

Molecular Line Parameters, Impact on Climate Models and the Quantum-Pascal

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Abstract: Infrared absorption spectroscopy is one of the most powerful techniques for determining gas compositions. A key input parameter for this method is the absorption line strength, which also has a significant impact on atmospheric and climate models. Line strengths can either be determined experimentally, as demonstrated in this work for three of the strongest absorption lines of carbon monoxide (CO), or calculated using ab-initio theoretical methods. Improving and experimentally validating theoretical line strengths offers the fundamental advantage that complete absorption spectra can be calculated with higher accuracy, leading to more reliable spectroscopic knowledge for climate models. At the Physikalisch-Technische Bundesanstalt (PTB), CO absorption line strengths in the fundamental band in the 4.5 μm wavelength range (R8-R10) were experimentally determined at 296 K, yielding values of $4.452(16)\cdot 10^{-19}$, $4.217(16)\cdot 10^{-19}$, and $3.851(15)\cdot 10^{-19}$ cm molecule $^{-1}$ respectively. These results show excellent agreement with the latest theoretical values recently reported by University College London, at sub-percent level. In contrast, line strengths currently used in widely applied databases such as HITRAN deviate from the experimental results by 0.66 %, 1.32 %, and 1.21 %, respectively.

1 Introduction

In this contribution we will exemplify recent achievements made during the Quantum-Pascal project in high-resolution tunable diode laser spectroscopy. To this end, we discuss new absorption line strengths measurements, performed at PTB. Available first data are for line strengths of carbon monoxide in its fundamental band in the 4.5 μm wavelength range. Our data is in excellent agreement with the values predicted by theorists from the University College London (UCL). This data serves as a benchmark for quantum chemistry calculations, which are, in turn, of fundamental relevance to current climate models. With the present measurement design, realized at the PTB, uncertainties of molecular line strengths are foreseen to achieve the sub permille level. Finally, we discuss the close links between the so-called Quantum-Pascal, gas metrology and climate action.

2 Theory

The Lambert–Beer law describes the attenuation of an electromagnetic wave propagating through an absorbing

medium. The fractional loss in intensity, $\frac{I}{I_0}$, over an infinitesimal path length, dL , is given by:

$$dI(\nu) = -\alpha(\nu) I(\nu) dL \quad (1)$$

where $\alpha(\nu)$ is the absorption coefficient given at the frequency ν . Neglecting scattering and other extinction processes, integration yields:

$$I(\nu) = I_0(\nu) e^{-\alpha(\nu)L} \quad (2)$$

The absorption coefficient is proportional to the number density ρ . For a single absorption line centered at ν_0 , this leads to:

$$I(\nu) = I_0(\nu) e^{-\alpha(\nu - \nu_0)\rho L} \quad (3)$$

In tunable laser absorption spectroscopy (TLAS), the laser frequency is ideally scanned across an isolated absorption line, and the integrated absorbance is measured as:

$$A_{\text{line}} = \int -\ln\left(\frac{I(\nu)}{I_0(\nu)}\right) d\nu \quad (4)$$

The frequency-integrated absorption coefficient defines the line strength parameter S as follows:

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$$S = \int \alpha(\nu - \nu_0) d\nu \quad (5)$$

Combining equations (4) and (5) yields the integrated Lambert–Beer law in its logarithmic form.

$$A_{\text{line}} = S \rho L \quad (6)$$

Using the ideal gas law, which is a sufficiently good approximation for the low pressures of several pascals used in this work:

$$\rho = P / (k_B T) \quad (7)$$

with the gas temperature T , the Boltzmann constant k_B and the gas pressure P , the final experimental equation becomes:

$$A_{\text{line}} = S P L / (k_B T) \quad (8)$$

Theoretical line strength parameters are temperature-dependent and are usually given for a reference temperature of 296 K. This temperature was used for the experimental assessment of S in this work, so no further consideration of temperature dependence is necessary.

