

Zero gas impurities - detection of H₂S



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Objective

The aim was to develop analytical methods/techniques that are suitable to detect a large group of compounds to improve efficiency and to reduce costs of analysis of zero gas. In particular, a method for simultaneous detection of H₂O, H₂S and CO₂ was investigated by MIKES and PTB. The research at MIKES focused on the use of near-infrared laser spectroscopy for the detection of H₂S in small concentrations (< 100 ppbv).

Method

In order to meet the targeted detection limit in H₂S detection by laser spectroscopy, an extremely sensitive method is required. In practice, this means cavity-enhanced spectroscopy, such as cavity ring down spectroscopy (CRDS). Simulations were done in order to find the optimum spectral region for the spectrometer. The strongest absorption lines of H₂S in the NIR can be found at 2.64 μm, but these lines are strongly interfered by water absorption lines (c.f. Fig. 1). Therefore, we ended up using one of the strongest lines of the ν₁+ν₂+ν₃ combination band of H₂S at 1.574 μm. This line is approximately an order of magnitude weaker than the lines at 2.7 μm, but also the water interference is significantly smaller (c.f. Fig. 2).

The experimental work was done using a commercial CRD spectrometer, manufactured by Picarro Inc. (Fig. 3). The spectrometer was characterized, calibrated, and slightly modified for the measurements of H₂S. The line strength of the H₂S line used for the measurements (@ 1574.5 nm, or 6351.0 cm⁻¹) was determined at MIKES, as this information was not available in the literature. In addition, the effect of water and CO₂ spectral interference on the H₂S measurement was determined in collaboration with PTB.

