# Absolute frequency measurement of $^{12}C^{16}O_2$ laser lines with a femtosecond laser comb and new determination of the $^{12}C^{16}O_2$ molecular constants and frequency grid

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ABSTRACT

Absolute frequency measurements of a $CO_2$ laser stabilized on saturated absorption resonances of $CO_2$ laser lines are reported. They were performed using a femtosecond-laser frequency comb generator and two laser diodes at 852 nm and 782 nm as intermediate oscillators, with their frequency difference phase-locked to the $CO_2$ laser. 20 $^{12}C^{16}O_2$ laser lines in the P and R bands at 9 µm were measured with a relative uncertainty of a few $10^{-12}$ limited by the $CO_2$ frequency reproducibility. A new determination of the $CO_2$ molecular constants was obtained from these data and previous measurements in the 10 µm band. The $CO_2$ frequency grid was also calculated, with an improvement of two orders of magnitude compared to the previous grid of Maki *et al* [A.G. Maki, C.C. Chou, K. Evenson, L.R. Zink and J.T. Shy, J. Mol. Spectrosc. 167, (1994) 211-224].


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# 1. Introduction

CO$_2$ lasers deliver a dense grid of emission lines in the spectral region 28-31 THz (9-12 µm) and have been widely used to calibrate high resolution molecular spectra. They can be easily stabilized on narrow sub-Doppler resonances providing reference frequencies with uncertainties of a few kHz. Such accuracy can be transferred to other spectral regions by generation of harmonics, sum or difference of CO$_2$ lasers frequencies, for example in the 60 THz or 87 THz regions of OCS absorption lines [1, 2]. The saturated fluorescence technique on CO$_2$ developed by Freed and Javan [3] is commonly used for stabilization and gives easy access to all laser lines. With this technique, Bradley *et al* [4] established in 1986 a CO$_2$ frequency grid with uncertainties of 3 to 10 kHz. This grid was then updated and extended by Maki *et al* [5], with uncertainties of less than 1 kHz and 2 kHz for the J< 40 lines of, respectively, the 10 and 9 µm band of the CO$_2$ isotopomer. Note that an alternative frequency grid exists in the 10 µm region, which is based on the stabilization of CO$_2$ lasers on direct saturated absorption lines of OsO$_4$ [6-8]. This grid provides higher accuracies between 50 Hz and 1 kHz, but it is in coincidence with a relatively small number (23) of laser lines, in the 10 µm band of the normal CO$_2$ isotopomer laser.

The CO$_2$ grid was recently severely tested by 2 groups. First at Bonn University some frequency differences of CO$_2$ laser lines were measured [9] leading to strong discrepancies with [5]. As an example, the deviation from Maki's values reaches 17 kHz for the frequency difference between the 9 µm transitions $^{12}C^{16}O_2$ P(34) and $^{13}C^{16}O_2$ R(22), despite a reproducibility better than 1 kHz. In our group it was observed for the first time in 1986 a saturation signal of CO$_2$ laser lines in an external cell at room temperature [10]. An uncertainty of 50 Hz was obtained on the R(10) line at 10 µm by connection to the OsO$_4$ grid [11]. Together with the P(12) and P(14) measurements, these data were included in the calculation of Maki. In 1997, twenty absolute frequencies of $^{12}C^{16}O_2$ laser lines around 10 µm were determined with accuracies between 100 Hz and 1 kHz [12]. For this purpose, the laser was stabilized on the molecular signal detected in transmission of a Fabry-Perot cavity [13]. This set of measurements revealed again some discrepancies of several kHz with the data published by Bradley *et al* [4] and Maki *et al* [5], larger than the uncertainties. Finally, for three transitions in the 10 µm region, the frequency of a laser stabilized with the saturated fluorescence technique was measured by connection to the OsO$_4$ grid, which permitted to evaluate the pressure shift [14]. All these results showed that a new calibration of the CO$_2$ grid is needed, as already pointed in [12] and [14].

