Supporting Information

Relaxation dynamics of aniline in methanol: the photoionization channel

Raúl Montero,[*,1,2] Iker Lamas,[1] Marta Fernández-Fernández,[1] Andrew W. Prentice,[3] Dave Townsend,[3,4] Martin J. Paterson,[3] Asier Longarte[*,1]

[1]*Departamento de Química Física. Universidad del País Vasco (UPV/EHU). Apart. 644, 48080 Bilbao, Spain.*

[2]*SGIker Laser Facility, Universidad del País Vasco (UPV/EHU), Leioa, Spain.*

[3]*Institute of Chemical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK.*

[4]*Institute of Photonics & Quantum Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK.*

*Corresponding authors: asier.longarte@ehu.es; raul.montero@ehu.es

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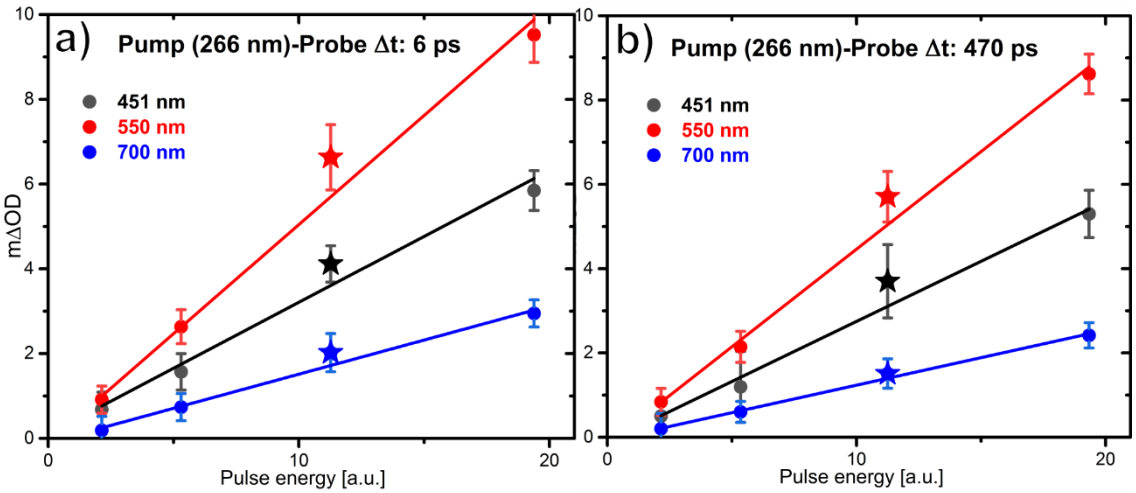
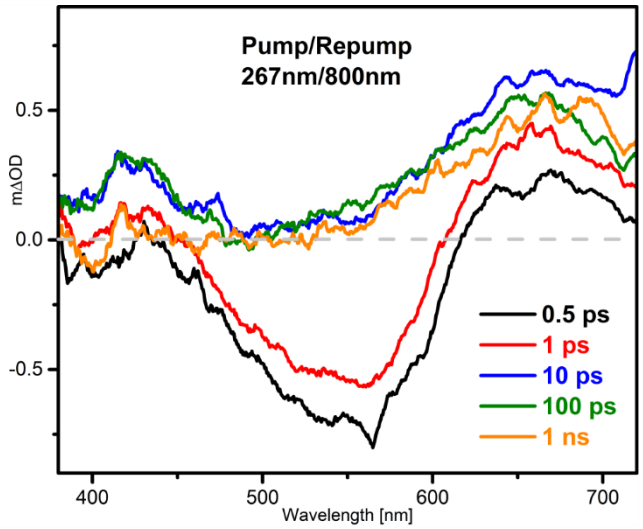
SI1. Dependence of the absorption signal on the pump energy

Dependence of the absorption signal, at the indicated probe wavelengths, on the pump energy at 6 (a) and 470 ps (b) pump-probe delays. The points marked with the star correspond to the energies employed in the TA measurements reported in the manuscript.



SI2. Pump-repump-probe experiments with repump at 800 nm

Pump (267 nm)–repump (800 nm)–probe spectra collected for aniline in methanol at fixed pump–repump delay (τ_1 = 20 ps) and at the indicated repump–probe delays (τ_2).



SI2. CAM-B3LYP and XMS-CASPT2(8e,9o) vertical excitation energies.

Table SI2. CAM-B3LYP and XMS-CASPT2(8e,9o) vertical excitation energies (VEE) for the most stable structures of the aniline$(H_2O)_1$ and aniline$(CH_3OH)_1$ clusters.

Structure	S_1		S_2		S_2-S_1 [eV]
	VEE [eV] (nm)	Character	VEE [eV] (nm)	Character	
CAM-B3LYP					
1-aniline$(H_2O)_1$	5.08 (244)	ππ*	5.40 (230)	πRydberg	0.32
2-aniline$(H_2O)_1$	4.64 (267)	πRydberg	4.82 (257)	ππ*	0.18
1-aniline$(CH_3OH)_1$	5.06 (245)	ππ*	5.38 (230)	πRydberg	0.32
2-aniline$(CH_3OH)_1$	4.84 (256)	ππ*	4.93 (251)	πRydberg	0.09
XMS-CASPT2(8e,9o)					
1-aniline$(H_2O)_1$	5.05 (246)	ππ*	5.79 (214)	πRydberg	0.74
2-aniline$(H_2O)_1$	4.86 (255)	ππ*	5.18 (239)	πRydberg	0.32
1-aniline$(CH_3OH)_1$	5.38 (230)	ππ*	5.77 (215)	πRydberg	0.39
2-aniline$(CH_3OH)_1$	4.93 (251)	ππ*	5.34 (232)	πRydberg	0.41