Broadband and highly sensitive comb-assisted cavity ring down spectroscopy of CO near 1.57 μm with sub-MHz frequency accuracy

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Abstract

A self-referenced frequency comb has been combined with a Cavity Ring Down (CRD) spectrometer to achieve a sub-MHz accuracy on the derived positions of the absorption lines. The frequency emitted by the Distributed Feedback (DFB) laser diode used in the spectrometer, was obtained from the frequency of its beat note with the closest mode of the frequency comb. This delivers excellent frequency accuracy over a broad spectral region with sensitivity (Noise Equivalent Absorption) of 1×10^{-11} cm^{-1} $Hz^{-1/2}$.

This set up is used to measure the absorption spectrum of CO over a wide range corresponding to the 3−0 band (6172.5−6418.0 cm^{-1}). Accurate values of line centers are measured for a total of 184 lines of four CO isotopologues, namely $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{12}C^{17}O$ present in "natural" abundances in our sample. The measurements include the first extensive study of the 3−0 band of $^{12}C^{18}O$ and $^{12}C^{17}O$, of the 4−1 hot band of $^{12}C^{16}O$ and the detection of new high-J transitions of the 3−0 band of $^{12}C^{16}O$ up to J= 34. The line centers were corrected for the self-pressure shift and used to derive the upper state spectroscopic parameters. The obtained standard deviation of about 300 kHz and 500 kHz for the 3-0 band of $^{12}C^{16}O$ and of the minor isotopologues, respectively, is a good estimate of the average accuracy of the reported line centers. The resulting 3−0 line list of $^{12}C^{16}O$ provided as Supplementary Material includes 69 reference line positions with a 300 kHz accuracy for the 6183−6418 cm^{-1} region.

1.   Introduction

The ability to measure frequencies of transitions with a high accuracy is important in order to obtain traceable reference spectra and provide frequency references. An increasing number of demanding applications also drives this need for frequency standards. For example, the detection of terrestrial mass planets around M dwarfs, and radial velocity surveys with high-resolution spectrographs in the near-infrared (NIR) show a growing interest and require wavelength reference standards in the whole 1.0–1.8 µm wavelength region [1]. Sounding of the greenhouse gases by active methods also requires frequency uncertainties to be minimized in order to reach the targeted precision on gas column densities [2]. This is especially the case with the measurement of atmospheric CO_2 at 1.6 µm where frequency errors of online lasers need to be lower than ±0.3 MHz to ensure a 0.25% precision [2]. Moreover as noticed in a recent IUPAC technical report on water transitions [3]: *Lack of calibration standards is identified as hindering the accurate determination of water energy levels*

The accurate line-center retrieval is of fundamental importance in optical communications, where there is the need of wavelength references for the wavelength-division multiplexing (WDM) systems. Much work has thus been devoted to provide reference frequencies in the C-band (6390–6536 cm^{-1}) which is the most used band for optical fiber communication [4,5 and references therein]. The P16 $\nu_1+\nu_3$ line position of $^{13}C_2H_2$ known with a 0.1 MHz standard uncertainty has been adopted by the Comité International des Poids et Mesures (CIPM), as a recognized reference for absolute optical frequency in the spectrum [6]. The $^{12}C_2H_2$ and $^{13}C_2H_2$ isotopologues of acetylene provide reference frequencies in the 1510–1550 nm (6450–6620 cm^{-1}) region [5,7]. These acetylene frequencies have been measured at a few kHz level using Doppler-free spectroscopic techniques, like saturation spectroscopy [5]. However, saturation requires high optical powers and strong absorption lines, limiting the spectral coverage.

Until recently, very few accurate near infrared frequency references were available outside the C–telecom band [8]. Picqué et al. [9] measured positions of 36 transitions with a ± 1 MHz accuracy from Fourier transform spectra calibrated with reference acetylene lines. In order to provide wavelength references covering the L band for optical fiber communication (6154–6390 cm^{-1}), Swann and Gilbert [10] reported positions for 14 and 18 lines of the same 3−0 band for the $^{12}C^{16}O$ and $^{13}C^{16}O$ isotopologues, respectively with an accuracy of a few tens MHz. For this purpose, the diode laser light was frequency doubled and used for saturation spectroscopy of transitions of rubidium, known with ±0.4 MHz accuracy.

In recent years, frequency combs (FC) have allowed considerable developments for measurements of transition frequencies with sub MHz uncertainties. Using Pound-Drever-Hall-locked frequency-stabilized Cavity Ring Down Spectroscopy (FS-CRDS), Domysławska et al. [11] reported position uncertainties between 0.9 and 2.9 MHz for the oxygen B-band near 14450 cm^{-1}. With the same FS-CRDS approach, Truong et al. [12] measured the frequency of one CO_2 transition near 6336 cm^{-1} with an uncertainty of ~9 kHz while, very recently, Long et al. reported $^{12}C^{16}O_2$ transition frequencies at the kHz-level from 1.6 to 7.8 µm [13]. As far as a high sensitivity is not required, dual comb spectroscopy as proposed by Zolot et al. [14] can provide broad-band frequency references in the near infrared. In their work, the Doppler-limited spectra of methane and acetylene were recorded with a comb tooth resolved dual comb spectroscopy. Methane and acetylene line positions were reported with 0.2 MHz accuracy in the 5870–6130 cm^{-1} and 6430–6630 cm^{-1} region, respectively.