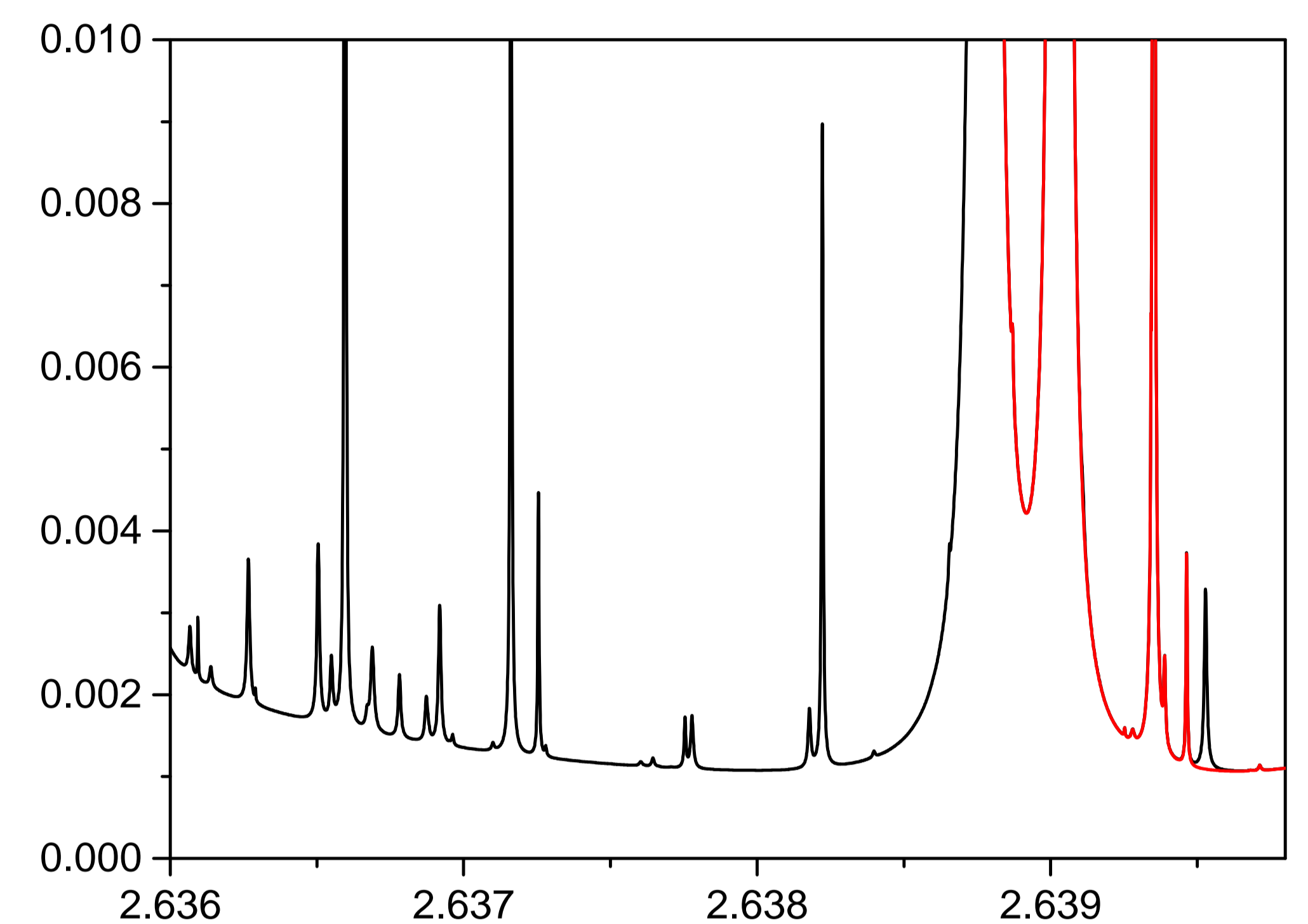
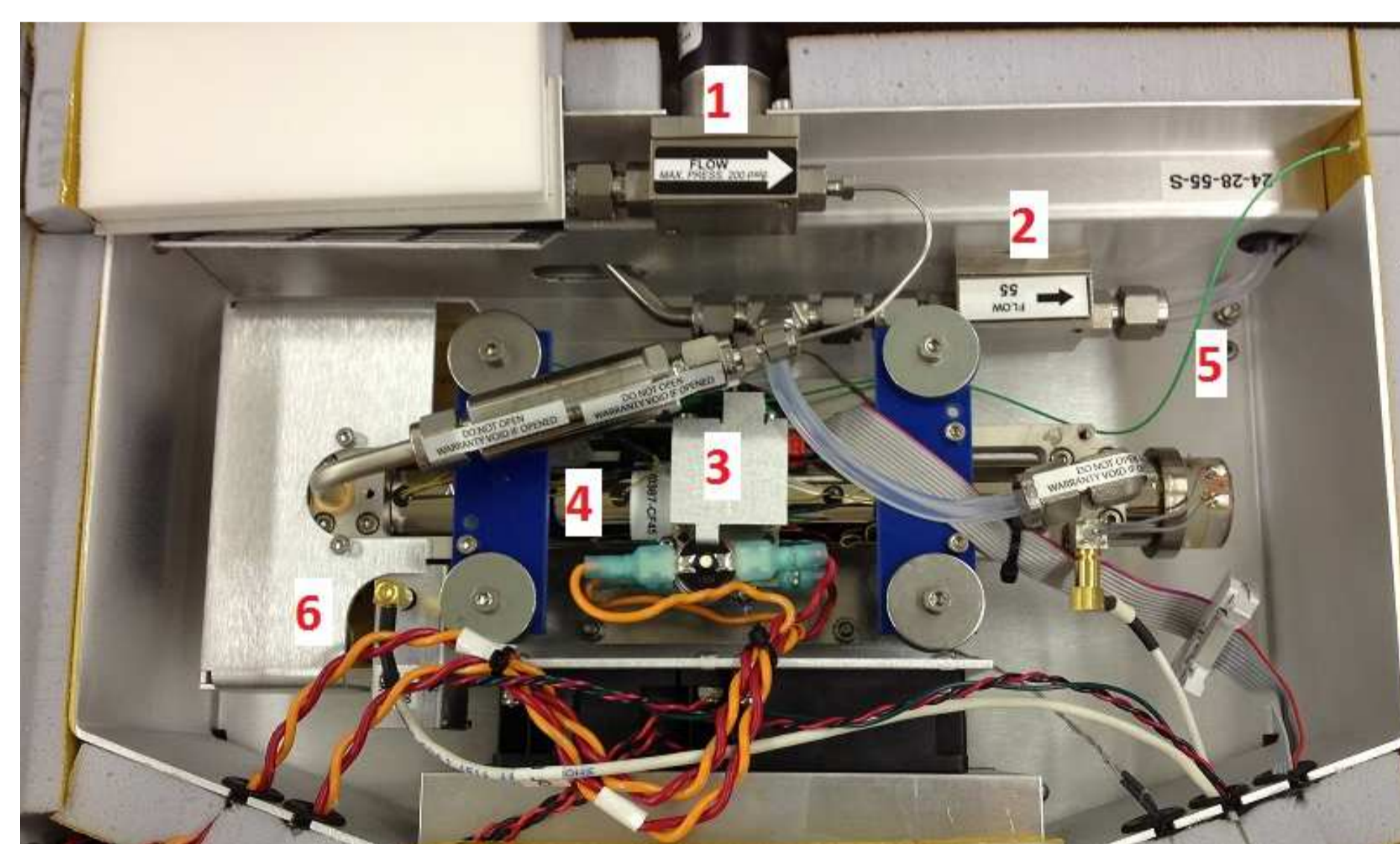
