Traceable CO_2-$\mathrm{R}(12)$ Line Intensity for Laser-Spectroscopy-Based Gas Analysis Near 2 μm

Gerardo J. Padilla-Víquez, Jorge Koelliker-Delgado, Olav Werhahn, Karl Jousten, and Detlef Schiel

Abstract—We determined the CO_2-$\mathrm{R}(12)$ line intensity (2-μm region) employing direct absorption spectroscopy improved by several high-accuracy-oriented new developments, with a relative uncertainty of 0.5%, $k = 1$. All the input quantities are traceable and the uncertainty was evaluated *Guide to the Expression of Uncertainty in Measurement* compliant. Our result for the line intensity is in agreement with the high-resolution transmission molecular absorption database value but 1.4% smaller. It was applied to partial pressure measurements of CO_2 in N_2 for samples of gravimetric-traceable known amount of CO_2 fractions. The differences of the results obtained from direct absorption spectroscopy and the gravimetric values were 0.4% or less.

Index Terms—Chemical analysis, infrared (IR) measurements, intensities of molecular spectral lines, IR spectroscopy, molecular spectra, partial pressure measurements, semiconductor lasers.

I. INTRODUCTION

TUNABLE-DIODE-LASER-ABSORPTION-SPECTROSCOPY (TDLAS)-based diagnostics have been employed in a wide range of gas analysis applications in recent years. The accurate measurement of partial gas pressures and gas concentrations are important tasks needed in many different fields like environmental control [1], semiconductor and other industrial processes [2], and medical diagnostics [3]. Carbon dioxide (CO_2) is a compound which plays an important role in all the mentioned fields. The line intensity of the observed transition is the crucial parameter for quantitative analysis of any absorption spectrum and has to be known as accurately as possible.

A comparison of available data shows that the disagreement of reported CO_2 line intensities is frequently $\pm 10\%$ or even larger [4]. The uncertainty in line intensities of the high-resolution transmission molecular absorption database (HITRAN) [5] database could range from $< 1\%$ up to $\geq 20\%$,

G. J. Padilla-Víquez is with the Laboratorio Costarricense de Metrología (Lacomet) Ciudad de la Investigación de la UCR, San Pedro de Montes de Oca, 2050 Costa Rica, on leave from PTB—Berlin, Germany (e-mail: gpadilla@lacomet.go.cr).

J. Koelliker-Delgado is with the Centro Nacional de Metrología (CENAM), Queretaro, 76241 Mexico, on leave from PTB—Braunschweig, Germany (e-mail: jkoellik@cenam.mx).

O. Werhahn and D. Schiel are with the Physikalisch-Technische Bundesanstalt (PTB), D-38116 Braunschweig, Germany (e-mail: Olav.Werhahn@ptb.de).

K. Jousten is with the Physikalisch-Technische Bundesanstalt (PTB) D-10587 Berlin, Germany (e-mail: Karl.Jousten@ptb.de).

depending on the substance, the individual line, and where the results come from. The uncertainties given in the databases or papers are often not evaluated in conformance with the internationally recognized practice stated in the *Guide to the Expression of Uncertainty in Measurement* (GUM) [6]. The Physikalisch-Technische Bundesanstalt (PTB) has started a project to improve the measurements of several CO_2 line intensities, so that they can be measured in a traceable manner and with an accuracy as high as possible. To this end we constructed a three-channel laser spectrometer with several new features, both in hardware and software, which delivered the desired improvements.

II. THEORY

The Lambert–Beer law of absorption, for an isolated line, without interference from other absorbing lines and without stimulated emission, can be written in the form

$$I(\nu) = I_0(\nu) \exp\left\{-k(\nu - \nu_\mathrm{c}) \cdot n \cdot L\right\} \tag{1}$$

where $I(\nu)$ is the transmitted intensity of the radiation at wavenumber $\nu (\nu = 1/\lambda)$, $I_0(\nu)$ is the incident intensity entering the absorbing media, n is the molecular density of the absorbing media (number of absorbing molecules per volume), L is the path length of the radiation through the absorbing media, and $k(\nu - \nu_\mathrm{c})$ is the absorption coefficient of the absorbing media at wavenumber ν for the absorption line centered at ν_c.

