J. Am. Chem. Soc. **1988**, *110*, 3874–3879

Substituent Effects on Solvent Dependence of the Bandshape of Charge-Transfer Transitions in *N*-Pyridinium Phenolates

A. M. Kjaer and J. Ulstrup*

Contribution from the Chemistry Department A, Building 207, The Technical University of Denmark, 2800 Lyngby, Denmark. *Received November 18, 1987*

Abstract: The solvatochromic absorption bands for "betaine-1", "betaine-22", and "betaine-29" (2,4,6-triphenyl-*N*-(4-hydroxyphenyl)-2,4,6-triphenyl-*N*-(2,6-dimethyl-4-hydroxyphenyl)- and 2,4,6-triphenyl-*N*-(3,5-dodecamethylene-4-hydroxyphenyl)pyridinium ions, respectively) in a range of polar, apolar, protic, and aprotic solvents have been investigated. The bands can be accurately fitted by a single harmonic high-frequency mode Franck–Condon envelope of Gaussian solvent-broadened sub-bands. Multiphonon band analysis including both molecular modes and the solvent dynamics indicates that the solvent broadening for betaine-29 in polar solvents correlates well with $\epsilon_0^{-1}-\epsilon_s^{-1}$, ϵ_0 being the optical and ϵ_s the static dielectric constant, not only for aprotic solvents but also for normal alcohols. This is different from the behavior of 2,4,6-triphenyl-*N*-(3,5-di-*tert*-butyl-4-hydroxyphenyl)pyridinium ion ("betaine-26") for which the high-frequency solvent vibrational spectral part was previously found to be important. Bands for apolar solvents are independent of the solvent and are much wider than what corresponds to a structureless dielectric medium, pointing to other than purely electrostatic coupling mechanisms. Both the molecular frequencies and coordinate displacements are largely independent of the solvent, emphasizing their molecular character, and the frequency value of about 1600 cm^{-1} suggests that C–O or C–N stretching is involved. Spectral data for "betaine-1" and "betaine-22" could only be obtained for alcohol solvents and chloroform. The C–O/C–N mode at 1600 cm^{-1} can also be identified for these compounds. In addition, the band features suggest that coupling both to O–H stretching modes and to less isotope sensitive solvent modes is important.

1. Introduction

Dynamic properties of nuclear motion in different liquid solvent polarization modes are strongly reflected in time-resolved fluorescence in the nano-, pico-, and femtosecond ranges[1-10] and in the bandshape features of optical absorption and emission bands for charge-transfer transitions.[11] Solvent dynamics is most directly reflected in the former, the theoretical handling of which rests on stochastic chemical rate theory.[12] Absorption and emission bands for solute molecules, by their reflection of vibrationally averaged solvent effects, are less diagnostic as to the precise pattern for solute–solvent interactions. For this and other reasons solvent induced band maximum, width, and shape features have frequently been handled in terms of cruder, less solvent specific models such as inhomogeneous broadening[13] or by means of empirical concepts such as the solvent donor and acceptor formalism.[14]

Rather detailed solvent structural effects can, however, still be incorporated into dynamic solute molecular bandshape theory. As long as the solute–solvent coupling can be regarded as linear, a powerful frame is the concept of vibrationally[15-20] and spatially[21] dispersive solvent dielectric permittivity functions or other Green's functions for the environmental response to the molecular solute field. For homogeneous isotropic media this function incorporates the whole environmental frequency spectrum, either directly from experimental dielectric or infrared spectral data for the pure solvents[22] or in terms of suitable Debye- or resonance-like representations[23] of the individual solvent absorption bands. The dielectric formalism can be extended to incorporate spatial dispersion in the different polarization branches.[21] The vibrationally and spatially dispersive dielectric permittivity can be related to molecular solvent properties by statistical mechanical theories.[24] Within such frames suitable probes for strong solute–solvent interaction and environmental solvent structural effects are optical absorption and emission bands of charge-transfer transitions in solute molecules, in which the ground and excited orbitals are exposed to the solvent, and major electronic charge redistribution accompanies the transition. Such systems are, for example, donor–acceptor complexes,[26-28] ion pairs,[29-36] mixed-valence com-

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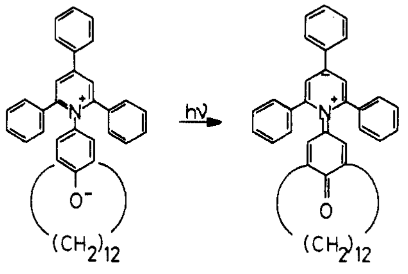

Figure 1. Schematic view of the solvatochromic charge transfer transition in *N*-pyridinium phenolates. The figure shows specifically "betaine-29". "Betaine-1" has no ring substituents, while "betaine-22" has a methyl substituent in the 2- and 6-positions (relative to the *N*-pyridinium ring atom) of the phenolate ring.

pounds,[37-43] and certain classes of large aromatic organic molecules.[1-5,44-47]

In a recent report[48] we have provided a detailed bandshape analysis of the "solvatochromic" charge-transfer band of 2,4,6-triphenyl-*N*-(3,5-di-*tert*-butyl-4-hydroxyphenyl)pyridinium ion ("betaine-26"[44-46]) for a wide range of protic, aprotic, polar, and apolar solvents. This analysis rested both on solvent dynamics in the form of the frequency dispersive dielectric permittivity function and on the dynamics of the molecular nuclear motion, in a way which has not previously been reported. Two main conclusions emerged from the analysis. First, the molecular parameters extracted from the bandshape features were largely independent of the solvent, substantiating the molecular nature of this part of the electronic-vibrational coupling. Secondly, the different solvents exhibited broadly three kinds of behavior. Polar, aprotic solvents behave as structureless dielectric media, characterized solely by their optical (ϵ_0) and static (ϵ_s) dielectric constants. Apolar, aprotic solvents display rather constant bandshape features in spite of widely different values of the bulk dielectric constants. This is indicative of other solute–solvent interactions than purely electrostatic forces. Finally, protic solvents reveal features indicative of hydrogen bonding and other specific solute–solvent interactions.

