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# Solvatochromic Shifts: A Reconsideration

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Solvatochromic shifts in molecular spectra are often used to determine excited-state dipole moments. In comparing results with the more accurate gas-phase Stark effects studies, large discrepancies are obtained in the few cases in which both types of studies have been carried out. We attempt to reconcile the two techniques by reanalyzing solvatochromic shift measurements in the situation in which a field-induced perturbation by a nearby state is possible. It is found that, in the high field limit, if we reinterpret solvatochromic shift studies as measuring an effective dipole moment which is a function of the dipole moments of both states and the transition moment between the two states, a possible explanation of the discrepancy is obtained. This is demonstrated to be reasonable in the only case (aniline) for which sufficient data are available. We also include examination of field-induced intensity borrowing as well as certain cavity-induced resonances and magnetic field induced effects. Finally we suggest some experiments to test the extent to which this reinterpretation is needed.

## Introduction

The utilization of solvatochromic shifts to determine dipole moment changes in various organic molecules has resulted in a considerable body of literature over the years, and rather than review the topic, the references contained in several recent articles[1,2] are adequate for a survey. Solvatochromic shifts of spectral bands are caused by the rather large electric fields experienced by a solute molecule due to polarization of the surrounding solvent molecules. These are often called reaction fields. 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 $\mu$ 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 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 $\mathbf{F}$ 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

$$f(D) = 2(D - 1)/(2D + 1) \quad \text{and} \quad f(n^2) = 2(n^2 - 1)/(2n^2 + 1)$$

In the spirit of the Franck−Condon principle, it is presumed that excitation or emission, being electronic in character, take place rapidly on optical excitation, while the polarized solvent shell, involving essentially nuclear motions, is rather slow to respond, maintaining the configuration 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),

$$\Delta E_{\mathrm{abs}} = -\mu_0(\mu_1 - \mu_0)\mathrm{a}^{-3}\{f(D) - f(n^2)\}$$

while for emission the corresponding expression is

$$\Delta E_{\mathrm{em}} = -\mu_1(\mu_0 - \mu_1)\mathrm{a}^{-3}\{f(D) - f(n^2)\}$$

By measuring solvent shifts as a function of solvent polarizability, it is presumed that the dipole moment changes can be extracted. As might be expected, this technique is especially suited for large organic molecules which are soluble in a range of solvents and has been applied extensively to such systems. Note the above expressions are only the leading terms in more elaborate theories, which also involve polarizabilities as well as higher order terms in $\Delta\mu$. However, unless one or more of the dipole moments involved are zero, the terms presented here are dominant and usually used in determining dipole moment changes. Difficulties such as determination of the value of $a$ may be circumvented by, for example, taking appropriate ratios of shifts observed in absorption and fluorescence. Further complications due to exciplex formation or hydrogen-bonding solvents can also easily be handled.

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**TABLE 1: Observed Dipole Moment Changes in Polyatomic Molecules Using Gas-Phase Stark Effect. Note the Comparison with Several Solution-Phase Solvatochromic Measurements**

| molecule | $\Delta\mu$ (D) gas | $\Delta\mu$ (D) soln | ref |
|---|---|---|---|
| formaldehyde ($H_2CO$) | 0.78 | | 5 |
| propynal ($H_2C_3O$) | 1.69 | | 6 |
| formyl fluoride (HFCO) | 1.07 | | 7 |
| difluorodiazirine ($N_2CF_2$) | 1.5 | | 8 |
| fluororbenzene | 0.30 | | 9 |
| chlorobenzene | 0.23 | | 10 |
| *p*-chlorofluorobenzene | 0.32 | | 11 |
| *m*-chlorofluorobenzene | 0.20 | | 12 |
| benzonitrile | 0.31 | | 13 |
| phenol | 0.20 | | 14 |
| aniline | 0.85 | 3.5 | 14,15 |
| *p*-fluorophenol | 0.44 | | 16 |
| *p*-fluoroaniline | 0.82 | 3.5 | 16,17 |
| styrene | 0.13 | | 18 |
| indole | 0.14 | 1.04 | 19,20 |

However, as has been pointed out[3] there are some further difficulties with the utilization of solvent-induced shifts to determine excited-state dipole moments. Firstly, since the method is inherently of low resolution ($10-1000$ cm$^{-1}$) due to the size of the molecules involved and the condensed phase, any distortions to the spectra due to other effects might be masked. Spectral lines of large molecules in condensed phases tend to be inhomogeneously broadened, resulting in considerable ambiguity in interpreting the genesis of the observed bands. Spectra often cannot be observed in the low field limit or preferably under field-free conditions, making it impossible to determine the exact field dependence of the observed shifts, much less attest to their linearity. The latter is of considerable concern since the internal fields achieved are so large ($10^4$ to $10^5$ kV/cm) as to call into question the linear dipole approximation assumed in the theory. Furthermore, the presence of high fields may cause mixing of nearby states, which are expected to be increasingly abundant in larger molecules, and this effect may be difficult to detect in spectra with many broad, overlapping bands.

