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Solvatochromic Shifts Reconsidered: Field-Induced Mixing in the Nonlinear Region and Application to Indole

John R. Lombardi[†]

Department of Chemistry and Center for Analysis of Structures and Interfaces (CASI),
The City College of New York, Convent Avenue at 138th Street, New York, New York 10031

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In previous work we showed that the observed discrepancy between gas-phase Stark effect measurements of excited-state dipole moments and those measured by solvatochromic shifts could be explained by possible intervention of a nearby excited state. Field-induced mixing of the two excited states causes solvent shifts that are linear in the high-field limit, where most solvent field studies are carried out, but the excited-state dipole moment must be replaced by an effective dipole moment. This effective moment is a combination of the excited-state dipole moments of both states as well as the transition moment between the two states. This new moment may have effects both on the solvent shifts observed and on the intensities. In the low-field gas-phase limit, the shifts are also linear but caused by the simple excited-state dipole moment. In the intermediate field region, the solvent shifts are expected to be decidedly nonlinear. The effective dipole moment is shown to be field-dependent near an avoided crossing of the two excited states, and this results in nonlinear behavior of the solvent reaction field. By identification of the onset of nonlinearity or, even better, by the fitting of the solvent shift observed to predicted expressions, the individual contributions to the effective dipole moment can be unraveled. We show how this theory can be applied to observed solvent shifts in the molecule indole, which has been observed throughout the nonlinear region. Consistent dipolar parameters that reconcile gas-phase and solution-phase results are obtained.

Introduction

The utilization of solvatochromic shifts to determine the value of excited-state dipole moments in numerous molecules has resulted in a considerable body of literature. In two recent papers[1,2] we have shown that the usual interpretation of solvatochromic shifts as arising from a simple change in dipole moment between the ground and excited states must, in many circumstances, be called into question. This is due to the severe discrepancies between the results of solvatochromic shift measurements and those obtained from the more accurate gas-phase Stark effect measurements. We attributed those discrepancies to the possible intervention of a nearby state, which may be coupled to the excited state by the solvent field. By estimating typical density of states, we further showed that there is a high probability of encountering a nearby state for molecules of the size normally studied by solvent shifts. This field-induced mixing of two nearby states may result in drastic changes in the apparent solvent shift, requiring a reinterpretation of the solvatochromic shift as caused by an *effective* dipole moment that is a mixture of the dipole moments of the two excited states involved. In the previous work, it was pointed out that typical solvent fields are much larger than those used in gas-phase Stark studies. In the gas-phase Stark effect, very low fields result in a linear spectral shift relatively unaffected by the nearby state and we may assume no mixing is involved. The derivative of this shift with applied field is proportional to the dipole moment of the excited state. In contrast, in the high-field limit, the spectral shift is still linear, but in this case, the derivative of the shift must be interpreted as due to the effective dipole moment. In the intermediate field region, we expect a rather nonlinear behavior of the observed spectrum. Since in both limits the spectral response is linear, we recommended that before solvatochromic shift results were interpreted as due solely to the dipole moment of the excited state, studies be carried out over a larger range of solvents to search for the onset of nonlinearity. By the study of the effect in the nonlinear region, it should be easy to sort out the low-field and the high-field limits, as well as to extract all the needed parameters to apply the theory fully. In this paper we shall examine the theory in the nonlinear region more carefully.

Considerable work has been carried out in recent years on the molecule indole,[3−17] for which it is well-known that the two lowest excited states, the ^1L_a and the ^1L_b, lie quite close to each other. This is one of the cases in which the gas-phase dipole moment change[18] ($\Delta\mu = 0.14$ D) differs greatly from that reported from solvatochromic shift measurements[17] ($\Delta\mu = 1.04$ D). Fortunately, solvatochromic shift measurements have been carried out[19] over a wide enough range of solvents to see a distinct nonlinearity in the observed shifts. Furthermore, they clearly establish that the two excited levels are inverted by increasing solvent polarity. Thus, it might be expected that indole will serve as a good test case of the solvent-induced mixing theory, especially in the region of state crossing.

