

**Supporting Information:**

**A Time-Resolved Vibrational Analysis of Excited  
State Ab-Initio Molecular Dynamics to  
Understand Photorelaxation: the Case of the  
Pyranine Photoacid in Aqueous Solution**

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## Computational details

The pyranine solute was located at the center of a water molecules sphere of a radius 19 Å; the structureless solvent surrounding the explicit sphere completes the hybrid explicit/implicit solvation model. Non periodic boundary conditions account for the interactions between the explicit molecular system and the implicit bulk solvent with both the electrostatic and dispersion-repulsion interactions. The solvent molecules are explicitly represented by the TIP3P water model, while the implicit bulk solvent by the polarizable continuum model, in conductor-like version (C-PCM). The explicit system itself is treated at different levels of theory according to the hybrid QM/MM ONIOM extrapolation scheme. In particular, the pyranine molecule is described by DFT and TD-DFT in the ground ( $S_0$ ) and  $S_1$  excited state, respectively, by adopting the global hybrid B3LYP functional and the 6-31g(d,p) basis set. The so-built energy potential ruled the AIMD simulations in both ground and excited state. The ground state sampling was performed by means of the atom-centered density matrix propagation (ADMP) method. After 5 ps of equilibration, the trajectory was collected for 10 ps with a time step of 0.2 fs, keeping a constant temperature of 298 K. From the ground state trajectory, five configurations representative of the equilibrium, with both coordinates and momenta have been chosen as starting points for the propagation of the excited state dynamics. In order to collect the excited state trajectories, a Born-Oppenheimer ab-initio dynamics was instead employed, where the excited state energies and gradients were calculated on-the-fly by TD-DFT in its linear response formalism. All the ground and excited state AIMD trajectories, used for the wavelet-based vibrational analysis, were generated using the Gaussian16 suite of programs. The 6-31g(d,p)/b3lyp/CPCM level of theory was also adopted for the calculation of the harmonic vibrational frequencies of the pyranine molecule in the ground and excited state minimum energy structure. The effects of the solvent was included by means of the C-PCM model.

The wavelet transform (WT) is a multiresolution analysis, i.e. the analyzing time window is adapted like a *zoom lens* to the simulated signal. WT is capable of capturing both low and high frequencies contribution with an optimal resolution. The frequency resolution ( $\Delta\nu$ ) is inversely proportional to the time resolution ( $\Delta\tau$ ), according to the ( $\Delta\nu\Delta\tau \geq 1/(4\pi)$ ).

We plotted the magnitude square of the transform  $|W(\nu, t)|^2$ . The intensities are reported in arbitrary units and the values of  $|W(\nu, t)|^2$  represents the contribution to the signal of the instantaneous frequency. The intensity therefore is the results of the wavelet integration of the time dependent signal. Every time dependent vibrational signal ( $\dot{\mathbf{Q}}_{\text{ES}}(\mathbf{t})$ ) (see Equation 2 and 3 of the main text) is wavelet transformed, therefore the signal intensities cannot be compared among different wavelet spectra.

Table S1: AIMD and harmonic frequencies in  $\text{cm}^{-1}$  of the principal vibrational modes. Harmonic frequencies refer to the  $S_0$  and  $S_1$  minimum energy structure computed at B3LYP/6-31g(d,p)/C-PCM level of theory.

	Exp	AIMD $S_0$	Harmonic $S_0$	Harmonic $S_1$
Vertical breathing	191	190	217	217
Ring deformation + COH rocking	362	360	349	349
Horizontal breathing	460		461	459
Out of plane ring deformation	630	620	660	662
Deformation + H out-of-plane	952	910	981	976
COH rocking + H ring rocking	1138/1154	1156	1156	1153

