Solvent Effects on the $\pi^* \leftarrow n$ Transition of Acetone in Various Solvents: Direct Reaction Field Calculations

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The direct reaction field model was used to calculate the solvent shift of the $n-\pi^*$ transition of acetone in eight different solvents. The computed shifts correspond excellently to experimental values. We found that dispersion interactions are an essential part of the model for correctly describing the shifts in both polar and apolar solvents. Improving the quality of the basis set generally improves the results, mainly due to an increase in electrostatic interactions.

Introduction

Solvent effects play a very important role in chemistry since most chemical reactions and biological processes take place in solutions. The properties of molecules and the interactions between them in solution can differ greatly from the properties and interactions in vacuum, the state to which most quantum chemical calculations refer.

A well-known example is the effect of solvents on the electronic spectra, which has been the subject of many experimental[1−3] theoretical[4−8] studies. The importance of these effects is illustrated by the $E_T(30)$ solvent polarity scale[9] which is based on the solvatochromic shifts of the $n-\pi^*$ transition in the pyridinium *N*-phenolate betaine dye. Another, computationally more accessible, example is presented by acetone in which the $n-\pi^*$ transition shows a blue shift in polar solvents and a red shift in apolar solvents.

As shown in an earlier paper[6] the blue shift is caused mainly by the electrostatic interactions. The solvent shell orientation is adapted to the electrostatic interactions in the ground state; the excitation process is much faster than the reorientation of the solvent shell. Thus the excited-state solute is surrounded by the solvent shell that was adapted to the ground-state interactions, and the interaction of the excited-state solute with the solvent shell will be less favorable than the interaction of the solvent shell with the ground-state solute. This causes an increase in excitation energy.

Red shifts in $n-\pi^*$ transitions are caused mainly by dispersion effects. The excited state always has a larger polarizability than the ground state because an electron is promoted to a more diffuse orbital in which it is more polarizable. Thus the dispersion interaction of the excited solute with the solvent will be larger than the dispersion interaction of the ground-state solute with the solvent. The excitation energy decreases, resulting in a red shift.

The first attempts to incorporate solvent effects in calculations are based on a dielectric continuum description[10] of the solvent. These models have been used with reasonable success; however, there are important limitations. They employ a macroscopic property of the solvent, the dielectric constant, to model the interactions on a microscopic scale; this means they can never accurately describe specific solvent−solute interactions, e.g., hydrogen bonding.[4,6] Another drawback is the need to reparametrize the model for each different solvent.

These difficulties can be resolved by using explicit solvent models. A number of these have been developed over the last years.[7,11] Most of them are based on a Lennard−Jones type force field for the dispersion and short range repulsion terms and point charges for modeling electrostatic effects. Recently, polarization effects were added to these models to include induction interactions;[5,8,12] however, the explicit polarizabilities are not used for modeling the dispersion. The Lennard−Jones parameters are fitted to ground-state interaction energies so no distinction can be made between dispersion interaction in the ground state and the excited states without reparametrizing for the excited states. For this reason these models fail to reproduce red shifts in the $n-\pi^*$ transition of acetone in apolar solvents.

These problems do not appear in our direct reaction field (DRF)[13−16] model that uses explicit polarizabilities for induction and polarization interactions as well as dispersion. In this paper we will demonstrate that our model reproduces both blue shifts and red shifts excellently without reparametrizing for different solvents or different states. We will describe the main features of the DRF model and compare them to other models, after which we will discuss the application of the DRF model to the solvent shifts in the $n-\pi^*$ transition of acetone in eight different solvents.

Theory

The DRF model is a hybrid QM/MM model in which the classical part (the solvent shell) is modeled by groups (A,B,...) of point charges, radii, and polarizabilities on each atom. These parameters can all be derived from monomer properties, either from experiment or calculations. Point charges can be calculated from ab initio wave functions on the monomers (A,B,...) using a dipole preserving population analysis[17] or by fitting charges to the electrostatic potential.[18] For the radii experimental values van der Waals radii can be used, but calculated values can also be obtained (e.g., from the quadrupole moment or polarizabilities). Atomic polarizabilities can be obtained by fitting them to experimental or calculated molecular polarizabilities in a procedure developed by Thole.[19,20]