N-Pyridinium phenolates cover a broad class of compounds which all possess an exceedingly solvent sensitive solvatochromic charge transfer transition in the visible or near infrared spectral range.[44-47] The transition has been used as a basis for the empirical E_T solvent polarity scale[46] and corresponds roughly to intramolecular electron transfer as shown in Figure 1. In view of the rather diverse detailed solvent behavior for betaine-26, in which two bulky *tert*-butyl groups are located on each side of the electron-donating phenolate group, further insight into the subtler points of bandshape theory can be anticipated by investigations of other betains with different substituents. In this work we report such data for other betaines: (a) 2,4,6-triphenyl-*N*-(4-hydroxyphenyl)pyridinium ion ("betaine-1"[44-47]), with no substituents in the phenol part; (b) 2,4,6-triphenyl-*N*-(2,6-dimethyl-4-hydroxyphenyl)pyridinium ion ("betaine-22"[44-47]), in which two sterically hindered methyl substituents cause a twist of the coplanar pyridinium and phenol ring arrangement; (c) 2,4,6-triphenyl-*N*-(3,5-dodecamethylene-4-hydroxyphenyl)pyridinium ion, in which the long chain of methylene groups partially screen the phenolate group from the external solvent, similar to the *tert*-butyl groups in betaine-26. The bandshape parameters and the pattern for solute–solvent interaction are indeed specific both to the solvents and to the betaine substituents.

2. Experimental Section

Materials. Betaine-1, betaine-22, and betaine-29 were prepared by combining the "upper" part, 2,4,6-triphenylpyrylium perchlorate, with the primary amine group in the "lower" part, i.e., with 4-aminophenol (betaine-1), 3,5-dimethyl-4-aminophenol (betaine-22), and with 2,6-dodecamethylene-4-aminophenol (betaine-29). The "upper" and "lower" constituents were prepared separately. This scheme is a general route to a wide variety of *N*-pyridinium compounds,[49] and the following procedures, slightly modified from the procedures reported in ref 44–46 and 50, were used.

2,4,6-Triphenylpyrylium Perchlorate. This compound was prepared and characterized as in ref 44–46 and 50: mp 248–249 °C as reported in ref 44.

2,4,6-Triphenyl-*N*-(4-hydroxyphenyl)pyridinium Perchlorate. This compound was prepared from 2,4,6-triphenylpyrylium perchlorate and 4-aminophenol by the procedure in ref 44: mp 250 °C as in ref 44.

3,5-Dimethyl-4-aminophenol.[51] 2,6-Dimethylphenylhydroxylamine (5 g) was added to 75 mL of 1:15 w/w ice-cooled aqueous sulfuric acid. After 30 min the precipitate (nitrosoxylene) was filtered and washed with dilute sulfuric acid. The solution was acidified with dilute sulfuric acid and extracted with diethyl ether. By subsequent addition of excess sodium hydroxide, extraction with diethyl ether to remove 2,6-xylidene, and neutralization of the aqueous phase with dilute sulfuric acid, 3,5-dimethyl-4-aminophenol precipitated. The product was recrystallized from boiling water: yield, 0.41 g; mp 180.5–181.5 °C as in ref 51.

2,6-Dimethylphenylhydroxylamine.[51] 1-Nitro-2,6-xylene (10 g) was dissolved in 25 mL of ethanol, 1 g of ammonium chloride in 10 mL of water was added, and the solution was heated to 65–70 °C. Zinc powder (15 g) was added over 17 min. After 1 min the solution was cooled, filtered, and washed with warm ethanol. The filtered solution was poured into 100 mL of ice water, and the precipitate was isolated and washed with petroleum ether: yield, 6.3 g; mp 98.5 °C as in ref 51.

2,4,6-Triphenyl-*N*-(2,6-dimethyl-4-hydroxyphenyl)pyridinium Perchlorate. 3,5-Dimethyl-4-aminophenol (0.4 g), 1.12 g of 2,4,6-triphenylpyrylium perchlorate, and 0.4 g of sodium acetate were refluxed in 25 mL of ethanol for 2 h. By addition of perchloric acid, unreacted 2,4,6-triphenylpyrylium salt was precipitated. "Betaine-22" was precipitated by adding 3 mL of water to the solution. The product was filtered, washed with water, and dried over silica gel: yield, 0.42 g; Mp 171–172.5 °C (lit. 166–167 °C[46]). The molar extinction coefficient at 424 nm: 953 dm^3 mol^{-1} cm^{-1} (lit. 985 dm^3 mol^{-1} cm^{-1} [46]).

2,6-Dodecamethylene-4-nitrophenol.[52,53] The sodium salt of nitromalonaldehyde was prepared from mucobromic acid (Ega Chemie) by the procedure in ref 52. It was converted to 2,6-dodecamethylene-4-nitrophenol by reaction with cyclopentadecanone (Fluka) by the procedure in ref 53: mp 110.1 °C (lit. 109 °C[53]).