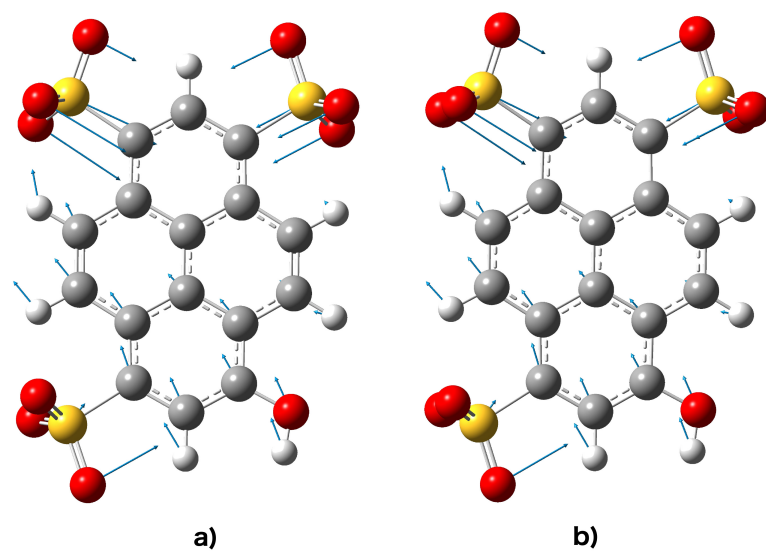


Figure S1: Composition of the skeletal breathing mode calculated in the a)  $S_0$  ( $217 \text{ cm}^{-1}$ ) and b)  $S_1$  ( $217 \text{ cm}^{-1}$ ) minimum.

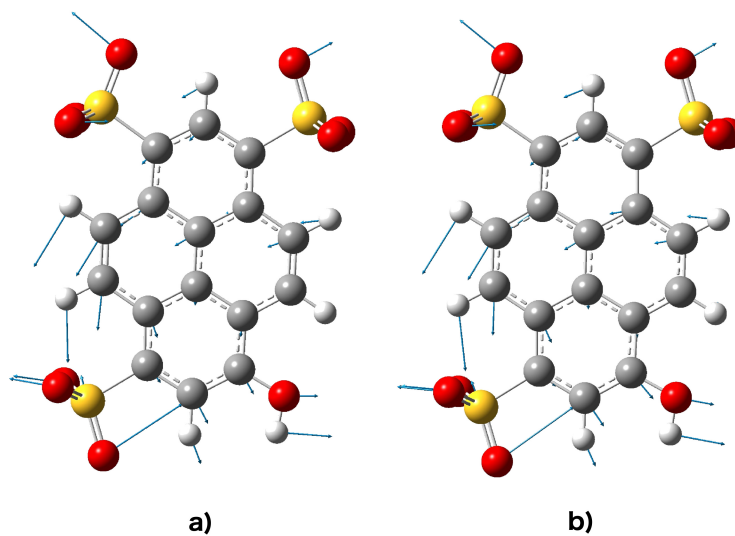


Figure S2: Composition of the ring deformation associated to COH phenolic rocking mode calculated in the a)  $S_0$  ( $349\text{ cm}^{-1}$ ) and b)  $S_1$  ( $349\text{ cm}^{-1}$ ) minimum.

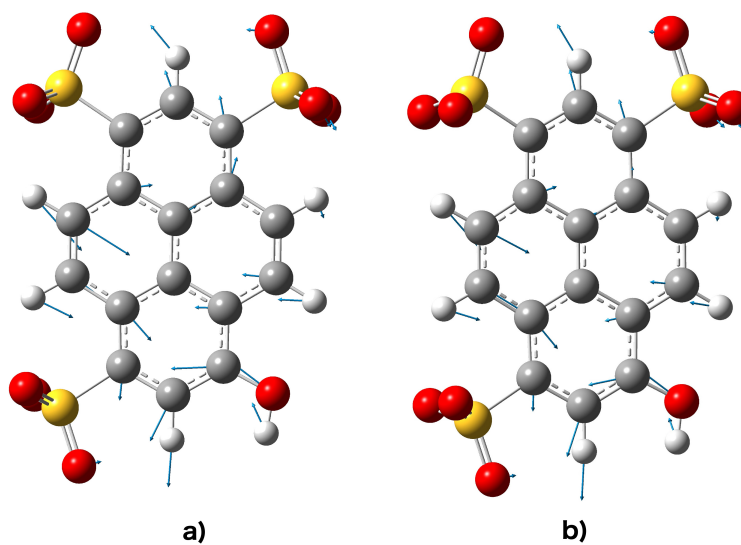


Figure S3: Composition of the horizontal breathing calculated in the a)  $S_0$  ( $461\text{ cm}^{-1}$ ) and b)  $S_1$  ( $459\text{ cm}^{-1}$ ) minimum.

