

## MO 15: Rotational- and Vibrational-resolution Spectroscopy

Time: Thursday 11:00–13:00

Location: F142

## Invited Talk

MO 15.1 Thu 11:00 F142

**Excited state dipole moments from rotationally resolved Stark spectroscopy** — ●MICHAEL SCHMITT, MATTHIAS ZAJONZ, and MARIE-LUISE HEBESTREIT — Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie I, Universitätsstraße 26.43.02

Rotationally resolved electronic Stark spectroscopy is a versatile tool for the accurate determination of rotational constants of molecules in both electronic states, connected by the electronic transition, centrifugal distortion constants, barriers to hindered internal motions, transition dipole moments, and the permanent dipole moments of both states. The latter provide an easy access to the electronic nature of the excited state, because they differ in size and in direction for different electronic states. The most reliable values for dipole moments of ground and electronically excited states are obtained from gas phase electronic Stark experiments, since the dependence of the frequency shift of individual rovibronic lines from the electric field strength yields immediately the dipole moment in ground and excited state. A variation of the solvatochromic effect will be presented, namely the thermochromic effect, which is able to yield dipole moment changes upon electronic excitation of molecules in solution that are largely independent of the solvent used, to close the gap between gas phase dipole moment changes and those obtained in solutions. Although used for many years in organic chemistry, the Lippert-Mataga theory has severe deficiencies, which will be highlighted in the contribution. We will present a thorough analysis of the photo-physics of the six different positional isomers of cyanoindole in the gas phase and in solution.

MO 15.2 Thu 11:30 F142

**High resolution continuous wave spectroscopy on the  $A^2\Sigma^+ \leftarrow X^2\Pi_{3/2}$  transition in nitric oxide** — ●PHILIPP NEUFELD<sup>1,3</sup>, PATRICK KASPAR<sup>1,3</sup>, FABIAN MUNKES<sup>1,3</sup>, ALEXANDER TRACHTMANN<sup>1,3</sup>, YANNICK SCHELLANDER<sup>2,3</sup>, ROBERT LÖW<sup>1,3</sup>, TILMAN PFAU<sup>1,3</sup>, and HARALD KÜBLER<sup>1,3</sup> — <sup>1</sup>Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart — <sup>2</sup>Institut für Großflächige Mikroelektronik, Universität Stuttgart, Allmandring 3b, 70569 Stuttgart — <sup>3</sup>Center for Integrated Quantum Science and Technology (IQST), Universität Stuttgart

Within the scope of the development of a new kind of gas sensor [1,2], we employ Doppler-free saturated absorption spectroscopy on the  $A^2\Sigma^+ \leftarrow X^2\Pi_{3/2}$  transition in nitric oxide (NO) for different total angular momenta  $J$  on the  $P_{12}$  branch. Spectroscopy is performed in continuous wave operation at 226 nm in a 50 cm long through-flow cell. Via phase sensitive detection by a lock-in amplifier the hyperfine structure of the  $X^2\Pi_{3/2}$  state of NO is partially resolved. The data is compared to previous measurements, showing good agreement. Investigation of the dependence of the spectroscopic feature on power and pressure, should yield hyperfine constants, natural transition linewidth and the collisional cross-section between NO molecules. [1] P. Kaspar et. al., OSA Optical Sensors and Sensing, 19-23 July, 2021 [2] J. Schmidt et. al., Appl. Phys. Lett. 113, 01113 (2018)

MO 15.3 Thu 11:45 F142

**Determination of the ortho-to-para ratio of  $H_3^+$  in a cryogenic ion trap** — PHILIPP SCHMID, CARSTEN CZAPCZYK, THOMAS SALOMON, OSKAR ASVANY, and ●STEPHAN SCHLEMMER — I. Physikalisches Institut der Universität zu Köln, Köln, Germany

A clean sample of ortho (o) and para (p)  $H_3^+$  is prepared in a cryogenic 22-pole ion trap by removing one nuclear spin species. This isolation is reached on time scales below one second by a selective excitation of the  $\nu_2$  vibrational mode of  $H_3^+$  addressing a rotational state associated with one of the two species. In subsequent collisions of the excited  $H_3^+$  with He the vibration-to-translation (V-T) energy transfer produces fast  $H_3^+$  of the addressed spin configuration which then leaves the trap via a small electrostatic barrier. Following this protocol the o/p-ratio of  $H_3^+$  coming from the ion source is determined to be 1:1, as expected. In the presence of normal hydrogen, n- $H_2$ , in the cryogenic ion trap the o/p-ratio of  $H_3^+$  reaches a stationary value close to 1:3 which is rationalized by the ordering of the lowest energy states of o- $H_3^+$  and p- $H_3^+$ . This work shows that nuclear spin specific and also structural isomer specific preparation and analysis is now possible in cryogenic ion traps. With this aid action spectra of isomer mixtures can be disentangled and it will become possible to determine isomer branching

ratios of chemical reactions, as well as to study state-specific reactions like for the fundamental  $H_3^+ + H_2$  collision system considered in this work.

