Investigation of tunable diode laser absorption spectroscopy for its application as primary standard for partial pressure measurements

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Abstract. Partial pressures in vacuum systems can be quite accurately measured by tunable diode laser absorption spectroscopy in the infrared. To examine the possibility for its application as primary standard, for CO\textsubscript{2} in the 2-µm-region we made full traceability to the respective SI unit for each input quantity of the model, evaluated the results according to the ISO guide to the expression of uncertainty in measurement, and validated the method successfully by comparison with gravimetrically produced samples of CO\textsubscript{2} in N\textsubscript{2}.

1. Introduction
The measurement of partial pressures in vacuum is usually accomplished by quadrupole mass spectrometers. These, however, cannot be calibrated in a general way so that the results of a calibration can be used for any given mixture and pressure. They also lack of long-term stability, show non-linearities at higher pressures (> 10\textsuperscript{-4} Pa) \cite{1}, generate residual gases by themselves and dissociate molecules.

Absorption methods in the infrared, on the other hand, do not affect the vacuum under investigation in any sense, promise much higher accuracy, are per se stable in indefinite times, and work well in the pressure range of fine vacuum (0.1 Pa to 1000 Pa), where quadrupole mass spectrometers can only be used with differential pumping schemes.

In an earlier investigation \cite{2} we demonstrated that by tunable diode laser absorption spectroscopy (TDLAS) it is possible to measure partial pressures of CO with high accuracy and acceptable resolution (10\textsuperscript{-5} Pa). We wanted to continue from there and see, if the method is also suitable to build a primary standard. Three tasks had to be fulfilled for this: Obtain a complete traceability to the SI units of all input quantities in the measurement model, calculate the uncertainties associated with the experimental results according to \cite{3} and validate the method in a safe way. It was applied to CO\textsubscript{2} detection.

2. Measurement Model
The measurement model equation is based on the Lambert-Beer law of absorption. For an isolated line, without interference from other absorbing lines and without stimulated emission, it can be written in the form:
\[
I(v) = I_0(v) \exp\left\{ - S \cdot \Phi(v - \nu_c) \cdot n \cdot L \right\}, \tag{1}
\]

where \(I(v)\) is the transmitted intensity at wave-number \(v\), \(I_0(v)\) is the incident intensity entering the absorbing media, \(n\) is the number density of the same, \(L\) is the path length through the absorbing media, and \(S\Phi(v - \nu_c)\) is the absorption coefficient of the absorbing media at wave number \(v\) for the absorption line centered at \(\nu_c\) with \(S\) as the line intensity at 296 K and \(\Phi(v - \nu_c)\) the form function.

Rearrangement of (1) using the ideal gas law and the fact that \(\Phi\) is normalized to 1 over the full wave-number range leads to the absorbance curve area \(A_{\text{line}}\).

\[
A_{\text{line}} = -\int_{-\infty}^{+\infty} \ln\left\{ \frac{I(v)}{I_0(v)} \right\} dv = S \cdot \frac{p}{kT} \cdot L. \tag{2}
\]

The line intensity \(S\) and partial pressure \(p\) are

\[
S = A_{\text{line}} \cdot \frac{kT}{p} \cdot L^{-1} \quad \text{and} \quad p = \frac{A_{\text{line}} \cdot kT}{S} \cdot L^{-1} \tag{3}
\]

respectively. It was necessary to determine the line intensity \(S\) in our laboratory before being able to determine accurate partial pressures, since the uncertainties of \(S\), if given in the literature [4], were too high for our purposes.

It is customary [5] to average the different values of \(S\) from the individual measurements. Having the possibility to vary both \(p\) and \(L\) in our apparatus we could obtain a straight \(A_{\text{line}}\) vs. \([p \cdot L \cdot (kT)^{-1}]\) line, which slope is equal to the line intensity \(S\). Systematic errors may be detected as an intercept. Instead of a simple linear regression analysis we applied a functional-structural linear analysis that delivers parameters which can be consistently interpreted as physical quantities [6].

![Figure 1. Experimental set up of the tunable diode laser absorption spectrometer for partial pressure measurement. From [9] © 2007 IEEE.](image)

3. Experimental
Figure 1 shows the experimental set-up, which is described in detail elsewhere [7]. As light source we used a DFB laser diode emitting around 4987 cm\(^{-1}\). The laser beam was split into three channels. The first served as detector channel after focussing the beam into the UHV Herriott cell, the second to detect the power fluctuations of the laser diode (reference channel), the third to measure the wave number sweep of the laser diode by a free space etalon (wave number or frequency marker channel).

