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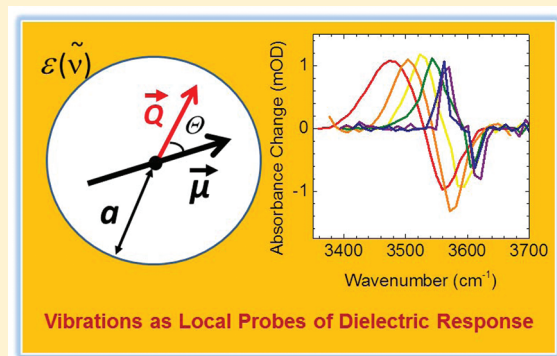
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 Supporting Information

ABSTRACT: We investigate the OH stretch vibrational frequency shifts of a prototype photoacid, 2-naphthol (2N), when dissolved in solvents of low polarity. We combine femtosecond mid-infrared spectroscopy and a theoretical model based on the Pullin–van der Zwan–Hynes perturbative approach to explore vibrational solvatochromic effects in the ground S_0 and the first electronically excited 1L_b states. The model is parametrized using density functional theory (DFT), at the B3LYP/TZVP and TD-B3LYP/TZVP levels for the 2N chromophore in the S_0 and 1L_b states, respectively. From the agreement between experiment and theory we conclude that vibrational solvatochromic effects are dominated by the instantaneous dielectric response of the solvent, while time-dependent nuclear rearrangements are of secondary importance.



Coupling between the electronic and nuclear degrees of freedom of solute and solvent results when a molecule is embedded in a solvent.¹ Traditional studies of solvation have utilized UV–vis electronic spectroscopy,^{2–5} where changes in solute–solvent couplings caused by electronic excitation can be deduced from solvatochromic frequency shifts of the electronic absorption or emission bands, which are typically on the order of several hundreds of wavenumbers. Solute–solvent couplings also affect the frequency position of the vibrations of a solute. These solvatochromic frequency shifts are typically 2 orders of magnitude smaller. In theory, the solute–solvent couplings have been analyzed by the Onsager solvation model where the solute is represented by a point dipole embedded in a spherical Onsager cavity interacting with a dielectric continuum representing the surrounding solvent molecules.^{6,7} For weakly hydrogen-bonded molecular systems in the electronic ground state, the experimental vibrational frequency shifts have been linked to perturbation theory of the solvated oscillator potential.^{8–10} In contrast, for electronic excited states, such a direct link between observed frequency shifts and molecular properties has yet to be established. In this paper, we will provide a first example where vibrational solvatochromic shifts and perturbation theory will be connected to solute properties governing these in both electronic ground and first excited states.

Realizing that solvent rearrangements caused by the electronic charge redistribution of the solute proceed on time scales characterized by the dielectric relaxation of the solvent,^{11–13} theoretical approaches, most notably the van der Zwan–Hynes relation,¹⁴ have incorporated the time-dependent dielectric response of the

solvent to take this into account. Whereas the important van der Zwan–Hynes relation has successfully been used in a large number of solvation studies of dye molecules exploring transient electronic absorption and emission signals,^{15–17} it has only been applied a few times to describe time-dependent vibrational frequency shifts,^{18–20} without, however, quantifying the underlying molecular parameters governing these shifts.

We investigate the solvation effects on the OH stretching mode of 2-naphthol (2N, see Figure 1), in a collection of nonpolar or weakly polar solvents, where explicit hydrogen bonding between the 2N solute and the solvent is understood not to take place. 2N is a prototype photoacid, which is several orders of magnitude more acidic in the electronically excited state. This property has enabled photoinduced proton transfer studies in protic solvents.^{21–23} IR spectroscopy of the OH stretching mode can provide key insight into hydrogen-bonding properties of 2N in the electronically excited state and may reveal the underlying mechanisms of photoacidity. Solvatochromism of electronic or vibrational transitions of hydrogen-bonded 2N has been investigated with descriptions based on empirical linear free energy relationships^{24,25} using the Kamlet–Taft approach.^{26,27} To understand OH stretching frequency shifts of hydrogen-bonded 2N on a microscopic level, however, one first has to characterize its behavior in solvents without specific interactions. To that effect, we present an experimental and theoretical study of the OH stretching mode of 2N in solvents ranging from *n*-hexane to 1,

