

MO 6: Ultrafast

Time: Thursday 14:00–15:30

Location: H2

MO 6.1 Thu 14:00 H2

Ultrafast Spectroscopy of Excited States of Novel Ru and Cu Photosensitizers — ●MIGUEL ANDRE ARGÜELLO CORDERO¹, PIT JEAN BODEN², MARTIN RENTSCHLER⁴, PATRICK DI MARTINO-FUMO², WOLFGANG FREY³, YINGYA YANG⁴, MARKUS GERHARDS², MICHAEL KARNAHL⁴, STEFAN LOCHBRUNNER¹, and STEFANIE TSCHIERLEI⁴ — ¹Institute for Physics, University of Rostock — ²Chemistry Department, TU Kaiserslauter — ³Institute of Organic Chemistry, University of Stuttgart — ⁴Institute of Physical and Theoretical Chemistry, TU Braunschweig

Newly synthesized Ru based photosensitizers with an extended π -system were found to exhibit long lived excited states with lifetimes of 1.7 and 24.7 μ s after optical excitation. The applied biipo ligand coordinates via a phenanthroline moiety, which is extended with a naphthalimide unit. In order to replace the rare noble metal, a Cu based analogion was developed. Nanosecond transient absorption (TA) measurements revealed, that in the Cu complex, non-emissive excited state are populated which exhibit even much longer lifetimes.

In the present work, we investigate this complex and the plain ligand by femtosecond TA spectroscopy and observe rich intramolecular relaxation dynamics. The shortest lifetime of 0.3 ps can be assigned to a flattening of the geometrical structure of the complex after optical excitation. The second exponential component of 3.3 ps reflects probably ISC to a triplet MLCT-state. However, the associated spectral signatures decay with a time constant of 10 ps. This may point to a transfer of the excited electron from the MLCT-state to a LC-state.

MO 6.2 Thu 14:15 H2

Ultrafast 2D-IR spectroscopy probes tRNA-Magnesium contact ion pairs — ●JAKOB SCHAUSS, ACHINTYA KUNDU, BENJAMIN P. FINGERHUT, and THOMAS ELSAESSER — Max Born Institute for Nonlinear Optics and Short-Pulse Spectroscopy, Berlin, Germany

The negative charge of nucleic acids makes them susceptible to interactions with their surrounding water shell and the ions embedded within. Magnesium ions in particular are known to strongly interact with RNA molecules, for example in the folding of functional RNA from an elongated chain into the native, condensed form. The interactions that play a role in the folding process are highly debated, partially due to the lack of non-invasive probes on the microscopic level.

Here, we use femtosecond 2D-IR spectroscopy of phosphate backbone vibrations to investigate the formation of transfer RNA/Mg²⁺ contact ion pairs (CIP). Phosphate vibrations have been shown to sense changes in the water environment upon RNA melting [1] and report on CIP formation in model systems [2]. The experimental results on tRNA agree well with molecular dynamics simulations that show stabilization of tRNA tertiary structure through contact ion pairs. Particularly in highly congested regions of the tRNA, the magnesium ions are instrumental in efficiently compensating the high negative charge density [3].

- [1] A. KUNDU *et al.*: *J. Phys. Chem. B*, 124, 2132-2138 (2020)
- [2] J. SCHAUSS *et al.*, *J. Phys. Chem. Lett.* 10, 6281-6286 (2019)
- [3] J. SCHAUSS *et al.*: *J. Phys. Chem. B*, 125, 740-747 (2021)

MO 6.3 Thu 14:30 H2

Unraveling collective coordinates influencing time-resolved x-ray absorption spectra of ionized urea and its dimer through machine learning — ●YASHOJ SHAKYA^{1,2}, LUDGER INHESER¹, CAROLINE ARNOLD^{1,2,3}, RALPH WELSCH^{1,3}, and ROBIN SANTRA^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg, Germany — ²Department of Physics, Universität Hamburg, Hamburg, Germany — ³Hamburg Centre for Ultrafast Imaging, Hamburg, Germany

Probing the early dynamics of chemical systems following ionization is essential for our understanding of radiation damage. Time-resolved x-ray absorption spectroscopy (TRXAS) on a femtosecond timescale can provide crucial insights into the ultrafast processes occurring upon ionization due to its element-specificity. However, even with theoretical simulations, getting a clear interpretation of the spectra can be challenging due to the high dimensionality of the data.

