# Isotopologue trace gas detection using multipass cavity Raman scattering

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**Abstract:** Feedback-assisted multipass-cavity spontaneous Raman scattering is demonstrated as an effective method of isotopologue analysis. Deuterium concentration precision near one part-per-million in water was obtained by direct vapor and indirect dihydrogen measurements.

Differentiation of naturally occurring isotopologues within a substance is a nontrivial task because of similar chemical properties and trace abundance. Well-established methods of isotopologue spectroscopy include isotope ratio mass spectrometry (IRMS), cavity ring-down spectroscopy (CRDS), off-axis integrated cavity output spectroscopy (ICOS), and quantum cascade tunable infrared laser differential absorption spectroscopy (QC-TILDAS) [1]. Although these techniques are effective for trace detection, they generally involve rather expensive, bulky and dedicated instrumentation. Spontaneous Raman scattering (SRS) can be applied simultaneously to a wide variety of chemical species and potentially provides an economical alternative. However, due to weak differential scattering cross-sections, gas SRS requires an enhancement mechanism based typically on waveguides [2] or optical resonators [3].

We report here deuterium isotopic characterization using an SRS enhancement approach that employs a blue multimode laser diode receiving feedback from a multipass optical cavity [4]. As illustrated in Fig. 1, light entering the near-concentric multipass cavity refocuses about 80 times and eventually retraces its path, which is enabled by slight off-axis alignment of the mirrors. The reflecting laser light returns to the laser diode, narrowing its spectral bandwidth to less than 0.1 nm with the help of an intermediate volume Bragg grating (VBG). The laser diode/multipass cavity/VBG system thus constitutes an external cavity diode laser (total cavity length $\approx$7.5 m). The forward and backward scattered spontaneous Raman emission is coupled out with an inline spectral filter and detected by a grating spectrometer.

We probed the deuterium concentration of various water samples using two methods. In the first, liquid water is evaporated underneath the multipass cavity foci and the concentration of HDO is measured. In the second, hydrogen gas generated from a water sample is probed for its relative concentration of HD.

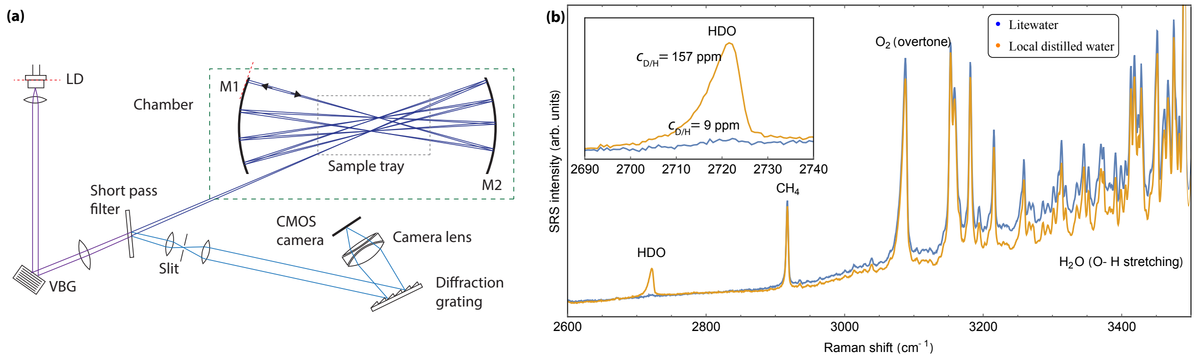

Fig. 1: (a) Schematic diagram of VBG-coupled multimode-laser-diode/multipass-cavity with only 8 double passes depicted. (b) Spectral overview of 8h-long measurements at atmospheric pressure for distilled water and Litewater with a headspace humidity of 50%. The HDO Raman signal is observed at 2721 cm$^{-1}$.

Fig. 1 summarizes the results obtained by the direct measurement of HDO from water vapor in the spectral range from 2600 cm$^{-1}$ to 4300 cm$^{-1}$ covering the O-H stretching vibrations. Local distilled water (deuterium concentration near 157 ppm) and deuterium depleted “Litewater” (nominal deuterium concentration of 5 ppm) show spectral signatures that differ in the peak at 2721 cm$^{-1}$, the HDO Raman Q-branch band associated with the O-D stretching vibration. With the magnitude of this peak we relate the concentration of HDO in $H_2O$ to the deuterium concentration defined as $c_{D/H} = n_D/n_H$, where $n_D$ is the number of deuterium atoms, and $n_H$ the number of hydrogen atoms, by

