Cavity-enhanced Absorption Spectroscopy for Trace Gas Detection with Frontier

Introduction

Detecting gases at low concentrations with FT-IR requires long pathlengths to increase absorption. The conventional approach employs a multi-pass White Cell where the light beam is reflected between two mirrors that are angled so that the beam emerges past one of the mirrors after a number of reflections, giving pathlengths up to tens of meters. In cavity-enhanced measurements, a highly collimated beam is reflected between two mirrors with a small amount of radiation emerging through the mirrors at each reflection. By using highly reflective mirrors the effective pathlength can be several thousand times greater than the separation between the mirrors. This gives the possibility of detecting gases at low concentrations in relatively small volumes, for example in looking for metabolites in breath.

Cavity-enhanced absorption spectroscopy (CEAS) has similarities with the better known cavity ringdown technique (CRDS) which measures the signal decay as a laser pulse emerges through one of the mirrors after successive reflections. By measuring the increase in the rate of decay caused by an absorbing species, CRDS can measure ppb concentrations of small molecules. The ringdown technique has typically been applied to small molecules where the wavelength of a NIR laser source can be tuned across very narrow individual lines of the spectra. In contrast this report describes CEAS using a broadband source applied to larger molecules where the spectra are broader.

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The measured signal is the sum of light that has passed through the cavity different numbers of times. Figure 1 shows that fraction of light transmitted as a function of the number of reflections for different reflectivities. The reflectivity of the mirrors is typically greater than 99.95% so that a significant fraction of the light undergoes thousands of reflections. When the separation between the mirrors is L and the reflectivity is R the effective pathlength is L/(1-R). For a 25 cm separation and reflectivity of 0.9995 the effective pathlength is 500 meters. Because there is no single pathlength the Beer-Lambert law does not apply. Instead the relationship between concentration, C, and incident and transmitted intensities, I_0 and I, is given by: $C \propto (I_0 - I)/ I$.[1]
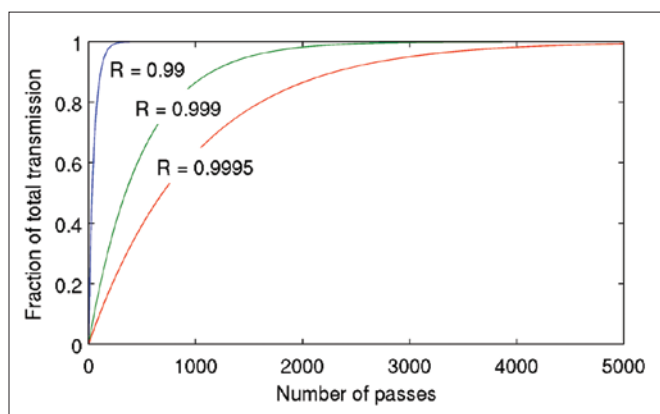

Figure 1. The fraction of intensity transmitted vs. the number of passes.

The high reflectivity of the mirrors means that only a very small fraction of the source radiation enters the cavity. For this reason laser sources have generally been used. The work described here was aimed at reducing the cost and complexity of the technique by using a near IR superluminescent diode (SLED) as the light source.[2]

Experimental

The light source was a fiber-coupled SLED with an output of 10 mW centered at 6000 cm^{-1} and bandwidth approaching 400 cm^{-1}. The cavity was positioned between the source and the emission port of a near IR Frontier™ fitted with an InGaAs detector. Aligning the system proved far easier than when using a monochromator because of the large circular aperture of the spectrometer. The principal target species was 1,3-butadiene, which is a common hazardous air pollutant. Spectra were measured at 4 or 16 cm^{-1} resolution. The cavity length was 25 cm and mirror reflectivity was measured to be up to 99.98%. This gives a pathlength enhancement factor of 5000 resulting in an effective pathlength of 1.25 km. A schematic of the system is shown in Figure 2.
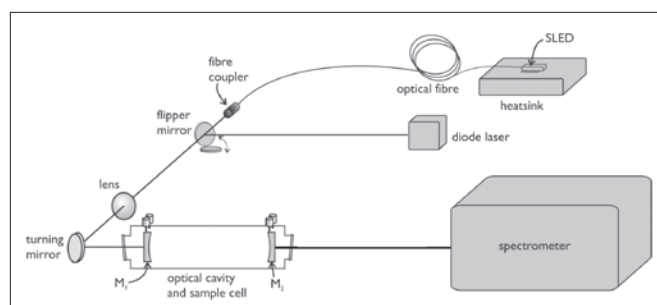

Figure 2. Schematic of experimental setup.

