Monte Carlo Quantum Mechanical–Configuration Interaction and Molecular Mechanics Simulation of Solvent Effects on the $n \rightarrow \pi^*$ Blue Shift of Acetone

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Received May 2, 1994[•]

Abstract: A Monte Carlo simulation method, making use of a combined quantum mechanical–configuration interaction and molecular mechanics (QM-CI/MM) potential, is described to examine the solvatochromic blue shifts of the $n \rightarrow \pi^*$ transition of acetone in aqueous and organic solvents. The calculation correctly predicts the spectral blue shifts of acetone in polar solvents, while the experimentally-observed dispersion red shift in nonpolar solvents was not reproduced. The discrepancy is attributed to the use of nonpolarizable potential functions for the solvent, which exclude explicit solute–solvent dispersion interactions. Nevertheless, the results reported in this paper demonstrate the viability of simulation studies of solvent effects on electronic excitation. The method provides the opportunity to investigate photochemical processes and reactions in solution.

Introduction

Solvatochromic shifts of electronic transitions are widely used to probe solute–solvent interactions in solution and to generate a quantitative solvent-polarity scale.[1] For example, it is well-known that the $n \rightarrow \pi^*$ electronic transition of carbonyl compounds undergoes a blue spectral shift in polar solvents.[1,2] The experimental findings have been attributed to specific hydrogen-bonding interactions and solvent dielectric effects, which stabilize the ground state more than the less-dipolar excited state.[1–3] Solvent-induced red shifts of the carbonyl $n \rightarrow \pi^*$ transition have been observed in nonpolar solvents, resulting from the difference between solute–solvent dispersion energies of the two states.[2] The dispersion energy is present in all solvents; however, the effect only becomes prominent in nonpolar solvents such as carbon tetrachloride, benzene, and cyclohexane.[1d,2,4]

Theoretical treatments of electronic spectra are well established.[5,6] However, quantum mechanical methods are primarily confined to isolated molecules in gas phase. Study of solvent effects on electronic transitions was pioneered by McRae and Bayliss, who employed a classical reaction field method by treating the solute molecule as a spherical cavity embedded in a macroscopic continuum medium.[2,7] The continuum reaction field model has been used by Zerner and co-workers with the intermediate neglect of differential overlap (INDO/S) Hamiltonian combined with configuration interaction (CI) calculations.[6d,8] The continuum models provide useful qualitative and quantitative insights into solvent effects on electronic transition.[1] Nevertheless, the difficulty associated with the continuum reaction field model is the choice of the cavity size (although realistic molecular cavities have been used by others),[9] and exclusion of specific solute–solvent interactions. Consequently, it is often necessary to adopt a supramolecular approach by including a few solvent molecules in the quantum mechanical calculation.[3,10]

Microscopic investigations of solvent effects on spectroscopy have been described by Warshel and co-workers, who employed a quantum mechanical extension of consistent force field to conjugate molecules (QCFF/PI) Hamiltonian in molecular dynamics simulations of mero dyes.[11] In this approach, the solute molecule is treated quantum mechanically, while the solvent is represented by a Langevin dipole model or by an all-atom solvent model (SCAAS).[11a] Encouraging results have been obtained. Recently, Levy and co-workers carried out a molecular dynamics simulation of formaldehyde in water to investigate the solvent effects on its absorption spectrum,[12] while DeBolt and Kollman reported results of similar calculations on acetone and formaldehyde in water, methanol, and CCl_4.[13] Levy and co-workers also performed ab initio Hartree–Fock calculations on 70 configurations of the supramolecular system selected from their molecular dynamics trajectory. These simulations demonstrated the capability of microscopic treatment of the solvent effects on electronic spectra with statistical mechanical sampling. However, in the latter applications, empirical potential functions are used for both the solute and solvent molecules, which are typically difficult to parametrize for these processes.

[•] Abstract published in *Advance ACS Abstracts*, September 15, 1994.

