

## ABSOLUTE FREQUENCY DETERMINATION OF SUPER-NARROW CO<sub>2</sub> SATURATION PEAKS OBSERVED IN AN EXTERNAL ABSORPTION CELL

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We have succeeded in observing very narrow saturation resonances (hwhm = 2.1 kHz) of room temperature CO<sub>2</sub> by monitoring directly the absorption of a CO<sub>2</sub> laser beam in an external absorption cell. Through successive recordings of the CO<sub>2</sub> lines and OsO<sub>4</sub> lines of known absolute frequency, we have been able to perform a preliminary determination of the frequencies of three CO<sub>2</sub> lines (respectively P(12), P(14) and R(10) of the 10.4 μm band) with an accuracy of the order of one kilohertz. A good agreement is found with previous measurements based on the saturated 4.3 μm fluorescence method. The main interest of this new method is to provide values for the frequencies in the free-flight regime.

### 1. Introduction

Ever since the discovery of the Lamb dip in CO<sub>2</sub> lasers [1,2] it has been a long-term unsatisfied dream to obtain directly narrow saturated absorption peaks in pure room-temperature CO<sub>2</sub> at low pressure. Because of the weakness of such signals, only indirect techniques such as the saturated fluorescence [6–10] or the inverted Lamb dip technique with a hot CO<sub>2</sub> cell inside the laser resonator [3–5] could be used. None of these methods has ever been able to yield a linewidth below ~100 kHz, essentially because of their intrinsic requirement for a high pressure and a high laser power. In these conditions, the baseline tilts and the numerous other known and unknown sources of asymmetry and shift may give rise to systematic errors which appear to be very difficult to reduce below the 3–5 kHz level. This is the reason why, for high accuracy spectroscopic needs, our group has developed an alternate grid of frequency markers, based on the narrow OsO<sub>4</sub> saturation resonances, which covers the spectral region 940–980 cm<sup>-1</sup> [9,11] and among which two lines have now a remarkable accuracy of their measured absolute frequency: respectively 1 kHz and 50 Hz for the OsO<sub>4</sub> markers corresponding to CO<sub>2</sub> P(14) [13] and to CO<sub>2</sub> R(10) [14]. In the course of this 1980 set of measurements, we also demonstrated

a ~20 kHz systematic shift of the CO<sub>2</sub> absolute frequency values in the P branch through a comparison of OsO<sub>4</sub> with CO<sub>2</sub> saturated fluorescence peaks in an external cell. This shift was confirmed by direct frequency connections between the P and R branches and, corrected for, in recent CO<sub>2</sub> tables [12].

It appeared to us in 1984 that the computerized long-term frequency control techniques developed for our spectrometer offered the possibility to use long integration time combined with a long optical path length (108 m) of high wavefront quality and therefore a new chance to observe the CO<sub>2</sub> resonances directly at very low pressure (0.7 to 1.5 × 10<sup>-2</sup> Pa) and power (a few hundred μW) and hence with a very narrow linewidth (2 to 3 kHz hwhm) [15,16]. The only major difficulty left then was to keep track of the long term drifts of the reference laser and we shall see below how this problem has been solved.

### 2. Presentation of our measurement method and experimental conditions

All the measurements reported in this paper have been performed with the 10 μm Villetaneuse saturation spectrometer which has been fully described elsewhere [17]. For these measurements we have used

only two low pressure  $\text{CO}_2$  lasers. The first one, which we usually call "reference laser", is used here as a transfer laser and is locked, by the third harmonic method, to a saturated absorption peak obtained in auxiliary absorption cells (absorption length = 6 m,  $w = 1.4$  cm). The nature of the molecule used here has no importance, as such, since the goal pursued is only to obtain the best long-term stability (i.e. during several hours) in addition to a good spectral purity ( $\sim 10$  Hz) for the reference laser. All that is needed, is the best possible signal-to-noise ratio for any saturation peak derivative in close coincidence with the  $\text{CO}_2$  laser line that one wishes to study. The second laser is frequency-offset locked and, for this purpose, the beat note of the two lasers is phase-locked to the radio-frequency produced by a synthesizer (HP 3325A) and directly counted by a frequency counter (HP 5328A) with a relative accuracy of  $2 \times 10^{-8}$ . The frequency tuning of the laser is then achieved by scanning digitally the synthesizer frequency with a microcomputer (HP 9826) which ensures a very linear correspondence between laser frequency and detection channel numbers. This second laser beam is expanded, spatially filtered and enters into a large absorption cell where it forms a three-fold standing wave of waist radius  $w \approx 4$  cm and total optical path (back and forth) of 108 m. This measurement laser is frequency modulated at one kilohertz and the first derivative signals of saturation peaks are recorded by the microcomputer after synchronous detection through a lock-in amplifier. The principle of the method is then to record both the  $\text{CO}_2$  laser line and the closest  $\text{OsO}_4$  line of known absolute frequency in order to determine their frequency interval. Unfortunately it was not possible to record the two lines quasi-simultaneously as could have been done with the absorption cell filled with a mixture of  $\text{CO}_2$  and  $\text{OsO}_4$  because experimental conditions were too different for the two gases (pressure, laser intensity, modulation index, integration time constant, ...). The cell was therefore filled successively with  $\text{CO}_2$  and  $\text{OsO}_4$  and it was thus essential to take into account the frequency drifts of the reference laser during the time of the experiment. To keep track of these drifts, the  $\text{CO}_2$  and  $\text{OsO}_4$  lines were recorded 6 to 7 times, with, for each recording, the precise time of its end and its duration. For all our experiments it appeared that the drifts had essentially linear and quadratic components which have been calculated by lin-

