MO 20: Theoretical Molecular Physics

Time: Thursday 14:30–16:45   Location: HS 3042

MO 20.1   Thu 14:30   HS 3042

Dynamics of AlF-AlF: Potential energy surface and intermediate complex characterization — •Xiangyue Liu[1], Weiqi Wang[1], and Jesús Pérez-Ríos[2,3] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — [2]Department of Physics and Astronomy, Stony Brook University, Stony Brook 11794, New York, USA — [3]Institute for Advanced Computational Science, Stony Brook University, Stony Brook 11794-3800, New York, USA

Diatomic metal-fluorine molecules are crucial for cryogenic buffer gas cooling, widely used in precision spectroscopy and laser cooling. Recently, AlF has gained attention for laser cooling due to its efficient laboratory production and highly-diagonal Franck-Condon matrix. This study focuses on the undesirable formation of AlF-AlF dimer complexes. We developed an accurate machine-learning potential energy surface for the AlF-AlF complex at the coupled-cluster theory level. Based on the resulting PES, *ab initio* molecular dynamics simulations have been performed, revealing primary reaction mechanisms. The lifetime of the intermediate AlF-AlF complex at different temperatures has been estimated.

MO 20.2   Thu 14:45   HS 3042

Exotic charged molecules and Rydberg glue — •Daniel J. Bosworth[1,2], Peter Schmelcher[1,2], and Matthew T. Eiles[3] — [1]Zentrum für Optische Quantentechnologien, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany — [2]The Hamburg Centre for Ultrafast Imaging, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany — [3]Max Planck Institute for the Physics of Complex Systems, 01187 Dresden, Germany

Neutral-ion interactions are of fundamental interest in physics and chemistry. Recent experiments are starting to explore them within the quantum regime. The sensitivity of Rydberg atoms to electric fields enables them to form weakly-bound diatomic molecular ions. These dimers bind on micrometer length scales due to the Rydberg's large induced dipole moment, which is the leading-order term in the ion-neutral interaction series. In this theoretical work, we explore the role of the higher-order terms in this interaction series. We first consider a system of a pair of cations interacting with a Rydberg atom at long-range. Surprisingly, we reveal that the Rydberg's quadrupole compensates the enormous Coulomb repulsion between the cation pair, forming a metastable trimer with mixing between states in neighbouring n-manifolds. We discuss the rapid decay of these trimers due to charge transfer of the Rydberg electron. Additionally, we reveal that the quadrupole interaction term introduces a dependence on the sign of the ion's charge, which can significantly alter non-adiabatic couplings between Rydberg states. Such modified couplings would not only affect vibrational dynamics, but also molecular lifetimes.

MO 20.3   Thu 15:00   HS 3042

The effects of dipole self energy in a molecular Tavis-Cummings model — •Lucas Borges, Markus Kowalewski, and Thomas Schnappinger — Department of Physics, Stockholm University, AlbaNova University Center, SE-106 91 Stockholm, Sweden

Theoretical studies in polariton photochemistry describe the molecular and photonic field interactions within the long-wavelength limit. The Pauli-Fierz Hamiltonian in the length gauge representation features a linear light-matter interaction term and a squared dipole self-energy (DSE) term, which assures a stable ground state for the total system. However, this representation blurs the distinction between photon and matter degrees of freedom. We performed nuclear wave functions dynamics from one to three MgH^+ molecules interacting with a single photonic mode in an optical cavity at the electronic strong-coupling regime. We investigate how additional DSE terms in the interaction Hamiltonian affect the system by producing new inter-molecular energy transfer pathways.

