

**HIGH-RESOLUTION OVERTONE SPECTROSCOPY AND DYNAMICS OF
STRONGLY AND WEAKLY BOUND SPECIES**

M. Herman

Laboratoire de Chimie quantique et Photophysique, CP160/09, Université libre de
Bruxelles, av. Roosevelt, 50; B-1050 Belgium

Over the last years, our group at ULB has been concerned with the high-resolution overtone spectroscopic investigation of strongly and weakly bound species, accounting for some dynamical issues, with recent results concerning NH_3 , OCS and a review [1]. A summary of our activity and some of the latest results we have obtained will be presented and detailed. Both experimental and more theoretical aspects will be concerned, focussing on challenging experiments to produce assignable data and on the required concepts to interpret them.

[1] K. Didriche et al, J. Chem. Phys. **138**, 11101 (2013); M. Herman and D.S. Perry, Phys. Chem. Chem. Phys. **15**, 9949 (2013); T. Földes et al, Mol. Phys. **2014**, 10.1080/00268976.2014.904944; D. Golebiowski et al., JQSRT, submitted for publication.

PRECISE MOLECULAR SPECTROSCOPY AND THEORY
OF SPECTRAL LINE SHAPES

Roman Ciuryło

¹Institut Fizyki, Uniwersytet Mikołaja Kopernika, ul. Grudziądzka 5/7, 87-100 Toruń,
Poland

The recent development of the Doppler limited spectroscopy made possible spectral line shape measurements with the ultra-high signal to noise ratio higher than 10^5 [1]. In the same time the use of the optical frequency comb allowed determination of line positions with precision at the kHz level [2]. Now, the precise spectral line shape measurements are not only possible for strong molecular transition but also for very weak transitions thanks to the cavity enhanced techniques [3]. This progress resulted in precise line shape measurements which are useful for fundamental research on the atomic interaction in molecular systems [4] or the spectroscopic determination of Boltzmann constant [5]. The development of laboratory technics is accompanied by the development of satellite instrumentation allowing spectroscopic measurements with the subpercent accuracy for the remote sensing of greenhouse gases in the Earth atmosphere [6]. Therefore, there is a need for new spectroscopic databases having subpercent accuracy, as well.

Analysis of precise spectroscopic data in most cases needs to go beyond the standard Voigt profile. Beside the Doppler and collisional broadening and shifting, the other effects such as: the speed-dependence of collisional broadening and shifting, the Dicke narrowing, the correlation between velocity-changing and phase or state changing collisions, and finally the dispersions line asymmetry should be taken under consideration. This need stimulated development of analytical line shape models [7] as well as *ab initio* approaches to the line shape calculations based on molecular dynamic simulation [8] or numerical solution of transport-relaxation equation [9]. Thanks to multispectrum fitting approach [10] the correlation between fitted parameters can be significantly reduced. This allows to resolve importance of each effect on the measured spectra. Nevertheless, analytical line profiles should be validated with an *ab initio* line shape calculations. An ultimate interpretation of the measured spectra should be done based on the direct comparison with the *ab initio* line shape calculations [11].

- [1] A. Cygan et al., Phys. Rev. A **85**, 022508 (2012)
- [2] G. W. Truong et al., J. Chem. Phys. **138**, 094201 (2013)
- [3] S. Kassi and A. Campargue, J. Chem. Phys. **137**, 234201 (2012)
- [4] E. J. Salumbides et al., Phys. Rev. D **87**, 112008 (2013)
- [5] L. Moretti et al., Phys. Rev. Lett. **111**, 060803 (2013); C. Lemarchand et al., Metrologia **50**, 623 (2013)
- [6] C. E. Miller et al., C. R. Physique **6**, 2387 (2005)
- [7] D. Robert et al., J. Mol. Struct. **517**, 393 (2000); R. Ciuryło et al., J. Quant. Spectrosc. Radiat. Transf. **68**, 257 (2001)
- [8] J.-M. Hartmann et al., Phys. Rev. A **87**, 013403 (2013); Phys. Rev. A **87**, 032510 (2013)
- [9] R. Blackmore, J. Chem. Phys. **87**, 791 (1987); R. Ciuryło et al., Phys. Rev. A **65**, 012502 (2002); P. Wcisło et al., Phys. Rev. A **88**, 012517 (2013)
- [10] D. C. Benner et al., J. Quant. Spectrosc. Radiat. Transfer **53**, 705 (1995); A. S. Pine and R. Ciuryło, J. Molec. Spectrosc. **208**, 180 (2001)
- [11] A. D. May et al., Can. J. Phys. **91**, 879 (2013)

NEW LIFE FOR AN OLD TOPIC: CONFORMATIONAL STUDIES OF BIOMOLECULES BY MICROWAVE SPECTROSCOPY

Alberto Lesarri

Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid (Spain)

This contribution will present an overview of the capabilities of microwave (MW) spectroscopy today. In the last decade the scope of MW spectroscopy has expanded considerably, associated to technical improvements and order-of-magnitude gains in sensitivity and bandwidth [1]. As a result, different kinds of structural problems are now tractable. The discussion will be limited to the conformational and structural investigation of neutral biochemical building-blocks, examining how far we are of treating molecular systems of real chemical interest, i.e., biologically functioning molecules. In particular, results will be presented on 7-membered puckered rings (caprolactone, oxacycloheptene, ...), 6-membered pyranoses found in sugars (ribose [2], fructose [3], ...) and bicyclic decane motifs found in steroids (2-decalone, lupinine [4]). Examples of weakly-bound intermolecular clusters will include dimers and trimers like (sevoflurane)₂, sevoflurane...benzene [5], (phenol)₂ and (phenol)₃ [6]. In all cases the rotational spectra provide valuable information on the intra and intermolecular factors controlling the molecular structure, in particular hydrogen bonding and stereoelectronic effects.

