

A 21: Ultrafast Dynamics II (joint session MO/A)

Time: Thursday 11:00–13:00

Location: F102

A 21.1 Thu 11:00 F102

Isosteric molecules in the time-domain — ●MAXIMILIAN POL-LANKA, CHRISTIAN SCHRÖDER, and REINHARD KIENBERGER — Chair for Laser and X-ray Physics, E11, Technische Universität München, Germany

We report on photoemission timing measurements performed on isosteric molecules in the gas phase on attosecond timescales. Comparing the photoemission time delay between the respective σ and π orbitals in the inner and outer valence states of CO₂ and N₂O leads to a deeper insight into the characteristics of isosterism in the time-domain. Additionally, the isoelectronicity of CO and N₂ is investigated in detail as a complementary study. Due to the similarities in molecular structure (isostericity) and electronic configurations (isoelectronicity) the pure effect of the specific molecular/orbital characteristics is expected to be probed. We are not only able to experimentally assess the relative photoemission delay between respective outer and inner valence states, but also performing absolute photoemission timing via attosecond streaking spectroscopy using iodomethane (I_{4d} state) as a reference. The experimental data show great similar tendencies but also differences between the compared molecular orbitals, which are determined but not completely understood up to now. Therefore, further theoretical considerations and accurate modelling of the process of laser-dressed photoionization and the information encoded in photoemission timing measurements on molecular targets are necessary. This will help us gaining a greater understanding of the correlations between molecular geometry and photoemission time and therefore the isosteric influence.

A 21.2 Thu 11:15 F102

RABBITT experiments in a vibrationally active ammonia molecule — ●LISA-MARIE KOLL¹, DAVID SORRIBES ORTIZ², IGNACIO MARTÍNEZ CASASÚS², TOBIAS WITTING¹, LORENZ DRESCHER^{1,4}, OLEG KORNILOV¹, MARC JJ VRAKING¹, FERNANDO MARTÍN³, and LUIS BAÑARES² — ¹Max Born Institute, Berlin — ²Universidad Complutense de Madrid — ³Universidad Autónoma de Madrid and IMDEA Nanociencia — ⁴University of California, Berkeley

Many RABBITT (Reconstruction of Attosecond Beatings By Interferences of Two-photon Transitions) experiments have been carried out so far for (rare gas) atoms to disentangle the evolution of an electronic wave packet by measuring the photoemission time delays. In molecules, the experiments are more complicated due to the nuclear degrees of freedom. Previously, RABBITT experiments could resolve vibrations in the photoelectron spectrum of N₂ [1], and N₂O [2]. Here, we present RABBITT experiments on NH₃ using the velocity map imaging (VMI) technique. NH₃ belongs to the C_{3v} symmetry group and, as a result of the photoionization process, symmetry is shifted to the D_{3h} conformation in NH₃⁺. The ionization of ammonia is accompanied by rich vibrational structure, such as the long vibrational progression in the ν_2 umbrella inversion mode of the X_{2A₂} state. These RABBITT experiments present an interesting and challenging case for full-dimensional theoretical calculations and help to demonstrate the capability of the RABBITT method to study in depth vibronic dynamics in polyatomic molecules. [1] S. Haessler et al., Phys. Rev. A 80, 01140R (2009) [2] L. Cattaneo et al., Nature Phys. 14, 733 (2018)

A 21.3 Thu 11:30 F102

Control of ion+photoelectron entanglement in an attosecond pump-probe experiment — ●LISA-MARIE KOLL, TOBIAS WITTING, and MARC JJ VRAKING — Max Born Institute, Berlin, Germany

Quantum mechanical entanglement is a vibrant topic, culminating in this year's Nobel price award. In attosecond science, it is common to use radiation in the extreme ultra-violet (XUV) regime to study atomic and electronic dynamics. Due to their high photon energy any sample (solid, liquid or gaseous) placed in their path is ionized, creating a bipartite quantum system, i.e. an ion+photoelectron. Entanglement between those sub-systems can have measurable consequences for any attosecond experiment [1]. To illustrate the role of entanglement in photoionization we designed an experimental protocol, which utilizes a pair of phase-locked XUV pulses [2] and an IR pulse to ionize hydrogen molecules. The initially entangled ion+photoelectron system created by the XUV photoionization process is converted by the IR pulse into a coherent superposition of the gerade and ungerade electronic state

of the ionic molecule leading to the observation of electronic localization [3]. By changing the time delay between the two XUV pulses the degree of ion+photoelectron entanglement is controlled and as a consequence the degree of electronic coherence. This can lead to the suppression of the observable electronic localization for certain time delays.

- [1] L.-M. Koll et. al., Physical Review Letters 128, 043201 (2022)
- [2] L.-M. Koll et al., Optics Express 30, 7082-7095 (2022)
- [3] G. Sansone et al., Nature 465, 763-766 (2010)

A 21.4 Thu 11:45 F102

High-order spectroscopy at 100 kHz repetition rate — ●KATJA MAYERSHOFER¹, SIMON BÜTTNER¹, TIM SCHEMBRI^{2,3}, MATTHIAS STOLTE^{2,3}, FRANK WÜRTHNER^{2,3}, and TOBIAS BRIXNER^{1,3} — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ³Center for Nanosystems Chemistry (CNC), Universität Würzburg, Theodor-Boveri-Weg, 97074 Würzburg

With our new laser setup we can carry out shot-to-shot femtosecond spectroscopy experiments at 100 kHz repetition rate, which decreases the measurement time to a few seconds for conventional coherent two-dimensional spectroscopy experiments. For the shot-to-shot measurements an acousto-optical modulator pulse shaper was implemented, which can arbitrarily shape pulses at 100 kHz repetition rate, and we detect full spectra with a line camera at 100 kHz. The increase in repetition rate and the ability to measure shot-to-shot also leads to a better signal-to noise ratio as a larger number of averages can be measured in the same time frame as previous measurements. As an exemplary measurement, we show data taken using the new development of fifth-order transient absorption spectroscopy. This method can be used to analyze the exciton dynamics in J-type coupled merocyanine dye films, which are interesting in view of their optoelectronic properties.[1]

- [1] A. Liess, et al., Adv. Funct. Mater. 2019, 29, 1805058.

