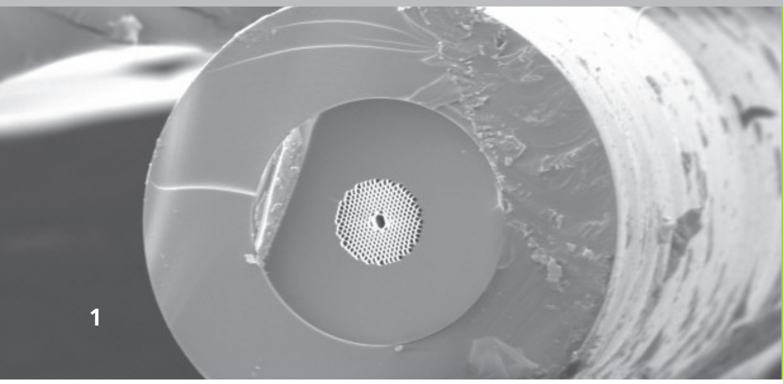
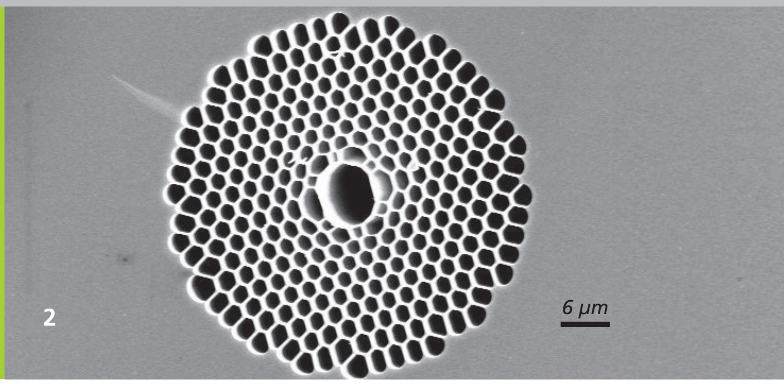
FRAUNHOFER INSTITUTE FOR PHYSICAL MEASUREMENT TECHNIQUES IPM




*1 Hollow-core photonic crystal fiber: The sample gas and the Raman excitation laser are coupled into the inner core of the fiber.*
*2 Zoom-in on the inner core (nominal diameter 7µm): light and gas interact in the long confined structure of the core.*

# RAMAN SPECTROSCOPY OF GASES

## COMPLETE GAS CHARACTERIZATION WITH A SINGLE TECHNIQUE

### Raman spectroscopy has a lot to offer

Raman spectroscopy bears great potential as a process analytical technology (PAT) tool for the identification and quantification of complex gas mixtures. In comparison to similarly specific spectroscopy techniques – such as infrared spectroscopy – the transformation of vibrational spectroscopy to the visible spectral region offers significant optical advantages in light sources and detectors and lends itself to integration with fiber optic setups.

In addition, Raman spectroscopy does not rely on molecular dipoles, which enables the technique to monitor important process gases like molecular oxygen, nitrogen and hydrogen which are invisible to infrared absorption spectroscopy.

### Raman spectroscopy in hollow-core photonic-crystal fibers

Raman spectroscopy on gases does face challenges, most notably the low sensitivity, which is exacerbated when applied to gases due to their low molecule density. It has been shown that hollow-core photonic-crystal fibers (HC-PCF) can supply a solution by enhancing the light-matter-interaction path by several orders of magnitude. The HC-PCF with its micron-sized, hollow inner core is used to guide gas, laser excitation light and scattered Raman-Stokes light, providing the means to collect Raman signals from significantly enhanced volumes.

Below, we present first results on HC-PCF-based signal enhancements for 785 nm excitation wavelengths and provide data on gas exchange rates in HC-PCF which are crucial for the data acquisition rate in industrial application.

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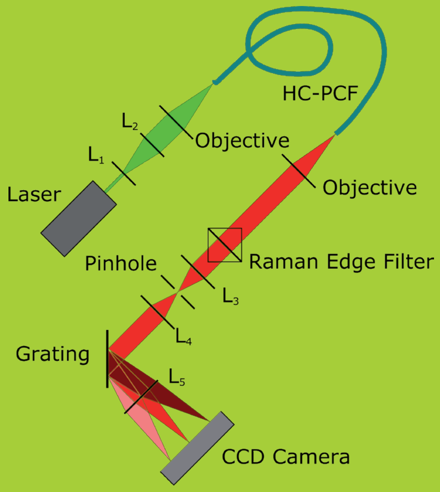