The integral over the $k(\nu - \nu_\mathrm{c})$ absorption coefficient in wavenumber domain across a single isolated absorption line is what forms the quantity defined as the line intensity (denoted customarily as S)

$$S = \int_{-\infty}^{+\infty} k(\nu - \nu_\mathrm{c}) d\nu. \tag{2}$$

It is important to remind that although the Lambert–Beer law does not show an explicit dependence on temperature, the spectral absorption coefficients $k(\nu - \nu_\mathrm{c})$ do depend on temperature and therefore the line intensity S also does. It is customary to report the S value at some conventional temperature, like 296 K.

Rearrangement of (1) and substituting (2) leads by

$$A_\mathrm{line} = -\int_{-\infty}^{+\infty} \ln\left\{\frac{I(\nu)}{I_0(\nu)}\right\} d\nu = S \cdot n \cdot L \tag{3}$$
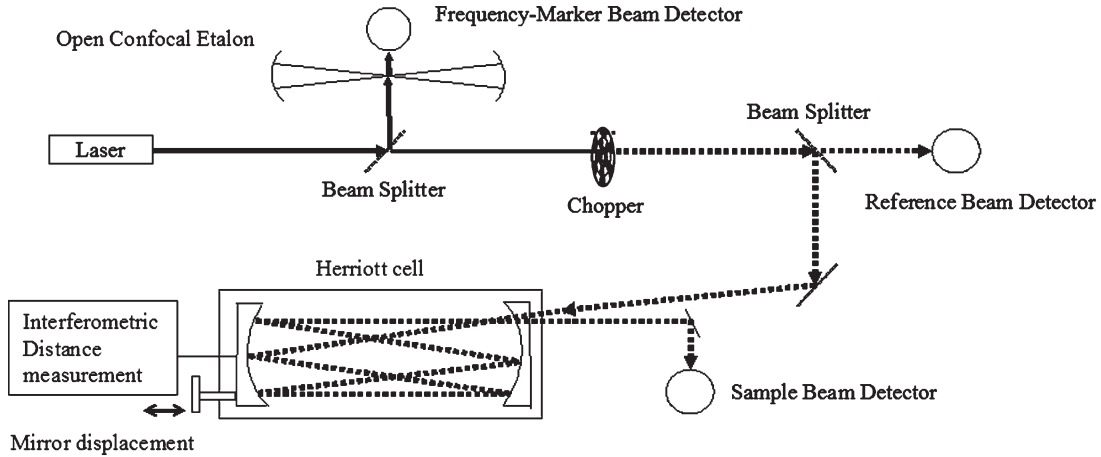
Fig. 1. Schematic representation of our spectrometer.

to the absorbance curve area A_{line}. The molecular density in vacuum conditions can be expressed by the gas temperature T and pressure p employing the ideal gas law, such that

$$A_{\text{line}} = S \cdot \frac{p}{k_{\text{B}} \cdot T} \cdot L \qquad (4)$$

with k_{B} being the Boltzmann constant.

The line intensity S can be determined from measurements of the integrated area A_{line} at different pressures p, temperatures T, and/or path lengths L, with rearrangement of (4)

$$S = \frac{A_{\text{line}} \cdot k_{\text{B}} \cdot T}{p \cdot L}. \qquad (5)$$

It is customary [7] to average the different values of S from the individual measurements.

Nevertheless some authors have analyzed the data as a linear model, applying a linear regression analysis to the A_{line} versus $[p \cdot L \cdot \{k_{\text{B}} \cdot T\}^{-1}]$ curve, whose slope would be equal to the line intensity S. Some kind of systematic errors may be detected as a nonnegligible intercept (note that (4) can be regarded as linear model, with intercept equal to zero). We have gone further on this regard, as linear regression is not the best tool in order to assign physical interpretation to the parameters of the model. Instead, a functional-structural linear analysis delivers parameters which can be consistently interpreted as physical quantities [8], [9], so we have used this tool in analyzing our data.

