

MO 4: Electronic Spectroscopy I

Time: Monday 14:00–16:30

Location: f142

Invited Talk

MO 4.1 Mon 14:00 f142

Structure and dynamics of gas phase metal clusters — ●BERND VON ISSENDORFF — Physikalisches Institut, Universität Freiburg, Germany

One of the clearest examples of a quantum size effect is the electron shell structure of simple (and not so simple) metal clusters, which has been studied in detail since the beginning of cluster physics. Photoelectron spectroscopy on size-selected clusters turned out to be an ideal tool to monitor this special electronic structure. Angle resolved photoelectron spectroscopy is even able to yield information about the wavefunctions of the electrons, as well as on the dynamics of the photoemission process [1]. The recent years have seen a constant improvement of the experimental techniques as well as of the theoretical methods used to simulate the results, which yields a new quality of insight, as was for example demonstrated for complex systems like zinc clusters [2]. Additionally the rapid development of new light sources like high intensity synchrotrons, free electron lasers and high harmonic sources offers a huge potential for experiments on clusters. I will discuss a number of experiments which have been done recently or are under development.

- [1] C. Bartels et al., *Science* 323, 1323 (2009)
 [2] A. Aguado, *Nanoscale*, 10, 19162 (2018)

MO 4.2 Mon 14:30 f142

Threshold Photoelectron Spectroscopy of IO and HOI — ●DOMENIK SCHLEIER¹, ENGELBERT REUSCH¹, LISA LUMMEL¹, PATRICK HEMBERGER², and INGO FISCHER¹ — ¹Institute for physical and theoretical Chemistry, Würzburg, Germany — ²Paul-Scherrer-Institute (PSI), Villigen, Switzerland

IO and HOI represent key intermediates and precursors in the formation iodine oxide particles (IOPs). During their formation they catalytically destroy ozone and ultimately influence cloud lifetimes, contributing negatively to earths radiative balance. Both molecules have been characterized using multiple spectroscopic techniques like UV/Vis, IR, EPR, microwave spectroscopy and photoelectron detachment. However, information on the cations and thermodynamic data is still scarce. We therefore employ PEPICO (Photoelectron Photoion Coincidence) spectroscopy to record mass-selected threshold photoelectron spectra (ms-TPES). The CRF-PEPICO (Combustion Reactions Followed by PEPICO) setup at the vacuum ultraviolet (VUV) beamline of the Swiss Light Source (SLS) uses a slow-flow reactor in which IO and HOI were produced from photolyzing an I₂/O₃ mixture at 532 nm. The ionization energies were determined to be 9.71 ± 0.02 eV and 9.79 ± 0.02 eV for IO and HOI, respectively. While HOI⁺ shows a vibrational frequency of 660 cm⁻¹, IO⁺ exhibits a spin-spin splitting resulting in the separation the 3Σ⁻ ground states. This splitting results in two different determined vibrational frequencies for the cation of 810 cm⁻¹ and 730 cm⁻¹.

MO 4.3 Mon 14:45 f142

From wavelike dynamics to anomalous diffusion: Exciton transport in polymers of varying length, observed by EEI2D spectroscopy — ●PAVEL MALÝ¹, JULIAN LÜTTIG¹, ARTHUR TURKIN¹, JAKUB DOSTÁL^{1,2}, CHRISTOPH LAMBERT¹, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, 12116 Prague, Czech Republic

Exciton transport and interaction in molecular aggregates and polymers are key processes in solar light harvesting and organic electronics. While the initial dynamics following photoexcitation proceeds in a delocalized, wavelike fashion, the subsequent exciton transport has diffusive character. In this work we use our newly-developed exciton-exciton interaction two-dimensional (EEI2D) spectroscopy [1], in combination with microscopic theoretical modelling, to study exciton dynamics and annihilation in squaraine copolymers of varying length [2]. By directly probing interacting exciton pairs, we observe the transition from wavelike to diffusive exciton motion, dependent on the exciton delocalization length relative to the polymer size. Contrary to the common assumption, we find that the exciton diffusion has anomalous, sub-diffusive character, indicating trapped excitons. Our results demonstrate the potential of high-order spectroscopy, such as EEI2D,

to provide new insights into exciton transport and interaction.