We recently developed a comb-linked CRDS spectrometer relying on the measurement of the beat note frequency between one of the modes of a self-referenced frequency comb (SRFC) and a small part of the light emitted by a Distributed Feedback (DFB) laser diode used as a source for CRDS. The frequency measurements are performed "on the fly" with no stabilization of the length of the CRDS cell and no locking of the laser frequency to the CRDS cavity, which makes this approach simpler than FC linked-FS-CRDS [11,12,13]. With this system, we could determine line frequencies with accuracy as good as 20 kHz by averaging several spectra of $^{12}C_2H_2$ transitions near 1.5 µm [15]. As a result, the developed CRD spectrometer offers excellent performances both in terms of frequency accuracy and sensitivity (noise equivalent absorption, α_{min}, better than 1×10^{-10} cm^{-1}). The same simple method of accurate frequency calibration of our CRDS spectra can be applied to the set of 90 DFB laser

diodes at our disposal allowing for routine CRDS recordings with high frequency accuracy over a broad spectral region from 1.26 to 1.72 μm. Our comb approach is used here over a broad spectral range to complete existing NIR reference measurements in the region with sub-MHz accuracy frequency measurements of CO transitions over the whole 6170–6420 cm^{-1} spectral range.

After a description of the experimental setup (Part 2), we will detail the data analysis in Part 3. In Part 4, the accuracy of the line centers will be estimated. Part 5 will be devoted to a comparison to previous studies of the CO bands under consideration.

2.   Experimental setup

A detailed description of our fibre-connected CRD spectrometer can be found in Refs. [16,17,18]. The 1.40-m long CRD cell is fitted with high reflectivity mirrors leading to ring down times up to 700 μs. Noise equivalent absorption coefficients at the 5×10^{-11} cm^{-1} level are routinely achieved [19,20,21]. As mentioned above, DFB laser diodes are used as light sources. Each of them allows for a 30 cm^{-1} spectral coverage by changing continuously the laser temperature from -10°C to 60°C. In this work, an Er-based 100-MHz SRFC (FFS model from Toptica) is coupled to the CRD spectrometer to provide absolute calibration to the frequency axis of the recorded spectra.

A fraction of the DFB laser light (~10%) is sent into a commercial Fizeau type wavemeter (HighFinesse WSU7-IR, 5 MHz resolution, 20 MHz accuracy over 10 hours) to measure the emitted frequency with a typical refresh rate of 100 Hz. Another fraction (10%) is superimposed to the SRFC onto an InGaAs photodiode (100 MHz band width) to obtain a beat note frequency, f_{bn}, between the DFB laser frequency and the nearest mode of the comb. A fast acquisition card (250 MHz-16 bits, by GAGE) is used to digitize the beating note. The beat note frequency is then determined at a 3 kHz repetition rate using a peak determination procedure after Fourier transform. At each determination, the measured frequency of the DFB laser, v_{meas}, is retrieved from:

$$v_{meas} = f_{CEO} + nf_{rep} \pm f_{bn}$$
Eq. 1

The f_{CEO} and f_{rep} radiofrequencies (RF) are the carrier-envelope offset frequency [22] and the repetition rate of the SRFC which are stabilized to 20 MHz and 100 MHz, respectively, using a 10 MHz rubidium frequency standard with a relative instability of 10^{-12} in one second. The comb order n is retrieved from the frequency measurement given by the wavemeter, whose accuracy is better than half the comb mode spacing. The sign of f_{bn}, which may vary during the frequency scans of the DFB, is assigned from that of the first derivative of $f_{bn}(t)$. When the DFB laser frequency is monotonically increasing over time, an increasing value of f_{bn} corresponds to a beating between v_{meas} and the comb mode n with $nf_{rep} + f_{CEO} < v_{meas}$, leading to a positive sign for f_{bn}. On the other hand, a decreasing value of f_{bn} over time corresponds to a beating between v_{meas} and the comb mode n+1 with $(n+1)f_{rep} + f_{CEO} > v_{meas}$, leading to a minus sign for f_{bn}. The uncertainty of the v_{meas} frequency is limited by the determination of f_{bn} measured with an uncertainty of about ±400 kHz mainly coming from the jitter of the DFB source during the beat note measurement. According to the fact that a line is typically described by 100 spectral points, inside its full width, the uncertainty on the line center determination is expected to be 10 times better. However the shot to shot noise of the ring downs also affects this determination, thus increasing the uncertainty on the line position to typically a few hundreds of kHz as described in the following.

The CRDS cell was filled with high purity carbon monoxide (Alphagaz 99.997 % stated purity) at three pressures (0.020, 1.00 and 10.0 mbar) depending on the intensity of the lines to be measured. The ring-down cell temperature and pressure were monitored during the spectrum acquisition by temperature sensors (TSic 501, IST-AG, ±0.1°C accuracy) fixed on the cell surface and two capacitance gauges (model 626B from MKS Instruments; 1 Torr and 10 mbar, 0.25% accuracy of reading), respectively. The spectra were recorded at temperatures remaining within 296.8 ± 0.3 K.

Figure 1 illustrates the achieved sensitivity coming with a dynamic range of four orders of magnitude. The noise equivalent absorption coefficient is at the 6.5×10^{-11} cm^{-1} level with no averaging

of the ring downs. The investigated spectral region, 6172.5–6418.0 cm^{-1}, was covered by the use of 12 DFB laser diodes, as illustrated in Figure 2 where an overview of the measured CO transitions is presented. The high dynamic range offered by our instrument and the use of various values for the total pressure of carbon monoxide, from 0.02 to 10 mbar, allow us to determine the positions for transitions with intensities ranging from 5.1×10^{-29} to 2.2×10^{-23} cm/molecule, i.e. over more than 5 orders of magnitude. A total of 184 line positions were accurately measured for four CO isotopologues, namely $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{12}C^{17}O$ present in "natural" abundances in our sample. As discussed below the average accuracy of these positions is better than 500 kHz, favorably comparing with previous determinations: these are limited in number to 32 positions from [10] and 36 from [9] with an estimated uncertainty from 12 to 30 MHz and of 1 MHz, respectively (see Figure 2).