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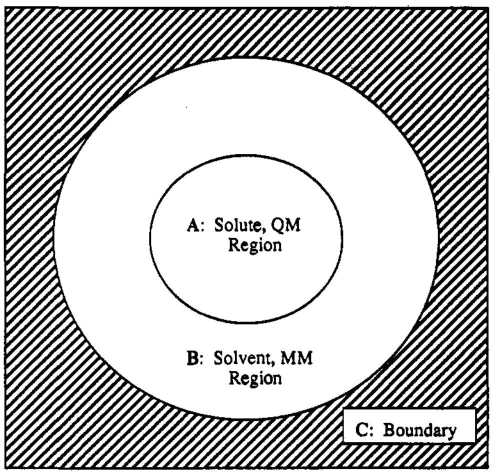

Figure 1. Schematic representation of the partition of a condensed-phase system.

In this paper, we describe a combined quantum mechanical–configuration interaction and molecular mechanical (QM-CI/MM) method to explore the solvent effects in electronic spectroscopy. In this approach, the chromophore solute molecule is treated by quantum mechanical molecular orbital (MO) theory, while the surrounding solvent is represented by empirical potential functions.[14,15] To obtain the energy of electronic excitation of the solute in solution, configuration interaction calculations are carried out throughout the simulation, while the ground-state CI energy is used to determine the Monte Carlo trajectory. Thus, electronic polarization of the solute by the surrounding solvent molecules is treated by the MO calculation.[15] However, in order to reduce the computation time, the mutual induced dipole–induced dipole dispersion interactions between the solute and solvent molecules are not explicitly included in the present implementation. Consequently, the method is not expected to predict the dispersion red shift for the carbonyl n → π* transition in nonpolar solvents. In the following, a brief outline of the theory and its implementation will first be given. Then, the method will be illustrated by computing the solvent spectral shifts of the n → π* transition of acetone in aqueous and organic solutions.

Theoretical Background

The combined QM-CI/MM potential for simulation of solvent effects on electronic spectroscopy is based on a method that has been used previously to study chemical reactions in solution.[11,14,15] The procedure relies on a partition of the condensed-phase molecular system into several regions (Figure 1). In this work, region A, which typically consists of the solute molecule, is treated quantum mechanically. Region B contains the surrounding solvent molecules, which are represented by classical, empirical potentials in statistical mechanical simulations. Region C specifies the boundary conditions for the rest of the bulk solution system, which may be treated by periodic boundary conditions or by a continuum model. Within the Born–Oppenheimer approximation and assuming no charge transfer between regions, the Hartree–Fock wave function for the solute molecule in region A is written as a single Slater determinant of occupied molecular orbitals, $\{\psi_i\}$, and the MO's are linear combinations of atomic orbitals, $\{\phi_\mu\}$.[16] Consequently, the effective Hamiltonian can be separated into three terms:

$$\hat{H}_{\mathrm{eff}} = \hat{H}^{\circ}_{\mathrm{X}} + \hat{H}_{\mathrm{Xs}} + \hat{H}_{\mathrm{ss}} \tag{1}$$

where $\hat{H}^{\circ}_{\mathrm{X}}$ is the Hamiltonian of the solute in region A, $\hat{H}_{\mathrm{ss}}$ is the solvent–solvent interaction energy in region B, and $\hat{H}_{\mathrm{Xs}}$ is the solute–solvent interaction Hamiltonian.[14] Throughout this paper, the subscript X represents the solute molecule in region A, which is treated quantum mechanically, whereas s designates the classical solvent molecules in region B, which is described by empirical potential functions. The molecular orbital coefficients, $\{c_{\mu i}\}$, are obtained by solving standard self-consistent field (SCF) Hartree–Fock equations by including the $\hat{H}_{\mathrm{Xs}}$ term in the Fock matrix, **F**.