Field-Induced Solvatochromic Shifts: Nonlinear Region

When a molecule comes under the influence of an electric field, perturbations to the energy may be expressed as an added term to the Hamiltonian operator:

$$H' = -\mu\cdot\mathbf{F}$$

where μ is the molecular dipole moment and $\mathbf{F}$ is the applied field. On excitation (or emission), the solute molecule is presumed to undergo a change in dipole moment $\Delta\mu$, resulting

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[†] E-mail: lombardi@sci.ccny.cuny.edu. Web site: http://www.sci.ccny.cuny.edu/~lombardi.

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in spectral shifts. These shifts are then

$$\Delta E = -\Delta\mu \cdot \mathbf{F}$$

If the field is externally applied to a molecule in the gas phase, then the direction and magnitude of **F** may easily be controlled. However, when the molecule of interest is embedded in a solvent, the field may be considered to arise from polarization of the surrounding molecules by the dipole moment of the molecule itself. This is called the reaction field, which may be written

$$\mathbf{F} = (\mu/a^3)\{f(D) - f(n^2)\}$$

where a is usually taken to be the molecular radius, D is the static dielectric constant of the solvent, and n is the refractive index of the solvent. $f(D)$ and $f(n^2)$ are the "Onsager polarity functions" given by and

$$f(D) = 2(D - 1)/(2D + 1)$$

$$f(n^2) = 2(n^2 - 1)/(2n^2 + 1)$$

It is also convenient to let $f(D,n) = f(D) - f(n^2)$.

It is usually presumed that excitation or emission, being electronic in character, takes place rapidly on optical excitation, while the polarized solvent shell, involving essentially nuclear motions, is rather slow to respond, maintaining the orientation corresponding to the polarization due to the initial ground (or excited) state. Thus, the spectral shifts are caused largely by the interaction of the change in dipole moment with the reaction field induced by the molecule in the initial state of the transition. The leading term in the solvatochromic shifts may then be written for absorption (the ground state is designated 0 and the excited state is 1):

$$\Delta E_{\text{abs}} = -\mu_0 \cdot (\mu_1 - \mu_0) a^{-3} f(D,n)$$

while for emission the corresponding expression is

$$\Delta E_{\text{em}} = -\mu_1 \cdot (\mu_0 - \mu_1) a^{-3} f(D,n)$$

By measurement of solvent shifts as a function of solvent polarizability, it is presumed that the dipole moment changes can be extracted. This is usually found to be linear in most of the solvents typically utilized in such experiments. The observed dipole moment change is then obtained by measuring the shift in the band maximum ω_{MAX} and $\Delta\mu = -\,\partial\omega_{\text{MAX}}/\partial\text{F}$. Note that $\Delta\mu = (\mu_1 - \mu_0)$ and that $\mathbf{F} = \mu_0 a^{-3} f(D,n)$ for absorption and $\mathbf{F} = \mu_1 a^{-3} f(D,n)$ for emission.

We now consider a molecule with a ground state (designated 0) and two excited states (1 and 2). Under zero-field conditions, we assume a zero-order Hamiltonian H_0 with eigenvalues E_0, E_1, and E_2 and corresponding eigenfunctions ψ_0, ψ_1, and ψ_2. For molecular electronic states, we assume a large gap between the ground state and the two (possibly nearby) excited states. On application of an electric field **F** (either an externally applied field or a reaction field), the new Hamiltonian is

$$H = H_0 + H'$$

and in order not to restrict ourselves to the low-field limit, we will diagonalize the Hamiltonian in the basis of zero-order eigenfunctions of the excited states. The requisite matrix elements are

$$H_{11} = E_1 - \mu_1 \cdot \mathbf{F} \qquad H_{22} = E_2 - \mu_2 \cdot \mathbf{F} \qquad H_{12} = -\,\mu_{12} \cdot \mathbf{F}$$

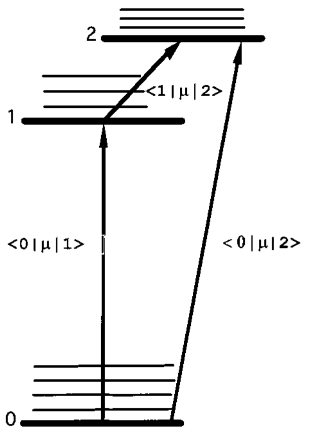

Figure 1. Energy level diagram for field-induced perturbations. The ground state (0) has an allowed transition to the excited state (1) through $\langle 0|\mu|1\rangle = \mu_{01}$ and a second excited state (2) to which a transition from the ground state may or may not be allowed by $\langle 0|\mu|2\rangle = \mu_{02}$. States 1 and 2 may be coupled by an external field only if $\langle 1|\mu|2\rangle = \mu_{12}$ is nonzero.

