The near-IR absorption spectra of gaseous trace constituents using Fourier-transform broadband cavity-enhanced absorption spectroscopy

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INTRODUCTION

In Fourier-transform broadband cavity-enhanced absorption spectroscopy (FT-BBCEAS), the concept of absorption enhancement in an optically stable cavity over a broad spectral range, is combined to the high spectral resolution performance of a Fourier-transform (FT) detection. The latter is required to resolve the fine structure of important atmospheric compounds and their isotopes in the infrared.

This project is to ultimately improve the sensitivity, selectivity and versatility of cavity-enhanced absorption spectroscopy for trace gas monitoring through the development of a field instrument which combines "classical" Fourier transform spectroscopy (FTS) with incoherent broadband cavity enhanced absorption spectroscopy (IBB-CEAS). First, a laboratory setup measures absorption lines in the near-infrared (NIR) of several possible trace species, at low pressures to avoid interferences from laboratory ambient gases, as well as to avoid spectral broadening. This information is being built into a database before a hardware for field deployment is built.

In this work, two configurations of a FT-IBBCEA setup were tested/validated by measuring the near-infrared spectrum of (a) methyl iodide (CH_3I), molecule of interest in the marine boundary layer and whose radioactive isotopes need to be closely monitored in the environment of nuclear power plants, (b) NO_2, prominent air pollutant resulting from the oxidation of nitrogen oxide emitted by cars and industries, and of (c) methyl cyanide (CH_3CN), a molecule of considerable atmospheric importance which is generated in fires.

EXPERIMENTAL SETUP

An FT-BBCEAS system was setup in the laboratory (Fig. 1). Two cavity lengths *d* (165 cm or 644 cm) and two light sources (a superquiet Xe arc lamp, Hamamatsu, 75W, or a supercontinuum fibre laser, Fianium, 6W) were tested . A pair of highly reflective mirrors constituted the cavity. Thanks to a fibre the output light was coupled into a FT spectrometer (FTS Brüker Vertex 80, max resolution 0.07 cm^{-1}) supplied with a InGaAs photodiode sensor. The cavity was closed with a steel pipe and it was pumped down before introducing trace compounds.

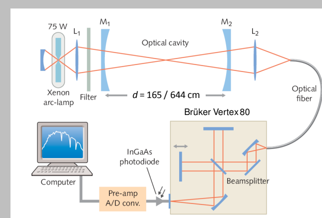


Fig.1a. Arrangement of an FT-BBCEAS system [1]

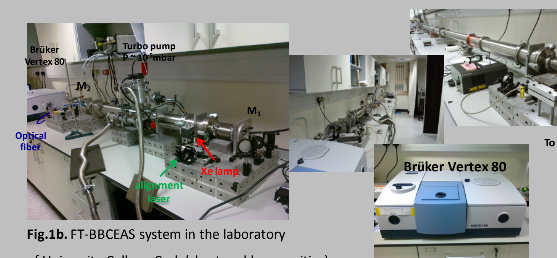


Fig.1b. FT-BBCEAS system in the laboratory of University College Cork (short and long cavities)

