# **Electronic Supplementary Information**

# The effect of solvent relaxation in the ultrafast time-resolved spectroscopy of solvated benzophenone.

Elena Zvereva,<sup>a,b,c</sup> Javier Segarra-Martí,<sup>d\*</sup> Marco Marazzi,<sup>a,b\*</sup> Johanna Brazard,<sup>e</sup> Artur Nenov,<sup>f</sup> Oliver Weingart,<sup>g</sup> Jérémie Léonard,<sup>e</sup> Marco Garavelli,<sup>f</sup> Ivan Rivalta,<sup>d</sup> Elise Dumont,<sup>d</sup> Xavier Assfeld,<sup>a,b</sup> Stefan Haacke,<sup>e</sup> and Antonio Monari<sup>a,b\*</sup>

- b. CNRS, Laboratoire de Physique et Chimie Théoriques. Vandoeuvre-lès-Nancy, 54506 France
- c. A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre, Russian Academy of Sciences, Arbuzov str. 8, 420088 Kazan, Russia
- *d.* Univ Lyon, Ens de Lyon, CNRS, Université Claude Bernard Lyon 1, Laboratoire de Chimie UMR 5182, F-69342, Lyon, France
- e. Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg and Labex NIE, 23 rue du Loess, 67034 Strasbourg Cedex, France.
- f. Università di Bologna, Dipartimento di Chimica Industriale "Toso Montanari" viale del Risorgimento 4, Bologna, Italy.
- g. Heinrich-Heine-Universität Düsseldorf, Institut für Theoretische Chemie und Computerchemie, Universitätsstr. 1, 40225 Düsseldorf, Germany

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*a.* Université de Lorraine – Nancy, Laboratoire de Physique et Chimie Théoriques. Vandoeuvre-lès-Nancy, 54506 France

#### 1. Molecular dynamics details

To simulate the bulk phase, periodic boundary conditions were applied, including a cutoff to turn off the interactions between atoms that are more than 9.0 Å apart, by the Particle Mesh Ewald (PME) method.<sup>S1</sup> Temperature was controlled using Langevin dynamics<sup>S2</sup> with collision frequency of 1 ps<sup>-1</sup>. A time step of 2 fs was used to integrate Newton's equations of motion. The pressure was maintained at 1 atm by the Monte Carlo thermostat.

The system was pre-equilibrated as follows: an energy minimization of 8000 steps was performed (4000 steps using the steepest descent algorithm followed by 4000 steps using the conjugate gradient algorithm) prior to (*i*) 200 ps molecular dynamics (MD) to heat the system up to 300 K in the NVT canonical ensemble, followed by (*ii*) a 200 ps MD equilibration in the NPT isothermalisobaric ensemble at 300 K and 1 atm to acquire the correct density. Finally, a 100 ns MD production run was performed.

# 2. RASPT2 details and results

Restricted active space self-consistent field (RASSCF)<sup>S3</sup> and its second-order perturbation theory extension (RASPT2)<sup>S4,S5</sup> were used as implemented in the MOLCAS 8 package.<sup>S6</sup> All bonding  $\pi$  valence orbitals and the n<sub>o</sub> were included into the RAS1 subspace, while all anti-bonding valence  $\pi^*$  orbitals comprised the RAS3 subspace. Five holes/electrons were allowed into the RAS1/RAS3 subspaces, respectively, leading to RASPT2(5,8|0,0|5,7). Atomic Natural Orbital basis of large type (ANO-L)<sup>S7,S8</sup> were employed in their triple- $\zeta$  (VTZP) contraction. This particular choice of active space and basis set was taken following a previous extensive benchmark showing it to be the most accurate affordable approach in gas-phase.<sup>S9</sup>

One representative trajectory was chosen to be computed at the RASPT2(5,8|0,0|5,7)/VTZP level at the different delay times (0, 100, 200 and 300 fs) to assess the relative accuracy of the B3LYP/6-311++G<sup>\*\*</sup> 2D spectra reported in the main text (Figure 6). Water molecules were explicitly included in the quantum mechanical region when they featured 3.0 Å or less from the oxygen in the carbonyl group of benzophenone. To compute the temporal evolution of the fingerprints along the excited state relaxation we used a simplified 'snapshot' protocol previously reported.<sup>S10</sup>



# 3. Experimental pump-probe spectra in methanol and hexane

**Figure S1.** Experimental pump-probe spectra for BP in methanol (left) and hexane (right) following excitation to  $S_1$  state.

# 4. Comparison between 2DES spectra calculated at TD-DFT and RASPT2 level

The DFT functional selected for a reliable simulation of pump-probe and 2DES is B3LYP (Figures 3 and 6 in the main text). This means, as explained in the Methods section, that this functional was selected for single point QM/MM calculations for each of the snapshots of the S0 (for t=0 fs) and S1 (for t=100, 200, 300 fs) QM(CAM-B3LYP)/MM dynamics.

