

Semi-empirical AM1 calculation of the solvent effect on the fluorescence spectra of some dihydroquinolinones[☆]

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Abstract

The CONductor-like Screening MOdel of solvent–solute interactions of Klamt and Schüürmann, COSMO, at the semiempirical AM1 level of MO calculations, augmented by limited singles and doubles configuration interaction, proves useful for the study of solvent induced shifts of fluorescence spectra. Optimization of geometry of ground S_0 and excited S_1 states for each solvent separately provides estimates of the changes of solvation energy accompanying the electron transition process and helps the understanding of the related solvent–solute reorganization and fluorescence mechanisms. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The observed shifts of the electronic absorption and emission bands of organic compounds induced by solvents are commonly understood as an indication of the extent of charge reorganization of solute molecules upon electronic excitation, resp. radiative excited state deactivation [1]. A more detailed consideration of solvent–solute interactions within the reaction potential concept should describe solvent shifts in the electronic absorption spectra as an indication of the extent of influence of inertial solvent reorganization on

the instantaneous charge reorganization of solute molecules upon electronic excitation. Solvent shifts of emission (fluorescence) bands reflect, conversely, the influence of equilibrium solvent arrangement around the excited solute, rearranging inertially due to the instantaneous charge redistribution upon radiative deactivation to the ground electronic state [2].

A variety of approaches to the theoretical treatment of solvent effects have been developed [2–6] [7–9] and applied to studies of organic reactions and dynamic processes in solution [10,11], as well as to studies of UV–Vis spectroscopic phenomena [4–8,11–13]. However, still no methodology for the prediction of solvent shifts of electron absorption spectra seems to gain general acceptance and applicability. A solvation model within the AM1

[☆] Part III of the series solvent induced shifts of electronic spectra. Part I: see [38]; Part II: see [44]

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semi-empirical MO parametrization has been used for the interpretation of the charge transfer mechanism of fluorescence in para-substituted dimethylanilines [14]. AM1/CONductorlike Screening Model (COSMO) calculations including explicit treatment of the excited states in a CI framework have been used to check the applicability of a COSMO to electronic absorption spectra [15]. Two papers treating solvent effects on fluorescence spectra of 2,5-distyrylpyrazine [16] and 4-(4'-*N,N*-dimethylaminophenyl)-3,5-dimethyl-1,7-diphenyl-bis-pyrazolo-[3,4-b;4',3'-e]-pyridine (DMA-DMPP) [17] theoretically use the pair excitation configuration interaction (PECI, see the discussion Section 6) and a reaction field approach [10,11] to calculate the corresponding emission frequencies. More work on the interpretation of fluorescence mechanisms and the nature of fluorescent excited states as influenced by solvents is reported by Catalan et al. [12,13], and Parusel et al. [18].

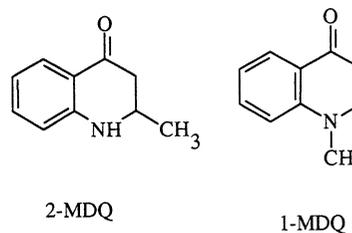
Several kinds of models consider quantum mechanically the solute molecule and place it in a cavity within some statistical environment, represented as a dielectric continuum [3,10]. Other models represent the solvent-solute interaction using hybrid approaches, e.g. quantum mechanical for the solute molecule with a semiempirical Hamiltonian and, e.g. molecular mechanics for the solvent [4–7]. Reliable results are obtained for molecular geometries using the same kind of hybrid with an *ab initio* Hamiltonian for the solute molecule and a classical force field for appropriately arranged solvent molecules [19]. Two approaches are at hand for this kind of study. First, parameterized models of solvation energies in a number of solvents take into account cavitation, dispersion and hydrophobic interactions by means of an empirical function of the solvent accessible surface (SAS), of molecules [20]. Another model considers the interaction of induced charges of a dielectric solvent continuum over the SAS and solute charge distribution by means of Green functions [21,22] to describe the electrostatic screening only, ignoring dispersion and other components of solvent-solute interactions. The latter computationally extremely effective algorithm is implemented in a couple of popular

