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Ultrafast OH-stretching frequency shifts of hydrogen-bonded 2-naphthol photoacid-base complexes in solution

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Abstract. We characterize the transient solvent-dependent OH-stretching frequency shifts of photoacid 2-naphthol hydrogen-bonded with CH_3CN in the S_0- and S_1-states using a combined experimental and theoretical approach, and disentangle specific hydrogen-bonding contributions from nonspecific dielectric response.

Photoacids have been extensively used in studies of photoinduced proton transfer [1,2,3]. However, the molecular/electronic origin of photoacidity remains poorly understood [4]. In order to understand the decrease in pK_a induced by the electronic excitation of 2-naphthol, the ultrafast response of the OH-stretching mode is studied as it provides a direct probe of the local structure and dynamics of hydrogen bonds in photoacid-base complexes. Our study combines ultrafast spectroscopy and theoretical modelling based on an analytical perturbative theory and *ab initio* quantum chemistry calculations. We correlate the OH-stretching frequency shifts in the ground and excited electronic states with the electronic charge redistributions induced by optical excitation, and we analyze the effect of solute-solvent interactions. Our findings are expected to be particularly relevant to proton transfer mechanisms of photoacids either in solution or embedded in complex biological environments such as photosensor proteins (*e.g.*, green fluorescent protein).

A marked red-shift of the OH-stretching mode, induced by hydrogen bonding with the solvent, can be observed for the steady-state IR spectra of 2-naphthol (2N) in the S_0-state (Figure 1a). Transient UV-pump-IR-probe spectra of 2N measured in the same solvents at a pulse delay of 10 ps reveal an even larger frequency shift in the first electronic excited ^1L_b-state (Figure 1b). For example, in dichloromethane (DCM) while the OH-stretching mode exhibits a frequency shift of ~80 cm^{-1} in the S_0-state compared to the reported uncomplexed gas phase values, this shift is of ~105 cm^{-1} in the ^1L_b-state. In the presence of a hydrogen bond to the solvent such as in DMSO-d_6, the effect is much more pronounced with a 531 cm^{-1} shift in the S_0-state, and 1134 cm^{-1} in the ^1L_b-state.
We determine the relative importance of specific interactions, including photoacid-base hydrogen bonding, and non-specific dielectric couplings with the surrounding solvent, in order to explore the perturbation of OH-stretching modes. We correlate the OH-stretching frequency shifts to the electronic nature of the OH groups in specific electronic states of photoacids by extending the perturbative theoretical model originally developed by Pullin, augmented by the van der Zwan-Hynes relationship. We then employ *ab initio* quantum chemistry calculations to provide the

molecular parameters for the Pullin-van der Zwan-Hynes (PvdZH) model, computed at the density functional theory level for the ground state (i.e. using the B3LYP/TZVP method) and the excited states (i.e. using the TD-B3LYP/TZVP method). Since TD-DFT calculations yield an incorrect excited state ordering, namely ^1L_b lies above ^1L_a, the spectroscopy-oriented configuration interaction (SORCI+Q) method was used with the 6-31G (d) basis set [5] implemented in the ORCA 2.6.19 program package. Compared to TDDFT, SORCI+Q allows us to selectively include π- and lone-pair electrons into the active space (i.e. the space of actively involved electronic states by excitation). For 2N-MeCN, by including all of the π-electrons and the lone-pair electrons from N-atom in MeCN, the computed state ordering agrees with the experimental measurements (Figure 2a), whereas for uncomplexed 2N, including all of the π-electrons leads to the correct state ordering.

The resulting analysis allows us to quantify the observed frequency shifts of 1-naphthol (1N) and 2-naphthol (2N) in the S_0- and ^1L_b-states in weakly polar solvents (n-hexane to 1,2- dichloroethane (1,2-DCE), i.e. no involvement of hydrogen bonds) [6,7]. The rates of the observed frequency red-shifts with the increase of dielectric constants of solvents are found to be governed by the combined effect of a few molecular parameters of specific electronic states, such as molecular dipole moments, and the first and second derivatives of the dipole moment along the OH-stretching coordinate, and the degree of anharmonicity of the OH stretching vibration.

We expanded this methodological approach to hydrogen-bonded complexes of 2N with CH_3CN in a set of solvents of low polarity. Figure 1c shows that the observed frequency red-shift upon hydrogen bond formation in such a 1:1 complex dissolved in cyclohexane amounts to 150 cm^{-1} compared to uncomplexed 2N, i.e. 2N is considered to form a weakly hydrogen-bonded complex with CH_3CN. The OH-stretching vibration of the 2N-CH_3CN complex follows a similar dependence