In this paper, 20 absolute frequency measurements of the R and P bands of the $^{12}C^{16}O_2$ laser lines around 9 µm are presented. The measurement uncertainty is ranging from 50 to 500 Hz. The set-up exploits two major experimental developments (Fig. 1). First, the revolution recently introduced in the field of frequency comparisons by the femtosecond laser which provides a perfect frequency comb permitted us to directly measure the frequency of a CO$_2$ laser versus an ultrastable 100MHz reference. Second, this reference generated from a H-maser itself controlled with the TAI (International atomic time) at BNM-SYRTE (Paris Observatory) was transferred through a 43-km optical fiber to our laboratory with a negligible degradation of the spectral properties [15]. Using these frequencies and previous measurements at 10 µm [8, 11, 12] we determined with an improved accuracy the rotational constants for the three vibrational levels implied in the transitions. Finally a new calculation of the frequency grid for the normal CO$_2$ isotopomer was performed. A comparison with the previous grid is also given.

## 2. The CO₂/CO₂ frequency standard

The experimental set-up is shown on Fig. 2. The measurement of the $CO_2$ laser line frequency is based on the stabilization of the $CO_2$ laser on a narrow saturated absorption resonance, detected in transmission of a Fabry-Perot cavity. This set-up was initially developed for the stabilization onto a saturated absorption of $OsO_4$ [13].

   The molecular gas is contained in a 1.5 m long symmetric Fabry-Perot cavity with a waist of 4.5 mm and a finesse of about 200. Typical conditions are a pressure of 0.1 Pa and a laser power of 1 mW inside the cavity. The saturated absorption is detected in transmission of the cavity. Compared to the case of the simple external cell, this allows a gain on the signal contrast proportional to the finesse of the cavity, and a better control of the laser beam geometry. The laser frequency is modulated at $f_1$=24.75 kHz and $f_2$=6.4 kHz. Using first-harmonic detection at $f_1$, the cavity resonance is locked to the laser frequency with a bandwidth of about 100 Hz. A second servo-loop with the same bandwidth then locks the laser frequency to the molecular line with a third-harmonic detection at $3f_2$. Each correction signal is applied to a piezoelectric transducer mounted on a mirror of the cavity and the laser, respectively. The peak-to-peak width of the saturated absorption resonance is about 25 kHz, to be compared to the typical 600 kHz width of the saturated fluorescence signal [14]. The signal to noise ratio is about 2000 in a bandwidth of 1 Hz. The residual offset is less than 5 % of the signal amplitude, due to the third-harmonic detection. However, since it can induce some frequency shift of the order of 500 Hz, it is compensated with the following procedure: the laser frequency is alternatively blue and red-shifted 200 kHz from the line and the corresponding offsets are measured on a digital voltmeter with a time constant of 1s. The mean value is then set to 0 by applying an offset voltage at the output of the lock-in amplifier.

   Fig. 3 displays the relative Allan deviation of the stabilized $CO_2$ laser, as calculated from the absolute frequency measurement (see section 3). It is $6.2 \times 10^{-13} \tau^{-1/2}$ between 1s and 100 s, a factor 3 better than the previous measurements [12]. This progress is related to the better signal to noise ratio of the reference line. In [12], an electrooptic modulator was used to generate the modulated beam feeding the Fabry-Perot cavity, resulting in a drastic reduction of the available power. Here, with the present set-up about 10 times more power is used for the absorption line. As a result a third-harmonic detection can be used, which is more favourable for the long-term stability and absolute frequency measurement.

## 3. Absolute frequency measurements

### 3.1 The fs comb

   The principle of frequency measurements using a femtosecond laser comb has been widely described [16-18], and the specific set-up used in this experiment (Fig. 1) was initially employed in the measurement of an $OsO_4$ frequency, as recently published in detail [15]. In the frequency domain, a mode-locked Ti:Sa laser produces a comb of modes spaced by the repetition rate $f_{rep}$ of the pulses. This comb spans more than the $CO_2$ laser frequency, and this can be exploited so that the $CO_2$ laser controls the separation between two modes of the comb.