In this theoretical study, we investigate the response of urea and its dimer to ionizing radiation and how it can be probed via TRXAS. We show how statistical analysis techniques, in particular partial

least square regression, can unravel specific structural dynamics in a molecule that induce changes in its TRXAS. By applying this technique, collective coordinates that most influence TRXAS are obtained from simulated ab initio nonadiabatic trajectories of valence-ionized urea and its dimer. For urea, this leads to the possibility of tracing specific molecular vibrations in its TRXAS. For its dimer, where ionization triggers a proton transfer, we show how the spectra can reveal the progress of the transfer.

MO 6.4 Thu 14:45 H2

Increasing ion yield CD in femtosecond photoionization of a prototypical chiral molecule using Optimal Control Theory — ●MANEL MONDELO-MARTELL, DANIEL BASILEWITSCH, CHRISTIANE P. KOCH, and DANIEL M. REICH — Freie Universität Berlin, Berlin, Germany

Molecular chirality is the property of some chemical compounds to have non-superimposable mirror images - enantiomers. These isomers interact identically with non-chiral probes, but show different behaviour when subjected to chiral objects, thus the characterization and separation of enantiomers is both complex and very relevant. A particularly fundamental characterization technique is the so-called circular dichroism (CD), i.e. the difference in absorption of circularly polarized light by the two enantiomers.

CD with monochromatic light is usually a weak effect since it relies on differences in the magnetic transition dipole moments of the enantiomers. Previous work[1] qualitatively showed that shaping the light probes can affect the absorption profile of two enantiomers. Here, we use Optimal Control Theory to maximise the CD signal of the $A \leftarrow \pi^*$ transition in fenchone. Since this transition is dipole forbidden, we can use the interplay of multipolar interaction terms as a resource for the pulse optimization. We show that CD of oriented ensembles can be increased up to a 100% by selectively exciting the electronic state of only one enantiomer. We also get a significant increase when including orientational averaging for fenchone molecules in the gas phase.

- [1] D. Kröner, *J. Phys. Chem. A* 115, 14510 (2011).

MO 6.5 Thu 15:00 H2

Is CCSD(T) a proper standard for dipole moment calculations? An analysis considering diverse diatomic species — ●XIANGYUE LIU¹, LAURA MCKEMMISH², and JESÚS PÉREZ-RÍOS¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany — ²School of Chemistry, UNSW Sydney, Sydney, NSW 2052, Australia

Coupled cluster with single, double, and perturbative triple excitations [CCSD(T)] is considered one of the most accurate electronic structure methods and has been widely used as a reference in benchmarking studies. The present work investigates the accuracy of CCSD(T) reproducing experimental ground state electric dipole moments and equilibrium distances of diatomic molecules. The results show that core-correlations are essential to some molecules, e.g., bi-alkali and main-group metal halides, to reach a satisfactory agreement with experimental measurements. However, for dipole moments of molecules involving transition metal atoms, CCSD(T) is not accurate enough even when including core-correlations. In addition, our work shows the relevance of using experimental data to benchmark theoretical quantum chemistry methods.

MO 6.6 Thu 15:15 H2

The Kicked Rotor and its Metrics of Chaos — ●CIAN HAMILTON and JESÚS PÉREZ RÍOS — Fritz Haber Institute, Berlin, Germany

The kicked rotor is a prototypical simple model that encompasses both order and chaos in classical and quantum variants. As a result, it has been extensively studied, although it is still not yet fully understood.

We have conducted a numerical exploration into both the classical and quantum kicked rotor, although from a different approach. As a result, we find that the transition from order to the chaos of the classical kicked rotor follows a hyperbolic tangent function depending on the kick strength by characterising the fractal dimension of the phase-space.

On the quantum front, we have been able to find how the localisation length for the wavefunction depends on the two quantum parameters controlling the system's dynamics. Similarly, by looking into the av-

erage kinetic energy after many kicks, we expect to have some hints about the emergence of quantum chaos and its correspondence with the classical dynamics. Finally, we have explored other areas of the

kicked rotor, including how sensitive the system is to the dynamic kick period and dynamic kick strength.