3 Methods

A tunable laser absorption spectroscopy setup was optimized to measure several of the strongest absorption line strengths of CO. This setup was previously used to measure water vapour absorption line strengths with sub-percentage uncertainties [1]. It now utilizes a quantum cascade laser and a shorter single path cell ($l=29$ mm) which can be evacuated for reference measurements or filled with the absorbing CO gas. The emission frequency of the QCL is tunable over several CO absorption lines of the fundamental band between 2175 cm^{-1} and 2185 cm^{-1} . The frequency-dependent transmission signals measured by fast and highly sensitive photo detectors, are then converted into absorbance and finally numerically integrated to get the measurement parameter A_{line} (Eq. 8). The CO gas pressure and temperature are monitored using a calibrated Capacitive Diaphragm Gauge and multiple calibrated Standard Platinum Resistance Thermometers, respectively. This is summarized as ‘Gas handling’ in Figure 3.1. For the numerical integration of the absorption signal precise knowledge of the relative laser frequency tuning is required. Therefore, the QCL is frequency-locked to a high finesse, indirectly tunable Fabry-Perot resonator, (Scanning FPI in Figure 1) and additionally sent through an evacuated Herriott-Cell (TAC in Figure 1) with an optical path length of 6.4 m, which serves as an optical interferometer which serves as an etalon. Analyzing the fringe pattern of the interference signal gives rise to the absolute frequency tuning of the QCL during TLAS measurements. The experimental setup is integrated into a thermal enclosure stabilized to 296 K using an ultra-stable water bath in combination with several radiators and air fans.

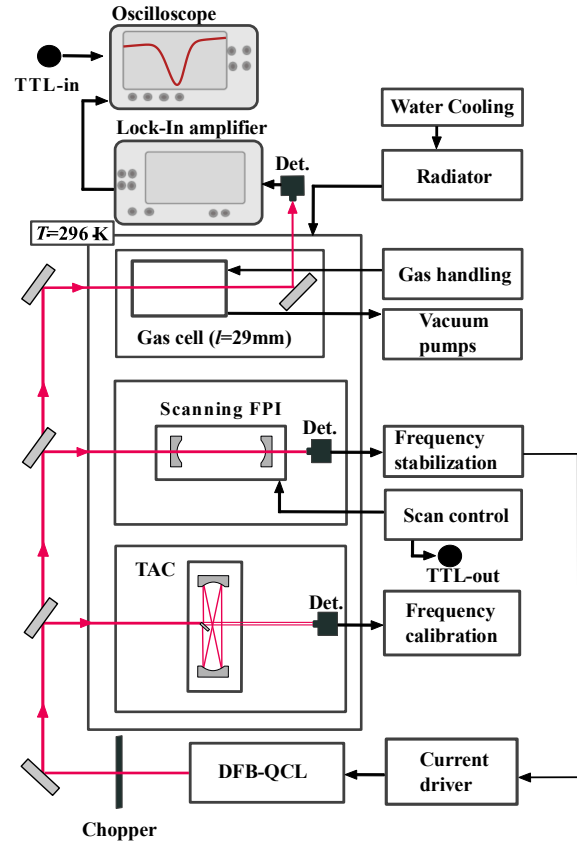


Figure 1: Experimental setup used to perform the line strength measurements for the three different CO absorption lines of the fundamental band.

4 Results

The absorbances of the R8, R9 and R10 absorption lines of the R-branch in the fundamental CO band were measured at different CO pressures between 5 Pa and 50 Pa. Figure 2 illustrates the R branch of the three CO isotopologues with the highest abundance ($^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$) around 2150 cm^{-1} , where the absorption measurements were performed (data taken from the HITRAN API [2]).