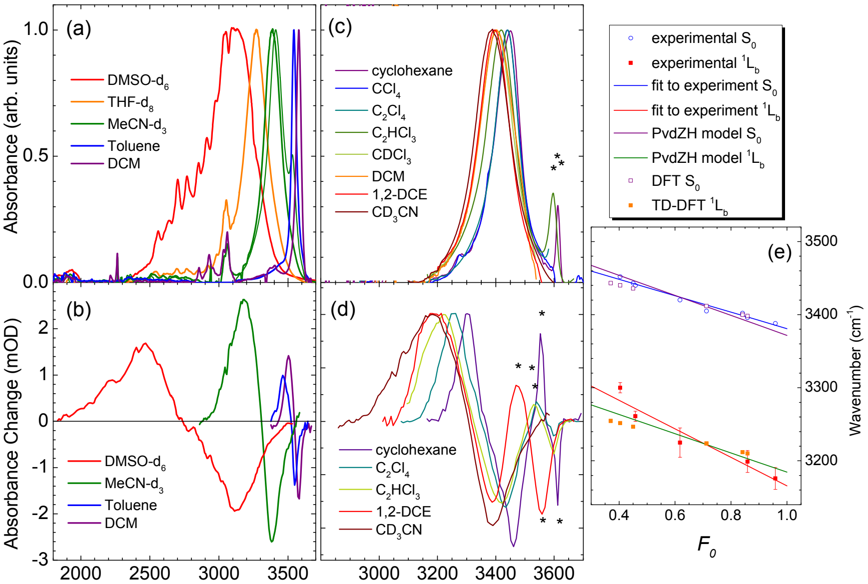

Fig. 1. (a) Steady-state and (b) UV-pump-IR-probe spectra measured for 2N dissolved in different solvents at a pulse delay of 10 ps, showing the marked frequency shifts of the OH-stretching mode for 2N in the S_0 and ^1L_b-states. (c) Steady-state FT-IR and (d) transient UV-pump-IR-probe spectra of 2N-CH_3CN complexes, measured in solvents with varying polarity. Asterisks denote OH-stretching bands of uncomplexed 2N molecules. The observed frequency shifts measured in the S_0- and ^1L_b-states are plotted in (e), together with calculated curves using the perturbative Pullin-van der Zwan-Hynes approach, as well as using (TD-)DFT with PCM modelling of the solvent, using the optimized molecular structures as depicted in the upper right of the figure.

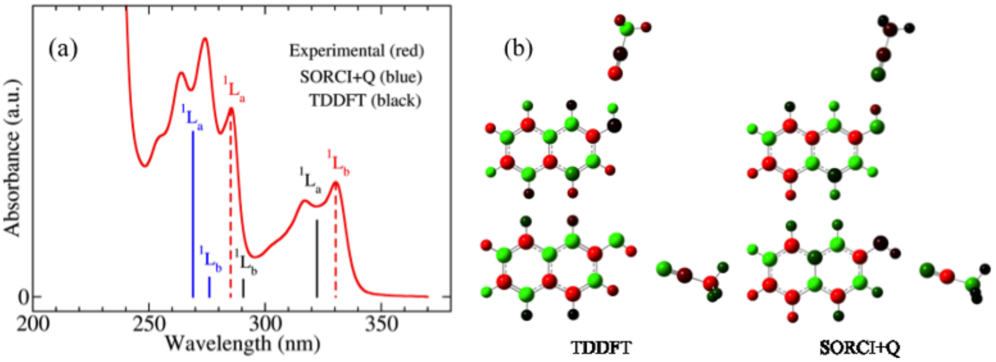

Fig. 2. (a) Ordering of the ^1L_a and ^1L_b excited states for the 2N-CH_3CN complex obtained by experimental UV-vis spectrum (red, 2N in CH_3CN solution), SORCI+Q calculations (blue, cis-2N-CH_3CN complex), and TDDFT calculations (black, cis-2N-CH_3CN complex). (b) Charge flow induced by the $S_0 \rightarrow {}^1L_b$ excitation of 2N-CH_3CN, computed by (TD-) DFT and SORCI+Q. The maximal negative change (i.e., increasing electron density) is represented in red, and the maximal positive change (i.e., decreasing electron density) is represented in green.

with $F_0 = (2\varepsilon_0-2)/(2\varepsilon_0+1)$, where ε_0 is the static dielectric constant of the solvent, as measured before for uncomplexed 2N (Figure 1e). This strongly suggests that treating a 2N-CH_3CN complex as a single solvated complex provides a valid physical insight to analyze the observed frequency shifts.

Figure 1d shows the transient UV-pump-IR-probe spectra of 2N-CH_3CN complexes. The measured frequency shifts of 2N-CH_3CN in the ^1L_b-state are also plotted in Figure 2e. We have quantified the slopes in Figure 1e by using the PvdZH model, with molecular parameters computed from *ab initio* calculations, and compared our predicted frequency shifts to that obtained by a direct OH-stretching normal mode analysis performed at the (TD-) DFT levels with the standard polarizable continuum model (PCM) solvation technique as implemented in Gaussian 09. Two stable conformers, which differ by the orientation of the O-H$\cdots$N vector relative to the aromatic ring of 2N (Figure 2b), were used in the analysis. Whereas a similarly consistent correspondence between experiment and theory for the slopes of frequency shifts is obtained for 2N-CH_3CN in the S_0-state, a marked deviation in the ^1L_b-state is apparent. This may be an indication that modelling of solvent-induced OH-stretching frequency shifts for stronger hydrogen-bonded complexes (such as 2N-CH_3CN in the ^1L_b-state), where anharmonicities of the OH-stretching potential are more pronounced, necessitates a sophistication of the description of these complexes extending to states involving conjugate (photo) base-conjugate acid configurations [8].

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