$$F_{\mu\nu} = F^{\circ}_{\mu\nu} + H^{\mathrm{Xs}}_{\mu\nu} \tag{2}$$

where $F^{\circ}_{\mu\nu}$ is the Fock matrix element for an isolated solute molecule, and the one-electron integral, $H^{\mathrm{Xs}}_{\mu\nu}$, represents solute–solvent interactions. The total energy of the ground-state single determinant is given as follows:[14d]

$$E^{\mathrm{HF}}_{\mathrm{tot}} = E^{\mathrm{HF}}_{\mathrm{X}} + E^{\mathrm{HF}}_{\mathrm{Xs}} + E_{\mathrm{ss}} \tag{3}$$

in which $E^{\mathrm{HF}}_{\mathrm{X}}$ is the Hartree–Fock energy of the solute in solution, E_{ss} is evaluated separately with empirical potentials for the solvent, and

$$E^{\mathrm{HF}}_{\mathrm{Xs}} = \langle \Psi^{\mathrm{HF}}_{\mathrm{sol}} | \hat{H}_{\mathrm{Xs}} | \Psi^{\mathrm{HF}}_{\mathrm{sol}} \rangle = \sum_{\mu\nu} P^{\mathrm{HF}}_{\mu\nu} H^{\mathrm{Xs}}_{\mu\nu} + \sum_{s}\sum_{M} \frac{q_s Z_M}{R_{sM}} + E_{\mathrm{vdW}} \tag{4}$$

In eq 4, $\Psi^{\mathrm{HF}}_{\mathrm{sol}}$ is the Hartree–Fock wave function of the solute in solution, which minimizes the energy of the Hamiltonian, $\hat{H}^{\circ}_{\mathrm{X}} + \hat{H}_{\mathrm{Xs}}$, q_s is the sth solvent partial charge, Z_M is the Mth solute nucleus charge, R_{sM} is the distance separating solute and solvent atomic centers, and E_{vdW} is the van der Waals interaction energy between the QM and MM regions. Parameters in the van der Waals term have been specified previously.[15] The Hartree–Fock density matrix, $P^{\mathrm{HF}}_{\mu\nu}$, is defined as a sum over the occupied orbitals.[16]

$$P^{\mathrm{HF}}_{\mu\nu} = 2\sum_{i=1}^{n} C_{\mu i} C_{\nu i} \tag{5}$$

Using the Hartree–Fock wave function, $\Psi^{\mathrm{HF}}_{\mathrm{sol}}$, as the reference state, the CI (configuration interaction) wave function for region A can be constructed and is given as follows:

$$\Psi^{\mathrm{CI}}_{\mathrm{sol}} = a_0 \Psi^{\mathrm{HF}}_{\mathrm{sol}} + \sum_{I} a_I \Psi_I \tag{6}$$

where Ψ_I's are the excited-state determinants, including singly excited, doubly excited, etc., states, which are formed by replacing occupied spin orbital(s) in $\Psi^{\mathrm{HF}}_{\mathrm{sol}}$ with virtual spin orbital(s). The CI coefficients can be obtained as normalized eigenvectors of the CI matrix, whose element is defined as $\langle \Psi_I | \hat{H}^{\circ}_{\mathrm{X}} + \hat{H}_{\mathrm{Xs}} | \Psi_J \rangle$. Eigenvalues of the CI matrix correspond to the CI total energies of the solute ground state and various excited states.[6,16]

The total ground-state energy of the condensed-phase system is then

$$E^{\mathrm{CI,g}}_{\mathrm{tot}} = \langle \Psi^{\mathrm{CI,g}}_{\mathrm{sol}} | \hat{H}_{\mathrm{eff}} | \Psi^{\mathrm{CI,g}}_{\mathrm{sol}} \rangle = E^{\mathrm{CI,g}}_{\mathrm{X}}(\Psi^{\mathrm{CI,g}}_{\mathrm{sol}}) + E^{\mathrm{CI,g}}_{\mathrm{Xs}} + E_{\mathrm{ss}} \tag{7}$$

in which the superscripts indicate the electronic state and wave function, and

$$E^{\mathrm{CI,g}}_{\mathrm{Xs}} = \sum_{\mu\nu} P^{\mathrm{CI,g}}_{\mu\nu} H^{\mathrm{Xs}}_{\mu\nu} + \sum_{s}\sum_{M} \frac{q_s Z_M}{R_{sM}} + E_{\mathrm{vdW}} \tag{8}$$

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In eq 8, $P^{CI,g}_{\mu\nu}$ is the ground-state one-particle density matrix of the CI wave function, eq 6, which can be conveniently determined by a difference density method.[6b,17]

$$P^{CI,g}_{\mu\nu} = P^{HF}_{\mu\nu} + \Delta P^{CI,g}_{\mu\nu} \qquad (9)$$

where $\Delta P^{CI,g}_{\mu\nu}$ represents the change in the HF density matrix due to the CI expansion (eq 6). In the combined Monte Carlo QM-CI/MM simulation, the Metropolis sampling is carried out on the basis of the total energy given by eq 7.

