

MO 5: Electronic Spectroscopy

Time: Tuesday 11:00–13:00

Location: F142

MO 5.1 Tue 11:00 F142

Highly-resolved Stark effect measurements of Rydberg states in nitric oxide — ●FABIAN MUNKES^{1,4}, PATRICK KASPAR^{1,4}, PHILIPP NEUFELD^{1,4}, ALEXANDER TRACHTMANN^{1,4}, YANNICK SCHELLANDER^{2,4}, LARS BAUMGÄRTNER^{3,4}, ROBERT LÖW^{1,4}, TILMAN PFAU^{1,4}, and HARALD KÜBLER^{1,4} — ¹Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart — ²Institut für Großflächige Mikroelektronik, Universität Stuttgart, Allmandring 3b, 70569 Stuttgart — ³Institut für Intelligente Sensorik und Theoretische Elektrotechnik, Universität Stuttgart, Pfaffenwaldring 47, 70569 Stuttgart — ⁴Center for Integrated Quantum Science and Technology (IQST), Universität Stuttgart

We demonstrate Stark effect measurements at room temperature of high-lying Rydberg states in nitric oxide. These states are generated using a three-photon continuous-wave excitation scheme. The readout is based on the detection of charged particles created by collisional ionization of Rydberg molecules. A theoretical discussion of the gained experimental results is given.

MO 5.2 Tue 11:15 F142

Threshold Photoelectron Spectra of fragments of AsMe3 and SbMe3 — ●EMIL KARAEV¹, MARIUS GERLACH¹, PATRICK HEMBERGER², and INGO FISCHER¹ — ¹Julius-Maximilians-Universität, Würzburg, Germany — ²Swiss Light Source, Villigen, Switzerland

Our group already investigated the pyrolysis products of methylated group V compounds $X = N^{[1]}$, $P^{[2]}$, $Bi^{[3]}$. While for the single methylated isomers of nitrogen we observed H-N-CH₂, N-CH₂ and H-N-CH, bismuth showed only Bi-CH₃. For phosphorus the isomers H-P-CH₂, P-CH₃ and P-CH₂ were detected. To complete our investigation of the 5th main group, trimethylarsenic and trimethylantimony were pyrolyzed. The emerging reactive species were characterized with the PEPICO setup of the VUV beamline of the synchrotron SLS in Switzerland. The resulting mass-selected threshold photoelectron spectra were interpreted using quantum chemical calculations and Franck-Condon simulations.

Our results show that antimony behaves similarly to bismuth, forming only Sb-CH₃. Arsenic on the other hand showed H-As-CH₂, As-CH₃ and As-CH₂, which is analogous to phosphorus.

MO 5.3 Tue 11:30 F142

Optical Absorption and Photodissociation Properties of Si_nO_m⁺ — ●TAARNA STUEMUND, MARKO FÖRSTEL, KAI POLLOW, EMIL MICKELIN, and OTTO DOPFER — IOAP, TU Berlin, Germany

The formation mechanisms of interstellar dust grains are still poorly understood. It is known, however, that these contain a significant amount of μm -sized silicate material [1]. So far only silicon monoxide (SiO) is identified in the interstellar medium [2]. We compare experimental data to quantum chemical calculations to understand photodissociation and optical absorption behavior, structures, and energies of possible Si_nO_m⁺ molecules that are potential and promising precursors. The experimental setup relies on action spectroscopy via mass spectrometry and resonant laser photodissociation of size-selected Si_nO_m⁺ clusters. These are generated via laser vaporization in a molecular beam expansion coupled to a quadrupole/time-of-flight tandem mass spectrometer and a broadly tuneable UV/VIS-OPO laser [3]. Preliminary data reveal competing fragmentation channels, their appearance energies and branching ratios, and the abundance and stability of neutral fragments. We highlight especially the spectrum of Si₃O₂⁺ measured by photodissociation and discuss it in an astrophysical context.

[1] K. Nagashima et al. *Nat.*, 2004, 428, 921-924[2] R. Wilson et al. *Astrophys. J.*, 1971 167, L97[3] M. Förstel et al., *Rev. Sci. Instrum.*, 2017, 88, 123110

MO 5.4 Tue 11:45 F142

The Electronic Spectrum of Si₂⁺ — ●KAI POLLOW, TAARNA STUEMUND, SOPHIE VERHOEVEN, EMIL MICKELIN, OTTO DOPFER, and MARKO FÖRSTEL — IOAP, TU Berlin, Germany

The first absorption lines of neutral Si₂ were measured 75 years ago. However, experimental information on the cation is rare. We recently

measured the first optical spectrum of Si₂⁺ via photodissociation spectroscopy[1]. We observe two vibronic band systems near 430 and 270 nm that are in very good agreement with high-level quantum-chemical calculations[2]. The measured vibronic transitions allow for determination of molecular constants in the ground and respective excited states. The optical spectrum of Si₂⁺ may enable astrophysical searches for this potential building block of interstellar silicate dust. We present the measured optical spectrum and compare it to quantum-chemical calculations.

[1] T. Studemund, K. Pollow, S. Verhoeven, E. Micken, O. Dopfer and M. Förstel *J.Phys.Chem.Lett.* 2022, 13 (33), 7624-7628.[2] Y. Liu; H. Zhai; X. Zhang; Y. Liu Ab initio calculation on the low-lying excited states of Si₂⁺ cation including spin-orbit coupling. *Chem. Phys.* 2013, 425, 156-161.