To the best of our knowledge, the present measurements are the first extensive ones for the 3−0 band of $^{12}C^{18}O$ and $^{12}C^{17}O$ and the 4−1 band of $^{12}C^{16}O$. This is a remarkable result if one considers that the natural isotopic abundance of $^{12}C^{17}O$ is only 3.68×10^{-4} [23].
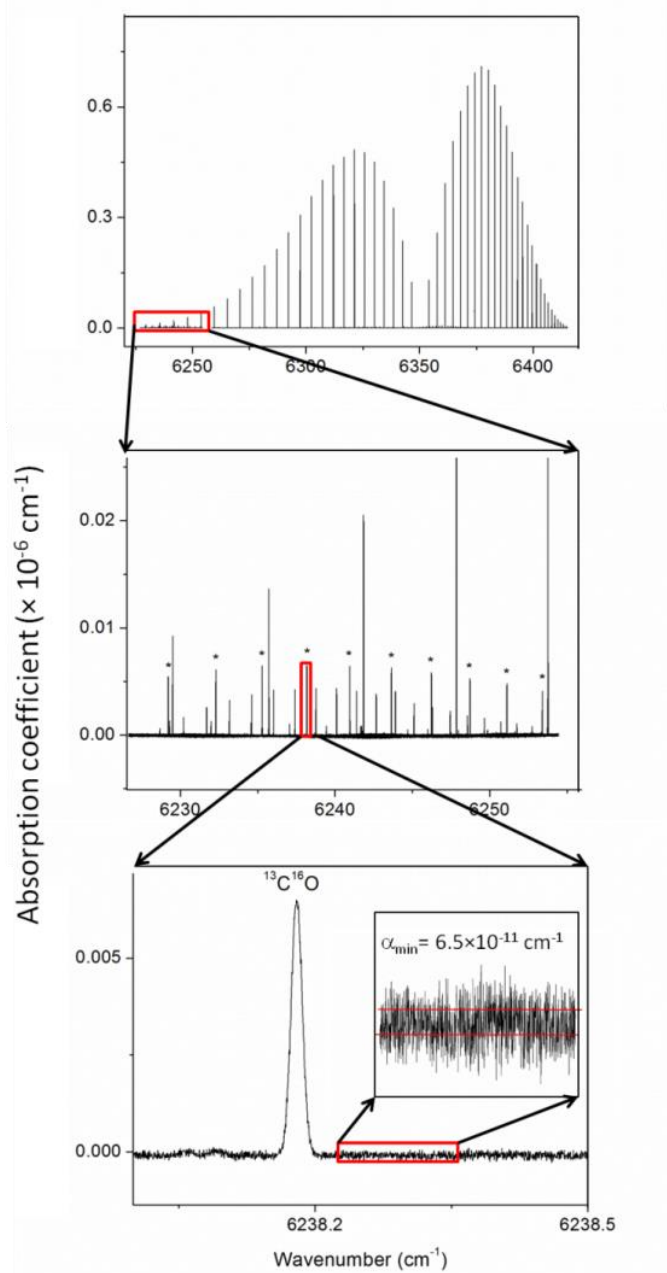

Figure 1. CW-CRDS spectrum of carbon monoxide in natural abundance in the region of the 3−0 band of $^{12}C^{16}O$ (P = 0.02 mbar). Three successive enlargements illustrate the high sensitivity and high

dynamic range of the recordings (noise equivalent absorption on the order of 6.5×10⁻¹¹ cm⁻¹). The stars in the middle panel mark the ¹³C¹⁶O lines of the 3−0 band.
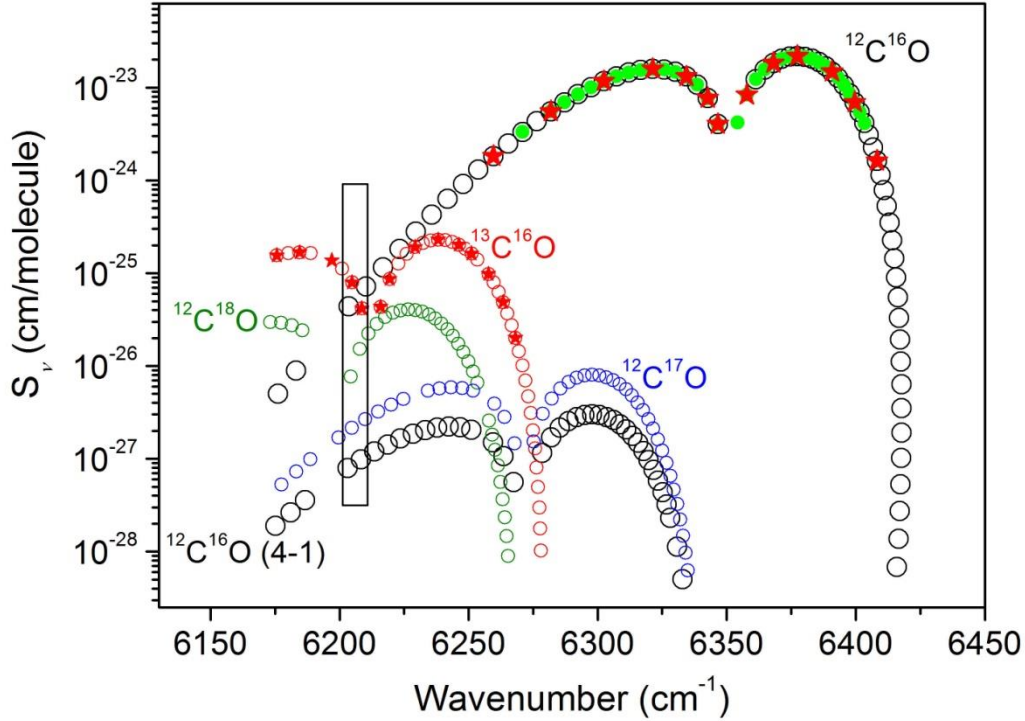

Figure 2. Overview of the CO transitions measured in this work (open circles) and comparison with literature data. Line positions of the 3-0 band of ¹²C¹⁶O were reported by Swann and Gilbert (red stars) [10] and Picqué et al. (green full circles) [9]. Some 3-0 ¹³C¹⁶O line positions were also determined by Swann and Gilbert (red stars) [10]. The rectangle highlights the 6201-6211 cm⁻¹ region where are located twelve lines analyzed by Wójtewicz et al. [24].

