

Invited Lectures A

September 4, Tuesday, 9:00 – 10:30

Ultra sensitive Cavity Ring Down Spectroscopy of methane and hydrogen between 1.26 and 1.71 μm .

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The fibered DFB laser CW-CRDS spectrometer developed in Grenoble allows recording absorption spectra with a typical noise equivalent absorption of $a_{\text{min}} \approx 5 \times 10^{-11} \text{ cm}^{-1}$, over the wide 5850-7920 cm^{-1} range. A detection limit of $a_{\text{min}} \approx 5 \times 10^{-13} \text{ cm}^{-1}$ has been achieved recently by averaging CRDS spectra for several hours.

The absorption spectra of methane and hydrogen have been investigated by CW-CRDS in order to fulfil important needs in planetary and atmospheric sciences and testing the most advanced theoretical calculations, respectively.

Empirical line lists were constructed from 5852 to 7919 cm^{-1} for methane at room temperature and at 80 K (Fig. 1). The WKMC (Wang, Kassi, Mondelain, Campargue) lists¹ include about 43000 and 46420 lines at $80 \pm 3 \text{ K}$ and $296 \pm 3 \text{ K}$, respectively. The “two temperature method” provided lower state energy values, E_{emp} , for about 24000 transitions. The clear propensity of the derived low J values of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ to be integer illustrates the quality of the lower state energy values. The WKMC list at 80 K has been successfully applied in a large range of temperature conditions existing on Titan¹, Uranus, Pluto, Saturn and Jupiter.

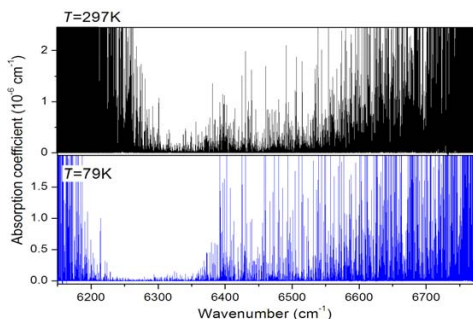


Fig. 1: Comparison of the CW-CRDS spectra of methane recorded at room temperature (upper panel) and 79 K (lower panel) in the 1.58 μm transparency window.

Very weak electric quadrupole transitions of the first overtone band of H_2 and D_2 were detected by CW-CRDS. They include the weakest hydrogen transitions reported so far by absorption spectroscopy (minimum intensity on the order of $1.8 \times 10^{-31} \text{ cm/molecule}$). Line intensities were obtained with a 2% uncertainty from a fit of the line profile using a Galatry line shape. The measured positions and intensities are found to agree very well with recent theoretical predictions which take into account relativistic and quantum electrodynamic corrections as well as effects of the finite nuclear mass².

[1] A. Campargue, L. Wang, S. Kassi et al. *Icarus*. **219**, 110 (2012).

[2] A. Campargue, S. Kassi, K. Pachucki, J. Komasa, *PCCP*. **14**, 802 (2012).