A 21.5 Thu 12:00 F102

High-resolution rapid-scanning two-dimensional electronic spectroscopy — ●NICOLAI GÖLZ, FRIEDEMANN LANDMESSER, DANIEL UHL, FRANK STIENKEMEIER, and LUKAS BRUDER — Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

Two-dimensional electronic spectroscopy (2DES) is an effective ultrafast spectroscopic technique to study dynamics of matter with a high spectro-temporal resolution. Extending the method to weakly perturbed molecular and cluster species in the gas phase permits very high spectral resolution [1,2]. However, in this case, the attainable resolution is limited by the acquisition time of corresponding long delay scans. To solve this problem, we have implemented a rapid-scanning method developed by the Ogilvie group [3] which reduces the acquisition time by up to 2 orders of magnitude. First results will be presented.

- [1] L. Bruder et al., Nat Commun 9, 4823 (2018)
- [2] U. Bangert et al., Nature Communications 13:1, 3350 (2022)
- [3] D. Agathangelou et al., J. Chem. Phys.155, 094201 (2021)

A 21.6 Thu 12:15 F102

Coherent multidimensional spectroscopy of molecular and cluster beam samples — ●YILIN LI, ARNE MORLOK, ULRICH BANGERT, DANIEL UHL, FRANK STIENKEMEIER, and LUKAS BRUDER — Institute of Physics, University of Freiburg, Germany

Coherent multidimensional spectroscopy is a versatile technique enabling further insights into intra- and inter-molecular couplings on ultrashort time scales. We have extended the method to molecular nanosystems prepared in the gas phase [1,2]. Recently we started analysing 2D beating maps to obtain information about the electronic and vibrational coherences in the systems, which are otherwise covered by linebroadening mechanisms. First results will be presented.

- [1] L. Bruder et al., Nat Commun 9, 4823 (2018)
- [2] U. Bangert, F. Stienkemeier, L. Bruder, Nat Commun 13, 3350 (2022)

A 21.7 Thu 12:30 F102

Simplifying the Analysis of Transient Absorption Data by Polarization Control — •YI XU¹, LARS MEWES¹, ERLING THYRHAUG¹, HEINZ LANGHALS², and JÜRGEN HAUER¹ — ¹Dynamical Spectroscopy, Department of Chemistry, Technical University of Munich, 85748 Garching, Germany — ²Department of Chemistry, Ludwig-Maximilians-Universität München, 81377 Munich, Germany

Ultrafast energy transfer in donor-acceptor (D-A) systems with orthogonal transition dipole moments (TDMs) is of fundamental interest due to its incompatibility with Förster theory. An in-depth theoretical treatment calls for specific experimental tools, which we provide by polarization-controlled transient absorption (TA) spectroscopy with broadband detection. We isolate pure donor and acceptor parts of the total signal. This provides a strategy to greatly reduce spectral congestion in complex systems. The polarization-associated spectra can be isolated to the contributions either parallel (S_z) or orthogonal (S_y) to the excitation TDM. The derived expressions read $S_z = 3 \cdot S_{MA} \cdot V_z(r(\lambda, t), \beta)$ and $S_y = 3 \cdot S_{MA} \cdot V_y(r(\lambda, t), \beta)$, where S_{MA} represents the magic angle spectra. The corresponding unit vectors $V_z(r(\lambda, t), \beta)$ and $V_y(r(\lambda, t), \beta)$ are both functions of the time resolved anisotropy $r(\lambda, t)$ and the angle β stands for differences between the TDMs defining the first and last light-matter interaction in a TA-sequence. We find that

$\beta \approx 30^\circ$ is an optimal choice to disentangle the D and A-signals. This proves the non-orthogonality within the “orthogonal” D-A system.

A 21.8 Thu 12:45 F102

Probing Nonadiabatic Dynamics with Attosecond Pulse Trains and soft X-ray Raman Spectroscopy — •LORENZO RESTAINO, DEEPENDRA JADOUN, and MARKUS KOWALEWSKI — Department of Physics, Stockholm University, Albanova University Centre, SE-106 91 Stockholm, Sweden

Ultrafast electronic coherences, generated by a photoexcited wave packet passing through a conical intersection, can be detected by linear off-resonant X-ray Raman probes. A hybrid femtosecond or attosecond probe pulse can be employed to generate a Raman spectrum that maps the energy difference between the involved electronic states. We investigate how attosecond pulse trains perform as probe pulses in the framework of this spectroscopic technique, instead of single Gaussian pulses. We explore different schemes for the probe pulse, as well as the impact of parameters of the pulse trains on the signals. We use two different model systems, representing molecules of different symmetry, and quantum dynamics simulations to study the difference in the spectra. The results suggest that such pulse trains are well suited to capture the key features associated with the electronic coherence.