

# THE DEVELOPMENT OF BROADBAND FOURIER TRANSFORM MICROWAVE SPECTROSCOPY TO OBSERVE MOTIONAL EFFECTS IN ROTATIONAL SPECTROSCOPY

B. H. PATE, *Department of Chemistry, University of Virginia, USA*

The analysis of pure rotational spectra of polyatomic molecules is a well-established field of high-resolution molecular spectroscopy. For many (if not most) molecules the spectrum can be quantitatively described by a distortable rotor Hamiltonian where the molecular rotational constants are directly related to the molecular geometry. For molecules that can adopt multiple conformations, the molecular rotational spectrum under thermal or molecular beam conditions can be understood as simply a set of distinct rotational spectra for each conformational geometry. This type of analysis requires that the molecular wavefunction is localized around a single nuclear configuration. For polyatomic molecules there is a threshold energy where intramolecular vibrational energy redistribution sets in. In a dynamical picture, the total vibrational energy of the molecule is exchanged between the vibrational normal-mode through the vibrational anharmonicity. For a molecule with multiple conformations, this vibrational energy flow can also lead to conformational rearrangement, or isomerization. Again in a dynamical picture, the molecular geometry undergoes time-dependent, large scale changes. These dynamics lead to motional effects in molecular rotational spectra that can be used to measure energy-resolved unimolecular isomerization rates. Effects of these dynamics on the rotational spectrum of a highly excited molecule will be described and illustrated by recent measurements using broadband Fourier transform microwave spectroscopy.

## APPLICATIONS OF CAVITY-ENHANCED DIRECT FREQUENCY COMB SPECTROSCOPY

ALEKSANDRA FOLTYNOWICZ, *JILA, National Institute of Standards and Technology and University of Colorado Department of Physics, University of Colorado, Boulder, Colorado 80309-0440, USA*; PIOTR MASŁOWSKI, *JILA, National Institute of Standards and Technology and University of Colorado Department of Physics, University of Colorado, Boulder, Colorado 80309-0440, USA and Instytut Fizyki, Uniwersytet Mikołaja Kopernika, ul. Grudziadzka 5/7, 87-100 Torun, Poland*; FLORIAN ADLER, KEVIN C. COSSEL, TRAVIS C. BRILES, AND JUN YE, *JILA, National Institute of Standards and Technology and University of Colorado Department of Physics, University of Colorado, Boulder, Colorado 80309-0440, USA*.

Cavity-enhanced direct frequency comb spectroscopy (CE-DFCS) is a newly developed highly sensitive technique that allows simultaneous detection of many molecular species due to the wide bandwidth and high spectral resolution provided by optical frequency combs.<sup>a</sup> By combining femtosecond laser-based optical frequency combs with enhancement cavities and broadband multichannel detection systems, the technique is capable of recording quantitative spectra with multi-terahertz bandwidth and resolutions ranging from gigahertz to sub-megahertz at absorption sensitivity of  $2.5 \times 10^{-10} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ .<sup>b</sup> We will present the principles of the technique and its most recent applications to human breath analysis and trace gas detection.

---

<sup>a</sup>M. J. Thorpe, K. D. Moll, R. J. Jones, B. Safdi and J. Ye, *Science* **311**, 1595-1599 (2006).

<sup>b</sup>M. J. Thorpe and J. Ye, *Appl. Phys. B* **91**, 397-414 (2008).

**Presentation mode:** lecture

**Time required:** 15 min

**Comment:** Please schedule this talk directly before the talk of Piotr Masłowski, *BROADBAND DIRECT FREQUENCY COMB SPECTROSCOPY OF MOLECULES IN THE MID-IR*

## BROADBAND DIRECT FREQUENCY COMB SPECTROSCOPY OF MOLECULES IN THE MID-IR

PIOTR MASŁOWSKI, *JILA, National Institute of Standards and Technology and University of Colorado, Department of Physics, University of Colorado, Boulder, Colorado, USA, Instytut Fizyki, Uniwersytet Mikołaja Kopernika, ul. Grudziadzka 5, 87-100 Torun, Poland*;  
ALEKSANDRA FOLTYNOWICZ, FLORIAN ADLER, KEVIN C. COSSEL, TRAVIS C. BRILES, AND JUN YE, *JILA, National Institute of Standards and Technology and University of Colorado, Department of Physics, University of Colorado, Boulder, Colorado, USA*.

