

Contributed Lectures H

Lecture Hall AII

August 31, Wednesday, 14:30 – 16:30

THz rotational spectroscopy of weakly polar CH₃D and non-polar CH₄ molecules using a widely tunable photomixing synthesizer based on a frequency comb

Cédric Bray¹, Arnaud Cuisset¹, Francis Hindle¹, Gael Mouret¹, Robin Bocquet¹, Vincent Boudon²

¹Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France, arnaud.cuisset@univ-littoral.fr, ² Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS-Univ. Bourgogne Franche-Comté, Dijon, France, vincent.boudon@u-bourgogne.fr

The Terahertz (THz) group of the Laboratory of Physical Chemistry of the Atmosphere has developed a THz synthesizer exploiting a photomixing source widely tunable between 0.3 and 3.3 THz with a frequency metrology precise to the ten kHz through the locking of optical laser sources on an ultra-stable frequency comb.¹ The performances of this unique instrument contribute to improve and complete international databases such as HITRAN or JPL by means of rotational spectroscopy studies (positions and line profiles) on stable and unstable species that play a key role in Earth or planetary atmospheres.^{2,3}

Recently, the sensitivity thresholds have been overcome through measurements on deuteromethane CH₃D, a primary target for measurements of the origin of atmospheric gases and methane CH₄, one of the most abundant gases in planetary atmospheres. Direct THz absorption measurements between 1 and 2.5 THz have been performed with an optical path of 20 m allowing line positions and line profiles studies of rotational transitions with intensities lower than 10⁻²⁵ cm⁻¹/(molecules.cm⁻²). In the case of CH₃D, the line positions of K multiplets with 6 < J < 10 have been measured for the first time with relative uncertainties better than 10⁻⁷ allowing to improve the accuracy of ground state molecular parameters⁴ and consequently, the prediction of pure rotational frequency and intensity transitions in the THz domain. In addition, a first determination of self-broadening coefficient from pure rotational transitions of CH₃D have been performed with measurements in a small pressure range from 1 to 4 mbar. Finally, we demonstrated the capability of the THz synthesizer to measure THz pure rotational transitions of non-polar CH₄ molecules where a very weak transition dipole moment is induced by centrifugal distortion effects. Our new measurements in the 2.5 THz region were compared with the distortion dipole rotational spectrum of CH₄ measured by Boudon *et al.* using synchrotron based FT-Far-IR spectroscopy.⁵ With a resolution of the order of tens of kHz, we improved by at least 2 orders of magnitude the accuracy of measured line frequencies providing a better agreement with simulations based on the tensorial formalism developed in the Dijon group for spherical-top molecules.

References

- [1] Hindle, F., et al., Appl. Phys. B, 2011. **104**: p. 763-768.
- [2] Martin-Drumel, M. A., et al., Ap. J. , 2015. **799**: 115.
- [3] Guinet, M., et al., J. Quant. Spectrosc. Radiat. Transfer, 2012. **113**: p. 1113-1126.
- [4] Drouin, B. J., et al., J. Quant. Spectrosc. Radiat. Transfer, 2009. **110**: p. 2077-2081.
- [5] Boudon, V., et al., J. Quant. Spectrosc. Radiat. Transfer, 2010. **111**: p. 1117-1129.

A far-infrared synchrotron-based study of the low-lying vibrational levels of malonaldehyde

E. Scott Goudreau, Dennis W. Tokaryk, Stephen C. Ross

Department of Physics and Centre for Laser, Atomic and Molecular Sciences,
University of New Brunswick, Fredericton, New Brunswick, Canada, dtokaryk@unb.ca

Malonaldehyde ($C_3O_2H_4$) has a ring structure featuring a hydrogen atom whose nucleus tunnels between two equivalent sites near the oxygen atoms. All fundamental vibrational energy levels in the molecule are thus split into two quantum tunnelling components.

We have taken spectra (~ 60 - 1600 cm^{-1}) of malonaldehyde at 0.0010 - 0.0015 cm^{-1} resolution, using the Fourier transform spectrometer on the far-infrared beamline of the Canadian Light Source synchrotron. The data include several bands involving fundamental vibrations of the molecule. This allows for full rotational analyses of the bands, and gives precise values of the tunnelling splitting in each level. Our analysis shows that to simultaneously accommodate existing microwave and millimetre wave data¹ with our infrared measurements, it is necessary to recharacterize the rotational levels of the ground vibrational tunnelling pair.

Further, the components of the two lowest-lying excited vibrational levels have not yet been conclusively assigned. Our infrared data provide some insights that help clarify this situation. We will discuss our suggested assignments and the reasoning that leads to them.