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The total energy of the system consisting of a quantum mechanically described solute and a discrete classical solvent is given by:

$$\Delta U^{\mathrm{discr}} = \Delta U^{\mathrm{QM}} + \Delta U^{\mathrm{MM}} + \Delta U^{\mathrm{QM/MM}} \tag{1}$$

in which U^{QM} is the expectation value of the vacuum Hamiltonian over the nonvacuum wave function. The interactions in the classical part can be written as:

$$\Delta U^{\mathrm{MM}} = \sum_{\substack{i\in A,j\in B\\ A>B}} q_i^A \nu_{ij}\, q_j^B + \frac{1}{2}\sum_{\substack{i\in A,j\in B\\ A,B\\ rs\notin AB}} q_i^A\ f_{ir}\, A_{rs}\ \ f_{sj}\, q_j^B + \Delta U^{\mathrm{MM}}_{\mathrm{disp}} + \Delta U^{\mathrm{MM}}_{\mathrm{rep}} \tag{2}$$

with $\nu_{sp} = 1/|\mathbf{r}_p - \mathbf{r}_s|$, the Coulomb potential in **p**, brought about by a source in **s**, and $f_{sp} = -\nabla_p\, \nu_{sp}$ is the corresponding electric field. The first two terms are the Coulomb interaction and the induction interaction (also called 'screening of the electrostatic interaction'). q_i^A is the *i*th point charge of classical group *A*. The A_{rs} are elements of the matrix **A**, which can be considered as the total polarizability of a system of molecules (see below). For clarity we note here that in eq 2 all interactions within monomers are set to zero.

For the classical dispersion interaction, we use the Slater–Kirkwood expression:

$$\Delta U^{\mathrm{MM}}_{\mathrm{disp}} = \sum_{i<j}\frac{1}{4R^6}\,\frac{\mathrm{Tr}(\boldsymbol{\alpha}_i \mathbf{t}(\mathbf{i},\mathbf{j})^2 \boldsymbol{\alpha}_j)}{(\sqrt{\alpha_i/n_i} + \sqrt{\alpha_j/n_j})} \tag{3}$$

in which $\mathbf{t}(\mathbf{i};\mathbf{j})$ is the interaction tensor for the induced dipoles at **i** and **j**. For the short range repulsion the CHARMM expression is used:

$$\Delta U^{\mathrm{MM}}_{\mathrm{rep}} = \sum_{i<j}\frac{3}{4}\,\frac{\bar{\alpha}_i \bar{\alpha}_j (r_i + r_j)^6}{(\sqrt{\bar{\alpha}_i/n_i} + \sqrt{\bar{\alpha}_j/n_j})}\, r_{ij}^{-12} \tag{4}$$

in which $\bar{\alpha}_i$, n_i, and r_i are the isotropic polarizability, number of valence electrons, and radius of atomic center *i*, respectively, and r_{ij} is the distance between centers *i* and *j*. We use the integral number of valence electrons of an atom and the same atomic polarizabilities that go into the electrostatic, response, and dispersion terms, leaving only the atomic radii as independent parameters.

Coupling of the Classical and Quantum System. The static electric field, brought about by the point charges, can easily be introduced in the solute Hamiltonian. Adding reaction field effects due to interaction with classical polarizabilities, however, is more difficult. The coupling of the quantum mechanical solute and the polarizable solvent system can be done by performing a so-called coupled-SCF procedure described by Thompson[12] in which the wave function has to be solved from a nonlinear equation:

$$[\ \hat{H}^{\mathrm{Q}} + \ \hat{H}^{\mathrm{RF}}(\Phi_{\mathrm{Q}})]\Phi_{\mathrm{Q}} = E(\Phi_{\mathrm{Q}})\Phi_{\mathrm{Q}} \tag{5}$$

$\hat{H}^{\mathrm{Q}}$ is the normal vacuum Hamiltonian, $\hat{H}^{\mathrm{RF}}$ is the reaction field Hamiltonian which is dependent on the wave function itself because it includes the dipole moments induced by the quantum system (in the classical polarizable system). This nonlinear equation has to be solved in an iterative scheme in which first the induced moments are calculated:

$$\mu_p = \alpha_p[\ \ f_p + \sum_{q\neq p}\ f\ (m_q,p) + \ f^{\ \mathrm{Q}}_{\ p}(\Phi_{\mathrm{Q}})] \tag{6}$$

f_p is the static field in *p*, $f\,(m_q,p)$ is the field in *p* due to a (classically induced) moment in *q*, and $f^{\ \mathrm{Q}}_p$ is the field in *p* due to the quantum system. These induced moments are put into the reaction field Hamiltonian $\hat{H}^{\mathrm{RF}}$, which is then used to calculate a new wave function which is in turn used to generate new induced moments, etc., until convergence is reached. In this way the solute feels the average response of the classical polarizabilities to the field due to the solute (i.e., the average reaction field), and the induction interaction between the quantum system and the classical system can be calculated.