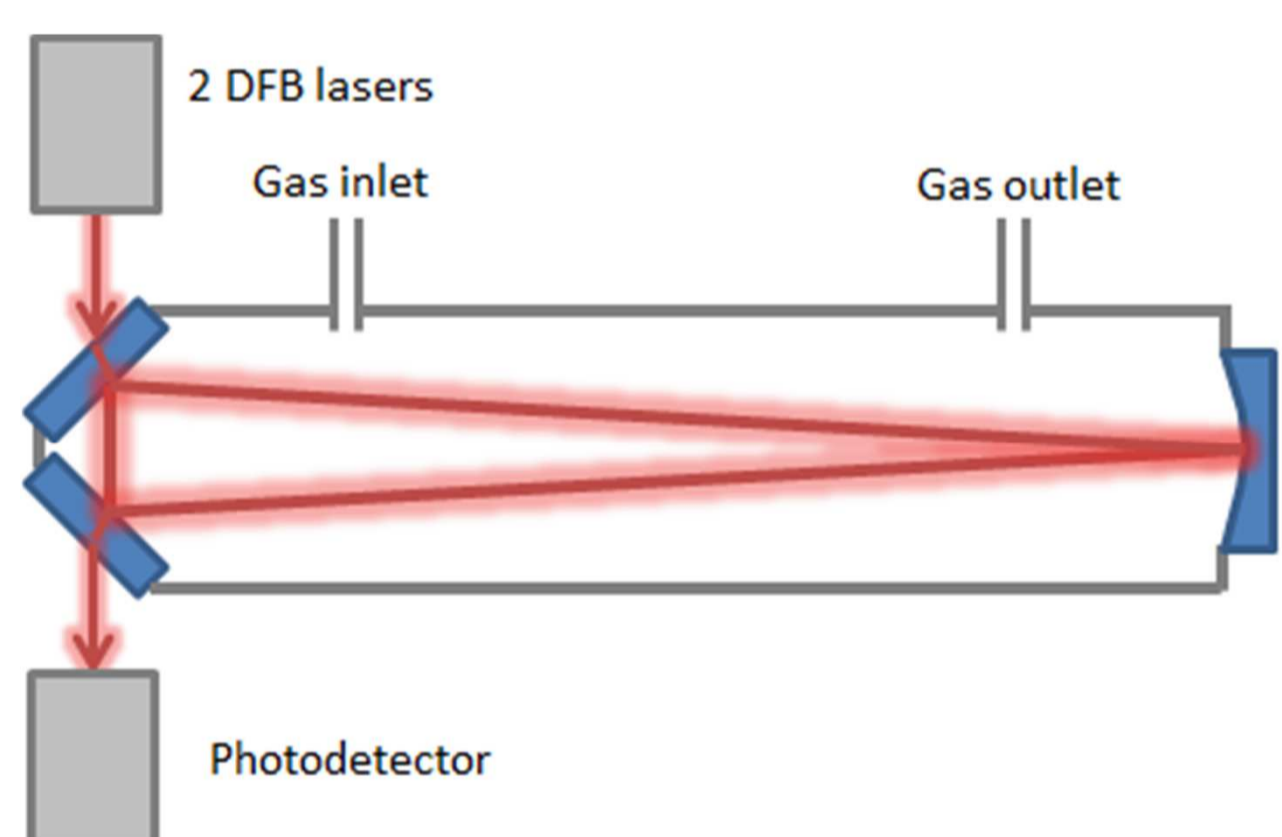