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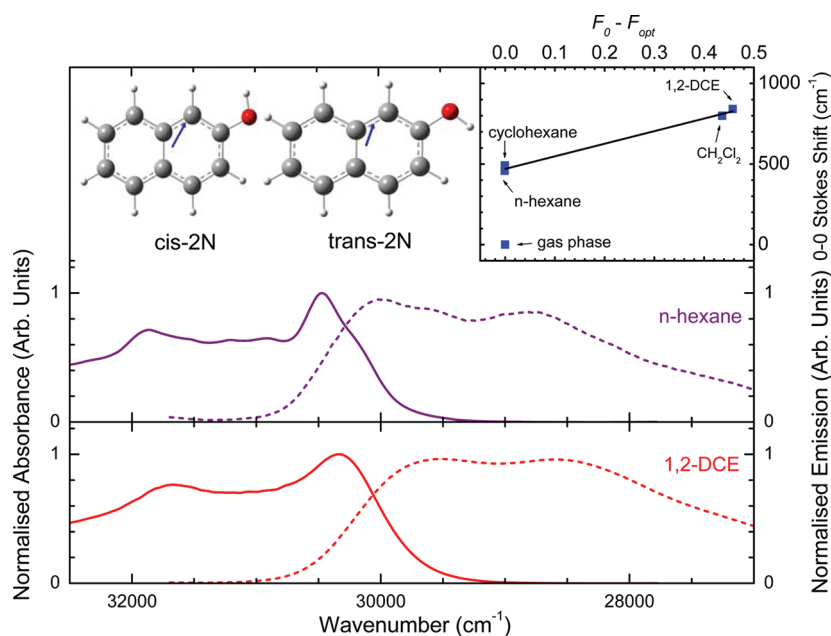


Figure 1. UV/vis absorption and emission spectra of 2N in *n*-hexane and 1,2-dichloroethane (1,2-DCE). The upper right inset shows the Lippert–Mataga plot of the 0–0 Stokes shift between the electronic absorption and emission origin transitions as function of $F_0 - F_{\text{opt}} = (2\epsilon_0 - 2)/(2\epsilon_0 + 1) - (2\epsilon_\infty - 2)/(2\epsilon_\infty + 1)$, from which $\Delta\mu^0 = \mu_e^0 - \mu_g^0 = 0.61 \pm 0.05$ D can be derived. The molecular structures of *cis*-2N and *trans*-2N are depicted as well with the electronic S_0 – 1L_b transition dipole moment shown as a blue arrow, with oscillator strength $f = 0.0150$ (*cis*-2N) and $f = 0.0097$ (*trans*-2N).

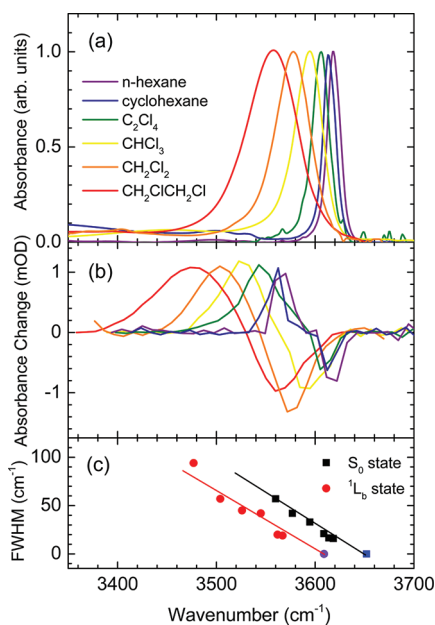


Figure 2. (a) Steady-state IR spectra of 2N; (b) transient IR spectra of 2N measured at 10 ps pulse delay; (c) correlation between the solvent-dependent frequency shift and transition bandwidth of 2N in the S_0 (black squares) and 1L_b (red dots) electronic states, including gas phase values for 2N (blue square and purple dot, respectively).