Given these difficulties, one would expect that researchers in the field would make an extensive effort to check the reliability of the method by comparison with other, more reliable but perhaps less generally applicable, techniques. A natural comparison would presumably be with gas-phase Stark effect measurements. These measurements involve examination of splittings of rotational lines due to externally applied electric fields. The technique is inherently of very high resolution (often 0.015 cm$^{-1}$) and utilizes relatively low electric fields ($1-10$ kV/cm) which are under the control of the experimenter, and observations can easily be made in the field-free limit. The limitation of this method, however, is the requirement that the molecule be small enough to be easily examined in the gas phase and have sufficiently stable states that sharp rotational structure may be observed in the electronic spectrum. Thus, many molecules of interest cannot be examined this way, and we must of consequence resort to lower resolution techniques in condensed phases. In Table 1 is presented a list of a large fraction of the molecules for which gas-phase Stark measurements have been made. (Numerous diatomic and triatomic molecules have been left out because they are not likely to be useful for comparisons with solvent shift studies. For a more comprehensive list see a very valuable review by Liptay.[4]) Included are the only measurements on these same molecules that could be found by solvatochromic shifts. Note that despite the fact that there are at least 15 possible candidates for comparison between the two techniques, solvatochromic studies have only been made in three.

It is quite worrisome that in all of the cases in which comparisons can be made the solvatochromic shift results for $\Delta\mu$ exceed the gas-phase measurements by factors of 4 or more. Since there are only three comparable results, this does not necessarily mean that all measurements will disagree by this amount, so that it is all the more necessary that further measurements be made from this or some expanded list. In any case, these discrepancies cannot be reconciled by appeal to experimental error, and we must search for a systematic explanation in the inherent limitations of the solvent shift method. The most likely correction to be expected would be through higher order terms in the electric field interaction. In fact as mentioned above, some of these have already been taken into account in the theory by inclusion of terms in the polarizability. Quantum mechanically, an expression for the polarizability may be derived by second-order perturbation theory as a sum over dipole moment matrix elements connecting to all the other states of the system divided by zero-order energy level differences. In this way contributions from all the other states in the system may be taken into account. The problem is that the perturbation expansion breaks down in the circumstance in which one of the perturbing states lies too close to the state of interest. In such a case we must consider the possibility of strong field induced mixing of one or more nearby states, and we must abandon perturbation theory for the more powerful and general technique of linear variation theory.

The possibility of a nearby state for the lowest lying allowed transition in aniline (293.8 nm) has been examined by several researchers, not only using high-resolution gas-phase spectroscopy[21] but also at lower resolution and higher pressures (and fields) with Stark modulation spectroscopy.[22] In these studies some of the likely properties of the perturbing state were obtained, indicating that it is quite different in orbital nature from the ($\pi-\pi^*$) state observed in field-free conditions. Further confirmation of the existence of a new nearby state was provided independently by comparison with solution and gas-phase results.[23] These researchers suggested that the perturbing state was Rydberg in origin, a conclusion that is consistent with the previous observations. Note that even if transitions to the perturbing state are forbidden from the ground state, and thus the state is not observed in the gas phase, as long as the transition moment between the two nearby excited states is nonzero, the states can be mixed by fields, and effects on the spectrum can be observed.

Evidence in *p*-fluoroaniline is less extensive. Nonlinearities in the gas-phase spectra were not observed, but the similarities in the observed dipole moment changes to those of aniline[24] hint at the lack of strong modification of the aniline molecule due to fluoro substitution. In the crystal at low temperature, where only weak crystal field interactions are expected,[25] the dipole moment change observed by Stark spectroscopy ($\Delta\mu =$ 1.61 D) was somewhat larger than that observed in the gas phase, but still considerably smaller than the solvatochromic results (see Table 1). The increasing size of the effective dipole moment change with increasing field utilized in the different experiments (gas phase to crystal to solution) may possibly be construed as evidence for field-induced mixing, although more definitive experiments would be required to constitute proof.