Similar expressions can be written for the excited states. Consequently, the spectral shift accompanying solvation at an instantaneous solvent configuration is determined by the difference of total excitation energies in solution, $\Delta E^{g\to e}_{tot}(\Psi^{CI}_{sol})$, and in the gas phase, $\Delta E^{g\to e}(\Psi^{CI}_{gas})$, which may be further decomposed into specific terms:

$$\Delta\nu = E^{g\to e}_{tot}(\Psi^{CI}_{sol}) - E^{g\to e}(\Psi^{CI}_{gas}) = \Delta\Delta E^{g\to e}_{X} + \Delta E^{g\to e}_{Xs} \qquad (10)$$

where $\Delta\Delta E^{g\to e}_{X} = \Delta E^{g\to e}_{X}(\Psi^{CI}_{sol}) - \Delta E^{g\to e}(\Psi^{CI}_{gas})$, which represents a change in the energy gap of the solute ground and excited states in solution and in the gas phase, while $\Delta E^{g\to e}_{Xs}$ is the difference in solvation energy due to the solute electronic excitation. Karelson and Zerner recently provided a nice analysis, demonstrating that the solvent effects are naturally included into such a CI treatment.[8]

Since electronic transition is much faster than the time required for solvent relaxation, positions of the surrounding solvent molecules do not change appreciably during the absorption process.[1,18] Consequently, at the instant of its formation, the excited state of the solute is surrounded by the solvent cage whose geometry and orientation correspond to the potential surface of the ground state, although the solvent electronic polarization will respond to the change in charge density of the solute from its ground state to the excited state. The difference in solvation energy between this Franck–Condon excited state and the equilibrium ground state is largely responsible for the spectral shift, which can be evaluated according to

$$\Delta E^{g\to e}_{Xs} = E^{CI,e}_{Xs} - E^{CI,g}_{Xs} = \sum_{\mu\nu}(P^{CI,e}_{\mu\nu} - P^{CI,g}_{\mu\nu})H^{Xs}_{\mu\nu} \qquad (11)$$

where $P^{CI,g}_{\mu\nu}$ and $P^{CI,e}_{\mu\nu}$ are the one-particle density matrices of the solute in the ground state and excited state in solution.

Finally, the solvent effect on electronic transition is determined by taking a Boltzmann average over solvent configurations generated in statistical mechanical Monte Carlo or molecular dynamics simulation:

$$\langle\Delta\nu\rangle = \frac{1}{N}\sum_{i=1}^{N}\Delta\nu_i \qquad (12)$$

where $\langle\Delta\nu\rangle$ designates an ensemble average of the spectral shift based on the ground-state potential surface and N is the number of configurations sampled in the simulation.

Several points should be addressed here. In our present implementation, the instantaneous change in electronic polarization of the solvent upon solute excitation is not specifically computed because pairwise, effective potential functions are used for the solvent to reduce the computer time. This is certainly a severe limitation, which shall not allow the method to predict the dispersion red shift for n → π* transition in nonpolar solvents.[11a] Incorporation of a polarizable solvent model and the results will be reported in a future publication. However, it should be noted that electronic polarization of the solute molecule by the surrounding solvent field is included in the present study through eq 2. For polar solvents, particularly those that can form hydrogen bonds, the major contribution to the spectral shift is from dipole–dipole and dipole–induced dipole interactions. Thus, the present method should provide reasonable results for systems involving strong solute–solvent interactions.

A convenient and widely used method for spectroscopy is the CIS (configuration interaction singles) treatment,[6] which is examined in this work. To increase the applicability of the QM-CI/MM simulation method to study chemical reactions, we also consider the full CI method.[16] However, an unavoidable practical difficulty in condensed-phase simulation using the combined QM-CI/MM potential is that one has to limit the number of orbitals and electrons allowed in the CI expansion because the computer time required for these calculations can quickly become unbearable even with supercomputers. Consequently, relatively small active space must be used in the CI calculation.[19] In this paper, we compare the results obtained from finite CI calculations as well as the size dependence of the CI expansion.

