Electron Transfer Induced Vibrational Excitation

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Electron transfer (ET) between a molecule and a semiconductor can be accompanied by vibrational excitation of the resulting cation due to Frank-Condon overlap [1]. The energy that is necessary for exciting these high-energy vibrational modes reduces the excess energy of the transferred electron and leads to an electron transfer spectrum. This spectrum caries information that is analog to the vibrational wavepacket that is involved in the ET process, including its coherent beating that results from the periodic encounter of the transition state. The dynamics of the wavepacket, and in particular its coherence time, provides insight into the strength of donor/acceptor coupling and the adiabaticity of the process. This information is important but not readily available for ET systems comprising a large number of possible electron acceptor states, because neither the rate of the reaction nor the electronic spectrum allow unambiguous assignment. We apply pump-degenerated four wave mixing (p-DFWM) to identify vibrational modes that couple to excited states and to the formation of cations in molecules that are chemically bound to semiconductor surfaces and undergo electron transfer upon photo excitation. We are able to follow the evolution of the vibrational modes, determine their lifetime and de-excitation pathways. Fig.1 shows Zn-tetraphenyl porphyrin as an example. The perimeter stretch mode couples strongly to electronic Soret band excitation. The mode shifts to higher energies at later times which shows that the original prepared state is a hot excited state [2]. The vibrational mode gains energy while the wavepacket moves towards the bottom of the anharmonic potential. P-DFWM has been used to study molecular excited state dynamics before, here we are applying it to solid-state heterogeneous electron transfer systems.

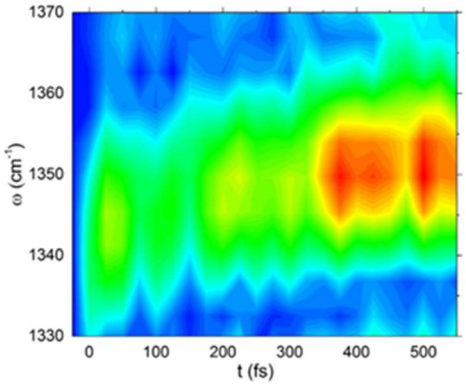

Fig 1 a) Evolution of a Zn-TTP perimeter stretch mode.

References:

[1] J. Nieto-Pescador, B. Abraham, L. Gundlach, JPCL. 5, 3498 (2014)

[2] B. Abraham B., J. Nieto-Pescador, L. Gundlach, JPCL. 7, 3151 (2016)