

MO 4: Spectroscopy of Cold Molecules and Complexes

Time: Monday 17:00–19:00

Location: N 25

MO 4.1 Mon 17:00 N 25

C₆₀⁺ Near-IR Emissions: Astronomical Relevance. —
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Recently, five Diffuse Interstellar Bands (DIBs) were assigned to C₆₀⁺ [1,2]. While investigating C₆₀⁺ in various cryogenic matrixes, we have observed LIF in the near-IR, when exciting the near-IR vibronic bands of C₆₀⁺. Power dependence measurements revealed a one-photon LIF process. In contrast, excitation in the UV does not lead to the emission of C₆₀⁺ in the vicinity of its NIR absorptions. We propose to search for C₆₀⁺ near-IR emissions in the fullerene containing reflection nebulae.

References

1. Campbell, E. K., Holz, M., Gerlich, D., and Maier, J. P. 2015, *Nature*, 523, 322.
2. Walker, G. A. H., Bohlender, D. A., Maier, J. P., and E. K. Campbell. 2015, *ApJL*, 812, L8.

MO 4.2 Mon 17:15 N 25

Cryo IR spectroscopy of a tetranuclear cobalt carbonyl complex in isolation — •SEBASTIAN DILLINGER¹, JENNIFER MOHRBACH¹, JOHANNES LANG¹, PIERRE BRAUNSTEIN², and GEREON NIEDNER-SCHATTEBURG¹ — ¹Fachbereich Chemie und Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany — ²Laboratoire de Chimie de Coordination, Institut de Chimie, UMR 7177 CNRS, Université de Strasbourg, 67081 Strasbourg, France

We present well resolved Infrared Multiple Photon Dissociation (IR-MPD) spectra of isolated [Co₄(CO)_n(dppa-H⁺)]⁺ (n = 3 - 10, dppa = NH(PPh₂)₂) in the carbonyl stretching region at cryogenic temperatures (26 K). [1] The [Co₄(CO)₁₀(dppa-H⁺)]⁺ complex [2] serves as precursor for the stepwise elimination of CO via collision induced dissociation (CID). The recorded spectra reveal several bands which shift by reduction of the CO coverage. This hints at an according change of coordination motif. DFT calculations help to elucidate the effects of the decreasing CO coverage on the structure and the spin multiplicity of the complex. We will discuss first data of a mixed CO-N₂ complex [Co₄(CO)₈(N₂)₁(dppa-H⁺)]⁺.

- [1] J. Mohrbach et al., *J. Mol. Spectrosc.*, 2016 (accepted)
- [2] C. Moreno et al., *J. Organomet. Chem.*, 1993, 452, 185

MO 4.3 Mon 17:30 N 25

Multi-spectroscopic analyses of diphenyl ether complexes with tert-butyl alcohol and water in the electronic ground and excited state — •DOMINIC BERNHARD¹, FABIAN DIETRICH¹, MARIYAM FATIMA², ANJA POBLITZKI³, MARTIN SUHM³, MELANIE SCHNELL², and MARKUS GERHARDS¹ — ¹Fachbereich Chemie, TU Kaiserslautern — ²MPI für Struktur und Dynamik der Materie, Hamburg — ³Institut für Physikalische Chemie, Universität Göttingen

Diphenyl ether (DPE) represents a system with competing docking sites for alcohols leading to OH-O and OH- π structures. Recently the DPE – methanol complex was investigated in a multi-spectroscopic work in the electronic ground state (S₀) where a dominating OH- π structure was found in agreement with theory. In the electronically excited state (S₁) the OH- π interaction is strengthened which was revealed in a combined IR/UV spectroscopic and theoretical work. Starting from these findings complexes of DPE with *tert*-butyl alcohol and water are investigated which are supposed to be completely different dispersion energy donors. For both complexes FTIR, microwave and mass- and isomer-selective IR/R2PI spectra were recorded revealing two co-existing OH-O and OH- π isomers in the S₀ state which are surprisingly in *both* cases predicted to be almost equally stable. In the S₁ state of DPE – *tert*-butyl alcohol vibrational spectra could be recorded separately for both isomers using UV/IR/UV spectroscopy; a retention of each structural motif is obtained, but the OH-O bond is weakened for the OH-O arrangement and the OH- π interaction is strengthened in the case of the OH- π isomer.

