

MEASUREMENT AND VALIDATION OF WATER VAPOR LINE STRENGTHS IN THE 1.4-2.7 μm RANGE BY HIGH SENSITIVITY TDLAS

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Line strengths of nine water vapor absorption lines in the wavelength range between 1.37 and 2.71 μm with line strengths of 10^{-23} - 10^{-21} cm/molecule have been measured using direct tunable diode laser absorption spectroscopy (dTDLAS). Four light sources have been used: three DFB diode lasers with wavelengths around 1.37 μm , 2.55 μm and 2.71 μm for measuring one application-specifically selected absorption line with each laser, and a VCSEL radiating around 1.39 μm for the measurement of six further absorption lines. Especially the absorption lines in the 1.37 μm and 1.39 μm region are frequently used for spectroscopic hygrometry. Hence a better knowledge of the line strength and their uncertainties will lead to more reliable water vapor measurements in applications such as combustion-analysis and environmental sciences. The spectrometer contained a single pass gas cell with 0.77 m path length and a photodiode (InAs or InGaAs, depending on the wavelength range). The measurements were done at 10-100 Pa pressures and at room temperature. The gas cell was filled with pure water vapor.

The obtained line strength results were compared to data available in the HITRAN 2012 database [1]. An overall good agreement was observed, however, uncertainties of our line strength results are significantly lower than that in HITRAN 2012. Another important difference is that we aimed to achieve traceability and comprehensive, transparent uncertainty estimation [2]. Accordingly, we analyzed the influence of each input parameter on the line strength results. We have identified that the most important factor determining the final uncertainty is the line area, mainly due to the uncertainty (1-2 %, $k=1$) of the laser tuning coefficient. The concentration of the gas sample also had a similar uncertainty contribution due to the challenges in preparing pure water vapor samples. Standard uncertainties of other parameters including pressure and temperature of the gas sample, the optical path length and the isotopic composition of the sample are below 0.15%. Taking into account all these parameters the standard uncertainty of the line strengths is in the 1.5-3% range ($k=1$ - confidence interval of 66 %).

In order to validate the measured line strength values we carried out absolute concentration measurements on gas mixtures provided by traceable humidity generators [3]. Very good agreement has been found, e.g. differences between the measured and the reference concentrations were smaller than 2% in the 50-20000 ppm concentration range.

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UNDERSTANDING THE INTERNAL TORSION AND BENDING MOTION OF DIMETHYL ETHER VIA ISOTOPIC STUDIES

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Dimethyl ether (DME) is well suited to study the large amplitude internal motion of two methyl groups. The internal torsion exhibits strong coupling effects of both rotors and also with the C-O-C bending mode. Furthermore DME is of astrophysical interest and the main isotopologue as well as the singly ¹³C substituted species have been detected in the interstellar medium [1, 2].

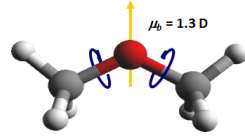


Fig. 1: Structure of DME. Grey for carbon atoms and red for oxygen.

DME is an asymmetric top with Ray's asymmetric parameter $\kappa = -0.9$ and a permanent dipole moment $\mu = 1.3$ D (see Figure 1). The molecule is well-studied by means of high resolution spectroscopy, although there are still some important open questions left, especially in case of the ¹³C substituted species [3, 4]. Calculated band center frequencies of the torsional motion obtained from high level *ab initio* calculations still deviate from experimental values, and comparison to ¹³C substituted species is so far restricted to few measurements of pure rotational transitions [4].

Recently, we recorded first high resolution broadband spectra of pure samples of singly and doubly ¹³C substituted DME in the region of 70 cm⁻¹ to 500 cm⁻¹ with a resolution of 30 MHz using the FT-IR spectrometer at the AILES beam-line of the SOLEIL synchrotron. Here we present our first analysis of the C-O-C bending mode of all three isotopologues and preliminary results for the first torsionally excited states. For the C-O-C bending mode the recorded spectra are well described by a standard Watsonian set of molecular parameters (see Figure 2). We expect the new measurements to foster quantum chemical modelling of large amplitude motion, and to enable assignments for astrophysical observations at the confusion limit.

