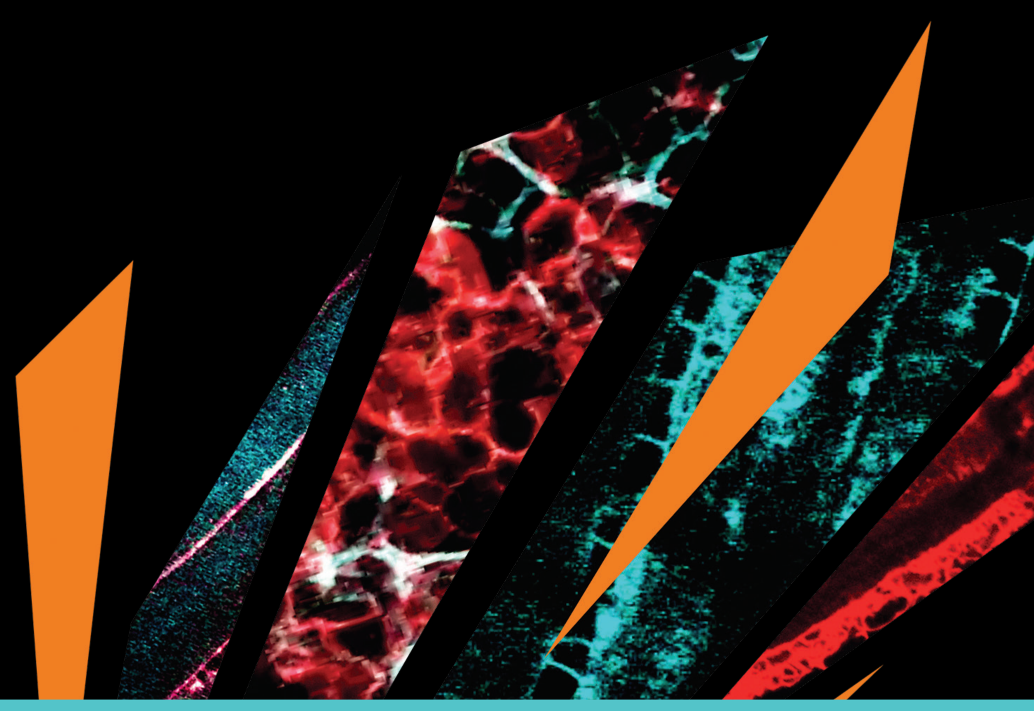

Multi-species, high resolution mid-infrared spectroscopy via fiber delivery

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Introduction

Optical parametric oscillators (OPOs) with broadband out put in the mid-infrared are well suited as sources for high resolution, high sensitivity multi-species IR spectroscopy due to their good beam quality, broad bandwidth, and high brightness. Spectroscopy applications such as atmospheric sensing often require remote delivery over open-paths up to km in length whereas fiber delivery is desired for inaccessible environments such as pipelines or reaction vessels.

Here we explore a flexible, easy to use, high-resolution technique for conducting remote stand-off, or fiber delivered, multi-species spectroscopy in a cluttered landscape containing both narrow and broad absorption features.

We perform quantitative, high resolution (≈0.033 cm^{-1}), time-resolved measurement of water, methane, methanol and C_2H_7NO (MEA) concentrations via fiber delivery of the OPO light. This demonstrates monitoring of hazardous chemicals in enclosed environments for health and safety reasons.

Methods

OPO light is routed through a Michelson interferometer before being coupled into a delivery fiber. Interferograms are recorded before the fiber and after a 10.5 m Herriott cell. The cell is connected to a closed-loop air delivery system into which chemicals can be injected to simulate changes in air quality. The cell and air delivery system can also be heated.