2,6-Dodecamethylene-4-aminophenol.[53] 2,6-Dodecamethylene-4-nitrophenol (1 g) was dissolved in a 6% sodium hydroxide solution in 50

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mL of water and 25 mL of ethanol. The solution was heated to boiling, and sodium dithionite powder was added until the color vanished. The solution was diluted with a few milliliters of water, and the product (a viscous oil) was isolated by benzene extraction, subsequent removal of benzene by distillation under slight vacuum, and drying over silica gel.

2,4,6-Triphenyl-*N*-(3,5-dodecamethylene-4-hydroxyphenyl)pyridinium Perchlorate. The 2,6-dodecamethylene-4-aminophenol product was dissolved in 15 mL of ethanol, and 1.3 g of 2,4,6-triphenylpyrylium perchlorate and 0.3 g of sodium acetate were added. The solution was refluxed for 2.5 h under nitrogen, concentrated perchloric acid was added until precipitation occurred, and the mixture was cooled in a refrigerator. The initially reddish precipitate was filtered and washed several times with ether which gradually turned it into a light yellow product: yield, 1.0 g; mp 299–300 °C as in ref 46.

Solvents and Other Reagents. Millipore water (4-Housing Milli-Q system) and analaR grade organic solvents were dried and further purified as in ref 48. Other reagents were of highest grade quality available.

Betaine solutions were prepared by dissolving the betaines in a small amount of methanol, adding excess sodium methanolate, and removing the methanol in an argon stream. The appropriate amount of argon-saturated organic solvent was then added. Addition of sodium methanolate prevents hydrogen bonding and spectral blue-shifts from possible remaining acid trace impurities but does not affect the optical spectral bandshapes.

Spectral Recordings. The spectrophotometer (Varian 2300), cells, data recording, and numerical processing were all the same as reported previously.[48]

3. Charge-Transfer Bandshape Functions for Strong Solute–Solvent Interactions

A fundamental element of optical charge-transfer bandshapes is that the dynamics of the solvent polarization modes, as opposed to static inhomogeneous broadening, is what causes the broadening of individual vibronic absorption lines. The formalism which has evolved from this view is available elsewhere,[11] and we summarize here only a few elements of which explicit use is made in the following.

The molar extinction coefficient for transition between a ground ("g") and excited ("e") electronic state in a solute–solvent system for which both levels are strongly coupled to the solvent environment, is[11]

$$\nu_{\mathrm{eg}}(\nu) = \frac{2\pi}{(\ln 10)(3c)}\, h\nu \frac{\beta}{\hbar} |M_{\mathrm{eg}}|^2 K(\nu) \tag{1}$$

where c is the light velocity in the solvent, h Planck's constant, $\hbar = h/2$, M_{eg} is the transition dipole moment, $\beta = (k_{\mathrm{B}}T)^{-1}$, k_{B} being Boltzmann's constant, T the temperature, and ν is the incoming light frequency. The bandshape function, $K(\nu)$, incorporates all the properties of the solute–solvent interaction in the ground and excited states.

Strong coupling solely to a broadly frequency dispersive solvent gives a Gaussian bandshape near the absorption maximum[11]

$$K(\nu) = \frac{2(\pi)^{1/2}}{\beta\Delta_{\mathrm{s}}} \exp\left[-\frac{(h\nu - h\nu_{\mathrm{m}})^2}{\Delta_{\mathrm{s}}^{-2}}\right] \tag{2}$$

Both the maximum, $h\nu_{\mathrm{m}}$, and the width, Δ_{s}, depend crucially on the solvent vibrational dispersion and on the coupling strength. More specifically, the maximum, $h\nu_{\mathrm{m}}$, is $h\nu_{\mathrm{m}} = E_{\mathrm{s}} + \Delta F_{\mathrm{o}}$ where ΔF_{o} is the free energy gap between the ground and excited states and E_{s} the solvent reorganization free energy. The latter is determined by the spectral function of the solvent permittivity, $\epsilon(\omega)$, and by the dielectric induction field difference between the electronic charge distributions in the ground and excited states, $\Delta\vec{D}(\vec{r})$, viz.[11,16–20]

$$E_{\mathrm{s}} = \frac{1}{\beta}\int_{\mathrm{o}}^{\omega_{\mathrm{c}}} \frac{\mathrm{d}\omega}{\omega} \mathrm{f}(\omega); \qquad \mathrm{f}(\omega) = \frac{\beta}{2\pi^2}\frac{\mathrm{Im}\,\epsilon(\omega)}{|\epsilon(\omega)|^2}\int \mathrm{d}\vec{r}[\Delta\vec{D}(\vec{r})]^2 \tag{3}$$

where ω_{c} is an upper "cutoff" frequency for the solvent vibrational spectrum. The Gaussian band width is[11,18]

$$\Delta_{\mathrm{s}} = (2E_{\mathrm{s}}k_{\mathrm{B}}T)^{1/2}\left[\int_{\mathrm{o}}^{\omega_{\mathrm{c}}} \mathrm{f}(\omega) \coth\left(\frac{1}{2}\beta\hbar\omega\right) \mathrm{d}\omega\right]^{1/2} \tag{4}$$

In the high-temperature limit, which appears to be adequate in the present analysis, E_s and Δ_{s} take the following well-known form

$$E_{\mathrm{s}} = \frac{1}{8\pi}(\epsilon_{\mathrm{o}}^{-1} - \epsilon_{\mathrm{s}}^{-1}) \int \mathrm{d}\vec{r}[\Delta\vec{D}(\vec{r})]^2; \qquad \Delta_{\mathrm{s}} = (2E_{\mathrm{s}}k_{\mathrm{B}}T)^{1/2} \tag{5}$$

The Gaussian form in eq 2 is inadequate in the spectral wings, and higher order cubic and quartic terms in the exponent become important, depending on the details of the solvent frequency dispersion.[11]