ESA spectra were generated by convoluting the computed ensemble S1-Sn oscillator strengths and excitation energies in eV with a Gaussian function of 0.15 eV FWHM. The resulting spectra were then converted to wavelengths.

Indeed, also the CAM-B3LYP functional was employed (Figure S2), finding divergences in the energetics concerning the assignments of the S1-ESAs, as compared especially to RASPT2 results.<sup>S9</sup> Hence, B3LYP was preferred.

Since the RASPT2 method is more accurate but highly demanding from the computational point of view, the 2DES was simulated only for one representative trajectory and compared with the selected B3LYP functional (Figure S3). As expected, the high-energy window is vastly different, since the doubly excited states (DEs) dominate the overall intensity, as also partially found by DFT/MRCI (see next section). On the other hand, for both levels of theory signals are recorded in the 17000-20000 cm<sup>-1</sup> window, even though at higher intensity for TD-DFT. Concerning the low-energy window (around 12000 cm<sup>-1</sup>), both TD-DFT and RASPT2 show the S1-ESA1 signal, more intense by the multiconfigurational treatment, due to DEs, especially at 200 and 300 fs.



 $\Omega_1 \,({
m x}\,\,10^3\,{
m cm}^{-1})$ 

Figure S2. 2DES calculated at CAM-B3LYP/6-311++G(d,p) level for the 82 ensemble trajectories



**Figure S3.** Comparison of 2DES simulated for a representative trajectory: B3LYP/6-311++G(d,p) (left) and RASPT2(5,8|0,0|5,7)/ANO-L-VTZP (right) levels of theory. Assignments are shown for the RASPT2 2DES, indicating double excitations:  $\pi$ - $\pi$ \* DE.

## 5. DFT-MRCI details and results

Excitation energies and transition dipole moments were computed for 82 QM/MM trajectory snapshots at 0, 100, 200 and 300 fs using the DFT/MRCI approach, as mentioned in the main text. As for the other levels of theory, all water molecules within a distance of 3 Å of the benzophenone oxygen were calculated explicitly as QM water molecules, while the remaining water molecules were described by an electrostatic field using the TIP3P charges.

Concerning DFT/MRCI details, an energy selector of 0.8, a selector threshold of 0.003 and the "tight" parameter set computing the first 30 singlet states were employed. The initial reference space included 12 orbitals, 12 electrons and single excitations. After convergence, the calculation was repeated with a newly generated reference space based on the previous CI-wavefunction to include all important configurations.

The obtained results are shown in Figures S4 and S5. Especially, the linear absorption spectrum (Figure S4) is in agreement with the TD-DFT and experimental results shown in the main text (Figure 1b), recording a slight red shift. Concerning the pump-probe spectra (Figure S5), DFT/MRCI gives a similar description compared to TD-DFT: three main spectral regions due to S<sub>1</sub>-ESAs are found, one in the high energy section (300-350 nm), a second one in the 500-600 nm

regime and the third one above 950 nm. The sharp peak around 300 nm is due to excitations to higher energy states (S20-S27). These states partly include double excitations with respect to the ground state. The main difference between TD-DFT and experiments (Figure 3 of the main text) and DFT/MRCI lies in the 500-600 nm band: by TD-DFT, the intensity is almost constant from 100 to 300 fs, while by DFT/MRCI a decrease in time is observed. On the other hand, by both TD-DFT and DFT/MRCI methods a consistent blue shift in time is recorded for the low energy band (> 950 nm).



**Figure S4.** Benzophenone linear absorption spectrum in water solution, simulated as a convolution of Gaussian functions (FWHM = 0.3 eV).



**Figure S5.** Benzophenone time-resolved pump-probe spectra, simulated as a convolution of Gaussian functions (FWHM = 0.3 eV), by TD-DFT (up) and DFT/MRCI (down) methods.

#### 6. Water behaviour

During the excited state dynamics, water molecules tend to be attracted by the carbonyl group of benzophenone. To highlight this, here we show the averaged number (for all 82 QM/MM trajectories) of water molecules having at least one hydrogen atom at a maximum distance of 3 Ångström from the oxygen atom of benzophenone, as a function of time (Figure S6). Data are taken at 0, 100, 200 and 300 fs.





**Figure S6.** Left: representative snapshot at 0 fs, showing only the water molecules (two) in the vicinity of the benzophenone carbonyl group. Right: Graph showing the average number of water molecules near the carbonyl group, that tends to increase with time on the S1 state.

# TD-DFT CASSCF Occupied Virtual Occupied Virtual Image: Comparison of the stress of the stress

#### 7. Orbitals corresponding to S<sub>1</sub>-ESAs

**Figure S7.** Main contributions to the S<sub>1</sub>-ESA1,2,3,4,5, at both TD-DFT (B3LYP/6-311++G<sup>\*\*</sup>) and multiconfigurational (CASSCF/ANO-L-VTZP) level of theory. At CASSCF level, only singly excited configurations are shown.

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