III. DETERMINATION OF LINE INTENSITY BY TDLAS

A. Experiment

The pressure of the pure (99.995%) CO_2 gas was measured by a capacitance diaphragm gauge (CDG) in the range (36.43 $\pm$ 0.11) Pa to (136.00 $\pm$ 0.41) Pa, the relative uncertainty of the pressure measurements was 0.3% ($k = 1$). The CDG was calibrated on a primary standard for vacuum pressure in our laboratory.

The temperature measurement was carried out by two miniature PT100 thermometers located inside the gas cell and suspended by their four connecting wires. By this, we avoided

to measure the gas cell walls temperature as an indirect method for measuring the gas temperature. This allowed us to reduce the gas temperature uncertainty by two orders of magnitude compared with the earlier situation (and common practice), when only the gas cell walls temperatures were recorded; i.e., we dropped the temperature uncertainty from 0.2% to 0.002% ($k = 1$) [9].

To increase both the accuracy and the sensitivity of the measurement, the absorption path length was maximized by use of a multireflection Herriott cell [10]. Special to our system is that the Herriott cell is installed in an ultrahigh vacuum (UHV) chamber and that the distance of the two spherical mirrors with curvature R can be changed from $R/2$ to R where $R = 1000$ mm nominally. By changing the mirror positions, a suitable number of reflections and absorption path length L can be chosen. L was determined by application of the mathematical properties of a Herriott Cell, which permits to calculate the total path length traveled by the ray for each closed-path configuration. To that end, it is necessary to know the effective radius of curvature of the mirrors of the Herriott cell. We developed a simple technique [9] to traceably measure the radius of curvature of the cell mirrors with an uncertainty of only 0.01% ($k = 1$), without taking the cell apart from its vacuum chamber. With all these measures, the determination of the total path length L was accomplished with an uncertainty varying from 0.07% to 0.04% for the several configurations realized (L varied from (717.78 $\pm$ 0.47) cm to (1613.29 $\pm$ 0.58) cm, $k = 1$).

Fig. 1 shows the experimental setup, which is described in detail elsewhere [9]. As light source, we used a distributed feedback laser diode operated near ambient temperature and emitting around $\nu_{\text{c}} = 4987$ cm^{-1}. The laser beam was splitted into three channels. The first served as detector channel after focusing the beam into the UHV Herriott cell, the second to detect the amplitude modulation and intensity fluctuations of the laser diode (reference channel), the third to measure the wavenumber sweep of the laser diode by a free space (air) etalon specially developed for this application (wavenumber marker channel).

The accuracy of the determination of the laser's wavenumber sweep is very crucial to the overall accuracy. For this reason,
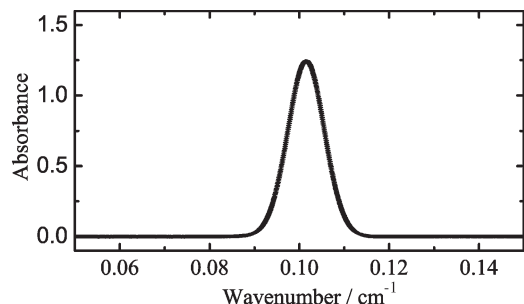
Fig. 2. Example of a laser sweep across the CO$_2$-R(12) line: absorbance $-\ln(I/I_0)$ versus wavenumber ν.

Fig. 3. Measured absorbance curve areas for the CO$_2$-R(12) line centered at 4987.3 cm^{-1}. The line intensity $S_{\mathrm{R}(12)}$ was determined from the slope of the dashed functional-structural line.

great care was taken to determine this *in situ* and in real time during the measurements of A_{line}. The results were verified by cross checking the free spectral range (FSR) of the etalon with the wavenumber distance between the CO$_2$ R(32) and R(33) lines, close to the R(12) line. The FSR of our etalon was (0.010375 ± 0.000016) cm^{-1} $(k = 1)$.

