Contributed Lectures G

Lecture Hall AII

August 31, Wednesday, 11:00 – 12:30

Accurate CRDS and OF-CEAS measurements of the water vapor self-continuum absorption in four near infrared atmospheric windows.

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Accurate water vapor absorption continuum measurements are performed by Cavity Ring Down Spectroscopy (CRDS) and Optical-Feedback-Cavity Enhanced Laser Spectroscopy (OF-CEAS) at selected spectral points of the transparency windows centered around 4.0, 2.1 and 1.25 µm. The temperature dependence of the absorption continuum at 4.38 µm is measured in the 23-39 °C range. The self-continuum water vapor absorption is derived either from the baseline variation of spectra recorded for a series of pressure values over a small spectral interval or from baseline monitoring at fixed laser frequency, during pressure ramps. In order to avoid possible bias approaching the water saturation pressure, the maximum pressure value was limited to about 16 Torr, corresponding to a 75% humidity rate.

After subtraction of the local water monomer lines contribution, self-continuum cross-sections, C_S, were determined with a few % accuracy from the pressure squared dependence of the spectra base line measured for a series of pressure values up to about 15 Torr.

Together with our previous CRDS and OF-CEAS measurements in the 2.1 and 1.6 µm windows, the derived water vapor self-continuum provides a unique set of water vapor self-continuum cross-sections for a test of the MT_CKD model in four transparency windows. A review of the previous experimental results is presented together with a comparison to the MT_CKD model (See Fig. 1). Our accurate measurements disagree with recent FTS measurements. Although showing some important deviations of the absolute values (up to a factor of 4 at the center of the 2.1 µm window), the overall frequency dependence of the MT_CKD2.5 model is validated.

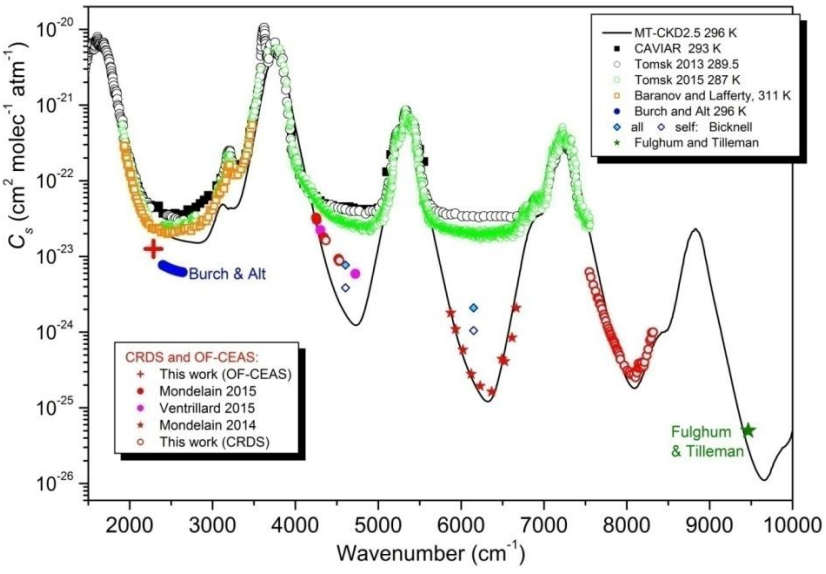

Fig. 1: Comparison of the experiment determinations of self-continuum cross-sections of water vapor near room temperature to the MT_CKD2.5 model.

The microwave spectra of planar aromatic heterocycles- Inertial defects behavior

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The simplest tricyclic aromatic nitrogen heterocyclic molecules 5,6 benzoquinoline and 7,8 benzoquinoline are possible candidates for detection of aromatic systems in the interstellar medium. Therefore the pure rotational spectra have been recorded using frequency-scanned Stark modulated, jet-cooled millimetre wave absorption spectroscopy (48-87 GHz) and Fourier Transform Microwave (FT MW) spectroscopy (2-26 GHz) of a supersonic rotationally cold molecular jet. Guided by ab initio molecular orbital predictions, spectral analysis of mm wave spectra, and higher resolution FT MW spectroscopy provided accurate rotational and centrifugal distortion constants together with ^{14}N nuclear quadrupole coupling constants for both species. The determined inertial defects, along with those of similar PANH and PAH species are used to extend the work of Oka[1] and develop an empirical formula for calculation of inertial defects of aromatic ring systems.

$$\Delta_0 = -\sum_{l=1-n} \frac{33.715}{\nu_l} + 0.0107\sqrt{I_{cc}}$$

The predictive ability of the formula is shown to be excellent for planar species with a number of pronounced out of plane vibrations. Fig 1. Below indicates the goodness of fit of experiment to theory for a subset of the species. The resultant constants are of sufficient accuracy to be used in potential astrophysical searches.

