Supporting Information for "Local excitation approximations to time-dependent density functional theory for excitation energies in solution"

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I. MD SIMULATIONS

We performed MD simulations for aqueous acetone and pyridine using the OPLS-AA force field.[1,2] For acetone, a cubic box (25 Å × 25 Å × 25 Å) containing 519 SPC water molecules and one acetone molecule was used, and for pyridine the box length was set to 24.91 Å and contains 511 SPC water molecules plus one pyridine molecule. The canonical ensemble was sampled using a Nosé-Hoover thermostat and long-range Coulomb interactions were treated using Ewald summation. Van der Waals interactions were truncated at 1.2 nm.

Following geometry optimization and an equilibration period of 600 ps, we performed a production simulation of 60 ps with a 1 fs time step, saving a snapshot every 1 ps. These 600 configurations were used in the subsequent TDDFT calculations. In gas phase, the MD simulations were performed in the same way, except that the box only contained one solute molecule and the initial structure of acetone or pyridine was optimized at the B3LYP/6-311++G* level.

Figure 1 shows the radial distribution functions for O(acetone)–O(water), O(acetone)–H(water), N(pyridine)–O(water), and N(pyridine)–O(water). In the case of aqueous acetone, the first O–H peak lies at 1.80 Å, indicating hydrogen bond formation between the oxygen of acetone and the hydrogen of water. The first O–O peak lies at 2.80 Å. Given the H_2O bond length of $\approx$ 1 Å, this indicates that the $\mathrm{O}\cdots\mathrm{H{-}O}$ angle is close to 180°, another important criterion for hydrogen bonds. The same conclusions hold for the aqueous pyridine simulations.

II. HOMO ENERGY LEVELS

Table I provides values of $-\varepsilon_{\mathrm{HOMO}}$ for several different combinations of functionals and basis sets. Values listed are the minimum values obtained from any of the 600 snapshots for which TDDFT calculations were performed. Even for functionals such as PBE0 and B3LYP, the onset of the ionization continuum is located no lower than 6.4 eV above the ground state (and much higher for long-range-corrected functionals), which is well above the distribution of $^1n\pi^*$ states in aqueous acetone and pyridine.

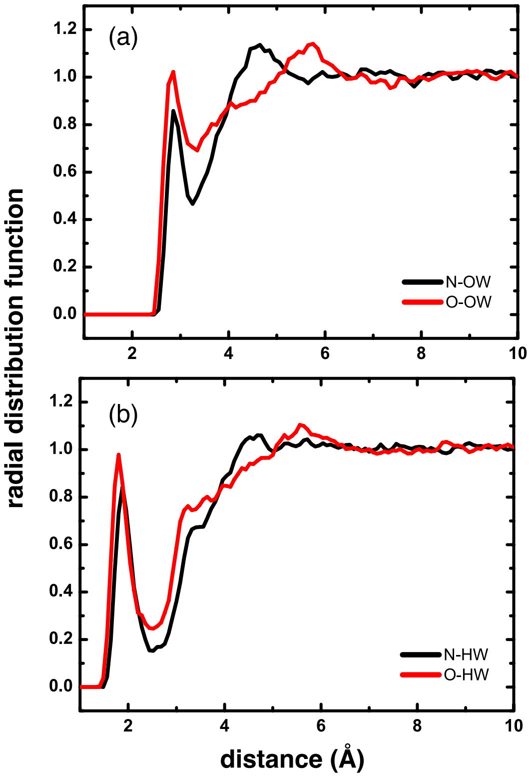

FIG. 1: Radial distribution functions (a) between the the water oxygen (“OW”) and either the acetone O atom or pyridine N atom, and (b) between the water hydrogen atoms (“HW”) and the same atoms in acetone and pyridine.

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[1] Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.

[2] Kaminski, G. A.; Friesner, R. A.; Tirado-Rives, J.; Jorgensen, W. L. *J. Phys. Chem. B* **2001**, *105*, 6474–6487.

TABLE I: Minimum values of $-\varepsilon_{\mathrm{HOMO}}$ (in eV) for 600 configurations of aqueous acetone and aqueous pyridine.

Molecule	Method	Isolated	Cluster
Acetone	PBE0/6-311G*	6.85	6.39
	PBE0/6-31+G*	6.99	6.63
	PBE0/6-311++G*	7.01	6.69
	B3LYP/6-311++G*	6.80	6.45
	ωB97X-D/6-311++G*	8.92	8.65
	LRC-ωPBEh/6-311++G*	8.87	8.57
Pyridine	PBE0/6-311++G*	7.02	6.85
	B3LYP/6-311++G*	6.77	6.61
	ωB97X-D/6-311++G*	8.92	7.26
	LRC-ωPBEh/6-311++G*	8.89	8.65