2-dichloroethane. A solvent-dependent frequency downshift and broadening of the band was observed, as well as a small transient frequency downshift in the most polar solvent. Using a perturbative approach to take into account the solvent-induced OH stretching frequency shifts, we show that the ratio of OH stretching frequencies of 2N in the S_0 and S_1 states is governed

by the solvent dielectric constant and by a factor comprising the electrical dipole moment and its first and second derivatives as well as the vibrational force constant and cubic anharmonicity. This approach is further validated by quantum chemical calculations of these molecular parameters of 2N in both the S_0 and S_1 states. A quantitative agreement between theoretically predicted and experimentally observed vibrational frequency shifts demonstrates the potential of the method for using a vibrational marker as a local dielectric probe by monitoring vibrational frequency shifts.

The electronic S_0 – S_1 transition dipole moment of 2N is polarized along the long axis of the molecule (the S_1 state is of 1L_b nature using Platt's notation²⁸). Figure 1 shows the associated UV/vis electronic absorption and emission spectra of this transition in *n*-hexane and 1,2-dichloroethane. A frequency red-shift of about 250 cm^{-1} occurs when going from gas phase 2N^{29–31} to nonpolar *n*-hexane. A further frequency shift of the electronic absorption origin of only 140 cm^{-1} is then observed from *n*-hexane ($\epsilon_0 = 1.88$) to 1,2-dichloroethane ($\epsilon_0 = 10.1$). An analysis of the observed Stokes shift between the electronic absorption and emission of 2N in a larger collection of solvents using the Lippert–Mataga expression^{2,3} has shown that the increase in electrical dipole upon electronic transition is of moderate size: 0.5 D (see inset of Figure 1).³²

As evidenced from Figure 2a showing the linear ground-state IR spectra, an increase in the magnitude of solute–solvent interactions upon increasing solvent polarity clearly results in a frequency red-shift and broader spectral width. A linear correlation between the solvent-dependent OH stretching frequency and the bandwidth exists (Figure 2c), which even fits the known value of gas phase 2N.^{29,30} For hydrogen-bonded molecular systems such a correlation has been reported before.³³ This simple correlation also holds for uncomplexed 2N, which is

surprising given the amount of experimental and theoretical findings accumulated on ultrafast dynamics of OH stretching modes in the last two decades.^{34–37} These studies decisively established that many mechanisms, ranging from the solute vibrational population lifetime, the solute vibrational mode anharmonicity, as well as the magnitude and time scale of the fluctuating solvent motions, contribute to the line broadening.

The transient IR spectra recorded at a pulse delay of 10 ps are shown in Figure 2b. They are characterized by a bleach at the OH stretching frequency of ground-state 2N and an increase in absorbance at a lower frequency marking the frequency position of the OH stretching mode of 2N in the S_1 state. This signal appears within the time resolution of 150 fs, and, apart from 1,2-dichloroethane (vide infra), no further spectral rearrangements were observed at longer pulse delays. As ground-state bleach and excited-state absorption signals partially overlap, a line shape fitting routine was applied to the transient spectra. Interestingly we find that the resulting values, depicted in Figure 2c as red dots, also follow a linear correlation between the OH stretching frequency and bandwidth for electronically excited 2N, albeit with a different slope than for 2N in the S_0 state. Extrapolation leads to the value for the OH stretching frequency of gas phase 2N, shown as the purple dot, in accordance with the reported value.^{30,38}