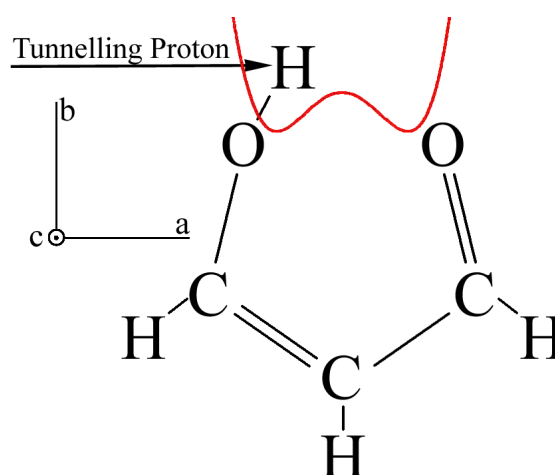


Fig. 1: Schematic of the malonaldehyde molecule and of the potential energy function for the proton-tunnelling motion between the oxygen atoms.

References

- [1] T. Baba, T. Tanaka, I. Morino and K. M. T. Yamada, *Detection of the tunnelling-rotation transitions of malonaldehyde in the submillimeter-wave region*, J. Chem. Phys. **110** (1999) 4131-4133.

Non Bonding Interactions, Internal Dynamic and Pre-Reactivity of the Adducts of Formic Acid with Various Families of Organic Compounds

Walther Caminati¹, Luca Evangelisti¹, Lorenzo Spada¹, Weixing Li¹, Alberto Lesarri², Juan Carlos López², Susana Blanco².

¹Dipartimento di Chimica "G. Ciamician" dell'Università, Via Selmi 2, I-40126 Bologna, Italy, walther.caminati@unibo.it; ²Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, Paseo de Belén, 7, E-47011, Valladolid, Spain, lesarri@qf.uva.es

Mixtures of formic acid with several alcohols, ethers, esters and ketones have been supersonically expanded as pulsed jets. The obtained cool plumes have been analyzed by Fourier transform microwave spectroscopy. It has been possible to assign the rotational spectra of the 1:1 adducts of formic acid with ethers, ketones, esters, but not with every kind of alcohols.

The conformational shapes and geometries of these adducts, the topologies of their intermolecular hydrogen bonds and the effects of the internal dynamics on the rotational spectra will be presented.

An explanation is given of the failure of the assignments of the rotational spectra of the adducts of formic acid with some alcohols.

The far infrared synchrotron rovibrational spectrum of oxetane

Omar Mahassneh¹, Jennifer van Wijngaarden²

¹University of Manitoba, Canada, mahassno@myumanitoba.ca; ²University of Manitoba, Canada, vanwijng@cc.umanitoba.ca

The rotationally-resolved vibrational spectrum of trimethylene oxide or oxetane ($\text{C}_3\text{H}_6\text{O}$) was recorded in the region from 650 through 1200 cm^{-1} using synchrotron radiation coupled to a Bruker IFS125HR FTIR spectrometer (resolution 0.00096 cm^{-1}) at the Canadian Light Source. The observed bands correspond to more than a dozen fundamental vibrations, hot bands and combination bands in this region with many extra features arising due to the facile ring puckering motion (ν_{18} : 52.9 cm^{-1}) which was previously characterized.¹ The ongoing analysis of the strong *b-type* bands corresponding to asymmetric in-plane CO stretching (ν_{23} : 1008 cm^{-1}) (Figure 1) will be presented along with the identification of Coriolis perturbations that arise due to interaction with energy levels related to in-plane CC stretching (ν_{24} : 940 cm^{-1} , ν_6 : 1033 cm^{-1}).²

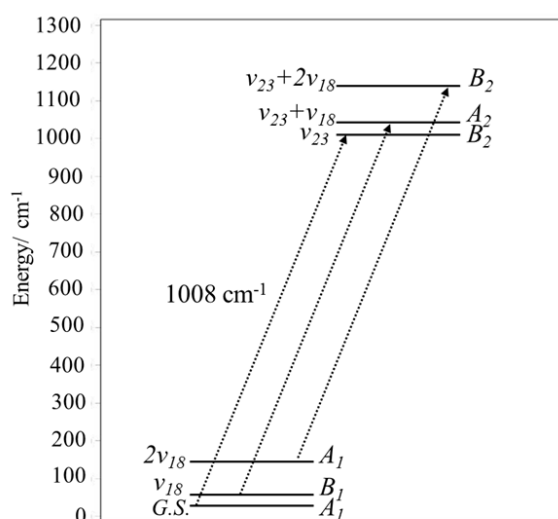


Fig. 1: Energy level diagram for the ν_{23} fundamental of oxetane and associated hotbands involving excited quanta of ring puckering (ν_{18}).

References

- [1] G. Moruzzi *et al.*, J. Mol. Spectrosc. **219**, 152 (2003).
- [2] Bánhegyi *et al.* Spectrochim. Acta. **39A**, 761 (1983).