A more elegant approach is presented by the *direct* reaction field model[13–16] (DRF) in which the effect of the solvent polarizability is introduced directly into the vacuum solute Hamiltonian ($H^{\ 0}$):

$$H = \ H^{\ 0} + \ H^{\ \mathrm{es}} + \ H^{\ \mathrm{rf}} \tag{7}$$

with $H^{\ \mathrm{es}}$ and $H^{\ \mathrm{rf}}$ the electrostatic and reaction potential *operators.* The interaction energy between a quantum mechanically described solute and a system of (classical) point charges and polarizabilities **A** (i.e., the solvent, see below)—for a single determinant, closed shell wave function—is given by:

$$\begin{aligned}\Delta U^{\mathrm{QM/MM}}_{\mathrm{int}} = {} & \sum_{A,i,j} q_i^{\ A} \nu_{ij} Z_j + \mathrm{e}\sum_{A,i} q_i^{\ A}\langle\nu\rangle_i + \sum_{A,i,j,r,s} q_i^{\ A}\ \ f_{ir}\, A_{rs}\ \ f_{sj} Z_j + \mathrm{e}\sum_{A,k,j,r,s} q_j^{\ A}\ \ f_{jr} A_{rs}\langle\ \ f\ (s;k)\rangle + {} \\ & \frac{1}{2}\sum_{i,j,r,s} Z_i\ \ f_{ir}\, A_{rs}\ \ f_{sj}\, Z_j + \mathrm{e}\sum_{i,k,r,s} Z_i\ \ f_{ir}\, A_{rs}\langle\ \ f\ (s;k)\rangle + \frac{\gamma}{2}\mathrm{e}^2\sum_{k,r,s}\langle\ \ f\ (k;r) A_{rs}\ \ f\ (s;k)\rangle = {} \\ & \frac{1}{2}\mathrm{e}^2\sum_{k,l,r,s}\langle\ \ f\ (k;r)\rangle_r\, A_{rs}\Big(1 - \frac{\gamma}{2}P_{12}\Big)\langle\ \ f\ (s;l)\rangle + \Delta U^{\mathrm{QM/MM}}_{\mathrm{rep}}\end{aligned} \tag{8}$$

In the first two terms of eq 8 we see the electrostatic interactions of nuclei and electrons with the point charges. The third term contains the interactions of the point charges with the dipoles induced by the nuclei and vice versa. The fourth represents the interaction between the point charges and the dipoles induced by the electrons and vice versa. The fifth and sixth terms are the screening of the nuclear repulsion and attraction, respectively (part of the induction). The seventh term contains the interaction of each electron with its own induced dipoles, and the eighth is the interaction of each electron with the dipoles induced by the other electrons; hence it is a two-electron term. The last term contains the induction interaction and part of the dispersion. The scaling factor, γ, is for the dispersion which is discussed below, and P_{12} is the permutation operator. If one takes $\gamma = 0$, term 7 disappears and in term 8 only the induction part remains. In order to distinguish between source and recipient in the expectation values of the field—e.g., $\langle\ \ f\ (k;s)\rangle$, i.e., the electric field at **s** due to electron *k*—we have made explicit the electron labels (*k*,*l*) and the electronic charge (e) so as to avoid ambiguity in the signs of the various terms. In eq 8 the cost of inducing all the dipoles in the classical system has already been included.

The repulsion term in eq 8 is the same as in eq 4, although we may optionally get the radii of the QM atoms "on the fly" instead of fixing them on their vacuum values. The difference of the expectation values

$$\langle\Psi|H\ |\Psi\rangle - \langle\Psi^0|H\ {}^0|\Psi^0\rangle + \Delta U_{\mathrm{rep}}^{\mathrm{QM/MM}} = \Delta U_{\mathrm{int}}^{\mathrm{QM/MM}} \tag{9}$$

contains all first- and second-order contributions usually obtained when Ψ refers to a supermolecule SCF calculation, and more. We can rewrite the expectation value of $H\ ^{\mathrm{rf}}$ as:

$$\langle H\ ^{\mathrm{rf}}\rangle = -\frac{1}{2}\langle\ f\ ^{\dagger}\mathbf{A}\ \ f\ \rangle = -\frac{1}{2}\langle\ f\ \rangle^{\dagger}\mathbf{A}\langle\ f\ \rangle - \frac{1}{2}\{\langle\ f\ ^{\dagger}\mathbf{A}\ \ f\ \rangle - \langle\ f\ \rangle^{\dagger}\mathbf{A}\langle\ f\ \rangle\} = \Delta U_{\mathrm{DRF}}^{\mathrm{ind}} + \Delta U_{\mathrm{DRF}}^{\mathrm{disp}} \tag{10}$$

The first term in eq 10 is the DRF induction interaction. The term between braces, { }, the difference between the expectation value of the DRF Hamiltonian and the average reaction field term, is the *unscaled* DRF dispersion interaction. It has been shown to be just the difference between the screened self-energy and the screened exchange contribution[14] (see eq 8). Moreover it has been shown[6,13,16] that this expression approximately equals the second-order perturbation theory (SOP) expression for dispersion, apart from a scaling factor:

$$\Delta U_{\mathrm{disp}}^{\mathrm{SOP}} \approx \left\{\frac{E_{\mathrm{solvent}}^{\mathrm{i}}}{E_{\mathrm{solute}}^{\mathrm{i}} + E_{\mathrm{solvent}}^{\mathrm{i}}}\right\}\Delta U_{\mathrm{disp}}^{\mathrm{DRF}} = \gamma\Delta U_{\mathrm{disp}}^{\mathrm{DRF}} \tag{11}$$