The excited-state eigenvalues of the perturbed Hamiltonian are then

$$E_{\pm} = \frac{1}{2}(E_1 + E_2 - (\mu_1 + \mu_2) \cdot \mathbf{F}) \pm \frac{1}{2}\{(E_1 - E_2 - (\mu_1 - \mu_2) \cdot \mathbf{F})^2 + 4(\mu_{12} \cdot \mathbf{F})^2\}^{1/2}$$

As a matter of convention, we will assume $E_2 > E_1$. If it turns out that $\mu_2 > \mu_1$, then it can be seen that the states will cross at $(\mu_1 - \mu_2) \cdot \mathbf{F} = (E_1 - E_2)$ if μ_{12} is zero. The crossing is avoided for $\mu_{12} \neq 0$, and the energy levels are decidedly nonlinear in their field dependence in this region. In the high-field limit (and any value for μ_{12}) we obtain

$$E_{+} = \frac{1}{2}(E_1 + E_2) - \mu_{\text{eff}}^{-} \cdot \mathbf{F}$$

$$E_{-} = \frac{1}{2}(E_1 + E_2) - \mu_{\text{eff}}^{+} \cdot \mathbf{F}$$

where

$$\mu_{\text{eff}}^{\pm} = \frac{1}{2}(\mu_1 + \mu_2) \pm \frac{1}{2}\{(\mu_1 - \mu_2)^2 + 4\mu_{12}^{\,2}\}^{1/2}$$

It is clear that under these circumstances we must reinterpret the results of solvatochromic shift measurements, replacing the excited-state dipole moment with the effective dipole moment:

$$\Delta\mu = -\partial\omega_{\text{MAX}}/\partial\text{F} = \mu_{\text{eff}}^{+} - \mu_0$$

This is a restatement of the most important result of our previous paper.[1] In cases where the dipole moment of the perturbing state (μ_2) is quite different from that of the observed state (μ_1), we might expect the high-field (solvatochromic shift) results to be quite different from the low-field (gas-phase) results. This is especially true if there is an avoided crossing ($\mu_2 > \mu_1$). In the low-field limit the effective dipole moment is that of state 1, i.e., $\mu_{\text{eff}}^{+} = \mu_1$, while in the high-field limit it is given by $\mu_{\text{eff}}^{+} = (1/2)(\mu_1 + \mu_2) + (1/2)\{(\mu_1 - \mu_2)^2 + 4\mu_{12}^{\,2}\}^{1/2}$. In both these limits, the energy levels change linearly with field and there is no difficulty in determining the reaction field for emission, since

$$\mathbf{F} = \mu_{\text{eff}}^{+} f(D,n)/a^3$$

However, in the region of an avoided crossing, near $(\mu_1 - \mu_2)\cdot\mathbf{F} = (E_1 - E_2)$, the energy levels are changing nonlinearly with the field, and it is necessary to recognize that the effective dipole moment is field-dependent. In this case we choose

$$\mu_{\rm eff}^{+}(F) = -\partial \mathrm{E}_{-}/\partial F$$

Since $E_- = (^1/_2)(E_1 + E_2 - (\mu_1 + \mu_2)\cdot\mathbf{F}) - (^1/_2)\{(E_1 - E_2 - (\mu_1 - \mu_2)\cdot\mathbf{F})^2 + 4(\mu_{12}\cdot\mathbf{F})^2\}^{1/2}$, taking the derivative, we obtain

$$\mu_{\rm eff}^{+}(F) = -\partial E_-/\partial F = \frac{1}{2}(\mu_1 + \mu_2) + \frac{1}{2}\{(\mu_1 - \mu_2)[E_1 - E_2 - (\mu_1 - \mu_2)\cdot\mathbf{F}] + 4\mu_{12}^{2}F\}/\{(E_1 - E_2 - (\mu_1 - \mu_2)\cdot\mathbf{F})^2 + 4(\mu_{12}\cdot\mathbf{F})^2\}^{1/2}$$

