

Contributed Lectures B

September 4, Tuesday, 11:00 – 12:30

Chirped-pulse broadband rotational spectroscopy of large molecules

V. Alvin Shubert, David Schmitz, Thomas Betz and Melanie Schnell

Center for Free-Electron Laser Science, Hamburg, Germany;
Max-Planck-Institut für Kernphysik, Heidelberg, Germany,
melanie.schnell@asg.mpg.de

Important technological advances have enabled the recent development of the broadband chirped-pulse Fourier transform microwave spectroscopy technique. In the experiment, the microwave frequency is linearly swept (with, to date, a demonstrated bandwidth of 12 GHz) within a short time. This chirp efficiently polarizes the molecular sample at all resonances within its frequency range. The speed of this new technique removes one of the major disadvantages of cavity-based Fourier transform microwave spectroscopy, which has been its slowness. As a consequence, rotational spectroscopy is moving towards investigations concentrating on determining the structure and dynamics of ever larger and more complex molecules, e.g. the study of isomerization reactions. In this contribution, we will present our newly built COMPACT chirped-pulse spectrometer based in Hamburg, its recent applications to large and complex molecules, and our recent findings, such as stepwise multiple excitations in benzonitrile and the interaction between internal rotation and nuclear quadrupole moment in parahalotoluenes.

Towards a MEMS Based External Cavity Tunable Infrared Laser for Spectroscopic Applications

T. M. Fahim Amin¹, Quamrul M. Huda², Yuebin Ning³, Graham McKinnon⁴, John Tulip⁵, Wolfgang Jäger⁶

¹Department of Chemistry and Department of Computer and Electrical Engineering, University of Alberta, Canada, tmfahim@ualberta.ca; ²Department of Chemistry and Department of Computer and Electrical Engineering, University of Alberta, Canada, mqhuda@ualberta.ca; ³Norcada, Inc., Canada, yuebin@norcada.com; ⁴Norcada Inc., Canada, graham@norcada.com; ⁵Boreal Laser, Inc., Canada, jtulip@telus.net; ⁶Department of Chemistry, University of Alberta, Canada, wolfgang.jaeger@ualberta.ca

Laboratory high resolution molecular spectroscopy has benefitted greatly from the tremendous advances in infrared diode laser technology in recent years. However, the high cost and often limited tuning range currently hinder their more widespread use in commercial applications, such as trace gas sensing, industrial process control, and medical diagnostics.

Diode lasers in external cavity configuration overcome the tuning range problem, but are currently assembled from discrete components and are fairly complex as a result. Microelectromechanical systems (MEMS) technology offers the possibility to integrate optical components for the external cavity laser on chip level dimensions and can be used for mass production.

A MEMS comb drive actuator will be used to rotate and translate the optical components of the external cavity to provide a wide laser tuning range. In this presentation, details about the external laser design will be shown and our progress in MEMS actuator design and fabrication will be given.

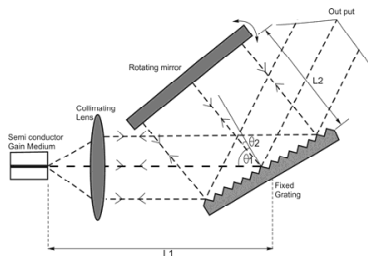


Fig. 1: External cavity laser in Littman-Metcalf configuration.

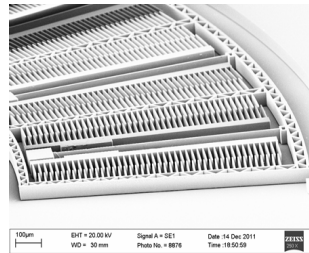


Fig. 2: Detail of a virtual pivot point rotary comb actuator.

Chirped pulse rotational spectroscopy and structures of the hexamer, heptamer and nonamer water clusters

Cristobal Pérez,¹ Matt T. Muckle,¹ Daniel P. Zaleski,¹ Nathan A. Seifert,¹
Berhane Temelso,² George C. Shields², Zbigniew Kisiel,³ Brooks H. Pate¹

¹Department of Chemistry, University of Virginia, McCormick Road, Charlottesville, VA 22903, USA (brookspate@virginia.edu); ²Dean's Office, College of Arts and Sciences and Department of Chemistry, Bucknell University, Lewisburg, PA 17837, USA (George.shields@bucknel.edu); ³Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland (kisiel@ifpan.edu.pl)

Studies of small water clusters provide an entry point to understanding the intricate hydrogen bonding networks in liquid water and have been the object of much experimental and theoretical work. The hexamer cluster level is the first in which the global minimum geometry departs from the simple ring geometry and takes on the form of a three-dimensional, cross-linked structure. Theory predicts three low energy forms: the prism, cage and book conformers. Rotational spectra of all three forms have now been observed simultaneously in supersonic expansion by means of chirped-pulse, Fourier-transform microwave spectroscopy.¹ Variation of carrier gas provided unambiguous experimental evidence that it is the cage form that is the most stable of the three.

The sensitivity of the chirped-pulse experiment allowed observation of all six singly substituted ¹⁸O species obtained by using 15% enriched H₂¹⁸O. The rotational constants of seven isotopic species available for each hexamer facilitated precise determination of oxygen framework geometry for all three of these clusters, in spectacular 0.01-0.02 Å agreement with O...O distances from vibrationally averaged *ab initio* calculations. Rotational spectra of the lowest energy forms of the water heptamer, (H₂O)₇, and the nonamer, (H₂O)₉, clusters have also been observed, and the ¹⁸O substitution study for the heptamer allowed determination of its oxygen framework geometry. These results and their connections with the properties of bulk water will be discussed.

