

MO 14: Vibrational and Rotational Spectroscopy

Time: Wednesday 14:00–16:30

Location: f142

Invited Talk

MO 14.1 Wed 14:00 f142

Elucidating transition metal clusters and complexes in cryo isolation — ●GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie and State Research Center OPTIMAS, TU Kaiserslautern, Germany

We utilize cryogenic ion trapping to record adsorption and activation kinetics, normal vibrations and magnetic moments of isolated transition metal (TM) clusters and their coordination complexes when held isolated void of environmental interferences. The characterization of such intrinsic properties in combination allows for far fetching conclusions on e.g. the morphologies and adsorbate induced reorganization of TM clusters, and the magnetostructural correlations within oligomeric TM complexes. We refer to published [1-7] as well as to most recent yet unpublished results [8-9].

[1] S. Dillinger, J. Mohrbach, J. Hewer, M. Gaffga, GNS, PCCP 17, 10358 (2015). [2] J. Mohrbach, S. Dillinger, GNS, J. Phys. Chem. C 121, 10907 (2017). [3] J. Mohrbach, S. Dillinger, GNS, J. Chem. Phys. 147, 184304 (2017). [4] S. Dillinger, J. Mohrbach, GNS, J. Chem. Phys. 147, 184305 (2017). [5] S. Dillinger, M. P. Klein, A. Steiner, D. C. McDonald, M. A. Duncan, M. M. Kappes, GNS, J. Phys. Chem. Lett. 9, 914 (2018). [6] M. P. Klein, A. Ehrhard, S. Dillinger, J. Mohrbach, GNS, Topics in Catalysis 61, 106 (2018). [7] J. Lang, J. M. Hewer, M. Klein, C. van Wüllen GNS, PCCP 20, 16673-16685 (2018). [8] D. V. Fries, M. P. Klein, A. Steiner, H. Schwarz, GNS, work in progress [9] A. Steiner, M. P. Klein, C. Wiehn, M. Prosenč, P. Armentrout, GNS, work in progress

Invited Talk

MO 14.2 Wed 14:30 f142

Rotational Studies of (chiral) Molecules/Complexes in Jets (& Flames) — ●JENS-UWE GRABOW — Leibniz Universität, Hannover, Germany

Rotational spectroscopy is the most precise and unambiguous method to detect and characterize molecular species important in environmental and astro-chemistry.

The dual excitation-emission propagation in-phase/quadrature-phase modulation passage-acquired coherence technique (DEEP-IMPACT) Fourier-transform microwave (FTMW) spectrometer delivers broadband spectra at a resolution similar to the resolving power of the narrowband but more sensitive excitation pulse-induced coherence coaxial orientation beamresonator arrangement (EPIC-COBRA) FTMW spectroscopy.

Nevertheless, the single-horn feed used in the dual off-axis parabolic reflector arrangement limits the applicable excitation power and therefore is severely reducing the polarization efficiency. Rotating of the field vector direction of the linearly polarized microwave radiation allows for a dual-feed horn. This novel setup prevails the high spectral resolution but increases the sensitivity dramatically while allowing the very high-power needed for less polar species. In this contribution we present the apparatus in detail as well as experimental results obtained with the EPIC-COBRA FT-MW spectrometer that also adopts instrumental aspects of the DEEP-IMPACT FTMW technique. Furthermore, we will try to elucidate the nature of double-quantum coherence and some of its recent applications towards chiral molecules as well as jet-sources to observe more reactive intermediates produced in combustion reactions.

MO 14.3 Wed 15:00 f142

IR Photodissociation spectra of $\text{Si}_x\text{H}_{4x-4}^+$ ($x=4-8$): Evidence for Si-H-Si proton bridges — ●MARTIN ANDREAS ROBERT GEORGE and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany

Silicon hydride clusters (Si_xH_y^+) play a significant role in plasma chemistry and astrochemistry. Despite this importance their structural and energetic properties are largely unexplored. Building upon our previous investigations of Si_2H_6^+ [1], Si_2H_7^+ [2], Si_3H_8^+ [3], we present infrared photodissociation (IRPD) spectra of previously unknown Si_xH_y^+ ions of the form $\text{Si}_x\text{H}_{4x-4}^+$ with $x=4-8$ ($\text{Si}_4\text{H}_{12}^+$ - $\text{Si}_8\text{H}_{24}^+$) [4]. Our spectral analysis, supported by dispersion-corrected density functional calculations, reveals that all $\text{Si}_x\text{H}_{4x-4}^+$ ions have at least one Si-H-Si bridge. The characteristic fingerprint of these three-center two-electron (3c-2e) bonds is the strongly IR active anti-symmetric stretch fundamental of the Si-H-Si bridge. The frequency

of this vibration depends strongly on the structural and energetic details of the Si-H-Si bridge. Our investigations reveal the correlations between the properties of the various Si-H-Si bridges (bond distances, bond angles, binding energies, stretch frequencies). The bond strength varies from strong symmetric 3c-2e chemical bonds to weak hydrogen or van der Waals bonds. [1] M. Savoca et al. (2013), Phys. Chem. Chem. Phys., 15, 2774 [2] M. Savoca et al., Angew. Chem. Int. Ed. (2013), 52, 1568 [3] M.A.R. George et al., Chem. Eur. J. (2013), 19, 15315-15328 [4] M.A.R. George, O. Dopfer (2019), Int. J. Mass Spectrom. (2019), 435, 51

MO 14.4 Wed 15:15 f142

Contact Ion Pairs of Phosphate Groups in Water — ●JAKOB SCHAUSS, ACHINTYA KUNDU, BENJAMIN P. FINGERHUT, and THOMAS ELSAESSER — Max-Born-Institut, Berlin, Deutschland

Negatively charged phosphate groups in the RNA backbone are key to the formation of an ordered solvation shell around the molecule. Interactions of these phosphate groups with alkali and alkaline earth ions in the surrounding solvent strongly impact RNA structure and folding dynamics. Dynamics of ionic arrangements as well as molecular coupling mechanisms of these interactions still escape our current understanding.

In our investigations we employ 2D infrared spectroscopy and microscopic density functional theory simulations on phosphate vibrations. Using the model system dimethyl phosphate in water with an added excess of Mg^{2+} , Ca^{2+} , and Na^+ ions we were able to observe and analyze the formation of contact ion pairs. [1]

[1] Schauss et al., *J. Phys. Chem. Lett.*, **10**, 6281-6286 (2019)

MO 14.5 Wed 15:30 f142

Dynamics of polar polarizable rotors acted upon by unipolar electromagnetic pulses — ●MALLIKARJUN KARRA¹, MARJAN MIRAHMADI², BURKHARD SCHMIDT², and BRETISLAV FRIEDRICH¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Institut für Mathematik, Freie Universität Berlin, Berlin, Germany

We study, analytically as well as numerically, the dynamics that arises from the interaction of a polar polarizable rigid rotor with single unipolar electromagnetic pulses of varying length with respect to the rotational period of the rotor. In the sudden, non-adiabatic limit, we derive analytic expressions for the rotor's wavefunctions, kinetic energies, and field-free evolution of orientation and alignment. The corresponding time-dependent Schrödinger equation is solved numerically in the finite pulse-width regime, extending all the way to the adiabatic limit where general analytic solutions beyond the field-free case are no longer available. The effects of the orienting and aligning interactions as well as of their combination on the post-pulse populations of the rotational states are visualized as functions of the orienting and aligning kick strengths in terms of population quilts, while the evolution of the wavepacket itself is visualized in terms of space-time probability densities. In the intermediate temporal regime, we find that the wavepackets as functions of the orienting and aligning kick strengths show resonances that correspond to diminished kinetic energies at particular values of the pulse duration. Based on this surprising finding, we propose a scheme for the rotational cooling of molecules via iterative 'braking'.

MO 14.6 Wed 15:45 f142

Wide range, high resolution M-IR spectroscopy of C_2H_2 — ●ULRICH EISMANN¹, DAVID B. FOOTE², MATT CICH², WALTER HURLBUT², DANIEL J. CHRISTENSEN³, FELIX ROHDE¹, and CHRIS HAIMBERGER² — ¹TOPTICA Photonics AG, Lochhamer Schlag 19, D-82166 Graefelfing, Germany — ²TOPTICA Photonics, Inc., 5847 County Rd. 41, Farmington, NY 14425, USA — ³now with Lumencor Inc., 14940 NW Greenbrier Parkway, Beaverton, OR 97006 USA

Continuous-wave optical parametric oscillators are a flexible tool for high-resolution spectroscopy, potentially covering from the D-UV to the M-IR range, with tunable narrow-linewidth output powers exceeding 10 W and versatile frequency referencing.