semiempirical program packages [23] and seems very attractive for the purpose of studying the title effects on large organic molecules. An additional attractive feature of this COSMO is that it represents dielectric screening energies as $(\epsilon - 1)/(\epsilon + x)$, where $0 < x < 2$ appears in Onsager's solution for the multipole screening at the center of a spherical cavity [22] and is set to 0.5 in the actual algorithm. The above expression resembles Onsager's permittivity function $(\epsilon - 1)/(2\epsilon + 1)$ and is close indeed to the empirical function of Lippert and Mataga [24–28]

$$\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1),$$

used to describe solvent effects on electronic absorption and emission spectra of organic molecules [29].

This paper describes a treatment of the fluorescence emission spectra of 2- and 1-methyl-2,3-dihydro-4(1H)-quinolinone, 2-MDQ and 1-MDQ, in a number of solvents of different polarity by the means of semiempirical AM1 calculations using the COSMO methodology with varying extent of configuration interaction. The two compounds are chosen due to the observed large solvent shifts of their fluorescence emission maxima, ca. 5000 cm^{-1} or more than 0.6 eV, a range large enough to eliminate the acceptable error of theoretical calculations, 0.1 eV.



2. Theory

A point open to discussion is whether the COSMO formalism is suitable for the calculation of excited state geometries and emission spectra. To this end, we may consider, after Tomasi and Persico [2] (see also Zerner [4–7]), various Hamiltonian models for the description of electronic

excitation, resp. radiative deactivation in solution. In general, the Hamiltonian is defined as $HM = H(0)M + Vs$, where the interaction operator Vs is determined at the SCF level for the initial electronic state, and HM is used in CI calculations of both the ground S_0 and the first excited S_1 state. In model A two terms of Vs must represent the work required for slow and fast solvent polarization to be added to the total energy. Model B uses no term for the slow solvent polarization in Vs . Thus, various models of solvent–solute interactions can be described as variations of the interaction operator Vs defining the respective reaction fields [2,4–7]. Both models A and B would indeed be deficient with respect to explicit minimization of the solvation free energy functional [2] at either SCF or CI level [21]. However, numerical differences between models A and B are small [2,4–7] and, hopefully, between any of these and the exact solution of the corresponding nonlinear Schroedinger equation will be small enough. Substantial ground for the latter expectation is provided by the fact that the COSMO formalism [22] derives explicitly from the SCF minimization of the electrostatic free energy of solvation [21]. We are aware, however, that dispersion contributions to the solvent induced shift of electronic absorption maxima can be as large as 2000 cm^{-1} [8].

Calculations of UV–Vis absorption energies are traditionally carried out at the geometry of the ground S_0 state, and Klamt has developed a version of COSMO to account for nonequilibrium solvent effects on electronic excitation, e.g. from the S_0 to the S_1 electronic state [15]. This treatment requires S_0 solute geometry optimization accounting for the corresponding solvent. However, insufficient attention seems to have been paid to the geometry change on excitation from the ground to an excited state during electronic excitation to the widespread opinion that excited state molecular geometries (almost) cannot be optimized by semiempirical MO methods [30] and the more so with regard to geometry differences affecting spectroscopic properties passing from the gas phase to solution.

Another concern is with the instantaneous solvent polarization energy, which is normally explicitly included in theoretical calculations of