There is still less evidence for a nearby state in indole. Mataga and Kubota[26] give theoretical arguments that the $^1L_a$ and $^1L_b$ states are energetically close, but once again this hardly

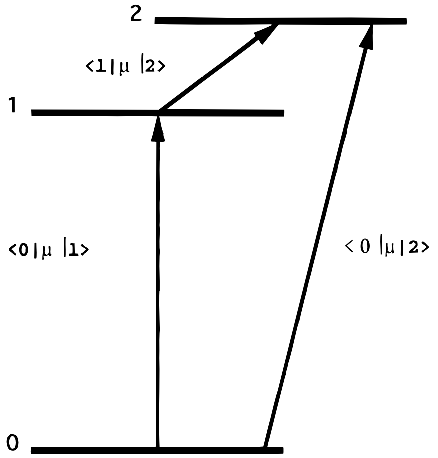

**Figure 1.** Energy level diagram for field-induced perturbations. The ground state 0 has an allowed transition to excited state 1 through $\langle 0|\mu|1\rangle$ and a second excited state 2 to which a transition from the ground state may or may not be allowed by $\langle 0|\mu|2\rangle$. States 1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

constitutes proof that they do interact through the mechanism of field-induced perturbation. Further work is clearly in order.

It is the purpose of this paper to consider the effect of a nearby state on solvatochromic shifts and to explore the proper reinterpretation of the observed results in cases when a solvent reaction field induces mixing. As mentioned above, this is possible even when transitions to the perturbing state are forbidden (or weak), and it is therefore unobserved in zero field. In the next section we examine the effect on frequency shifts due to field-induced perturbations, and in the following section, we consider the effects on the intensity profile of the presumably inhomogeneous band. Finally we explore briefly several other possible effects. One is due to the possibility of a cavity resonance. Another, which has not previously been examined, but could under certain circumstances be influential is magnetic field perturbations. We also suggest some experimental approaches worthy of further study.

## Field-Induced Solvatochromic Shifts

We 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 $\psi_0$, $\psi_1$, and $\psi_2$. For molecular electronic states, we assume a large gap between the ground state and the two (possibly nearby) excited states. These are illustrated in Figure 1. The zero-order transition moments between the states are

$$\mu_{01} = \langle\psi_0|\mu|\psi_1\rangle \qquad \mu_{02} = \langle\psi_0|\mu|\psi_2\rangle \qquad \mu_{12} = \langle\psi_1|\mu|\psi_2\rangle$$

While, for forbidden transitions, one or more of these may be zero, considering the most general case first, we will presume them to be nonzero. 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

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

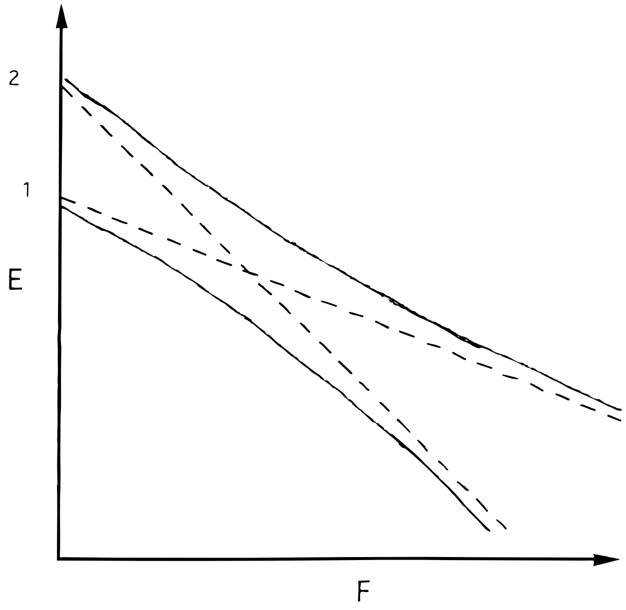

**Figure 2.** Effect of field-induced perturbation on the energy levels of two interacting states as a function of applied field. In zero field the states are at energies $E_1$ and $E_2$. Assuming $E_2 > E_1$ and that $\mu_2 > \mu_1$, it can be seen by the dashed lines that if $\mu_{12}$ is zero (no mixing), the lines will cross. The crossing is avoided for $\mu_{12} \neq 0$, in which case the solid lines represent $E_+$ (upper curve) and $E_-$ (lower curve). Note that in this case in the high-field limit (and assuming $\mu_{12}$ is small) the effective dipole moment (represented by the slope of the curve) of the lower state is closer to that of the upper zero-field state (2).

