Supplementary Materials: A simplified treatment for efficiently modeling the spectral signal of vibronic transitions: application to aqueous Indole

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S1 Benchmark of DFT functionals for the calculation of the gas phase vibronic transitions

The following functionals were considered to calculate the gas phase vibronic transitions of indole: B3LYP[1], CAM-B3LYP[2], PBE0[3], M06-2X[4] and ωB97X-D[5]. For each of those functionals we calculated the optimized geometries (both for the ground and the excited states) and their corresponding frequencies using TD-DFT and 6-311+G(d) as the basis set. All the calculations were performed using Gaussian16[6]. We show the results obtained for the geometry corresponding to the ground state minimum in Table S1.

Table S1: Gas phase excitation energies (ΔE) and electric transition dipole square length ($|\mu|^2$) for the ground state $\longrightarrow L_b$ and ground state $\longrightarrow L_a$ transitions of indole calculated using different functionals. We highlighted in bold the functionals in which the order of the L_b and L_a states is inverted compared to the results obtained with EOM-CCSD/6-311+G(d) (i.e. $\Delta E(L_b) < \Delta E(L_a)$, see main text).

	L_b		L_a	
	ΔE (eV)	$\|\mu\|^2$ (a.u.)	ΔE (eV)	$\|\mu\|^2$ (a.u.)
B3LYP	**4.8483**	0.2800	**4.7081**	0.6588
CAM-B3LYP	4.9920	0.3141	5.0388	0.8928
PBE0	**4.9476**	0.3154	**4.8229**	0.6784
M06-2X	5.0527	0.3951	5.1028	0.8294
ωB97X-D	5.0089	0.2906	5.0637	0.9129

From these results we immediately discarded B3LYP and PBE0 because of the inaccurate description of the L_b and L_a electronic states, in particular inverting the order of those states.

With the remaining functionals (i.e. CAM-B3LYP, M06-2X and ωB97X-D) we calculated the gas phase vibronic spectrum corresponding to the ground state $\longrightarrow L_b$ transition (see Figure S1) using the method implemented in Gaussian16[7,8] and no significant difference was observed. A larger basis set was also tested with M06-2X, namely aug-cc-pVTZ[9] (see Figure S1), which provided similar results.

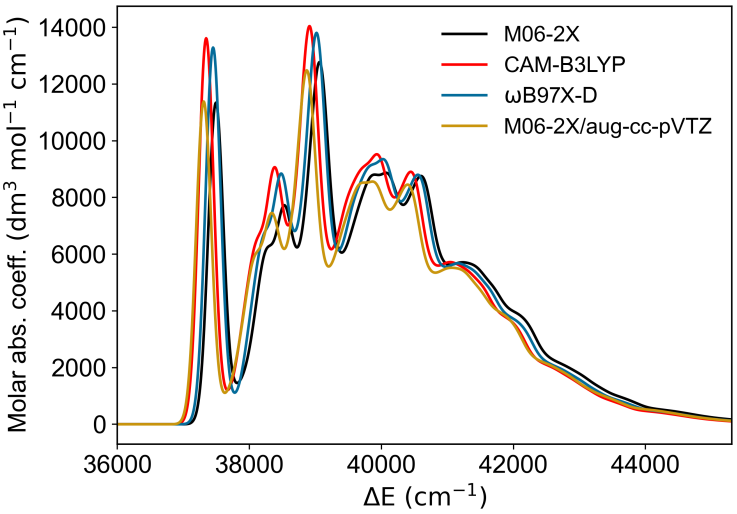

Figure S1: Gas phase vibronic spectra corresponding to the ground state $\longrightarrow$ L_b transition calculated using the method implemented in Gaussian16 (see main text) and M06-2X (black and yellow), CAM-B3LYP (red) and ωB97X-D (blue) as functionals and 6-311+G(d) as the basis set, expect when mentioned (in which case aug-cc-pVTZ was used).

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