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Innovative optical spectrometers for ice core sciences and atmospheric monitoring at polar regions

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In this talk recent developments accomplished from a collaboration between the Laboratoire Interdisciplinaire de Physique (LIPhy) and the Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) both in Grenoble (France), are discussed, covering atmospheric chemistry of high reactive species in polar regions and employing optical spectrometers for both *in situ* and laboratory measurements of glacial archives.

In the framework of an ANR project, a transportable spectrometer based on the injection of a broadband frequency comb laser into a high-finesse optical cavity for the detection of IO, BrO, NO_2 and H_2CO has been realized.[1] The robust spectrometer provides shot-noise limited measurements for as long as 10 minutes, reaching detection limits of 0.04, 2, 10 and 200 ppt (2σ) for the four species, respectively. During the austral summer of 2011/12 the instrument has been used for monitoring, for the first time, NO_2, IO and BrO at Dumont d'Urville Station at East of Antarctica. The measurements highlighted a different chemistry between East and West coast, with the halogen chemistry being promoted to the West and the OH and NO_x chemistry on the East.[2]

In the framework of a SUBGLACIOR project, an innovative drilling probe has been realized. The instrument is capable of retrieving *in situ* real-time vertical profiles of CH_4 and δD of H_2O trapped inside the ice sheet down to more than 3 km of depth within a single Antarctic season. The drilling probe containing an embedded OFCEAS (optical-feedback cavity-enhanced absorption spectroscopy) spectrometer will be extremely useful for (i) identify potential sites for investigating the oldest ice (aiming 1.5 Myrs BP records for resolving a major climate reorganization called the Mid-Pleistocene transition occurred around 1 Myrs ago) and (ii) providing direct access to past temperatures and climate cycles thanks to the vertical distribution of two key climatic signatures.[3] The spectrometer provides detection limit of 0.2 ppbv for CH_4 and a precision of 0.2‰ on the δD of H_2O within $\sim$1 min of integration time. The spectrometer and the home-made gas sampling has been tested during an oceanographic campaign last summer in the Mediterranean Sea, measuring the vertical distribution of CH_4 dissolved in seawater. The project is now moving forward its final goal which consists of employing the probe for a first test season at Concordia station during the Austral summer of 2016/17, and then for the "oldest ice challenge" drilling season scheduled in the Austral summer of 2017/18.

Finally, preliminary results on the isotope ratio measurements of $CO^{18}O$,$^{13}CO_2$ and $^{13}CO^{18}O$ will be presented. A novel spectrometer, based on OFCAES technique employing a Quantum Cascade Laser around 4.4 μm wavelength, offers a precision below 0.05 ‰ for the three isotopic anomalies, for 200 ppmv of CO_2 samples. The optical device will be employed for laboratory experiments coupling it with a continuous ice-crushing extraction system for analyzing trapped bubbles of gas in Antarctica ice cores.

[1] R. Grilli, G. Méjean, S. Kassi, I. Ventrillard, C. Abd-Alrahman, and D. Romanini, "Frequency Comb Based Spectrometer for in Situ and Real Time Measurements of IO, BrO, NO_2, and H_2CO at pptv and ppqv Levels.," *Environ. Sci. Technol.*, vol. 46, no. 19, pp. 10704–10, Oct. 2012.

[2] R. Grilli, M. Legrand, A. Kukui, G. Méjean, S. Preunkert, and D. Romanini, "First investigations of IO, BrO, and NO_2 summer atmospheric levels at a coastal East Antarctic site using mode-locked cavity enhanced absorption spectroscopy," *Geophys. Res. Lett.*, vol. 40, pp. 1–6, Feb. 2013.

[3] R. Grilli, N. Marrocco, T. Desbois, C. Guillerm, J. Triest, E. Kerstel, and D. Romanini, "Invited Article: SUBGLACIOR: An optical analyzer embedded in an Antarctic ice probe for exploring the past climate," *Rev. Sci. Instrum.*, vol. 85, no. 111301, pp. 1–7, 2014.