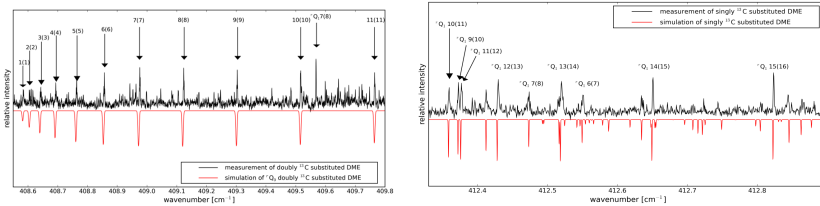


Fig. 2: Experimental and simulated spectra of the C-O-C-bending mode for a) singly and b) doubly ¹³C substituted DME

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**SELF-, N₂-, O₂- AND AIR- BROADENING COEFFICIENTS OF HFC-32
RO-VIBRATIONAL- AND ROTATIONAL- TRANSITIONS FOR ATMOSPHERIC
APPLICATIONS**

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Difluoromethane (CH₂F₂, HFC-32) has been proposed as a valid replacement for both CFCs and HCFCs (in particular HCFC-22), and its mixture with CF₃CH₃, CF₃CH₂F, and CF₃CHF₂ is widely used as refrigerant. Because of the commercial applications, the atmospheric concentration of CH₂F₂ has increased rapidly since 1990s and its abundance was 3 pptv in 2005. As such, CH₂F₂ appears to be a relevant atmospheric pollutant, and thus it needs to be considered in radiative transfer calculations and atmospheric models.

Despite the undisputable atmospheric relevance of HFC-32, also highlighted by the number of investigations dealing with this compound, to our knowledge the determination of its line-by-line spectroscopic parameters have never been attempted.

This contribution reports on the determination of the CH₂F₂ line-by-line parameters, with particular emphasis on pressure broadening coefficients, for both ground state- and ν_7 band-transitions, by means of MW and IR absorption spectroscopy, respectively. In particular, measurements for a number of ν_7 band transitions, lying in the 8.2 μm region, have been carried out at the Laboratory of Molecular Spectroscopy of Venice (LMS-Ve), while those in the ground vibrational state have been performed at the Laboratory of Millimeter/Submillimeter-wave Spectroscopy of Bologna (LMS-Bo). The experiments have been carried out at room temperature on self-broadened CH₂F₂ and also perturbing the radiating species by means of N₂ and O₂ molecules, thus obtaining self-, N₂-, O₂- and air-broadening coefficients; in addition, for ro-vibrational transitions, integrated absorption coefficients have also been determined. Broadening parameters obtained for ground state transitions have resulted greater than the corresponding ones for ν_7 band transitions and both series of experiments have shown no clear trend concerning the quantum number dependence of the collisional decay rates.

**RECENT LINE-SHAPE AND DOPPLER THERMOMETRY STUDIES INVOLVING
TRANSITIONS IN THE $\nu_1+\nu_3$ BAND OF ACETYLENE**

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The line positions for transitions in the $\nu_1+\nu_3$ band are often used as a frequency standard by the telecom industry and also needed for planetary atmospheric studies. Four relevant studies have been recently carried out in our group and will be discussed briefly below.

(1) N₂-broadened line widths and N₂-pressure induced line shifts have been measured for transitions in the $\nu_1+\nu_3$ band of acetylene at seven temperatures in the range 213–333K to obtain the temperature dependences of broadening and shift coefficients. The Voigt and hard-collision line profile models were used to retrieve the line parameters. This study has been published in *Molecular Physics*, 110 Issue 21/22 (2012) 2645-2663.

(2) Six nitrogen perturbed transitions of acetylene within the $\nu_1+\nu_3$ absorption band have been recorded using a 3-channel diode laser spectrometer. We have examined C₂H₂ spectra using a hard collision (Rautian) profile over a range of five temperatures (213 K–333 K). From these fits we have obtained the N₂- broadening and narrowing coefficients of C₂H₂ and examined their temperature dependence. The experimentally measured narrowing coefficients have been used to estimate the nitrogen diffusion coefficients. The broadening coefficients and corresponding temperature dependence exponents have also been compared to that of calculations completed using a classical impact approach on an ab initio potential energy surface. We have observed a good agreement between our theoretical and experimental results. This study was published in *Canadian Journal of Physics* 91(11) 896-905 (2013).

