

## MO 4: Electronic II

Time: Tuesday 10:30–11:30

Location: MO-H5

MO 4.1 Tue 10:30 MO-H5

**Near-Field scanning optical microscopy of molecular aggregates: the role of light polarization** — ●SIDHARTHA NAYAK<sup>1</sup>, FULU ZHENG<sup>2</sup>, and ALEXANDER EISFELD<sup>1</sup> — <sup>1</sup>MPIPKS, Dresden, Germany — <sup>2</sup>BCCMS, University of Bremen, Bremen, Germany

Strong Interaction between transition dipoles of molecules leads to formation of delocalized excitonic eigenstates of molecular aggregates. Using a scattering scanning near-field optical microscope setup one can record position dependent absorption spectra[1] from which we can reconstruct the wavefunctions[2]. In this contribution we focus on the dependence of the spectra on the direction and polarization of the incoming electromagnetic radiation, which induces a Hertz dipole with a specific orientation at the tip-apex. Within a simple description based on the eigenstates of the aggregate, We find that the spatial patterns of the spectra have a strong dependence on the orientation of this tip-dipole, which can be understood by considering three basic functions that only depend on the arrangement of the aggregate and the molecule-tip distance, but not on the orientation of the tip-dipole[3]. This approach is validated by a more detailed description where the incoming radiation and the interaction between tip and molecules is explicitly taken into account.

[1] X. Gao and A. Einfeld, *J. Phys. Chem. Lett.* 9, 6003 (2018)

[2] F. Zheng, X. Gao and A. Einfeld, *Phys. Rev. Lett.* 123, 163202 (2019)

[3] S. Nayak, F. Zheng and A. Einfeld, *J. Chem. Phys.* 155, 134701 (2021)

MO 4.2 Tue 10:45 MO-H5

**Detecting Chirality in Mixtures Using Nanosecond Photoelectron Circular Dichroism** — ●SIMON RANECKY<sup>1</sup>, BARATT PARK<sup>2,3</sup>, PETER SAMARTZIS<sup>4</sup>, IOANNIS GIANNAKIDIS<sup>4</sup>, DIRK SCHWARZER<sup>2</sup>, ARNE SENFTLEBEN<sup>1</sup>, THOMAS BAUMERT<sup>1</sup>, and TIM SCHÄFER<sup>2</sup> — <sup>1</sup>Uni Kassel — <sup>2</sup>Uni Göttingen — <sup>3</sup>Texas Tech Lubbock (USA) — <sup>4</sup>IESL-FORTH Iraklio (Greek)

The ionization of randomly oriented chiral molecules with circularly polarized light leads to an asymmetric angular photoelectron distribution. Depending on the handedness of the molecules and the sense of rotation of the incident light, more electrons are scattered forward or backward with respect to the direction of the incident light. This effect is called photoelectron circular dichroism (PECD). Its size can reach more than 10% for pure enantiomers and decreases for lower enantiomeric excesses (e.e.). It can be applied to determine the e.e. of chiral substances with a precision below 1% [1].

Tunable narrowband nanosecond lasers in combination with a cold molecular beam achieve vibrational resolution in resonance-enhanced multiphoton ionization [2]. As a proof of principle, we made four mixtures of pure enantiomers of fenchone and camphor and selectively ionized either fenchone or camphor by tuning the wavelength to the band origin of their B-band and measured their background suppressed PECD. We were able to discriminate the enantiomers of both sub-

stances. This opens the perspective to determine the e.e. in mixtures.

[1] A. Kastner et al., *ChemPhysChem*, 17, 1119 - 1122, (2016)

[2] A. Kastner et al., *Phys. Chem. Chem. Phys.*, 22, 7404, (2020)

MO 4.3 Tue 11:00 MO-H5

**The gas-phase infrared spectra of the 2-methylallyl radical and its high-temperature reaction products** — ●TOBIAS PREITSCHOPF<sup>1</sup>, FLORIAN HIRSCH<sup>1</sup>, ALEXANDER LEMMENS<sup>2</sup>, ANOUK RIJS<sup>2</sup>, and INGO FISCHER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Deutschland — <sup>2</sup>Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7, 6525 ED Nijmegen, The Netherlands

The resonance-stabilized 2-methylallyl radical, 2-MA, is considered as a possible intermediate in the formation of polycyclic aromatic hydrocarbons (PAH) in combustion processes. In this work we report on its contribution to molecular growth in a high-temperature microreactor and provide species- and isomer-selective IR/UV ion dip spectra of the various jet-cooled reaction products, employing free electron laser radiation in the mid-infrared region. Small (aromatic) hydrocarbons such as fulvene, benzene, styrene, or para-xylene, as well as polycyclic molecules, like (methylated) naphthalene, were identified with the aid of ab initio DFT computations. Several reaction products differ by one or more methyl groups, suggesting that molecular growth is dominated by (de)methylation in the reactor.

MO 4.4 Tue 11:15 MO-H5

**Formation and spectroscopic investigation of molecular clusters of phthalocyanine and water in superfluid helium nanodroplets** — ●JOHANNES FISCHER and ALKWIN SLENCZKA — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93053 Regensburg, Germany

Superfluid helium nanodroplets serve as a gentle and ultracold (T = 0.37 K) host system for molecular and atomic species as well as weakly bound (van der Waals) clusters [1]. The latter can be synthesized *in situ* by successive pick-up of different species by the droplets. We will present an extended investigation of a cluster consisting of a single phthalocyanine and one water molecule, that possesses a multitude of isomeric structures in helium droplets [2]. The attachment of water to phthalocyanine becomes influential on spectroscopic observables like electronic and vibrational transition frequencies, line shapes, and intramolecular dynamics upon electronic excitation. This study discusses all these features by means of fluorescence excitation spectra and dispersed emission spectra. The number of configurational variants identified thereby provides evidence that for some of these cluster isomers the contribution of the surrounding helium goes beyond the stabilization of local minima in the phthalocyanine to water potential hypersurface. [1] A. F. Vilesov et al., *Angew. Chem. Int. Ed.*, **43**, 2622, (2004). [2] J. Fischer et al., *J. Phys. Chem.*, **123**, 10057, (2019).