Changing the mirror positions of a multi-reflection Herriott cell [8] the number of reflections can be chosen. The determination of the total path length \(L\) (7 m to 16 m) was accomplished with an uncertainty as low as 0.04% for the configurations realized. The accuracy of the determination of the
laser’s wave number sweep is very crucial to the overall accuracy. The results were verified by cross checking the free spectral range of the etalon with the wave number, respectively wave number “distance” between the CO\textsubscript{2} R(32) and R(33) lines.

The laser wave number was scanned across the absorption line by modulating the current in the laser diode in a triangular pattern at a repetition rate of about 10 Hz. Lock-in technique (chopper frequency 3 kHz) was applied to eliminate the relatively high background due to thermal radiation.

For higher accuracy the zero-transmission reference level was determined independently for each measurement, by admitting enough gas to reach the 100% absorption plateau (Fig. 2). To predict the input intensity on the detection channel, all the channels were also recorded without gas in the chamber.

![Figure 2. Example ([7]) of a scan across the CO\textsubscript{2}-R(12) line. Total (100%) absorption at high pressure (thick black), predicted signal at zero absorption on the sample beam detector (grey), and measured signal on the sample beam detector (thin black). The transformation from time to wave number is not completely linear, but 10 ms roughly corresponds to 1.76·10\textsuperscript{-2} cm\textsuperscript{-1}.](image)

Each transmission spectrum contains 2500 points. Our own developed processing system handled both the recording of data as well as the algorithm to evaluate the line intensities and partial pressures and the calculation of their uncertainties according to [3]. The pressure of the pure CO\textsubscript{2} gas (36 Pa to 136 Pa) and the total pressure in gas mixtures was measured by a capacitance diaphragm gauge (CDG) calibrated on a primary standard for vacuum pressures in our laboratory with a relative uncertainty of 0.3%. The temperature measurement was carried out by two calibrated mini PT100 thermometers located inside the vacuum chamber [7].

4. Results

As already mentioned, before starting partial pressure measurements we measured the line intensity \( S_{R(12)} \). Both \( p \) and \( L \) were varied to get sufficient redundancy of data. Fig. 3 shows the \( A_{\text{line}} \) vs. \( pL\cdot(k_B T)^{-1} \) curve for 28 measurements. The best-fit line passes through the origin with an intercept of 5.8·10\textsuperscript{-5}±1.4·10\textsuperscript{-4} cm\textsuperscript{-1} compatible with zero. The slope of the Functional-Structural linear model gave us the final result for our measurement of the CO\textsubscript{2}-R(12) line intensity as \( S(296 \text{ K}) = (1.2550±0.0062)\cdot10^{-21} \text{ cm/molecule} \) \((k = 1, 26 \text{ degrees of freedom})\).

The validation and application of the presented R(12) line intensity figure has been carried out by measuring the partial pressure in known gas mixtures (Table 1).

| Sample | Gravimetrically prepared | Our measurement |
|--------|--------------------------|-----------------|
| PTB    | (0.051743 ± 0.000046) mol/mol | (0.05170 ± 0.00042) mol/mol |
| BAM C49286 (Bundesanstalt für Materialprüfung) | (1068.0 ± 2.9) µmol/mol | (1064 ± 21) µmol/mol |
5. Discussion and conclusions
With tunable diode laser absorption spectroscopy as a primary standard we showed that it is possible to make traceable and ISO GUM compliant measurements of line intensities, partial pressures and amount of substance fractions (with measured total pressures from secondary standards). The gas absorption line used was in the weaker absorption band of the second harmonic of CO$_2$. With the stronger absorption band it would be possible to reduce the resolution limit from 0.1 Pa here by about a factor of 1000, i.e. our resolution limit would be of the order of $10^{-4}$ Pa.

TDLAS in the manner presented could be used to detect partial pressures of diatomic gas species in the fine vacuum range and up to about 10 kPa of total pressure without the need of calibrating the instrument. It can be used as well to calibrate other partial pressure analyzers in this pressure range. Similar set-ups as ours with reduced size and accuracy might even be promising to replace existing and less stable measurement methods in the fine vacuum regime.

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