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

In order to increase the accuracy of the transmission (i.e., absorbance) measurements, the zero-transmission reference level was determined independently for each measurement, by admitting enough gas in the chamber until the 100% absorption plateau was evident and recorded. Furthermore, all the channels were recorded also without gas in the chamber, before and after the absorption measurements, in order to construct a transformation function to predict the input intensity of the detection channel based on the simultaneous measurement of the reference channel.

Each transmission spectrum contains 2500 points and is the mean of 70 individual spectra taken within 10 s. The temperature and pressure readings were performed in real time, almost simultaneously with each transmission spectrum.

We developed an "Integrated Processing System for Integrated Absorbance Measurements" (IPSIAM) which handled the automatic reading and recording (on PC) of all the input quantities (spectra, pressures, temperatures) as well as their later analysis to find the line intensities (with pure gas) or partial pressures (with gas mixtures). These programs incorporated in full detail the necessary steps to calculate the uncertainties according to GUM and required minimal intervention by the operator (high automatization level). Given the high density of digitalization points for the spectra, and the complete coverage of the absorption line including its "wings," we implemented in IPSIAM a direct numeric integration method to find A_{line}, avoiding any spectral line profile fit.

B. Results

Fig. 2 shows, as an example, one of our absorbance measurements across the CO$_2$-R(12) line. The bars for the standard uncertainties at both axes are not visible since they are quite
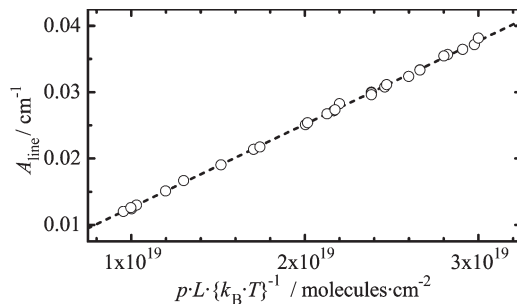
small compared to the size of the symbols and the scale of the drawing. Both p and L were modified to get sufficient redundancy of data. The measured gas temperature exhibited also small fluctuations around the average room temperature, so that all the measured integrated absorbances $A_{\mathrm{line}}(T)$ were corrected to a reference temperature $T_0 = 296$ K using a linear model for our range of temperatures [5], [9].

A total of 28 independent measurements were analyzed to find the $S_{\mathrm{R}(12)}$ value. Fig. 3 shows the A_{line} versus $[p \cdot L \cdot \{k_{\mathrm{B}} \cdot T\}^{-1}]$ curve for the 28 measurements. If the best fit line does not pass through the origin, this would indicate possible systematic offset errors. Our measurement series, however, were compatible with the assumption that $A_{\mathrm{line}}([p \cdot L \cdot \{k_{\mathrm{B}} \cdot T\}^{-1}] = 0) = 0$, because from the functional-structural analysis, we obtained an intercept b which was smaller than its standard uncertainty

$$b = 5.8 \cdot 10^{-5} < 1.4 \cdot 10^{-4} = u(b).$$

The slope of the functional-structural model gives us the final result for our measurement of the CO$_2$-R(12) line intensity $S(T_0)$ at reference temperature $T_0 = 296$ K

$$\mathrm{R}(12) : S(T_0) = (1.2550 \pm 0.0062) \cdot 10^{-21} \text{ cm/molecule}$$

$$(k = 1 \text{ with 26 degrees of freedom}). \tag{6}$$

The relative uncertainty of our measurement of the CO$_2$-R(12) line intensity (line center at $\nu_{\mathrm{c}} = 4987.3087$ cm^{-1}, [5]) is therefore 0.49% $(k = 1)$. Our measurement is 1.4% smaller than the corresponding HITRAN value [5], but in agreement with HITRAN given the large uncertainty of that value, as can be seen in the comparison of Table I. In that table, the "Direct" column presents the result given by applying (5) directly to each individual measured A_{line} value and averaging the 28 measurements (after temperature-correction to $T_0 = 296$ K). We applied functional-structural linear analysis because the slope is interpreted as a physical quantity—S. Regression analysis delivers in general two different possible values for the slope, although in this case both values $(1.2549 \pm 0.0062) \cdot 10^{-21}$ cm/molecule and $(1.2557 \pm 0.0062) \cdot 10^{-21}$ cm/molecule., are statistically compatible with the functional-structural result [8], [9].