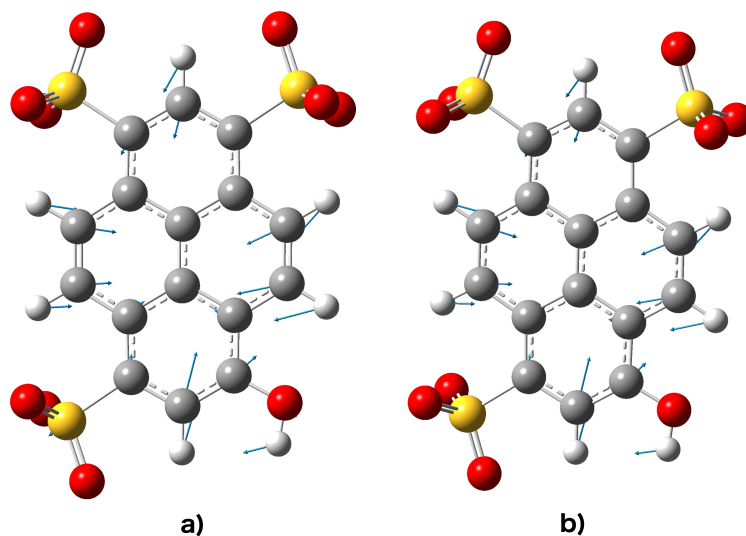


Figure S4: Composition of the ring wagging and breathing combination mode calculated in the a)  $S_0$  ( $660\text{ cm}^{-1}$ ) and b)  $S_1$  ( $662\text{ cm}^{-1}$ ) minimum.

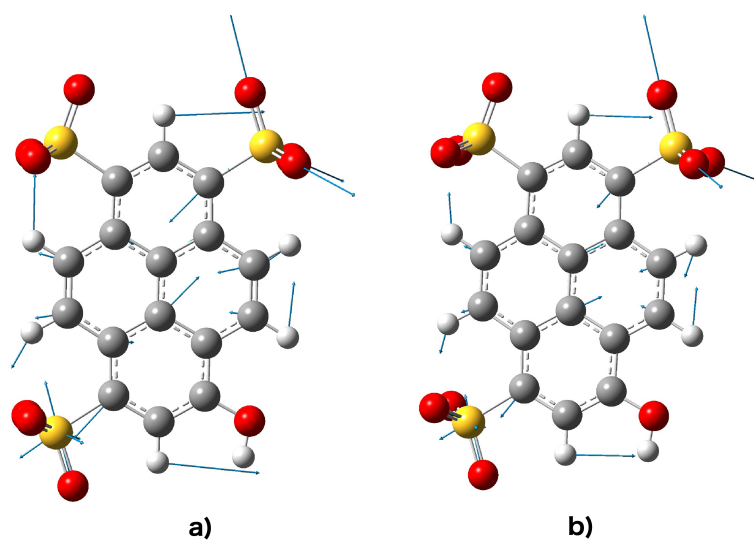


Figure S5: Composition of the ring deformation associated to Hydrogen out of plane mode calculated in the a)  $S_0$  ( $981\text{ cm}^{-1}$ ) and b)  $S_1$  ( $976\text{ cm}^{-1}$ ) minimum.



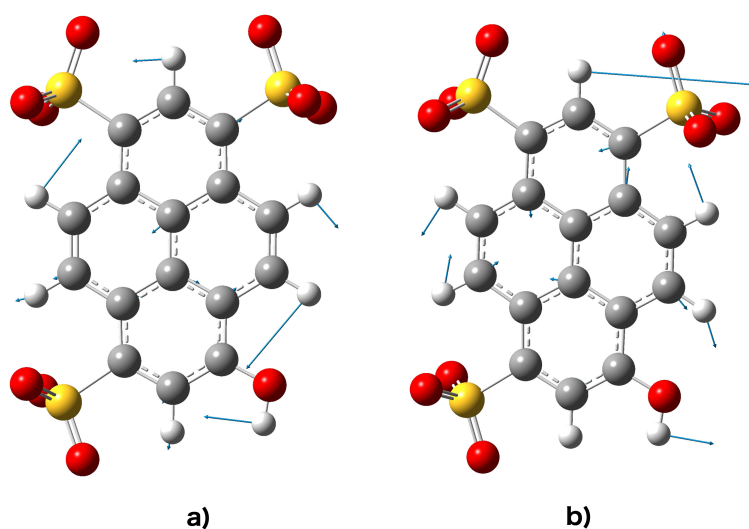


Figure S6: Composition of the CHO phenolic rocking associated to nearby hydrogen rocking mode in the a)  $S_0$  ( $1156\text{ cm}^{-1}$ ) and b)  $S_1$  ( $1153\text{ cm}^{-1}$ ) minimum.