

MO 30: Molecular Spectroscopy and Theoretical Approaches

Time: Friday 14:30–16:15

Location: HS XVI

MO 30.1 Fri 14:30 HS XVI

High-resolution rovibrational spectroscopy of H_5^+ — ●SAMUEL MARLTON, PHILIPP SCHMID, THOMAS SALOMON, JANOS SARKA, DIVITA GUPTA, OSKAR ASVANY, and STEPHAN SCHLEMMER — University of Cologne, Cologne, Germany

H_5^+ is an extremely floppy molecular ion that is so complex that it pushes the limits of foundational concepts in spectroscopy and molecular physics such as molecular structure, normal modes of vibration, typical group theoretical treatments, and the separation of vibrational and rotational degrees of freedom. Using leak-out spectroscopy (LOS) it is finally possible to measure infrared transitions of H_5^+ with high resolution.[1] In this experiment, H_5^+ ions are stored in a cryogenic (20 K) 22-pole ion trap and irradiated with an infrared laser. Photoexcited ions collide with neutral He gas atoms to transfer the vibrational internal energy of the ion into kinetic energy, giving the ion sufficient kinetic energy to leak out of the trap and be detected. The LOS spectrum is constructed by measuring the leak-out ion yield as a function of laser frequency. We employ LOS to measure the H_5^+ vibrational band centred at 940 cm^{-1} (a combination band exciting the central proton hop and outer hydrogen separation), which is a promising step to understanding extremely floppy molecules.

[1] Schmid et al., 2022, J. Phys. Chem. A., 126(43), pp.8111-8117.

MO 30.2 Fri 14:45 HS XVI

Experimental symmetry assignments of protonated methane rovibrational levels — ●SAMUEL MARLTON, PHILIPP SCHMID, OSKAR ASVANY, and STEPHAN SCHLEMMER — University of Cologne, Cologne, Germany

Protonated methane (CH_5^+) does not consist of one proton and four hydrogen atoms but all five protons are equivalent, all entertaining bonds with the central carbon atom. This makes the molecule floppy with an irregular rovibrational spectrum, which remains unassigned. [1,2] The nuclear spins of the five protons combine to a total nuclear spin of $I = 1/2, 3/2$ or $5/2$, which—due to the Pauli exclusion principle—combine with ro-vibrational states of corresponding symmetry $A_2 \cong I = 5/2$, $G_2 \cong I = 3/2$, and $H_2 \cong I = 1/2$ with abundance ratios of 6:4:2. Using leak-out spectroscopy (LOS), [3] we provide direct experimental symmetry assignments by measuring these abundance ratios. In our experiment, CH_5^+ ions stored in a cryogenic ion trap are irradiated with an infrared laser. Photoexcited ions collide with neutral gas atoms (Ne) to eventually transfer vibrational energy into kinetic energy, giving the ion sufficient kinetic energy to leak out of the trap. We assign symmetry labels to transitions by measuring the fraction ($2/12$, $4/12$, or $6/12$) of CH_5^+ ions that leak-out of the trap when each transition is resonantly excited. This approach will help construct a ground state term diagram. [1] White et al., 1999, Science, [2] Asvany et al., 2015, Science, [3] Schmid et al., 2022, J. Phys. Chem. A.

MO 30.3 Fri 15:00 HS XVI

Spatially resolved spectroscopy of Rydberg states in nitric oxide — ●YANNICK SCHELLANDER¹, FABIAN MUNKES², ALEXANDER TRACHTMANN², FLORIAN ANSCHUTZ², ETTORE EDER², HANNA LIPPMANN², MERIEM MAVLUTOVA², MARIUS WINTER¹, ROBERT LÖW², PATRICK SCHALBERGER¹, TILMANN PFAU², HARALD KÜBLER², and NORBERT FRUEHAUF¹ — ¹Institute for Large Area, University of Stuttgart, Stuttgart, Germany — ²5th Institute of Physics, University of Stuttgart, Germany

High-resolution continuous-wave (cw) laser spectroscopy of nitric oxide (NO) molecules has been performed to study the energy-level structure. Special focus is on effects of electric fields on high Rydberg states. The photo-excitation is based on a resonance enhanced three-color three-photon excitation scheme. In contrast to theory, the measurements show states with no frequency shift. The reason for this effect is most likely an inhomogeneous electric field distribution. This is caused by field attenuations near the cell walls resulting from charge carrier accumulations on these. Therefore, charge carriers generated near the cell walls experience a much lower electric field than expected. To further investigate the charge carrier effects and prove the given explanation, spatially resolved measurements of the ionization currents are performed. These kinds of measurements are enabled by an electrode / transimpedance amplifier array based on thin-film technology.

Other thinkable applications of such a sensor array could be the determination of the dynamic density distribution by turbulent gas flow or in resonance-enhanced multiphoton ionization experiments.

