

Supplementary Material for

**“Solvent Effects on Vibronic Coupling in a Flexible Bichromophore:  
Electronic Localization and Energy Transfer  
induced by a Single Water Molecule”**

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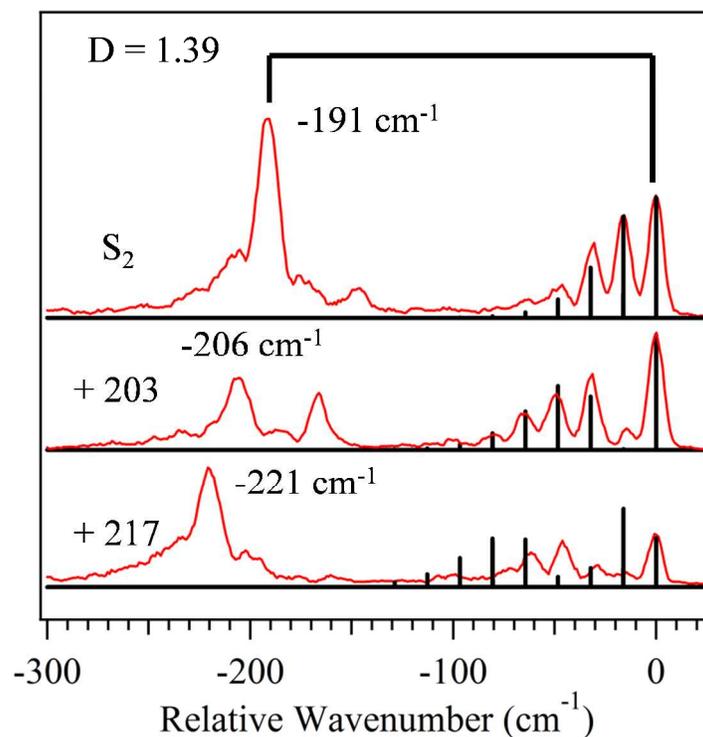
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1. Low frequency portion of the DFL spectra of the +189, +203, +217  $\text{cm}^{-1}$  bands of DPOE- $\text{H}_2\text{O}$ , with Franck-Condon fits to the progression in the 16  $\text{cm}^{-1}$  mode (**Figure S1**).
2. The resonant two-photon ionization spectra monitoring (a) the  $\text{DPOE}^+$  mass channel without water, (b) the  $\text{DPOE}^+$  mass channel with water, and (c) the  $\text{DPOE}-(\text{H}_2\text{O})_1^+$  mass channel (**Figure S2**).

## 1. Frank-Condon Fits to the emission spectra of DPOE-(H<sub>2</sub>O)<sub>1</sub>.

Figure S1 presents the first 300 cm<sup>-1</sup> of the DFL spectra of the transitions +189, +203, and +217 cm<sup>-1</sup> above the S<sub>1</sub> origin of the *tgt* conformer of DPOE-H<sub>2</sub>O complex. All three spectra are comprised of two parts assignable to the S<sub>2</sub> and S<sub>1</sub>(v) contributions to the excited state level. The three transitions are assigned to the S<sub>0</sub>-S<sub>2</sub> 0<sup>0</sup><sub>0</sub> and a short progression in the lowest frequency vibration of the complex involving a rocking of the H<sub>2</sub>O molecule/DPOE framework, mode 93. The DFL spectra in Figure S1 show how this Franck-Condon activity involving ν<sub>93</sub> were fit using an Excel spreadsheet based Franck-Condon fitting program using the recursion formulae in Henderson et al.<sup>1</sup> Stick diagrams in Figure S1 show the best-fit result for a displacement parameter of D=1.39.

The remaining emission is S<sub>1</sub>(v) emission come from the portion of each excited state wave function due to S<sub>1</sub>(v) “background” levels that carry no oscillator strength in absorption, and therefore are “dark” states that are mixed with the S<sub>2</sub> 0<sup>0</sup><sub>0</sub>, 93<sup>1</sup>, and 93<sup>2</sup> bright states carrying the oscillator strength in absorption from the ground state zero-point level. These S<sub>1</sub>(v) levels undergo Δv=0 emission back to corresponding levels in the ground state, appearing with shifts from resonance fluorescence that are within a few cm<sup>-1</sup> of their energy in excess of the S<sub>1</sub> origin in excitation. This emission is analogous to the “clump emission” observed and characterized in diphenylmethane.<sup>1,2</sup>