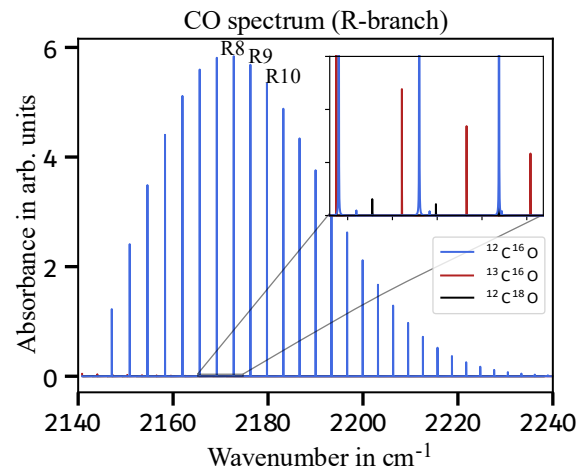


Figure 2: R branch of the three CO isotopologues between 2140 cm^{-1} and 2240 cm^{-1} . Using the TLAS setup in Figure 1, the line strengths of the R8, R9 and R10 absorption lines of the main isotopologue were investigated.

The experimentally obtained, pressure dependent line areas A_{line} (Eq. 8) were analyzed against $PL(k_B T)^{-1}$ as seen in Figure 3. The respective line strengths of the three absorption lines can be obtained from the slopes of the linear fits.

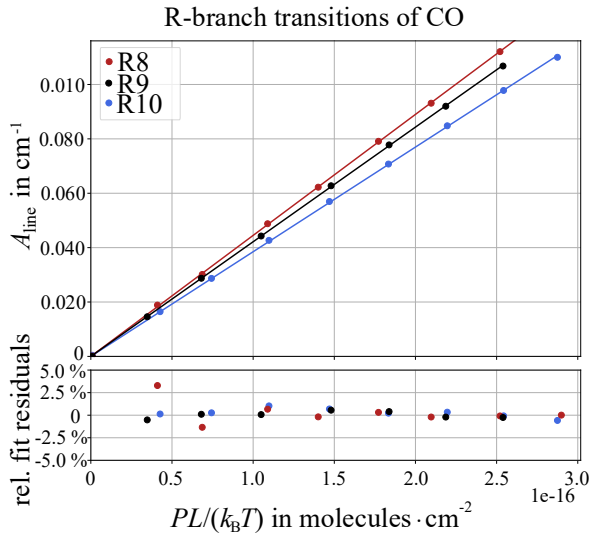


Figure 3: Pressure dependent CO line areas of the R8, R9 and R10 absorption lines. The residuals of the linear fits are shown below the experimental data.

The experimentally obtained line strengths values S are given in Table 1 together with their line positions and the expanded relative measurement uncertainties $\mu_{\text{rel}}(S)$.

Table 1: Experimental results for S at 296.00(2) K

Line	Wavelength in cm^{-1}	S in 10^{-19} cm/molec	$\mu_{\text{rel}}(S)$ in % ($k=2$)
R8	2176.2835	4.452(16)	0.34
R9	2179.7719	4.217(16)	0.37
R10	2183.2238	3.851(15)	0.37

5 Discussion

The experimental results are compared with the theoretical values from the HITRAN2024 database [2] and with the latest calculations from the University College London (UCL) [3] in Table 2.

Table 2: S at 296 K in comparison with theoretical values from HITRAN [2] and UCL [3].

Line	$S/S_{\text{HITRAN}} - 1$	$S/S_{\text{UCL}} - 1$
R8	0.66 %	-0.35 %
R9	1.32 %	0.28 %
R10	1.21 %	0.14 %

The experimentally determined line strengths of the three absorption lines agree with theoretical calculations within the expanded uncertainty and the relative difference between experiment and calculation is better than 0.35 %. The difference between the experimental results presented in this paper and the respective line strengths listed in the HITRAN database is between 0.66 % and 1.32 %, suggesting that the line strengths in the database are slightly too large.

Table 3 shows the exemplary expanded uncertainty budget for the R8 line strengths measurement. The highest contribution to the measurement uncertainty comes from the statistical noise of the data when performing the linear fit (Figure 3). Other significant factors that contribute to the overall measurement uncertainty are the gas pressure and temperature measurements, the gas purity of the commercial CO gas, the laser linewidths of the QCL, the measurement of the optical path lengths of the CO gas cell and finally the isotopologue mixture of the commercial CO gas.

