

# Ultrafast Photoinduced Charge Transfer of 1-Naphthol and 2-Naphthol Photoacids to Halogenated Solvents

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**Abstract:** We explore the fluorescence quenching behaviour of 1-naphthol and 2-naphthol photoacids in halocarbon solvents with time-correlated single-photon-counting and femtosecond IR-spectroscopy, and conclude that halocarbon solvents facilitate an efficient de-excitation mechanism through solute-solvent electron transfer.

**OCIS codes:** (320.7150) Ultrafast spectroscopy; (300.6250) Spectroscopy, condensed matter; (300.6340) Spectroscopy, infrared

Photoacid molecules have been utilized as a means to phototrigge proton transfer dynamics. This has been used to much effect in dedicated ultrafast spectroscopic photoacid-base neutralization studies [1]. The underlying mechanism for photoacidity on the other hand is still a topic for debate. In contrast to conventional pictures where optical excitation leads to (partial) charge transfer away from the electronegative atom in the proton donating group, state-of-the-art quantum chemical calculations have indicated that the net charge flow in the photoacid is rather minor. Instead the driving force for photoacidity is understood to be due to much larger charge density changes in the conjugated photobase side of the Förster cycle [2,3]. One local probe of the hydrogen bond is the O-H stretching mode, that will show a direct correlation between hydrogen bond strength and O-H stretching frequency shift, albeit one has to take into account the substantial effect of solute-solvent interactions. In a recent combined experimental and theoretical study, it was shown that for complexes of 2-naphthol and other aromatic alcohols hydrogen-bonded with acetonitrile the O-H stretching mode frequency can be correlated to photoacidity, and to the hydrogen bond structure in terms of O...N or O-H distances. Interestingly the effect of photoexcitation of 2-naphthol did not have an overtly local Mulliken charge change on the oxygen or hydrogen atom [4], which would confirm the picture of photoacidity predominantly driven by charge changes in the conjugate photobase upon electronic excitation.

To provide an alternative access to charge distribution changes induced by photoexcitation, we investigate the excited-state dynamics of 1-naphthol and 2-naphthol in halocarbon solvents such as CCl<sub>4</sub>, C<sub>2</sub>Cl<sub>4</sub>, and CHCl<sub>3</sub>. These solvents induce a major fluorescence quenching, suggesting a solute-solvent interaction where electronic charge flow is the underlying mechanism. To determine the electronic excited-state lifetimes of 1-naphthol and 2-naphthol, we present time-correlated single-photon counting (TCSPC) measurements of the fluorescence emission, as well as femtosecond IR spectroscopic measurements to follow the dynamics through potentially dark states, as well as possible ground-state recovery. We observe a major electronic excited state lifetime shortening for CCl<sub>4</sub>, and to some extent C<sub>2</sub>Cl<sub>4</sub>, whereas for CHCl<sub>3</sub> the effect is smaller. Interestingly, we observe a significant effect on the lifetime when having the naphthol photoacid hydrogen-bonded to acetonitrile, suggesting the charge flow upon photoexcitation may be altered due to the hydrogen bonding interaction.

Figure 1a,b shows the TCSPC results, measured with 40 ps time resolution, obtained on 1-naphthol and 2-naphthol. A clear lifetime shortening is apparent in these measurements. We were not able to time-resolve the fluorescence decay of 1-naphthol in CCl<sub>4</sub>, suggesting its lifetime is shorter than 40 ps. To follow the excited-state dynamics with more detail, as well as better time resolution, we have performed femtosecond IR spectroscopic measurements of both the O-H stretching region around 3550-3620 cm<sup>-1</sup> and of the fingerprint region around 1200-1300 cm<sup>-1</sup> (see Fig. 2a,b). Upon photoexcitation a small red-shift of the O-H stretching band occurs [4], followed by a decay of the O-H stretching band in the S<sub>1</sub>-state, and a partial bleach recovery of the O-H stretching band of the S<sub>0</sub>-state on time scales of a few picoseconds to hundreds of picoseconds, depending on the halocarbon solvent used. The observed dynamics in the TCSPC and femtosecond IR spectroscopic measurements have strong similarities to other donor-acceptor systems where photoexcitation induces forward electron transfer, followed by a slower back-electron transfer, leading to ground state recovery [5,6].