MO 30.4 Fri 15:15 HS XVI

Recent achievements and future prospects in precision spectroscopy of tritium-substituted molecules — ●VALENTIN HERMANN — Tritiumlabor Karlsruhe, Karlsruhe Institute for Technology, Karlsruhe, Germany

Precision spectroscopy of tritium-substituted molecules provides essential data for refining molecular energy models and supports applications in fusion research, where monitoring tritium-containing species is crucial. Recent advancements include high-resolution FTIR spectroscopy of tritiated water isotopologues (HTO, DTO, T₂O), revealing over 4500 new absorption lines with accuracies up to $5.6 \times 10^{-5}\text{ cm}^{-1}$. NICE-OHMS (Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectroscopy) has also been applied to HT, achieving unprecedented spectral accuracy of 21 kHz.

Future projects aim to expand high-accuracy measurements to additional tritium-substituted species and to systematically improve line intensities for enhanced spectroscopic databases. The planned investigation of tritiated methane will support fusion research by enabling more accurate detection and monitoring of tritiated hydrocarbons, which are critical for fuel cycle control.

MO 30.5 Fri 15:30 HS XVI

The connection between the Exact Factorization and the Born-Huang representation of the molecular wave function — ●PETER SCHÜRGER¹, YORICK LASSMANN², FEDERICA AGOSTINI¹, and BASILE CURCHOD² — ¹Institut de Chimie Physique, University Paris-Saclay — ²Centre for Computational Chemistry, School of Chemistry, University of Bristol

In recent years, the exact factorization (EF) formalism sparked a lot of interest in the non-adiabatic dynamics community and led to the development of various new promising methods for non-adiabatic molecular dynamics simulations [see e.g. PCCP, 26, 26693-26718 (2024)]. In EF, the molecular wave function is written as a product of a time-dependent conditional and time-dependent marginal amplitude. The EF is usually presented as “qualitatively” different in its formalism, compared to the more traditional Born-Huang (BH) representation, i.e. the adiabatic representation of the molecular wave function [JPC A, 126, 1263-1282 (2022)]. Here, I will present a new perspective on the foundations of EF [ChemRxiv (2024)], that does not rely on a probabilistic interpretation and that strengthens the connection between EF and BH. Specifically, EF is a basis set that can be derived from BH and the adiabatic basis by introducing a time-dependent unitary transformation. Features of the EF, like the partial normalization condition and the gauge freedom, arise naturally in our formalism. Furthermore, equations of motion can be derived in this EF basis. I will conclude by presenting some applications of EF to simulate the ultrafast dynamics of fulvene and 4-(dimethylamino)benzonitrile (DMABN).

MO 30.6 Fri 15:45 HS XVI

A Hierarchical Approach to Quantum Many-Body Systems in Structured Environments — KAI MÜLLER¹, KIMMO LUOMA², and ●CHRISTIAN SCHÄFER³ — ¹Institut für Theoretische Physik, Technische Universität Dresden, D-01062 Dresden, Germany — ²Department of Physics and Astronomy, University of Turku, 20014 Turku, Finland — ³Department of Physics, Chalmers University of Technology, 412 96 Göteborg, Sweden

Open quantum systems featuring non-Markovian dynamics are routinely solved using techniques such as the Hierarchical Equations of Motion (HEOM) but their usage of the system density-matrix renders them intractable for many-body systems. Here, we combine the HEOM with the BBGKY hierarchy to reach a consistent and rigorous description of open many-body systems and their quantum dynamics. [Kai Müller, Kimmo Luoma, and Christian Schäfer, arXiv:2405.05093.] We demonstrate first the strength and limitations of this stacked hierarchy for superradiant emission and spin-squeezing of established quantum optical models before presenting its full potential for quantum many-body systems. In particular, we explicitly simulate the impact of charge noise on the dynamic of the Fermi-Hubbard model subject to

a structured bath comprising cavity and vibro-phononic environment. Lastly, we discuss few-emitter lasing to further elaborate the flexibility of the stacked hierarchy. Our work establishes an accessible, yet rigorous, route between condensed matter and quantum optics, fostering the growth of a new domain at their interface.

MO 30.7 Fri 16:00 HS XVI

Calculating excitonic interactions using transition currents with application to PTCDA — ●GRACE HSIAO-HAN CHUANG and ALEXANDER EISFELD — Max Planck Institute for the Physics of Com-

plex Systems, Nöthnitzer Str 38, Dresden

We calculate the excitonic interaction of the PTCDA dimer without overlapping molecular wavefunctions, focusing on transition charge and current density. These quantities are derived from post-processing the numerical wavefunction using electronic structure theory. Additionally, we present a homemade algorithm designed to efficiently and cost-effectively capture these two quantities. To validate the dipole approximation, we also compute accurate numerical values for a typical arrangement of PTCDA on a monolayer.