For $A(F) = E_1 - E_2 - (\mu_1 - \mu_2)\cdot\mathbf{F}$ and $B(F) = 2\,\mu_{12}\cdot\mathbf{F}$, this may be written more simply:

$$\mu_{\rm eff}^{+}(F) = \frac{1}{2}(\mu_1 + \mu_2) + \frac{1}{2}[(\mu_1 - \mu_2)A + 2\mu_{12}B]/\{A^2 + B^2\}^{1/2}$$

Note that at the avoided crossing $A(F) = 0$, and if we expand this expression in the vicinity of small values of A, we obtain

$$\mu_{\rm eff}^{+}(F) = \frac{1}{2}(\mu_1 + \mu_2) + \left(\mu_{12} - \frac{1}{2}(\mu_1 - \mu_2)[E_1 - E_2 - (\mu_1 - \mu_2)\cdot\mathbf{F}]/\{2\mu_{12}\cdot\mathbf{F}\}\right) + O(A^2/B^2)$$

Remembering that at the crossing $E_1 - E_2 = (\mu_1 - \mu_2)\cdot\mathbf{F}$, we obtain for the effective dipole moment $\mu_{\rm eff}^{+} = (^1/_2)(\mu_1 + \mu_2) + \mu_{12}$. Thus, we may summarize our results in the three limits:

low field: $\mu_{\rm eff}^{+} = \mu_1$

at avoided crossing: $\mu_{\rm eff}^{+} = \frac{1}{2}(\mu_1 + \mu_2) + \mu_{12}$

high field: $\mu_{\rm eff}^{+} = \frac{1}{2}(\mu_1 + \mu_2) + \frac{1}{2}\{(\mu_1 - \mu_2)^2 + 4\mu_{12}^{2}\}^{1/2}$

Note that by measurement of the solvatochromic shifts over a wide enough range, it is possible to make observations in all three regions. Since there are three parameters, namely, μ_1, μ_2, and μ_{12}, it is possible to completely characterize the dipolar properties of the excited states involved. However, under many circumstances (e.g., when $\mu_{02} = 0$, the second excited state is hidden) the parameter $E_1 - E_2$, which determines the avoided crossing point, is also unknown. A good estimate of this parameter can be obtained by examining the value of f at which nonlinearity of the solvatochromic shifts occurs. We should remember that in absorption the solvent field is determined by the ground-state dipole moment

$$\Delta E_{\rm abs} = -\mu_0\cdot(\Delta\mu)a^{-3}\,f(D,n) \qquad \{\Delta\mu = \mu_{\rm eff}^{+} - \mu_0\}$$

while for emission the corresponding expression is

$$\Delta E_{\rm em} = \mu_{\rm eff}^{+}\cdot(\Delta\mu)a^{-3}\,f(D,n) \qquad \{\Delta\mu = \mu_{\rm eff}^{+} - \mu_0\}$$

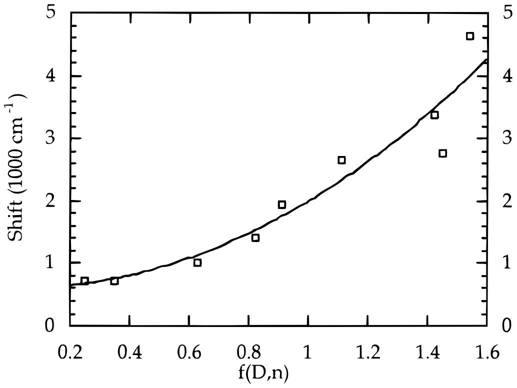

Figure 2. Solvatochromic shifts for emission in indole. The solid curve is a quadratic least-squares fit of the data. The parameters for the fit are $0.616 + 0.117f + 1.50f^2$ with a confidence level of 0.92. Note the onset of nonlinearity in the range $f(D,n) = 0.6{-}0.8$ (near the solvent ethyl acetate).