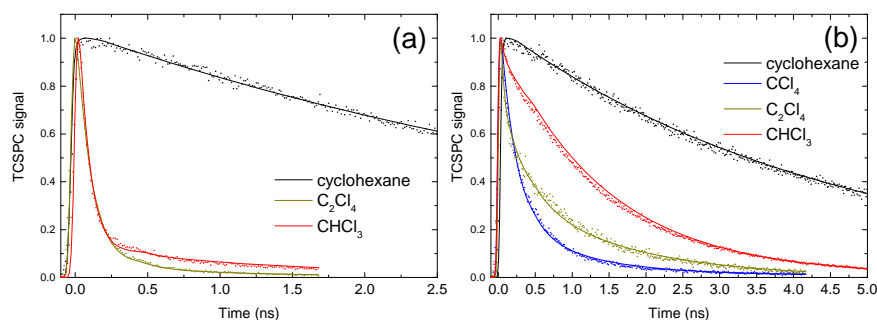


Fig. 1 TCSPC measurements on 1-naphthol and 2-naphthol in halogenated alkanes. Multiexponential fitting the shortest time constants for 1-naphthol:  $C_2Cl_4$   $\tau_1=100ps$  and  $CHCl_3$   $\tau_1=70ps$ . For 2-naphthol these are:  $CCl_4$   $\tau_1<30ps$  (0.45);  $\tau_2 = 200 ps$  (0.3),  $C_2Cl_4$   $\tau_1=200 ps$  (0.8) and  $CHCl_3$ :  $\tau_1<40ps$  (0.2);  $\tau_2=1.4 ns$  (0.8)

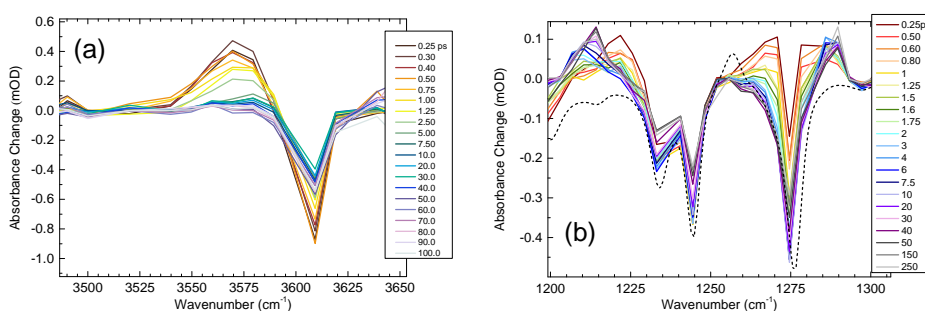


Fig. 2 Transient IR spectra of 1-naphthol in  $CCl_4$ , measured in O-H stretching and fingerprint regions, showing the picosecond excited state decay, and formation of an intermediate charge transfer state.

To model the electron transfer (ET) mediated excited state decay of 1-naphthol and 2-naphthol, we used a kinetic model based on ET rates calculated using Marcus Theory [7] (Eqn.1, Fig. 3b), and isomerization rates calculated using the Eyring equation (Eqn. 2).

$$k_{ET} = \frac{2\pi}{\hbar} \frac{|H_{AD}|^2}{\sqrt{4\pi k_B T \lambda}} \exp\left[-\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}\right] \quad (1)$$

The free energy ( $\Delta G$ ) and reorganization energy ( $\lambda$ ) were calculated at the DFT (B3LYP/6-31+G(d,p)) level of theory and corrected using excitation energies obtained at the TD-DFT level (B3LYP [8]/6-31+G(d,p)) in Gaussian 09 [9]. The electronic coupling  $|H_{AD}|$  was calculated at the DFT (B3LYP/TZ2P) level of theory using ADF [10,11]. All calculations were performed in a polarizable continuum model (PCM) to mitigate the computational burden of explicitly modeling solvent molecules (Fig. 3a).