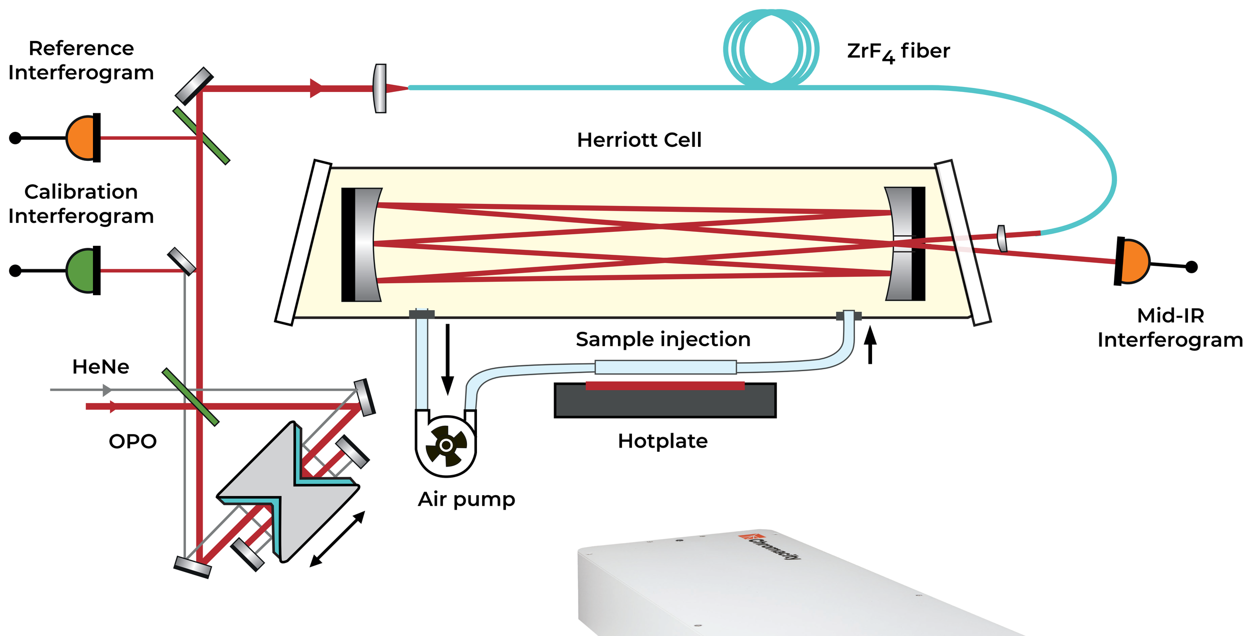

Fig. 1 Experimental setup

Photo Chromacity OPO

References

[1] Kara, O., et.al., "Open-path multi-species remote sensing with a broadband optical parametric oscillator", Opt. Express 27(15), (2019).

[2] Johnson, K., et.al., "High resolution ZrF4-fiber-delivered multi-species infrared spectroscopy", OSA Continuum, 3(12), 3595-3603 (2020).

[3] Gordon, I.E. et.al, "The HITRAN 2017 molecular spectroscopic database," J. Quant. Spectrosc. Radiat. Transfer 203, 3–69 (2017).

Chromacity Near-IR OPO

Good beam quality → high resolution, long path lengths
High brightness → long path lengths, high sensitivity
Broad bandwidths → simultaneously probe multiple species