Computational Details

Statistical mechanical Monte Carlo simulations are performed with the MCQUB/BOSS program,[20] in which the quantum mechanical energies are evaluated using Stewart's MOPAC program.[21] Since CI calculations will be carried out throughout the fluid stimulation in order to generate the Monte Carlo trajectory and to compute the excitation energy in solution, a computationally efficient method must be used. We have adopted as in the past the Austin Model 1 (AM1) Hamiltonian,[22] and modified the multielectron configuration interaction (MECI) module in MOPAC to incorporate the combined QM-CI/MM potential.[19,21] The MCQUB program takes advantage of the MECI features within MOPAC, and allows the user to conveniently choose the CIS Hamiltonian in Monte Carlo simulations. Understandably, it is always desirable to use small CI expansions, while retaining a reasonable description of the physical properties, since the computer memory and cpu time will increase rapidly as the number of active orbitals and electrons increases.[19] The Monte Carlo calculation is performed using standard methods.[23] The following gives an outline of the present computational procedure.

(1) For a given solvent configuration, the Hartree–Fock reference wave function is determined with the combined AM1/OPLS Hamiltonian, using a procedure described previously.[14d]

(2) Then, the CI matrix is constructed and diagonalized, from which the ground-state and excited-state energies as well as eigenvectors are obtained. The Monte Carlo Metropolis sampling is based on the ground-state CI potential energy, although we note that simulations of excited states can similarly be carried out. Solute–solvent interaction energies for both the ground and excited states are determined according to eq 8 by employing the corresponding one-particle density matrix of the CI wave function.

(3) The next step is to generate a new configuration by randomly moving the solute, a solvent molecule, or the volume; then, steps 1 and 2 are repeated.

(4) Finally, the ensemble average and statistics are analyzed and printed out.

To illustrate the performance of this combined QM-CI/MM potential for simulation of the solvent effects on electronic transition, we have computed the n → π* spectral shifts of acetone in water, methanol, acetonitrile, chloroform, and carbon tetrachloride. Although solvent effects on any excited states can be determined from the CI calculation, only the low-energy transitions are of interest here. In this paper, we report the solvatochromic shifts for excitations of acetone to the lowest singlet (S_1) and triplet (T_1) states. The carbonyl n → π* $S_0 \to S_1$ transition

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Table 1. Computed Solvent Spectral Shifts for the n → π* Electronic Transition of Acetone (cm^{-1})[a]

solvent	ϵ	$\langle\Delta\nu\rangle(S_0 \to T_1)$	$\langle\Delta\nu\rangle(S_0 \to S_1)$	exptl($S_0 \to S_1$)
CCl_4	2.2	6 ± 5	5 ± 4	−490
$CHCl_3$	4.8	298 ± 22	277 ± 21	50
CH_3CN	35.9	568 ± 31	535 ± 29	
CH_3OH	32.7	807 ± 65	763 ± 60	570
H_2O	78.3	1765 ± 87	1694 ± 84	1560

[a] The gas-phase reference excitation energies for this CI(100) calculation are 27 441 and 24 955 cm^{-1} for the $S_0 \to S_l$ and $S_0 \to T$ transitions, respectively. Spectral shifts are relative to the gas-phase value.