TABLE I
MEASURED CO_2-R(12) LINE INTENSITY $S_{R(12)}$

Parameter	Direct	Slope	HITRAN
$S_{R(12)}/\ 10^{-21}$ cm·molec^{-1}	1.2582	1.2550	1.273
u_r / % ($k = 1$)	± 0.77	± 0.49	± (2 to 5)
Deviation from HITRAN / %	-1.2	-1.4	--

TABLE II
COMPARISON OF CO_2 PARTIAL PRESSURE MEASUREMENTS

Sample	Gravimetric-reference value of CO_2 / %	TDLAS-absolute measurement of CO_2 / %	Relative Difference
BAM-C49286	0.10680 ± 0.00029	0.1064 ± 0.0021	-0.37 %
PTB-mixture	5.1743 ± 0.0046	5.170 ± 0.042	-0.08 %

IV. APPLICATION TO PARTIAL PRESSURE MEASUREMENTS

The validation and application of the presented R(12) line intensity measurement has been carried out by measuring the partial pressure and the amount of CO_2 fraction in gas mixtures with well known content. These experiments were performed with the same apparatus and in addition with a second spectrometer setup [11]. For the partial pressure measurements, we proceeded exactly as for the line intensity measurements, except that at the end the IPSIAM system calculated the partial pressure under knowledge of the proper line intensity, given by (6), and using a rearrangement of (5)

$$p = \frac{A_{line} \cdot k_B \cdot T}{S \cdot L}. \tag{7}$$

The amount of CO_2 fraction was calculated by the ratio of CO_2 (partial) pressure p, given by (7), to the measured total gas pressure P_{total} (directly measured with the CDG).

We measured the partial pressure of CO_2 in two mixtures: A sample of the mixture coded C49286, prepared by the Bundesanstalt für Materialprüfung (BAM), which is a certified reference gas mixture of (1068.0 ± 2.9) µmol/mol (0.1068%) of CO_2 in N_2; and a PTB gravimetrically prepared sample of (0.051743 ± 0.000046) mol/mol (5.1743%) of CO_2 in N_2. The reported uncertainties are standard uncertainties $(k = 1)$. These two values are traceable to mass standards through the gravimetric preparation process.

The absolute measurements of the CO_2 partial pressures of these two samples, using our system, were 0.1064% ± 0.0021% for the BAM-C49286 sample and 5.170% ± 0.042% for the PTB sample $(k = 1)$. Our results are, respectively, only 0.37% and 0.08% smaller than the gravimetric-reference values. Table II summarizes the results of the partial pressure measurements. The reported uncertainties were evaluated taking into account the uncertainties of all the input quantities of our measurement model, as required by the GUM. Detailed information of the uncertainty evaluation is given elsewhere [9]. It is worth noting the statistical confirmation of the GUM-compliant uncertainty determination of our measurements. For instance, we realized 15 independent measurements of the PTB sample. The average of the 15 standard uncertainties found by IPSIAM for the 15 CO_2 partial pressure measurements was 0.0394%, while the standard deviation of the 15 CO_2 partial

pressure measurements was 0.0392%, i.e., the statistical dispersion of results confirmed the correctness of the uncertainty evaluation according to GUM.

V. DISCUSSION AND CONCLUSION

Integrated absorption spectroscopy is a measuring technique that can be used to make traceable measurements of line intensities, partial pressures, and amount of substance fractions. To this end, several conditions must be met in several fields including the experimental setup, the processing system, and the implementation of a measurement assurance program capable to demonstrate the traceability of the measurement results. We have demonstrated this possibility by setting up a 3-channel TDLAS spectrometer, the development of our IPSIAM software, and the implementation of the key elements of a measurement assurance program as part of our experiment.