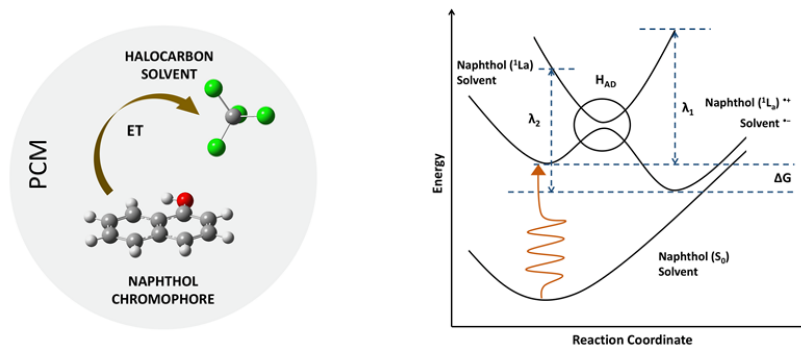


Fig. 3 (a) Donor-acceptor system in PCM & (b) Schematics of Marcus energy manifolds for the system.

Rates of isomerization were obtained from the Eyring equation (2) using energies obtained from a C-C-O-H dihedral scan (Fig. 4a)

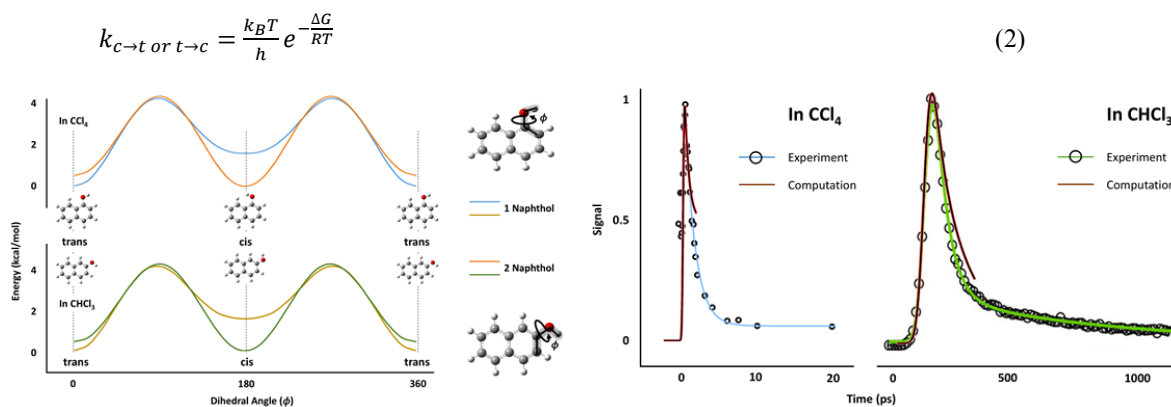


Fig. 4 (a) Dihedral scan for calculation of energy barriers & (b) Comparison of excited state decay (early time) spectra for 1-naphthol in  $\text{CCl}_4$  and  $\text{CHCl}_3$ .

The decay spectra (Fig. 4b) computed for the case where (starting with equally distributed cis & trans isomers in excited state) trans isomers isomerize first to cis before getting oxidized, are in complete agreement with the experimental spectra. We are currently involved in a more thorough modeling of the system with multiple solvent molecules that appear to be necessary, to capture the complete picture of multiexponential decay over the entire reaction timescale.

In conclusion, we observe an efficient deexcitation pathway on picosecond time scales for the electronically excited photoacids 1-naphthol and 2-naphthol, that we ascribe to electron transfer to the halogenated alkane solvent, followed by back electron transfer resulting in ground state recovery. Modelling of this using Marcus theory suggests that the mechanism is driven by multiple solvent molecules interacting with the  $\pi$ -aromatic electronic levels of these photoacids. Altered ET rates of hydrogen bonded photoacids suggests that charge distribution changes induced by hydrogen bonding may be reflected in solute-solvent electronic couplings.

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