is symmetry forbidden, which accounts for its small absorption coefficient, while the $S_0 \to T_1$ transition is both symmetry and spin forbidden, which appears via spin–orbit coupling at low-energy regions in the spectrum (ca. 500–700 nm) with very small oscillator strength.[18] Acetone is selected in this study because there have been numerous experimental and theoretical investigations, providing an excellent source of data for comparison.[2,4,12,13,24] Furthermore, the observed spectral shift of acetone (λ_{max}) in solution covers a large energy range, from a 490 cm^{-1} red shift in CCl_4 up to a 1500 cm^{-1} blue shift in aqueous solution, relative to the gas-phase spectrum.[2,4] In all calculations, the AM1 Hamiltonian is adopted for acetone.[22] The CI calculations include a total of 100 configurations of all excitations for a 5-orbital/6-electron active space (2 unoccupied and 3 doubly occupied orbitals). In addition, two sets of CIS computations are performed, one consisting of 5 orbitals/13 configurations (2 unoccupied, 3 doubly occupied orbitals) and the other 10 orbitals/51 configurations (5 unoccupied, 5 doubly occupied orbitals). For the solvents in the combined AM1-CI/MM potential, the TIP4P model is used for water and the OPLS functions are employed for organic solvents.[25] The combined AM1/OPLS model has been used in Hartree–Fock calculations to investigate a number of aqueous and organic solution systems; the results are encouraging.[26]

Statistical mechanical Monte Carlo simulations are performed for systems of cubic boxes containing 260 water and methanol, and 125 acetonitrile, chloroform, and CCl_4 molecules plus 1 acetone. In all calculations, the isothermal–isobaric (NPT) ensemble is employed at 25 °C and 1 atm along with periodic boundary conditions. A cutoff distance of 9.5 Å is used for the aqueous solution, whereas 10.5–12 Å is adopted for organic solvents. The acceptance rate is controlled at about 40–45% of all attempted moves. Each simulation covers at least 1×10^6 configurations for equilibration, followed by additional 1.5×10^6 configurations for averaging. All calculations are carried out on IBM RS6000/370 workstations in our laboratory.

Results and Discussion

The computed n → π* spectral shifts accompanying solvation are listed in Table 1, while the energy components (eq 10) are recorded in Table 2. Uncertainties of the calculated spectral shifts are estimated from fluctuations for averages of 10^5 configuration blocks. Solute–solvent structural data including radial distribution functions (rdfs) were also recorded during the simulation; however, they are not reported here since the primary goal of this work is to examine solvent spectral shifts in electronic transitions. The computed rdfs are in accord with those reported in early studies.[12,13]

As expected, the present model is not able to predict the experimentally-observed red shift in the $S_0 \to S_1$ excitation of acetone in CCl_4 because the effect of the solvent polarization by the solute electronic transition is not specifically evaluated. In this study, we have adopted a pairwise potential function for the solvent,[25] which effectively ignores the specific mutual solute–solvent dispersion interaction. Such interactions, however, are believed to be primarily responsible for the spectral shift toward low energy (red shift).[1d,2,24b,27] This certainly is a major limitation of the present model, although improvement can be made by employing a polarizable potential for the solvent (see below).[11] However, this combined QM-CI/MM Monte Carlo method correctly predicts the large blue shifts of acetone in methanol and water. Importantly, the qualitative trend of solvent effects on the solvatochromic spectral shift is found to be in accord with experiments.[1,2] As the solvent polarity and hydrogen-bonding ability increase, the n → π* transition moves toward the higher energy region (blue shift). In water and methanol, the computed blue shifts for the $S_0 \to S_1$ excitation are 1694 and 763 cm^{-1}, respectively, which compare favorably with the experimental data (1560 and 570 cm^{-1}).[2] For CCl_4, a small blue shift of 5 cm^{-1} is predicted, while the changes are 277 and 535 cm^{-1} in $CHCl_3$ and CH_3CN. Note that the spectral shift in CH_3CN is predicted to be smaller than in CH_3OH, although the former has a greater dielectric constant. Overall, the Monte Carlo simulation overestimates the solvatochromic shifts to the blue by about 140–500 cm^{-1}, with the largest errors occurring in nonpolar solvents. Nevertheless, in view of the fact that the AM1 theory is not specifically parametrized for predicting electronic spectroscopy of organic compounds and the simple approximation of the solvent model, the results obtained here are encouraging.

