Tunable diode laser based absorption spectroscopy for line strength measurements of CO_2 at 2.7 µm – traceability and uncertainty assessment

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Spectroscopic line parameters are frequently measured by broadband techniques like Fourier-transform infrared spectroscopy (FTIR) to derive data for whole spectral bands. Results are collected in databases and are often used for absolute amount fraction determinations or model calculations. FTIR provides an extremely wide spectral coverage, however at the cost of a reduced spectral resolution of 10^{-2} to 10^{-3} cm^{-1}. On the other hand, tunable diode laser absorption spectroscopy (TDLAS) is a measurement technique which is suitable for studying individual absorption lines with higher spectral resolution (in the range of 10^{-4} cm^{-1})[1]. By concentrating on single absorption lines and single line parameters, more accurate measurements might be possible, and a more comprehensive uncertainty assessment can be given. Reliable line strengths of individual lines with corresponding uncertainties can be used as anchor points for the validation of larger data sets, e.g., measured by FTIR spectroscopy[2]. Furthermore, TDLAS has the potential to perform traceable measurements, in this case, to provide traceable line strength values. From the metrological point of view, this is quite important, since traceability increases reliability of the results and through a standardized uncertainty assessment[3] ensures comparability of data obtained from different measurements.

In our present work we combined TDLAS with metrological principles and report line strengths of two $^{12}C^{16}O_2$ lines in the $\nu_1+\nu_2$ band around 2.7 µm[4]. We put special emphasis on traceability and a concise, well documented uncertainty assessment. In our presentation we give a detailed uncertainty budget, discussing individual input quantities that contribute to the line strength uncertainty. We have found that in our experiments the laser tuning coefficient and the gas handling procedure were the two major uncertainty contributors. Smaller, but not negligible uncertainty contributions originate from the temperature, pressure and isotopic composition of the gas sample, path length of the gas cell, emission spectrum of the laser and choice of the line profile function. Relative expanded uncertainties (k = 2, corresponding to 95% confidence level) of the obtained CO_2 line strengths are in the 1-1.3% range. The measured line strength values are in agreement with literature data (line strengths listed in the HITRAN 2008 and GEISA 2011 databases), but show at least a factor of two lower and considerably better defined uncertainties, as well as traceability has been achieved for most of the input parameters. To the best of our knowledge such studies have sparsely been reported before. Line strengths presented here are planned to be used for traceable measurement of CO_2 amount fractions in zero gas standards[5].

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