where $E_{\mathrm{solute}}^{\mathrm{i}}$ and $E_{\mathrm{solvent}}^{\mathrm{i}}$ are the ionization energies of the quantum mechanical solute and the classical solvent, respectively. We can compare the DRF dispersion to the London formula for dispersion for a dimer interaction:

$$\Delta U_{\mathrm{disp}}^{\mathrm{London}} = \frac{-E_{\mathrm{i}}^{\mathrm{A}}\ E_{\mathrm{i}}^{\mathrm{B}}}{E_{\mathrm{i}}^{\mathrm{A}} + E_{\mathrm{i}}^{\mathrm{B}}}\frac{3\alpha_{\mathrm{A}}\alpha_{\mathrm{B}}}{2R^6} = \gamma\frac{-3\alpha_{\mathrm{A}}(E_{\mathrm{i}}^{\mathrm{B}}\alpha_{\mathrm{B}})}{2R^6} \approx \gamma\Delta U_{\mathrm{disp}}^{\mathrm{DRF}} \tag{12}$$

where fragment B is treated quantum mechanically in the DRF dispersion expression. It is clear that the dispersion interaction not only depends on the polarizability but also on the ionization potentials of both fragments. The ionization potential of B is introduced explicitly in γ but is also implicitly present in $\Delta U_{\mathrm{disp}}^{\mathrm{DRF}}$—through the wave function used. It should be noted that the London formula is based on a one-center expansion—i.e., a point polarizability—whereas in the DRF interactions multicenter expansions are used.[13] The DRF dispersion expression therefore gives a much better description.

We redefined the reaction field operator according to eq 11,[13] i.e., by scaling with γ the integrals for screening of the one-electron self-energy and of the two-electron exchange contributions (see also eq 8). This is only possible if the exchange interaction is explicitly under control, i.e., only for single-determinant wave functions. When using $\gamma = 0$, the wave function does not feel the effect of dispersion with the classical system and the method renders in fact the average reaction field (ARF) method rather than the DRF approach. With this definition of ARF the functional minimized is the same as that of the coupled SCF approach and, hence, leads to identical Fock operators. Thus, although they are constructed along different paths, they lead to the same SCF wave function.

With $\gamma \neq 0$ the quantum system does feel the effect of dispersion which will modify the wave function. This in turn will lead to a somewhat different induction interaction as illustrated below.

The matrix **A**—used in eqs 2, 8, and 10—is a (super)matrix representing the total linear response of the complete discrete classical part, in which all particles interact self-consistently. Taking a set of points {**p**} with polarizabilities $\{\alpha_p\}$ in a uniform electric field $\mathbf{F}^0$, we have for the induced dipole moment in point **p**:

$$\mathbf{m}_p = \boldsymbol{\alpha}_p(\mathbf{F}^0(\mathbf{p})\ \sum_{q\neq p}^{N^{pol}}\mathbf{t}(\mathbf{p};\mathbf{q})\ \mathbf{m}_q) \tag{13}$$

A formal solution for $\{\mathbf{m}_p\}$ can be found by collecting the N^{pol} equations into a single supermatrix equation of dimension $N^{\mathrm{pol}} \times N^{\mathrm{pol}}$:

$$\mathbf{M} = \boldsymbol{\alpha}(\mathbf{F}^0 - \mathbf{TM}) \tag{14}$$

where $\mathbf{F}^0$ and **M** are $3\mathbf{N}^{\mathrm{pol}}$ dimensional vectors and α and **T** are square $3N^{\mathrm{pol}} \times 3N^{\mathrm{pol}}$ matrices. The supervectors and supermatrices are blocked into $3N^{\mathrm{pol}}$ and $3N^{\mathrm{pol}} \times 3N^{\mathrm{pol}}$ elements, respectively: $\mathbf{M}_p = \mathbf{m}_p$, $\alpha_{pq} = \alpha_p\partial_{pq}$, $\mathbf{T}_{pq} = \mathbf{t}(\mathbf{p};\mathbf{q})(1 - \partial_{pq})$, and ∂_{pq} is the Kronecker delta. Then

$$\mathbf{A} = (\boldsymbol{\alpha}^{-1} + \mathbf{T})^{-1} \tag{15}$$

may be considered as an ordinary polarizability matrix (but of an N^{pol} membered system):

$$\mathbf{M} = \mathbf{FA} = \mathbf{F}(\alpha^{-1} + \mathbf{T})^{-1} \tag{16}$$

A is obtained either by an exact matrix inversion or by solving the associated linear equations by iteration. We note that eq 16 is a self-consistent solution for any field, e.g., the electric field of QM during any stage of, e.g., the Hartree−Fock procedure, and can be expressed in terms of integrals over any basis set, which can be added to the vacuum Hamiltonian.

The {**t**(**p**;**q**)} are, when appropriate, screened according to the method described by Thole[19] in which (atomic) polarizabilities are taken as related to (model) charge distributions, the widths of which are related to the $\{\alpha_p\}$. This leads also to a consistent screening of the potentials and fields of interaction for overlapping charge distributions.