(3) An extension of the previous study was to analyze the room temperature for the same six transitions using the Voigt, Rautian, Galatry, Rautian–Galatry and Correlated Rautian profiles. For the entire pressure range, we have tested the applicability of these line-shape models. Except for Voigt profile, Dicke narrowing effect has been considered in all mentioned line-shape models. The experimental results for the narrowing parameters have been compared with calculated values based on the theory of diffusion. This study is published in the *Journal of Quantitative Spectroscopy and Radiative Transfer* 140 (2014) 58–66.

(4) In this paper we present accurate measurements of the fundamental Boltzmann constant based on a line-shape analysis of acetylene spectra in the $\nu_1+\nu_3$ band recorded using a tunable diode laser. Experimental spectra recorded at low pressures have been analyzed using both the Voigt model and the Speed Dependent Voigt model that takes into account the molecular speed dependence effects. These line-shape models reproduces the experimental data with high accuracy and allow us to determine precise line-shape parameters for the transitions used, the Doppler-width and then determined the Boltzmann constant, k_B . This study is in press in the *Journal of Chemical Physics*.

FOUR-WAVE MIXING SPECTROSCOPY OF THE $\text{NO}_3 \tilde{B}^2E' - \tilde{X}^2A_2'$ SYSTEM

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The nitrate free radical, NO_3 , is one of the simplest nitrogen oxides and important intermediates in atmospheric chemistry, but rigorous assignment of the vibrational structure of the \tilde{X}^2A_2' state remains elusive. In this work, useful information was obtained on the vibrational assignment on NO_3 free radical generated in a supersonic free expansion. The $\tilde{B}^2E' - \tilde{X}^2A_2'$ transition was investigated by four-wave mixing (4WM) spectroscopy. Nitrate free radical was generated by pyrolysis of N_2O_5 via ceramic tubing (inside diameter ϕ 1 mm and about 30 mm length) surrounded out-side by a heater mounted just after the nozzle orifice of a commercial pulsed valve (Series 9, General Valve). The laser induced fluorescence (LIF) spectrum was measured with the 4WM spectra simultaneously. To obtain information on the vibrational structure of the \tilde{X}^2A_2' state of NO_3 , two-color 4WM spectroscopy is required, but the current measurement is restricted to degenerate (one-color) 4WM (D4WM) spectroscopy. The broad 0_0^0 band of the $\tilde{B}^2E' - \tilde{X}^2A_2'$ transition does not consist of one sub-band, but of several bands. The intensity distribution of the sub-bands of the D4WM spectrum is similar, but not identical to that of the LIF spectrum.

A STUDY OF THE MOLECULAR STRUCTURE AND SPECTROSCOPIC PROPERTIES OF 2-FORMYLPHENYLBORONIC ACID PINACOL ESTER BY EXPERIMENTAL METHODS AND QUANTUM CHEMICAL CALCULATIONS

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The molecular structure and vibrations of 2-formylphenylboronic acid pinacol ester (2fpbape) were investigated by infrared spectroscopic techniques. The theoretical calculations for the molecular structure and spectroscopic studies were performed with DFT (B3LYP) and 6-311++G(d,p) basis set calculations using the Gaussian 09 program [1]. FT-IR spectra were recorded in the solid phase, the ^1H and ^{13}C NMR spectra were recorded in DMSO solution. After optimizing the geometry of the molecule, vibrational wavenumbers and fundamental vibrations modes were carried out on the basis of the total energy distribution (TED) of the vibrational modes calculated with SQM program [2]. The proton and carbon chemical shifts were determined by GIAO method for the gas and solvated phases (DMSO and water). The results of theoretical calculations for the spectra of the title compound were compared with the observed spectra.

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**MEASUREMENTS OF CO₂ LINE PARAMETERS IN THE 9250-9500 CM⁻¹ AND
10700-10800 CM⁻¹ REGIONS**