- [1] J. Dostál et al., *Nat. Commun.* 2018, 9, 2466-2473
 [2] P. Malý et al., *Chem. Sci.* 2020, DOI:10.1039/C9SC04367E

MO 4.4 Mon 15:00 f142

Time- and frequency-resolved TOF-MS and photoion imaging on tetracene multimers — ●MARCO FLOCK and INGO FISCHER — University of Würzburg, Institute of Physical Chemistry

Singlet fission (SF) describes the spin-allowed splitting of a photoexcited singlet state into two triplet states localized at two chromophores in a molecular system. To enable SF, the triplet energy of the chromophore must be half or lower than its singlet energy. This condition is fulfilled by tetracene making it a promising model system for the investigation of the SF process. The photophysical properties of the tetracene dimer and trimer were investigated by time- and frequency-resolved time of flight (TOF) photoionization and photoion imaging experiments in a molecular beam. The latter ones allow the exclusion of signals originating from fragmentation of higher order clusters. Frequency-resolved measurements revealed an ongoing red-shift of the dimer and trimer absorption compared to the monomeric species. Time-resolved measurements offered a completely different behavior for all three species: While monomeric tetracene shows no activity on the ps timescale, the dimer signal decays monoexponentially on the order of 100 ps and the trimer species shows a two-step relaxation with time constants of around 50 ps and 1 ns. The observed dynamics can be attributed to photophysical processes after photoexcitation and thus might play a role in the SF process of tetracene multimers.

MO 4.5 Mon 15:15 f142

Dispersed fluorescence spectroscopy on Cyanoindoles — ●HENRICH CHRISTIAN and SCHMITT MICHAEL — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

The fluorescence of tryptophan and its derivatives is utilized for the spectroscopy of proteins. Through the introduction of substituents with different inductive (and mesomere) effects in different positions of the indole chromophore, the polarity of the environment can be affected. The energetic order of the two first electronically excited singlet states of indole, L_a and L_b strongly depends on this polarity. Different positions of the cyano group lead into different stabilization of these two states. We used laser induced fluorescence and dispersed fluorescence spectroscopy along with Franck-Condon theory in order to determine the changes of the geometry in the cyanoindoles upon electronic excitation. We perform fits of the rotational constants from high resolution laser induced spectroscopy and the Franck-Condon factors of different $L_a/L_b \rightarrow S_0$ transitions of cyanoindoles.

MO 4.6 Mon 15:30 f142

High resolution laser induced Stark spectroscopy: Position dependent study on 3-, 4- and 5-Cyanoindole — ●MARIE-LUISE HEBESTREIT, HILDA LARTIAN, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

In this contribution we present investigations of the electronic nature of 3-, 4- and 5-cyanoindole [1-3]. Indole and most of its derivatives have two close lying electronically excited singlet states labeled 1L_a and 1L_b in the nomenclature of Platt, which can be distinguished by the orientation of their transition dipole moment and by the magnitude and orientation of the permanent dipole moment [4,5]. In combination with *ab initio* calculations it is possible to determine the electronic nature for the lowest excited states via rotationally resolved Stark spectroscopy. The studies showed 1L_a character for the lowest excited state of 4- and 5-cyanoindole, while for 3-cyanoindole the lowest excited state was determined to be an 1L_b state. Reasons for this behavior are given by the influence of the inductive and mesomeric effect of the cyano group and the resulting electron density flow in the chromophor, depending if the cyano group is attached at the pyrrole ring or at the benzene ring.

- [1] Schneider et al, *Phys. Chem. Chem. Phys.*, 2018, **20**, 23441
 [2] Hebestreit et al, *Phys. Chem. Chem. Phys.*, 2019, **21**, 14766
 [3] Wilke et al, *Chem. Phys. Chem.*, 2016, **17**, 2736.
 [4] Platt, *J. Chem. Phys.*, 1949, **17**, 484.
 [5] Weber, *Biochem. J.*, 1960, **75**, 335.

