

Contributed Lectures M

September 7, Friday, 11:00 – 12:30

Flexible molecules: a challenge for rotational spectroscopy and computational methods: The rotational spectra of 2-fluorobenzylamine, and methylaminoethanol

Sonia Melandri; Camilla Calabrese; Assimo Maris; Luca Evangelisti; Walther Caminati

Department of Chemistry "G. Ciamician", University of Bologna, Via Selmi 2, I-40126 Bologna, Italy. sonia.melandri@unibo.it

The high number of low energy conformations and the presence of large amplitude motions taking place through shallow potential energy surfaces are peculiar of flexible molecules which represent a challenge for rotational spectroscopy. The conformational space of such molecules is generally shaped by non bonding interactions occurring within the molecule or with the surroundings. These interactions can be changed drastically through substitution of even a single atom.

We report the rotational study of 2-fluorobenzylamine (2FBA) and methylaminoethanol (MAE) performed by Molecular Beam Fourier Transform Microwave Spectroscopy (MBFTMW) and Free Jet Absorption Microwave Spectroscopy (FJAMW). For these species it has proved essential to compute the complete potential energy surfaces related to the low amplitude modes. This has been calculated at the B3LYP/6-311++G** level of theory while the stable geometries have been characterized MP2/6-311++G**.

The study of 2FBA is an example of the effects of fluorine substitution which is a common technique to change the physicochemical properties of materials and drugs. The rotational spectra show the presence of two of the four stable conformers predicted with quantum chemical calculations: the global minimum is stabilized by an intramolecular hydrogen bond between the fluorine atom and one hydrogen of the aminic group, another conformer is characterized by a complex tunnelling motion of the aminic hydrogen atom and a third one relaxes because of the low barrier to interconversion. Significant differences with respect to benzylamine have been observed.

The interest in the conformational properties of MAE is twofold: in the first place, aminoethanol and thus also MAE can be considered precursors of aminoacids in the interstellar medium¹ and secondly, the MAE side chain is present in important biological molecules such as adrenaline. The conformational preferences of MAE are dominated by the intramolecular hydrogen bond between the OH and NH₂ groups and its flexibility and asymmetry generate a very high number of conformers. 24 stable conformations have been predicted and two conformers were observed by FJAMW spectroscopy with our 60-72 GHz spectrometer. With respect to a previous study² we have extended the observed frequency range, partly reassigned the rotational spectrum of one of the conformers and determined the nuclear quadrupole constants. The search for higher energy conformers has also been undertaken.

References

- [1] S. Charnley, in Proceedings of the workshop: The bridge between the Big Bang and Biology, CNR, Italy 1999.
- [2] R. E. Penn and L.W. Buxton, *J. Mol. Spectrosc.* **56**, 229, 1975.

Rotational Spectra of Sugars: The Six Most-Stable Conformations of Ribose

Emilio J. Cocinero¹, Alberto Lesarri², Patricia Écija¹, Francisco J. Basterretxea¹,
Jens-Uwe Grabow³, José A. Fernández¹, Fernando Castaño¹

¹Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Ap. 544, 48080 Bilbao (Spain); emiliojose.cocinero@ehu.es

²Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid (Spain); lesarri@qf.uva.es

³Institut für Physikalische Chemie & Elektrochemie, Gottfried-Wilhelm-Leibniz Universität Hannover, 30167 Hannover (Germany)

Sugars have been elusive to spectroscopic studies. Here we report a rotational study of the aldopentose ribose. Aldopentoses are structural polymorphs which exhibit alternative linear or cyclic forms, closing either five-membered (furanose) or six-membered (pyranose) rings. In both rings α or β anomers are possible depending on the orientation of the hydroxy group at the anomeric carbon. β -Furanose is predominant in ribonucleosides and other biochemically relevant derivatives, but is β -furanose the native form also of free ribose? Recent condensed-phase X-ray¹ and older NMR² studies delivered conflicting results. In order to solve this question we conducted a microwave rotational study on D-ribose using ultrafast UV laser vaporization.³ The spectrum revealed six conformations of free ribose, preferentially adopting β -pyranose chairs as well as higher-energy α -pyranose forms. The spectrum also allowed for unambiguous distinction between different orientations of the hydroxy groups, which stabilize the structures by cooperative hydrogen-bond networks. No evidence was observed in the gas-phase of the α/β -furanoses or linear forms found in the biochemical derivatives.