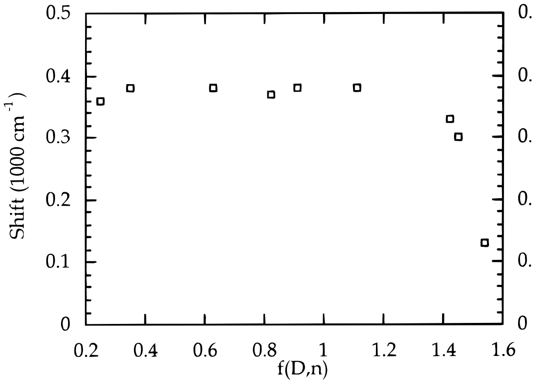

Figure 3. Solvatochromic shifts for absorption to the ^1L_b band of indole. Note the onset of nonlinearity around $f(D,n) = 1.4$ (near the solvent methanol).

Since $\mu_{\rm eff}^{+}\cdot$ varies depending on $f(D,n)$, we expect that the onset of nonlinearity may be observed at different points in absorption than emission. It is also clear that there will be a region in which the observed fluorescence shift is nonlinear. By extrapolation of the high-field and low-field straight lines, the crossing point will be at their intersection. We then have at the crossing for emission

$$E_1 - E_2 = (\mu_1 - \mu_2)\cdot\mathbf{F}^{\rm em} = (\mu_1 - \mu_2)\cdot\mu_{\rm eff}^{+}(F)\,f_c^{\rm em}(D,n)/a^3$$

where $f_c^{\rm em}$ is the value of $f^{\rm em}$ at the state crossing. Carrying out a similar procedure for absorption, we have at the crossing

$$E_1 - E_2 = (\mu_1 - \mu_2)\cdot\mathbf{F}^{\rm abs} = (\mu_1 - \mu_2)\cdot\mu_0(F)\,f_c^{\rm abs}(D,n)/a^3$$

Thus, assuming the cavity radius does not change much between absorption and emission, we obtain the useful relation

$$\frac{\mu_{\rm eff}^{+}\cdot\cos\gamma_e}{\mu_0\cos\gamma_0} = \frac{[(^1/_2)(\mu_1 + \mu_2) + \mu_{12}]\cos\gamma_e}{\mu_0\cos\gamma_0} = \frac{f_c^{\rm abs}}{f_c^{\rm em}}$$

In this expression γ_e and γ_0 are the angles between the effective excited and ground-state dipole moments and the direction of $\mu_1 - \mu_2$. This is especially valuable in that the parameter a has been eliminated.

Application to the Solvatochromic Shifts in Indole. The spectrum of indole provides a good test of the theory, since the parameters are all known. Both good gas-phase measurements exist and the solvatochromic shift studies cover a sufficiently wide range such that the nonlinear regions are clearly covered. In Figures 2 and 3 we present the solvatochromic shifts for both emission and absorption.[19] In both cases, for low values of $f(D,n)$ the shift is nearly flat. In absorption, the flatness extends all the way to rather high values of $f(D,n)$. Around $f(D,n) = 1.5$ (corresponding approximately to 1.7×10^7 V cm^{-1} D^{-1}), sharp nonlinearity sets in. In fluorescence, by contrast, the entire curve is quite nonlinear, and although it is difficult to pinpoint the exact onset, it is clearly in the region 0.7−0.8. Lami and Glasser estimate 0.8 (corresponding approximately to 0.9×10^7 V cm^{-1} D^{-1}). They take this to be the point at which the solvent polarity causes a crossing of the ^1L_b with the ^1L_a state. The above theory shows that this is in fact an avoided crossing if $\mu_{12} \neq 0$. Assuming no change in cavity radius, we may infer $f_c^{\mathrm{abs}}/f_c^{\mathrm{em}} \approx 2$. We shall use this later as a check on the theory.

