

Supporting Information to:
Computing the inhomogeneous broadening of electronic
transitions in solution: a first-principle quantum mechanical
approach.

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1 Treatment of Non polar contribution to the broadening

As anticipated in the text of the article, the inhomogeneous broadening of non-polar solvents should thus be almost zero, also for a electronic transition involving a substantial dipole moment shift. On the other hand experiments show that the spectral band in solution are usually broader than that recorded in the gas phase, also in a non polar solvent. Also this effect has been investigated in several theoretical papers.(see Citations in the text) One possibility to explain this result is that in non-polar solvents 'non-electrostatical' dynamical solvent effects (vide infra) play a more significant role than in polar solvents, which are instead ruled by electrostatic interactions. The initial and final states of the transition could have a different polarizability and this could induce changes in the solvation shell also in non-polar solvents (see also the recent paper of Frediani et al.) Another possibility involves instead the use of a fixed cavity within our calculations, i.e. we compute λ by using the same cavity for the ground and the excited state. In this way we likely fully account for the equilibration of the solvent degrees of freedom related to the ro-librational motions of the solvent molecules, for example, the re-alignment of the molecular dipole moments

to the excited state density. On the other hand, it is possible that we underestimate the effect due to the 'breathing' of the solvent cage around the solute, i.e. that in the equilibrium configuration the average solute-solvent distance is different with respect to the *neq* one.

As highlighted by Kim et al. this effect can be included in continuum models by changing the cavity size. As a preliminary step towards a refined theoretical and computational treatment of this aspect, we have computed the *neq* and *eq* vertical absorption energies (VAE) by using a different α value for the cavity radii (vide supra). As shown in tables 1 of the text, a change of $\pm 10\%$ of the radii is sufficient in CEX to shift the vertical transition energy by $\sim 200\text{ cm}^{-1}$. As a consequence, a breathing mode of the cavity changing the radii by $\pm 5\%$ would induce a periodic fluctuation of the transition energy of $\sim 400\text{ cm}^{-1}$. The present analysis cannot be considered quantitative, since different values would have been obtained by different choice of the cavity models/radii. We here just want to highlight the presence of a chemical physical effect, looking for additional theoretical/experimental efforts (e.g. by performing suitable dynamical studies explicitly including solvent molecules.) The value we got is not far from the FWHM of the Gaussian we have used in the convolution in cyclohexane (650 cm^{-1}) in order to match the experimental bandwidth reported by Maroncelli and coll. (J. Phys. Chem. 1995 99, 17311)

2 Dependence of our results on the PCM model

Our estimates of λ are not significantly affected by the PCM parameters employed in the calculations. In fact W_{pol} computed by employing a discrete scheme to solve the electrostatic problem within PCM (like those implemented in releases of Gaussian less recent than Gaussian 09) are within 50 cm^{-1} the values reported in Table 1 of the article main text. In order to check the dependence on the choice of the radii used to build the PCM cavity we have performed test calculations by using the cavity built according to the UAHF model (V. Barone, M. Cossi, J. Tomasi, J. Chem. Phys. 1997, 107, 3210). The computed W_{pol} for C153 are within 100 cm^{-1} the UAO results.

Table 1: Non equilibrium ν_A , equilibrium ν_A and solvent reorganization energy (λ) in cm^{-1} computed for C153 in DMSO and cyclohexane at the SS-PCM/TD-PBE0/6-31G(d) level for different choices of the radii size (α parameter) by using UA0 radii

	ν_A NEQ	ν_A EQ	λ_A	W_{pol}	ν_A NEQ	ν_A EQ	λ
	DMSO				Cyclohexane		
$\alpha=0.9$	23000	21700	1300	1700	25500	25500	0
$\alpha=0.95$	23400	22200	1200	1650	25700	25700	0
$\alpha=1.0$	23700	22600	1100	1600	25900	25900	0
$\alpha=1.05$	24000	23000	1000	1500	26000	26000	0
$\alpha=1.1$	24300	23300	1000	1500	26200	26200	0