Our system was capable to measure the R(12) line intensity of CO_2 of the $\nu_1 + 2\nu_2 + \nu_3$ band near 2 µm with an expanded relative uncertainty of 1.0% ($k = 2$, about 95% level of confidence), and of 1.4% for individual measurements; which signifies an improvement in the level of accuracy of a factor of 4 (probably a factor of 10) in terms of the uncertainty figures given in HITRAN [5]; but even more important, it represents a strong quality improvement in traceability for these types of measurements.

The application of the CO_2-R(12) line intensity value to the TDLAS absolute measurement of partial pressures of CO_2 in N_2 was successful and demonstrated the equivalence of two different traceability chains for the same measurand (partial pressure or amount of substance fraction): one to mass standards (gravimetric values) and the other to pressure and temperature standards (TDLAS values).

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Jorge Koelliker-Delgado received the degree in chemical engineering from Celaya Institute of Technology, Celaya, Mexico, in 1993, the Master's degree in environmental engineering from Instituto Tecnologico y de Estudios Superiores de Monterrey, Monterrey, Mexico, in 1995, and the Doctor's degree from Technical University of Braunschweig, Braunschweig, Germany, in 2006.

Since 1997, he has been working with the National Metrology Center of Mexico, where he performs measurement services and research in the field of gas analysis. His main fields of research are environmental measurements and spectroscopy.

Olav Werhahn received the Diploma in physics from University of Hanover, Hannover, Germany, in 1995 and the Dr. rer. nat. degree from University of Göttingen, Göttingen, Germany, in 1999.

From 1996 to 1999, he was with the Max-Planck-Institute for Flow Research, Göttingen, working on the infrared (IR) spectroscopy of hydrogen-bonded clusters. Since 2000, he has been with the German NMI, PTB, Braunschweig, Germany. He worked on projects devoted to laser safety and laser spectrometry. He is currently working on laser-spectrometric methods in gas analysis for the Department of Metrology in Chemistry.

Karl Jousten received the Ph.D. degree in physics from University of Heidelberg, Heidelberg, Germany, in 1987.

From 1985 to 1990, he was working on a new gaseous field ion source for nanobeams in Heidelberg and on the high-frequency modulation of a liquid metal ion source at the Oregon Graduate Center, Corvallis. Since 1990, he has been working in the field of vacuum metrology with PTB, Berlin, Germany, heading this section since 1992. In 1993, he started a project of the exploration of laser-absorption spectroscopy in the IR for measurement of partial pressures in fine and high vacuum. This paper is the latest result of these investigations.

Gerardo J. Padilla-Víquez received the M.Sc. degree from Costa Rica University, San Pedro, Costa Rica, in 1999 and the Ph.D. degree from Technical University of Berlin, Berlin, Germany, in 2005, both in physics.

From 2002 to 2005, he was working on the investigation of tunable-diode laser-absorption spectroscopy (TDLAS) for its application to partial pressure measurements at the vacuum metrology laboratory of the National Metrology Institute (NMI) of Germany—Physikalisch-Technische Bundesanstalt (PTB), Berlin. Since 1994, he has been working in several fields of metrology with the NMI of Costa Rica—Laboratorio Costarricense de Metrología (Lacomet), mainly in the area of pressure metrology, heading this laboratory from 1994 to 2001. Currently, he is Chief of the Physical Metrology Department at Lacomet and Teacher of Physics and Metrology at the Costa Rica University.

Detlef Schiel received the Diploma in chemistry and the Dr. rer. nat. degree, both from Technical University of Braunschweig, Braunschweig, Germany, in 1975 and 1980, respectively.

Since 1979, he has been with the German NMI, PTB, Braunschweig, working in the fields of IR and Raman spectrometry. Since 1988, he has been Head of the working group for inorganic analysis, he is currently responsible for the development of primary methods of measurements in inorganic and gas analysis by means of thermal ionization mass spectrometry, inductively coupled plasma mass spectrometry, inductively coupled plasma optical emission spectroscopy, and TDLAS in the department of Metrology in Chemistry.