The excited-state eigenvalues of the perturbed Hamiltonian are then

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

while the new eigenfunctions may be written

$$\phi_+ = \sin(\beta)\,\psi_1 + \cos(\beta)\,\psi_2 \quad \text{and} \quad \phi_- = \cos(\beta)\,\psi_1 - \sin(\beta)\,\psi_2$$

where

$$\beta = (1/2)\arccos[1 + \alpha^2]^{-1/2}$$

$$\alpha = 2H_{12}/(H_{11} - H_{22}) = -2\mu_{12}\cdot\mathbf{F}/[E_1 - E_2 - (\mu_1 - \mu_2)\cdot\mathbf{F}]$$

In Figure 2 we illustrate the effect of applied field on the new energy levels $E_\pm$. It is assumed, for purposes of illustration in this case, that $E_2 > E_1$ and that $\mu_2 > \mu_1$. In the zero-field limit, the levels are identical to $E_1$ and $E_2$ . In low field the lines are nearly linear with slopes given by their respective dipole moments. It can be seen by the dashed lines that if $\mu_{12}$ is zero (no mixing), the lines will cross. The crossing is avoided for $\mu_{12} \neq 0$, in which case the solid lines represent $E_+$ and $E_-$. In the intermediate field region $(\mu_1 - \mu_2)\cdot\mathbf{F} \cong E_1 - E_2$, the energies are decidedly nonlinear. Note that in the high-field limit ($(\mu_1 - \mu_2)\cdot\mathbf{F} \gg E_1 - E_2$ and for small $\mu_{12}$) the effective dipole moment (represented by the slope of the curve) of the lower state ($E_-$) is closer to that of the upper zero field state (2), while that of the upper state ($E_+$) is closer to that of the lower zero-field state (1). It is as though the two states have switched dipole moments. In the high field limit (and any value for $\mu_{12}$) we obtain

$$E_{\pm} = (1/2)(E_1 + E_2) \pm \mu_{\text{eff}}\cdot\mathbf{F}$$

where

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

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. In cases where the dipole moment of the perturbing state ($\mu_2$) is quite different from the observed state ($\mu_1$), we might expect the high-field (solvatochromic shift) results to be quite different from the low-field (gas-phase) results. Even if $\mu_1 \cong \mu_2$ we expect a measurable difference when $\mu_{12}$ is not negligible.

The only case in which we have both unambiguous gas-phase Stark effect measurements and solvatochromic shift measurements is aniline, and it is worth examining the results in light of this analysis. From the previously mentioned ref 21 we have for aniline (by symmetry all dipole moments are parallel to the $C_2$ axis of the molecule, and we need not consider the vector natures of the dipole moments)

$$\mu_1 = 2.45\text{ D} \qquad \mu_2 = 6.0\text{ D} \qquad \mu_{12} = 0.5\text{ D}$$

From the intermediate-field Stark modulation results[22] we obtain the value of the energy level difference of the spectral origins $E_2 - E_1$ to be on the order of 10 cm$^{-1}$, so that it is clear that the solvatochromic shift observed is in the high-field limit. Substituting we obtain

$$\mu_{\text{eff}}{}^{+} = 6.07\text{ D} \quad \text{and} \quad \mu_{\text{eff}}{}^{-} = 2.39\text{ D}$$

Due to the low resolution of the solvatochromic shift results, transitions separated by 10 cm$^{-1}$ cannot be resolved. These parameters correspond to the situation illustrated in Figure 2 (in the high-field limit $(\mu_1 - \mu_2)\cdot\mathbf{F} \gg E_1 - E_2$ and for small $\mu_{12}$), where the dipole moments are interchanged. Utilizing the ground-state dipole moment of $\mu_0 = 1.53$ D, we predict $\Delta\mu = \mu_{\text{eff}}{}^{+} - \mu_0$ to be 4.5 D. Although this number differs somewhat from that observed in solvatochromic shift studies (3.7 D, see Table 1), the discrepancy is a lot less than that using the previous interpretation. Part of this remaining discrepancy may be due to intensity effects discussed in the next section. (The magnitude of experimental errors in solvatochromic shift measurements is not entirely clear. If we take the usual spectroscopic estimate of error to be on the order of the line width, say several hundred cm$^{-1}$, most of the remaining discrepancy for the reinterpreted aniline results disappears.)

In all of the above we have assumed that the (zero-field) observed transition in question is a single, spectroscopically isolated vibronic band and that inhomogeneous broadening presumably is due to solvent−solute interactions. However, considering their relative width, we must also include the possibility that additional inhomogeneities arise from unresolved overlapping of adjacent vibronic bands. In this case, it is likely that the field-induced effect will not be constant over the whole band. This is due to the variation of the perturbation strength with different vibronic levels. Probably the two most likely sources of this effect are due to variations in both $\mu_{12}$ and $E_1 - E_2$ across the band. The zero-field energy level separation clearly varies, and we must reinterpret $E_1 - E_2$ to be the difference in *vibronic* levels at each point in the band, including intensity from each vibronic transition which contributes to the observed band. Along these lines an interesting effect on the electric dipole moment with varying triplet−triplet ($T_1 - T_2$) separations has been observed in the phosphorescence spectrum of 2,4,5-trimethylbenzaldehyde[27] in durene crystals.

