CFEL SCIENCE

SEMINAR

27th February 2013 - 11:00 a.m.

CFEL-bldg. 99, seminar room IV

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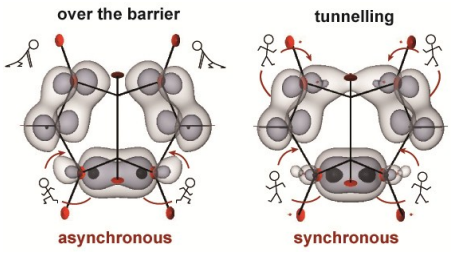
Quantum dynamics of electron-nuclear fluxes in chemical processes: initialization, analysis and design of measurements by molecular high order harmonic spectroscopy

The talk will be divided into two parts: The first one will deal with electron-nuclear fluxes in pericyclic reactions in the electronic ground state, exemplified for the degenerate Cope rearrangement of semibullvalene, see Figure 1. Specifically, we discover that electronic bond-to-bond fluxes may proceed either synchronously or asynchronously, depending on the preparation of the reactants [1, 2]: Reactions with energy E well above the barrier B proceed asynchronously - even during synchronous nuclear rearrangements - whereas reactions with energy well below B proceed synchronously. The former scenario (E > B) can be initialized by means of selective laser pulses [3] whereas the latter (E < B) corresponds to coherent tunneling at cryogenic temperatures [4].

The second part will deal with the design of experiments to measure these quantum fluxes: We study numerically pump-probe schemes using a midinfrared, intense few-femtosecond probe laser pulse which generates molecular high-order harmonics (MHOHG) from a coherent superposition of electron-nuclear wave packets prepared by a weak femtosecond UV pump pulse from an initial bound state in the molecular ions H_2^+ and T_2^+. We show that by varying the time delay between the intense probe pulse and the UV pump pulse by a few hundred attoseconds one alters the MHOHG signal intensity by orders of magnitude. The periodicity of the MHOHG intensity variations as function of the time delay is equal to the period of the electron oscillation in the coherent superposition which varies with internuclear distance. Finally, we relate this high sensitivity of MHOHG spectra to opposing electron velocities (fluxes) in the electron wave packets of the recombining (recolliding) ionized electron and of the bound electron in the initial coherent superposition of two electronic states [5, 6, 7].



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[2] Bredtmann, T.; Manz, J. *Angew. Chemie. Int. Ed.* **2011**, *50*, 12652.
[3] Bredtmann, T.; Manz, J. *J. Chem. Sci.* **2012**, *124*, 121.
[4] Zhang, X.; Hrovat, D. A.; Borden, W. T. *Org. Lett.* **2010**, *12*, 2798.
[5] Bredtmann, T.; Chelkowski, S.; Bandrauk, A. D. *Phys. Rev. A* **2011**, *84*, 021401(R).
[6] Chelkowski, S.; Bredtmann, T.; Bandrauk, A. D. *Phys. Rev. A* **2012**, *85*, 033402.
[7] Bredtmann, T.; Chelkowski, S.; Bandrauk, A. D. *J. Phys. Chem. A* **2012**, *DOI:10.1021/jp3063977*.

Host: Robin Santra - CFEL Theory Division