   The basic technique is shown in Figure 4. The laser diode at 852 nm is phase locked to a fs mode. The sum of the diode and $CO_2$ frequencies is generated in a crystal of $AgGaS_2$ and a second laser diode, at 782 nm, is phase locked to the sum. Finally a second fs mode is phase locked to this diode by feeding back to the fs cavity length. With the notation of Figure 4, the frequencies are related as $f(CO_2) = pf_{rep} - \Delta_0 + \Delta_1 + \Delta_2$, where $|\Delta_0|$, $|\Delta_1|$ and $|\Delta_2|$ are the frequencies of the synthesizers driving the 3 phase-lock loops.

The repetition rate, $f_{rep}$, can be measured by directing part of the fs laser output onto a high-speed diode. Comparing the output with the frequency $\Delta_3$ of another synthesizer, the frequency difference $\delta = \left| f_{rep} - \Delta_3 \right|$ is then counted with a reciprocal frequency counter. The integer $p$ (approx. 31000) and the signs of $\Delta_0$, $\Delta_1$, $\Delta_2$ are established unambiguously because the $CO_2$ frequency is already well known. The $CO_2$ frequency and, subsequently the relative Allan deviation, is then directly deduced from the measurement of $f_{rep}$.

All synthesizers and the frequency counter of this experiment are referenced to a 100 MHz standard generated at BNM-SYRTE. This standard is generated from a hydrogen maser, itself linked to the TAI (International Time Unit) or compared to a Cs fountain [19]. The 100 MHz signal is transferred to LPL via a 43 km optical fibre as an amplitude modulation on a 1.55 µm carrier generated by a laser diode. It is down-converted and used to phase lock the harmonic of a 5 MHz quartz oscillator, which thus provides the 10 MHz reference for the synthesizers and the counter. The relative Allan deviation of this system is $3.10^{-13}$ for 1s. Since this is well below the relative Allan deviation of the $CO_2$ laser line stabilization, this reference does not limit the frequency measurement.

### 3.2 Absolute frequency determination

Fig. 5 displays the frequency measurements over a period of 45 days for the P(22) line of the 9 µm band. Between 3 and 8 measurements were obtained during one day, each of them corresponding to the averaging of a few tens of 1 s gate frequency measurements. Between each measurement, the frequency stabilisation loop was opened and the line offset was checked. The uncertainty for each day (1-$\sigma$ statistical uncertainty) is around 15 Hz, when the daily deviation from the overall mean frequency is approximately 3 times larger.

The mean frequency over the series of measurements was found to be $< \nu(P(22)) > = 31\ 328\ 961\ 496{,}109\ (51)$ kHz. The uncertainty is the mean $\sqrt{\sigma_{stat}^2 + \sigma_{disp}^2}$ of the statistical uncertainty $\sigma_{stat}$ and the day-to-day reproducibility $\sigma_{disp}$. We calculate $\sigma_{stat}^2 = 1 \Big/ \left( \sum \frac{1}{\sigma_i^2} \right)$, where $\sigma_i$ is the 1-$\sigma$ statistical uncertainty for each day. $\sigma_{disp}$ corresponds to the half dispersion of the set of the measurements. It is about 50 Hz for P(22), and this was set as the minimum value for $\sigma_{disp}$ for all the $CO_2$ lines. By this way, we took into account the frequency dependence on the daily experimental parameters, even if only two or three series of measurements were performed.

Finally, depending on the laser line, the uncertainty ranges between 50 and 500 Hz. It increases for the low and high values of J, for which the $CO_2$ laser lines are weaker.

We carried out some preliminary studies of the $CO_2$ laser line frequency shift on the parameters of the frequency stabilization setup : power of the laser beam, modulation amplitude, 3-f or 5-f detection, $CO_2$ pressure. Changing these parameters by a factor 1.5 did not induce any frequency shift larger than 50 Hz, which is less than the measurement uncertainty.

## 4. Results and discussion

### 4.1 Experimental results at 9 µm

Table 1 displays the absolute frequency for 20 lines of the 9 µm band, together with the frequency difference to the $CO_2$ frequency grid of Maki [5]. This frequency difference is

illustrated on Fig. 6 and invites two comments. First, the shifts are significantly larger than the error bars. Second, they are not constant and the minimum is not found for the low values of J.

The calculation of Maki exploited a lot of measurements of frequency differences between $CO_2$ lines, and only a few absolute frequency measurements. For the 9 μm band two absolute frequency measurements were performed in the past : R(10) with an uncertainty of 4.5 kHz [20, 21] and R(12) with an uncertainty of 15 kHz [22].