Additional coupling to local modes modifies the bandshape function which now becomes an envelope of absorption lines between all the local mode vibronic components of the transition, each broadened by the solvent bandshape function in eq 2. It turns out that the data to be considered in the following are adequately represented by a single local displaced harmonic oscillator. The bandshape function is then[11,16–20]

$$K(\nu) = \frac{2(\pi)^{1/2}}{\beta\Delta_{\mathrm{s}}} \sum_{n=-\infty}^{n=\infty} \Phi_n \exp\left[-\frac{(h\nu - h\nu_{\mathrm{m}} + n\hbar\Omega_{\mathrm{c}})^2}{\Delta_{\mathrm{s}}^2}\right]$$

$$\Phi_n = I_{|n|}\left(\frac{\Delta_{\mathrm{c}}^2}{sh\left(\frac{1}{2}\beta\hbar\Omega_{\mathrm{c}}\right)}\right) \exp\left[\frac{1}{2}\beta\hbar\Omega - \frac{1}{2}\Delta_{\mathrm{c}}^2 \coth\left(\frac{1}{2}\beta\hbar\Omega_{\mathrm{c}}\right)\right] \tag{6}$$

where Ω_{c} is the local mode vibrational frequency and Δ_{c} its equilibrium coordinate displacement. $I_{|n|}$ is the modified Bessel function of order $|n|$.[54] Equation 6 can straightaway be extended to any number of local modes,[55] as for example in ref 48 and 55.

4. Bandshape Parameters for *N*-Pyridinium Phenolates

Absorption spectra for "betaine-29" were recorded for a wide range of polar, apolar, protic, and aprotic solvents, with a far wider range of the solvent parameter $\epsilon_{\mathrm{o}}^{-1} - \epsilon_{\mathrm{s}}^{-1}$ than what is possible for mixed-valence compounds. Absorption spectra for the weakly or unsubstituted betaine-22 and betaine-1, respectively, could, on the other hand, only be obtained for normal alcohols and for chloroform, as these betaines were insoluble or decomposed in other common solvents. In all cases the solvatochromic charge transfer band was well separated from other bands and could be analyzed to give unambiguous bandshape parameters.

The bands are always notably asymmetric, with a slower fall-off on the high-frequency side of the maximum (cf. Figure 2 in ref 48). This is indicative of strong coupling to molecular high-frequency modes. Coupling to the high-frequency vibrational tail of the hydroxylic solvent spectra may also cause such an effect, but the molecular modes must be important as the effect is maintained in all aprotic solvents for which the spectral data could be obtained.

The bandshape for the three betaines and all the solvents were always well represented, with small variances, by eq 1 and 6. It is very notable that this extends to all the normal alcohols, as these were poorly represented by eq 6 for betaine-26. Figures 2–4 show the bandshape parameters Δ_{s}, Ω_{c}, and Δ_{c} extracted by least-squares fitting of eq 1 and 6 to the on-line data. The figures and the parameter values reveal the following picture.

(A) The solvent band width, Δ_{s}, for betaine-29 is well correlated with $(\epsilon_{\mathrm{o}}^{-1} - \epsilon_{\mathrm{s}}^{-1})^{1/2}$ in the range 0.45–0.73 for the latter. The intercept is insignificant, indicative of little reorganization in low-frequency molecular modes. It is notable and quite different from the behavior of betaine-26 that this correlation covers both aprotic polar and hydroxylic solvents. In this respect all these solvents thus behave as entirely structureless dielectric media for betaine-29. The corresponding solvent reorganization free energies range from 0.8 eV for methanol to 0.25 eV for iodobenzene.

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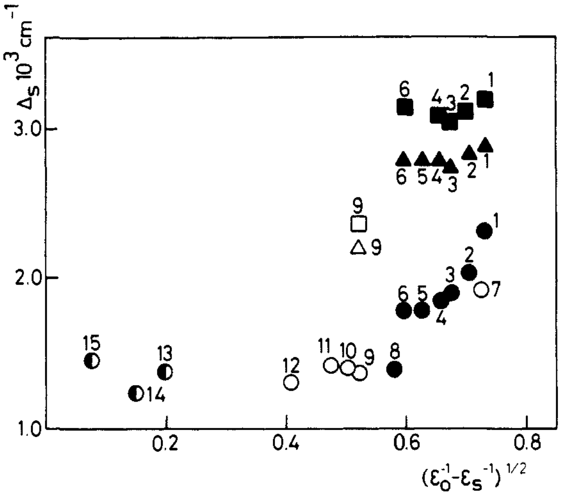

Figure 2. Solvent band widths, Δ_s, in units of 10^3 cm^{-1} for the three betaines. Solvatochromic absorption band parameters are obtained by least-squares fits of eq 6 to the data and plotted against the solvent "polarity" parameter $(\epsilon_0^{-1}-\epsilon_s^{-1})^{1/2}$. Filled symbols represent alcohol solvents, open symbols polar aprotic solvents, and half-filled symbols aprotic apolar solvents. Circles refer to "betaine-29", triangles to "betaine-22", and squares to "betaine-1". The ordinate scale represents betaine-29, while the data points for betaine-22 and betaine-1 are shifted vertically upwards by 0.2 and 0.6 units. The numbering refers to the following solvents: 1, methanol; 2, ethanol; 3, 1-butanol; 4, 1-pentanol; 5, 1-octanol; 6, 1-decanol; 7, acetonitrile; 8, *tert*-amyl alcohol; 9, chloroform; 10, chlorobenzene; 11, bromobenzene; 12, iodobenzene; 13, dioxane; 14, toluene; 15, benzene.