absorption spectra. With fluorescence, however, we have to keep in mind the fact, that fluorescent electronic states are long enough living species, with approximate lifetimes three orders of magnitude (ca. 10^{-9} s) larger than the time of a molecular vibration and solvent shell relaxation (ca. 10^{-12} s). Therefore, we may consider the geometries of fluorescent electronic states, usually S_1 , as perfectly optimizable within the original COSMO formalism with no allowance for nonequilibrium solvent shell arrangement, contrary to the treatment of UV absorption spectra by Klamt [15]. Using these equilibrium S_1 geometries we may circumvent the nonequilibrium treatment of solvation [31] and thus obtain zero order approximate emission energies, i.e. $S_1 \rightarrow S_0$ energies, by a basic COSMO/SDCI geometry optimization, using the terminology of Klamt [15,22]. To account for solvent polarization, we may calculate additionally the solvation energy of a S_0 electronic density distribution at the equilibrium S_1 geometry. The difference between S_1 and S_0 solvation energies at the S_1 equilibrium geometry would then represent the instantaneous correction to the emission energy to the first order of approximation. Our suggestion is to apply the following ‘relaxation cycle’ of COSMO calculations in order to find the required corrections to the absorption, viz. the emission energies of the solute:

1. CISD calculation of the equilibrium geometry of the S_0 state in the solvent, with geometry optimization.
2. Single point CISD calculation of the S_1 energy, electronic distribution, and solvation energy at the S_0 geometry.
3. CISD calculation of the equilibrium geometry of the S_1 state in the solvent, with geometry optimization.
4. Single point CISD calculations of the S_0 energy, electronic distribution, and solvation energy at the S_1 geometry.

The instantaneous polarization energy for the $S_0 \rightarrow S_1$ electronic excitation (that is, for the longest wavelength absorption transition) would thus be given by the difference

$$E_{\text{pol}}^{\text{abs}} = \Delta H_{\text{soln}}^{(2)} - \Delta H_{\text{soln}}^{(3)}$$

that is, the relaxation energy of the solvent shell in the S_1 state after the excitation. For the fluorescent deactivation $S_1 \rightarrow S_0$ the instantaneous polarization energy would be

$$E_{\text{pol}}^{\text{em}} = \Delta H_{\text{solv}}^{(4)} - \Delta H_{\text{solv}}^{(1)},$$

i.e. the relaxation energy of the solvent shell in the S_0 state after the excitation.

The suggested method of calculation accounts for the geometry changes of the solute, and in addition the solvent reorganization process, thus being consistent with the idea of a ‘conductor-like screening’ interaction only of solute and solvent, that is, with the basic assumptions of COSMO [22].

3. Computational details

Semiempirical AM1 MO calculations are carried out with the MOPAC 93 [23] program package. Gradient geometry optimizations are done initially at the HF level for the closed shell ground state structure S_0 , as usual in earlier MO studies of electronic absorption spectra. However, we further optimize the excited S_1 geometry including configuration interaction [32] using the microstate formalism [33] with a limited number of single and double excitations, namely two electrons in two orbitals, with a total of five active orbitals. All optimizations are first carried with the default BFGS procedure [34,35], then continued with the EF procedure of Baker [36,37] until gradient norm less than $0.05 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$ is achieved with all values of ϵ between 2 and 80 for the entire range of solvents used in the experiment [38]. This is not always possible with the excited S_1 state; in such cases the optimization of corresponding structures was persistently repeated to reduce the gradient norm to no more than $1.0 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$. The positions of the fluorescence maxima are calculated as vertical singlet transition energies $S_1 \rightarrow S_0$ at the optimized geometry of the S_1 species. We note that the final reduction of gradient norm from 1.0 to below $0.05 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$ changes the $S_1 \rightarrow S_0$ transition energy by only ca. 3 cm^{-1} .

An independent estimate of solvation energy contributions is obtained by AM1 SM1 [20] calculations of solvation energies in water. Geometry optimizations of large molecules by AM1 SM1 are very time consuming; therefore we use optimized AM1 COSMO geometries for $\epsilon = 78.4$ and single point calculations by the AMSOL [20] program package to evaluate the various contributions to the solvation energy explicitly.