In contrast to traditional views,³ electronic excitation of photoacids is now understood to involve only minor electronic rearrangement from the OH group to the aromatic ring.³⁹ Electronic excitation of gas phase 2N to the 1L_b state thus only induces small changes in electron density of the OH group of 2N.^{39–41} In the gas phase, one distinguishes two possible conformers of 2N, *cis* and *trans*, where these designations represent the relative orientation of the OH group with respect to the naphthalene ring (Figure 1).⁴² For *cis*-2N, the intramolecular electronic charge redistribution is responsible for the small increase of the electrical dipole moment from 1.01 D in the S_0 state to 1.17 D in the S_1 state.³¹ Similar values have been deduced for 2N in room temperature solution,^{32,43} where, because of the small energy difference between the *cis* and *trans* conformers, likely an ensemble average of *cis*-2N and *trans*-2N exists. The experimentally observed OH stretching frequency shift for *cis*-2N from 3652 cm^{-1} (S_0) to 3609 cm^{-1} (S_1)^{30,38} reflects such a moderate weakening of the OH bond. However, such small frequency shifts may also be due to a change in the anharmonicity of the OH stretching potential. To discount such an effect, we have performed quantum chemical calculations of *cis*-2N and *trans*-2N in both S_0 and S_1 states. From this analysis we learn that the gas phase value for the anharmonic shift $\omega_e\chi_e$, defined as $\omega_e\chi_e = \nu_{\text{OH}}(\nu = 0 \rightarrow \nu = 1) - \nu_{\text{OH}}(\nu = 0 \rightarrow \nu = 2)/2$, remains basically unaffected upon electronic excitation. Furthermore, we calculate that embedding 2N in solvents such as those studied here does not change the anharmonicity significantly compared to the gas phase value. We were able to verify this for the electronic ground state by measuring the vibrational overtone of the OH stretch in the different solvents employed in this study. Only very small anharmonicity changes were recorded, similar to the previously reported data on the OH stretching mode of phenol.⁴⁴ As such, we conclude that the small frequency shift of 43 cm^{-1} for *cis*-2N (similar values are expected for *trans*-2N) upon electronic excitation is not caused by a mere change in anharmonicity of the OH stretching mode, but instead is predominantly caused by electronic charge rearrangements.

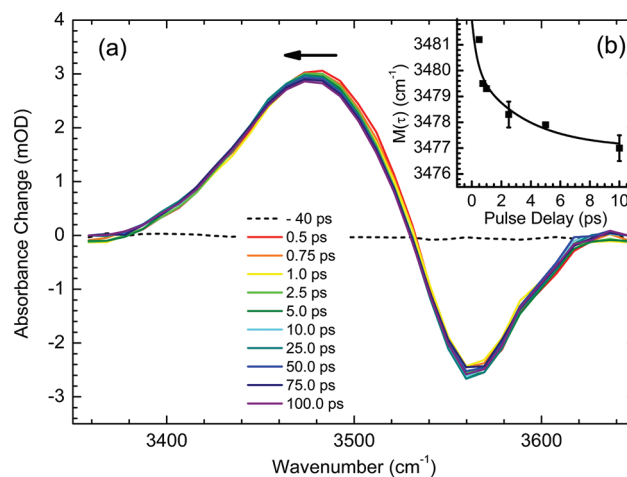


Figure 3. (a) Transient IR spectra of the OH stretching mode of 2N in 1,2-dichloroethane; (b) time-dependent frequency shift of the OH stretching mode showing a small delayed downshift at early pulse delays. Biexponential fitting parameters of this shift were taken without change from Table 2 of ref 45 with $A_1 = 0.34$ and $\tau_1 = 0.26$ ps, $A_2 = 0.66$ and $\tau_2 = 3.5$ ps.

