Raman spectroscopy is an established technique for identifying and quantifying chemical substances. Similar to IR absorption spectroscopy, it is based on querying the characteristic energy levels of a molecule and provides a fingerprint emission spectrum of a given compound. In contrast to IR spectroscopy, the light-molecule-interaction is coupled to the polarizability instead of the molecular dipole moment – enabling Raman to detect homo-nuclear gases such as hydrogen, oxygen, and nitrogen.

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 view of 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 such as molecular hydrogen, oxygen, and nitrogen which are invisible to infrared absorption spectroscopy. However, in comparison to IR spectroscopy, Raman suffers from a weak transition probability and associated poor signals.

To overcome these challenges and exploit the technique’s potential, Fraunhofer IPM is exploring a variety of techniques to enhance Raman signals and apply Raman spectroscopy even in low-cost applications. Here, we outline a cost-effective H₂ sensor setup to selectively quantify hydrogen in arbitrary gas matrices.

**Raman spectroscopy and gases**

Basic hydrogen (H₂) sensors, such as those based on thermal conductivity, suffer from cross-sensitivities. With these sensors, accurate H₂ quantification is only possible if the residual gas matrix is known, since other gases also influence the thermal conductivity. For demanding applications, selective H₂ determination without cross-sensitivities is desirable. Raman spectroscopy – as a vibrational spectroscopy tool – offers a solution here and can detect homo-nuclear gases without cross-sensitivities.

**Raman detection with filters and large detectors**

Traditional Raman spectroscopy uses spectrographs to analyze the sample’s scattered light. In order to squeeze this light through the entrance aperture of a spectrograph, collecting from a focused, small sample volume is essential. In contrast to this, a Raman sensor designed to only detect H₂ just needs a narrow-band transmission filter on the H₂ Raman wavelength to selectively quantify Raman light.

We thank the German Federal Ministry of Education and Research (BMBF) for funding within the TransHyDE-project Safe Infrastructure, funding code 03HY202G.
Therefore, a large-scale detection with a significant field of view, e.g. with a camera detector, is possible and may enhance Raman signals significantly. Fraunhofer IPM is exploring this approach with a setup shown in figure 1: The beam of a 532-nm-laser is imaged onto a large detector chip, the scattered light is collected perpendicularly and can be filtered by varying Raman gas filters. Figure 2 shows images recorded with air as a sample. The laser beam is visible when using \( \text{N}_2 \) or \( \text{O}_2 \) Raman filters, however, using a methane filter does not provide a signal. Figure 3 shows the results of some nitrogen:argon concentration steps and demonstrates the potential of filter-based detection.

**Raman signal enhancement**

The large-scale image detector used in the experiments above can be exploited even further: By using retro-reflectors, the laser beam (which doesn’t lose any significant amount of power when exciting Raman light) may be tossed back and forth several times through the field of view of the imaging optics – and thus multiply the resulting Raman signal. In the end, this enhancement together with low requirements on laser and camera performance will enable Raman gas sensors with price points formerly unreachable for Raman-based systems.

**Target specifications**

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<th>Specification</th>
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<td>Target gas</td>
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