4. Results

Computed AM1 emission energies for the $S_1 - S_0$ electronic transition of 2-MDQ along with experimental fluorescence data in 17 solvents [38] are listed in Table 1. Calculated AM1 radiative emission $S_1 - S_0$ energies for 1-MDQ in 7 solvents are given along with the corresponding experimental data [38] in Table 2. The calculated dipole moments for 1-MDQ are 3.80 D, S_0 , and 5.13 D, S_1 , in the gas phase and 5.78 D, S_0 and 9.96 D, S_1 at $\epsilon = 24.6$, ethanol. The corresponding values for 2-MDQ are 3.65 D, S_0 ; 5.24 D, S_1 in the gas phase and 5.77 D, S_0 , and 9.23 D, S_1 at $\epsilon = 78.4$, water. The S_1 excited state geometries of considered dihydroquinolines remain almost planar as in the ground S_0 state, with the only exception of 1-MDQ in water, where an additional conformational minimum, twist chair, is found. However, no dual fluorescence is observed for this compound, see below.

The SCF vectors show that the n-orbital of 1-MDQ and 2-MDQ is the third highest occupied molecular orbital (HOMO-2), while the first excited singlet and triplet states arise from pure $\pi\pi^*$ excitations from HOMO to the lowest unoccupied molecular orbital, LUMO, T_1 ; HOMO to LUMO + 1, T_2 ; and HOMO-1 to LUMO, S_1 . Inspection of the CI matrix and the state vectors confirms the pure $\pi\pi^*$ nature of the lowest excited states.

To obtain an independent estimate of neglected dispersion and cavitation contributions to the solvation energy we use single point AM1 SM1 calculations [20] at the ground S_0 and planar excited S_1 state geometries of 2-MDQ and 1-MDQ. For the calculated total solvation energy

of 2-MDQ in the S_0 state, $-8.7 \text{ kcal mol}^{-1}$, the contribution from dispersion and cavitation energy is $-1.7 \text{ kcal mol}^{-1}$, that is, ca. 20% of the total solvent contribution. For the same molecule in the S_1 state the calculated total solvation energy is $-14.4 \text{ kcal mol}^{-1}$, while the dispersion plus cavitation contribution remains $-1.7 \text{ kcal mol}^{-1}$, that is, $> 15\%$. For 1-MDQ, the total solvation energy for the S_0 state is -11.1 kcal

mol^{-1} , with a contribution of dispersion plus cavitation terms of $-1.2 \text{ kcal mol}^{-1}$, $> 15\%$, while for the S_1 state the corresponding values are -19.3 and $-1.0 \text{ kcal mol}^{-1}$, ca. 5% of the solvent contribution.

Finally, to estimate the instantaneous polarization energy from the solvent relaxation cycle outlined above, we calculate the solvation energies of 2-MDQ and 1-MDQ as the difference of their

Table 1

Experimental fluorescence maxima $\nu_{\text{Fl}}^{\text{exp}}$, calculated AM1 vertical S_1-S_0 emission energies $\nu_{\text{Fl}}^{\text{calc}}$ and differences in solvation energy between S_0 and S_1 of 2-MDQ, in various solvents^a