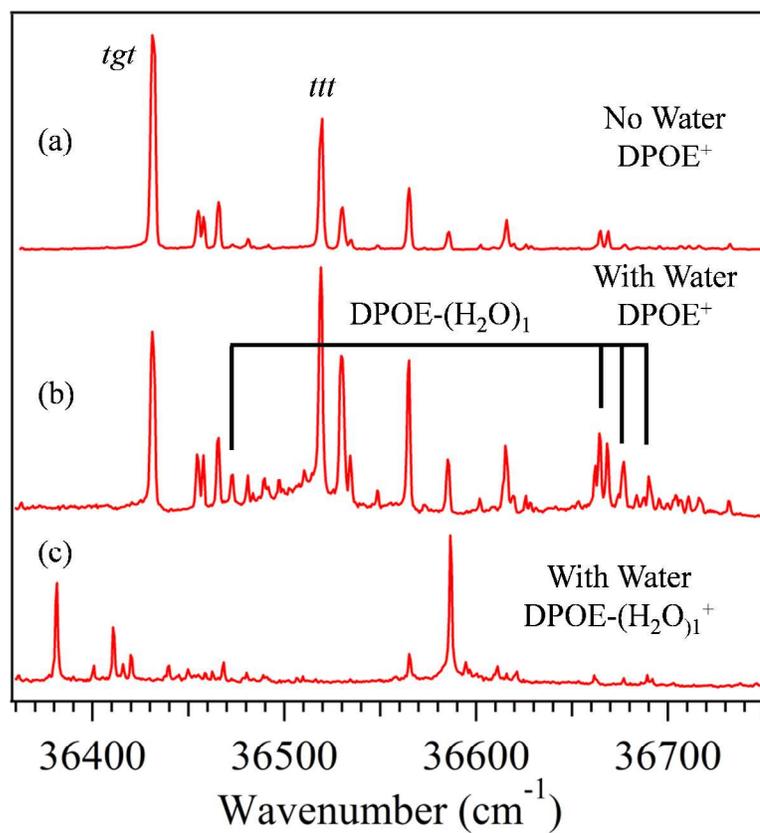
**Figure S1.** The displacement parameter ( $D$ ) for the normal coordinate in the ground and excited state was determined to be 1.39. Harmonic Franck-Condon integrals were calculated using the recursion relations outlined by Henderson et al.<sup>3</sup> The clump emission at  $+189\text{ cm}^{-1}$  from the resonance fluorescence is due to vibronic levels in the  $S_1$  manifold.

## 2. Resonant two-photon ionization spectrum.

**Figure S2** shows a portion of the R2PI spectra without (a) and with (b, c) water present in the expansion, when monitoring the DPOE monomer (a, b) and the  $[\text{DPOE-H}_2\text{O}]^+$  mass channels (c). The transitions assigned to the  $\text{DPOE-(H}_2\text{O)}_1$  complex appear most clearly among the transitions of the DPOE monomer in the monomer mass channel, with the complex undergoing fragmentation following photoionization with high efficiency. This is analogous to the efficient fragmentation that occurred in benzene- $(\text{H}_2\text{O})_n$  clusters, in which the preferred geometries of the ionized clusters are very different than their neutral counterpart, leading to poor Franck-Condon factors to energies below the dissociation threshold for the complex.<sup>4,5</sup> The transitions in the

$[\text{DPOE-H}_2\text{O}]^+$  mass channel are assigned to the  $\text{DPOE-(H}_2\text{O)}_2$  cluster, which also fragments with near unit efficiency by loss of a single  $\text{H}_2\text{O}$  molecule, in this case appearing in  $[\text{DPOE-H}_2\text{O}]^+$  mass channel, with no significant interference in the  $\text{DPOE}^+$  monomer mass channel where we detect the  $\text{DPOE-(H}_2\text{O)}_1$  complex. As a result, the RIDIR spectra recorded for the  $\text{DPOE-H}_2\text{O}$  complex in  $S_0$ ,  $S_1$ , and  $S_2$  states have no interference from  $\text{DPOE-(H}_2\text{O)}_2$ .

This is most relevant to the  $S_2$ -state RIDIR spectrum, in proving that the four OH stretch fundamentals observed in that spectrum (Figure 4c) are exclusively from the  $\text{DPOE-(H}_2\text{O)}_1$  complex. It is worth noting that an IR-induced fragmentation of the 1:2 cluster into the  $\text{DPOE}$  monomer mass channel would appear as a gain rather than as a depletion, while we observe only depletion. The spectroscopy of the larger  $\text{DPOE-(H}_2\text{O)}_n$  clusters with  $n=1-4$  will be taken up elsewhere.<sup>6</sup>



**Figure S2.** The resonant two-photon ionization spectrum (a) the DPOE<sup>+</sup> mass channel without water (b) the DPOE<sup>+</sup> mass channel with water and (c) the DPOE-(H<sub>2</sub>O)<sub>1</sub><sup>+</sup> mass channel. The tie lines in (b) mark the S<sub>1</sub> 0<sup>0</sup><sub>0</sub> and S<sub>2</sub> 0<sup>0</sup><sub>0</sub>, 93<sup>1</sup><sub>0</sub>, and 93<sup>2</sup><sub>0</sub> transitions.

## REFERENCES

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