

Impact of Hydrogen Bonding on the Vibrational Relaxation of para-Nitroaniline

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After photo-physical and photo-chemical processes in solution the re-distribution of excess energy is crucial for the stabilization of the reaction products. para-Nitroaniline (pNA) is a very suitable model system for these processes: After photo-excitation it undergoes a rapid 300 – 500 fs internal conversion (IC) to its electronic ground state and thereby releases 25000 cm⁻¹ of excess energy. The transfer of this energy to its solvent surroundings has been studied in dependence of the solvent nature by pump-probe spectroscopy in the visible¹. This yields a global measure for the vibrational excitation and its dynamics. Here, time-resolved IR experiments on pNA in different solvents are presented aiming at mode specific information (see Figure 1).

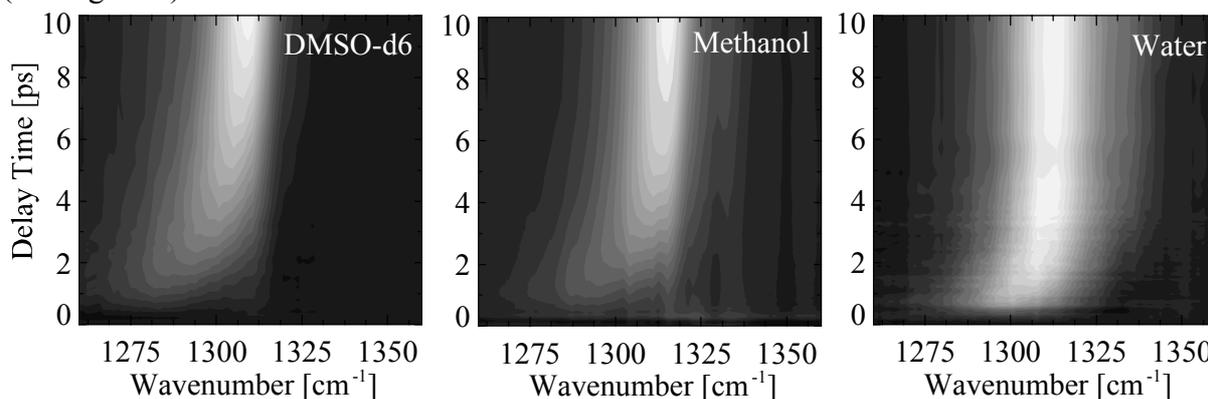


Figure 1: Time resolved IR-data of pNA in different solvents. The data shown is corrected for the bleaching signal observed at zero delay time. Lighter grey corresponds to increased bleach corrected absorption. Dark black surfaces represent no absorption changes.

From a comparison with time resolved non resonant Raman data² one can conclude that the recorded peak shifts are a manifestation of excited low frequency modes which couple anharmonically to the NO₂–stretch vibration. This symmetric NO₂–stretch vibration responds to ultrafast IC with a pronounced down shift of its IR resonance frequency (see Figure 1). The amplitudes of these shifts and their relaxation time constants depend on the solvent, the values being: DMSO-d₆: -29cm⁻¹, 3.1 ps, methanol: -25cm⁻¹, 2.1 ps and water -15cm⁻¹, 1.6 ps. The results indicate that the relaxation of the low frequency modes – observed via the anharmonic coupling to the mid IR-mode - depends on the hydrogen bonding capabilities of the solvent.

¹ S.A. Kovalenko, R. Schanz, H. Hennig, and N. P. Ernsting, „Cooling dynamics of an optically excited molecular probe in solution from femtosecond broadband transient absorption spectroscopy“, *Journal of Chemical Physics*, **2001**, *115*, 3256-3273.

² T. Schrader, A. Sieg, F. Koller, W. Schreier, Q. An, W. Zinth, P. Gilch, „Vibrational relaxation following ultrafast internal conversion: comparing IR and Raman probing“, *Chemical Physics Letters*, **2004**, *392*, 358-364