| Number | Solvent | ϵ | ET(30) ^b (kcal mol ⁻¹) | $\nu_{\text{Fl}}^{\text{exp}}$ (cm ⁻¹) | $\nu_{\text{Fl}}^{\text{calc}}$ (cm ⁻¹) | ΔH_{solv} (kcal mol ⁻¹) |
|--------|--------------------|------------|---|--|---|--|
| 1 | Hexane | 1.88 | 30.9 | 25 300 | 25 981 | 693 |
| 2 | Cyclohexane | 2.02 | 31.2 | 25 200 | 25 893 | 752 |
| 3 | Diethyl ether | 4.34 | 34.6 | 24 000 | 24 674 | 1414 |
| 4 | Ethylacetate | 6.02 | 39.1 | 23 300 | 24 189 | 1631 |
| 5 | Tetrahydrofuran | 7.58 | 37.1 | 23 400 | 23 911 | 1771 |
| 6 | 1,2-dichloroethane | 10.4 | 41.9 | 23 200 | 23 570 | 1928 |
| 7 | Acetone | 20.7 | 42.2 | 22 700 | 23 061 | 2194 |
| 8 | Acetonitrile | 37.5 | 46.0 | 22 300 | 22 780 | 2303 |
| 9 | DMSO | 49.0 | 45.0 | 22 000 | 22 688 | 2348 |
| 10 | Cyclohexanol | 15.0 | 46.9 | 20 600 | 23 264 | 2093 |
| 11 | 1-Butanol | 17.51 | 50.2 | 20 500 | 23 169 | 2138 |
| 12 | 1-Propanol | 20.33 | 50.7 | 20 300 | 23 076 | 2177 |
| 13 | Ethanol | 24.55 | 51.9 | 20 200 | 22 968 | 2226 |
| 14 | Methanol | 32.70 | 55.5 | 20 000 | 22 803 | 2282 |
| 15 | 1,2-Ethanediol | 37.70 | 56.3 | 19 900 | 22 785 | 2296 |
| 16 | Glycerol | 42.50 | 57.0 | 19 600 | 22 742 | 2342 |
| 17 | Water | 78.39 | 63.1 | 19 700 | 22 602 | 2408 |

^a Multiple regression analysis for 2-MDQ fluorescence in aprotic solvents: $\nu_{\text{exp}} = 2326 + 0.885 \nu_{\text{calc}} - 0.097 \Delta H_{\text{solv}}$ and $R = 0.982$, Standard error = 178 cm^{-1} .

^b ET(30), an empirical solvent parameter [41].

Table 2

Experimental fluorescence maxima and calculated AM1 vertical S_1-S_0 emission energies, and differences in solvation energy, between S_0 and S_1 of 1-MDQ in various solvents

| Number | Solvent | ϵ | $\nu_{\text{Fl}}^{\text{exp}}$ (cm ⁻¹) | $\nu_{\text{Fl}}^{\text{calc}}$ (cm ⁻¹) | ΔH_{solv} (kcal mol ⁻¹) |
|--------|---------------|------------|--|---|--|
| 1 | Cyclohexane | 2.02 | 24 600 | 25 601 | 1306 |
| 2 | Diethyl ether | 4.34 | 23 400 | 24 012 | 2212 |
| 3 | Ethylacetate | 6.02 | 22 400 | 23 589 | 2499 |
| 4 | Acetone | 20.70 | 21 800 | 21 962 | 3297 |
| 5 | Acetonitrile | 37.50 | 21 600 | 21 271 | 3546 |
| 6 | Athanol | 24.55 | 19 700 | 21 798 | 3370 |
| 7 | Water | 78.39 | 18 800 | 21 175, 17 609 ^a | 3654, 5474 ^a |

^a The optimization of the S_1 state of 1-MDQ in water is difficult. Persistent optimization results in a conformational change of the dihydropyridine ring and reordering of excited singlet and triplet states. See also [14] for changes of nitrogen pyramidalization in the S_1 state related to observed dual fluorescence.

Table 3

Calculated AM1 CISD/COSMO heats of formation of 2-MDQ and 1-MDQ in the gas phase and in acetonitrile solution for the solvent relaxation cycle^a

| | $H_f(1)$ | $H_f(2)$ | $H_f(3)$ | $H_f(4)$ | H_f , RHF ^b |
|---------------|----------|----------|----------|----------|--------------------------|
| 2-MDQ | -21.5 | 63.6 | 57.4 | -20.1 | -14.4 |
| 2-MDQ in MeCN | -30.4 | 45.7 | 38.0 | -27.2 | -27.4 |
| 1-MDQ | -10.9 | 74.5 | 69.7 | -8.2 | -3.9 |
| 1-MDQ in MeCN | -18.7 | 56.6 | 47.1 | -13.7 | -6.3 |

^a Units are kcal mol⁻¹.