The transition moment and consequently $\mu_{\text{eff}}$ may also vary. In the Born−Oppenheimer approximation we may write the vibronic wave function as a product of electronic and vibrational functions $\psi_{\text{ev}} = \psi_{\text{e}}\chi_{\text{v}}$, and since the dipole moment operator is a function only of the electronic coordinates, we have

$$\mu_{12} = \langle\psi_1|\mu|\psi_2\rangle = \langle\psi_{\text{e}1}|\mu|\psi_{\text{e}2}\rangle\langle\chi_1|\chi_2\rangle$$

where we assume the first factor depends only on electronic state and does not vary much over the band, while the second factor, $\langle\chi_1|\chi_2\rangle$, the Franck−Condon overlap integral, may change considerably across the band. A complete analysis of solvatochromic shifts would have to take into account these variations as well. Note in the rotationally resolved gas-phase Stark spectrum of aniline, even within a *single* vibronic band[21] vastly different field effects were observed in the $^{R}$R branch in comparison with the $^{P}$P branch.

In the circumstances in which the molecule is in a high electric field, there are two consequences. First the effective dipole moment could be quite different from the dipole moment of the individual states even though a linear field dependence is observed. In principle this situation can be distinguished from the one in which no perturbing state (2) is present by studies in the low-field limit and searching for nonlinearity; in solution this cannot easily be done, since even fairly nonpolar solvents often produce relatively high reaction fields. Thus, in practice it may be impossible to distinguish the perturbed case from the unperturbed case without resorting to comparison with the gas-phase results. The second consequence of the presence of innately high fields in polar liquids is that the wave functions of the two interacting states are strongly mixed, each containing some of the character of the other. Transitions to otherwise weak or forbidden transitions become allowed through a form of field-induced intensity borrowing. When spectra are inhomogeneously broadened, this leads to intensity shifts caused not only by the dipole moments of the states but also by transfers of intensity from one transition to a nearby one. This effect will be examined in the next section.

## Field-Induced Intensity Borrowing

In addition to the strong nonlinear effects on the energy levels of an excited state discussed in the previous section, an intervening state that can be coupled by a field can also have a strong influence on the spectral intensities. As the field increases, the wave functions of the two excited states become increasingly mixed. Each takes on more of the character of the other, and we might expect them to exchange spectral intensity as well. In high resolution we expect this to manifest itself with the appearance of new transitions where one was previously forbidden, with the concomitant reduction in intensity of the allowed transition. This is analogous to intensity-borrowing effects resulting from the well-known Herzberg−Teller theory. However, in lower resolution situations, this effect may show up perhaps as a new shoulder or asymmetry on an otherwise allowed band. The net effect may be to cause a measurable shift in the spectral peak in addition to that predicted above for the energy levels. Once again, in solution, since the bands are already inhomogeneously broadened, and not necessarily symmetric, and since extrapolation to lower fields is difficult, it may be impossible to unravel this effect on the observed bands. However, it is at least worthwhile to examine here the nature and magnitude of the effect in a typical case.

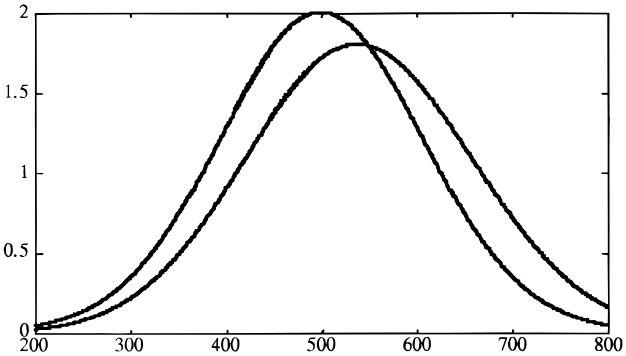

**Figure 3.** Effect of field-induced mixing on the intensity of a spectral line in the limit of large α. It is assumed that two initial states have transitions at (0 → 1) 500 cm$^{-1}$ and (0 → 2) 600 cm$^{-1}$, respectively, and each with a bandwidth of 150 cm$^{-1}$. In zero field ($\alpha = 0$) we assume $\mu_{02} = 0$, and all the intensity resides in the 0 → 1 transition. This is shown as the higher peak. The second peak is obtained with $\alpha = 5$ and the other parameters kept constant. Note the apparent shift in the band peak of approximately 40 cm$^{-1}$.