In general the polarizabilities are constructed following Thole's original recipe and parametrization for obtaining (molecular) polarizabilities with experimental accuracy. This model has been reparametrized also for computed polarizabilities from specific basis sets.[20] The advantage of this way of treating the relay matrix is that only atomic polarizabilities are needed as input, while changes in geometry will be automatically reflected in **A**. Optionally one may reduce parts of **A** first to group polarizabilities so as to reduce the dimensionality of the problem. For a detailed description of the DRF model and its implementation, the reader is referred to the paper published recently by de Vries et al.[13]

Thus in the DRF model the energy can be obtained as the expectation value of the DRF Hamiltonian without the need for an iterative solution scheme. Furthermore the electrons in the quantum system are directly correlated with the classical charge distributions modeled by polarizabilities; thus the dispersion interaction between classical and quantum system is included. When a wave function for an excited state is used in stead of that for the ground state, the dispersion interaction will be different, so the DRF model allows to model the effect of dispersion on spectral transitions.

Computational Details

In order to randomly generate nonequilibrium solvent geometries, statistical mechanical Monte Carlo (MC) simulations were

TABLE 1: Comparison of Treating Reaction Field Effects as First-Order Correction and Self-Consistently for a Single Solvent Conformation (4-31G)[a]

	H^{RF} as pert	H^{RF} self-cons	H^{RF} self-cons, $\gamma = 0$
E_{el}	+2072	+2153	+2144
E_{disp}	−1154	−1179	0
E_{ind}	+605	+647	+654
E_{pol}	−362	−387	−387
E_{q}	−67	−144	−151
E_{tot}	+1094	+1090	+2260

[a] In the last column the average reaction field values are given (all values in cm^{-1}).

performed in which the solvent as well as the solute was treated classically. Both solvent and solute geometries were kept rigid in the MC sampling. The solute and solvents we used are sufficiently rigid to justify this simplification. Modeling solutes and solvents in which considerable changes in the geometry can be expected, e.g., relatively strong acids like formic acid or fluoroacetic acid where the proton can be (partly) transferred to the carbonyl oxygen (experiments have shown very large blue shifts in these solvents[3]), should of course include sampling over the internal degrees of freedom. This requires, however, a molecular dynamics (MD) approach rather than the MC method. The gradients, necessary for a DRF/MD treatment, only just have been coded in our group and are presently being tested.

The acetone solute was surrounded by 52 solvent molecules (40 for dioxane, cyclohexane, and benzene) which were kept inside a sphere of a radius chosen to approximately obtain the experimental density of the system. The force field we used is the classical interaction part of our DRF model,[16] as given in eqs 1−4. The point charges were fitted to the electrostatic potential from ab initio calculations in points selected according to the CHELPG[18] scheme, as implemented in Gaussian 94.[21] Atomic polarizabilities were derived from fits to experimental molecular polarizabilities.[19,20]

The systems were equilibrated in 500 000 moves. After this, a data collection run of 100 000 moves was conducted from which 100 randomly chosen conformations were saved for later analysis. This procedure is different from the earlier approach,[6] in which an QM/MM Monte Carlo simulation was performed with a limited number of moves (∼15 000), and has the advantage of sampling a greater part of configuration space at less computational cost. This new procedure also makes the use of larger basis sets possible. The spectral transitions in the saved conformations were then calculated in QM/MM calculations using the DRF model.[13−15] In these calculations the static potential was treated self-consistently, and the reaction field effect was calculated as a first-order correction to the energy (so the wave function is not modified by the reaction field). That this is justified can be seen from Table 1 where the contributions to the shift of a single conformation of acetone in water are compared to the contributions in the case where the reaction field effects are treated self-consistently also. Although the different terms differ somewhat, the difference in the total shift is negligible. Table 1 also shows the values for the case that $\gamma = 0$; i.e., we used the average reaction field approach here. We see that all terms differ somewhat from the case where dispersion effects are included, but the differences are very small (the dispersion contribution is zero here of course). We can conclude that dispersion modifies the wave function slightly but the effects of this modification on, e.g., the induction interaction is negligible: i.e., the induction in the DRF approach is nearly equal to the induction in the ARF approach.

TABLE 2: Dispersion Scaling Parameters Computed from Experimental Ionization Energies (Eq 11)[a]

molecule	γ S_0	γ S_1
water	0.565	0.679
MeCN	0.557	0.671
CCl_4	0.543	0.662
$CHCl_3$	0.543	0.657
MeOH	0.528	0.645
dioxane	0.485	0.605
cyclohexane	0.503	0.621
benzene	0.488	0.607

[a] The S_1 state was taken 3.72 eV above S_0, the excitation energy in the DZP basis. Experimental ionization energies were taken from ref 24.