^b This RHF column represents the ground state closed shell computational results.

heats of formation in the gas phase and in acetonitrile solution ($\epsilon = 37.5$), using the optimized CISD geometries of the corresponding S_0 and S_1 states to obtain a S_1 solvent relaxation energy of -1.5 kcal mol⁻¹, or ca. 520 cm⁻¹, and a S_0 relaxation energy of 1.8 kcal mol⁻¹, or ca. 630 cm⁻¹, see the necessary data in Table 3.

5. Fluorescence properties

1-MDQ and 2-MDQ exhibit relatively intense fluorescence in polar deaerated solvents with a quantum yield $Q_f = 0.2$ – 0.5 ; the singlet lifetimes $^1\tau$ are in the range 5 – 20 ns. The radiative rate constant K_f is of the order of 10^7 s⁻¹. The electronic spectra are shifted to longer wavelengths with increasing solvent polarity. The solvent effect on the emission spectra is more pronounced than on the absorption ones, e.g. in the case of 2-MDQ the red shift of the longest wavelength absorption maximum is 1200 cm⁻¹ when passing from cyclohexane to acetonitrile, while the shift of the fluorescence maximum is 2700 cm⁻¹. These experimental data [38,39] suggest that the first excited singlet state S_1 is of $\pi\pi^*$ character. The observed solvent and substituent effect on the electronic spectra as well as the results from the performed quantum-chemical calculations indicate that the lowest $^1(\pi\pi^*)$ state has a partial intramolecular charge transfer (ICT) character, i.e. upon excitation to $S_1(\pi\pi^*)$, an electron displacement from the nitrogen to the carbonyl group occurs. This may account for the experimentally observed (1) pronounced effect of the substituent on the nitrogen on the electronic spec-

tra which may be explained by its influence on the electron density at the N atom and thereby on the charge transfer from the nitrogen atom to the carbonyl group, and (2) the much larger bathochromic displacement of the fluorescence maxima upon increase of solvent polarity relative to the absorption ones.

The solvent effects on the fluorescence properties in aprotic solvents are consistent with the general type of solvent interaction. The ground state dipole moment of 2-MDQ $\mu_g = 4.5$ D and its change upon excitation $\Delta\mu = 5.2$ D have been determined [38] using the Lippert equation [24–28] and the correlation method of Varma and Groenen [40]. In protic solvents, however, there is a break in the experimental data relative to the aprotic ones both in the plot of the Stokes' shift versus the empirical function of Lippert [24–28] $\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)$ and in the dependence of the energy of the fluorescence maxima on the empirical solvent parameter ET(30) [41], which is an indicator of the electrophilicity of the solvent, see Table 1. The variation of the fluorescence quantum yield also can be divided into two groups according to the nature of the solvent [38]. In aprotic solvents it increases as the emission frequency decreases. Although the studied compounds fluoresce at longer wavelengths in protic solvents, see Table 1, the quantum yield is smaller than in acetone and acetonitrile, and decreases with the emission frequency. In deuterated solvents the fluorescence spectra remain unchanged in form and position relative to these in the normal ones; while the quantum yield is unaffected in CDCl₃, fluorescence intensity is enhanced in C₂H₅OD and D₂O

[38]. The stronger non-radiative deactivation of the studied compounds in protic solvents than in aprotic ones and the deuterium isotope effects indicate that the OH group of the solvent plays a specific role in the radiationless deactivation as a result of hydrogen bond formation with the solute in the excited state [38]. The vibrational modes of the intermolecular hydrogen bonds are considered to act as accepting modes in the internal conversion to the ground state.

The above spectral data, fluorescence quantum yield measurements, and isotope effects suggest solvent–solute complexation in the first excited singlet state and explain the break of emission frequency–solvent polarity relationships between protic and aprotic solvents. The excess of stabilization energy of the S_1 excited state due to hydrogen bonding of the protic solvent to 2-MDQ can be estimated from the difference between the energies of the emission maxima in

CH_3OH and CH_3CN [38], which have the same polarity, and is found to be of the order of 2300 cm^{-1} .