Tunable from 1.4 – 4 μm

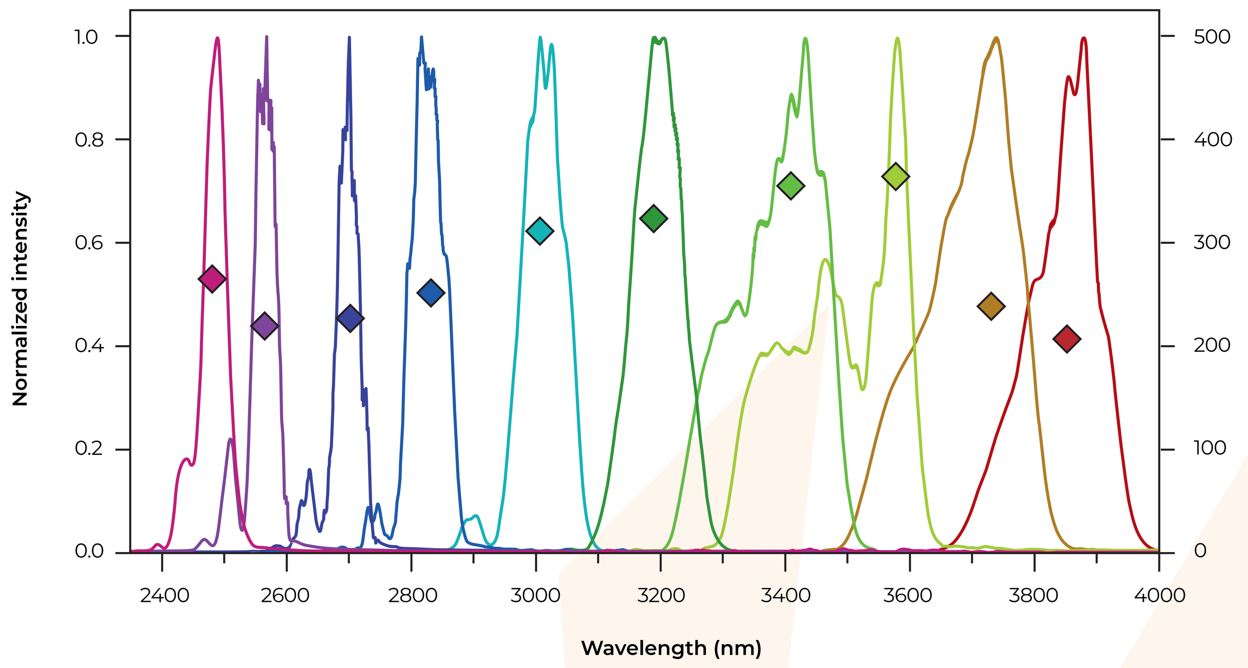

Fig. 2 Typical idler spectra from Chromacity OPO

Spectral Fitting

The fitting algorithm [1, 2] is a global optimization in which the illumination spectrum is modelled as a many-point spline and co-optimized with database spectra [3] of all participating gas species to obtain their concentrations. For species with line-like absorption features, this means baseline correction can be done without the need for a reference spectrum (see Fig. 3b).

For improved accuracy where there are broad absorption features, the ratio of the reference detector spectrum to the freely fitted envelope of a cell filled with only ambient air constitutes a transfer function. For subsequent measurements in the presence of additional chemical species, the spectral envelope can be retrieved by multiplying the reference detector spectrum by this transfer function (see Fig. 3a & 3c).

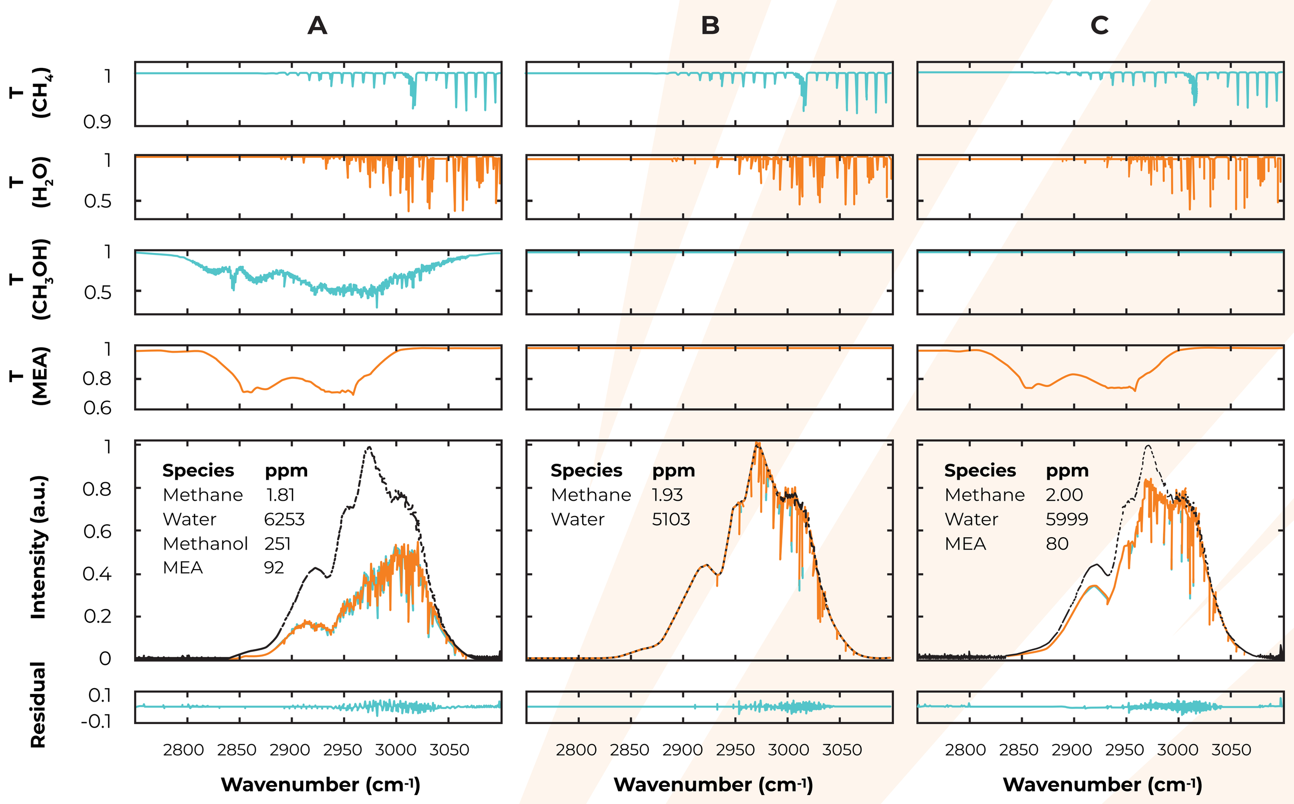

Fig. 3 Average of 64 spectra from cell containing (a) MEA and methanol, (b) only air, and (c) MEA. Main plots compare measured spectrum (orange) to the best-fit (blue). The co-fitted illumination envelope is shown by the dashed line. Fitted contributions of each chemical species are plotted as transmission spectra above the main plot. The residual is shown at the bottom.