3.   Line position determination
3.1.   Fitting procedure

The different spectra were fitted using an interactive least squares multi-line fitting program (http://fityk.nieto.pl/) assuming a Voigt profile with the Gaussian component fixed to the theoretical value of the Doppler broadening. The fitting program provides the line center and the corresponding integrated absorption coefficient, A_{ν_0} (cm⁻²). The line intensity, S_{ν_0} (cm/molecule), of a rovibrational transition centered at ν_0, was obtained from:

$$A_{\nu_0} = \int_{line} \alpha(\nu)d\nu = PS_{\nu_0}(T)/kT \qquad \text{Eq. 2}$$

where ν is the wavenumber in cm⁻¹; $\alpha(\nu)$ is the absorption coefficient in cm⁻¹ obtained from the cavity ring down time, τ (in s): $\alpha(\nu)=1/c(1/\tau - 1/\tau_0)$ where c is the speed of light and τ_0 is the ring down time of the empty cavity; P and T are the measured pressure and temperature, respectively, and k is the Boltzmann constant.

Most of the line parameters determined in this work were derived from the 1.00 mbar spectra. For the weakest lines of the 3−0 band of ¹²C¹⁶O ($R(J)$ lines with $J \geq 28$), the 10.0 mbar spectra were used while the spectra at 0.02 mbar were used to retrieve the line parameters of the strongest 3-0 ¹²C¹⁶O lines ($P(J)$ lines with $J \leq 22$ and $R(J)$ lines with $J \leq 24$). Indeed, for these strong transitions, at higher pressures, the light transmitted through the CRD cell was insufficient for accurate estimation of the

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ring down time. In case of multiple determinations of the line parameters due to partial overlapping between the spectral intervals covered with successive laser diodes, the average value was adopted.

3.2. Pressure-shift corrections

In spite of the low pressure values of the recordings, the self-pressure shifts of the line center have to be considered in order to get accurate line centers in the zero pressure limit. In Ref. [9], Picqué et al. reported self-pressure shifts varying between -250 to -100 kHz/mbar for 36 lines of the 3−0 band of $^{12}C^{16}O$ with J values up to 19 (see Fig. 3). These values, reported with an uncertainty of about 30 kHz/mbar, were adopted to extrapolate our line positions at zero pressure for the same band of the same isotopologue, leading to significant corrections for the line centers retrieved from recordings at 1.0 and 10.0 mbar. For the high J lines, not measured in [9], we used values extrapolated from a linear fit of the measured pressure shifts between m = -6 to -17 and m = 6 to 20, respectively (see Figure 3) (m is −J in the P branch and $J+1$ in the R branch). It is important to notice that the extrapolated pressure shifts for the R branch are consistent with the pressure shift values that we could estimate from our spectra recorded at 1 and 10 mbar for the R29−R37 transitions (see Figure 3). These lines are mainly very weak high J lines. The error bar given on Fig. 3 result from the uncertainty on the determination of these line positions.

As showed in Fig. 3, pressure shifts reported in [9] are in a very good agreement with the less complete data set determined by Swann and Gilbert in [10] for 14 and 18 lines of the 3−0 band of $^{12}C^{16}O$ and $^{13}C^{16}O$, respectively. In this latter work, very similar pressure shifts were measured for $^{12}C^{16}O$ and $^{13}C^{16}O$ showing no isotopic dependence (Figure 3). We thus adopted the $^{12}C^{16}O$ values of Ref. [9] to correct the 3−0 line positions of the minor CO isotopologues.

The pressure shift values measured in [9] and [10] are in good agreement with the work of Jacquemart et al. [25] but deviate systematically by about 50 kHz/mbar from those reported by Sung and Varanasi in [26]. This difference may results in a systematic bias of -50 kHz on the center at zero pressure of the lines measured at 1 mbar.
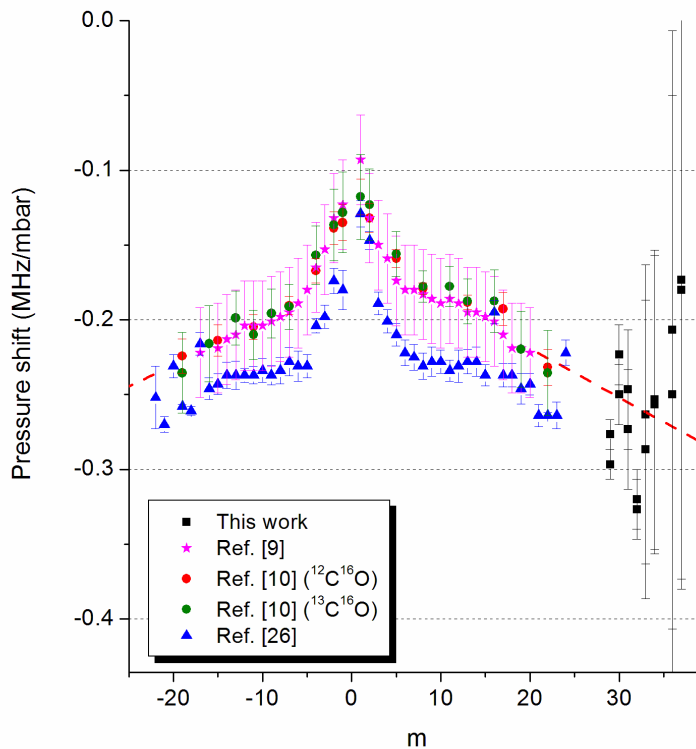
Figure 3. Pressure shifts for different transitions of the 3–0 band of $^{12}C^{16}O$ measured in Refs. [9] (pink stars), [26] (blue triangles), [10] (red circles) and in this work for high J values (black squares). Dashed lines correspond to high J extrapolations of the pressure shift values measured in [9]). $^{13}C^{16}O$ values from Ref [10] are also displayed (green circles).