6. Discussion

Fig. 1 shows a plot of the calculated versus the experimental fluorescence transition energies of 2-MDQ in 17 solvents. $\nu_{\text{fl}}^{\text{exp}}$ versus $\nu_{\text{fl}}^{\text{calc}}$ clearly decomposes into two linear relationships. Higher emission frequencies for aprotic solvents are reproduced with a correlation coefficient $R = 0.991$ and a slope $B = 0.934$. The experimental emission maxima of 2-MDQ in protic solvents are shifted bathochromically versus the calculated energies. The correlation between the calculated and experimentally observed emission energies is still satisfactory, $R = 0.962$, but the slope becomes $B = 1.515$. Correcting the $S_1 - S_0$ emission energies of 2-MDQ for protic solvents with the additional stabilization energy of the S_1 state, due to hydrogen bonding with the solvent, 2300 cm^{-1} , we obtain a common linear relationship between observed and calculated emission energies with correlation coefficient $R = 0.989$ and slope $B = 0.948$.

Calculated and experimental emission frequencies for 1-MDQ in aprotic solvents only show a good correlation with $R = 0.962$ and slope $B = 0.697$.

The pair double-excitation correlation interaction, PECl, adopted by Clark [10,11,42] for the semiempirical MO treatment of molecular electronic spectra can be classified as a model A type of approach [2,4–7]. It is justified from the point of view of ensuring sufficient, and never excessive, account for the static electron correlation [43] with proper account for ground state participation. That approach proved satisfactory for the calculation of electronic absorption spectra [10,11] using optimization of the ground S_0 state geometry only. However, the same treatment would not be justified for fluorescence spectra because of (1) the different geometries of the S_0 and S_1 states; (2) the virtually different solvent–solute interactions in the ground and the excited states, and (3) the molecular relaxation effects following the light

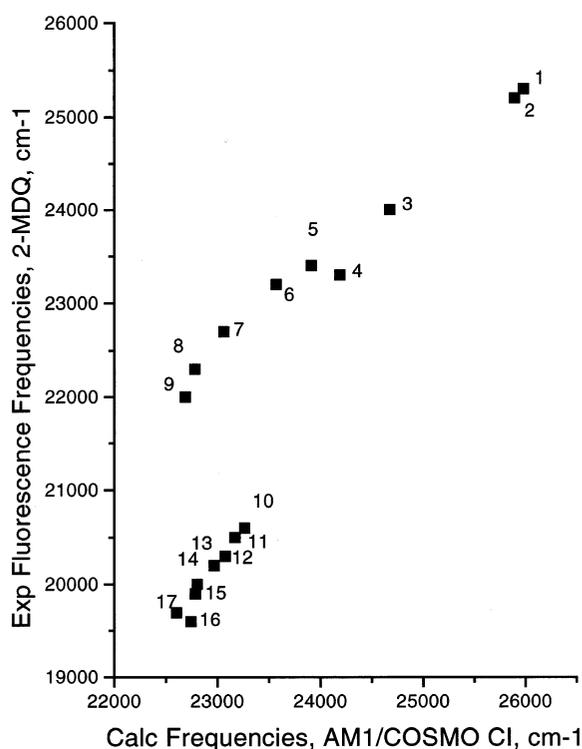


Fig. 1. Scatter plot of experimental versus calculated fluorescence. Frequencies of 2-MDQ in various solvents. Data points are numbered as in Table 1.

absorption, respectively emission. Therefore, as an initial approximation we choose to comprehensively optimize geometries of both S_0 and S_1 states and refrain from limiting the CI to the pair excitations only. This would of course leave the problem of determining the necessary active space of the CISD expansion in order not to overcount the extent of electron correlation correction to the calculated energies. Our intention is to find the appropriate active space empirically in order to see if there are general values of the number of electrons to be used in the CI treatments and of the number of active orbitals for various classes of molecules. As we make no provision for slow solvent reorganization, our calculations represent a model B type of approach [2,4–7].