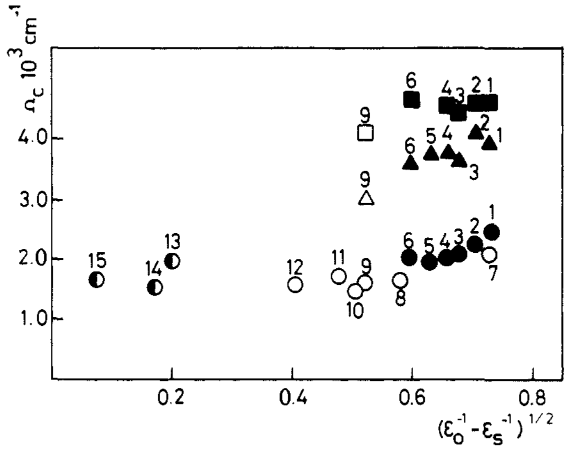

Figure 3. Dependence of the molecular vibrational frequency, Ω_c, in units of 10^3 cm^{-1}, obtained by least-squares fitting of eq 6 to the data, on $(\epsilon_0^{-1}-\epsilon_s^{-1})^{1/2}$. Same symbols and numbering as in Figure 2. Data points for betaine-22 and betaine-1 shifted vertically upwards by 1.0 and 2.0 units, respectively, relative to the ordinate scale shown.

The $(\epsilon_0^{-1}-\epsilon_s^{-1})^{1/2}$ range from 0.45 to 0.73 is roughly the range where correlations have been obtained for mixed-valence compounds in aprotic solvents. Figure 2 shows that less polar solvents do not fit the correlation for betaine-29. Rather, for $(\epsilon_0^{-1}-\epsilon_s^{-1})$ smaller than about 0.4 Δ_s becomes constant and gives a value of $E_s \approx 0.2$–0.25 eV. This behavior is similar to that observed for betaine-26. In both cases the solute–solvent coupling thus remains strong for apolar solvents. The nature of the coupling must, however, be different from that of the more polar solvents and rather originates from multipolar, dispersion, or pseudopotential-like forces.

While the solvent band width for betaine-29 in normal alcohol solvents follows the $(\epsilon_0^{-1}-\epsilon_s^{-1})$ correlation, the two weakly substituted betaines have almost constant band widths over a $(\epsilon_0^{-1}-\epsilon_s^{-1})$ variation of 20%. The solvent behavior is apparently quite system specific. A constant band width could be indicative of constant local structural features, say polarization correlation length or Kirkwood "*g*-factor". The latter, as extracted from high field dielectric measurements indeed shows little variation for the alcohols considered here.[56]

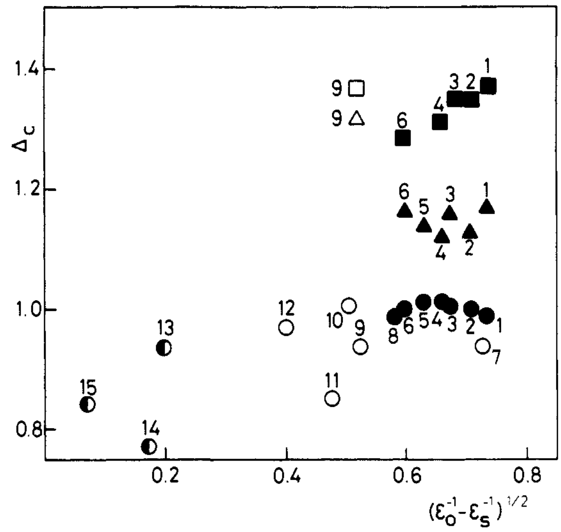

Figure 4. Dependence of the dimensionless equilibrium coordinate displacement, Δ_c, obtained by least-squares fit of eq 6, on $\epsilon_0^{-1}-\epsilon_s^{-1}$. Numbering and symbols the same as in Figure 2 and 3. The data points for betaine-22 and betaine-1 are shifted vertically upwards by 0.3 and 0.4 units, respectively, relative to the ordinate scale.

(B) Of the molecular quantities the coordinate displacement of betaine-29 is practically constant for all the solvents, including the alcohols. Its value is 0.9 ± 0.1 which is close to that for betaine-26. The coordinate displacements of betaine-1 and betaine-22 are independent of the solvent over the narrower polarity range feasible here and have the same numerical values as for betaine-29. All this substantiates the molecular nature of this quantity.

The molecular vibrational frequency for betaine-29 is solvent independent for all the aprotic solvents. The value is 1600 ± 150 cm^{-1}, i.e., very close to the value for betaine-26 and corresponding to significant reorganization at the phenolate site. Ω_c increases almost linearly with increasing $(\epsilon_0^{-1}-\epsilon_s^{-1})^{1/2}$ for the alcohols, giving a value of 2500 cm^{-1} for the most polar alcohol, methanol. In striking contrast to the behavior of betaine-26, all these values are still quite representative of real physical solute–solvent properties involving O–H stretching or bending motion. The behavior of betaine-22 follows closely that of betaine-29 in this respect. Ω_c again increases linearly with increasing $(\epsilon_0^{-1}-\epsilon_s^{-1})^{1/2}$, giving a value of 2950 ± 150 cm^{-1} for methanol. The values for betaine-1 are about 2600 ± 100 cm^{-1} and practically independent of the solvent. The actual values of Ω_c, Δ_c, and Δ_s for the three betaines are summarized in Table I.

