

MO 28: Poster: Theory: Molecular Dynamics

Time: Thursday 16:00–18:00

Location: P1

MO 28.1 Thu 16:00 P1

Energy transfer among distant quantum systems in spatially shaped laser fields — ●OLIVER KÜHN¹, GUENNADDI PARAMONOV¹, and ANDRE DIETER BANDRAUK² — ¹Institut für Physik, Universität Rostock, Germany — ²Laboratoire de Chimie Théorique, Faculté des Sciences, Université de Sherbrooke, Canada

The quantum dynamics of two H atoms with a separation of 5.3 nm excited by ultrashort ($t_p = 5$ fs) and spatially shaped laser pulses is studied by the numerical solution of the non-Born-Oppenheimer time-dependent Schrödinger equation within a 3D model, including the internuclear distance R and the two z coordinates of the electrons. Different types of a spatial laser field envelope are considered which either excite both atoms (A and B) or atom A only. In both cases an efficient energy transfer from atom A to atom B has been found. The ionization of atom B achieved mostly after the end of the laser pulse is close to or even higher than that of atom A. It is shown that with a narrow spatial envelope of the laser field, the underlying mechanisms of the energy transfer from A to B and the ionization of B are the Coulomb attraction of the laser driven electron by the proton of atom B and a short-range Coulomb repulsion of the two electrons when their wave functions significantly overlap in the domain of atom B. In the case of a broad Gaussian spatial envelope of the laser field, the opposite process also occurs with a smaller probability: the energy is transferred from the weakly excited atom B to atom A, and the ionization of atom A is also induced by the electron-electron repulsion in the domain of atom A due to a strong overlap of the electronic wave functions.

MO 28.2 Thu 16:00 P1

Lineshapes of absorption- and circular dichroism spectra of molecular aggregates — ●KLAUS RENZIEHAUSEN and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We perform time-dependent quantum calculations on the absorption and circular dichroism (CD) spectroscopy of molecular aggregates. The interplay between vibrational motion, geometry, electronic coupling and aggregate size to arrive at a certain lineshape is analyzed in detail. The numerical results are interpreted in terms of analytical considerations [1], and a comparison to experiment is given [2].

[1] F.C. Spano, *J. Chem. Phys.*, **122**, 234701 (2005). [2] Z. Chen *et al.*, *Chem. Eur. J.* **13**, 436 (2007).

MO 28.3 Thu 16:00 P1

Excited State Solvation Dynamics of a Polarity Probe — CHRISTOPH ALLOLIO and ●DANIEL SEBASTIANI — Physics Department, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

The fluorescent dye *N*-methyl-6-quinolone (MQ) can be used as a probe for the local infrared spectrum in the liquid phase.[1] Femtosecond spectroscopy has given indirect access to its excited state solvation dynamics via the time dependent Stokes shift. In its protonated form (HMQ), the molecule is also a photoacid.[2] Recent results have extended its application to biochemical environments.[3] Using ab-initio molecular dynamics we examine the solvation dynamics of MQ in its ground and excited state. We discuss the effect of MQ electronic excitation on the solvent environment, focussing on the effects on hydrogen bonding and electrostatic screening. The results are compared to spectroscopical data and benchmark calculations.

1 Pérez Lustres, J. L.; Kovalenko, S. A.; Mosquera, M.; Senyushkina, T.; Flasche, W.; Ernsting, N. P. *Angew. Chem. Int. Ed.*, **44**, 5635-5639 (2005)

2 Pérez Lustres, J. L.; Rodriguez-Prieto, F.; Mosquera, M.; Senyushkina, T.; Ernsting, N. P.; Kovalenko, S. A. *J. Am. Chem. Soc.*, **129**, 5408-5418 (2007)

3 Sajadi, M.; Ajaj, Y.; Ioffe, I.; Weingärtner, H.; Ernsting, N. P. *Angew. Chem. Int. Ed.*, **49**, 454-457 (2010)

MO 28.4 Thu 16:00 P1

Water molecules in ultrashort intense laser pulses — ●SIMON PETRETTI¹, ALEJANDRO SAENZ¹, ALBERTO CASTRO², and PIERO DECLEVA³ — ¹Humboldt-Universität zu Berlin, Germany — ²Universidad Zaragoza, Spain — ³Università di Trieste, Italy

Ionisation of water molecules exposed to ultrashort intense laser pulses is studied theoretically within a newly developed single-active-electron approximation [1,2]. In this approach the three-dimensional time-dependent Schrödinger equation describing one electron in the combined field of a multi-centred molecular core and the laser field is solved numerically.

It is shown that for a laser wavelength of 800 nm and for a variety of laser intensities the alignment-dependent ionisation of single orbitals can be interpreted and explained by means of the orbital structure. This is demonstrated by a three-dimensional representation of the ionisation yield of the orbitals that reflects well their shape.

One of the key characteristics of water molecules is their relatively large dipole moment. Thus, it is in principle not only possible to consider aligned, but also oriented molecules in which, e.g., the molecular dipole moment points parallel or anti-parallel to the laser field. It is shown that the ion yield in ultrashort phase-stabilized laser pulses strongly depends on the absolute orientation.

[1] Awasthi *et al.*, *Phys. Rev. A*, **77**, 063403 (2008).

[2] Petretti *et al.*, *Phys. Rev. Lett.*, **104**, 223001 (2010).

MO 28.5 Thu 16:00 P1

Rotational effects on enantioseparation — ●ANDREAS JACOB and KLAUS HORNBERGER — Max-Planck-Institut für Physik komplexer Systeme, Dresden

Recently, several ideas to separate enantiomers have been proposed, i.e. to split molecules in a left handed configuration from their right handed mirror state [1,2]. They are based on the dynamics caused by the equations of motion in an adiabatic basis produced by laser induced gauge potentials. Since the effect of molecular rotation has been neglected in these studies, we want to study the influence of the orientation state on the enantioseparation by numerical integration of the full molecular rotation state.

[1] Li, Bruder and Sun, *Physical Review Letters* **99**, 130403 (2007)

[2] Li and Shapiro, *Journal of Chemical Physics* **132**, 194315 (2010)

MO 28.6 Thu 16:00 P1

A Wigner function for molecular rotation states — ●TIMO FISCHER and KLAUS HORNBERGER — Max Planck Institute for the Physics of Complex Systems, 01187 Dresden, Germany

We construct a phase space representation of the rotation states of an asymmetric top molecule, relying on the fact that the configuration space is the Group $SO(3)$. We evaluate the Wigner function for asymmetric top eigenstates and provide Weyl symbols for the relevant angular momentum operators. This formalism is then compared to a second approach applicable to physical systems with Lie Group symmetries. The latter makes use of generalized coherent states to define an adequate phase space formulation satisfying the Stratonowich-Weyl correspondence.