MO 20.4   Thu 15:15   HS 3042

Cavity-Born-Oppenheimer Hartree-Fock: Vibronic-Strong-Coupling beyond a single molecule — •Thomas Schnappinger and Markus Kowalewski — Department of Physics, Stockholm University, Sweden

When a molecule interacts with the vacuum field of a nanoscale cavity, strong coupling reshapes the potential energy surfaces to form hybrid light-matter states called polaritons. Recent experiments show that this strong coupling between light and matter is capable of modifying chemical and physical properties. The situation in which the quantized cavity modes are coupled via their characteristic frequency to vibrational degrees of freedom of molecules is called vibrational strong coupling (VSC). In the VSC regime, the chemistry of a single electronic state (mostly the ground state) and its vibrational spectroscopy are influenced by the cavity interaction. In this theoretical contribution we use the ab-initio Cavity-Born-Oppenheimer-Hartree-Fock approach to study the effect of VSC on the ground state properties of single molecules and small ensembles of such molecules. We are able to optimize cavity-coupled molecular systems and can calculate vibropolaritonic IR spectra, since we have implemented analytical gradients. Our ab-initio treatment allows us to study the interactions between individual molecules mediated by the cavity. These interactions give rise to local strong coupling effects that allow the modification of chemical reactivity in the VSC context.

MO 20.5   Thu 15:30   HS 3042

Multi-state mapping approach to surface hopping — •Johan Runeson and David Manolopoulos — Physical and Theoretical Chemistry Laboratory, University of Oxford, UK

Many important problems in physics and chemistry involve non-adiabatic dynamics: nuclear motion on two or more coupled electronic potential energy surfaces. The most popular method to treat this problem is fewest-switches surface hopping (FSSH), which involves stochastic hops of classical nuclear trajectories between adiabatic electronic states. This method can be used with *ab initio* potentials and is widely applied in photochemistry. However, its long-standing problems are overcoherence and violation of detailed balance. A new 'mapping approach to surface hopping' (MASH) [1] appears to resolve many of these issues: it avoids *ad hoc* decoherence corrections and provably relaxes to the correct quantum–classical equilibrium. Although originally developed for two states, we have extended the method to any number of states and applied it to a variety of problems, including gas-phase photochemistry, spin-boson models, and exciton transfer in photosynthetic systems [2]. In all cases, we find MASH to be more accurate as well as more numerically tractable than FSSH. The talk will summarize this development and mention some current exciting applications, including charge transport in organic materials.

[1] J. R. Mannouch and J. O. Richardson, J. Chem. Phys. 158, 104111 (2023). [2] J. E. Runeson and D. E. Manolopoulos. J. Chem. Phys. 159, 094115 (2023).

MO 20.6   Thu 15:45   HS 3042

Open quantum system approach to non-adiabatic molecular physics — Michael Reitz[1], •Nico Bassler[2,3], Raphael Holzinger[4], Ágnes Vibók[5,6], Gábor Halász[5], and Claudiu Genes[3,2] — [1]Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, California 92093, USA — [2]Department of Physics, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), D-91058 Erlangen, Germany — [3]Max Planck Institute for the Science of Light, D-91058 Erlangen, Germany — [4]Institut für Theoretische Physik, Universität Innsbruck, A-6020 Innsbruck, Austria — [5]Department of Information Technology, University of Debrecen, H-4002 Debrecen, Hungary — [6]ELI-ALPS, ELI-HU Non-Profit Ltd, H-6720 Szeged, Hungary

Non-adiabatic molecular phenomena, i.e., processes due to the breakdown of the Born-Oppenheimer approximation, govern the fate of most photophysical and photochemical processes. We propose here an open quantum system approach based on quantum Langevin equations to non-adiabatic molecular physics, with relevance during or after the process of photoexcitation and in the presence of a dissipative, thermal environment. Based on a linear vibronic coupling model, we derive analytical expressions for the non-radiative transition rates of processes occurring at the intersection between two potential energy surfaces such as internal conversion and conical intersections. Our work allows for an intuitive understanding of these processes in terms of multi-phonon sidebands and establishes a connection between open quantum system dynamics, molecular quantum optics, and quantum chemistry.