Table 2. Energy Components of the Total Solvatochromic Shifts (cm^{-1})[a]

	$S_0 \to T_1$			$S_0 \to S_1$		
solvent	$\langle\Delta\nu\rangle$	$\Delta E_{\mathrm{Xs}}^{g\to e}$	$\Delta\Delta E_{\mathrm{X}}^{g\to e}$	$\langle\Delta\nu\rangle$	$\Delta E_{\mathrm{Xs}}^{g\to e}$	$\Delta\Delta E_{\mathrm{X}}^{g\to e}$
CCl_4	6	8	−2	5	6	−1
$CHCl_3$	298	370	−73	277	289	−12
CH_3CN	568	769	−201	535	596	−61
CH_3OH	807	973	−166	763	789	−27
H_2O	1765	1906	−144	1694	1625	68

[a] $\Delta\Delta E_{\mathrm{X}}^{g\to e}$ is obtained by taking the difference between $\langle\Delta\nu\rangle$ and $\Delta E_{\mathrm{Xs}}^{g\to e}$. Standard errors for $\Delta E_{\mathrm{Xs}}^{g\to e}$ are of the same order as those of $\langle\Delta\nu\rangle$ in Table 1.

The solvent effects on other excited states may also be determined in the Monte Carlo QM-CI/MM simulation. Of particular interest is the excitation to the triplet state. Energy changes due to solvation for the T_1 state are given in Table 1. Again, it should be noted that these energies are computed with the solvent cage corresponding to the ground state of the solute molecule. Experimental data concerning solvent effects on the $S_0 \to T_1$ transition do not appear to be available since the process is both symmetry and spin forbidden, which typically occurs with very low oscillator strength (10^{-7} to 10^{-9}).[18] The results indicate that the solvent effects move the absorption band further to the short wavelength than the $S_0 \to S_1$ transition since the decrease in molecular dipole moment is greater in the $S_0 \to T_1$ transition than in the $S_0 \to S_1$ transition.[13,28] This observation is in agreement with findings by DeBolt and Kollman.[13]

Self-consistent reaction field (SCRF) models, treating the solvent as a continuum dielectric medium, were primarily used in the past to predict solvent effects on electronic transitions, notably Zerner's ZINDO program.[6a,8] Clearly, the SCRF method will not predict the red shift of the carbonyl n → π* transition, accompanying a decrease in molecular dipole moment, in nonpolar solvent since the solvent dielectric constant will always be greater than that of a vacuum ($\epsilon_0 = 1$). To overcome this difficulty, Rosch and Zerner recently developed a perturbation method combining separate calculations for the solute and solvent molecules.[27] The theory was successfully applied to acetone, benzene, naphthalene, and chrysene in cyclohexane, which all show large red shifts relative to the gas-phase spectra. In this

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Table 3. Comparison of Computed Spectral Shifts for the Acetone $n \rightarrow \pi^*$ Excitations in Water (cm^{-1})[a]

method	$S_0 \rightarrow T_1$	$S_0 \rightarrow S_1$
CI(100)	1765 ± 87 (1906 ± 85)	1694 ± 84 (1625 ± 80)
CIS(13)	1535 ± 57 (1778 ± 51)	1283 ± 50 (1754 ± 50)
CIS(51)	1277 ± 72 (1792 ± 82)	1039 ± 67 (1771 ± 82)
exptl		1560

[a] Total spectral shifts are given first, followed by solvation contributions in parentheses.

method, the dispersion energy shifts were treated as a correction to the continuum SCRF calculation.[8,27] Analogously, the method may be used to correct results obtained from the present combined QM-CI/MM Monte Carlo simulations.

In a recent report, Karelson and Zerner investigated the solvatochromic $n \rightarrow \pi^*$ blue shift using the INDO/S Hamiltonian along with the SCRF treatment.[3] They proposed that the origin of the solvatochromic blue shift of $n \rightarrow \pi^*$ transition in protic solvents is due to a simple medium dielectric effect, which "lowers the ground state energy of the solute molecule substantially more than it lowers the excited-state energy".[3] This is opposed to an alternative explanation, which suggests that interactions with the solvent lower the energy of the lone-pair orbital, while the π^* orbital is less affected.[3] Overall, our simulation results are in good accord with Zerner's proposal. The energy components contributing to the total solvent spectral shift are listed in Table 2. Clearly, the spectral shifts are dominated by solvent stabilization of the ground state over that of the excited states. The energy gap between the ground state and excited state actually becomes smaller relative to the gas phase thanks to distortion of the solute wave function in solution (except for the $S_0 \rightarrow S_1$ transition in water), while the effects appears to be larger for the $S_0 \rightarrow T_1$ excitation than for $S_0 \rightarrow S_1$.