MO 4.4 Mon 17:45 N 25

[B₁₂Cl₁₁]⁻: An anionic superelectrophile? — MARKUS ROHDENBURG¹, •MARTIN MAYER², MAX GRELLMANN², CARSTEN JENNE³, TOBIAS BORRMANN¹, FLORIAN KLEEMISS⁴, VLADIMIR

A. AZOV¹, KNUT R. ASMIS², SIMON GRABOWSKY⁴, and JONAS WARNEKE⁵ — ¹University of Bremen, Institute of Applied and Physical Chemistry — ²Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig — ³Bergische Universität Wuppertal, Fakultät für Mathematik und Naturwissenschaften — ⁴University of Bremen, Institute of Inorganic Chemistry and Crystallography — ⁵Physical Science Division, Pacific Northwest National Laboratory, USA

Noble-gas (Ng) binding at room temperature is characteristic of super-electrophilic dications. Here, we report on the binding of krypton and xenon by the closo-dodecaborate anion [B₁₂Cl₁₁]⁻. The [B₁₂Cl₁₁Ng]⁻ complexes are thermodynamically stable species with Ng binding energies of 80 to 100 kJ/mol and contain B-Ng bonds with a significant degree of covalent interaction. The electrophilic nature of the boron binding site in [B₁₂Cl₁₁]⁻ is spectroscopically confirmed by the observation of a blue shift of the CO stretching mode in [B₁₂Cl₁₁CO]⁻. The characteristic electric field in front of the reactive site of [B₁₂Cl₁₁]⁻ results in a barrier for polar molecules, promoting the formation of Ng-complexes that are not detected with reactive cations like C₆H₅⁺. This introduces the new chemistry of "dipole discriminating electrophilic anions". Implications for noble gas compounds and the fundamental concept of electrophilicity are discussed.

MO 4.5 Mon 18:00 N 25

Optical photodissociation spectroscopy of metal lumichrome ionic complexes using the 22-Pole BerlinTrap — •DAVID MÜLLER, PABLO NIETO, ALAN GÜNTHER, ALEX SHELDRICK, and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin

Flavin-containing systems act as light sensors in plants and as blue-light receptors in fungi due to their wide spectral absorption from the VIS to the UV. They differ in their substituents at the N10 position. The simplest flavin without any substituent is lumichrome (LC). Most experiments concerning flavins were performed in solution, but not on isolated gas phase ions. Hence, the influence of the solvent and the ions is not fully understood yet. We report first vibronic spectra of protonated lumichrome H⁺LC [1] and metalated lumichrome (M⁺LC, M = Li-Cs). The gas-phase ions are generated in an ESI-source, mass-selected by a QPMS and cooled in a cryogenic 22-pole trap. After laser irradiation (380-500 nm) the fragments are mass-selected by an orthogonal ReTOF mass spectrometer. This design enables us to detect all fragments and the parent ion simultaneously. By comparison to quantum chemical calculations, we can assign the N5 position as the protonation site and the O4 position as the metalation site.

- [1] A. Günther et al., *J. Mol. Spectrosc.* (2016), in press DOI:10.1016/j.jms.2016.08.017

MO 4.6 Mon 18:15 N 25

Vibrational Blue Shift of coordinated N₂ in [Fe₃O(OAc)₆(N₂)_n]⁺: "Non Classical" Dinitrogen Complexes — •JOHANNES LANG, JENNIFER MOHRBACH, SEBASTIAN DILLINGER, JOACHIM HEWER, and GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie und Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany.