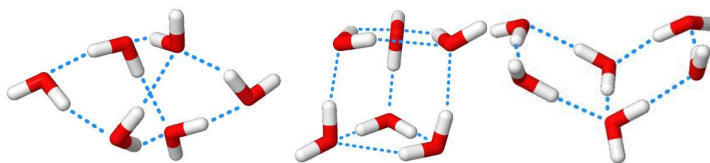


Fig. 1: The observed cage, prism and book geometries of the water hexamer, (H₂O)₆.

References

- [1] C. Perez, M.T. Muckle, D.P. Zaleski, N.A. Seifert, B. Temelso, G.C. Shields, Z.Kisiel, B.H. Pate, *Science* **336**, 897, 2012.

Comb-assisted spectroscopy of molecular ions in the MIR**Oskar Asvany, Jürgen Krieg, Stephan Schlemmer**

I. Physikalisches Institut, Universität zu Köln, Germany, asvany@ph1.uni-koeln.de

A commercial mid-infrared optical parametric oscillator (OPO) with optical output around 2564-3125 cm^{-1} is combined with a frequency comb in the near-infrared for highly accurate frequency measurement. The idler frequency of the OPO is determined with a wavemeter to an accuracy of better than 50 MHz, and then measured very accurately by analyzing the pump and signal beat frequencies with the comb. The beat readout is done via two spectrum analyzers (or counters). The setup allows for a wide and continuous scanning ideal for recording unknown spectra of cold molecules. The potential of this approach is demonstrated by measuring a rovibrational line of CH_5^+ in a cold ion trap. The spectrum analyzers currently limit the error of the frequency determination to about 150 kHz with ample room for future improvements.

Laboratory and Space Infrared Detection of C_{60}^+ .

Dmitry Strelnikov¹, Artur Boettcher¹, Bastian Kern¹ and Manfred Kappes¹

¹Institute of Physical Chemistry, KIT, Karlsruhe, Germany, dmitry.strelnikov@kit.edu;

Mass-selected C_{60}^+ deposition into cryogenic neon and argon matrices followed by infrared and UV-Vis absorption measurements allowed us to detect a new infrared band, originating from C_{60}^+ . Another infrared absorption band attributed previously to C_{60}^+ was re-assigned as C_{60}^+ . We compared the laboratory infrared absorption spectra of C_{60}^+ to the infrared emission spectra, measured by Spitzer telescope of different circumstellar sources, where C_{60} was recently detected. Several astronomical objects were found, where emission features of C_{60}^+ , including the previously unknown infrared band of C_{60}^+ can be unequivocally observed. Laboratory measurements were supported by DFT and TD-DFT calculations.

Depletion spectroscopy of water and water-methane clusters in superfluid helium nanodroplets

Shengfu Yang,¹ Andrew M Ellis,¹ Ben Shepperson,¹ Adrian Boatwright,¹ Feng Cheng¹ and Daniel Spence¹

¹ Department of Chemistry, University of Leicester, UK, sfy1@le.ac.uk

Helium nanodroplets are large helium clusters typically containing 10^3 - 10^6 helium atoms.¹ They are superfluid and have an exceptionally high thermal conductivity; as a result, foreign species, when captured by helium nanodroplets, can be cooled rapidly to the equilibrium temperature of helium nanodroplets, 0.38 K, by evaporative loss of helium atoms.² Most atoms and all molecules enter helium nanodroplets rather than sit on the surface; when more than one dopant is picked up, agglomeration of dopants will occur. Due to the superfluidity and the ultra-low temperature, helium nanodroplets offer an idea cryogenic environment for the formation and the investigation of molecules and molecular clusters.

We have formed water clusters and binary clusters formed by water and methane inside superfluid helium nanodroplets and have investigated the vibrational spectra by depletion spectroscopy technique.³ Infrared spectroscopy have been recorded at different ion channels in the mass spectrum, such as $m/z = +19, +37, +55, etc.$, which allows the correct assignment of each peak (see Figure 1). In addition to depletion signals which correspond to the absorption of photons and the consequent depletion of helium nanodroplets, we have also observed *enhancement* signals in the photon counter which indicate long-lived vibrational states of water and water-methane clusters.

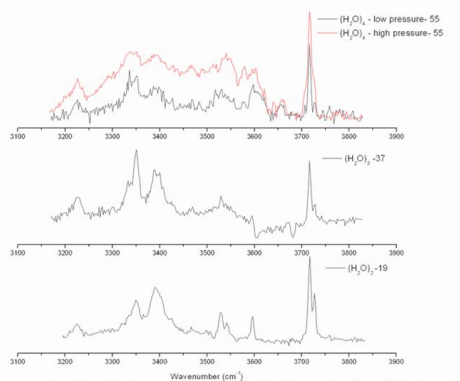


Fig. 1: Spectra of water clusters recorded at different ion channels.

References

- [1] J. P. Toennies and A. F. Vilesov, *Angew. Chemie Int. Ed.* **43**, 2662, 2004.
- [2] W. L. Lewis, B. E. Applegate, J. Sztáray, B. Sztáray, T. Baer, R. J. Bemish and R. E. Miller, *J. Am. Chem. Soc.* **126**, 11283, 2004.
- [3] M. Y. Choi, G. E. Douberly, T. M. Falconer, W. K. Lewis, C. M. Lindsay, J. M. Merritt, P. L. Stiles, and R. E. Miller, *Int. Rev. Chem. Phys.* **25**, 1952, 2006.