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The absorption spectra of natural carbon dioxide have been recorded in two wavenumber ranges 9250-9500 and 10700-10800 cm⁻¹ of the near infrared region using spectrophotometric complex based on an IFS 125 HR Fourier transform spectrometer and a 30 meters multipass cell with the White optical system [1]. The spectra were recorded at room temperature, spectral resolution of 0.03 cm⁻¹, path length of 727 m and at pressure range from 298 to 674 mbar. In total 444 line positions and intensities of 11 bands of 3 isotopologues ¹⁶O¹²C¹⁶O, ¹⁶O¹³C¹⁶O and ¹⁶O¹²C¹⁸O have been retrieved in the 9250-9500 cm⁻¹ range. The 20032-00001 band of ¹⁶O¹²C¹⁸O and four hot bands 30032-10001, 30033-10002, 30034-10002 and 22232-02201 of the principal isotopologue were observed for the first time. In addition in the 10700-10800 cm⁻¹ region we have registered 36 lines of three bands 30032-00001, 30033-00002 and 31132-01101 of the principal isotopologue. The line intensities of these bands have been measured for the first time. Using these line intensities two effective dipole moment parameters for the $\Delta P = 15$ series of transitions have been fitted. Here $P = 2V_1 + V_2 + 3V_3$ is the polyad number (V_i are vibrational quantum numbers). The comparison of the measured line intensities to those from the AMES line list [2] has been done.

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**FOURIER TRANSFORM OPTICAL FREQUENCY COMB SPECTROSCOPY IN
THE MID-INFRARED BASED ON DOUBLY RESONANT OPO**

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We report a sensitive and robust Fourier transform spectrometer operating in the 3.0-5.6 μm range based on a synchronously pumped femtosecond optical parametric oscillator (OPO). The pump source is a 2 μm Tm: fiber laser delivering 3 W of power in 100 fs pulses with ~ 417 MHz repetition rate. The doubly resonant OPO (similar to the one described in Refs. [1, 2]) based on an OP-GaAs crystal, operating non-degenerately, delivers over 20 mW of combined power in signal and idler laser beams. Operating at different OPO-cavity lengths allows for tuning the signal and idler beams over the whole operating range, with simultaneous bandwidth in each of the frequency windows of 0.5 μm or more.

The spectrometer is equipped with a 100 m multipass cell and the fast scanning delay line with the optical path delay limited to 64 cm, corresponding to a resolution of 468 MHz, which is suitable for measurements of pressure broadened lines under atmospheric conditions. Due to the use of the multipass cell with broadband mirrors, the whole bandwidth of the OPO can be used for measurement. The obtained detection limit for absorption equals $1.7 \times 10^{-7} \text{ cm}^{-1}$ in 100 seconds acquisition time, in 30000 detection channels simultaneously, which corresponds to $1 \times 10^{-8} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ per spectral channel. The operating frequency range allows access to strong molecular transitions in the so-called fingerprint region, important for numerous applications based on trace gas detection in gas phase [3]. To test the experimental setup, the measurements of molecular species such as methane, carbon monoxide, isoprene and ethane were performed, reaching detection limits in terms of concentration in the tens of ppb range or lower. Moreover, thanks to the dual band operation of the non-degenerate OPO, simultaneous access to two spectral windows allows for the measurements of different spectral bands of the molecule of interest, with line intensities that can differ by orders of magnitude. This effectively increases the dynamic range in concentration, removing the need for sample dilution for strongly absorbing samples.

The presented system delivers high resolution, fast acquisition and access to a wide variety of molecules in a simple and robust experimental setup. It has the potential to reach even higher sensitivity when combined with an enhancement cavity [4, 5], although at the cost of complexity.

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NH₃ SPECTRA IN THE 2.3 MICRONS REGION

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In this work we deal with the observation of the ammonia molecule isotopologues (¹⁴NH₃ and ¹⁵NH₃) in the 2.3 microns region. Compared to our recently published data [1] a study of the spectra temperature dependence and enlargement of the covered spectral range is presented. The spectra were recorded in the 7m path long, cryogenically cooled Herriott cell in temperatures ranging from 160 to 296K. As a tunable laser source the Vertical External Cavity Surface Emitting Laser (VECSEL) have been used, offering a broad tunability with a narrow line width (below 1MHz) and a single TEM₀₀ mode emission in the spectral range from 4270 to 4350 cm⁻¹. To treat the spectra, an approach based on the relative line intensities temperature dependencies was used in order to increase the precision of lower state energies estimations. This process was practically the same as the one we applied recently in the 1.5 micron region [2]. The retrieved values of transitions lower states together with the line centres and intensities were used to identify transitions quantum states. Afterwards these results were compared to the previously published line list based on experimental data – the HITRAN database as well as to the theoretical predictions by Yurchenko et al. [4] and Huang et al. [5].

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