MO 5.5 Tue 12:00 F142

State selective diagnostics and spectroscopy of H₃⁺ in a heavy ion storage ring — ●AIGARS ZNOTINS¹, LUKAS BERGER¹, FLORIAN GRUSSIE¹, DAMIAN MÜLLER¹, OLDRICH NOVOTNY¹, FELIX NUSSLEIN¹, ANDREAS WOLF¹, ARNAUD DOCHAIN², XAVIER URBAIN², and HOLGER KRECKEL¹ — ¹Max-Planck-Institut für Kernphysik, Heidelberg, Germany — ²Institute of Condensed Matter and Nanoscience, Louvain-la-Neuve, Belgium

The significance of the triatomic hydrogen ion H₃⁺ for astrochemistry is well-established. It is a key contributor in a network of ion-neutral reactions that govern interstellar chemistry at low temperature and density. Additionally, as the simplest polyatomic molecule, H₃⁺ is an important benchmark system for theoretical calculations.

Due to a lack of a permanent dipole moment, laboratory spectroscopy of H₃⁺ remains a non-trivial endeavor. The highest-lying H₃⁺ levels experimentally reported have been identified by transitions from the H₃⁺ ground state to energies around 16500 cm⁻¹. Considering that the dissociation limit of H₃⁺ is at approximately 35000 cm⁻¹, more than half of the energetic landscape remains unexplored.

In this work, we discuss the possibility and requirements to extend H₃⁺ spectroscopy into the energy region above 20000 cm⁻¹. An approach for multi-color action spectroscopy is proposed to state-selectively investigate highly excited states of H₃⁺ in a cryogenic ion storage ring environment. We present model calculations describing the laser diagnostic schemes, based on a comprehensive H₃⁺ linelist.

MO 5.6 Tue 12:15 F142

Electronic Photodissociation Spectroscopy of Diamondoid Cations in a Cryogenic Trap — ●PARKER CRANDALL, SIMONE STAHL, VIKTORIA LOVASZ, MARKO FÖRSTEL, and OTTO DOPFER — Technische Universität Berlin, Berlin, Germany

Similarities have been observed between the infrared spectra of diamondoids and unidentified IR emission bands seen in the spectra of young stars with circumstellar disks.^{1,2} It is also suggested that their radical cations could contribute to features in the largely unassigned diffuse interstellar bands due to their low ionization energy and absorption in the visible range.³ However, the optical spectra of these cations have only recently begun to be measured experimentally, which is required for astronomical identification. Here, we present the optical spectra of the radical cations of adamantane (C₁₀H₁₆⁺)⁴, diamantane (C₁₄H₂₀⁺)⁵, and 1-cyanoadamantane (C₁₁H₁₅N⁺). These spectra were recorded by photodissociation of mass-selected ions in the gas phase at 5 K using a tandem mass spectrometer coupled to a cryogenic 22-pole ion trap. The experimental results are compared to photoelectron spectra and time-dependent DFT calculations for interpretation. All spectra reveal broad structures that are attributed to lifetime broadening and Franck-Condon congestion arising from geometric changes and/or Jahn-Teller distortion. The astrophysical implications of these ions will also be discussed.

MO 5.7 Tue 12:30 F142

Measuring fluorescence-detected two-quantum photon echoes using cogwheel phase cycling — ●AJAY JAYACHANDRAN, STEFAN MÜLLER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

We describe two-quantum photon echo spectroscopy, a new technique that enables one the selective characterization of doubly excited states. This technique is analogous to the popular ‘photon echo’ experiment [1], which encodes the dynamic information associated with singly excited states.

We transfer the core principle, i.e., a rephasing contribution that removes the effect of inhomogeneous broadening, to doubly excited states, and we extract the signal experimentally using cogwheel phase cycling of three-pulse sequences and fluorescence detection. We verify the applicability of cogwheel phase cycling, which has proven useful in two-dimensional nuclear magnetic resonance spectroscopy to reduce overall measurement time in comparison to nested phase cycling [2], by extracting the two-quantum photon echo without any signal aliasing.

We study how exciton–exciton annihilation of squaraine molecular aggregates of varying chain length [3] can be quantified by accessing the homogenous linewidth of the biexciton state which is obtained from the two-quantum photon echo.

[1] S. Asaka et al., *Phys. Rev. A* **29**, 2286-2289 (1984).

[2] M. H. Levitt et al., *J. Magn. Reson.* **155**, 300-306 (2002).

[3] P. Malý et al., *Chem. Sci.* **11**, 456-466 (2020).

MO 5.8 Tue 12:45 F142

Near-field scanning optical microscopy of topologically protected excitons in molecular aggregates — ●SIDHARTHA NAYAK,

CHRISTOPHER W. WÄCHTLER, and ALEXANDER EISFELD — MPIPKS, Dresden, Germany

Delocalized excitonic eigenstates of molecular aggregates are responsible for the energy transfer from an incoming radiation into the aggregate. Static disorder, which can arise from an imperfect environment of each molecule, reduces the exciton transport and large disorders can even localize the exciton. It has been shown theoretically that a two-dimensional periodic array of tilted and interacting molecules in a homogeneous magnetic field shows topologically protected edge states [1] which are robust under local disorder. With a scattering scanning near-field optical microscope setup, one can not only record position dependent absorption spectra [2] but also reconstruct the wavefunctions from these spectra [3]. In this contribution we study theoretically the near field spectra of the aforementioned 2D aggregates in which the molecules experience a disordered environment because of the probing metallic tip. Due to the topological protection, the edge states are robust even in the presence of the metallic nanoparticle, such that the recorded spectrum shows clear signatures of these edge states.

[1] J. Y. Zhou, S. K. Saikin, N. Y. Yao and A. Aspuru-Guzik, *Nature materials* **13**, 1026-1032 (2014)

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

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