

MO 3: Theory: Quantum Chemistry and Molecular Dynamics

Time: Monday 16:30–18:45

Location: F 102

Invited Talk

MO 3.1 Mo 16:30 F 102

Mechanisms of Triplet Generation and Depletion in Organic Molecules — ●CHRISTEL M. MARIAN — Theoretical and Computational Chemistry, HHU Düsseldorf, Germany

Inter-system crossing (ISC) plays a central role in photochemistry, photobiology, and photodynamic therapy. While a high triplet quantum yield is desirable for photosensitizers, rapid quenching of the T1 state is preferable for photoprotectors. A prerequisite for the understanding of the underlying mechanisms is the knowledge of the excited states and their interactions.

State-of-the-art quantum chemical methods can help to shine light on the cascade of relaxation processes following the primary photo excitation. The combined density functional and configuration interaction method (DFT/MRCI) has proven to yield high-quality electronic excitation spectra. Electronic spin-orbit matrix elements are calculated using the SPOCK program package while vibrational contributions to ISC rates are determined using the SNF and VIBES programs.

The mechanisms of triplet formation and depletion have been investigated for a variety of organic chromophores. Here, only a few model cases are presented: Flavone where the ISC mechanism follows the well-known El-Sayed rules, porphyrin where vibronic spin-orbit coupling between the S1 and T1 states is responsible for the high triplet quantum yield, and flavin where a solvent or protein environment have a significant impact on the ISC mechanism. Efficient triplet quenchers such as cyclooctatetraenes or diphenylhexatrienes are found to possess fast relaxation pathways to the electronic ground state.

MO 3.2 Mo 17:00 F 102

Relativistic srDFT-MP2 for the dimers of group 18 of the periodic system. — ●OSSAMA KULLIE and TROND SAUE — Laboratoire de Chimie Quantique CNRS/ Uni Strasbourg, 4, rue de Blais Pascal, 67070 Strasbourg, France. Email:okullie@chimie.u-strasbg.fr

In this talk I will present the well established short-range density functional (srDFT) in the theoretical chemistry, in which the Coulomb operator in the Hamiltonian is separated in two parts, a short-range part and a long-range part. The short-range part is treated by the virtue of a standard density functional like LDA, GGA whereas the long-range part is treated by the wave function methods or post Hartree-Fock methods like second-order Moller-Plesset perturbation MP2 or coupled-cluster method CCSD(T). The results will be demonstrated with calculations using the relativistic DIRAC-package[1] for the rare gas dimers Rg₂ of group 18 of the periodic system, where the bonding is weak and known to be van der Waals like or due to London dispersion force. [1]http://wiki.chem.vu.nl/dirac/index.php/Dirac_Program

MO 3.3 Mo 17:15 F 102

Untersuchung des Konformerensraums des flexiblen Neurotransmitters Melatonin — ●MIRIAM WOLLENHAUPT und MICHAEL SCHMITT — Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie

Der Konformerensraum des Neurotransmitters Melatonin wurde in den niedrigsten elektronischen Singlettzuständen mit Hilfe der coupled cluster Methode CC2 in der Näherung der resolution of identity (RI) untersucht. Die Ergebnisse für die Energetik und die Strukturen der verschiedenen Konformere, die sich in der Orientierung der Seitengruppe unterscheiden, werden diskutiert und mit den Ergebnissen von kürzlich erhaltenen rotationsaufgelösten elektronischen Spektren des Melatonins verglichen. Neben den Grundzuständen wurden auch die niedrig liegenden elektronisch angeregten Singlet-Zustände untersucht, die sich in der Nomenklatur nach Platt als L_a- und L_b-Zustand klassifizieren lassen.

MO 3.4 Mo 17:30 F 102

Semiclassical dynamics of open quantum systems — CHRISTOPH-MARIAN GOLETZ, WERNER KOCH, and ●FRANK GROSSMANN — Institut für Theoretische Physik, TU Dresden, 01062 Dresden, Germany

The applicability of the Semiclassical Hybrid Dynamics (SCHD) [1] can be extended to the finite temperature case. Results obtained for the thermalization process of a harmonic as well as an anharmonic oscillator can then be compared to those obtained using the recently developed Semiclassical Brownian Motion method (SCBM) [2]. Since

the SCHD method includes individual reservoir modes explicitly, their distribution can be tailored to accurately reflect all aspects of the environmental influence. Details that need to be taken care of in constructing the finite equivalent of the infinite bath are discussed and different contributions to the thermalization process are identified.