The literature review included in Refs. [26] and [27] indicates that the self-pressure line shifts in the 1–0, 2–0 and 3–0 bands of $^{12}C^{16}O$ increases significantly with the vibrational excitation. For the newly observed 4–1 band, we adopted the same values as for the 3–0 band corresponding to the same variation of vibrational quantum numbers. The spectrum of the 4–1 transitions being recorded at 1.0 mbar, this assumption is expected to be valid in a good approximation and to add a minor contribution to the uncertainty of the 4–1 line positions extrapolated to the zero pressure limit.

In summary, the self-pressure line shifts bring corrections to the line center up to about 3 MHz for the few *R(J)* lines recorded at 10 mbar and were evaluated on the basis of the coefficients given in Ref. [9], which were reported with a ±30 kHz/mbar error bar. Taking into account the systematic discrepancy with Ref. [26] of the order of 50 kHz/mbar, the extrapolation at zero pressure is believed to contribute to the error budget of the line center by less than 80 kHz for all lines recorded at 1 mbar or less.

The complete list of retrieved line centers before and after correction of the self-pressure shifts is provided as Supplementary Material. In few cases, particularly for some very weak lines of $^{12}C^{18}O$ and $^{12}C^{17}O$ and of the 4–1 band of $^{12}C^{16}O$, the accuracy of the line center determination was affected by parasitic absorption features from impurities of water and CO_2. Those lines (marked with a star in the line list) are excluded from the forthcoming discussion on the accuracy of our line center determinations.

4. Accuracy of the line center values

The comparison of the derived line centers to previous measurements will be discussed in the next section. As our position values are believed to improve the accuracy for most of the line centers of the considered bands of CO, we use two alternative (and partly redundant) approaches to test the accuracy of our line centers: *(i)* a fit of the upper state band parameters whose quality gives a quantitative estimation of the precision of the line centers; *(ii)* ground state combination differences (GSCD) which allow using for comparison very accurate ground state energy values derived from microwave data.

In fact, these comparative analysis provide a test for the precision and not for the accuracy. However, recent comparison of C_2H_2 line positions against values known with kHz accuracy [5], has shown that only a very small systematic bias (<20 kHz) affects the frequency axis of our comb-calibrated CRDS spectra [15]. As a consequence, the tests below can also be considered as a validation of the accuracy of our line position values.

Both analyses use the ground state energy levels derived from the spectroscopic constants provided by the CDMS database [28,29]. These constants were obtained from a fit of rotational transitions in the microwave range and are listed in Table 1 for the four considered CO isotopologues. They allow reproducing the ground state energy levels with typical standard deviations less than 30 kHz. The CDMS line lists of CO were calculated using these constants and part of these lines was adopted for the HITRAN database [23]. Our choice to use the original constants instead of the HITRAN values is justified by the fact that the number of digits provided in the HITRAN lists is insufficient and does not fully account for the quality of the original CDMS data.

4.1. Quality of the fit of the band parameters

The rovibrational constants of the *v*=3-4 upper states were derived from a fit of the measured line positions, corrected from the self-pressure shifts, using the standard expression for the ro-vibrational energy levels:

$$E_v(J) = G_v + B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + ...$$

Eq. 3

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where J is the angular momentum quantum number, G_v corresponds to the vibrational term, B_v is the rotational constant, D_v and H_v are centrifugal distortion constants.

The ground state constants were constrained to their CDMS values as given in the upper part of Table 1 while the $v=1$ constants were taken from Farrenq et al. [31]. The maximum J value used in the fit of the lower and upper levels is also given in Table 1. The standard deviations for the (Obs.- Calc.) differences range between 260 and 490 kHz for the $v=3$ levels of the four studied isotopologues. These values can be considered as an estimation of the accuracy of our line center values. The transition frequencies computed from the spectroscopic parameters of Table 1 are provided in the Tables attached as Supplementary Material. These Tables list the centers calculated for all $P(J)$ and $R(J)$ lines with J values up to the maximum J value included in the fit, corresponding to transitions with intensities ranging from 5.1×10^{-29} to 2.2×10^{-23} cm/molecule. Their claimed uncertainty is 300 kHz and 500 kHz for the 3-0 band of $^{12}C^{16}O$ and of the $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{12}C^{17}O$ minor isotopologues, respectively. Let us underline that 0.3 MHz accuracy on the line center determination represents less than 0.15% of the $^{12}C^{16}O$ Doppler width (0.22 GHz HWHM). Note that the sample pressure is measured with a 0.25% accuracy which leads to a negligible error on the reported line positions (at the kHz level or below).

Table 1. Spectroscopic constants (in MHz) for the vibrational states of CO isotopologues involved in this work. The results of the fit performed from rotational lines in the CDMS database [28,29] are given in the upper part of the Table for the v=0 lower state. The spectroscopic constants for the v=1 lower state were derived from the Dunham coefficients obtained in Ref. [31]. These lower state constants being fixed, the upper states constants were derived from a fit of the transition wavenumbers measured in this work and are reported in the lower part of this Table.