Fig. 1. Simulated spectra of 150 μmol/mol water vapor and 4 μmol/mol CO₂, with and without 0.1 μmol/mol H₂S at 150 mbar pressure. The background is mostly caused by water. The optical path length is 3000 m. The simulation is based on the HITRAN 2008 database. The arrow indicates one of the absorption lines of H₂S that could be used for the measurements without insurmountable problems due to water interference.

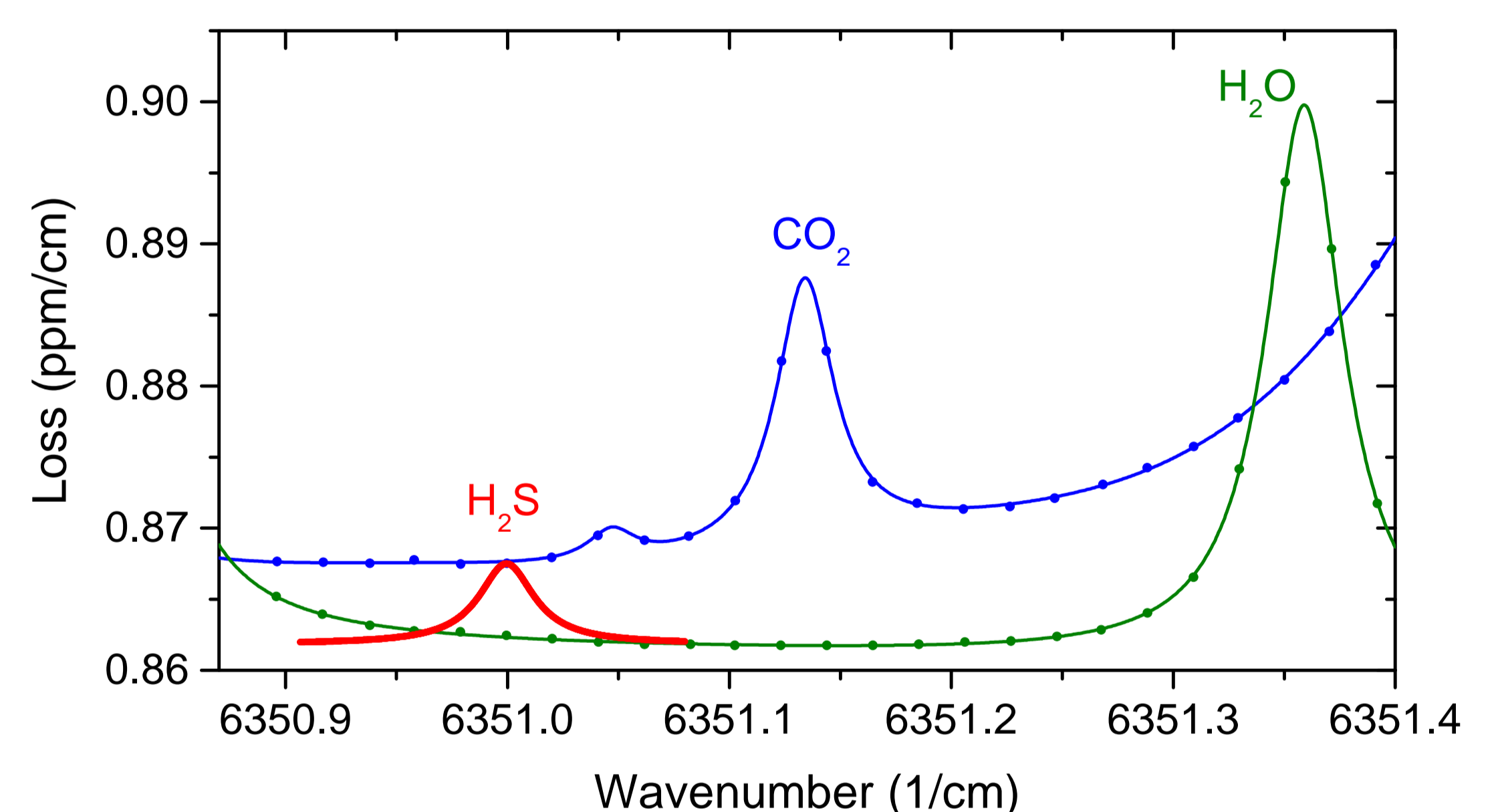


Fig. 2. Cavity-ring-down spectra of 2.66% of H₂O (green curve) and 0.86% of CO₂ (blue curve) in the spectral range used for the H₂S measurements. The spectrum of 448 ppb of H₂S is shown in red for comparison.

Results

- The H₂S line strength at 6351 cm⁻¹ determined to be $S = 1.09 \times 10^{-22}$ cm/molecule ($\pm 5\%$)
- The H₂S detection limit was determined to be 48 ppb (SNR = 2, 1-s measurement time), which is well below the target. This was determined using a sample which contains relatively high concentrations of residual H₂O (1130 ppm) and CO₂ (446 ppm). In practice, with zero gas standards, these impurities (and consequently the spectral interferences) are much smaller, and hence the H₂S detection limit is better.
- The residual (uncompensated) interference of water and carbon dioxide on H₂S were determined to be -1.4 ppb/% H₂O and -5.4 ppb/%CO₂, respectively. Thus, the spectral interferences on zero gas analysis are negligible, unless fast changes of CO₂ appear - see Fig. 4. (CO₂ concentration changes faster than 30 s cannot be compensated for in the present experimental setup).

