

MO 4: Electronic Spectroscopy

Time: Monday 10:30–12:30

Location: S HS 002 Biologie

Invited Talk MO 4.1 Mon 10:30 S HS 002 Biologie
Determination of Excited State Dipole Moments for Complex Systems - From Gas to the Condensed Phase — ●MICHAEL SCHMITT, MARIE-LUISE HEBESTREIT, MIRKO LINDIC, MATTHIAS ZAJONZ, and MICHAEL SCHNEIDER — Heinrich-Heine-Universität, Institut für Physikalische Chemie I, 40225 Düsseldorf, Germany

While in the gas phase, rotationally resolved electronic Stark spectroscopy is a versatile tool for the accurate determination of the permanent dipole moments in both states connected by the electronic transition, the situation in solution is less favorable. Although conceptually simple and broadly applied, solvatochromic shifts for the determination of excited state dipole moments are inaccurate and lead sometimes to completely false results.

A variant, using thermochromic shifts, leads to more reliable results, but still has some pitfalls. On the other hand many molecules are thermally labile and cannot be brought into the gas phase without decomposition. In this contribution, we compare the values of excited state dipole moments from Stark spectroscopy with those from thermochromic shifts, and show some improvements to the method. The range of small (20 atoms) to large (more than 100 atoms) is covered, hereby.

MO 4.2 Mon 11:00 S HS 002 Biologie
Photoelectron circular dichroism observed on the nanosecond timescale — ●ALEXANDER KASTNER, TOM RING, ROXANA SAVULEA, HAN-GYEOL LEE, HENDRIKE BRAUN, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

The asymmetry of photoelectron angular distributions from randomly oriented enantiomers of chiral molecules in the ionization with circularly polarized light arises in forward/backward direction with respect to the light propagation direction. This effect is known as photoelectron circular dichroism (PECD) and has been investigated by single-photon [1, 2] as well as resonance-enhanced multi-photon ionization using a femtosecond laser [3, 4]. Highly structured asymmetries in the range of $\pm 10\%$ on bicyclic Ketones were observed featuring pronounced dependence on photoelectron energy and electronic character of intermediate state for fenchone [5]. In addition, we were able to generalize the idea of a chiro-optical response to rotationally tailored fields [6].

Here we report on observation of PECD when using a Nd:YAG nanosecond laser. The possibility to use an ordinary nanosecond laser reduces the technical requirements to apply PECD in analytics.

- [1] I. Powis, *Adv. Chem. Phys.* 138, 267-329, (2008)
- [2] L. Nahon et al., *J. El. Spectr.* 204, 322-334, (2015)
- [3] C. Lux et al., *Chem. Phys. Chem.* 16, 115-137, (2015)
- [4] A. Kastner et al., *Chem. Phys. Chem.* 17, 1119-1122, (2016)
- [5] A. Kastner et al., *J. Chem. Phys.* 147, 013926, (2017)
- [6] P. V. Demekhin et al., *PRL*, *accepted*, (2018)

MO 4.3 Mon 11:15 S HS 002 Biologie
Simulation of molecular photoelectron spectra within the Dyson orbital formalism — ●TOBIAS MÖHLE, SERGEY I. BOKAREV, and OLIVER KÜHN — Universität Rostock, Inst. f. Phys.

Photoelectron spectroscopy is an important tool for studying the electronic structure of molecular systems, but reliable predictions challenge theoretical models to date. In the weak-field limit, using a perturbative approach and neglecting inter-channel-interactions, the difficulties are two-fold: First, the bound electrons must be described accurately enough to obtain reasonable excitation energies in a wide range. Second, accurate intensities require a proper representation of the photoelectron wave function.

For the bound part we use time-dependent density-functional theory in combination with optimally tuned range-separated hybrid functionals. This leads to fairly good energetics in the valence region of water, benzene, Cu_4^- and S_8 . The level of approximation for the photoelectron spectrum influences the outcome strongly: The popular frozen-orbital approximation, where the transition energies correspond to the (Kohn-Sham) orbital energies, is outperformed by Dyson-orbital based simulations by far. Using the latter, the sudden approximation gives reasonable results in many cases. However, to account for the kinetic-energy-dependence of intensities, the photoelectron must be taken into

account explicitly. While it is often described on a very approximate level, a route towards a more reliable description is presented, using a finite element scheme amended by infinite elements to ensure the correct asymptotic behaviour of the wave function.

MO 4.4 Mon 11:30 S HS 002 Biologie
Excited state dipole moment of 2-((4-methoxyphenyl)ethynyl)-3-(1-methyl-1H-indol-3-yl)quinoxaline via condensed phase thermochromic spectroscopy — ●MIRKO LINDIC, MATTHIAS ZAJONZ, TIM OBERKIRCH, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

The dipole moment of 2-((4-methoxyphenyl)ethynyl)-3-(1-methyl-1H-indol-3-yl)quinoxaline in the first excited singlet state was investigated using the method of thermochromic shifts of the fluorescence emission and absorption spectra.

Using the mentioned molecule as example some questions about the determination of excited state dipole moments in solution will be discussed: Which influence does the solvent cavity have dealing with large molecules? How is the dipole moment composed in a dye with multiple chromophores? How could quadrupole effects play a role in condensed phase measurements?

