Geophysical Research Abstracts,
Vol. 11, EGU2009-6146-1, 2009
EGU General Assembly 2009

Cavity Enhanced absorption spectroscopy with an Optical Comb: Detection of atmospheric radicals in the near UV.

G. Méjean, S. Kassi, and D. Romanini

Laboratoire de Spectrométrie Physique, CNRS UMR 5588, Université J. Fourier de Grenoble, Saint Martin d'Hères, corresponding author : guillaume.mejean@ujf-grenoble.fr

The atmospheric chemistry community suffers a lack of fast, reliable and space resolved measurement for a wide set of very reactive molecules (e.g. radicals such as OH, NO3, BrO, IO, etc.). Due to their high reactivity, these molecules largely control the lifetime and concentration of numerous key atmospheric species. The concentrations of radicals are extremely low (ppbv or less) and highly variable in time and space. Measuring their concentration is often extremely laborious, expensive and requires heavy equipment (chemical sampling and treatment followed by mass spectrometry and/or chromatography).
We recently introduced an optical spectroscopy technique based on a femtosecond laser oscillator, "Mode-Locked Cavity-Enhanced Absorption Spectroscopy", that we propose to develop into an instrument for in situ measurement of local concentration of traces of reactive molecules [1-3].
We have already demonstrated the possibility of measuring part in 1E12 by volume concentrations of radicals of high atmospheric interest, such as IO or BrO [4], as needed for monitoring these species in the environment. We apply cavity-enhanced absorption spectroscopy in the near UV range using a frequency-doubled Ti:Sa modelocked femtosecond laser. Efficient broadband injection of a high finesse cavity is obtained by matching this optical frequency-comb source to the comb of cavity transmission resonances. A grating spectrograph and a detector array disperse and detect the spectrum transmitted by the cavity carrying the absorption features of intracavity molecules. IO traces were obtained by mixing together controlled flows of gaseous iodine and ozone inside a high finesse cavity (F∼6000). A Chameleon Ultra II ML-Laser (gracefully lent during 1 month by Coherent Inc.) was frequency doubled to address an absorption band of IO at 436 nm. A locking scheme allowed the cavity transmission to be smooth and stable. The transmitted light was dispersed using a high resolution (0.07nm) grating spectrograph (HR4 Jobin-Yvon) and collected with a cooled CCD linear array (1024 pixels). As the cavity finesse was measured by the ringdown time, and the IO absorption cross section is known, we could estimate that we had produced 0.2 ppbv of IO.
The absorption noise level (7E-10cm-1 after 10s averaging) corresponded to a detection limit of 3 ppt par racine de Hertz. It is to be noted that the mirrors yielding a finesse of 6000 around 436 nm were centered at 460 nm, where the cavity finesse was measured to be about 20 000.
Moreover, modern solid state ML lasers are compact and could function reliably in environmental research stations. The spectral range from 500 down to 225 nm, accessible by efficient frequency doubling and tripling, includes strong absorption bands of important species; in particular, given their known optical cross sections, we estimate detection limits in the range 1-10 pptv for IO, BrO, OClO, OIO, and OBrO, sufficient for environmental measurements. ClO, HONO, HCHO, NO2, SO2, and O3 should be detectable down to 10-100 pptvs. The OH radical should be visible at 308 nm below 0.1 pptv, not far from typical ambient concentrations.

[1] T. Gherman and D. Romanini, 2002, Mode-locked cavity-enhanced absorption spectroscopy, Optics Express 10, 1033-1042.
[2] T. Gherman, S. Kassi, A. Campargue, and D. Romanini, 2004, Overtone spectroscopy in the blue region by Cavity-Enhanced Absorption Spectroscopy with a Mode-Locked femtosecond laser: Application to acetylene, Chem. Phys. Lett 383, 353-358.
[3] T. Gherman, E. Eslami, D. Romanini, S. Kassi, J.-C. Vial, and N. Sadeghi, 2004, High sensitivity broad-band mode-locked cavity-enhanced absorption spectroscopy: Measurement of Ar*(3P2) atoms and N2+ ions densities, J. Phys. D: Appl. Phys. 37, 2408-2415.

[4] G. Méjean, S. Kassi, and D. Romanini, 2008, Cavity Enhanced absorption spectroscopy with an Optical Comb: Detection of atmospheric radicals in the near UV, Optics Letters. 33, 1231-1234 (2008)