Due to this limited number of absolute frequency measurements, we expected that the frequency grid of Maki will be globally shifted. Here, there is a non-constant shift that we attribute to the various origin of the experimental data used by Maki for his fit. These data were recorded using the saturated fluorescence technique, but with different pressures, and without any 3-f detection to reduce the line offset. For instance, the high-J laser transitions were measured at 9.3 Pa instead of the conventional 5.3 Pa pressure [5]. In fact, our results are compatible with Maki's frequencies with the uncertainty of the absolute frequency measurements used by Maki to calibrate its grid.

### 4.2    Determination of the molecular constants at 9 and 10 μm

These new absolute frequency measurements complete the data already obtained in the 10 μm band with a saturated absorption spectroscopy at low pressure. Table 2 displays the absolute frequency of 19 lines measured with a similar uncertainty[1]. The frequencies have been derived from two sets of measurements. First, the frequency difference between $CO_2$ and $OsO_4$ reference lines was measured in our group [11, 12], second the absolute frequencies of the $OsO_4$ reference lines were recently re-measured at Paris Observatory [8]. A conservative uncertainty of at least 60 Hz was considered for the $OsO_4$ reference frequencies. This takes into account the fact that both set-ups at Paris Observatory and in our laboratory are slightly different.

A new set of constants for $CO_2$ can be deduced from all these 39 data at 9 and 10 μm. Following [5], the expressions for the rovibrational energy levels are written :

$$E(v, J)/h = G_v + B_v[J(J+1)] - D_v[J(J+1)]^2 + H_v[J(J+1)]^3 + L_v[J(J+1)]^4 \quad (1)$$

where the subscript v yields respectively 0, I and II for the vibrational upper level $(00^01)$ and lower levels $[02^00,10^00]_I$ and $[02^00,10^00]_{II}$. Here the standard spectroscopic notations for $CO_2$ are used : the transitions 0→I and 0→II correspond respectively to the 10 and 9 μm bands of $CO_2$.

The 14 parameters $v_I=G_0-G_I$, $v_{II}=G_0-G_{II}$, $B_0$, $D_0$, $H_0$, $L_0$, $B_I$, $D_I$, $H_I$, $L_I$, $B_{II}$, $D_{II}$, $H_{II}$, $L_{II}$ have been included in a least-squares fit performed with the Mathematica 4.1 software. The experimental data have been weighted with the square of the inverse of the uncertainties. Column 2 of table 3a displays the resulting molecular constants. We checked that each constant is relevant, i.e. the introduction of the highest order terms L's improves significantly the fit. The fit of the band II is more precise than the fit of the band I, which is due to the existence of data for the high J values in band II. Column 3 gives the previous determination from [5]. The present fit corresponds to a significant reduction of the uncertainty on the constants. We note a shift of the band centers $v_I$ and $v_{II}$ of 2,5 kHz and 6,7 kHz equal to 6σ and 4σ while the values of the other constants are in good agreement except for $H_0$ and $L_0$.

We also fitted the data with another set of constants to reduce the correlation between the corresponding rotational parameters of the different vibrational levels. We replaced $B_I$ by $\Delta B_I=B_I-B_0$, and $B_{II}$ by $\Delta B_{II}=B_{II}-B_0,...$ . The new results are displayed on Table 3b. Results are consistent with the previous fit. The values and uncertainties of the parameters not listed in

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[1] The R(8) line has also been measured. But its frequency has been removed from the data, since the $OsO_4$ reference line used for the measurement was later observed as a doublet [23].

Table 3b are exactly the same as in Table 3a. In fact, only $\Delta B_{II},\ldots \Delta L_{II}$ are more precisely determined than $B_{II},\ldots L_{II}$, because, probably, of a more adequate set of data for the fit of band II.

*4.3    New frequency grid at 9 and 10 μm*

The fit of the molecular constants can be also used to calculate a new frequency grid of the $CO_2$ laser lines, based only on data measured with saturated absorption spectroscopy. Table 4 shows these results, with a comparison to the experimental data.