The larger frequency shifts observed in solution should thus originate from solute–solvent interactions. A proper characterization needs to distinguish between the instantaneous electronic dielectric response and the finite nuclear contributions of the solvent. For most solvents studied, we did not detect further frequency shifts reflecting solvent shell rearrangements after the initial appearance of the OH stretching band of 2N in the S_1 state upon electronic excitation. Only in the more polar 1,2-dichloroethane is a time-dependent frequency downshift apparent (Figure 3a). This indicates that the magnitude of such shifts in solvents of lower polarity is even smaller and therefore below our experimental frequency resolution. It is interesting to note that the temporal behavior of the OH stretching frequency downshift observed for 2N in 1,2-dichloroethane with femtosecond infrared spectroscopy (Figure 3b) is identical to the transient shifts of electronic bands observed with femtosecond UV–vis electronic pump–probe experiments on 8-hydroxy-1,3,6-trisdimethylsulfonamide (HPTA) in the same solvent,⁴⁵ a molecule with much larger dipole moments in both electronic ground and excited states than 2N. As we photoexcite 2N around the electronic origin, vibrational cooling effects to the transient vibrational frequency shift within the S_1 state are expected to be negligible. In fact, transient frequency upshifts are expected to occur for vibrational cooling,^{46,47} whereas we observe a frequency downshift. Since we observe a single OH stretching resonance in all solvents used, exchange within the distribution of conformers with different rotation angles must be much faster than 300 fs. As a result the mechanism underlying the observed transient OH stretching frequency can be assigned to solvent shell rearrangement dynamics. In 1,2-dichloroethane the observed OH stretching frequency shift upon electronic excitation of 2N is 79 cm^{-1} . This amounts to a solvation-induced component of 36 cm^{-1} after taking into account the observed frequency shift observed in the gas phase. In comparison, the solvent shell rearrangement due to the non-instantaneous nuclear component of the dielectric response only leads to a time-dependent shift of 4 cm^{-1} . We can thus confidently conclude that the contribution from the (instantaneous) electronic part of the dielectric response dominates the solvent-induced

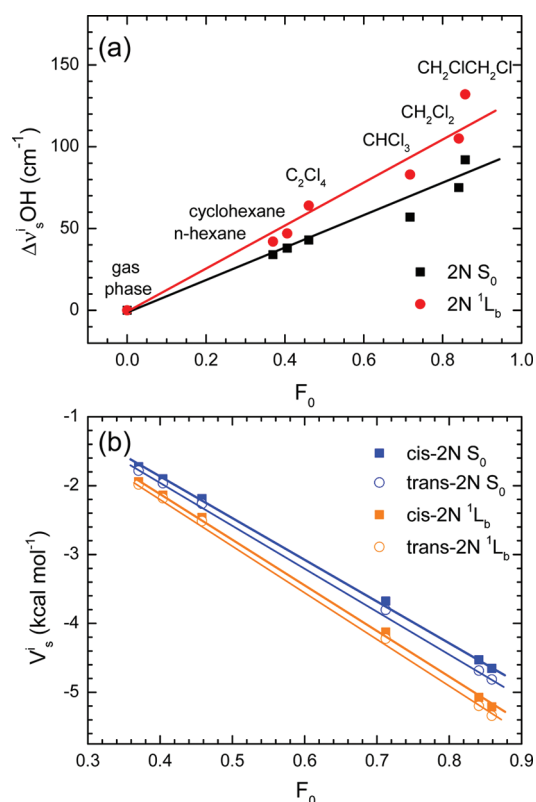


Figure 4. (a) Solvent-dependent vibrational frequency shift $\Delta\nu_s^i = \nu_0^i - \nu_s^i$ as function of F_0 measured for 2N in the S_0 and 1L_b states; (b) solvation energies of *cis*-2N and *trans*-2N as function of F_0 calculated at the B3LYP/TZVP level for the S_0 state and at the TD-B3LYP/TZVP level for the 1L_b state.

OH stretching frequency shifts of 2N in the solvents used in this study.