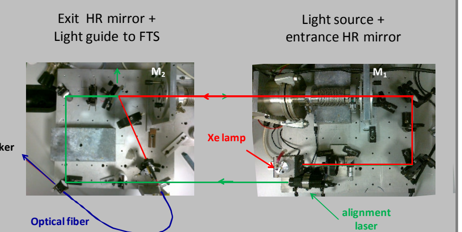


Fig.1c. Optical path

MEASURED ABSORPTION SPECTRA

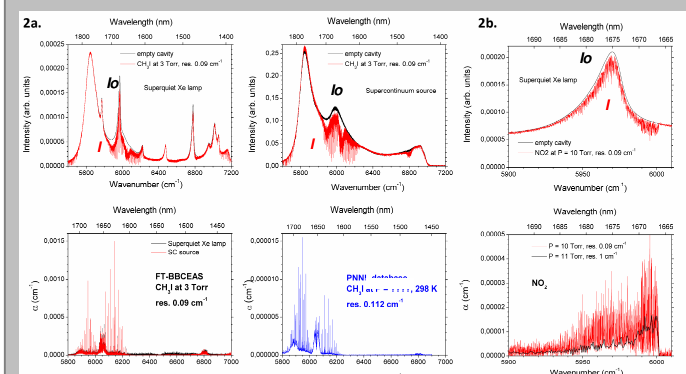


Fig.2. Measured cavity intensities, *I* and *Io*, and absorption coefficient, α, obtained in a 165 cm long cavity, over the wavenumber range [5800:7000] cm^{-1} for **2a.** CH_3I and **2b.** NO_2

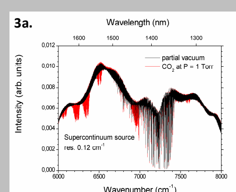
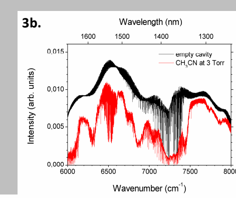
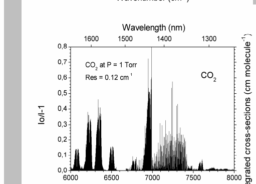
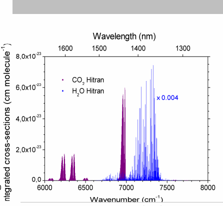
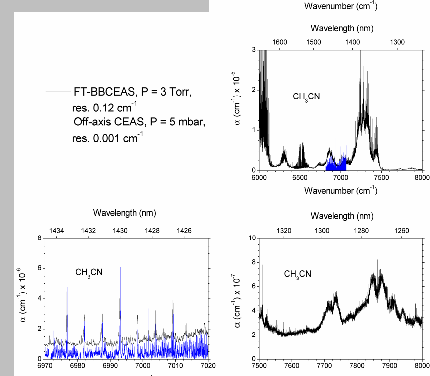


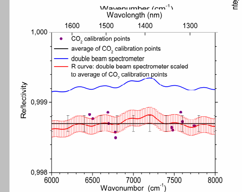
Fig.3. Measured cavity intensities, *I* and *Io*, and absorption coefficient, α, obtained in a 664 cm long cavity, over the wavenumber range [6000:8000] cm^{-1} for **3a.** CO_2 and **3b.** CH_3CN











CO_2 was used as calibration gas to measure the mirror reflectivity as a function of wavelength.

The reference, integrated absorption cross-sections were taken from the HITRAN database.

REFERENCES

[1]. J. Orphal and A.A. Ruth, *Opt. Express*, **16**, p. 19232 (2008).

[2]. S.E. Fiedler *et al.*, *Chem. Phys. Lett.* **371**, p. 284 (2003).

[3]. D.S. Venables*et al.*, *Environ. Sci. Technol.*, **40**, p. 6758 (2006).

SPECTRAL ANALYSIS

The absorption coefficient, $\alpha(\lambda)$, of the sample was calculated as follows [2]:

$$\alpha = \frac{(I_0 - I)}{I}\frac{(1-R)}{d} = n\sigma \qquad \text{Eq. (1)}$$

where $I_0(\lambda)$ and $I(\lambda)$ were the intensity spectra recorded in the empty cavity and in the presence of the absorbing species, respectively, $R(\lambda)$ was the mirror reflectivity curve and *d* was the length of the cavity. Concentration *n* of the absorbing species can be retrieved by fitting its absorption cross-sections $\sigma(\lambda)$ to the measured absorption coefficient. Reflectivity curve $R(\lambda)$ was established by recording the intensity spectrum of a known concentration *n* of a reference gas [3] whose integrated absorption lines are well known in the near-IR (Fig. 3).

SUMMARY

FT-IBBCEAS is a promising approach for lab and field studies because:

- It allows sensitive measurements of trace pollutants from landfill using their near-IR "fingerprints"
- Multiple species can be detected simultaneously for selectivity
- Long cavities (several metres separation) are feasible and increase the sensitivity of the system

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