Here, we demonstrate more than 50 nm of automatic, effectively-mode-hop-free idler tuning of our commercial source DLC TOPO by using stand-off digital control. We achieve an absolute accuracy in the low 10^{-3} cm^{-1} range ($\approx 100 \text{ MHz}$) at a scan speed of $2 \text{ cm}^{-1}/\text{min}$. We

present continuous spectroscopy on C_2H_2 and CH_4 near $3\ \mu m$. The M-IR frequency referencing is established by monitoring the pump and signal wavelengths in the N-IR using a wavelength meter, and our data suggests an improvement of the HITRAN database.

Our scheme can be extended to fully automatic operation within the entire $2.2 - 4.0\ \mu m$ idler emission range. For demonstration, we obtain similar performance at the minimum and maximum idler wavelengths. Using a frequency frequency comb as a reference, ultimate accuracies can be achieved, and we demonstrate measurements of the DLC TOPO locked to a commercial comb system DFC CORE.

MO 14.7 Wed 16:00 f142

IR/UV Ion Dip Spectroscopy of the 2-Methyl-Allyl-Radical and its High Temperature Bimolecular Reaction Products —

•TOBIAS PREITSCHOPF¹, FLORIAN HIRSCH¹, ALEXANDER LEMMENS², ANOUK M. RIJS², and INGO FISCHER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²FELIX Laboratory, Faculty of Science, Radboud University, Toernooiveld 7, 6525 ED Nijmegen, The Netherlands

As recent studies suggest, small hydrocarbon radicals such as the 2-methyl-allyl radical (2-MAR) are considered as highly reactive intermediates in combustion processes [1]. Studies of these isolated radicals are scarce but bear important information on their reactions for kinetic modelling of combustion processes.

In this work we investigate the gas phase IR-spectra of the 2-MAR and its high temperature bimolecular reaction products in a free jet using IR/UV Ion-Dip-Spectroscopy. This double resonance spectroscopic method combines the structural sensitivity of mid-infrared spec-

troscopy with mass information from UV photoionization. The 2-MAR is generated by flash pyrolysis from the corresponding bromide precursor. Additionally, the pyrolysis-tube serves as a flow reactor to foster bimolecular reactions. While a dye-laser ionizes the various products in a one-color two-photon process, the mid-IR-radiation is provided by the free electron laser FELIX, Nijmegen/NL. This intense IR light source can be scanned over the fingerprint region for unambiguous identification of the dilute reaction products.

[1] V. D. Knyazev et al., J. Phys. Chem. A. 1998, 102, 8932-8940

MO 14.8 Wed 16:15 f142

Millimeter Wave Spectrum of Styrene Oxide C_8H_8O —

•PASCAL STAHL¹, ARENAS BENJAMIN², SERGIO DOMINGOS², GUIDO W. FUCHS¹, MELANIE SCHNELL², and THOMAS GIESEN¹ — ¹Institute of Physics, University Kassel, Heinrich-Plett Str. 40, 34132 Kassel, Germany — ²Spectroscopy of Molecular Processes, DESY, Notkestraße 85, 22607 Hamburg, Germany

We investigated the astrochemically-relevant, chiral molecule styrene oxide C_8H_8O and analysed the rotational spectrum of its ground state. Chirped-pulse Fourier-transform microwave and millimeter-wave spectroscopy and frequency modulation absorption spectroscopy was applied to record spectra in the region of 2 GHz to 330 GHz. Spectral analysis produced a set of precise rotational constants and centrifugal distortion constants up to the sextic order. Our accurate predictions of styrene oxide into the (sub-)millimetre range are necessary for radio astronomy searches. In addition, we assigned the spectra of all singly-substituted ^{13}C and the ^{18}O isotopologues, which allowed us to investigate the gas-phase structure of the molecule.