The O-H Stretching Mode of a Prototypical Photoacid as a Local Dielectric Probe

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1. Solvent-Induced Vibrational Frequency Shifts (Pullin-van der Zwan-Hynes approach)

Numerous perturbative theoretical studies on the solute-solvent couplings affecting vibrational transitions have been reported.[1-8] We base our work on Pullin's derivation of the solvent induced vibrational frequency shifts that uses the Onsager model of a point dipole representing the solute embedded in a spherical cavity surrounded by a continuous solvent medium characterized by the macroscopic dielectric constant.[2] This derivation is closely related to that by Buckingham,[1] except for starting points in defining molecular Hamiltonians, and estimation of dielectric constant for different contributions in the expression for solvent-induced vibrational frequency shift. We extend this approach with the van der Zwan-Hynes relationship [9-11] to describe the time-dependent reaction field induced by the point dipole altered by electronic excitation.[12]

The Morse vibrational potential in the gas phase of the molecular system $V_i(Q)$ can be written as a Taylor expansion along the vibrational coordinate Q as:

$$V_i(Q) = D_i\left(1 - e^{-\alpha_i Q}\right)^2 = \frac{1}{2!}V_i'' Q^2 + \frac{1}{3!}V_i''' Q^3 + \dots \quad , \tag{S1}$$

where $V_i'' = 2D_i\alpha_i^2$, $V_i''' = -6D_i\alpha_i^2$ and D_i is the dissociation energy in the i electronic state. The gas phase electrical dipole moment in the electronic ground ($i = g$) and excited ($i = e$) states is expanded as:

$$\boldsymbol{\mu}_i(Q) = \boldsymbol{\mu}_i^0 + \boldsymbol{\mu}_i' Q + \frac{1}{2!}\boldsymbol{\mu}_i'' Q^2 + \dots \quad , \tag{S2}$$

The dielectric response of the medium surrounding the Onsager cavity with diameter a_i is taken into account with the following expressions for the reaction field $\mathbf{R}_i(Q)$:

$$\mathbf{R}_i(Q) = f_0 \mathbf{\mu}_i^0 + f_\infty \mathbf{\mu}_i' Q + \frac{f_\infty}{2!} \mathbf{\mu}_i'' Q^2 + \dots \qquad , \qquad \text{(S3)}$$

and:

$$f_0 = \frac{1}{a_i^3}\left(\frac{2\varepsilon_0 - 2}{2\varepsilon_0 + 1}\right) \quad , \quad f_\infty = \frac{1}{a_i^3}\left(\frac{2\varepsilon_\infty - 2}{2\varepsilon_\infty + 1}\right) , \quad f_{or} = f_0 - f_\infty \qquad , \qquad \text{(S4)}$$

where the static dielectric constant ε_0 and the dielectric constant at optical frequencies ε_∞ define the magnitude of the time-dependent vibrational frequency shift through the finite nuclear response function of the solvent f_{or}.

This gives the following relationship for the solvent induced vibrational frequency shift for the OH stretching mode Δv_s^g of 2N in the electronic ground state:

$$\frac{\Delta v_s^g}{v_0^g} = \frac{f_\infty}{2V_g''}\left[\left(2\mathbf{\mu}_g'' - \frac{V_g'''}{V_g''}\mathbf{\mu}_g'\right)\bullet\mathbf{\mu}_g^0 + \mathbf{\mu}_g'\bullet\mathbf{\mu}_g'\right] + \frac{f_{or}}{2V_g''}\left[\left(\mathbf{\mu}_g'' - \frac{V_g'''}{V_g''}\mathbf{\mu}_g'\right)\bullet\mathbf{\mu}_g^0\right]$$

$$\text{(S5)}$$

Δv_s^g is defined as the difference between the OH stretching frequencies of 2N in the gas phase and in solution: $\Delta v_s^g = v_0^g - v_s^g$. The quadratic and cubic terms V_g'' and V_g''' originate from the Taylor expansion of the OH stretching mode potential of gas phase 2N in the S_0-state, whereas $\mathbf{\mu}_g^0$ is the permanent dipole, and $\mathbf{\mu}_g'$ and $\mathbf{\mu}_g''$ are the linear and quadratic Taylor expansion terms of $\mathbf{\mu}_g^0$ along the OH stretching coordinate in the electronic ground state. A similar equation holds for the time-dependent solvent induced vibrational frequency shift for the OH stretching mode $\Delta v_s^e(t)$:

$$\frac{\Delta v_s^e(t)}{v_0^e} = \frac{f_\infty}{2V_e''}\left[\left(2\mathbf{\mu}_e'' - \frac{V_e'''}{V_e''}\mathbf{\mu}_e'\right)\bullet\mathbf{\mu}_e^0 + \mathbf{\mu}_e'\bullet\mathbf{\mu}_e'\right] + \frac{f_{or}}{2V_e''}\left[\left(\mathbf{\mu}_e'' - \frac{V_e'''}{V_e''}\mathbf{\mu}_e'\right)\bullet\mathbf{\mu}(t)\right]$$

$$\text{(S6)}$$

Here the time-dependent dipole moment $\mathbf{\mu}(t)$ takes into account the finite dielectric response of the solvent, by a time dependent change from $\mathbf{\mu}_g^0$ to $\mathbf{\mu}_e^0$:[12]

$$\mathbf{\mu}(t) = \mathbf{\mu}_g^0\left[1 - z(t)\right] + \mathbf{\mu}_e^0\, z(t) \qquad , \qquad \text{(S7)}$$

where μ_e^0 and μ_g^0 are the permanent dipole moments in the electronic excited and ground states, and $z(t)$ is the solvation coordinate changing from $z(t=0)=0$ at the initial solvent configuration and $z(t=\infty)=1$, when the equilibrium solvent configuration for 2N in the S_1-state has been reached. The solvation correlation function $C(t)$ is then connected to the time-dependent solvation coordinate $z(t)$:[9-11]

$$C(t) = \frac{\Delta v_S^e(t) - \Delta v_S^e(t=\infty)}{\Delta v_S^e(t=0) - \Delta v_S^e(t=\infty)} = 1 - z(t) \qquad . \qquad (S8)$$

Using Eq. (S4), Eqs. (S5) and (S6) can be rewritten into the following expressions:

$$\Delta v_s^i = S_i F_0 + C_i F_\infty \qquad , \qquad (S9a)$$

$$S_i = \frac{1}{2V_i''} \left[\left(\mu_i'' - \frac{V_i'''}{V_i''} \mu_i' \right) \bullet \mu_i^0 \right] \frac{v_0^i}{a_i^3} \qquad , \qquad (S9b)$$

$$C_i = \frac{1}{2V_i''} \left[\mu_i'' \bullet \mu_i^0 + \mu_i' \bullet \mu_i' \right] \frac{v_0^i}{a_i^3} \qquad . \qquad (S9c)$$

where $F_0 = \left(\frac{2\varepsilon_0 - 2}{2\varepsilon_0 + 1} \right)$ and $F_\infty = \left(\frac{2\varepsilon_\infty - 2}{2\varepsilon_\infty + 1} \right)$. Whereas the static dielectric constant ε_0 varies from 1.8 in n-hexane to 10.4 for 1,2-dichloroethane, the dielectric constant at optical frequencies ε_∞ remains about the same. We confirmed this by measuring the group delay for femtosecond pulses tuned at 3 μm in the solvents used in this study, deriving the refractive index n, and calculating $\varepsilon_\infty = n^2$. As a result, the observed solvent-dependent vibrational frequency shift of 2N in electronic state i can be approximated as a linear function of

$F_0 = \dfrac{2\varepsilon_0 - 2}{2\varepsilon_0 + 1}$ with a slope S_i governed by molecular parameters V_i'', V_i''', μ_i^0, μ_i' and μ_i'', as

well as the Onsager cavity size a_i, expressed in the main text as Eq. (1).

2. Methods and Instrumentation

2-Naphthol (99%, abbreviated as 2N), n-Hexane, cyclohexane, C_2Cl_4, $CHCl_3$, CH_2Cl_2 and 1,2-dichloroethane (Reagent Plus ≥99%) were all purchased from Aldrich. The solvents were then dried over molecular sieves and 2N was purified by recrystallization. The IR-spectra of the solutions were measured with a Varian 640 FT-IR spectrometer. Although none of the

solvents used in this study showed any characteristic water bands in their respective IR spectra, a measurement was performed in order to verify that possible minute amounts of water contamination had no bearing on our experiments. For this, we measured the FT-IR spectra of 2N in CH_2Cl_2 to which known quantities of water were added. We did not observe any change in either frequency or bandwidth of the band corresponding to the free OH stretch of 2N. This is not so surprising given that the addition of a base to a nonpolar solvent is known to deplete the free OH band without modifying its properties and results in the appearance of a new red-shifted and broadened band attributable to the hydrogen bonded complex with the base.[13] Unfortunately, at high water concentrations, such as those needed to observe this red-shifted band, disambiguation of 2N-water complexes with water dimers for a proper characterisation becomes problematic. It thus appears that the complexation constant between water and 2N is very low and as such, possible water contamination will not affect the measurements.

