STEPWISE SOLVATION EFFECTS ON THE EXCITED STATES OF A WEAKLY COUPLED BICHROMOPHORE: 1,2-DIPHENOXYETHANE-$(H_2O)_N$ (N=2-4) CLUSTERS

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1,2-Diphenoxyethane (DPOE) is a prototypical flexible bichromophore which was shown to consist of two conformers in the gas phase with the first two excited states split by 1 cm^{-1} or less.[a] Last year, we reported on the remarkable effects of asymmetric binding of a single H_2O molecule to DPOE, localizing the electronic excitation, and producing OH stretch IR spectra that report on the mixed electronic character of the excited state vibronic levels.[b] Here, we extend that work to DPOE-$(H_2O)_n$ clusters with n=2-4 with the goal of seeing how the degree of asymmetry and electronic coupling evolve as the number of water molecules bound to DPOE increases. Ground state IR spectra in the OH stretch region (3300-3750 cm^{-1}) sensitively probe the H-bonding networks present in the clusters. In the excited states, the stepwise addition of water molecules significantly changes the solvent-induced splitting of the excited states. Excited state IR spectroscopy is used to identify the (nominal) S_1 and S_2 origins, and to track the degree of S_1/S_2 character via the OH stretch transitions observed. The spectra provide novel insight to the way in which solvent molecules redistribute the electronic energy as the density of intermolecular vibrational modes grows with cluster size.

[a] E. G. Buchanan, *et al.*, *J. Phys. Chem. A*, submitted

[b] E. G. Buchanan, *et al.*, *67th International Symposium on Molecular Spectroscopy*, 2012, **WG08**