MO 15.4 Thu 12:00 F142

**Leak-out spectroscopy: a new, universal action spectroscopy method** — ●PHILIPP C. SCHMID, THOMAS SALOMON, SVEN THORWIRTH, OSKAR ASVANY, and STEPHAN SCHLEMMER — I. Physikalisches Institut, Universität zu Köln, Köln, Germany

Rotational-resolved vibrational spectra of molecular ions are recorded using action spectroscopy techniques in cryogenic ion traps [1]. Thereby the spectrum is identified as a change of the ion mass by fragmentation upon photon absorption, pre-dissociation of tagged ions or via laser induced chemical reactions. Although all these techniques have advanced significantly, action spectroscopy cannot be applied to many ions when the aforementioned methods fail to work. Here, we present a new method of action spectroscopy, called leak-out spectroscopy (LOS) [2]. LOS does not rely on a change in the mass of the ion, but on the transfer of internal energy of an excited ion to its translation energy upon the collision with a neutral partner. This allows the fast ions to escape the trap potentials and thus the spectrum can be recorded by detecting the ions leaving the trap. Based on this principle, LOS is intrinsically background free and suitable for virtually any ion. In recent measurements we used LOS to record the ro-vibrational resolved  $\nu_1$  C-H stretching vibration spectrum of l- $C_3H^+$ . [1] B.A. McGuire et al., Nature Review Physics 2(2020)402. [2] P.C. Schmid et al., J. Phys. Chem. A 126(2022)8111.

MO 15.5 Thu 12:15 F142

**Spectroscopic studies of acylium- and thioacylium ions** — ●SVEN THORWIRTH<sup>1</sup>, OSKAR ASVANY<sup>1</sup>, THOMAS SALOMON<sup>1</sup>, MARCEL BAST<sup>1</sup>, PHILIPP C. SCHMID<sup>1</sup>, MICHAEL E. HARDING<sup>2</sup>, IGOR SAVIC<sup>3</sup>, JOSÉ L. DOMÉNECH<sup>4</sup>, and STEPHAN SCHLEMMER<sup>1</sup> — <sup>1</sup>I. Physikalisches Institut, Universität zu Köln, Köln Germany — <sup>2</sup>Institut für Nanotechnologie, Karlsruher Institut für Technologie (KIT), Karlsruhe, Germany — <sup>3</sup>Department of Physics, Faculty of Sciences, University of Novi Sad, Novi Sad, Serbia — <sup>4</sup>Instituto de Estructura de la Materia (IEM-CSIC), Madrid, Spain

Acylium- and thioacylium ions, R-CO<sup>+</sup> and R-CS<sup>+</sup>, are classes of astrochemically important molecular ions that have received relatively little attention from molecular spectroscopy so far. Triggered by recent laboratory and astronomical observations of the polyatomic HC<sub>3</sub>O<sup>+</sup>, HC<sub>3</sub>S<sup>+</sup>, and CH<sub>3</sub>CO<sup>+</sup> species (see, Thorwirth et al. 2020, Cernicharo et al. 2021 and references therein) our laboratory investigations have now been extended towards other selected (thio)acylium species. Here, we would like to present a status report on our studies performed using various action spectroscopy schemes in combination with state-of-the-art ion traps.

Thorwirth, S., Harding, M. E., Asvany, O. et al. 2020, Mol. Phys. 118, e1776409

Cernicharo, J., Cabezas, C., Bailleux, S. et al. 2021, Astron. Astrophys. 646, L7

MO 15.6 Thu 12:30 F142

**Luminescent and excited state properties of bimetallic coinage metal NHC-complexes** — ●DANIEL MARHÖFER<sup>1</sup>, PIT BODEN<sup>1</sup>, SOPHIE STEIGER<sup>1</sup>, CHRISTOPH KAUB<sup>2</sup>, PETER ROESKY<sup>2</sup>, and GEREON NIEDNER-SCHATTEBURG<sup>1</sup> — <sup>1</sup>Dept. of Chemistry, TUK, Erwin-Schrödinger-Str. 52-54, 67663 Kaiserslautern — <sup>2</sup>Institute of Inorganic Chemistry, KIT, Engesserstr. 15, 76131 Karlsruhe

A series of bimetallic coinage metal complexes containing a specific, bipyridyl substituted, N-heterocyclic carbene ligand was investigated via luminescence spectroscopy as well as step-scan FTIR spectroscopy. The series contains the monometallic and the heterobimetallic gold complexes as well as the homobimetallic silver and copper compounds. The luminescence measurements were performed both in potassium bromide matrix and in (conditionally frozen) ethanoic solution. The emission lifetimes were determined via time-correlated single photon counting in the temperature range between 5 K and 290 K. The excited state structures were studied by electronic excitation by a pulsed UV laser followed by step-scan FTIR probing, allowing the determination

of the IR absorption of the electronically excited molecules. The obtained excited state spectra were then compared to both the ground state vibrational spectrum as well as the quantum-chemically calculated lowest energy singlet and triplet states' vibrational spectra. A pronounced dependence of the excited state IR absorption, the emission colour and the excited state lifetimes on the metal centers could be observed and finally assigned to cooperative effects in specific metal combinations.

MO 15.7 Thu 12:45 F142

**2DIR Spectroscopy of an Organic Azide Model** — •CLAUDIA GRÄVE, JÖRG LINDNER, and PETER VÖHRINGER — Clausius-Institut für Physikalische und Theoretische Chemie, Rheinische Friedrich-

Wilhelms-Universität Bonn, Wegelerstraße 12, 53115 Bonn, Germany

The photoinduced dynamics of azides is of great importance in organic chemistry but not yet understood, even at a qualitative level. We are currently utilizing ultrafast spectroscopy to address these dynamics.

Here, we report on first results from femtosecond two-dimensional infrared (2DIR) spectroscopy of 1-cyano-2-(4-azidophenyl)-acetylene to understand vibrational energy transfer (VET) to the solvent and intramolecular vibrational energy redistribution (IVR). Our 2DIR data show that IVR from the azide moiety through the phenyl ring onto the para-positioned cyano-acetylene group occurs on a time scale of 3.5 ps. In contrast, VET in chloroform solution requires 20 ps. Finally, a coherent vibrational quantum beat can be detected, which dephases within roughly 1 ps.