We analyze the observed solvent-induced OH stretching frequency shifts of 2N with perturbation theory for vibrational spectroscopy,⁷ which has been refined with the van der Zwan–Hynes relation to account for nuclear rearrangements of the solvent, in a similar fashion as applied before in the analysis of solvation effects on the C=O stretching mode of coumarin 102 in $CHCl_3$ upon electronic excitation,^{18,19} and the C≡O stretching modes of $[Re(R_2-bpy)(CO)_3Cl]$ ($R = COOH$ or $COOEt$; $bpy = 2,2'$ -bipyridine) complexes.²⁰ A direct link between the observed OH stretching frequency shifts in the electronic ground and excited states with molecular parameters can thus be made (see Supporting Information). Quantum chemical calculations provide an alternate method to achieve this, and while it was previously impossible to do this for the coumarin 102,^{18,19} and $[Re(R_2-bpy)(CO)_3Cl]$ ($R = COOH$ or $COOEt$; $bpy = 2,2'$ -bipyridine) complexes,²⁰ we now show that for 2N embedded in a solvent dielectric medium these molecular parameters can satisfactorily be calculated at the B3LYP/TZVP (2N in S_0) and TD-B3LYP/TZVP (2N in S_1) levels.

From our steady-state and transient IR spectra recorded at long pulse delays, we observe a linear dependence of the solvent-induced vibrational frequency shift of 2N in the S_0 state $\Delta\nu_s^g$ and of 2N in the 1L_b state $\Delta\nu_s^e(t = \infty)$ as a function of the solvent dielectric function $F_0 = (2\epsilon_0 - 2)/(2\epsilon_0 + 1)$ (Figure 4a). The experimental ratio for the slopes S_e/S_g of these curves is found to be 1.23 ± 0.05 . This linear dependence can be rationalized with

Table 1. Calculated Parameters of *cis*-2N and *trans*-2N in the S_0 and 1L_b States

term	<i>cis</i> -2N 1L_b	<i>cis</i> -2N S_0	<i>trans</i> -2N 1L_b	<i>trans</i> -2N S_0
$\mu''_i \cdot \mu_i^0$ ($D^2 A^{-2} amu^{-1}$)	-1.2257	-0.8876	-2.0618	-1.5944
$\mu'_i \cdot \mu_i^0$ ($D^2 A^{-1} amu^{-1/2}$)	1.0651	0.6820	1.5468	1.4097
$\mu''_i \cdot \mu'_i$ ($D^2 A^{-2} amu^{-1}$)	1.9995	1.4872	2.3046	1.9135
V'''_i/V''_i ($A^{-1} amu^{-1/2}$)	-7.1234	-7.1660	-7.1295	-7.1714
a_i (Å)	1.1762	1.1260	1.3071	1.4374
C_i (cm ⁻¹)	4.4674	3.8981	1.0214	0.9951
S_i (cm ⁻¹)	91.82	65.00	94.29	66.38
S_e/S_g	1.4126		1.4205	

the Pullin–van der Zwan–Hynes approach for solvent-dependent vibrational frequency shifts, assuming solvent dielectric relaxation has fully taken place, i.e., at long pulse delays (see Supporting Information). We derive that the slope ratio S_e/S_g can be written as

$$\frac{S_e}{S_g} = \frac{\left(\mu''_e - \frac{V'''_e}{V''_e} \mu'_e\right) \cdot \mu_e^0}{\left(\mu''_g - \frac{V'''_g}{V''_g} \mu'_g\right) \cdot \mu_g^0} \frac{\nu_0^g}{\nu_0^e} \left(\frac{a_g}{a_e}\right)^3 \quad (1)$$

Here the quadratic and cubic terms V''_i and V'''_i come from the Taylor expansion of the OH stretching mode potential, whereas μ_i^0 is the permanent dipole, and μ'_i and μ''_i are, respectively, the linear and quadratic Taylor expansion terms of the electrical dipole along the OH stretching coordinate, and ν_0^i is the OH stretching transition frequency of gas phase 2N in the electronic state $i = g$ or e . We calculate S_e/S_g using the results of our quantum chemical calculations (Table 1), with the experimental values for $\nu_0^{29,30}$. Given that the Onsager solvation energy V_s^i of 2N in the electronic state i is expressed as

