

MO 11: Infrared and Microwave Spectroscopy

Time: Tuesday 11:00–12:30

Location: F 107

MO 11.1 Tue 11:00 F 107

Fast acquisition of high-resolution microwave spectra with broadband FT-MW spectroscopy — ●DENNIS WACHSMUTH, DAVID A. DEWALD, MICHAELA K. JAHN, and JENS-UWE GRABOW — Institut für Physikalische Chemie, Gottfried Wilhelm Leibniz Universität Hannover, Germany

The need for quite precise predictions of molecular geometries and potential energy barriers to internal motions necessary to calculate rotational transition frequencies is a major obstacle in narrowband high-resolution microwave spectroscopy techniques. We present the recently developed in-phase/quadrature-phase modulation passage-acquired-coherence technique (IMPACT) Fourier-Transform spectrometer as a new experimental tool for high-resolution broadband measurements of rotational spectra, here implemented in the 2.0-26.5 GHz frequency range. This method combines the advantages of broadband spectrometers with the resolution of cavity based narrowband instruments and therefore accelerates the precise acquisition of wide spectral ranges. Since the design is based on the upconversion of a chirp in the -500 to +500 MHz base band from an arbitrary waveform generator to the desired signal band at microwave frequencies in one step, no disadvantageous frequency multiplication, filtering or difference frequency generation is necessary. After excitation of the supersonic jet-expansion comprising the molecular ensemble, the molecular response signal is downconverted and detected in the DC-centered base band, again in a single step. The obtained spectrum exhibits a linewidth of <5 kHz (HWHM), the signal frequency determination accuracy is <1 kHz.

MO 11.2 Tue 11:15 F 107

Schnelle Erfassung von großamplitudigen Bewegungen in 2,6-difluorophenol — ●DAVID A. DEWALD¹, MICHAELA K. JAHN¹, DENNIS WACHSMUTH¹, JENS-UWE GRABOW¹ und SURESH C. MEHROTRA² — ¹Gottfried Wilhelm Leibniz Universität Hannover, Deutschland — ²Dr. Babasaheb Ambedkar Marathwada University, Indien

Organische Moleküle mit großamplitudigen internen Bewegungen sind mit ihrer molekularen Dynamik von weitreichendem Interesse. Im Vergleich zu starren Molekülen sind sie jedoch deutlich schwerer durch ab-initio-Methoden zu berechnen. Unser kürzlich fertig gestelltes Breitband-Fourier-Transform-Mikrowellen (FTMW)-Spektrometer (in-phase/quadrature-phase-modulation-passage-acquired-coherence-technique (IMPACT)) eignet sich hervorragend zum Lokalisieren von ungenau vorhergesagten molekularen Signaturen. Wir illustrieren dies an einer Studie zur internen Dynamik des 2,6-difluorophenols (DFP) vor: Mit der IMPACT wurde das Molekularstrahl-FTMW-Spektrum von DFP im Frequenzbereich von 8-26 GHz erfasst. Das Spektrum belegt, dass sich die Gleichgewichtsposition des Hydroxyl H-Atoms, dirigiert durch eine intramolekulare Wasserstoffbrückenwechselwirkung zu einem der beiden F-Atome, innerhalb der Benzolringebene befindet. Das H-Atom tunnelt zwischen den beiden äquivalenten Positionen, was im Spektrum durch eine relativ große Aufspaltung der Rotationsübergänge sichtbar wird. Bei der Ermittlung der spektroskopischen Konstanten und des energetischen Abstands der Tunnelspezies half die Breitband-Methode durch die schnelle Erfassung der spektralen Informationen trotz mäßiger ab-initio Vorausrechnungen.

MO 11.3 Tue 11:30 F 107

High-Resolution Rotational Spectroscopy of polyaromatic molecules and determination of semiexperimental equilibrium structure of 1,3,4 oxadiazole — ●MICHAELA K. JAHN¹, JENS-UWE GRABOW¹, DON McNAUGHTON², JEAN DEMAISON³, and EMILIO J. COCINERO⁴ — ¹Physikalische Chemie, Leibniz-Universität Hannover, Germany — ²Monash University, Australia — ³Université de Lille I, France — ⁴Universidad del País Vasco, Spain

1,3,4-Oxadiazole (C₂H₂N₂O) is a five membered heterocyclic molecule, which appears as building block in a variety of pharmaceutical drugs. A spectroscopic analysis, aiming at the precise structure of the molecular unit, employed Fourier transform microwave spectroscopy of a supersonic jet observing the main and minor isotopologues in natural abundance. The extremely high resolution of the FTMW-instrument yields precise spectroscopic constants, including all elements of the nitrogen nuclear quadrupole coupling hyperfine tensors. Due to the large rotation of the principal axis system upon isotopic substitution, the de-

termination of the equilibrium structure is poisoned by vibrational effects. Reliable structures employing a combination of ab-initio results at different levels in approaches called iteratively reweighted fit, mixed regression and extrapolated structures. Additionally, for some polyaromatic, nitrogen containing systems, we show that quantum chemical predictions, employing DFT calculations with inexpensive basis sets, already compare well with the measured microwave spectra. The results of our rotational analysis provide the transition frequencies as prerequisite for deep radio astronomical searches in space.

