

The water vapor absorption continuum in the atmospheric windows at 4.0, 2.1, 1.6 and 1.25 μm

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While being implemented in most atmospheric radiative transfer codes, the amplitude, the temperature dependence and the physical origin of the water vapor absorption continuum constitute a long standing issue in molecular spectroscopy with direct impact in atmospheric and planetary sciences.

In this presentation we will review our recent measurements of the self- and foreign-water vapor continua at different spectral points of the atmospheric windows at 4.0, 2.1, 1.6 and 1.25 μm , by Cavity Ring Down Spectroscopy (CRDS) and Optical-Feedback-Cavity Enhanced Laser Spectroscopy (OF-CEAS) [1, 2]. The absorption continuum was derived either from the baseline variation of spectra recorded for a series of pressure values over a small spectral interval or from baseline monitoring at fixed laser frequency, during pressure ramps. After subtraction of the local water monomer lines contribution, self-continuum cross-sections, C_s , were determined with a few percent accuracy from the pressure squared dependence of the spectra base line level. The temperature dependence of the continuum of importance for atmospheric application was also obtained for some spectral points.

The measured cross sections constitute a unique set of accurate experimental constraints which have been used to adjust the last version (V3.2) of the semi-empirical MT_CKD water vapor continuum (Mlawer-Tobin-Clough-Kneizys-Davies) [3], widely incorporated in atmospheric radiative transfer codes (see Fig. 1).

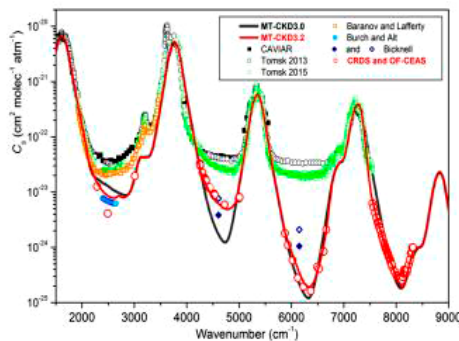


Figure 1. Comparison of the MT_CKD3.0 and 3.2 models (black and red solid lines, respectively) of the water vapor self-continuum cross-sections, C_s , in the 1500-9000 cm^{-1} range to an exhaustive collection of the experimental determinations available in the literature and obtained in this work (red circles).

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Sub-MHz deuterium spectroscopy and comparison with *ab initio* calculations of the line-shape effects

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In view of its simplicity, molecular hydrogen is the most appropriate chemically neutral system for testing quantum electrodynamics (QED) for molecules as well as for studies on new physics beyond the Standard Model [1] such as new forces. Theoretical predictions for energies of rovibrational transitions of hydrogen isotopologues are reaching $4 \cdot 10^{-5}$ cm⁻¹ accuracy [2–4]. In the Doppler limit line position of H₂, HD or D₂ becomes affected by the line-shape effects including its asymmetry [5]. Our experimental approach takes advantage of cavity-enhanced spectroscopy, and thereby we achieved sub-MHz level of accuracy on the weak quadrupole line position [4], typical for Doppler-free techniques.

To achieve kilohertz level of accuracy we applied *ab initio* quantum scattering calculations to describe the collisional line-shape effects. We performed measurements in several pressures to obtain determination of the line position free from systematic errors caused by incorrect line-shape characterisation. Similar *ab initio* line-shape model was tested in separate measurements with He perturber. Moreover, we extended our experiments to a wide range of temperatures and validated temperature dependences of line-shape effects. Line S(2) 2–0 of D₂ has been measured by the frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) method assisted by an optical frequency comb (OFC) [6,7], using experimental setup described in Refs. [8,9].

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The high-resolution spectrum of DC₃N recorded in the infrared and millimeter-wave regions: a global analysis

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The observation of deuterated species in astronomical environments allows the determination of the H/D isotopic ratio, from which physical and chemical properties of astronomical objects can be deduced. DC₃N has been detected in several sources, most recently in the solar-type protostar IRAS 16293-2422 [1]. The laboratory work carried out so far is however still partial, since it concerns mainly pure rotational transitions [2,3] and, to a less extent, low-resolution infrared spectra [4]. The present work aims at providing a broad set of laboratory data in the infrared, millimeter- and submillimeter-wave regions. The infrared spectrum of DC₃N has been recorded at high-resolution (0.004 and 0.008 cm⁻¹) between 450 and 1600 cm⁻¹, where the fundamental bands ν_4 , ν_5 , ν_6 and their hot and combination bands are located. Moreover, the rotational transitions in the ground vibrational state and in the excited states $\nu_4=1, 2$, $\nu_5=1, 2$, $\nu_6=1, 2$, $\nu_7=1, 2, 3, 4$, $\nu_4=\nu_7=1$, $\nu_5=\nu_7=1$, $\nu_6=\nu_7=1$ have been recorded between 240 and 300 GHz, with the goal to extend the measurements to 1 THz. A global analysis which, besides the usual ro-vibrational Hamiltonian terms, accounts also for the predicted anharmonic resonances, is in progress. Eventually, a list of rest frequencies will be produced, in order to assist astronomical searches.

