# Supplementary Online Material

# Photoinduced Proton Coupled Electron Transfer in 2-(2'-Hydroxyphenyl)-Benzothiazole

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# Detailed Computational Methodology

For all calculations which include solvent effects, the quantum chemical package GAUSSIAN [1] has been employed whereas calculations without consideration of any solvent effect have been performed with the quantum chemical package TURBOMOLE1 [2] [except of Fig. 2 (a)]. For the ground-state structure optimization (if not noted otherwise) and IR spectrum calculation, density functional theory (DFT) was used with the BP86 density functional [3,4] and Ahlrichs TZVP [5] basis set. For excited-state structure optimizations and IR spectra calculations, time-dependent DFT (TD-DFT) with the B3LYP density functional [6,7], as implemented in GAUSSIAN 09 and TURBOMOLE (Version 6.2), respectively, and the TZVP or TZVPP [5,8] basis sets were used as well as the Configuration Interaction Singles (CIS) method with the TZVP basis set. The B3LYP density functional in GAUSSIAN 09 employs the Vosko, Wild, and Nusair (VWN) correlation functional(III) [9] whereas the B3LYP density functional implementation in Turbomole version 6.2 uses the VWN(V) correlation functional [9]. In addition, IR excited-state spectra were obtained with the M06-2X [10] and CAM-B3LYP [11] density functionals. The electronic transition dipole moments of cis-enol from the ground to the first electronically excited state were obtained with TDDFT employing B3LYP and the TZVP or TZVPP basis set. The solvent tetrachloroethene is considered via the polarizable continuum model (PCM) using the integral equation formalism variant as implemented in GAUSSIAN 09. The normal modes, frequencies, and IR intensities as well as the anisotropy angles of certain normal modes were obtained with a modified and extended version of SNF [12,13] in the harmonic approximation. GAUSSIAN 09 and TURBOMOLE, respectively, were employed for the calculation of electronic energy gradients and electric dipole moments for distorted structures of the molecule of interest. This data was collected by SNF that evaluates the normal modes and IR intensities. For the differentiation, a three-point central difference formula [14] was applied and the step length for the differentiation was chosen to be 0.01 bohr. The electrostatic-potential-fitted (ESP) charges were obtained employing the Merz-Singh-Kollman [15,16] scheme as implemented in GAUSSIAN 09. Molecular structures and normal modes were visualized using the programs VMD [17] and JMOL [18], respectively.

Figure 1: IR spectra of HBT in the $S_1$-state with cis-keto* configuration, calculated with (a) TDDFT (B3LYP/TZVP), (b) TDDFT(B3LYP/TZVP/PCM)/CIS(TZVP/PCM), (c) TDDFT (CAM-B3LYP/TZVP/PCM), and (d) TDDFT (M06-2X/TZVP/PCM) are compared with the transient IR spectrum measured at 100 ps pulse delay (d).
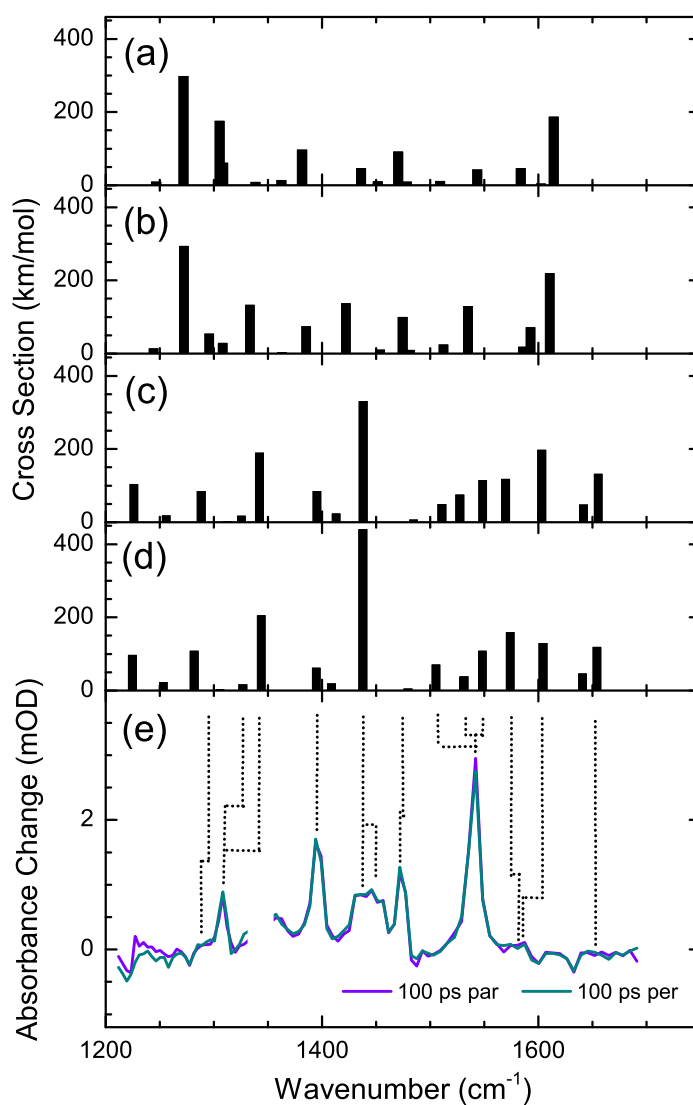
# Comparison of Experimentally Measured and Calculated Anisotropies

Table 1: Measured and calculated [TDDFT(B3LYP/TZVP/PCM)] anisotropy angles $\Theta$ of selected experimental bands / calculated normal modes $\Omega$ of cis-keto (in brackets: trans-keto*) in the first electronically excited state.

| $\Omega$ (cm$^{-1}$) | | $\Theta$ (°) | |
|---|---|---|---|
| Exp. | Theory | Exp. | TDDFT |
| 1305 | 1308 (1305) | $29 \pm 5$ | 39 (4) |
| 1397 | 626+794 (625+770) | $90-15$ | 90 (90) |
| 1439 | 1422 (1421) | $77 \pm 13$ | 52 (31) |
| 1475 | 1475 (1475) | $90-15$ | 68 (86) |
| 1475 | 1482 (1491) | $90-15$ | 62 (31) |
| 1535 | 1535 (1520) | $23 \pm 2.5$ | 16 (29) |

Table 2: Measured and calculated anisotropy angles Θ of selected experimental bands / calculated normal modes $\Omega$ of cis-keto in the first electronically excited state; the calculated values were obtained with normal modes employing TDDFT(B3LYP/TZVP/PCM) and electric-dipole moments computed with CIS(TZVP/PCM).

| $\Omega$ (cm$^{-1}$) | | Θ (°) | |
|---|---|---|---|
| Exp. | Theory | Exp. | (TDDFT/CIS) |
| 1305 | 1308 | 29 ± 5 | 12 |
| 1397 | (703+735) | 90−15 | 90 |
| 1439 | 1142 | 77 ± 13 | 36 |
| 1475 | 1475 | 90−15 | 68 |
| 1475 | 1482 | 90−15 | 38 |
| 1535 | 1535 | 23 ± 2.5 | 12 |

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