	G_v	B_v	D_v	H_v	N^a	$J_{Max}{}^b$	Stdev
Lower states [28,29,30,31]							
$^{12}C^{16}O$ v=0 [30]	0	57 635.968019(28)	0.18350489(16)	$1.7168(10)\times10^{-7}$	31	38	0.013
$^{12}C^{16}O$ v=1 [31]	64 253 651.1540	57 111.2415	0.1834871	1.6992×10^{-7}	--		
$^{13}C^{16}O$ v=0 [28,29]	0	55 101.0125196(254)	0.16768599(77)	$1.5069(85)\times10^{-7}$	23	30	0.031
$^{12}C^{18}O$ v=0 [28,29]	0	54 891.42052(15)	0.1664057(28)	$1.457(57)\times10^{-7}$	11	18	0.008
$^{12}C^{17}O$ v=0 [28,29]	0	56 179.991097(280)	0.1743296(62)	1.521×10^{-7} [f]	37	8	0.026
Upper states (This work)							
$^{12}C^{16}O$ v=3	190 381 373.343(72)	56 061.90989(75)	0.1834756(17)	$1.578(10)\times10^{-7}$	63	34	0.263
$^{12}C^{16}O$ v=4	252 259 442.10(42)	55 537.3302(81)	0.183576(39)	$2.74(45)\times10^{-7}$	34	24	1.060
$^{13}C^{16}O$ v=3	186 240 611.80(13)	53 629.8800(15)	0.1676683(45)	$1.463(30)\times10^{-7}$	36	32	0.395
$^{12}C^{18}O$ v=3	185 894 423.38(22)	53 428.6831(48)	0.166353 (22)	$1.03(25)\times10^{-7}$	25	24	0.487
$^{12}C^{17}O$ v=3	188 015 316.99(12)	54 665.3268(24)	0.1742917(84)	1.521×10^{-7} [f]	25	17	0.292

*Notes*_ ^{a} Number of input data used for the fit
^{b} Maximum value of the rotational quantum number included in the fit
[f] Value fixed in the fit.

4.2. Lower state combination difference relations

As a further check, let us consider to which extent GSCD relations are fulfilled. The $P(J+1)$ and $R(J-1)$ transitions share the same J upper rotational state and the quantity $\Delta(J) = P(J+1) - R(J-1)$ is simply the difference of the $(J+1)$ and $(J-1)$ ground state energy levels, independent on the upper energy level. $\Delta(J)$ values can be calculated with a very good accuracy (better than 60 kHz) from the CDMS constants (Table 1).

Band	N^a	$\Delta_{This\ work} - \Delta_{Literature}$ Average $\pm 1\sigma$ (MHz)
3–0 $^{12}C^{16}O$	27	0.068 ± 0.371

4−1 $^{12}C^{16}O$	12	-0.045 ± 1.730
3−0 $^{13}C^{16}O$	6	-0.179 ± 0.408
3−0 $^{12}C^{18}O$	4	0.300 ± 0.714
3−0 $^{12}C^{17}O$	7	-0.017 ± 0.364

Table 2. Comparison to accurate literature values of the lower state combination difference relations obtained from the P(J+1) and R(J-1) line centers determined in this work.
Notes:
ª Number of lower state combination differences used for the comparison.

Average value and standard deviations (1σ) of the differences between the $\Delta(J) = P(J+1) - R(J-1)$ values obtained from CDMS (v= 0) and Farrenq (v=1) and determined in this work are presented in Table 2 together with the number of pairs of lines used for the comparison. The obtained values which correspond to twice the error bar of the line centers are consistent with the standard deviation value obtained from the fit of the band parameters (Table 1).

5.   Discussion

Let us compare our line position values to the values provided in different line lists available in the literature.

5.1.   Comparison to the positions calculated by Farrenq et al.

In 1991, Farrenq et al. gathered 4500 unblended CO line positions measured from a high resolution solar spectrum from space and 14000 accurate laboratory measurements in order to derive an improved set of Dunham coefficients for the four main CO isotopologues [31]. This set of Dunham coefficients is expected to reproduce the laboratory data with accuracy better than 15 MHz (or 5×10^{-4} cm^{-1}) [31]. We present below a comparison of the line positions calculated with these coefficients with our experimental values for all the transitions reported in this study.

The 3−0 band of $^{12}C^{16}O$

Sixty three accurate line centers with upper J values up to 34 were determined for the 3−0 band of $^{12}C^{16}O$. The differences with the positions calculated using the Dunham coefficients [31] are plotted in Figure 4. For J values up to 20 the calculated frequencies agree within 1 MHz with our measurements, Farrenq's values being slightly larger. The deviations increase to about 2 MHz for J values around 30. The quality of agreement indicates that the ±15 MHz uncertainty reported in Ref. [31] is strongly conservative in our range of J values. Nevertheless, let us note that the same ±15 MHz uncertainty claimed in Ref. [31] is expected to hold for J values up to more than 120 for the v = 3 vibrational state.