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Sub-doppler metrology of HD

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Molecular hydrogen is the quantum molecular system to benchmark to challenge the fundamental physics, i.e., the Quantum Electrodynamics (QED), and the molecular Hamiltonians. Actually, soon or later, the accurate determination of the vibrational sequences of the molecular hydrogen isotopologues will open new perspectives for challenging the proton-to-electron mass ratio, and the proton radius size in a spectroscopy laboratory.

We will report on the first sub-Doppler determination of weak dipole transitions (forbidden in the Born-Oppenheimer approximation) in the $v : 2 \leftarrow 0$ overtone band of HD at $\lambda \sim 1.38 \mu\text{m}$. To saturate rovibrational transitions, we have implemented the Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS) technique locked against a Cs-clock referenced Optical Frequency Comb (OFC).

The experimental sensitivity ($\sim 10^{-12}/\text{cm}^{-1}/\text{Hz}^{1/2}$) allowed us to determine the frequency center of 3 transitions (R_1 , R_2 and R_3) with an accuracy of the order of 20 kHz, i.e., with a gain of 3 orders of magnitude compared with the previous determinations. Under low pressure conditions, the broadening and frequency shift coefficients have been determined.

However, the shape of the observed NICE-OHMS resonances suffer from unexpected abnormal asymmetry which may be attributed to the hyperfine structure of the rotational levels. Nevertheless, the shape of the NICE-OHMS dispersion resonances, as well as their lack of amplitude suggests possible interfering crossover resonances. Furthermore, our frequency determination[1] of the transition does not match the value recently proposed by S.-M. Hu's group obtained by saturated CRDS (Lamb-dip)[2], as well as it barely matches the value proposed the Naples group (Doppler-broadened CRDS). These different transition frequency determinations, and the unexplained resonance shape can open the door to possible controversy that we will try to surround.

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IR laser spectroscopy of the deuterated isotopologues of ammonia

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Laser spectroscopy is performed in the near infrared to study the deuterated isotopologues of ammonia. Previous studies predicted a band in the range 6500–6800 cm^{-1} [1]. First experiments show the evidence of transformation of the gas ND_3 introduced in the cell which yields to the formation of ND_2H and NH_2D . At a first glance, no ND_3 transitions are present in this range of energy. First analysis will be presented with the isolation of the spectrum of each species.

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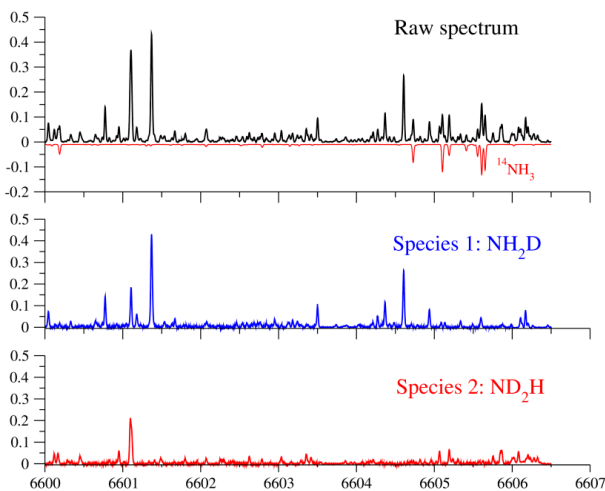


Fig. 1: Spectrum around 1514 nm. Impurity of $^{14}\text{NH}_3$ is present, the two spectra of NH_2D , ND_2H species have been isolated.

Photoacoustic spectroscopy of the oxygen a-band in support of OCO-2

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C2.6.

A number of remote sensing satellite missions using spectroscopic methods to interrogate atmospheric composition require accurate spectroscopic models for valid retrievals. The oxygen A-band (762 nm) is utilized for determination of air mass, solar pathlength, and surface pressure in remote sensing applications due to the uniform concentration of molecular oxygen throughout the atmosphere and the spectral isolation of the band. NASA's OCO-2 satellite uses the A-band as a reference to determine the global atmospheric carbon dioxide concentrations with an accuracy of 0.25%, placing stringent demands on our knowledge of the A-band spectral parameters. Current limitations in the A-band spectroscopic models, primarily from the treatment of line mixing (LM) and collision induced absorption (CIA), remain a significant source of error in carbon dioxide column retrievals. LM is manifested as intensity exchange due to collisional population transfer between closely spaced energy levels while CIA appears as a broad, weak continuum absorption feature arising from transient dipoles induced by molecular collisions. Photoacoustic spectroscopy, a zero-background technique with a large dynamic range, is an ideal method to observe these effects which become increasingly prominent at elevated pressures. We have developed a high precision (SNR>10,000), broadband photoacoustic spectrometer for recording full A-band spectra at room temperature. Unsaturated line-shapes are captured over a wide pressure range (300–3000 torr) to observe intensity exchange due to LM while maintaining high sensitivity to weak baseline features of CIA without interferences from instrumental background effects. Results from multispectrum fits of this data with non-Voigt line shapes showing insufficiencies in current A-band models will be presented.