Table 3: Uncertainty budget for R8 line measurement

Quantity	$\mu_{\text{rel}}(S)$ in % ($k=2$)	Type
Linear fit (S)	0.284	A
Pressure	0.120	B
Frequency calib.	0.126	B
Gas purity	0.030	B
Temperature	0.008	A
QCL linewidth	0.006	A
Optical pathlength	0.004	B
$^{13}\text{C}^{16}\text{O}$ contribution	0.004	B

The experiments reported in this paper are embedded in a larger framework at PTB. With the data's relevance for climate sciences, it belongs to the Innovation Cluster for Environment & Climate metrology [4]. With the application of spectroscopy, it also belongs to the QuantumPascal and MQB-Pascal projects [5, 6]. Detailing both aspects is beyond the scope of this paper. However, the determination of metrological traceable molecular line strengths is a core matter of metrology for climate sciences at PTB with various projects and other studies published before [7, 8, 9]. Line strength data impact climate sciences and related climate models wherever spectra and atmospheric transportation of radiation, i.e. sunlight matter. Networks of terrestrial, airborne, and satellite-borne measurement systems

monitor the planet to determine whether climate change is driven by human activity or natural processes. All of these rely on the knowledge of molecular line data, and metrological traceability of an increasing number of them will guarantee the reliability and comparability of the inferred atmospheric conditions.

6 Conclusion

With CO being (only) a greenhouse gas precursor this molecular species often serves as a benchmark for quantum chemical calculations and new measurement approaches [10]. With only two atoms the line strengths are easier to calculate than those of more complex molecular structures directly relevant to climate sciences. Also, for new measurements, the comparably easy to handle CO in spectroscopic experiments provides valuable insight often improving the measurement process.

Improved uncertainties of CO absorption line strengths do come with direct relevance for ongoing metrology research projects. This includes, for example, the current joint research projects PriSpecTemp (22IEM03) [7] and MQB-Pascal (22IEM04) [6] in the European Partnership on Metrology programme [European Association of National Metrology Institutes (EURAMET e.V.), European Partnership on Metrology, [11]]. Within PriSpecTemp, ratios of multiple CO absorption lines are used to determine gas temperatures with high accuracy. This is achieved by means of remote sensing techniques. The reliability of such spectroscopic thermometry critically depends on accurate and metrological traceable line strength data.

In the context of the new realization of the pascal based on density measurements, the lowest uncertainties are currently achieved using Fabry–Perot refractometry (FPR) with pure gases such as helium, argon, and nitrogen. This approach relies on precise measurements of gas refractivity. In comparison, absorption by CO, as investigated in this work, produces a signal which is orders of magnitude stronger and therefore particularly well suited for measurements at very low pressures.

At present, FPR addresses a pressure range from approximately 1 Pa to 300 kPa. The lower limit of this range, around 1 Pa, corresponds to optimal signal-to-noise ratios in the tunable laser absorption spectroscopy (TLAS) measurements presented here for an optical path length of about 1 m. Using the same experimental setup, optical path lengths of up to 100 m have been realized, enabling optimal measurements in the pressure range around 10 mPa.

By employing cavity-based techniques such as cavity ring-down spectroscopy (CRDS) and cavity-enhanced absorption spectroscopy (CEAS), effective optical path lengths of several kilometers can be achieved. This allows precise measurements of correspondingly lower CO partial pressures, extending well into the ultra-high vacuum regime (pressures below 10^{-6} Pa). As a result,

improved uncertainties established by FPR at higher pressures can, at least partially, be transferred to significantly lower pressure ranges.

Furthermore, our line strength results will help improve future CO measurements related to climate sciences and environmentally relevant measurements, e.g., in traffic exhaust assessments.

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