The intensity of transitions from the ground (0) state to the excited states $E_\pm$ is given in the most general case by the expression

$$I_\pm = |\langle \psi_0 | \mu | \phi_\pm \rangle|^2$$

$$I_+ = \sin^2(\beta)\, \mu_{01}^{\ 2} + 2\cos(\beta)\sin(\beta)\, \mu_{01}\, \mu_{02} + \cos^2(\beta)\, \mu_{02}^{\ 2}$$

$$I_- = \cos^2(\beta)\, \mu_{01}^{\ 2} - 2\cos(\beta)\sin(\beta)\, \mu_{01}\, \mu_{02} + \sin^2(\beta)\, \mu_{02}^{\ 2}$$

where the field dependent parameter $\beta$ is given in the previous section. In the zero-field limit $\alpha = 0$, $\beta = 0$, and $I_+ = \mu_{02}^2$, $I_- = \mu_{01}^2$ as expected. As the field increases, so does α, and the contributions from the two zero-field states become increasingly mixed. There are two limits in which α can become large. One is that for which $\mu_1 \cong \mu_2$ and $\mu_{12}\cdot\mathbf{F} \gg E_2 - E_1$. The other is when $(\mu_1 - \mu_2)\cdot\mathbf{F} \cong E_1 - E_2$, i.e., near an avoided crossing (see Figure 2). The limit of large α results in $\beta = \pi/4$, and we obtain simply

$$I_+ = (\mu_{01} + \mu_{02})^2 \quad \text{and} \quad I_- = (\mu_{01} - \mu_{02})^2$$

Note that if the transition to state 2 is forbidden ($\mu_{02} = 0$), in this (large α) limit both transitions have equal intensity. The transition 0 → 1(−) has shared half of its intensity with the 0 → 2(+) transition. Another interesting effect of field-induced perturbations can be seen in the situation in which both transitions are initially equal in intensity ($\mu_{01} = \mu_{02}$). With large α the intensity of $I_-$ vanishes.

In Figure 3 we illustrate the effect of field-induced mixing on the intensity of a spectral line in the limit of large α. It is assumed that two initial states have transitions at (0 → 1) 500 cm$^{-1}$ and (0 → 2) 600 cm$^{-1}$, respectively, and each is given a bandwidth of 150 cm$^{-1}$. We also assume $\mu_{02} = 0$ and that initially (in zero field, $\alpha = 0$) all the intensity resides in the 0 → 1 transition. This is shown as the higher peak centered at 500 cm$^{-1}$. The second peak is obtained with $\alpha = 5$, and the other parameters including line positions are kept constant. Note the apparent shift in the band peak of approximately 40 cm$^{-1}$. Furthermore the peak has become somewhat skewed. It can be seen that although this effect is small, and considerably less in magnitude than the frequency shifts from the previous section, it may still be of some significance and should be considered in a complete theory.

## Other Effects

Of course the above discussion does not include all possible effects on the solvent-shifted spectrum. As mentioned above, hydrogen bonding and exciplex formation have already been considered and need not be included here. However, there is an effect due to a cavity resonance that could result in solvent effects that deviate considerably from the usual theory. This effect was discussed originally by Corsetti and Kohler[28] but has been all but ignored since. It involves corrections to the reaction field due to the molecular polarizability. We consider a point dipole in the center of a sphere of radius $a$ with a surrounding medium of uniform dielectric constant $D$. The proper expression for the reaction field[29] is then

$$\mathbf{F} = fa^{-3}(\mu + \alpha\mathbf{F}) \quad \text{with} \quad f = 2(D-1)/(2D+1)$$

or, solving for $\mathbf{F}$,

$$\mathbf{F} = fa^{-3}\mu/(1 - \alpha a^{-3} f) = fa^{-3}\mu/(1 - \alpha/\alpha_C)$$

where we have defined a cavity polarizability $\alpha_C = a^3/f$. Note that whenever the molecular polarizability approaches the cavity polarizability $\alpha \cong \alpha_C$, the reaction field becomes large and severe nonlinear effects will be observed. Presumably this effect is not considered in the usual solvatochromic shift studies because they are in the limit where $\alpha \ll \alpha_C$. For example in aniline[2] $a^3 = 37$ A$^3$ and $\alpha = 11.7$ A$^3$. In the solvent hexane $f = 0.3697$, and therefore $\alpha \ll \alpha_C = 100$ A$^3$, so that in this case we do not expect nonlinearities due to a cavity resonance. Note, however, for some molecules this may not be true. For example retinals have been studied extensively due to their biological importance. In solvents with low internal fields (or in vitro) the effective dipole moment change of all-*trans*-retinal is near 1 D,[28] while at larger fields (in vivo) experiments[30] indicate an effective dipole moment change of 13.2 D. This decidedly nonlinear behavior may be interpreted as due to a large nonlinear contribution to the reaction field caused by rather large changes in the molecular polarizability (as much as 600 A$^3$). While this case might be considered rather extreme, it is still important that the possibility be included in consideration of the proper interpretation of solvatochromic shift experiments.