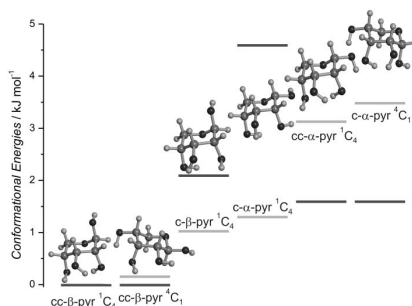


Fig. 1: The most stable conformations of D-ribose.³

[1] D. Šišak, L. B. McCusker, G. Zandomenighi, B. H. Meier, D. Bläser, R. Boese, W. B. Schweizer, R. Glymour, J. D. Dunitz, *Angew. Chem. Int. Ed.* **2010**, *49*, 4503.

[2] a) R. U. Lemieux, J. D. Stevens, *Can. J. Chem.* **1966**, *44*, 249. b) E. Breitmaier, U. Hollstein, *Org. Magn. Reson.* **1976**, *8*, 573.

[3] E. J. Cocinero, A. Lesarri, P. Écija, F. J. Basterretxea, J. U. Grabow, J. A. Fernández, F. Castaño, *Angew. Chem. Int. Ed.* **2012**, *51*, 3119.

Continuous-wave stimulated Raman spectroscopy inside a hollow-core photonic crystal fiber

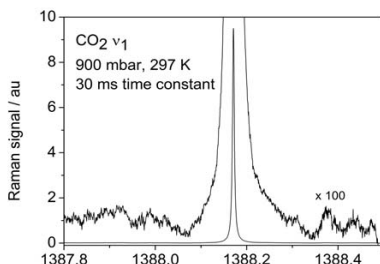
José-Luis Doménech¹, Maite Cueto²

Instituto de Estructura de la Materia (IEM-CSIC), Serrano 123, 28006 Madrid Spain

¹jl.domenech@csic.es; ²alfmaite@gmail.com

Hollow-core photonic crystal fibers¹ (HCPCF) have raised new opportunities to study light-matter interaction. Such fibers guide light due to the band-gap effect produced by an array of smaller channels which surrounds a central hollow core with a few μm diameter. The tight confinement of light inside the core, that can be filled with gases, as well as a long interaction length, make it possible to devise new ways to do low signal level spectroscopy, as is the case of high resolution stimulated Raman spectroscopy (SRS). Owyong et al.² demonstrated high resolution continuous wave SRS in 1978 and, shortly afterwards, he developed the *quasi*-continuous SRS technique, which today remains the best compromise between resolution and sensitivity for gas-phase high resolution Raman spectroscopy. In that set-up, a cw-single mode probe laser experiences a transient gain or loss of power caused by the interaction with a high peak power pulsed laser when their frequency difference matches that of a Raman-allowed transition of a sample. In the quasi-cw technique, the Fourier transform of the time profile of the pump pulses limits the instrumental resolution, typically a few 10^3 cm^{-1} .

In this work, we show the possibility of fully cw stimulated Raman spectroscopy, using a gas cell built around a HCPCF to overcome the limitations posed by the weakness of the stimulated Raman effect when not using pulsed sources. The interaction length (1.2 m), longer than that of a multiple pass refocusing cell, and the narrow diameter of the core (4.8 μm), can compensate for the much lower laser powers used in the cw set-up. On the other hand, the experimental complexity is considerably reduced and the instrumental resolution is pushed down to the MHz level (below 10^{-4} cm^{-1}), limited by the frequency jitter of the stabilized cw lasers. At present, we have demonstrated the feasibility of the experiment and proved a spectral resolution better than 0.005 cm^{-1} in the unresolved Q-branch of the ν_1 component of the Fermi dyad CO_2 at 1388 cm^{-1} .



