−EFP energy analysis can be generalized to analyze solvent-induced shifts of excitation energies by performing the full decomposition for both the ground and excited states and then subtracting the ground-state interaction energies from the excited-state interaction energies. Here, the relaxation energy E_{relax} is interpreted as the shift of the excitation energy of the solute at the solvated geometry. Then, the QM−EFP interaction contributions are direct solvent shift interactions. For the results presented in the following analysis of formaldehyde, the solvent shift interactions are denoted with the symbol Δ.

Using a single snapshot from an equilibrated 300 K Nosé—Hoover MD simulation of formaldehyde in 150 EFP1 water molecules, a comparison of the solvent shift decomposition of the lowest $n-\pi^*$ excited state with several QM—EFP methods is presented in Figure 6. All calculations employ the cc-pVDZ basis set.[60,61] While the first-order wave function is not available for MCQDPT, it is still instructive to show the relaxation energy and total solvent shift in comparison to the other methods.

Figure 6 provides several insights concerning the intermolecular interactions leading to solvent shifts of excitation energies. First, in every method, the dominant term in the $n-\pi^*$ solvent shift is the electrostatic interaction. The positive (blue) shift of the electrostatic interaction arises from a significant reduction of the dipole moment of the solute upon excitation. Further, the overestimation of the electrostatic contribution with CIS for the $n-\pi^*$ excitation occurs because CIS is known to overestimate the change in the dipole moment of the solute between the ground and excited states.[62] Most enlightening is that the changes in the both the solute and solvent polarization energies upon excitation of the solute are no larger than ~0.1 eV for all QM methods, and very little difference is observed between the fully self-consistent and Method 2 polarization methods. Again, the anomalous solute polarization energy, computed with CIS, appears to arise from the fact that the gas-phase polarizability of the $n-\pi^*$ excited state is predicted to be larger than that of the ground state. For the other methods, the ground-state polarizability is only slightly larger than the excited-state polarizability.

Summary. The effective fragment potential provides a viable approach for predicting and interpreting the effects of solvents on the properties of electronically excited states. The imminent implementation of QM—EFP exchange—repulsion and dispersion energy and gradients will broaden the applicability of this approach. An important reason for the success of the QM—EFP approach is that the EFP method includes self-consistent polarizability that allows the solvent to respond to the changing electron density of the solute upon excitation. There have been other applications of the QM/MM methodology that include solvent polarization response, including recent work by Li and co-workers.[64] Interested readers are referred to a very recent comprehensive review of such methods.[65]

> An important reason for the success of the QM—EFP approach is that the EFP method includes self-consistent polarizability that allows the solvent to respond to the changing electron density of the solute upon excitation.

AUTHOR INFORMATION

Corresponding Author
*E-mail: mark@si.msg.chem.iastate.edu.

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