MO 20.7   Thu 16:00   HS 3042

Molecular motion enhanced excitation transport in molecular aggregates despite internal molecular vibrations — ●Ritesh Pant[1], Varadharajan Srinivasan[2], Alexander Eisfeld[1], and Sebastian Wüster[2] — [1]Max Planck Institute for the Physics of Complex Systems, Dresden, Germany — [2]Indian Institute of Science Education and Research, Bhopal, India

Molecular aggregates can under certain conditions transport electronic excitation energy over large distances due to the long range dipole-dipole interactions [1]. It was shown earlier that the thermal centre-of-mass motion of molecules can enhance the efficiency of transport compared to the static case in the presence of diagonal disorder, when neglecting molecular vibration [2]. Our current research extends this understanding by examining the impact of molecular vibrations, with a particular focus on adiabatic excitation transport. To simulate quantum dynamics of the electronic excitation coupled to vibrations we use non-Markovian quantum state diffusion, solved through the hierarchy of pure states, combined with classical molecular dynamics for centre-of-mass motion of molecules [2, 3]. Using a specific model of torsional molecular motion, we can identify parameter regimes in which the motion aids excitation transfer even in the presence of vibrations, although adiabatic transport appears disrupted by vibrations.

[1] T. Brixner et. al., Adv. Energy Mater. 7, 1700236 (2017). [2] R. Pant et. al., Phys. Chem. Chem. Phys. 22, 21169 (2020). [3] D. Suess et. al., Phys. Rev. Lett. 113, 150403 (2014).

MO 20.8   Thu 16:15   HS 3042

Gas-phase sugar synthesis: The formation of protonated glycolaldehyde — ●Weiqi Wang[1], Hunarpreet Kaur[2], Sandra Brünken[2], and Jesús Pérez Ríos[3,4] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — [2]FELIX Laboratory, Faculty of Science, Radboud University, Toernooiveld 7c, 6525 ED Nijmegen, The Netherlands. — [3]Department of Physics and Astronomy, Stony Brook University, Stony Brook 11794, New York, USA — [4]Institute for Advanced Computational Science, Stony Brook University, Stony Brook 11794-3800, New York, USA

The investigation into the origins and processes of prebiotic synthesis in our universe is pivotal to unraveling the mystery of life's beginnings. Currently, the understanding of the chemical pathways leading to complexity is incomplete and mostly experiential.

A crucial initial step in understanding prebiotic synthesis involves exploring pathways that give rise to simple sugars. This study delves into the intricate reaction networks governing the formation of protonated glycolaldehyde, a key component in sugar synthesis. Through the *ab initio* molecular dynamics method, we systematically explore the entire relevant phase space. To identify the species observed in infrared (IR) experiments, we calculate IR spectra from simulations at finite ensemble temperatures or under specific kinetic temperature conditions. Furthermore, we determine the thermodynamic conditions within the experimental chamber.

MO 20.9   Thu 16:30   HS 3042

A Time-dependent Perspective on Resonant Inelastic X-ray Scattering of Pyrazine — ●Antonia Freibert[1], David Mendive-Tapia[2], Nils Huse[1], and Oriol Vendrell[2] — [1]University of Hamburg — [2]Heidelberg University

The developments of advanced x-ray sources have enabled the study of physical phenomena occurring on the intrinsic timescale of nuclear and electronic motion. One technique that gained considerable attention is resonant inelastic x-ray scattering (RIXS) and its extension into the ultrafast time domain. RIXS involves a coherent scattering process where the system is resonantly excited into short-lived core-hole states and subsequently decays back to the ground and valence excited states. This technique combines the element specificity of core-level spectroscopy with the ability to reach valence excited states across a wide spectral range and a spectral resolution that is not limited by the large core-hole lifetime broadening, making it a versatile and promising tool to study the local electronic structure in complex molecular systems.

I will present RIXS simulations of pyrazine at the nitrogen K-edge including wavepacket dynamics in both the valence- and core-excited state manifold. This allows to accurately depict dynamic processes occurring within the ultrashort core-hole lifetime and their manipulation through changes in excitation frequency. Additionally, I will discuss the impact of the spectral distribution of the incoming X-ray pulse and how it manifests in the resulting spectra striving for an optimal interplay between theory and experiment.