Another effect, which has not been previously discussed but may be worth exploring, is that of magnetic interactions. Even though under normal conditions we might expect magnetic perturbations to be rather small, just as for electric fields, there are possible magnetic configurations for which large effects could be observed. Magnetic fields can be generated internally in a liquid by the continual molecular motions of the dipoles of surrounding molecules. It is entirely possible that a reaction magnetic field is created by a molecular magnetic moment in a fashion similar to the reaction electric field usually invoked in solvatochromic shift theory. The resulting interaction of induced magnetic field with the magnetic moment is presumably quite small. However, in the absence of large electric effects such as for nonpolar molecules, it might be comparable to the higher order effects due to polarizability expected in the electric case and therefore not be negligible. Furthermore, every excited singlet state in a molecule has a corresponding, often nearby triplet state. It is the ubiquity as well as proximity of these triplet states that encourages speculation that they could be influential in solution spectra.

For magnetic fields where spin angular momentum is tightly coupled to the molecular frame (case a) or the orbital angular momentum (case c), the results are identical to the electric field case if $\mu$ is interpreted as the magnetic moment. If the spin is completely decoupled (pure case b), the results will be the same as the electric field for each spin component. Once again one might be concerned that magnetic transition dipoles are small. However, in the limit in which the electric transition dipole vanishes, such as in the 3500 Å transition of formaldehyde,[31] the magnetic field effect can become dominant.

In the intermediate coupling cases, a Hamiltonian must be considered which includes spin−orbit coupling terms. However, the magnetic field situation differs from the electric field situation in one very important respect. The parity selection rules for an electric perturbation are $+ \leftrightarrow -$, $+ \not\leftrightarrow +$, $- \not\leftrightarrow -$, while for a magnetic perturbation they are $+ \leftrightarrow +$, $- \leftrightarrow -$, and $+ \not\leftrightarrow -$. If in zero field two states lie close to each other, they may perturb each other due to small, field-independent terms in the Hamiltonian usually neglected (say spin−orbit). The selection rules for such a perturbation are $+ \leftrightarrow +$, $- \leftrightarrow -$, and $+ \not\leftrightarrow -$, so that if an electric field induced perturbation is observed, the two states could not possibly be perturbed in zero field. However, it is entirely possible for a magnetic field perturbation to affect states already mixed by a zero-field perturbation. Suppose state 1 has no magnetic moment and that state 2 does have a magnetic moment $\mu_M$. This is the situation to be expected with a singlet−triplet perturbation. Assume further that the states interact through a field-independent term $H_{SO} = \langle \psi_1 | A\mathbf{L}\cdot\mathbf{S} | \psi_2 \rangle$. Then we have

$$H_{11} = E_1 \qquad H_{22} = E_2 \pm \mu_M\cdot\mathbf{F} \qquad H_{12} = H_{SO}$$

and we obtain four separate levels given by

$$E_{++} = (1/2)(E_1 + E_2 + \mu_M\cdot\mathbf{F}) + (1/2)[(E_2 - E_1 - \mu_M\cdot\mathbf{F})^2 + 4H_{SO}{}^2]^{1/2}$$

$$E_{+-} = (1/2)(E_1 + E_2 - \mu_M\cdot\mathbf{F}) + (1/2)[(E_2 - E_1 - \mu_M\cdot\mathbf{F})^2 + 4H_{SO}{}^2]^{1/2}$$

$$E_{-+} = (1/2)(E_1 + E_2 + \mu_M\cdot\mathbf{F}) - (1/2)[(E_2 - E_1 - \mu_M\cdot\mathbf{F})^2 + 4H_{SO}{}^2]^{1/2}$$

$$E_{--} = (1/2)(E_1 + E_2 - \mu_M\cdot\mathbf{F}) - (1/2)[(E_2 - E_1 - \mu_M\cdot\mathbf{F})^2 + 4H_{SO}{}^2]^{1/2}$$