[1] C.-M. Goletz and F. Grossmann, J. Chem. Phys. **130**, 244107 (2009)

[2] W. Koch, F. Grossmann, J. T. Stockburger, and J. Ankerhold, Phys. Rev. Lett. **100**, 230402 (2008)

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MO 3.5 Mo 17:45 F 102

Vibronic transitions and quantum dynamics in molecular oligomers: a theoretical analysis with an application to aggregates of perylene bisimides — ●VOLKER ENGEL¹, JOACHIM SEIBT¹, THERESA WINKLER¹, KLAUS RENZIEHAUSEN¹, VOLKER DEHM², FRANK WÜRTHNER², and HANS-DIETER MEYER³ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ³Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg

Vibronic absorption spectra of molecular aggregates consisting of up to $N = 9$ monomer units are calculated employing methods of time-dependent quantum mechanics. Taking one vibrational degree of freedom for each monomer into account and treating one-exciton excited electronic states, this leads to a problem with N vibrations and N electronically coupled states. The demanding quantum propagation is carried out within the MCTDH (Multi-Configuration Time-Dependent Hartree) method. Spectral features of and population transfer in the aggregates are analyzed as a function of the aggregate size and the strength of the electronic coupling. Employing a model for oligomers of perylene bisimides it is shown how measured temperature-dependent absorption spectra correlate with the aggregate size. Furthermore, the exciton localization and dynamics in these aggregates is investigated.

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Calculation of the structure of H₃⁻ negative ion, and of its formation rate in the interstellar medium — MEHDI AYOUB¹, ●VIATCHESLAV KOKOULINE¹, ROMAIN GUÉROUT¹, MAURICE RAOULT¹, JACQUES ROBERT¹, ROLAND WESTER², and OLIVIER DULIEU¹ — ¹Laboratoire Aimé Cotton, CNRS, Université Paris-Sud, Orsay, France — ²Physikalisches Institut, Universität Freiburg, Germany

We computed a new accurate potential energy surface for the simplest negative triatomic ion H₃⁻. We determined its permanent dipole moment, bound states, rotational constants, predissociated vibrational resonances and their lifetimes. We also present the theory of radiative association of atoms and molecules, applied to the (H₂-H⁻) system. We suggest a way to detect H₃⁻ in the interstellar medium, which would be also a probe for the presence of H⁻.

MO 3.7 Mo 18:15 F 102

Quantum-induced symmetry breaking explains infrared spectra of CH₅⁺ isotopologues — ●SERGEI IVANOV, ALEXANDER WITT, and DOMINIK MARX — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany

Protonated methane, CH₅⁺, has been investigated intensively using a host of different experimental and theoretical techniques since decades, see Ref. [1] for a review. This is due to the correlated large amplitude motion of its five protons around the carbon nucleus that leads to so-called hydrogen scrambling and causes a fluxional molecular structure. Although the protons and deuterons can easily visit all five sites due to vivid scrambling motion, the occupation of the topologically different sites is found to be strongly non-combinatorial and thus non-classical. This is a purely quantum-statistical effect implying a breaking of the classical symmetry of the site occupations induced by zero-point fluctuations, which are governed by the different masses of H and D [2]. Importantly, this quantum-induced symmetry breaking is the key for understanding of the spectral changes occurring upon gradual deuteration of CH₅⁺. *Ab initio* MD in combinations with techniques based on Feynman's formulation of quantum statistical mechanics in terms

of path integrals allow us to fully reproduce the experimental spectra. Moreover, an in-house developed analysis technique enables full assignment of spectral features to molecular motions.

[1] P. Kumar P. and D. Marx, Phys. Chem. Chem. Phys. **8**, 573 (2006)

[2] D. Marx and M. Parrinello, Nature **375**, 216 (1995)

MO 3.8 Mo 18:30 F 102

On-The-Fly Computation of the Vibronic Spectrum of Formaldehyde — •JÖRG TATCHEN¹ and ELI POLLAK² — ¹Heinrich Heine University, Düsseldorf, Germany — ²Weizmann Institute of Science, Rehovot, Israel

Direct molecular dynamics without precomputed potential energy surfaces comprises a well-established tool in classical chemical reaction dynamics and nonadiabatic surface hopping. Developing analogous on-the-fly concepts for the true quantum regime where interference effects and tunneling are important is currently a very active area of research. In this work, we implement a semiclassical theory for the on-the-fly calculation of the $S_0 \rightarrow S_1$ absorption band of formaldehyde. Time-dependent density functional theory is used for the S_1 excited state potential energy surface. We obtain a reasonable description of the vibronic structure already from a frozen Gaussian theory using a few thousand trajectories.