(C) In order to illuminate the nature of the molecular mode pattern futher, a two-mode model was fitted to the data by means of the following generalized form of eq 6

$$K(\nu) = \frac{2(\pi)^{1/2}}{\beta\Delta_s}\sum_{n_1=-\infty}^{\infty}\Phi_{n_1}\sum_{n_2=-\infty}^{\infty}\Phi_{n_2}\exp\left[-\frac{(h\nu - h\nu_m + n_1\hbar\Omega_{c1} + n_2\hbar\Omega_{c2})^2}{\Delta_s^2}\right] \qquad (7)$$

where the subscripts 1 and 2 refer to the two molecular coordinates and Φ_{n_1} and Φ_{n_2} each have the same form as in eq 6. This procedure is the same as in ref 48, except that asymmetry and high-frequency vibrational tails in the solvent spectral part could now be omitted. Ω_{c1} and Δ_{c1} for one of the coordinates were fixed at 1600 cm^{-1} and 0.8, respectively, and the values of other one (Ω_{c2} and Δ_{c2}) were fitted by the least-squares analysis. The result remains somewhat entangled and is summarized in Table II. Ω_{c2} and Δ_{c2} for betaine-1 are again practically constant, Ω_{c2} being 2850

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[56] Ruff, I. *Acta Chim. Hung.* **1986**, *121*, 203.

Table I. Solvatochromic Bandshape Parameters for Betaine-1, Betaine-22, and Betaine-29 in Normal Alcohol Solvents[a]

betaine no.	solvent	$(\epsilon_0^{-1}-\epsilon_s^{-1})^{1/2}$	Δ_s	A	$h\nu_m$	Ω_c	Δ_c
1	methanol	0.732	2.58 ± 0.05	145 ± 2	21.91 ± 0.06	2.61 ± 0.10	0.96 ± 0.04
1	ethanol	0.706	2.51 ± 0.05	166 ± 2	20.67 ± 0.06	2.59 ± 0.09	0.95 ± 0.04
1	propanol	0.687	2.51 ± 0.04	188 ± 2	20.25 ± 0.05	2.70 ± 0.10	0.88 ± 0.04
1	butanol	0.674	2.45 ± 0.03	199 ± 2	19.79 ± 0.04	2.44 ± 0.06	0.95 ± 0.03
1	1-pentanol	0.657	2.49 ± 0.03	193 ± 2	19.70 ± 0.04	2.53 ± 0.07	0.91 ± 0.03
1	1-decanol	0.595	2.54 ± 0.04	204 ± 2	19.30 ± 0.05	2.67 ± 0.10	0.88 ± 0.03
22	methanol	0.732	2.67 ± 0.07	54 ± 1	21.16 ± 0.06	2.97 ± 0.15	0.87 ± 0.04
22	ethanol	0.706	2.63 ± 0.04	62 ± 1	20.06 ± 0.04	3.10 ± 0.12	0.83 ± 0.03
22	propanol	0.687	2.53 ± 0.05	80 ± 1	19.32 ± 0.07	2.64 ± 0.14	0.86 ± 0.05
22	butanol	0.674	2.59 ± 0.03	69 ± 1	19.13 ± 0.04	2.80 ± 0.11	0.82 ± 0.03
22	1-pentanol	0.657	2.59 ± 0.07	67 ± 1	18.63 ± 0.08	2.76 ± 0.20	0.84 ± 0.06
22	1-decanol	0.595	2.59 ± 0.10	66 ± 2	18.49 ± 0.12	2.64 ± 0.25	0.86 ± 0.09
29	methanol	0.732	2.36 ± 0.06	145 ± 3	17.96 ± 0.06	2.48 ± 0.09	0.99 ± 0.04
29	ethanol	0.706	2.05 ± 0.05	284 ± 5	16.68 ± 0.05	2.23 ± 0.07	1.03 ± 0.04
29	propanol	0.687	1.89 ± 0.05	357 ± 8	16.06 ± 0.05	2.06 ± 0.07	1.04 ± 0.04
29	butanol	0.674	1.85 ± 0.04	376 ± 6	15.90 ± 0.04	2.03 ± 0.05	1.06 ± 0.03
29	1-pentanol	0.657	1.79 ± 0.04	337 ± 6	15.50 ± 0.04	1.96 ± 0.06	1.06 ± 0.03
29	1-decanol	0.595	1.78 ± 0.03	359 ± 5	15.43 ± 0.03	2.02 ± 0.05	1.04 ± 0.03

[a] Obtained from single-mode analysis and linear solvent approximation (eq 1, 2, and 6). Δ_s, Ω_c, and $h\nu_m$ in units of 10^3 cm^{-1}. $A = (8\pi^{5/2}/\ln 10)(\nu/c)|M_{eg}|^2/\Delta_s$ in units of dm^3 mol^{-1} cm^{-1}. ϵ_0 is identified with the squared refractive index at the sodium D line, n_D. n_D and ϵ_s data are from ref 57 and 58.

Table II. Solvatochromic Bandshape Parameters for Betaine-1, Betaine-22, and Betaine-29[a]