The discovery of transition metal dinitrogen complexes in 1965 launched the ever growing research field of N₂ coordination chemistry. Spectroscopically, metal-N₂ bonding manifests itself by shifted N₂ stretching vibration frequencies in relation to the (IR inactive) frequency of the free N₂ molecule. Predominantly, N₂ complexes exhibit vibrational red shifts [1,2], which is well understood terms of the Dewar-Chatt-Duncanson (DCD) model [3].

Here, we present "non classical" dinitrogen complexes [Fe₃O(OAc)₆(N₂)_n]⁺ (n = 1,2,3) in the gas phase at cryo temperatures. Infrared photo dissociation (IR-PD) as well as density functional theory (DFT) calculations reveal blue shifted N₂ stretching vibration bands. A detailed analysis of the electronic and steric interplay between N₂ and the [Fe₃O(OAc)₆]⁺ unit indicates strengthened N-N bonds due to pronounced σ bonding and a lack of π back donation.

- [1] S. Dillinger, J. Mohrbach, J. Hower, M. Gaffga, G. Niedner-Schatteburg, *PCCP* 2015, 17, 10358-10362.
- [2] F. Studt, F. Tuczek, *J. Comp. Chem.* 2006, 27, 1278-1291.
- [3] G. Frenking and N. Fröhlich, *Chem. Rev.*, 2000, 100, 717-774.

MO 4.7 Mon 18:30 N 25

High density source for slow and internally cold polar molecules reaching a collision limited regime — •THOMAS GANTNER, MANUEL KOLLER, XING WU, SOTIR CHERVENKOV, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, 85748 Garching, Germany

We present a new source for intense beams of slow and internally cold polyatomic molecules. By employing buffer gas cooling, an intense beam of molecules is achieved, reaching a single state purity of up to 92% [1]. Subsequently, the molecules are decelerated by a centrifuge decelerator [2] to a kinetic energy corresponding to less than 1 K. This combination produces cold guided molecules at fluxes exceeding $10^{10}/\text{s}$ and densities of over $10^9/\text{cm}^3$. We thereby enter a regime where cold dipolar collisions can be observed directly in a quadrupole guide. Utilizing the technique for a range of molecules (ND_3 , CH_3F , CHF_3 , CF_3CCH , CH_3OH , and $\text{C}_3\text{H}_7\text{OH}$) demonstrates its wide applicability.

[1] X. Wu et al., ChemPhysChem 2016, 17, 3631

[2] S. Chervakov et al., Phys. Rev. Lett. 112, 013001 (2014)

MO 4.8 Mon 18:45 N 25

Characterising and Optimising of a Novel Laser Desorption Source — •NICOLE TESCHMIT^{1,2}, DANIEL HORKE^{1,2}, KAROL DŁUGOŁĘCKI¹, DANIEL GUSA¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center

for Free- Electron Laser Science, DESY, Hamburg — ²The Hamburg Center for Ultrafast Imaging, University of Hamburg — ³Department of Physics, University of Hamburg

The control of small and moderate-size gas-phase molecules, such as the spatial separation of different quantum states, conformers, and molecular clusters, has been demonstrated, using static and/or dynamic electric fields [1]. Here, we present a new laser-desorption source for the production of very cold molecular beams, which will extend the above-mentioned techniques to larger biologically important molecules, such as peptides. The molecular beam of a laser-desorption source is for the first time characterized using strong field ionization by a femtosecond laser, combined with a time of flight mass spectrometer. Strong field ionization allows the detection of all existing species (including molecular fragments produced by the desorption process) and atoms in the interaction region. The beam can now be fully characterized and the conditions optimized for the production of intact sample molecules in the beam and the separation of one conformer from the beam can be shown. This makes this source suitable for use with non-species selective techniques, like time resolved single molecule diffractive imaging experiments.

[1] Y.-P. Chang, D. A. Horke, S. Trippel, J. Küpper, Int. Rev. Phys. Chem. 34, 557 (2015)