

# Wavelength-meter controlled cavity ring-down spectroscopy for measurement of trace water vapor at ppt levels

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We developed a relatively simple technique to efficiently couple a laser frequency to a resonance frequency of a high-finesse cavity used in cavity ring-down spectroscopy (CRDS). The resonance frequency of the high-finesse cavity is stabilized with reference to the frequency of a helium-neon (He-Ne) laser. In this condition, the probe laser can easily be coupled to the cavity by controlling its frequency using a high-resolution wavelength meter, even using an inexpensive probe laser having a relatively broad spectral line width, such as a distributed-feedback (DFB) diode laser.

The method used to stabilize the resonance frequency of the cavity is essentially the same as that has been referred to as "frequency-stabilized (FS) CRDS [1]," but the technique to couple the laser with the cavity proposed in this study ("wavelength-meter controlled" technique) is relatively simple compared with those used in other studies on FS-CRDS.

The purpose of this study was to develop a CRDS-based trace-moisture analyzer capable of measuring trace water vapor (trace moisture) in N<sub>2</sub> even at ppt levels using the wavelength-meter controlled technique [2].

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# CRDS of the collision induced absorption (CIA) band of O<sub>2</sub> at 1.27 μm

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In our atmosphere, the  $a^1\Delta_g - X^3\Sigma^-g$  ( $v=0-0$ ) absorption band of oxygen near 1.27 μm is formed by the superposition of local absorption lines with a broad absorption feature due to short-lived collisional O<sub>2</sub>-O<sub>2</sub> and O<sub>2</sub>-N<sub>2</sub> complexes, namely the collision induced absorption (CIA). The local lines corresponding to magnetic dipole transitions (and very weak electric quadrupole transitions) are of importance for air mass determination in several programs like the ground-based Total Carbon Column Observing Network (TCCON) and the CNES satellite MicroCarb.

In the present work, the CIA coefficients of the oxygen band at 1.27 μm are measured by cavity ring down spectroscopy (CRDS) at room temperature. Twelve distributed feed-back laser diodes were used below 7920 cm<sup>-1</sup> together with an external cavity diode laser above this wavenumber. The  $B_{O_2-O_2}$ ,  $B_{O_2-N_2}$  and  $B_{O_2-Air}$  binary absorption coefficients are determined with a reduced uncertainty from series of low density spectra (from 0.36 to 0.85 amagat) of pure oxygen and N<sub>2</sub>+O<sub>2</sub> mixture with O<sub>2</sub>= 20.95%. The CIA was obtained by difference between the absorbing samples spectra and argon spectra recorded *for the same densities* after removal of the local contribution of the absorption lines. The achieved accuracy of the retrieved CIA relies on the high base line stability of the spectra (at the 2×10<sup>-10</sup> cm<sup>-1</sup> level). In addition, the adopted sub-atmospheric pressure values have the advantage to minimize the uncertainty related to the subtraction of the local lines. Although more accurate, our CIA coefficients show a good agreement with previous high pressure FTS values by Maté et al. [1] recommended by the HITRAN2016 database. For instance, deviations limited to a few % are noted for the  $B_{O_2-Air}$  coefficient.

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# Cavity-enhanced dispersion spectroscopy for the highest accuracy applications

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We demonstrate comparison between absorption and dispersion spectroscopy in the optical cavity to estimate applicability of both approaches to the highest-accuracy applications. In many cases of reference spectra, e.g. for atmospheric applications, high dynamic range of absorption is crucial. Such conditions often lead to not negligible systematic errors of retrieved line parameters, exceeding the noise level and in consequence sub-percent uncertainties of line intensities and line shape parameters are not achievable. In the case of widely used cavity ring-down spectroscopy (CRDS) its dynamic range is limited by a bandwidth of detection system.

In this study we compare accuracy and dynamic range of CRDS, cavity mode width spectroscopy (CMWS) [1] and cavity mode-dispersion spectroscopy (CMDS) [2]. The frequency axis is linked through the optical frequency comb to the primary frequency standard [3]. Comparison is done on spectra of a weak ro-vibrational line from (3-0) band of CO, measured simultaneously with all three methods and fitted with the Hartmann-Tran profile (HTP) [4,5] and multi-spectrum fitting technique [6,7]. We prove predictions from our earlier paper [2] that contrary to both absorption methods CMDS spectrum has no indication of any systematic errors at sub-per-mille level of line intensity, even at high-opacity conditions and signal-to-noise ratio above  $10^4$ . This immunity to systematic errors results directly from replacing the intensity by the frequency measurements.

Our results suggest a paradigm shift from absorption to dispersion spectroscopy in the most demanding applications, e.g. reference data for atmospheric studies and testing ab initio line parameters, Doppler thermometry, isotope ratio measurements and basic research related to testing the Standard Model. CMDS can also be implemented into high-resolution and broadband direct optical frequency combs spectroscopy [8,9].

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# H<sub>2</sub>-He scattering states observation with cavity ring-down spectroscopy

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We present observations of scattering states of H<sub>2</sub> perturbed by helium. We set together *ab initio* lineshape parameters calculated based on the H<sub>2</sub>-He interaction potentials [1] with highly accurate cavity-enhanced spectroscopic data using well physically justified line-shape profile – the Speed Dependent Billiard Ball profile (SDBBP) [2–3].

The system of hydrogen molecule in its ground electronic state perturbed by helium consists of only four electrons. It is a fundamental molecular system perturbed by an atom. The performed *ab initio* calculations of H<sub>2</sub>-He interaction potentials allowed us to derive line-shape parameters from first principles [1]. We compare the entirely *ab initio* SDBB profile with highly accurate experimental molecular transitions of H<sub>2</sub>. The achieved agreement between the *ab initio* and experimental spectra is at the level of 1%. Within this approach not only the shapes of experimental lines are reliably reproduced, but also the underlying physics of molecular collisions can be traced. Besides the analysis of the basic line-shape effects (such as relaxation or phase changes of the internal states of the molecule), we also analyse the more sophisticated ones such as speed-dependent effects or velocity changing collisions (complex Dicke narrowing parameter) [3–4], which are particularly pronounced for the H<sub>2</sub>/D<sub>2</sub>-He systems [1,5–7].

According to our knowledge, this is the first comparison of highly accurate experimental spectra with advanced *ab initio* models which includes the speed-dependent and velocity-changing collisions effects. It allows us to study quantum scattering for molecules as well as to validate *ab initio* quantum potentials in ranges very challenging for quantum chemistry methods (for instance, for highly stretched molecules).

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