Could solvent vibrational modes generate coherent oscillation in excited organic dye?

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The coherent oscillation in excited organic molecules are studied with 2DES. The use of different solvent enhances oscillations with the frequency of solvent modes. This was confirmed by using standard and deuterated DMSO. The same measurements on pure solvent reveal the Raman spectrum of solvent.

The effects of the solvent in absorption spectra of organic dyes were extensively studied since the fifties [1]. In ultrafast optical spectroscopy is often thought as a polarizable continuum or to fluctuate in the frequencies of transition inducing dephasing and decoherence [2].
Here we performed 2DES on systems consisting of a charge molecule (PEPEP) and highly dipolar solvents, where the coupling between molecule and solvent is expected to be maximized. Frequencies of oscillation are mainly investigated by Fourier transforming the 2DES signal along the population time and integrating the other frequencies axes, obtaining integrated FFT spectra. The oscillations of coherences in 2DES maps are found to be related to a specific mode of the solvent around 650 cm^{-1}. The frequency of this oscillation is present also in the Raman spectrum of PEPEP and in the CH_3CN sample but it is greatly enhanced in DMSO and d-6 DMSO that own a strong Raman band in that region. Moreover, the frequency of this oscillation is slightly shifted as a function of the solvent used.

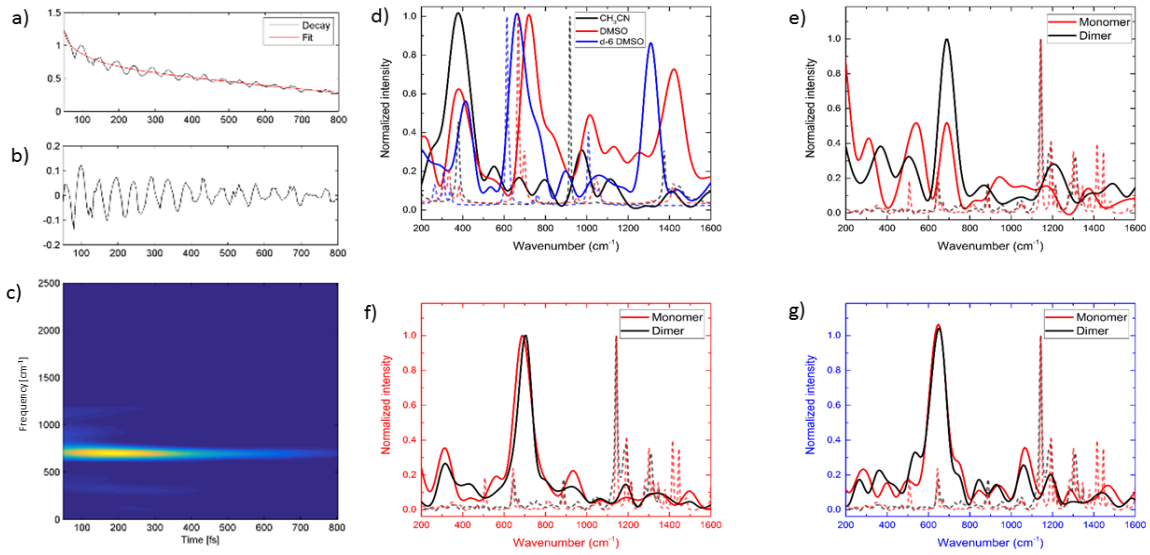

Fig.1 (a) Decay of 2DES signal of PEPEP charge molecule fitted by multi-exponential function. (b) Residuals of Multi-exponential fitting (c) Time frequency transform of the signal that evidence the decay of only one oscillation of frequency equal to a vibrational mode of the solvent used (DMSO). FFT spectra of pure solvents reveals their own Raman spectra (d). On the contrary, FFT spectra of the PEPEP molecule are weakly related to their own Raman spectra and strongly depend on the solvents used. Measurements are performed on CH_3CN (e), DMSO (f) and d-6 DMSO (f). In particular, in case of DMSO and d-6 DMSO the frequency enhanced is the mode of the solvent close to 700 cm^{-1}.

[1] H. E. Ungnade, "The Effect of Solvents on the Absorption Spectra of Aromatic Compounds," *J. Am. Chem. Soc.*, vol. 75, no. 2, pp. 432–434, 1953.

[2] W. W. Parson, *Modern Optical Spectroscopy: With Examples from Biophysics*. 2009.