betaine no.	solvent	$(\epsilon_0^{-1}-\epsilon_s^{-1})^{1/2}$	Δ_s	A	$h\nu_m$	Ω_{c2}	Δ_{c2}
1	methanol	0.732	2.52 ± 0.04	149 ± 2	21.73 ± 0.05	2.9 ± 0.1	0.79 ± 0.04
1	ethanol	0.706	2.43 ± 0.04	183 ± 2	20.54 ± 0.04	2.9 ± 0.1	0.76 ± 0.03
1	propanol	0.687	2.44 ± 0.03	194 ± 2	20.06 ± 0.03	3.0 ± 0.1	0.71 ± 0.03
1	butanol	0.674	2.40 ± 0.02	194 ± 2	19.64 ± 0.03	2.7 ± 0.1	0.74 ± 0.02
1	1-pentanol	0.657	2.43 ± 0.02	198 ± 1	19.53 ± 0.02	2.8 ± 0.1	0.72 ± 0.02
1	1-decanol	0.595	2.47 ± 0.03	210 ± 2	19.11 ± 0.03	3.0 ± 0.1	0.70 ± 0.03
22	methanol	0.732	2.58 ± 0.05	56 ± 1	20.93 ± 0.04	3.3 ± 0.2	0.72 ± 0.03
22	ethanol	0.706	2.58 ± 0.05	66 ± 1	19.86 ± 0.02	3.6 ± 0.2	0.69 ± 0.01
22	1-pentanol	0.657	2.51 ± 0.03	71 ± 1	18.93 ± 0.03	3.2 ± 0.2	0.63 ± 0.02
22	1-octanol	0.626	2.51 ± 0.05	70 ± 1	18.43 ± 0.05	3.1 ± 0.3	0.67 ± 0.05
22	1-decanol	0.595	2.44 ± 0.03	69 ± 2	18.25 ± 0.09	2.7 ± 0.3	0.73 ± 0.08
29	methanol	0.732	2.25 ± 0.04	151 ± 2	17.76 ± 0.04	2.6 ± 0.1	0.84 ± 0.04
29	ethanol	0.706	1.96 ± 0.04	289 ± 5	16.57 ± 0.03	2.4 ± 0.1	0.81 ± 0.03
29	butanol	0.674	1.81 ± 0.04	357 ± 7	16.00 ± 0.04	2.2 ± 0.1	0.79 ± 0.04
29	1-pentanol	0.657	1.75 ± 0.03	374 ± 5	15.82 ± 0.03	2.1 ± 0.1	0.81 ± 0.03
29	1-decanol	0.595	1.71 ± 0.02	361 ± 4	15.36 ± 0.02	2.2 ± 0.1	0.78 ± 0.02

[a] Obtained by means of the approximation based on two molecular modes and a linear solvent (eq 1, 2, and 7). Ω_{c1} and Δ_{c1} for one mode fixed at 1600 cm^{-1} and 0.8, respectively. Units as in Table I.

Table III. Comparison of the Solvatochromic Bandshape Parameters for Betaine-1, Betaine-22, and Betaine-29[a]

betaine no.	solvent	Δ_s	A	$h\nu_m$	Ω_{c2}	Δ_{c2}
1	methanol	2.56 ± 0.04	143 ± 2	21.76 ± 0.05	2.94 ± 0.13	0.78 ± 0.04
1	methanol-*O-d*	2.48 ± 0.05	152 ± 3	21.57 ± 0.06	2.58 ± 0.12	0.84 ± 0.05
1	ethanol	2.45 ± 0.04	170 ± 2	20.49 ± 0.04	2.85 ± 0.11	0.77 ± 0.03
1	ethanol-*O-d*	2.39 ± 0.04	175 ± 2	20.33 ± 0.05	2.55 ± 0.11	0.82 ± 0.04
22	methanol	2.58 ± 0.05	56 ± 1	20.93 ± 0.04	3.30 ± 0.18	0.72 ± 0.03
22	methanol-*O-d*	2.53 ± 0.05	58 ± 1	20.82 ± 0.05	3.09 ± 0.17	0.73 ± 0.04
22	ethanol	2.58 ± 0.03	66 ± 1	19.80 ± 0.02	3.6 ± 0.1	0.69 ± 0.01
22	ethanol-*O-d*	2.57 ± 0.04	66 ± 1	19.77 ± 0.03	3.6 ± 0.2	0.66 ± 0.02
29	ethanol	2.03 ± 0.04	287 ± 4	16.62 ± 0.03	2.56 ± 0.09	0.77 ± 0.03
29	ethanol-*O-d*	1.95 ± 0.04	267 ± 4	16.41 ± 0.03	2.32 ± 0.08	0.81 ± 0.03

[a] In methanol and ethanol with the parameter values for the O-deuteriated solvents (same model and units as in Table II).

± 100 cm^{-1} and $\Delta_{c2} \approx 0.8 \pm 0.05$. Also, Ω_{c2} still increases slightly with increasing $(\epsilon_0^{-1}-\epsilon_s^{-1})$ for both betaine-22 and betaine-29, the ranges now being 2700–3300 and 2200–2600 cm^{-1} when going from *m*-decanol to methanol, i.e., the values are higher than for the single-mode analysis. There is no such tendency for Δ_{c2} which is now 0.80 ± 0.02, 0.70 ± 0.02, and 0.75 ± 0.03 for betaine-29, betaine-22, and betaine-1, respectively. These frequency values are close to those typical for O–H stretching in strongly hydrogen bonded systems. However, the corresponding deuterium isotope effects are too small to be fully in line with "pure" proton motion.

(D) The local mode nature was finally checked by comparison of the spectral bandshape parameters for methanol and ethanol with the corresponding parameters for the O-deuteriated solvents. These results are summarized in Table III. The isotope effect for the molecular mode frequency Ω_{c2} is largest for betaine-1, namely 1.14 and 1.12 for methanol and ethanol, respectively. It is 1.10 for betaine-29 in ethanol, 1.07 for betaine-22 in methanol, and virtually absent for betaine-22 in methanol. Significant isotope effects are thus sometimes obtained. They are, however, much smaller than expected for pure O–H stretching which might otherwise be the kind of motion suggested by the values of Ω_{c2}. The isotope effects are furthermore rather specific both as to the solute and the solvent. In spite of the close resemblance of the extracted frequency values to that for O–H stretching, this local motion is therefore likely to represent composite proton and less isotope sensitive motion such as solvent molecular librations. In view of the difference between the different solute and solvent systems, the specific pattern for this motion is furthermore likely to be affected by the solute molecules and to differ from that of the pure solvents.