The grid was calculated from P(50) to R(40) and from P(30) to R(30) for the 9 μm and 10 μm band, respectively. For higher values of J, the uncertainties increase rapidly due to the lack of experimental data.

This grid represents an improvement of the accuracy by two orders of magnitude compared to the Maki's grid.

Note that the users of the $CO_2$ saturated fluorescence spectroscopy must take into account the pressure shift under their experimental conditions for the calibration of molecular spectra. A shift of $-1.7$ kHz for the standard pressure of 5.3 Pa was found on the 10P(14), 10R(10) and 10R(22) lines [14] but this figure can depend on the transitions.

## 5.  Conclusion

We have demonstrated the frequency stabilization of a $CO_2$ laser on the saturation signal of the corresponding $CO_2$ laser line. The absolute frequency was measured using the new technique of the femtosecond-laser frequency comb generator. We measured the absolute frequencies of twenty $CO_2$ laser lines on the 9 μm band with an uncertainty ranging from 50 to 500 Hz. The molecular constants for the 3 levels involved in the 9 and 10 μm laser lines are deduced from a fit of these present measurements and previous measurements in the 10 μm band [8, 12]. Their uncertainty is strongly reduced compared to the previous determination of [5]. This is particularly clear for the vibrational frequencies $\nu_I$ and $\nu_{II}$, for which only two absolute measurements with uncertainties 4.5 kHz and 15 kHz were available before this work. The fit leads also to a significant improvement of the $CO_2$ frequency grid. With these results $CO_2$ presents one of the best-known vibrational bands, together with the $\nu_3$ band of $SF_6$ [24] or with $I_2$ [25].

This fit could be improved with new line measurements in the 9 and 10 μm bands. Concerning the 10 μm band, the existing frequency data refer to $OsO_4$ transition frequencies in the vicinity of the $CO_2$ laser lines and are limited to J=26. Higher-J lines could now be measured with the present direct frequency measurement method. A similar work could be easily extended to other isotopomers of $CO_2$.

## Acknowledgements

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**FIGURE CAPTIONS**

FIGURE 1 : Block diagram of the measurement of the $CO_2$ laser line frequency. The frequency difference between two modes of the fs laser is locked to the $CO_2$ laser frequency to be measured. The repetition rate, $f_{rep}$, is then counted with a counter referenced to a 100 MHz signal delivered through an optical fiber by BNM-SYRTE (Paris Observatory)

FIGURE 2 : Experimental arrangement for the $CO_2$ laser stabilisation on the $CO_2$ laser line.

FIGURE 3 : Relative Allan deviation of the $CO_2$ laser frequency, when it is stabilized to a narrow $CO_2$ saturated absorption line.

FIGURE 4 : Simplified schematics of lasers and frequencies involved in locking of the fs system to the $CO_2$ laser frequency.

FIGURE 5 : Frequency measurements of the P(22) $CO_2$ laser line at 9 µm, versus date of measurement.

FIGURE 6 : Comparison between the calculated frequencies of Maki (triangles) and the present measurements (squares), for (a) P band (b) R band, at 9 µm. All the frequencies are referred to our data.


**TABLE CAPTIONS**

TABLE 1 : Measured absolute frequencies, in kHz, for the laser lines of the 9 µm band of $CO_2$

TABLE 2 : Absolute frequencies, in kHz, for the laser lines of the 10 µm band of $CO_2$ deduced from the measurements [12] and [8].

TABLE 3 : a) Molecular constants, in kHz, for the laser lines of the 9 and 10 µm bands of $CO_2$. Index 0 corresponds to the upper vibrational level of the transition, index I to the lower level of the 10 µm band, and index II to the lower level of the 9 µm band. Column 2 gives present results obtained with a 14-parameter fit of the 9 and 10 µm bands, column 3 gives the Maki's results. b) Alternate set of constants which represent the difference of the molecular constants of the lower and upper levels.

TABLE 4 : Frequency grid of the normal isotopomer of $CO_2$ : laser lines at 9 µm (left) and 10 µm (right). Column 1 : laser line label. Column 2 : calculated frequencies and uncertainties given by the fit. Column 3 : difference between observed and calculated frequencies; in brackets are given the uncertainties of the experimental data.