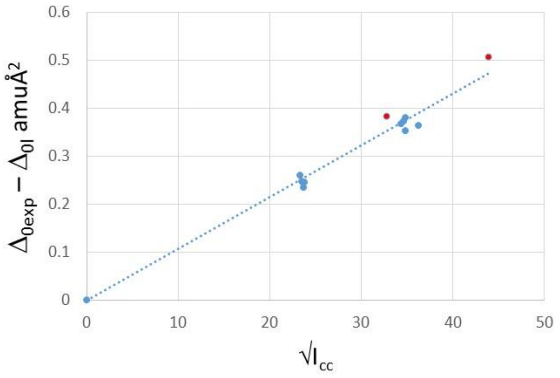

Fig. 1: A plot of $\Delta_{0exp} - \Delta_{0I}$ versus $\sqrt{I_{cc}}$, where Δ_{0I} is the 1st term in Equation 1, Δ_{0exp} is the experimental inertial defect and I_{cc} the moment of inertia around the principal axis c.

References

[1] Oka T. On negative inertial defect. Journal of Molecular Structure 1995,352-353:225–33.

High Resolution Free Jet Millimeter Wave Absorption Spectroscopy: a bridge to Astrochemistry

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Conventional absorption spectroscopy is still the workhorse in high-resolution rotational laboratory spectroscopy.[1] The data obtained from these kind of instruments are relevant for astronomical searches of complex molecules that represent excellent probes of the physical and chemical environments and history of the sources where they are detected.[2] Nowadays, observations performed by the Atacama Large Millimeter Array (ALMA) open up new opportunities to reveal the chemical complexity of solar systems analogues. At the same time the huge amount of data collected and the extremely rich surveys represent a challenge for the astrochemistry community. The chance to detect molecules with an increasing large number of atoms, goes hand in hand with the complexity of their conformational equilibria, often associated with large amplitude motions, that need to be analysed in laboratory before taking on an astronomical search. For this reason a strong interplay between the laboratory spectroscopists and the observational astronomers is increasingly required to be able to unravel the spectra, which are rather difficult to predict theoretically, mainly in the sub-mm wave region.

In this talk laboratory results on diols and thiols of potential astronomical interest, obtained using the only Free Jet Absorption Millimeter Wave (FJAMMW) spectrometer working at the University of Bologna,[3] will be presented. The rotational spectra (59.6 - 74.4 GHz, corresponding to 5.03 - 4.03 mm) reveal the presence of six conformers for 1,2-butanediol ($C_4H_{10}O_2$) and four conformers for 1,3-propanedithiol ($C_3H_8S_2$), proving the complexity of the conformational landscapes of these kind of compounds.

Moreover, taking advantage of the existing public ALMA data, some considerations on the rich molecular line spectrum of the Class 0 protostellar binary IRAS 16293-2422 will be discussed.

References

[1] S. Brünken, S. Schlemmer, arXiv:1605.07456, 2016

[2] E. Herbst, E. F. van Dishoeck, Annu. Rev. Astron. Astrophys. **47**, 427, 2009

[3] C. Calabrese, A. Maris, L. Evangelisti, L. B. Favero, S. Melandri, W. Caminati, J. Phys. Chem. A. **117**, 13712, 2013

Laboratory Rotational Spectroscopy Studies of Interstellar Molecules

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Up to date, over 180 molecules have been unambiguously identified in the interstellar medium (ISM) due to the ongoing astronomical observations complemented with elaborated laboratory studies. Many of these molecules are organic containing abundant interstellar elements H, C, N, and O. Unambiguous identification of specific species requires direct comparison of the particular frequencies observed in the astronomical line surveys with those known from laboratory experiments. The vast amount of data generated by ALMA and other astronomical facilities motivates laboratory spectroscopists to record and analyze rotational spectra of potential interstellar molecules. A general procedure is used in Valladolid combining time domain (MB-FTMW, CP-FTMW) and frequency domain (Stark microwave, mmw, sub-mmw) spectroscopy techniques to obtain precise sets of spectroscopic constants that could be used to search for individual species in the ISM. This is illustrated in the present contribution with several significant examples.

Towards the increase of Lamb-dip accuracy

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We report on the results of precise frequency measurements with the sub-Doppler spectrometer of the IAP RAS, N.Novgorod [1] for a set of interstellar molecules, which are important for radio astronomical studies of the star-forming regions. The investigations include a significant improvement of the frequency accuracy for rotational spectra of OCS [2], an explanation of «hf ratio anomalies» in the rotational spectra of HNCO, measurements of the hf constants in the torsion-rotational spectrum of CH_3OD and shifts of hf frequencies by the pressure and source intensity, which are especially strong in HC_3N. For all of the measured transitions, the relative accuracy of the line centers at mm-submm wavelengths in a Doppler velocity scale is ≤ 1 m/s.

References

[1] G.Yu. Golubiatnikov, S.P. Belov, I.I. Leonov, A.F. Andriyanov, I.I. Zinchenko, A.V. Lapinov, V.N. Markov, A.P. Shkaev, A. Guarnieri. Radiophysics and Quantum Electronics, **56**, 599, 2014.
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