Results

Spectra were measured at resolutions between 0.5 and 16 cm^{-1}. As the bands in the spectrum of 1,3-butadiene are relatively broad a resolution of 16 cm^{-1} is sufficient. Figure 3 shows cavity-enhanced spectra of butadiene at concentrations between 300 and 80 ppm. From separate measurements of the scan-to-scan noise the detection limit for 1,3-butadiene for a four minute measurement is estimated to be about 600 ppb.
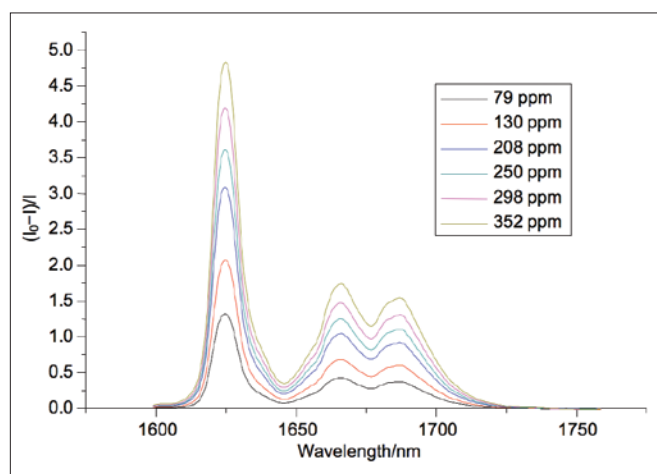

Figure 3. Spectra of 1,3-butadiene.

One of the principal attractions of cavity enhanced spectroscopy is the possibility to observe multiple species. Figure 4 shows spectra of isoprene, methane and a mixture containing 10 ppm methane and 120 ppm isoprene in air. At 4 cm^{-1} resolution, the fine structure of the methane spectrum can be seen superimposed on the broad bands of isoprene.
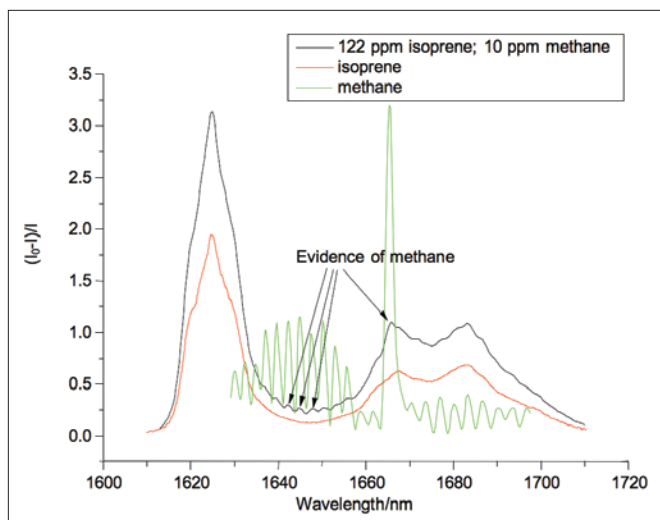
Figure 4. Spectra of isoprene (red), methane (green) and a mixture with 10 ppm methane and 120 ppm isoprene in air.

Summary

Cavity-enhanced absorption measurements with a SLED source and Frontier with an InGaAs detector can achieve ppm sensitivity for measuring 1,3-butadiene. Other hydrocarbon species have been measured with the same system. The spectral range can be increased by multiplexing SLED's but the very high reflectivities needed cannot be maintained over a wide spectral range.

Acknowledgment

References

1. M. Mazurenca, A.J. Orr-Ewing, R. Peverall, G.A. Ritchie, Annu. Rep. Prog. Chem. Sect. C, 2005, **101,** 100-142.

2. W. Denzer, M.L. Hamilton, G. Hancock, M. Islam, C.E. Langley, R. Peverall and G.A.D. Ritchie, *Analyst,* 2009, **134,** 2220-2223.

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