Before analysis of these results in light of the above theory, it is worthwhile to discuss dipole moment directions. If we take the long axis (A) of the molecule as the origin, dipole moment directions may be expressed in terms of θ, the angle from this axis in the direction of the N atom. Slater and Callis[15] have carried out very reliable semiempirical calculations on indole on the indo/s-sdci level. The values of θ for the ground (0), ^1L_b (1), and ^1L_a (2) states are determined to be −45°, −41°, and −27°, respectively. Also useful from these results is the value of $\mu_{12} = 0.27$ D, which is at −66°. Note that since μ_0 and μ_1 are nearly parallel, we will ignore the direction cosines between them, and the direction cosine between those states and state 2 is 0.97. Thus, we may replace μ_2 by $0.97\mu_2$ without much fear of discrepancy. Note also that the gas-phase Stark effect value for $\Delta\mu$ (0.14 D) is measured along the long molecular axis, and if it is to be compared with solvatochromic shift measurements or calculations, we must take it as a projection along the A axis. Thus, we refer to the axis at −45° by dividing by the direction cosine, that is, $\Delta\mu/\cos 45° = 0.20$ D.

Examining the curve for emission more carefully, we see that the source for the previously mentioned discrepancy between gas-phase and solvatochromic shift reports[1] for the excited-state dipole moment change stems from lack of a proper theory with which to interpret the results. Lami and Glasser[19] fit the curve to two separate straight lines, one for each of the two nearby excited states, and conclude that $\Delta\mu = 1.04$ D for the first excited state (^1L_b). This is inconsistent with the nearly flat shift observed in absorption, which is indicative of a much smaller dipole moment change.

We have examined the data more carefully, trying various nonlinear fits, and found that, given the quality of the data as well as taking account of the theory, the best fit is a quadratic of the form $0.616 + 0.117f + 1.50f^2$. This is shown as the solid curve in Figure 2. If we now consider the limit of low $f(D,n)$, the slope is 0.117. When $a = 3.4$ Å and $\mu_0 = 2.39$ D, this gives a $\Delta\mu = 0.26$ D,[20] which is in good agreement with both the gas-phase results ($\Delta\mu/\cos 45° = 0.20$ D) and the low-field solvatochromic absorption results ($\Delta\mu \approx 0$).

To obtain a high-field result, we take the derivative of the quadratic expression with respect to f at $f = 1$. This is 3.12, resulting in an expression for the high-field effective dipole moment change:

$$\mu_{\mathrm{eff}}^{+}\Delta\mu = \mu_{\mathrm{eff}}^{+}(\mu_{\mathrm{eff}}^{+} - \mu_0) = 16.6\ \mathrm{D}^2$$

Solving the resulting quadratic equation for μ_{eff}^{+}, we obtain a value of

$$\mu_{\mathrm{eff}}^{+} = 5.21\ \mathrm{D}$$

This is close to the value of 5.44 D obtained by Lami and Glasser for μ_2, the dipole moment of the second excited state (^1L_a). Using the calculated value of $\mu_{12} = 0.27$ D,[15] we obtain a value of $\mu_2 = 5.16$ D. (Note that this is not very sensitive to the value of μ_{12}.)

We may now carry out an independent check on the theory by calculating the value of μ_{eff}^{+} at the crossing. This is given by $(^1/_2)(\mu_1 + \mu_2) + \mu_{12}$, which is 4.05 D. We then may calculate the ratio $\mu_{\mathrm{eff}}^{+} \cos \gamma_e/(\mu_0 \cos \gamma_0) \cong \mu_{\mathrm{eff}}^{+}/\mu_0 = 1.9$. This is very close to the value of $f_c^{\mathrm{abs}}/f_c^{\mathrm{em}} = 2$ obtained above. This gives us added confidence that our analysis is correct.

We summarize the results on indole as follows. We have been able to obtain an interpretation of the solvatochromic results that is consistent with the gas-phase results as well as the best available calculations under the assumption that the lowest two excited states are coupled by a solvent field-induced mixing. The resulting dipole moments are

$$\mu_0 = 2.13 \pm 0.02\ \mathrm{D}$$
$$\mu_1 = 2.39 \pm 0.05\ \mathrm{D}$$
$$\mu_2 = 5.16 \pm 0.09\ \mathrm{D}$$
$$\mu_{12} = 0.27 \pm 0.09\ \mathrm{D}$$

Not only are these results internally consistent including both absorption and emission as well as with the gas phase, but they are supported by the excellent fits obtained to the data over a wide range of solvents, as well as the independent test provided by the ratio of the solvent fields at which an avoided crossing occurs.

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