The positions of 36 of our 63 studied transitions were also measured in Ref. [9] with an accuracy of 1 MHz from Fourier transform spectra calibrated with reference acetylene lines. In their work, Picqué and Guelachvili [9] compared their measurements with positions predicted with an accuracy of 1.5 MHz from Dunham coefficients provided by Farrenq through private communication (i.e. ten times better accuracy than reported in the original paper by Farrenq et al. [31]). By comparing our values with the positions measured and calculated in [9], we obtain mean differences of 0.66(38) MHz and 0.20(32) MHz, respectively. These values are fully consistent with the corresponding reported uncertainties (1 MHz and 1.5 MHz, respectively).
In summary, our measurements for the 3−0 band of $^{12}C^{16}O$ are in agreement with positions derived from the Farrenq's et al. work and provide a substantial increase of the level of accuracy, by more than an order of magnitude for the 20< J <34 lines, whose previous determinations were limited by a ±15 MHz [31] error bar.
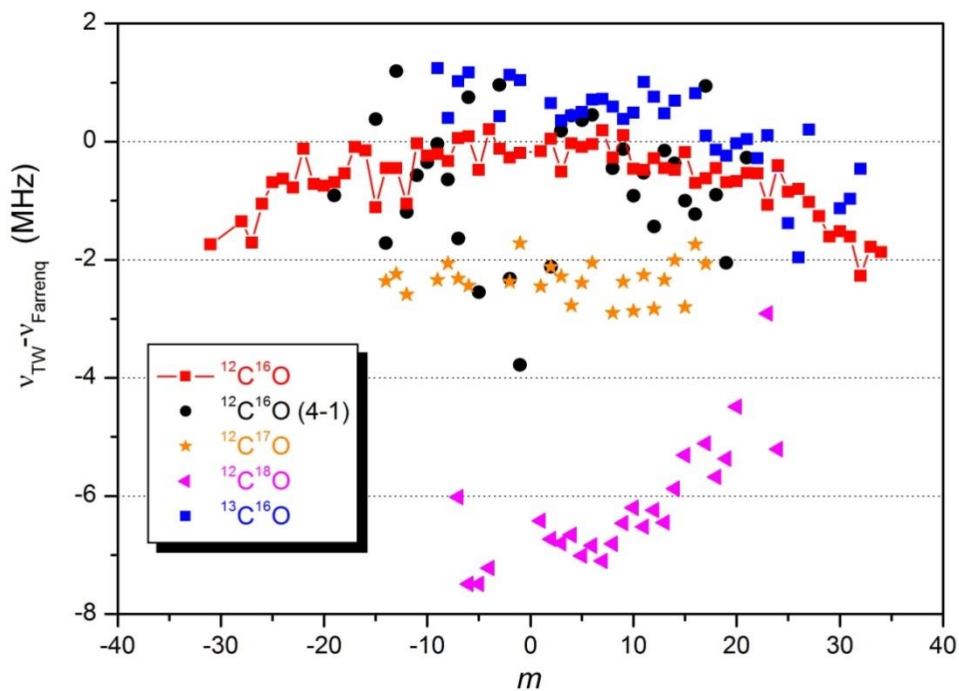
Figure 4. Differences (in MHz) between the measured CO line centers in this work (TW) and the corresponding values calculated from the Dunham coefficients given in Ref. [31] (m is −J in the P branch and J+1 in the R branch).

The 3−0 band of the minor CO isotopologues

To the best of our knowledge, the present measurements are the first extensive measurements of the 3−0 band of $^{12}C^{18}O$ and $^{12}C^{17}O$. The only previous detection for these two minor isotopologues is due to Wójtewicz et al. who recently reported the line profile analysis of five lines ($^{12}C^{17}O$ R0-R2 and $^{12}C^{18}O$ P15-P14) by frequency stabilized CRDS [24] (see Fig. 2). The only previous study of the 3-0 band of $^{13}C^{16}O$ is that of Swann and Gilbert [10] who used ^{13}C highly enriched sample and reported 18 line positions with an average accuracy of ±15 MHz. For sake of comparison, our analysis spans 36 line positions with accuracy better than 0.5 MHz for this isotopologue using a non enriched sample.

The Dunham expansion obtained by Farrenq et al. includes the mass dependence of Dunham coefficients and allows accounting for the line positions of $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{12}C^{17}O$ with a unique set of parameters. Figure 4 includes the comparison to the positions derived from the Dunham coefficients [31]. The achieved agreement is much better than the ±15 MHz uncertainty declared in Ref. [31]. The largest deviations are of the order of 7 MHz for the low J values of $^{12}C^{18}O$, while the $^{12}C^{17}O$ calculated line positions are systematically underestimated by about 2.5 MHz.

The 4−1 band of $^{12}C^{16}O$

The positions of 34 transitions of the newly observed 4−1 hot band of $^{12}C^{16}O$ have been measured with upper J values up to 24. The difference between these positions and the values calculated from the Dunham coefficients reported in [31] is -0.55(1.27) MHz, thus confirming again the accuracy of the values by Farrenq et al. within 1 MHz in our range of J values.

Using the v= 1 spectroscopic parameters from Ref. [31] and the v= 4 parameters presently derived from the 4−1 hot band, the 4−0 wavenumber values have been computed for comparison with our recent measurements of 10 line centers of the 4-0 transitions by CRDS near 8300 cm^{-1} [32]. In this latter work, the line positions were reported with a 30 MHz accuracy provided by the wavemeter used for the frequency calibration. Average and standard deviation (1σ) values of -7.6 ± 22.7 MHz are obtained, respectively, which is consistent with the 30 MHz accuracy.

5.2. Comparison to recent line lists

Other line lists available in the literature deserves to be considered. Very recently, using an approach similar to that of Farrenq et al., Velichko et al. derived a set of mass-independent Dunham parameters globally describing the vibrational energy levels of the CO molecule [33]. The input data set gathered by Velichko et al. was critically evaluated using the Ritz principle [34] and includes recent measurements. Nevertheless, the large majority of the set of more than 19000 transitions of $^{12}C^{16}O$, $^{13}C^{16}O$, $^{14}C^{16}O$, $^{12}C^{17}O$, $^{13}C^{17}O$, $^{12}C^{18}O$ and $^{13}C^{18}O$ used by Velichko et al. is due to Farrenq et al. and only limited changes are expected for the line positions under consideration. This is indeed what is observed on the overview comparison of the $^{12}C^{16}O$ 3-0 line positions, presented in Fig. 5. The average and *rms* deviations of the differences between the CRDS and calculated line positions are nevertheless improved: -0.10(36) MHz and 0.66(57) MHz for Velichko et al. and Farrenq et al., respectively.

Farrenq's calculations were also used to generate the HITRAN line list but line positions are provided with only four decimal digits in the HITRAN list (i.e. 10^{-4} cm^{-1}), which explains the larger dispersion on the position differences displayed in Fig. 5 (*rms* deviation of 1.07 MHz).