MO 4.7 Mon 15:45 f142

Exciton Interaction and Exciton Diffusion in Artificial Light-Harvesting Complexes Probed with High-Order Multidimensional Spectroscopy — •JULIAN LÜTTIG¹, BJÖRN KRIETE², TENZIN KUNSEL², PAVEL MALÝ¹, THOMAS L. C. JANSEN², JASPER KNOESTER², MAXIM S. PSHENICHNIKOV², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, Netherlands

Two-dimensional electronic spectroscopy (2DES) has become a powerful tool for the investigation of single-exciton dynamics in various molecular systems, e.g., self-assembled artificial light-harvesting complexes. Here we use the recently developed technique of exciton-exciton-interaction two-dimensional (EEI2D) spectroscopy to disentangle the exciton dynamics in single-walled and double-walled tubular aggregates [1]. The technique of EEI2D spectroscopy allows us to follow the transport of excitons through the different systems by measuring exclusively exciton-exciton annihilation. We combine the technique of EEI2D spectroscopy with a microfluidic system to identify the influence of the supramolecular structure on the single- and double-exciton processes. EEI2D spectroscopy uncovers the different processes of exciton diffusion, energy transfer and exciton-exciton annihilation in these artificial-light harvesting complexes.

[1] B. Kriete et al., *Nat. Commun.* **10**, 4651 (2019)

MO 4.8 Mon 16:00 f142

Direct measurement of multiexcitonic structure in colloidal CdSeS/ZnS quantum dots by multiple-quantum 2D fluorescence spectroscopy — •STEFAN MÜLLER, JULIAN LÜTTIG, LUISA BRENNEIS, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

The multiexcitonic states of semiconductor quantum dots are of great relevance for their optoelectronic applications such as lasers and photovoltaics. Especially hot multiexcitons are discussed to be involved in the mechanism of carrier multiplication, a process that can significantly enhance solar cell efficiencies [1]. However, it is difficult to observe hot multiexcitons directly spectroscopically due to their short lifetime.

To address this, we demonstrate our recently developed method of multiple-quantum two-dimensional (2D) fluorescence spectroscopy on colloidal CdSeS/ZnS alloyed core/shell quantum dots. We report a systematic measurement protocol that simultaneously probes biexcitonic and triexcitonic quantum coherences by fourth- and sixth-order nonlinear processes. This is achieved by appropriate phase cycling of fully collinear femtosecond multipulse trains in combination with fluorescence detection, as previously demonstrated [2]. Our results directly reveal various hot multiexcitonic states, enabling to measure the binding energies of these many-body species.

[1] R. D. Schaller et al., *Nat. Phys.* **1**, 189-194 (2005).

[2] S. Mueller et al., *Nat. Commun.* **10**, 4735 (2019).

MO 4.9 Mon 16:15 f142

Excited state lifetimes of indole, 3-,4-, and 5-cyanoindole and pKa values of cyanoindoles in the ground and first excited state. — •HILDA LARTIAN, MARIE-LUISE HEBESTREIT, CAROLIN BORBECK, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

In this contribution the excited state lifetimes of indole, 3-cyanoindole (d_1), 4-cyanoindole (d_1) and 5-cyanoindole in D_2O and ethylacetate solution, obtained from time correlated single photon counting (TC-SPC), are presented and compared to excited state lifetimes in the gas phase. The excited state lifetime of 4-cyanoindole (d_1) in ethylacetate and D_2O solution is longer than of bare indole and the other cyanoindoles. 4-cyanoindole (d_1) shows a different behavior in the gas phase and has a shorter lifetime than 3-cyanoindole (d_1), while 3-cyanoindole has a shorter excited state lifetime than 4-cyanoindole. The different behavior of 3-, 4-, and 5-cyanoindole is discussed on the basis of the different electronic nature of the electronically excited singlet states. Furthermore the pKa values of cyanoindoles in the ground and excited state have been measured using UV/Vis absorption spectroscopy. 2- and 3-cyanoindole have lower ground state pKa values (<13) than the other cyanoindoles (>14). Only for 4- and 7-cyanoindole a significant shift in pKa upon excitation can be detected which might be due to low fluorescence lifetimes of the other cyanoindoles.

[1] Schneider et al, *Phys. Chem. Chem. Phys.*, 2018, **20**, 23441

[2] Hebestreit et al, *Phys. Chem. Chem. Phys.*, 2019, **21**, 14766

[3] Wilke et al, *Chem. Phys. Chem.*, 2016, **17**, 2736.