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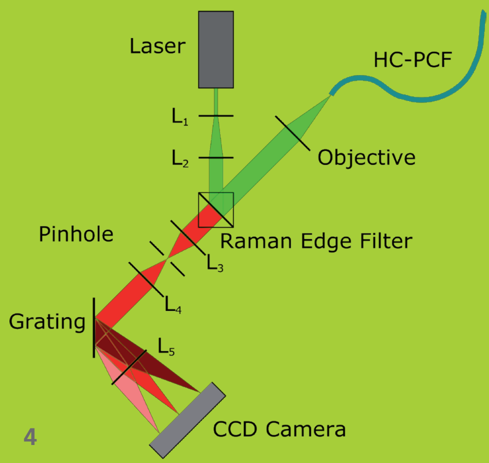


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## Signal enhancement

We used a Raman setup (schematic representation in figure 3) comprising a Raman excitation laser at 785 nm with an output power at the fiber entrance of approx. 20 mW. Figure 5 and 6 show the measured Raman spectra of air (atmospheric pressure) with integration times of 1 s and 100 s and demonstrate the huge potential of HC-PCFs in Raman gas detection: The marked regions show signals from oxygen (1 555 cm$^{-1}$), nitrogen (2 331 cm$^{-1}$) and even carbon dioxide (1 555 cm$^{-1}$), which has a concentration of around 400 ppm in air and is clearly detectable in the 100-s-integration measurement. In comparison to a free-focus-in-air setup we calculate a signal enhancement factor of approximately 800 (wavelength- and power-adjusted).

## Gas exchange

For an industrial application the gas exchange time in an HC-PCF with a micrometer-sized inner opening is crucial to the reachable data acquisition rate. Results from a 1.2-m-fiber and a pressure difference of 1 bar used for gas exchange show an exchange rate of approximately 100 s, which is too long for many industrial applications. However, this value shows a quadratic dependence on fiber length, so that a 0.6-m-fiber has an exchange rate of only 25 s and could be used with a more powerful laser to end up with a similar gas detection performance. As the limit of photo damage experienced in HC-PCFs is of the order of Watts, there is still a lot of signal potential available by increasing laser power.

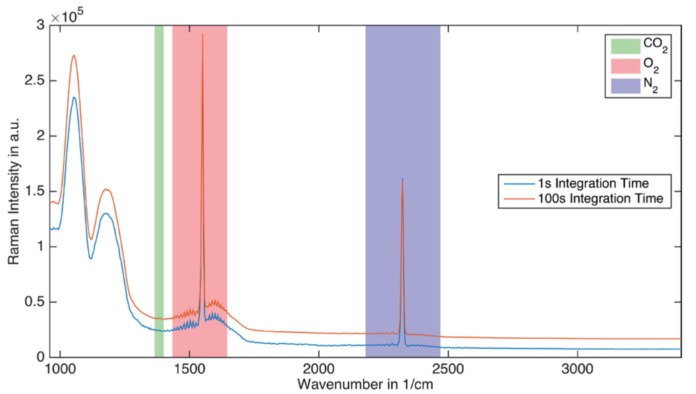
In summary, it is possible to find a balance between gas exchange rate and intrinsic Raman signal per laser excitation power for every practical application and Fraunhofer IPM would gladly evaluate your measurement challenge.

The spectroscopic system outlined above may easily be adapted to customer needs. Different fiber length geometries, different excitation wavelengths and diverse platform configurations may straightforwardly be implemented.

**3 + 4** *Two experimental setups to incorporate HC-PCF gas detection into a Raman spectrometer: the optics are coupled to the fiber either in back-scattering geometry or in transmission geometry.*

### Custom system development

Fraunhofer IPM is your competent partner for diverse spectroscopic applications. We offer an extended adaptation to your measuring needs including solutions for sample preparation, data analysis (image processing, chemometrics) and technical evaluation.

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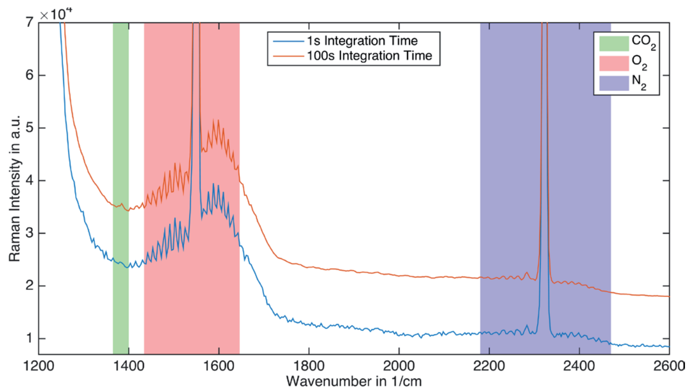


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