TABLE 3: Computed and Experimental Shifts (cm^{-1})[a]

solvent	4-31G basis	DZP basis	experimental[b]
H_2O	+1253 ± 463	+1493 ± 514	+1700 ± 200
MeCN	+345 ± 353	+478 ± 390	+400 ± 200
CCl_4	−273 ± 36	−278 ± 36	−250 ± 200
MeOH	+536 ± 794	+729 ± 862	+850 ± 200
$CHCl_3$	+79 ± 155	+123 ± 175	+150 ± 200
dioxane	−32 ± 310	+54 ± 354	0 ± 200
cyclohexane	−953 ± 73		-400 ± 200
benzene	−743 ± 205		−650 ± 200

[a] Uncertainties in the calculated values are root mean square deviations over the 100 conformations that were analyzed. Uncertainties in the experimental values are uncertainties in the position of the absorption maxima. [b] Experimental values were taken from refs 1 and 3.

The ground state of the acetone solute (S_0) was described by a closed shell RHF wave function and the singlet excited state (S_1) by an open shell ROHF wave function as implemented in HONDO8.1.[22] Although the SCF approximation is rather poor for excited states, it has been shown earlier[6] that it gives reasonable results when calculating shifts of the maximum. The vacuum transition energies for the $n-\pi^*$ transition are 26 962 and 30 043 cm^{-1} for the 4-31G and DZP basis, respectively, where the experimental value is 36 100 cm^{-1}. The scaling parameters for the dispersion interaction (see eq 11) are listed in Table 2.

Results and Discussion

We selected acetone to study the solvent effect on spectral transitions because it was computationally feasible and because there are abundant experimental data available for comparison. We selected the two most recent experimental reports[1,3] we were aware of to compile a list of experimental shifts in the solvents we simulated (see Table 3). Both authors agree on the shifts in most solvents within 200 cm^{-1}, the value we took as the uncertainty in the experimental values. This value reflects the uncertainty in the maximum position of the absorption peaks. The shifts in the $n-\pi^*$ transition, calculated in the 4-31G basis as well as in Dunning's polarized double zeta basis set (DZP),[23] are listed in Table 3.

As before,[6] the computed shift in water (1493 cm^{-1}) is reasonable, compared to the experimental data,[1,3] (1700 cm^{-1}). The shift in acetonitrile (478 cm^{-1}) agrees much better to the experimental value (400 cm^{-1}) than the value reported earlier, probably due to sampling over a larger number of conformations. The computed values for MeOH and $CHCl_3$, 729 and 123 cm^{-1}, respectively, also agree quite well with the experimental values (850 and 150 cm^{-1}). For dioxane experiments[3] show no appreciable shift, and our value of 54 cm^{-1} is

TABLE 4: Analysis of the Contributions to the Shifts[a]

solvent	basis	ΔE_{pol}	ΔE_{ind}	ΔE_{el}	ΔE_{disp}	ΔE_q	ΔE_{tot}
H_2O	DZP	−311	+577	+2503	−1204	−72	+1493
		(±110)	(±77)	(±526)	(±86)	(±36)	(±514)
	4-31G	−340	+649	+2266	−1228	−94	+1253
		(±101)	(±84)	(±486)	(±90)	(±45)	(±463)
MeCN	DZP	−336	+519	+1588	−1267	−26	+478
		(±108)	(±64)	(±407)	(±98)	(±18)	(±390)
	4-31G	−372	+591	+1445	−1276	−34	+345
		(±97)	(±59)	(±369)	(±98)	(±22)	(±353)
CCl_4	DZP	−68	+134	−3	−342	+1	−278
		(±8)	(±16)	(±18)	(±45)	(±0)	(±36)
	4-31G	−73	+145	−5	−340	0	−273
		(±10)	(±21)	(±16)	(±46)	(±0)	(±36)
MeOH	DZP	−469	+613	+2127	−1469	−73	+729
		(±196)	(±124)	(±953)	(±169)	(±50)	(±862)
	4-31G	−493	+708	+1915	−1502	−92	+536
		(±196)	(±144)	(±888)	(±179)	(±63)	(±794)
$CHCl_3$	DZP	−102	+173	+412	−358	−2	+123
		(±29)	(±40)	(±170)	(±74)	(±2)	(±175)
	4-31G	−106	+186	+360	−358	−3	+79
		(±31)	(±47)	(±147)	(±75)	(±3)	(±155)
dioxane	DZP	−432	+566	+1208	−1268	−20	+54
		(±126)	(±37)	(±409)	(±49)	(±16)	(±354)
	4-31G	−481	+663	+1102	−1286	−30	−32
		(±113)	(±42)	(±365)	(±53)	(±21)	(±310)
cyclohexane	4-31G	−208	+430	−29	−1146	0	−953
		(±16)	(±32)	(±42)	(±52)	(±0)	(±73)
benzene	4-31G	−271	+468	+401	−1337	−4	−743
		(±49)	(±57)	(±208)	(±178)	(±4)	(±205)

[a] Values are given in cm^{-1}. Values in parentheses are rms deviations over the conformations analyzed.

reasonably close to zero. The red shift in CCl_4 (-278 cm^{-1}) is excellent compared to the experimental value of -250 cm^{-1} reported by Hayes[3] but too low in comparison to the shift observed by Bayliss[1] (-450 cm^{-1}). The red shift in cyclohexane (-953 cm^{-1}) is much larger than the experimental value of -400 cm^{-1}. Finally the experimental red shift in benzene (-650 cm^{-1}) is reproduced quite well by our value of -743 cm^{-1} at the 4-31G level.