Steady-state electronic absorption spectra were recorded with a double-beam UV-vis spectrometer (Perkin-Elmer), and emission spectra were recorded with a spectrofluorometer (Spex Fluorolog). As self-association was found to occur in the non-polar solvents such as n-hexane or cyclohexane, the concentrations were kept as low as 20 mM. We observe a significantly lower emission quantum yield and a deviation of the emission band shape in $CHCl_3$ and in C_2Cl_4 (whereas major fluorescence quenching was even observed in CCl_4), preventing a precise determination of the electronic Stokes shift in these solvents. This effect, occurring on much longer time scales than we discuss here, are tentatively ascribed to a special exciplex interaction between these halocarbon solvents and 2N in the S_1-state, thereby shortening of the electronic excited state lifetime.

Ultrafast infrared spectra were recorded using an experimental set-up described previously.[14] Electronic excitation of 2N was achieved with pulses (3 µJ, 50 fs) generated by sum frequency mixing of the fundamental of a 1 kHz amplified Ti:sapphire laser (Tsunami oscillator with Spitfire Pro regenerative and booster amplifier stages, Spectra Physics) and visible pulses generated by a noncollinear optical parametric amplifier (NOPA). The excitation wavelength was tuned to the lowest energy peak of the ^1L_b transition for each solvent thereby ensuring minimal excess energy (328 to 330 nm). After passing an optical delay line, the pump pulses were focused onto the sample with a beam diameter of approximately 200 µm. Tunable mid-infrared pulses were generated by a double-pass optical parametric amplification followed by difference frequency mixing of signal and idler. The probe and reference pulses were obtained using reflections from a ZnSe wedge, and focused

onto the sample by means of an off-axis parabolic mirror (focal diameter 150 μm). The probe and reference pulses were dispersed in a polychromator (8-10 cm^{-1} resolution) and spectrally resolved absorbance changes were recorded simultaneously for each shot using a liquid nitrogen cooled HgCdTe double array detector (2x31 pixels). Pump-probe measurements were recorded under magic angle conditions between UV-pump and IR-probe. The time resolution was determined to be 150 fs based on the cross-correlation between the UV-pump and IR-probe pulses measured in a ZnSe semiconductor placed at the sample position. A peristaltic pump was used to circulate the sample through a flow cell (1 mm thick CaF2 windows separated by a 300 μm thick teflon spacer), to guarantee that a new sample volume was excited for every laser shot.

A *b initio* calculations were performed by using *Gaussian 09.*[15] The ground state geometry was optimized at the B3LYP/TZVP level, while the excited state geometry was optimized by TDDFT(B3LYP/TZVP), in either the gas phase, or embedded in a dielectric continuum. The same level of ab initio methods was applied for calculations of dipole moments, solvation energy, and normal mode analysis in both ground or ^1L_b excited states. The solvation energy calculations were performed based on the PCM model, after the geometry was optimized in the dielectric continuum. We note that the TDDFT method switches the order of the ^1L_a and ^1L_b excited states for both cis-2N and trans-2N. However, the states can be readily identified due to their distinct symmetry. We therefore compute all the molecular parameters, including dipole moments, and first and second dipole derivatives, for the ^1L_b excited state as described at the TDDFT level. The first derivatives of dipole moment in electronic state $i = e$ or g, with respect to the k-th normal mode ($\mu'_{i,k} \equiv \dfrac{\partial \mu_{i,k}}{\partial Q_{i,k}}$) were calculated by using the keyword of 'IOP(7/33=1)' as implemented in *Gaussian 09.* The second derivatives (i.e. the first derivatives of $\mu'_{i,k} \equiv \dfrac{\partial \mu_{i,k}}{\partial Q_{i,k}}$ with respect to the k-th normal coordinate) were calculated, as follows:

$$\mu''_{i,k} = \frac{\partial \mu'_{i,k}}{\partial Q_{i,k}} = \sum_j \frac{\partial \mu'_{i,k}}{\partial x_j} l_{jk} \qquad , \qquad (S9)$$

where l_{jk} is the transformation matrix from Cartesian to normal mode coordinates, and

$\dfrac{\partial \mu'_{i,k}}{\partial x_j}$ is calculated numerically by finite differences:

$$\frac{\partial \mu'_{i,k}}{\partial x_j} = \frac{\mu'_{i,k}\left(x_j + \delta x_j\right) - \mu'_{i,k}\left(x_j - \delta x_j\right)}{2\delta x_j} \qquad . \qquad \text{(S10)}$$

The harmonic and anharmonic force constants were calculated by using the keyword of 'freq(=anharmonic)' as implemented in *Gaussian 09*,[15] using the HF/6-31g method for the ground state, and using the CIS/6-31g method for the ^1L_b excited state.

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