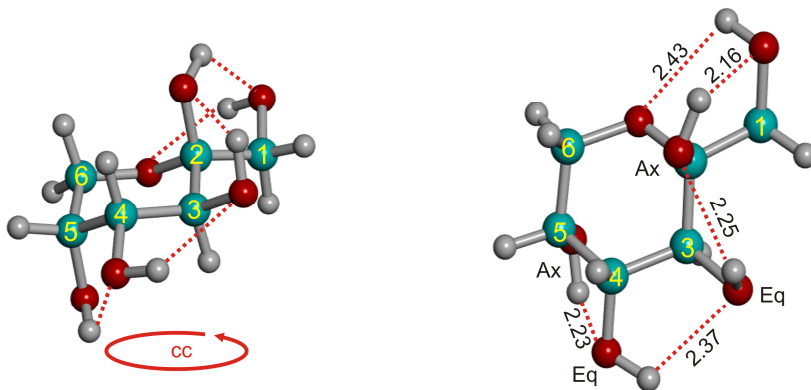


Figure 1. The most stable conformation of fructose [3] obtained by MW spectroscopy.

- [1] a) J. U. Grabow, "Fourier Transform Microwave Spectroscopy: Measurement & Instrumentation" in *Handbook of High Resolution Spectroscopy* (Ed.: M. Quack, F. Merkt), vol. II, pp. 723-800, Wiley: Chichester, 2010. b) S. T. Shipman, B. H. Pate, "New Techniques in Microwave Spectroscopy", *ibid.*, vol. II, pp. 801-828.
- [2] E.J. Cocinero, A. Lesarri, P. Écija, F.J. Basterretxea, J.U. Grabow, J.A. Fernández, F. Castaño, *Angew. Chem. Int. Ed.* **51**, 3119 (2012)
- [3] E.J. Cocinero, A. Lesarri, P. Écija, A. Cimas, B.G. Davis, F.J. Basterretxea, J.A. Fernández, F. Castaño, *J. Am. Chem. Soc.* **135**, 2845 (2013).
- [4] M.K. Jahn, D. Dewald, M. Vallejo-López, E.J. Cocinero, A. Lesarri, J.-U. Grabow, *J. Phys. Chem. A* **117**, 13673 (2013)
- [5] N.A. Seifert, D.P. Zaleski, C. Pérez, J.L. Neill, B.H. Pate, M. Vallejo-López, A. Lesarri, E.J. Cocinero, F. Castaño, I. Kleiner, *Angew. Chem. Int. Ed.* **53**, 3210 (2014)
- [6] N.A. Seifert, A.L. Steber, J.L. Neill, C. Pérez, D.P. Zaleski, B.H. Pate, A. Lesarri, *Phys. Chem. Chem. Phys.* **15**, 11468 (2013)

ARE YOUR SPECTROSCOPIC DATA BEING USED?

Iouli E. Gordon¹, Laurence S. Rothman¹, Jonas S. Wilzewski^{1,2}

¹ Harvard-Smithsonian Center for Astrophysics

Atomic and Molecular Physics Division, Cambridge MA 02138-1516, USA

² Fachrichtung Physik, Fakultät Mathematik und Naturwissenschaften

Technische Universität Dresden, Mommsenstraße 11, 01069 Dresden, Germany

Spectroscopy is an established and indispensable tool in science, industry, agriculture, medicine, surveillance, etc. The potential user of spectral data which is not available in HITRAN [1] or other databases, searches the spectroscopy publications. After finding the desired publication, the user very often encounters the following problems: 1) They cannot find the data described in the paper. There can be many reasons for this: nothing is provided in the paper itself or supplementary material; the authors are not responding to any requests; the web links provided in the paper have long been broken, etc. 2) The data is presented only in a reduced form, for instance, through the fitted spectroscopic constants. While this is a long-standing practice among spectroscopists, there are numerous serious problems with this practice, such as users getting different energy and intensity values because of different representations of the solution to the Hamiltonian, or even just despairing of trying to generate usable line lists from the published constants.

Properly providing the data benefits not only users but also the authors of the spectroscopic research. We will show that this increases citations to the spectroscopy papers and visibility of the research groups. We will also address the quite common issue when researchers obtain the data, but do not feel that they have time, interest, or resources to write an article describing it. There are modern tools that allow one to make these data available to potential users and still get credit for it. However, this is a worst case scenario recommendation, i.e., publishing the data in a peer-reviewed journal is still the preferred way. Similar discussion applies to unpublished computer codes.

The HITRAN database is supported by the NASA Earth Observing System (EOS) under the grant NNX11AF91G, and by the NASA Planetary Atmospheres program under grant NNX13AI59G.

[1] L. S. Rothman, I. E. Gordon, et al. *QSRT* **113**, 4-50 (2013).