Results

Detection limits of 290 ppb and 890 ppb are obtained for methane and MEA respectively using this setup with averaging of 64 spectra (see Fig. 4 a, c). The impact of an additional species with a complex spectrum (methanol) on the detection sensitivity of the others is also explored (see Fig. 4 b, d). Detection sensitivity is reduced, but not to an overwhelming degree. The precision, as indicated by the Allan deviation (Fig. 5), can also be readily quantified and shows the expected improvement with averaging for species with stable concentration (see methane in Fig. 5b).

Fig. 4 Detection sensitivity in ppm, from noise-equivalent absorption analysis, with its variation across the spectrum, for MEA (a, b) and methane (c, d). This is measured for a cell containing (a, c) only MEA and (b, d) MEA plus methanol.

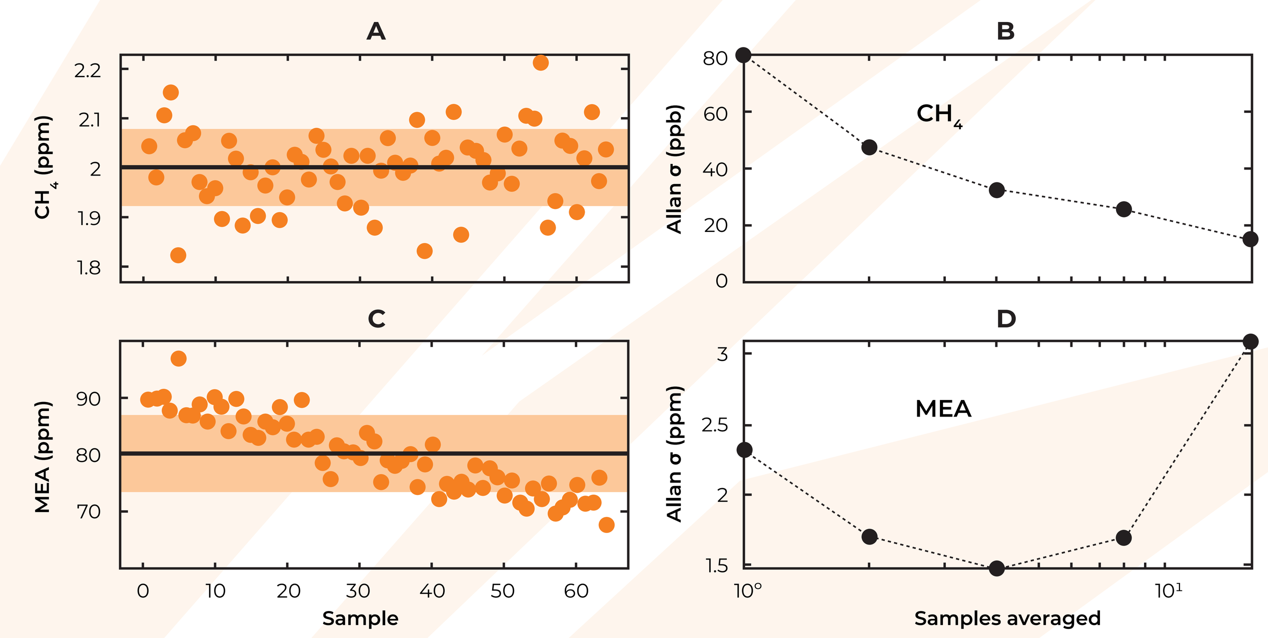

Fig. 5 Concentrations of (a) methane and (c) MEA recovered from 64 single-spectra fits for a cell containing MEA. The red region shows ± 1 standard deviation. Also shown are Allan deviations in concentration of (b) methane and (d) MEA.

Conclusions

1. The Chromacity Near-IR OPO is a high performance and affordable light source for multi-species IR spectroscopy.
2. Fitting algorithm enables quantitative measurement of chemical concentrations, even for species with broad continuum-like absorptions.
3. Remote delivery of the light is achieved, in this case via fiber but also possible over open paths.
4. Detection sensitivity and precision can meet relevant environmental monitoring specifications.

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