The uncertainties for the computed shifts given in Table 3 are root mean square deviations (rms) over the 100 conformations analyzed. These values do not indicate the error in the maximum position of the transition but rather reflect the broadness of the maxima mentioned by Bayliss.[1] In polar solvents the rms deviation is much larger than in apolar ones. This indicates, that in polar solvents, the shift in the transition is very much dependent on the orientation of the local dipoles in the solvent molecules in the first solvent shell, and a broad variety of orientations are present, causing broad absorption maxima. In apolar solvents the orientation is not that important and the deviation is much smaller. This is also evident from the rms deviations in the contributions to the shifts as shown in Table 4. The deviation for the electrostatic contribution is, in all cases where electrostatics are important, by far the most important contribution to the rms deviation.

An analysis of the contributions to the shifts is given in Table 4. ΔE_{el} and ΔE_{disp} denote the difference in electrostatic interaction (the first two terms on the right-hand side of eq 8) and dispersion interaction (term 7 and part of term 8 in eq 8) between the quantum system and the classical system in the ground state and excited state. ΔE_{ind} is a contribution due to the induction: the interaction between the quantum system and the moments induced by the quantum system (this interaction is found in terms 5, 6, and part of term 8 in eq 8). ΔE_{pol} consists of three parts: the interaction between the quantum system and the moments induced by the classical system (1), the interaction between the classical system and the moments induced by the quantum system (2) (these two terms are found in the third and fourth terms of eq 8), and the cost of inducing all dipoles (3) (which has already been subtracted from the interaction terms in eq 8). ΔE_q is the change of the intrinsic excitation energy of the quantum system, i.e., the difference between expectation value of the vacuum Hamiltonian over the vacuum wave function and the expectation value of the vacuum Hamiltonian over the nonvacuum wave function. This term contains the polarization cost for the dipole(s) induced in the quantum system by the classical system.

When analyzing the contributions to the shifts in polar solvents (H_2O, MeCN, and MeOH), it becomes clear that the dispersion component is essential in the quantitatively correct description of the excitation energy shift. Ignoring dispersion, the blue shifts would be overestimated by 1200−1500 cm^{-1}. This also holds for chloroform for which the blue shift would have been overestimated by 350 cm^{-1} without including dispersion. In 1,4-dioxane the electrostatic contribution, caused by a quadrupole type interaction—there is a considerable negative charge of -0.47 on the oxygen atoms in the point charge model—is balanced by the dispersion term to yield a net zero shift. In the cases of CCl_4, cyclohexane, and benzene there is very little electrostatic interaction, and dispersion dominates in these solvents, resulting in a red shift.

The effect of increasing basis set quality can be extracted from Table 4. Use of a better basis set increases the electrostatic contribution by up to 250 cm^{-1}. The effect on the other contributions is very small. This can be understood by examining the vacuum dipole moments and polarizabilities. The vacuum dipole moments of acetone in the 4-31G basis are 3.57 and 2.48 D for the ground and excited states, respectively. For the DZP basis these dipole moments are 3.36 and 1.48 D for the ground and excited states. Thus although the total dipole moment decreases upon going to a larger basis set (and approaching the experimental value of 2.88 D[24] closer), the difference between the dipole moment in the ground and excited states increases; the difference is 1.09 D for the 4-31G basis and 1.88 D for the DZP basis, leading to a larger difference in electrostatic interactions between the ground and excited states in the DZP basis.

When we look at the ground-state polarizabilities in both basis sets, 30.81 B^3 for the 4-31G basis and 33.34 B^3 for the DZP basis,[20] we see that the difference is less than 10%, so increasing the basis set will not have a large effect on the dispersion in the ground state. Calculating polarizabilities for the excited state is much more troublesome. Excited-state polarizabilities at the SCF level tend to become slightly smaller than the ground-state values where they are expected to be larger. The polarizabilities for the excited state are 28.26 and 31.83 B^3 for the 4-31G and DZP basis sets, respectively. As noted above, the dispersion interaction is not only governed by the polarizability but also by the ionization potentials of the solvent and solute, first of all through γ where the ionization energies are explicitly present and also by their implicit presence in ΔU^{DRF}_{disp}—as can be seen from eq 12. The ionization potential for the excited state used in γ was calculated by taking the excited state 3.72 eV—the (underestimated) excitation energy in the DZP basis—above the ground state, which leads to an overestimated ionization potential for the excited state. It has been shown earlier[6] that γ is not very sensitive to errors in the ionization potentials. The overestimated ionization potential does have an effect on the dispersion interaction due to its (implicit) presence in ΔU^{DRF}_{disp}. The underestimated excited-state polarizability of the solute in ΔU^{DRF}_{disp} is multiplied by the overestimated ionization potential of the SCF wave function (see eq 12); thus the overestimated ionization potential compensates for the underestimated polarizability. Further improving the basis set or wave function would increase the excited-state polarizability, but the ionization potential of this state would be decreased, leading to a very similar dispersion. Improving the basis set does not alter the trend of the shifts observed in different solvents, but in polar solvents the computed shifts compare significantly better to experimental values.

