Unravelling the Pathways of Ultrafast Vibrational Energy Flow in Hydrogen Bonds

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Hydrogen bonding plays a central role for the structural and dynamical properties of many condensed phase molecular systems. The theoretical modelling continues to pose a challenge because the quantum nature of the hydrogen comes along with a strong correlation between its motion and that of the environment. This is exemplified in the well-known dependence of the hydrogen's potential on the donor-acceptor distance in a simple A-H..B complex. It was only recently that details of the ultrafast dynamics of condensed phase hydrogen bonds have been unveiled by using nonlinear time-resolved infrared spectroscopy. [1]
In this contribution we will discuss aspects of the theoretical simulation of ultrafast hydrogen bond dynamics. This involves the determination of effective model Hamiltonians based on the combination of ab initio calculations for a small part of the system with spectral densities for the solvent interaction, which are derived from classical molecular dynamics.[2] The multidimensionality leads to a complex pattern of anharmonic couplings giving rise to various pathways for vibrational energy redistribution after hydrogen bond excitation. The dynamics of this process can be modelled by a Quantum Master Equation, which also serves to establish the link to the nonlinear infrared experiments.[3]
The theoretical approach will be discussed in some detail for the specific example of phthalic-acid-monomethylester[4] and first results for a model system mimicking the hydrogen bonds in adenine-thymine base pairs will also be given.

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[1] E. T. J. Nibbering, T. Elsaesser, "Ultrafast Vibrational Dynamics of Hydrogen Bonds in the Condensed Phase", Chemical Reviews, **2004**, 104, 1887-1914

[2] O. Kühn, H. Naundorf, "Dissipative Wave Packet Dynamics of the Intramolecular Hydrogen-Bond in o-Phthalic Acid Monomethylester", Physical Chemistry Chemical Physics, **2003**, 5, 79-86

[3] V. May, O. Kühn, »Charge and Energy Transfer Dynamics in Molecular Systems », Wiley-VCH, Weinheim, 2004.

[4] K. Heyne, E. T. J. Nibbering, T. Elsaesser, M. Petkovic, O, Kühn, « Cascaded Energy Redistribution upon O-H Stretching Excitation in an Intramolecular Hydrogen Bond », Journal of Physical Chemistry A, **2004**, 108, 6083-6086