CFEL SCIENCE

SEMINAR

16th October 2013 - 2:00 p.m.

CFEL-bldg. 99, seminar room IV

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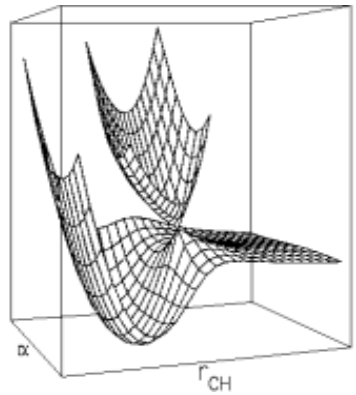
Ab initio-based quantum studies of nonadiabatic molecular photodynamics

A general introduction is given into the quantum-dynamical treatment of molecular motion following photoexcitation in the near UV spectral range. This generates the system in a highly non-equilibrium conformation in an excited electronic state whereby vibrational motion and various energy redistribution processes are initiated. The latter comprise also the nuclear and electronic degrees of freedom through which the usual Born-Oppenheimer separation betweens electrons and nuclei becomes invalid. Conical intersections of potential energy surfaces (see the illustrative figure) have emerged as prototypical scenarios signaling a complete breakdown of the Born-Oppenheimer approximation[1]. This leads to a thorough redistribution of the spectral intensity and a nonradiative transition between different potential energy surfaces proceeding on the same timescale as nuclear vibrations, i.e. femtoseconds. The coupled multimode nature of the nuclear wavefunction necessitates the use of efficient wavepacket propagation schemes, in particular, the MCTDH method[2].

In the talk, the general considerations are illustrated by suitable examples to highlight the most relevant phenomena. These are taken from our work on the photoelectron spectra of five-membered ring molecules[3] the UV excitation spectrum of SO_2[4] and benzenoid cations[5], featuring more than two strongly coupled electronic states.



1 W. Domcke, D.R. Yarkony, and H. Köppel (Eds.), Conical Intersections: Electronic Structure, Dynamics and Spectroscopy (World Scientific, Singapore, 2004).
2 M. H. Beck, A. Jäckle, G.A. Worth, and H.-D. Meyer, Phys. Rep. 324, 1 (2000).
3 H. Köppel, E. Gromov and A. Trofimov, Chem. Phys. 304, 35 (2004).
4 C. Leveque, A. Komainda, R. Taieb and H. Köppel, J. Chem. Phys. 138, 044320 (2013).
5 S. Faraji and H. Köppel, J. Chem. Phys. 137, 22A531 (2012).

Host: Robin Santra - CFEL Theory Division