$$V_s^i = -\frac{\mu_i^2}{a_i^3} \frac{F_0}{2} \quad (2)$$

we calculated the solvation energies at the B3LYP/TZVP (2N in S_0) and TD-B3LYP/TZVP (2N in S_1) levels (see Figure 4b). From the slopes of these curves we can derive the values of a_e/a_g for *cis*-2N and *trans*-2N (Table 1). It turns out that the ratios $(a_g/a_e)^3$ and ν_0^g/ν_0^e are small correction terms, and S_e/S_g is strongly governed by the factor containing the gas phase dipole moment terms. We estimate the in-products $\mu''_i \cdot \mu_i^0$ and $\mu'_i \cdot \mu_i^0$ as well as the ratio between cubic anharmonic and quadratic harmonic Taylor expansion terms V'''_i/V''_i (Table 1). We find that the $-(V'''_e/V''_e)\mu'_e \cdot \mu_e^0$ term strongly dominates while $\mu''_i \cdot \mu_i^0$ provides a significant correction to the total value for the slope for both the S_0 and the S_1 states of *cis*-2N and *trans*-2N. The sum of the two terms has a positive value for *cis*-2N and *trans*-2N, in accordance with the observed frequency downshift of the OH stretching band for solution phase 2N. For *cis*-2N we calculate $S_e/S_g = 1.4126$ and for *trans*-2N $S_e/S_g = 1.4205$. Since the energy difference between *cis*-2N and *trans*-2N and the barrier between these two conformers is less than kT , we obtain an average calculated value for 2N of $S_e/S_g = 1.4166$, which is somewhat larger than the experimentally determined value. While the calculated values for the intercept C_i are only a few wavenumbers for both *cis*-2N and *trans*-2N, smaller than the

experimental error, the calculated values for the slope S_i of the two rotamers in the two electronic states are about 10–20% less than the experimental values. A reason for this may be the neglect of the solute polarizability correction in the description used. While we have not found a value for the polarizability of 2N, a comparison with the known value for naphthalene suggests that a deviation of 10–20% is reasonable.

In conclusion, we have measured the solvent-induced frequency shifts of the OH stretching mode of 2-naphthol (2N) in solvents ranging from *n*-hexane to 1,2-dichloroethane, where no solute–solvent hydrogen bond interactions are understood to occur. The remarkably large OH stretching frequency shifts of up to 96 cm^{−1} in the S_0 state and 130 cm^{−1} in the 1L_b state in the most polar solvent 1,2-dichloroethane from the respective gas phase values can be rationalized with perturbation theory of solvent-induced vibrational frequency shifts based on the model of a point dipole inside an Onsager cavity embedded in a dielectric continuum. Whereas for previous applications of this approach an understanding of the underlying molecular quantities governing the observed frequency shifts in electronic excited states has been impossible, we demonstrate in the current work on 2N that these can be determined using (TD-)DFT quantum chemical calculations. The comparison of the values of these molecular quantities for 2N in the S_0 and the 1L_b states shows that electronic excitation only has minor effects on the electronic structure of the photoacid.

With this result we show that the combination of an experimental and theoretical analysis of vibrational frequency shifts of a molecular probe to monitor local dielectric properties can now be explored on different types of molecular vibrations located on functional units inside a broad range of biomolecular systems. Here the molecular probes may even be embedded in biomolecular systems undergoing structural changes, e.g., in the case of protein folding. The larger anharmonicity of OH and NH stretching modes typically causes larger solvent-induced frequency shifts than for other molecular vibrations. We show that the perturbative approach still holds for OH/NH stretching vibrations for weakly polar media, provided no specific interactions such as hydrogen bonding occur. Refinement of the method for hydrogen-bonded OH/NH stretching vibrations, where the OH/NH stretching potentials are significantly altered from the unbound case, will expand the applicability of the method. Further refinement may also result from a detailed analysis of the comparison of the deviations of the vibrational frequency shifts in the electronic ground and excited states from the linear dependence with respect to F_0 . With this comparison higher order effects such as a dependence of the solute dipole on the solvent polarizability or specific interactions in halocarbon solvents^{48,49} may be traced down.

■ ASSOCIATED CONTENT

S Supporting Information. Discussion of solvent-induced vibrational frequency shifts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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