5. Discussion

The bandshape analysis above substantiates our previous conclusions[48] based on betaine-26 that multiphonon bandshape theory which incorporates both solute molecular motion and the environmental dynamics, provides a powerful theoretical frame for solute–solvent interactions. Betaines are suitable probes in this respect because their intramolecular charge-transfer transitions are well isolated from other transitions, and they are accessible for wide ranges of solvents and display characteristic and strong variations of the bandshape features with the solvent.

Investigations of betaine molecules with different substituents, however, reveal an entangled pattern for the solute–solvent interactions which appears to be quite specific both as to the solvents and as to the betaine substituents. Two groups can be distinguished on the basis of their solute–solvent interaction behavior: (A) betaine-26 and betaine-29, both of which are heavily substituted and (B) unsubstituted or "weakly" substituted betaine-1 and betaine-22. We consider in turn these two groups.

The broad asymmetric solvatochromic absorption band of betaine-26 and betaine-29 for all aprotic solvents is well reproduced by a single high-frequency nuclear Franck–Condon envelope of Gaussian sub-bands. The molecular nature of this mode is strongly corroborated by the constancy of the vibrational frequency around 1600 cm^{-1} for both betaines over wide ranges of the solvent parameter $\epsilon_0^{-1}-\epsilon_s^{-1}$. The value corresponds to structural reorganization in the C–O or C–N bond system which are the ones most likely to be affected by photoexcitation. The coordinate displacements correspond to molecular reorganization energies in the range of 0.1–0.2 eV (0.2–0.25 eV for betaine-26 in alcohol solvents) or real coordinate displacements of 0.03–0.05 Å.

The solvent Gaussian sub-band width for both betaines are well correlated with $\epsilon_0^{-1}-\epsilon_s^{-1}$ for polar aprotic solvents and leaves little or no low-frequency molecular reorganization. In this respect aprotic polar solvents thus behave as structureless dielectric continuous media. This solvent polarity range is also the one over which band maxima for intervalence transitions in binuclear transition-metal complexes and $\epsilon_0^{-1}-\epsilon_s^{-1}$ are correlated.[38–40,42a] At lower values of $\epsilon_0^{-1}-\epsilon_s^{-1}$, Δ_s is approximately constant, indicative of other kinds of solute–solvent interaction such as multipole-, acoustic-, or pseudopotential-like.

Betaine-26 and betaine-29 behave markedly differently in alcohol solvents. Solvent broadening of the vibronic sub-bands for betaine-26 is poorly represented by a Gaussian. The simplest bandshape to provide both a good fit and physically reasonable molecular parameters involves two molecular modes and a cubic correction to the solvent broadening. The latter is representative of significant contributions from high-frequency "tails" in the solvent vibrational dispersion.[48] Moreover, the solvent dependence of the Gaussian component seems to be dominated by hydrophobic interactions rather than by solvent polarity effects. In contrast, the betaine-29 band is always well represented by a single molecular mode and Gaussian solvent broadening. We return to possible reasons for this difference below.

Two-mode analysis leads to somewhat larger molecular vibrational frequencies for the second nuclear coordinate for betaine-29 than for betaine-26. In both cases the frequencies suggest that O–H stretching is a significant element, but the relatively small deuterium isotope effects also indicate that the molecular motion is composite and involves significant contributions from less isotope sensitive solvent motion.

The solute–solvent behavior of betaine-1 and betaine-22 is different from that of betaine-26 and betaine-29. Apart from smaller molar absorbance at the absorption maximum, the steric effects of the two methyl substituents in betaine-22 furthermore seem to be insignificant. Betaine-1 and betaine-22 are insoluble or decompose in most of the aprotic solvents, and data could only be obtained for alcohol solvents and for chloroform. As for betaine-29, the solvatochromic bands were always adequately represented by a single molecular mode and a Gaussian solvent band. Both the solvent band width and the molecular vibrational frequency depend only insignificantly on the solvent as does the coordinate displacement for betaine-22, while some decrease of Δ_c with increasing $\epsilon_0^{-1}-\epsilon_s^{-1}$ is exhibited for betaine-1. This overall pattern is not changed by two-mode analysis, as shown in Tables I and II. The two betaines show somewhat different deuterium isotope effects, these effects being significantly larger for betaine-1 than for betaine-22 in both methanol and ethanol solution.

A clue to the spectral band difference between betaine-26 and the group of the other three betaines for alcohol solvents is perhaps offered by the following consideration. The electron-donating phenolate group in betaine-1 and betaine-22 is directly exposed to the external solvent. The bandshape might therefore largely reflect properties of the undistorted solvent, with due account of certain structural effects, reflected, for example, in the isotope effects. This pattern is largely maintained for betaine-29. The phenolate group is here only weakly screened from the solvent and the structural features of the latter little changed by the methylene chain which has to be in an extended conformation in order to stretch around the phenolate group. On the other hand, the voluminous *tert*-butyl groups in betaine-26 represent much more extended screening in all spatial directions than the methylene chain in betaine-29. Structural properties of hydrogen bonding solvents in particular can therefore be expected to be different from those of the bulk properties to a much larger extent. Hydrophobically induced solvent hydrogen bond network increase[59] would for example be in line with the much greater importance of the high-frequency part of the solvent vibrational spectrum as observed for betaine-26, compared with the other betaines.

Acknowledgment. We thank the Danish Natural Science Research Council for financial support.

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