References

- [1] P. St. Russell, *Science* **299**, 358, 2003
- [2] A. Owyong, C. W. Patterson, R. S. McDowell, *Chem. Phys. Lett.* **59**, 156, 1978

New model for *ab initio* ground electronic state potential energy surface of the ozone molecule and extended vibration predictions

Vladimir Tyuterev¹, Roman Kochanov^{2,1}, Sergei Tashkun², Filip Holka³, Peter Szalay⁴

¹GSMA, Université de Reims, France, vladimir.tyuterev@univ-reims.fr, ²LTS, Zuev Institute of Atmospheric Optics, Tomsk, Russia roman2400@rambler.ru, tashkun@rambler.ru, ³MST Faculty, Slovak University of Technology, Trnava, Slovak Republic, filip.holka@stuba.sk, ⁴Institute of Chemistry, Eotvos University, Budapest, Hungary, szalay@chem.elte.hu,

An accurate determination of the ozone potential energy surfaces (PES) is a prerequisite for theoretical calculations of complex kinetics of formation, dissociation, and recombination of the ozone molecule¹. Previous band centres predictions for recent analyses of high-resolution spectra²⁻⁵ which are expected to bring valuable information on the ozone properties have been carried out with empirically determined PES⁶. In order to extend the validity of the ground electronic state PES at higher energy range we propose a new analytical PES representation in order to describe a very complicated shape of the surface along the transition state to the dissociation. This work is based on new *ab initio* calculations approaching the present computational limits⁷, accounting for the extrapolation to complete basis set (CBS) limit, size-consistency and relativistic corrections. To build the PES along the minimum energy path we extended the electronic structure calculations of ref.7 to much larger grid of nuclear configurations. Graphical software useful for the study of the shape of the PES was developed. Vibration energies up to dissociation and the nodal structures of 3D variationally computed wave functions will be presented as well as comparisons of predictions with available experimental data²⁻⁵. Comparisons with previously available spline PES approximations⁸, the effect of the reef barrier and the normal mode assignment issues will be discussed.

References

- [1] R. Schinke, S. Grebenshchikov, M. Ivanov, et al, Ann. Rev. Phys. Chem. 57, 625 (2006)
- [2] A. Campargue, A. Barbe, M.R. De Backer-Barilly et al, PCCP, 10, 2925 (2008)
- [3] A. Campargue, A. Liu, S. Kassi, et al, J. Mol. Spectrosc., 255, 75 (2009)
- [4] A. Barbe, M.R. De Backer-Barilly, V. Tyuterev, et al, J Mol Spectrosc., 269,175 (2011)
- [5] E. Starikova, A. Barbe, M.-R. De Backer-Barilly et al JQSRT, in press (2012)
- [6] V. Tyuterev, S. Tashkun, D. Schwenke et al, CPL, 316,271-9 (2000)
- [7] F. Holka, P. Szalay, T. Muller, V. Tyuterev, JPC A, 114, 9927-9935 (2010)
- [8] R. Siebert, P.Fleurat-Lessard, R. Schinke, et al. JCP, 116, 9749 (2002)

High-precise spectrometry of the terahertz frequency range: methods and devices

Vladimir L. Vaks¹, Sergey I. Pripolzin¹, Alexander N. Panin¹ and Dmitry G. Paveliev²

¹Institute for Physics of Microstructures RAS, Russia, elena@ipm.sci-nnov.ru;

²Lobachevsky State University of Nizhny Novgorod, Russia, pavelev@rf.unn.ru

We present a high precise THz technique (frequency synthesizers and spectrometers) for various applications such as noninvasive medical diagnostics and security systems. The cornerstone of the presented devices is multipliers and mixers based on quantum superlattice structures.

We have realized the generation of THz radiation with using the subTHz synthesizers based on e.g. backward wave oscillator (BWO) (OV-76, 118-178 GHz) or Gunn generator (97.5-117.0 GHz) with phase-lock loop (PLL) of reference generator and frequency multipliers on nanostructures – quantum semiconductor superlattices (QSS). The QSS are more effective for frequency transformation and detection, due to the lower values of inertness and parasitic capacitances and presence of negative differential conductivity (till 1 THz) on the volt-ampere characteristic. The possibility of the generation of THz radiation harmonics with using the frequency multipliers on QSS was studied. The investigations with using IR Fourier spectrometer (“BOMEM” DA3.002) with helium Si-Composite Bolometer (4,2 K) were carried out. Experimentally we have got the 54th harmonic with frequency of 8.1 THz.

The application of harmonic mixers based on QSS allows essentially simplifying a THz synthesizer’s scheme and improving reliability and stability of the BWO operation in synchronization mode for all generation range (up to 1.25 THz). We have elaborated synthesizers of 667 - 857 GHz, 789 - 968 GHz, 882 - 1100 GHz frequency ranges.