For comparison, Levy and co-workers performed a molecular dynamics investigation of formaldehyde in water, employing empirical potential functions with partial charges derived from ab initio molecular electrostatic potentials.[12] Subsequently, 70 configurations were selected from the molecular dynamics trajectory to carry out Hartree–Fock MO calculations at the 6-31 + G* level. These authors obtained a blue shift of 1900 cm^{-1} and a bandwidth of 4400 cm^{-1}. DeBolt and Kollman reported molecular dynamics calculations of acetone and formaldehyde in water, methanol, and CCl_4, also with ab initio electrostatic potential-fitted charges.[13] They predicted blue shifts of 1680 and 1400 cm^{-1} for acetone in water and methanol, respectively. The spectral shift in CCl_4 was found to be about zero, similar to our observation. This is because nonpolarizable potential funtions were also used in their calculations.[13]

In Table 3, we examine the dependence of the computed spectral shift with respect to three CI treatments in aqueous solution. In addition to the 5-orbital/6-electron full CI treatment (100 configurations), CIS calculations with 13 configurations (5 orbitals/6 electrons) and 51 configurations (10 orbitals/10 electrons) are considered. The results shown in Table 3 suggest that the computed spectral shifts are dependent on the size of the CI calculation. The spectral shifts are somewhat underestimated using CIS, although surprisingly, the smaller CIS (13) simulation yields better agreement with experiments than the more extensive CIS (51) calculation. On the other hand, changes in solvation energy accompanying the electronic excitation are in general accord among these methods.

To conclude, we address treatments of the induced dipole–induced dipole dispersion interaction between the solute and solvent. The dispersion interaction favors the excited state over the ground state, leading to a bathochromic (red) shift of the $n \rightarrow \pi^*$ absorption for acetone in nonpolar solvents.[29] A proper quantum mechanical treatment of this effect would require consideration of interactions between singly excited configurations of both the solute and solvent molecules. Clearly, it is not practical to treat the entire solution system quantum mechanically in Monte Carlo simulations. It might be possible to construct a database of solvent configurations generated in the presence of the bulk solvent. Then, these configurations are allowed to interact with the solute configurations. This is similar to the method used by Rosch and Zerner.[27] An alternative approach is to employ an effective, polarizable empirical potential function for the solvent to introduce the mutual electronic polarization between the solute and solvent.[10,11] Finally, different van der Waals parameters may be derived for the ground and excited states to account for the difference in dispersion energy. Attempt is currently being made to incorporate these methods into our program.

Concluding Remarks

We have presented a Monte Carlo simulation method for studying the solvatochromic shift of the electronic spectra of organic compounds in solution, making use of a combined quantum mechanical–configuration interaction and molecular mechanical potential. In the present study, the Monte Carlo calculation is carried out based on the potential surface of the ground state, determined by the AM1-CI/OPLS model. This yields the excitation energies of the solute in the presence of an instantaneous solvent configuration, and the differential solvation energies of the solute in the ground state and its excited states. The simulations correctly predict the solvatochromic blue shift of acetone in polar solvents including acetonitrile, methanol, and water, while quantitative estimates of the spectral shift are greater than the experimental values. However, the dispersion red shift in CCl_4 was not reproduced. The discrepancy is attributed to the use of empirical potential functions for the solvent, which do not contain explicit polarization terms, thus excluding mutual solute–solvent dispersion interactions. Clearly, improvement of the method toward this direction is necessary. Although use of polarizable intermolecular potential functions (PIPF) for the solvent would tremendously increase the computer time required in these calculations, a number of approaches might be tested to incorporate the dispersion interactions. The results presented here demonstrate that it is viable to carry out condensed-phase simulations for processes involving electronic transitions. This shall provide the opportunity to study photochemical processes and chemical reactions involving the gas-phase excited state in solution.

Acknowledgment. Gratitude is expressed to the National Science Foundation and National Institutes of Health for support. I thank Professor M. C. Zerner for providing a preprint of ref 27.

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