

# Ultrafast IR Spectroscopy of O-H Stretching Modes in 2-Naphthol-Acetonitrile Photoacid-Base Complexes

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**Abstract:** The O-H stretching mode is a direct hydrogen-bond probe. In a combined femtosecond IR spectroscopic and quantum chemical approach, we demonstrate how this local marker directly reflects charge distribution changes induced in photoexcited photoacid-base complexes.

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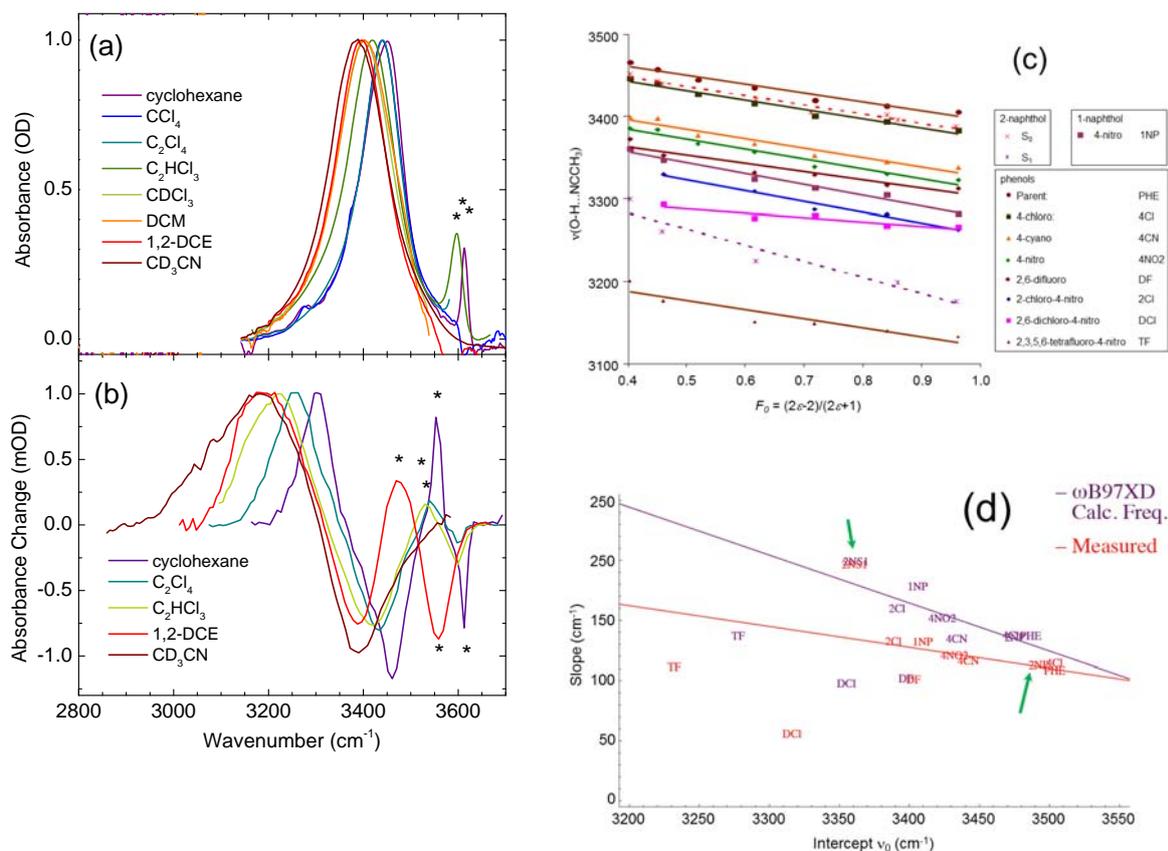
Photoacids are typically organic aromatic alcohols or protonated amines that exhibit a strong change in acidity (proton donating capability) upon electronic excitation. For example, the prototypical photoacid 2-naphthol (2N) undergoes a dramatic change of  $pK_a$  upon  $S_1 \leftarrow S_0$  photoexcitation, shifting from  $pK_a=9$  in the  $S_0$  state to  $pK_a=3$  in the  $S_1$  state. The  $pK_a$  values can be used to predict ultrafast proton transfer rates to accepting bases under aqueous conditions by using Marcus-type relationships that correlate free energy changes and reactivity according to the Förster cycle [1]. This has been supported by measurements of proton-to-solvent transfer rates and data on steady-state electronic absorption and emission spectra. Such considerations have also led to the understanding that an additional electronic excited-state level crossing is involved for 1-naphthol (1N), only recently probed to occur with a 60 fs time constant [2]. To further characterize the electronic excited states of photoacid-base complexes, we report here the ultrafast probing of O-H stretching modes. The correlation between the O-H stretching frequency and the H-bond distance is well established [3]. Stronger H-bonds tend to have shorter H-bond distances and larger red-shifted frequencies of the H-stretching oscillator. However, it has also been well understood that the differences in frequency values is caused by electrostatic interactions imposed by the surrounding solvent molecules, leading to spectral line broadening as exemplified by the O-H stretching band of water under ambient conditions.