In zero field we have the usual perturbation formula:

$$E_{\pm} = (1/2)(E_1 + E_2) \pm (1/2)[(E_2 - \mathrm{E}_1)^2 + 4H_{SO}{}^2]^{1/2}$$

while in high fields the energies are

$$E_{++} = (1/2)(E_1 + E_2) + \mu_M\cdot\mathbf{F}$$

$$E_{+-} = (1/2)(E_1 + E_2)$$

$$E_{-+} = (1/2)(E_1 + E_2)$$

$$E_{--} = (1/2)(E_1 + E_2) - \mu_M\cdot\mathbf{F}$$

so that with complete mixing the states behave as though one were unperturbed and the other has a effective moment of $\mu_M$, while the field has decoupled the zero-field spin−orbit coupling. This may be compared to the Zeeman effect in the gas phase, in which a similar effect is observed. Note that as in the electric field case, depending on the selection rules, considerable differences might be observed from the usual solvatochromic shift predictions, requiring a reinterpretation of those results. Also since the generation of the magnetic reaction field depends on the existence of a magnetic moment in the *initial* state of a transition, if we assume absorption is from a pure singlet state, there should be no magnetic effect on absorption. Magnetic field effects are only observable in emission.

Since these effects are expected to be small for most polar molecules, it is probably not worth the effort to test the applicability of these ideas. However, for nonpolar molecules, one easy test is to study the solvation shift of phosphorescence, in comparison with, say, the fluorescence shifts in the same molecule. To my knowledge, this has not been done, but might prove very interesting. Zero-order spin−orbit effects might be small in many normal organic molecules; however an interesting class of molecules that might yield results are the metalloporphyrins. Many are sufficiently symmetric to be nonpolar, but with judicious choice of metal, they have a variety of spin−orbit states that may be coupled or decoupled to a varying degree. They all have intense visible and ultraviolet spectra, as well as strong emission, and are soluble in a variety of solvents.

## Conclusions and Suggestions for Further Study

We have shown at least some ways in which the results of solvatochromic shift measurements may be reconciled with gas-phase Stark effect measurements by reinterpreting the solvatochromic shift results as measuring an effective dipole moment, possibly due to field-induced mixing of nearby electronic states. This effective moment is a complex function of the dipole moment of the observed excited state and that of the perturbing state. It might be argued that this effect depends on the near coincidence of two states and is therefore not generally applicable. However, we must consider the large number of low lying states predicted by theory, but are invisible within the confines of normal spectroscopy, which could become manifest in the presence of strong electric or magnetic fields. In fact at this point only for one molecule (aniline) are sufficient data available to carry out a complete analysis. This is all the more reason that solvatochromic studies be extended to most if not all of the molecules listed in Table 1. However, most molecules cannot be studied in the gas phase, so that it might be necessary to develop other techniques to examine the extent to which solvatochromic shifts might be reexamined.

As shown above, one valuable way to unravel the effects of field-induced mixing to extract dipole moments of individual states is to study effects in lower fields, in the nonlinear decoupling regime. However, it is difficult to do this with most normally utilized solvents at room temperature. One suggestion would be to carry out studies in matrix isolation. Numerous studies of spectroscopy of molecules in solid rare gas matrixes at low temperatures (below 35 K), as well as in liquid nitrogen (77 K), have shown that the perturbation of molecular parameters by the surrounding molecules is minimal and that such studies are good substitutes for gas-phase experiments when necessary. The dielectric properties of rare gas molecules are well-known, and cryogenic technology is well enough developed that it is routinely utilized in many laboratories. Small samples of rather large organic molecules embedded in such matrixes could easily be obtained. For truly valid comparisons, it might be necessary to carry out higher field solvent shift studies at low temperatures as well, examining of course the low-temperature effects on dielectric constants, but this in itself would be of interest. Other studies might involve low-temperature studies of molecules in hydrocarbon glasses or crystals. Heptanes and pentanes are especially well suited to these types of studies, and mixtures of isopentane and 3-methylpentane have been widely studied at 77 K. Solubility might be a problem, but there are numerous molecules for which that problem can be overcome. Note the hydrocarbons have low polarizabilities and do not perturb the solute much, but somewhat more than the rare gases, and they could be useful for intermediate field studies, where nonlinearities due to avoided crossings could become important. In fact several Stark effect studies have been carried out in polar free-base porphyrins[32−34] using the high-resolution technique of hole-burning spectroscopy. These molecules have strong absorption and emission spectra and would be good candidates for the experiments suggested above. Other effects due to dipolar coupling between the solute and amorphous solvent "two-level system” have been shown to drastically influence the effective dipole moment at low temperatures.[35,36] Since liquids at room temperature have an amorphous structure, experiments on the temperature dependence of effective dipole moments in amorphous media might be of interest.

In any case, until more definitive low-field comparisons can be made, prudence dictates that the dipole moments measured in solvatochromic shift experiments be interpreted as effective dipole moments, rather than claiming, without further examination, that they represent dipole moments of a single state.

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