The possibilities of using the quantum cascade lasers (QCL) with frequency sweeping and mixing the frequencies of diode lasers on fast switch for nonstationary gas spectroscopy as radiation sources of THz frequency range are investigated. The effect of heating the QCL which brings to changes of width of forbidden gaps of QCL structure and hence to changes of energy levels in the system and refraction coefficient of excited modes of structure is used for frequency sweeping of QCL radiation.

The analytical method of THz spectroscopy developed in IPM RAS is based on nonstationary effects (free damping polarization, fast sweeping the radiation frequency). The periodic switching the phase (or frequency) of radiation interacting in resonance with the medium leads to rising the processes of transient radiation and absorption, periodic appearing and decaying the macroscopic polarization induced. The subTHz spectrometer based on the phase-switching of the BWO’s radiation on the gas, and also time-domain registration is presented. The spectrometer of 1-2.5 THz frequency range (with registration of a signal in time area) based on solid-state radiation sources is performed. The gas spectrometers developed are intended for ecological monitoring; investigations in the chemistry of high pure substances; control of hi-tech processes as well as for medical diagnostics.

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Infrared spectroscopy of gaseous acetylene mixtures from low to high temperatures.

Miguël Dhyne^{1,2}, Pierre Joubert², Jean-Claude Populaire¹, Laurent Fissiaux¹,
Muriel Lepère¹

¹Laboratoire Lasers et Spectroscopies, PMR, University of Namur (FUNDP), Belgium;

²Institut UTINAM, University of Franche-Comté (Besançon), France,
miguel.dhyne@fundp.ac.be

In the last decades, laser spectroscopic techniques have been greatly improved, in particular their applications to atmospheric monitoring¹⁻³ and combustion diagnostics⁴. To retrieve the C₂H₂ abundance in some of these media, the broadening and shift coefficients of C₂H₂ lines and their temperature dependencies are needed.

This work is devoted to the study of the temperature dependence of the collisional broadening and shift coefficients of infrared absorption lines of self-perturbed acetylene and diluted in nitrogen, hydrogen and xenon.

Measurements are carried out by tunable diode-laser spectroscopy⁵ at very high resolution, for lines in the $\nu_4 + \nu_5$ ro-vibrational band, located around 1330 cm⁻¹. Different experimental conditions of pressure and temperature (extending from 170 K to 500 K) are considered. The determination of the broadening widths and shifts is realized by theoretical line profile (Voigt⁶, Rautian⁷, Galatry⁸) fits on the experimental lineshape.

For the H₂-C₂H₂ mixture, theoretical investigations are done in order to retrieve the temperature dependence of the broadening coefficients. These calculations are obtained using the semiclassical Robert-Bonamy⁹ approach based on an *ab initio* Potential Energy Surface (PES)¹⁰.

References

- [1] J. Rudolph, D.H. Ehhalt and A. Khedim, *J. Atmos. Chem.* **2**, 117, 1984.
- [2] W. Macy Jr., *Icarus* **41**(1), 153, 1980.
- [3] S.J. Kim, T.R. Geballe, K.S. Noll and R. Courtin, *Icarus* **17**, 522, 2005.
- [4] Z.S. Li, M. Linvin, J. Zetterberg, J. Kiefer and M. Aldén, *Proceeding of the Combustion Institute* **31**(1), 817, 2007.
- [5] L. Fissiaux, G. Blanquet, M. Lepère, *J. Quant. Spectrosc. Transfer* **113**, 1233, 2012.
- [6] B.H. Armstrong, *J. Quant. Radiat. Transfer* **7**, 61-88, 1967.
- [7] S.G. Rautian and I.I. Sobel'man, *Sov. Phys. Usp. Engl. Transl.* **9**, 701-16, 1967.
- [8] L. Galatry, *Phys. Rev.* **122**, 1218-230, 1960.
- [9] D. Robert, J. Bonamy, *J. Phys.* **40**, 923, 1979.
- [10] F. Thibault, S.V. Ivanov, O.G. Buzykin, L. Gomez, M. Dhyne, P. Joubert, M. Lepère, *J. Quant. Spectrosc. Radiat. Transfer* **112**, 1429, 2011.