We report for the first time high-resolution molecular spectra in the 2600 - 3600  $\text{cm}^{-1}$  range acquired with a mid-IR optical frequency comb (OFC) spectrometer. It is based on a femtosecond optical parametric oscillator (OPO), which is continuously tunable between 2200-3700  $\text{cm}^{-1}$  and delivers average output power up to 1 W<sup>a</sup>. This comb source is combined with Herriott cell with optical path of 36.4 m and Fourier transform spectrometer (FTS) to provide resolution of 0.005  $\text{cm}^{-1}$  (160 MHz), single-scan bandwidth of up to 300  $\text{cm}^{-1}$ , and absorption sensitivity of  $3.8 \times 10^{-8} \text{ cm}^{-1} \text{ Hz}^{-1/2}$  per spectral element. Due to the extremely high brightness of the OFC compared to traditional light sources used in classical Fourier transform spectroscopy, the spectrometer allows acquisition times of less than one minute while achieving broad bandwidth and high spectral resolution. Furthermore, the mid-infrared spectral range promises lower minimum detectable concentrations and a more comprehensive list of detectable molecules compared to near-infrared systems, which must rely on vibrational overtones for detection. The demonstrated measurements include many molecular species and their mixtures important for atmospheric research and breath analysis (such as  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_2\text{O}$ ,  $\text{C}_2\text{H}_6$ ,  $\text{H}_2\text{O}$ , isoprene etc.). The achieved concentration detection limits are in the parts-per-billion range. Applications and future development of the system will be discussed.

---

<sup>a</sup>F. Adler, K. C. Cossel, M. J. Thorpe, I. Hartl, M. E. Fermann, and J. Ye, *Opt. Lett.* **34**, 1330-1332 (2009)

**Presentation mode:** lecture

**Time required:** 15 min

**Comment:** Please schedule this talk directly after the talk of Aleksandra Foltynowicz, *APPLICATIONS OF CAVITY-ENHANCED DIRECT FREQUENCY COMB SPECTROSCOPY*

# FREQUENCY-COMB ASSISTED SPECTROSCOPIC INVESTIGATION OF H<sub>2</sub><sup>18</sup>O AND H<sub>2</sub><sup>17</sup>O MOLECULES BETWEEN 1.38 AND 1.42 $\mu\text{m}$

LIVIO GIANFRANI, EUGENIO FASCI, ANTONIO CASTRILLO, GIOVANNI CASA, *Dipartimento di Scienze Ambientali, Seconda Università di Napoli, Via Vivaldi 43, I-81100 Caserta, Italy*; ALESSIO GAMBETTA, MARCO MARANGONI, *Campus Point, Dipartimento di Fisica del Politecnico di Milano, Via Ghislanzoni 24, I-23900 Lecco, Italy*; GIANLUCA GALZERANO, PAOLO LAPORTA, *Istituto di Fotonica e Nanotecnologie - CNR and Dipartimento di Fisica del Politecnico di Milano, Piazza Leonardo Da Vinci 32, I-20133 Milano, Italy*.

We report what we believe to be the first extensive spectroscopic investigation of the H<sub>2</sub><sup>17</sup>O and H<sub>2</sub><sup>18</sup>O spectra in the near infrared, aided by a GPS-displined, self referenced, fiber-based, optical frequency comb synthesizer. Lamb-dip spectroscopy has been performed in the wavelength window between 1.38 and 1.42  $\mu\text{m}$  for a large number of line pairs of the  $\nu_1+\nu_3$  band, each of them sharing the excited level in a lambda scheme. We used an extended cavity diode laser frequency locked to a high-finesse optical cavity, inside which the saturation regime was reached<sup>a</sup>. Line by line, absolute frequency stabilization of the laser source is achieved by locking a preselected cavity mode to the center of the sub-Doppler resonance<sup>b</sup>. Absolute frequency measurements are carried out with a short-term precision of 3 kHz and a long-term repeatability of 15 kHz. Using this relatively complex apparatus, we are able to perform a very stringent test of recently developed methods for inverting experimental transition data and retrieving energy levels of small molecules. In particular, our results allow for a strict comparison with the so-called MARVEL procedure, standing for Measured Active Rotational-Vibrational Energy Levels<sup>c</sup>, which relies upon the use of all available spectroscopic data and validation by first-principles theoretical calculations. An extraordinary agreement was found for the energy separations between rotational levels of the H<sub>2</sub><sup>18</sup>O fundamental vibrational state, with a root-mean-square deviation of about 76 kHz. On the contrary, the line positions furnished by the same procedures seem to be less accurate than those of the HITRAN database.

---

<sup>a</sup>G. Gagliardi, G. Rusciano, and L. Gianfrani, *Appl. Phys. B* **70**, 883 (2000)

<sup>b</sup>G. Galzerano, E. Fasci, A. Castrillo, N. Coluccelli, L. Gianfrani, and P. Laporta, *Opt. Lett.* **34**, 3107 (2009)

<sup>c</sup>T. Furtenbacher, A. Császár, J. Tennyson, *J. Mol. Spectroscopy* **245**, 115 (2007)