Here, we focus on the study of O-H stretching modes of photoacid molecules in hydrogen-bonded complexes by analyzing the 2N-CH<sub>3</sub>CN model system. We combine ultrafast UV/IR pump-probe spectroscopy with ab-initio quantum chemistry calculations to parametrize the Pullin model of solvent-induced vibrational frequency shifts [4]. Calculations were performed with GAUSSIAN09, using density functional theory at the B3LYP/TZVP and  $\omega$ B97XD/TZVP levels of theory and excited state calculations at the TD-DFT level with implicit solvation using IEF-PCM. The complex exhibits a moderate solvent-induced vibrational frequency shift for the O-H stretching mode when changing the surrounding solvent from nonpolar cyclohexane to polar acetonitrile. With O-H stretching frequencies well-above 3000 cm<sup>-1</sup>, the observed O-H stretching bands reflect intramolecular charge distributions of the photoacid-base complexes as well as couplings with the surrounding solvent of a given polarity, while vibrational couplings to fingerprint combination/overtone bands as well as anharmonic couplings with H-bond modulation modes can be neglected. Figure 1a,b shows the steady-state and transient IR spectra of 2N-CH<sub>3</sub>CN complexes in various solvents after UV photoexcitation at 330 nm. Upon promotion to the  $S_1$ -state, the O-H stretching frequency downshifts primarily due to the underlying electronic excitation while the solvent rearrangements in the (sub)picosecond time scale have only a minor additional contribution [4]. The frequency shift exhibits a linear dependence on  $F_0 = (2\epsilon_0 - 2)/(2\epsilon_0 + 1)$ , where  $\epsilon_0$  is the static dielectric constant of the solvent (Fig. 1c). This is in line with our previous findings of uncomplexed 2N and 1N, which validates treating the 2N-CH<sub>3</sub>CN complexes as a point dipole immersed in a spherical Onsager cavity according to Pullin's derivation of the solvent-induced vibrational frequency shifts.

To obtain microscopic insights into the observed frequency changes of 2N-CH<sub>3</sub>CN, we compare our results with observed O-H stretching frequency shifts for a large collection of phenol-derivatives as well as a 1N-derivative (Fig. 1c). We plot the observed frequency shifts as a function of  $F_0$  and we derive the intercept as its hypothetical gas phase value ( $\epsilon = 1$ ;  $F_0 = 0$ ). The solute-solvent coupling sensed by the O-H stretching mode is represented by the

slope of the observed frequency shift. In this way, we have characterized the different aromatic alcohol complexes in a slope vs. intercept plot (Fig 1d) showing that the complexes can be characterized as regular acids.

Based on our findings, we conclude that a free-energy correlation with the vibrational spectroscopic observable, namely the O-H stretching marker mode of the 2N-CH<sub>3</sub>CN complexes can be made. As such O-H stretching frequency shifts follow changes in acidity (as characterized by the p*K<sub>a</sub>*-value). The underlying mechanisms of charge distribution changes govern how the solute-solvent couplings can have an impact on the O-H stretching potential, leading to solvent-induced O-H stretching frequency shifts. These mechanisms can be quantified using (time-dependent) density functional theory at the B3LYP/TZVP and ωB97XD /TZVP levels of theory using solvation continuum models.



**Figure 1:** (a) Steady-state IR spectra of 2N-CH<sub>3</sub>CN complexes in various solvents (asterisks denote uncomplexed 2N); (b) Transient IR spectra after UV photoexcitation at 330 nm; (c) The O-H frequency shift exhibits a linear dependence on  $F_0 = (2\epsilon_0 - 2)/(2\epsilon_0 + 1)$ , where  $\epsilon_0$  is the static dielectric constant of the solvent, which validates treating the 2N-CH<sub>3</sub>CN complexes (dashed curves) according to Pullin's model of the solvent-induced vibrational frequency shifts; (d) Values for the intercept and slope of various photoacid-base complexes, derived from experiment curves in (c), plotted in red, are compared with calculated values presented in purple. The 2N-CH<sub>3</sub>CN points are indicated with green arrows.

## References

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