The measurements results will also be compared with values from ab initio calculations to allow a critical view on the effects of solvent molecules in spectroscopic methods.

MO 4.5 Mon 11:45 S HS 002 Biologie
 Λ -doubling and Zeeman effect of $^2\Pi_{3/2}$ molecules in helium nanodroplets — ●WOJCIECH RZADKOWSKI and MIKHAIL LEMESHKO — Institute of Science and Technology Austria (IST Austria), Am Campus 1, 3400 Klosterneuburg, Austria

Fine-structure levels of $^2\Pi_{3/2}$ electronic state of diatomic molecules in the absence of external fields split into so-called Λ -doublets. In the presence of a magnetic field they split further, forming separate Zeeman levels. Both effects get strongly enhanced when the molecule is immersed into superfluid helium nanodroplets. This behavior lacks microscopic explanation, with only limited phenomenological models available.

We use the angulon quasiparticle [1] to build a joint microscopic model explaining both anomalous Λ - and Zeeman splittings. Our approach does not use extensive numerical calculations. Instead, a physically intuitive picture of bath-induced couplings between fine-structure levels of the molecule is introduced. The theory can be verified against experimental data readily available for OH molecule [2].

- [1] M. Lemeshko, Quasiparticle Approach to Molecules Interacting with Quantum Solvents, *Phys. Rev. Lett.* 118, 095301 (2017)
- [2] P. Raston, T. Liang, G. Douberly, Anomalous Λ doubling in the Infrared Spectrum of the Hydroxyl Radical in Helium Nanodroplets, *J. Phys. Chem. A* 117 (2013)

MO 4.6 Mon 12:00 S HS 002 Biologie
Optically-induced collapse of Mg foam in helium nanodroplets — ●LEV KAZAK¹, SEBASTIAN GÖDE², JOSEF TIGGESBÄUMKER¹, and KARL-HEINZ MEIWES-BROER¹ — ¹Institute of Physics, University of Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock, Germany — ²European XFEL GmbH, Holzkoppel 4, 22869 Schenefeld, Germany

Magnesium embedded in helium droplets exist in form of metastable network of atoms surrounded by the layer of helium or so-called foam. At the conditions where only one Mg atom is presented in droplet, resonant two-photon ionization spectroscopy in the vicinity of $3^1P_1 \leftarrow 3^1S_0$ atomic transition reveals a narrow peak at 279 nm, blue-shifted relative to free atom. When the number of Mg atoms increases, a second peak at 282 nm arise and independent on further change of number of atoms. The presence of this feature, indicates that Mg atoms in He droplet have a interatomic distance of about 10 Å. In present work, the results on photoelectron spectroscopy of activated Mg foam are present. Instead of a single photoemission line, complex photoelectron spectra are obtained when several magnesium atom are present in the droplet, but almost no specific doping dependence is observed. New photoelectron peaks are attributed to highly excited states of Mg atoms. Analysis of electron yield with respect to pick-up statistics reveals the maximum number of Mg atoms which could be

stabilized in foam. The behavior of photoelectron spectra indicates a foam collapse. The excess of energy during this process is transferred to single Mg atoms, leading to population of highly excited states.

MO 4.7 Mon 12:15 S HS 002 Biologie

Photo-dissociation of size and charge-state selected poly-anionic tin clusters — ●MARKUS WOLFRAM, STEFFI BANDELOW, ALEXANDER JANKOWSKI, STEPHAN KÖNIG, GERRIT MARX, and LUTZ SCHWEIKHARD — Felix-Hausdorff-Straße 6, Institut für Physik, Greifswald, Deutschland

In contrast to various other metals that dissociate by monomer evaporation [1, 2], excited tin clusters offer a broad range of decay products, as observed after electron-cluster interactions [3]. To get further insight into their decay pathways, size and charge-state selected clusters $\text{Sn}_n^{1-}/2^-$ were photo-excited at the ClusterTrap-setup [4] by 532-nm

Nd:YAG laser pulses.

For small mono-anionic precursor clusters containing up to about $n = 50$ atoms, Sn_{n-7}^{1-} , Sn_{n-10}^{1-} or Sn_{n-15}^{1-} are observed as preferred fragments. For the bigger clusters (between ca. $n = 50$ to 70) there is a transition to monomer evaporation. In the case of di-anionic precursors, clusters Sn_{n-10}^{1-} come along with Sn_{10}^{1-} , probably due to fission as in the case of the group-14 neighbor-element lead [5]. Furthermore, doubly charged fragment clusters as Sn_{n-7}^{2-} appear - a special feature not observed previously for di-anionic clusters.

- [1] L. Schweikhard et al., Eur. Phys. J. D 36, 179 (2005)
- [2] A. Herlert et al., Int. J. MassSpectrom. 249-250,215 (2006)
- [3] S. König et al., Eur. Phys. J. D 72, 153 (2018)
- [4] F. Martinez et al., Int. J. Mass Spectrom. 365-366, 266 (2014)
- [5] S. König et al., Phys. Rev. Lett. 120, 163001 (2018)