$$c_{\mathrm{HDO}} = \frac{2n_{\mathrm{H}}n_{\mathrm{D}}}{(n_{\mathrm{H}}+n_{\mathrm{D}})^2} = \frac{2c_{\mathrm{D/H}}}{(1+c_{\mathrm{D/H}})^2}, \tag{1}$$

because in the liquid state water molecules are able to freely exchange protons and deuterons. We are thus able to determine the deuterium concentration of Litewater as 8±1 ppm from a ratio of peaks normalized to peaks associated solely with $H_2O$. Relative to the Vienna Standard Mean Ocean Water (VSMOW) with concentration $c_{\mathrm{D/H,standard}}$ = 155.76 ppm, this corresponds to

$$\delta^2\mathrm{H} = \frac{c_{\mathrm{D/H,sample}} - c_{\mathrm{D/H,standard}}}{c_{\mathrm{D/H,standard}}} \times 1000 = -949 \pm 7‰. \tag{2}$$

However, to achieve such a precise detection of HDO, averaging over numerous measurements was necessary, effectively resulting in long exposure times. An inherent limitation in the direct measurement of water vapor is that the vapor concentration must be well below the dew point to avoid condensation on optical elements.

Alternatively, we can measure the concentration of deuterium of a byproduct of a water reaction. Figure 2 shows results of measurements of dihydrogen produced from the same samples as in Fig. 1 using a reaction with lye and aluminum foil. The advantage of this method over the direct measurement of water vapor is that high concentrations of the analyte, HD, may be generated.

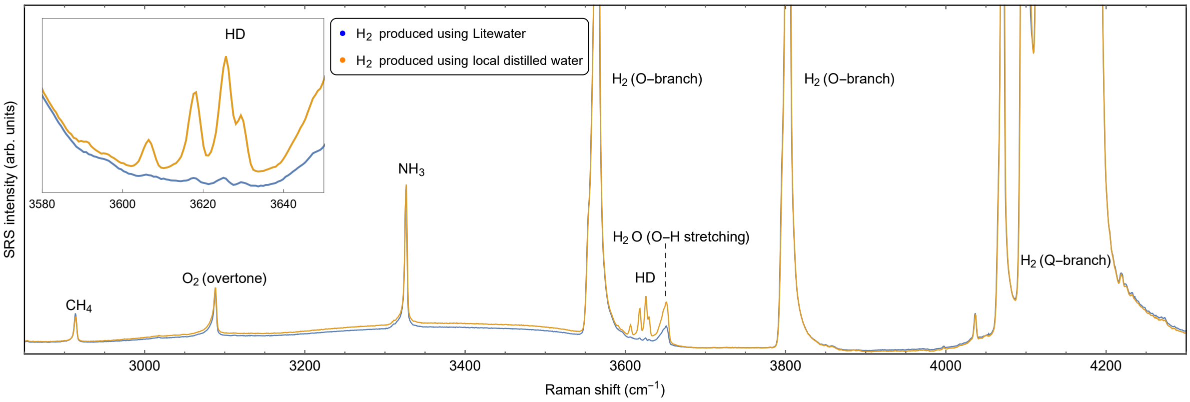

Fig. 2: Spectral overview of 1h-long measurements of gaseous $H_2$ produced using Litewater and local distilled water from the reaction $6\,H_2O + 2\,Al \xrightarrow{NaOH} 2\,Al(OH)_3 + 3\,H_2$.

As seen in Fig. 2, trace detection of HD (Raman band near 3620 $cm^{-1}$) is readily achieved so long as background humidity is not excessive. Here, the humidity level, proportional to the magnitude of the peak near 3650 $cm^{-1}$, was kept below 0.1% (water vapor concentration of 24 ppm) using zeolite desiccant. The inset of Fig. 2 reveals that the deuterium concentration is measurable with significantly less noise, despite a much shorter exposure time. Furthermore, the concentration of hydrogen in Fig. 2 was less than 10% in air near atmospheric pressure. Thus, if instead the chamber were filled with 100% hydrogen at atmospheric pressure, for instance by using water electrolysis, the same measurement of deuterium concentration could have been performed in only a minute, possibly with a precision rivaling the sub-permille $\delta^2$H level obtained by CRDS, IRMS, ICOS, or QC-TILDAS [1]. Quite generally, our experiments demonstrate the suitability of multipass cavity enhanced SRS for isotopologue spectroscopy, relevant for environmental, medical, and industrial applications.

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## References

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