HIGH SENSITIVITY CW-CRDS AND ICLAS SPECTROSCOPY OF WATER IN ATMOSPHERIC SPECTRAL WINDOWS.

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Highly sensitive absorption methods based on lasers (ICLAS) or high finesse cavities (CRDS) allows sensitivity which are typically two orders of magnitude higher than the one achieved by Fourier Transform Spectroscopy associated with multipass absorption cells. Using these methods, we have characterized the absorption spectrum of water in spectral regions corresponding to "atmospheric windows" where transitions are extremely weak. These transparency windows are of particular importance as they are used for astrophysical observations or for trace detection.

In particular we will detail the performances obtained in the 1.5 μm window (6100-6750 cm^{-1}), which was investigated by cw-CRDS using a series of DFB diode lasers with detectivity of the order of 10^{-10}-10^{-9} cm^{-1} leading to the determination of the line parameters (wavenumber and intensity) of a total of 5190 lines [1]. Different isotopologues of water ($H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$ and $HD^{16}O$) present in natural abundance in the sample contribute to the spectrum. For the main isotopologue, $H_2{}^{16}O$, 2130 lines were measured with line intensities as weak as 10^{-29} cm/molecule while only 926 lines (including a proportion of 30% inaccurate calculated lines) with a minimum intensity of 3×10^{-27} cm/molecule are provided by the HITRAN and GEISA databases.

The rovibrational assignment was performed by S. N. Mikhailenko and O. V. Naumenko, on the basis of the *ab initio* calculations by Schwenke and Partridge with a subsequent refinement and validation using the Ritz combination principle together with all previously measured water transitions relevant to this study. Compared with previous FTS investigations, even those performed with isotopically enriched sample, our results obtained with natural water extend significantly the knowledge of the energy level structure of the four mentioned water isotopologues: 172, 139, 71 and 115 new energy levels were determined for the $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$ and $HD^{16}O$ isotopologues respectively.

The spectrum analysis has showed that most of the transitions which cannot be assigned to water are very weak and are due to impurities such as carbon dioxide and ammonia, leaving only about 3% of the observed transitions unassigned.

As a second example [2], we will present the water spectrum recorded between 9520 and 10010 cm^{-1} by Intracavity Laser Absorption Spectroscopy based on a Vertical external Cavity Laser System Emitting Laser. Quantum well semiconductor structures have been used as amplifying media giving access to the 8800-10100 cm^{-1} region, not accessible by ICLAS-Ti:Sapphire. The rovibrational analysis performed by O. Naumenko has allowed determining 156 new energy levels belonging to a total of 13 vibrational states.

[1]. P. Macko, D. Romanini, S. N. Mikhailenko, O. V. Naumenko, S. Kassi, A. Jenouvrier, Vl. G. Tyuterev and A. Campargue High Sensitivity CW-Cavity Ring Down Spectroscopy of water in the region of the 1.5 μm atmospheric window. Journal of Molecular Spectroscopy (submitted).

[2]. O. Naumenko and A. Campargue. Rovibrational analysis of the absorption spectrum of H_2O around 1.02 μm by ICLAS-VeCSEL, Journal of Molecular Spectroscopy 221 (2003) 221-226.