MO 11.4 Tue 11:45 F 107

Internal Rotation and Nuclear Quadrupole Splitting in *p*-halo-toluenes (chloro-,bromo-,iodo-) — ●V. ALVIN SHUBERT, DAVID SCHMITZ, THOMAS BETZ, and MELANIE SCHNELL — Center for Free-Electron Laser Science, Hamburg, and Max-Planck-Institut für Kernphysik, Heidelberg, Germany

The presence of internal rotors and quadrupolar nuclei within a molecule give rise to microwave spectra exhibiting complex splitting patterns. These patterns offer insights into the internal dynamics and the influence of different substituents on the chemical and physical properties of large molecules. For example, the effect that the electronegativity of the halogen atoms has on the magnitude of the methyl group internal rotation barrier and the coupling between internal rotation and a quadrupolar nucleus. Such molecules containing both moieties have been previously studied,¹ and in order to further elucidate the combined effect, a series of *p*-halotoluenes (chloro-, bromo-, and iodo) were studied. We report the rotational spectra of these molecules in the frequency range 2-8.5 GHz obtained via the broadband microwave technique. The halogen atoms yield nuclear hyperfine splittings and the hindered methyl rotor with a barrier height, V_6 , gives rise to additional splittings in the spectra. We will discuss the effect of the halogen group on the internal rotation barrier, the coupling between the quadrupolar nuclei and internal rotation, and compare our results to ab initio calculations.

¹M. Schnell, J.-U. Grabow, *Angew. Chem. Int. Ed.* **45**, 3465-3470 (2006).

MO 11.5 Tue 12:00 F 107

First calibration of TAPiR (Tritium Absorption IR-spectroscopy) — ●ROBIN GRÖSSLE and ALEXANDER BECK — Karlsruher Institut für Technologie (KIT), Tritium Labor Karlsruhe

Future fusion facilities like ITER and Demo will have up to 3 kg of tritium and deuterium circulating in their fuel cycle. The estimated throughput will be about 1 kg per hour. One important capability of these tritium fuel cycles is to reprocess unburned fuel and to purify tritium and deuterium. For hydrogen isotopologue (H₂, D₂, T₂, HD, HT and DT = Q₂) processing the Isotope Separation System (ISS) is available, using a cascade of cryogenic distillation columns, which operate at 20 to 30 K, to concentrate the T₂.

IR-spectroscopy has been selected to proof its capability as a reliable, reproducible, fast and non invasive analytic technique for composition analysis of liquid hydrogen mixtures.

In this talk first calibration measurements of the TAPiR experiment where Q₂ can be liquefied and measured using a FTIR-spectrometer will be presented. For this purpose calibrated gas mixtures in combination with methods like LASER Raman spectroscopy (LARA) and quadrupole mass spectrometry (QMS) were used. The disadvantage of these methods is that they are not able to measure directly in the liquid phase. The preliminary results are very promising to bring TAPiR on its way to a Tritium accountancy method for fusion.

MO 11.6 Tue 12:15 F 107

First Measurements with TAPiR (Tritium Absorption IR-Spectroscopy) — ●ALEXANDER BECK and ROBIN GRÖSSLE — Karlsruher Institute of Technology (KIT), Karlsruhe, Germany

For a continual operation of the future fusion facilities like the International Thermonuclear Experimental Reactor (ITER) a constant feeding ratio of tritium and deuterium into the fusion chamber is essential. To ensure a constant feeding ratio, a system for measuring the tritium and deuterium concentration at certain steps in the fuel cycle has to be provided.

One important capability of these fuel cycles is to reprocess un-

burned fuel and to purge tritium and deuterium. For hydrogen isotopologue processing the Isotope Separation System (ISS) is available, applying a cascade of cryogenic distillation columns to enrich the T2.

Before reinjecting the tritium back to fusion process, its purity has to be measured to ensure the constant feeding ratio to the plasma. IR-spectroscopy has been selected to proof its capability as a reliable, reproduceable, fast and non invasive analytic technique for composition analysis of liquid hydrogen mixtures.

The development of an IR-sensor-system started with the TApIR experiment, a sample cell for IR-spectroscopy on the liquefied hydrogen isotopologues protium and deuterium. The first measurements have been taken and several aspects, like background development of the IR-source and the detector system need to be considered to extract the pure spectral information of the hydrogen isotopologues for further analysis.