Our findings disagree with the results of both Thompson[8] and Gao,[7] who also reproduced blue shifts in polar solvents quite well; however they did so with a model that did not include dispersion effects. It will be clear that adding dispersion to their models will lead to a drastic lowering of the blue shifts, indicating that their electrostatic contributions are much too small. This may be caused by the approximate nature of the wave function they use (semiempirical AM1), which is parametrized for heats of formation and not for spectroscopic use. Furthermore, semiempirical Hamiltonians are known to give a poor description for intermolecular interactions.[25]

Conclusions

We have shown that the DRF model gives an excellent description of the solvent effects on the $n-\pi^*$ transition in acetone, in both polar and apolar solvents without the need for reparametrization for different solvents. The experimental shifts are approximated very well. Using a small number of randomly chosen conformations from an extended classical Monte Carlo simulation gives results that are comparable to complete QM/MM calculations but offers the advantage of sampling over a larger part of configuration space at reduced computational cost. The contribution of the ubiquitous dispersion is important for the quantitative description of the shifts in both polar and apolar solvents. Without inclusion of the dispersion interaction, the blue shift in polar solvents can be overestimated greatly.

Improving the quality of the basis set does not alter the qualitative picture, but especially for polar solvents the quantitative agreement with experimental results becomes significantly better.

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References and Notes

(1) Bayliss, N. S.; Wills-Johnson, G. *Spectrochim. Acta* **1968**, *24A*, 551.

(2) Suppan, P. *J. Photochem. Photobiol.* **1990**, *A50*, 293.

(3) Hayes, W. P.; Timmons, C. J. *Spectrochim. Acta* **1965**, *21*, 529.

(4) Karelson, M.; Zerner, M. C. *J. Am. Chem. Soc.* **1990**, *112*, 9405.

(5) Gao, J. *Theor. Chim. Acta* **1997**, *96*, 151.

(6) de Vries, A. H. van Duijnen, P. Th. *Int. J. Quant. Chem.* **1996**, *57*, 1067.

(7) Gao, J. *J. Am. Chem. Soc.* **1994**, *116*, 9324.

(8) Thompson, M. A. *J. Phys. Chem.* **1996**, *100*, 14492.

(9) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.

(10) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.

(11) Gao, J.; Xia, X. *Science* **1992**, *258*, 631.

(12) Thompson, M. A.; Schenter, G. K. *J. Phys. Chem.* **1995**, *99*, 6374.

(13) de Vries, A. H.; van Duijnen, P. Th.; Juffer, A. H.; Rullmann, J. A. C.; Dijkman, J. P.; Merenga, H.; Thole, B. T. *J. Comp. Chem.* **1995**, *16*, 37; Erratum p 1445.

(14) Thole, B. T.; van Duijnen, P. Th. *Theor. Chim. Acta* **1980**, *55*, 307.

(15) van Duijnen, P. Th.; Juffer, A. H.; Dijkman, J. P. *J. Mol. Struct. (THEOCHEM)* **1992**, *260*, 195.

(16) van Duijnen, P. Th.; de Vries, A. H. *Int. J. Quant. Chem.* **1996**, *60*, 1111.

(17) Thole, B. T.; van Duijnen, P. Th. *Theor. Chim. Acta* **1983**, *63*, 209.

(18) Breneman, C. M.; Wiberg, K. B. *J. Comp. Chem.* **1990**, *11*, 361.

(19) Thole, B. T. *Chem. Phys.* **1981**, *59*, 341.

(20) van Duijnen, P. Th.; Swart, M. *J. Phys. Chem. A* **1998**, *102*, 2399.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Pittsburgh, 1995.

(22) Dupuis, M.; Farazdel, A.; Karma, S. P.; Maluendes, S. A. In *MOTECC*; Clementi, E., Ed.; ESCOM: Leiden, 1990.

(23) Dunning, T. H.; Hay, P. J. In *Methods in Electronic Structure Theory*; Schaefer, H. F., III, Ed.; 1977.

(24) *CRC Handbook of Chemistry and Physics*, 62nd ed.; CRC Press: Boca Raton, FL, 1981.

(25) Hobza, P.; Kabelac, M.; Sponer, J.; Mejzlik, P.; Vondrasek, J. J. *Comp. Chem.* **1997**, *18*, 1136.