Comparing calculated and experimental fluorescence frequencies of dihydroquinolines in various solvents, we quickly find that an active space of two electrons in two orbitals is sufficient to reproduce the energies of the observed fluorescence maxima, while a larger active space is prone to predict emission frequencies shifted to the red relative to the experiment. This result indicates that PECI [10,11,41] is a good approximation and separated electron pairs on double excitations in different MOs are too strong a correlation correction. Luckily enough, if the separated electron pair is situated on two adjacent MOs, the correction is sufficient to account for the amount of dynamic correlation in studied dihydroquinolines. On the other hand, increasing the number of active orbitals from 2 to 5 gradually improves the agreement between predicted and measured fluorescence maxima. Further improvement from larger numbers of active orbitals is only marginal.

The emitting state of 2,3-dihydro-4(1H)-quinolinones has a partial intramolecular charge transfer character. Therefore, the position of the fluorescence maxima shows a rather pronounced solvent dependence; for 2-MDQ it moves by 5600 cm^{-1} to the red on passing from hexane to water. The two linear correlations of the energy of the fluorescence maximum of 2-MDQ on calculated AM1 $S_1 - S_0$ transition energies for aprotic and protic solvents, Fig. 1, can be interpreted as an-

other indication of different solvent–solute interactions in the two types of solvents.

The different slopes of the ν_{exp} versus ν_{calc} relationships support the conclusion of the different nature of the emitting state of 2-MDQ in aprotic and protic solvents. The solvent effects in aprotic solvents are consistent with a usual continuum type of solvent–solute interaction. However, protic solvents seem to form solvent–solute complexes with excited 2-MDQ molecules, as deduced earlier from fluorescence experiments in deuterated solvents [38,39]. Present AM1/COSMO calculations with limited CISD, however, provide additional information on the nature of solvent–solute interactions in the excited states having significant charge separation, as demonstrated by the differences of calculated solvation energy of S_0 and S_1 states of 2-MDQ and 1-MDQ, see Tables 1 and 2, and single point AM1 SM1 data.

A measure of the solvent relaxation energy can be the difference of (electrostatic) solvation energies of ground S_0 and excited S_1 states, ΔH_{solv} , given in Tables 1 and 2. The more polar S_1 state is better solvated by polar solvents and calculated values ΔH_{solv} of 2-MDQ and 1-MDQ (Tables 1 and 2) increase smoothly with increasing solvent dielectric permittivity. Two-parameter regression analysis for 2-MDQ supplement this interpretation, showing that the solvent shift of the emission maximum of this molecule depends significantly more on the solvent relaxation process than on solute geometry change accompanying the transition from the S_1 to the S_0 electronic state. In other words, molecules with potentially large charge transfer in the excited state may require Model A type of calculations of solvent–solute interactions [2,4–7] in order to account for the significant solvent reorganization upon electronic excitation and for the interpretation of CT fluorescence. Model B calculations seem sufficient for the interpretation of remaining fluorescence mechanisms.

In qualitative terms, 1-MDQ should also experience significant charge transfer to the carbonyl group in the excited S_1 state. This is confirmed by the low slope of the corresponding ν_{exp} versus ν_{calc} relationship, see Table 2.

7. Conclusion

The COSMO methodology [22,23] proves a useful tool for the study of solvent induced shifts of fluorescence spectra of large molecules. An important requirement is the complete optimization of both ground S_0 and excited S_1 state geometries in each solvent, which in turn provides useful estimates of solvation energy differences between the ground and excited states of the solute and, respectively, of solvent–solute reorganization accompanying the light emission processes. While the neglect of dispersion and cavitation contributions to solvation energy can be considered a shortcoming of the COSMO methodology, for the studied molecules these constitute < 15–20% of the solvation energy in the ground S_0 state. For the S_1 fluorescence state dispersion and cavitation contributions to the solvation energies of studied polar molecules are generally > 10% and can be even lower than 1% of the total solvent effect. The use of a solvent relaxation cycle also gives an estimate of instantaneous polarization energy < 10% of the total solvent effect on the observed fluorescence spectra.

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