It is also worth comparing against the results obtained by Coxon and Hajigeorgiou [35]. These authors constructed an empirical potential energy function which was adjusted by direct fits of a collection of 21559 line positions. Using their vibrational terms and rotational constants of the *v*= 0 and *v*= 3 states (Table 5 of Ref. [35]), we computed the $^{12}C^{16}O$ positions of the 3-0 transitions. The comparison included in Fig. 5 shows a behavior mostly identical to that obtained with the positions of Velichko et al. (+0.15(39) MHz *versus* -0.10(36) MHz). This is again the consequence of the dominant impact of the experimental data of Farrenq et al. on the line position dataset used in the potential fit of Coxon and Hajigeorgiou.

Finally, let us consider the line list recently released by Li et al. [32]. In this work mostly devoted to the line intensity calculations of CO transitions, Li et al. determined a new piece-wise dipole moment function (DMF) consisting in a semi-empirical DMF near equilibrium internuclear distance (up to *v*= 6) completed by an *ab initio* DMF for large internuclear distances. The experimentally-determined potential energy function from Coxon and Hajigeorgiou [35] was used to compute the wavefunctions and the energy levels. Surprisingly, the transition frequencies of the 3-0 band provided by Li et al. [32] differ importantly from those of Ref. [35] (see Fig. 5). Although the current line position discrepancy would not affect studies of stellar atmospheres, we suggest that the line positions of Li et al should not be taken into next official releases of HITRAN and HITEMP.
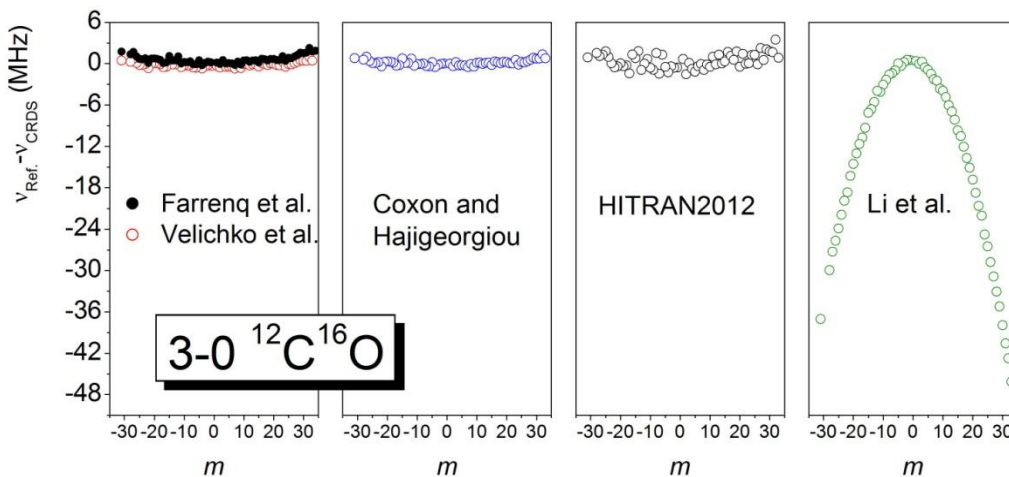

Figure 5. Differences (in MHz) between the $^{12}C^{16}O$ positions of the 3-0 transitions of various line lists available in the literature and those measured in the present work. From left to right: Farrenq et al. [31] and Velichko et al. [33], Coxon and Hajigeorgiou [35], HITRAN2012 [23] and Li et al. [32]. (m is –J in the P branch and J+1 in the R branch).

6.   Conclusion

This work is a first application of our comb-linked CRDS spectrometer. It consists in measuring the beat note frequency between the light emitted by one of our DFB laser diodes and the nearest mode of a self-referenced frequency comb. The method was recently introduced and detailed in [15] over a narrow spectral range on acetylene lines whose centers were found to coincide within 20 kHz with values measured at the kHz level by saturation spectroscopy [5]. In the present study, around 200 transitions of the second overtone band of carbon monoxide are reported with sub MHz accuracy over the wide 6170–6420 cm^{-1} range.

The advantage of our approach as compared to FC linked-FS-CRDS [11,12,13] is its simplicity, frequency measurements being performed "on the fly" with no stabilization of the length of the CRDS cell and no locking of the laser frequency.

By coupling a SRFC laser with our CRD spectrometers we have thus recorded spectra with a highly accurate frequency axis while maintaining the high sensitivity and high dynamic range of the CRDS technique and without any degradation of the data acquisition rate. This last point is crucial for application to extensive characterization of molecular absorption bands.

After correction of the pressure-shift effect, 63 line centers of the 3–0 band of $^{12}C^{16}O$ could be reproduced with a standard deviation of 260 kHz ($\approx 1 \times 10^{-5}$ cm^{-1}) using the standard polynomial expression of the rovibrational energy levels. This high accuracy relies on the negligible bias (<20 kHz [15]) of the frequency calibration of the spectra and on the quality of the CRDS spectra which were recorded with a Noise Equivalent Absorption of about 1×10^{-11} cm^{-1} Hz$^{-1/2}$. Note that the claimed accuracy of the center determination represents about one thousandth of the Doppler line width (300 kHz compared to 220 MHz HWHM). Another advantage provided by the CRDS sensitivity is that low pressure values (less than 1 mbar) can be used for the recordings, limiting pressure shift effects and then possible errors on the line center extrapolated to zero pressure. For instance, the 50 kHz/mbar disagreement on the self pressure shifts reported in the literature adds a 500 kHz uncertainty for the R(30)-R(39) lines which were measured at 10 mbar.

As a main output of this contribution, the full list of line centers of the various studied bands was calculated with the derived spectroscopic parameters. It provides accurate reference line positions over the wide 6170–6420 cm^{-1} range. The claimed accuracy for the 3-0 band of the main and of the minor isotopologues is 300 and 500 kHz respectively. These values agree with the most accurate positions available in the literature and represent an important gain in accuracy.

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