Gain measurements in optically-pumped ammonia near 1 THz

**Martin Mičica^{1,2}, Roman Motiyenko³, Mathias Vanwolleghem², Kamil Postava¹,
Laurent Margulès³, Jaromír Pištora¹, Jean-François Lampin²**

¹Nanotechnology Centre and IT4Innovations, VSB – TU Ostrava, Czech Republic,
martin.micica@vsb.cz;

²Institut d'Electronique, de Microélectronique et de Nanotechnologie, UMR CNRS
8520, Université de Lille 1, Villeneuve d'Ascq, France;

³Laboratoire de Physique des Lasers, Atomes et Molécules, UMR CNRS 8523,
Université de Lille 1, Villeneuve d'Ascq, France
mathias.vanwolleghem@univ-lille1.fr, jean-francois.lampin@univ-lille1.fr

Ammonia (NH₃) shows big potential as an active medium for optically pumped lasers¹ and amplifiers² working in the terahertz range. In our contribution we present gain measurements of population inverted pure inversion transitions in the $\nu_2=1$ vibrational state of ¹⁴NH₃. In this state the *sa*(3,3) transition has a frequency close to 1.073 THz and the *sa*(4,4) transition has a frequency close to 1.083 THz. The population inversion was obtained by optical pumping thanks to a CW mid-infrared (MIR) quantum cascade laser (QCL) tuned to 967.346 and 966.815 cm⁻¹, for the *asQ*(3,3) and the *asQ*(4,4) transitions respectively. For terahertz probing we employed a high performance multiplication chain consisting of Schottky diodes³ and a 4 K InSb-bolometer as a detector. Measurements were performed under different pressures of gaseous NH₃ and different pumping power. For the *sa*(4,4) transition, the highest gain of about 8 dB/m was obtained at an optimal pressure of about 30 μ bar (see Fig. 1). The linewidth of the QCL was smaller than the Doppler broadening of the NH₃ lines. By slight detuning of the QCL from the center of the MIR transition frequency it was possible to shift the gain peak in the terahertz transition along the broadened line. Some measurements done with a NH₃ laser¹ have also shown a gain of about 20 dB/m for the *sa*(3,3) transition².

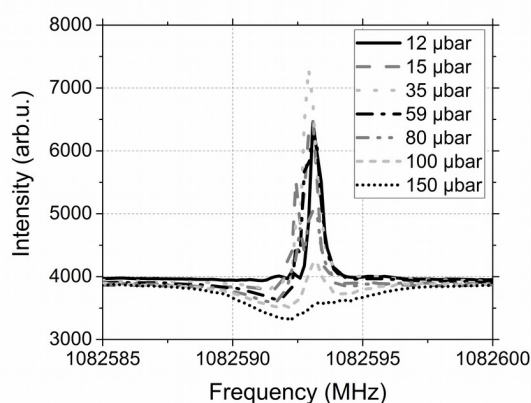


Fig. 1: Gain measurements around 1.083 THz for several NH₃ pressures, in a 40 cm-long cell. The optimal pressure is about 35 μ bars.

References

- [1] A. Pagies, G. Ducournau, J.-F. Lampin, *Applied Physics Letters Photonics* **1**, 031302 (2016).
- [2] M. Mičica, M. Vanwolleghem, A. Pagies, K. Postava, J. Pištora, J.-F. Lampin, submitted to IRMMW-THz 2016.
- [3] O. Zakharenko, R. A. Motiyenko, L. Margulès, T. R. Huet, *J. Mol. Spectrosc.* **317**, 41 (2015).

Rotational spectroscopy of non-covalently bound complexes of medium size organic molecules

Camilla Calabrese, Assimo Maris, Annalisa Vigorito and Sonia Melandri

Università degli Studi di Bologna, Dipartimento di Chimica “G. Ciamician”, via Selmi 2, I-40126 Bologna, Italy, sonia.melandri@unibo.it;

The conformational space of non-covalently bound complexes of medium size organic molecules is shaped by competing interactions occurring within the molecules or with the partners. It usually presents a high number of low energy conformations very close in energy with shallow potential energy barriers through which the molecular system can tunnel.

The conformational preferences of non-covalently bound complexes can be studied to a very high degree of accuracy by free jet rotational spectroscopy¹ and from the detailed structural and dynamical data that can be obtained, the site and geometry of the interaction and information on the binding energy can be inferred without ambiguity.

The questions usually addressed are: which is the preferred binding site, which type of interactions are established, and whether any conformational change takes place in the monomers upon complexation. Answers to these questions allow insight into the molecular interaction process at the molecular level, bridging the gap between gas-phase and bulk properties.

Chosen examples of published and unpublished results of complexes of medium-size organic molecules with different partners formed in a supersonic expansion and characterized by rotational spectroscopy will be discussed. The partner molecules are held together by hydrogen bonds, weak hydrogen bonds and lone-pair- π -hole interactions.

It will be shown how non-bonding interactions compete to shape the conformational space of the complexes, the structural changes brought to the conformers of the monomers by complexation and how these interactions can be drastically changed through atomic or functional group substitution.

References

- [1] M. Becucci and S. Melandri *Chem. Rev.* 2016, **116**, 5014–5037
DOI: [10.1021/acs.chemrev.5b00512](https://doi.org/10.1021/acs.chemrev.5b00512)