ear regression and, in this way, could be easily eliminated from the measurements of the  $\text{CO}_2$  and  $\text{OsO}_4$  lines intervals. The causes of such a drift are not yet well identified. The only clear fact is that the drift is highly dependent upon the quality of the reference saturation peak, as could be guessed. Possible origins for this drift are: (1) time-dependent electronic offsets in the detection system of the reference line, owing, for example, to a room temperature variation during the day; (2) a slow change of the pressure in the absorption cell which would induce a variation of the background of the detected signal and hence of the locking point of the laser on the saturation peak; (3) a change in interference state of fringes coming from optical feedback in the laser. Fortunately, the detailed knowledge of these causes is of little importance in the present case as far as the reference laser frequency drift remains at a reasonable level ( $\leq 10$  Hz/min) and can be compensated. The result is that the standard deviation of the measurement of the  $\text{CO}_2$ - $\text{OsO}_4$  frequency difference is of the same order as that obtained in a measurement of the difference between two simultaneously recorded molecular lines ( $\leq 50$  Hz). Examples of recordings of  $\text{CO}_2$  and  $\text{OsO}_4$  saturated absorption lines are given in figs. 1, 2 and 3, together with the time variation of the frequency drift of the reference laser in each experiment. The typical conditions which have been used in the experiments are the following:

— for  $\text{CO}_2$ , the pressure in the large cell was in the range of  $0.7$  to  $1.5 \times 10^{-2}$  Pa and the incident laser power was of the order of  $500 \mu\text{W}$ ; each recording lasted about 20 min (20 scans of 57 s with a 100 ms time constant over 500 frequency channels of 50 Hz each).

— for  $\text{OsO}_4$ , the pressure was  $\sim 3 \times 10^{-3}$  Pa and the incident power  $\sim 3 \mu\text{W}$ ; the total recording time was limited to 100 to 200 s (5 to 10 scans lasting 20 s each, with an integration time constant reduced to 30 ms over the same frequency range).

A fully quantitative discussion of the signal-to-noise ratio that can be reached with these conditions will be given in a near future paper.

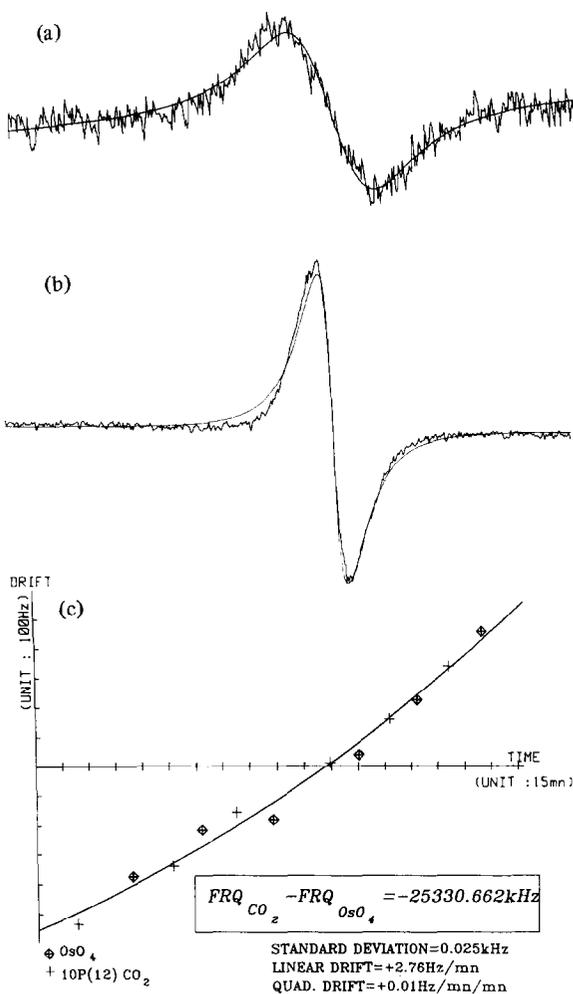


Fig. 1. (a) First derivative signal corresponding to the  $CO_2$  10P(12) saturated absorption line and Lorentzian derivative fit (hwhm = 3.08 kHz). The  $^{192}OsO_4$  line to which this  $CO_2$  line is compared is the P(39)  $A_1^3(u)$  line [15] for which a typical recording is displayed in (b) (hwhm = 1.60 kHz). This line exhibits a slight asymmetry and a non-Lorentzian character owing to a rather large modulation index. The reference laser is locked to the R(66)  $A_1^0 + F_1^0 + F_2^0 + A_2^0$  trigonal superhyperfine cluster of the  $\nu_3$  band of  $^{32}SF_6$  and (c) gives the frequency drift of this reference laser (as a function of time) for each of the twelve successive line recordings.

### 3. Results and comparison with previous measurements

Preliminary measurements have been performed for three laser lines of the  $10.4 \mu m$   $^{12}C^{16}O_2$  band: P(12),

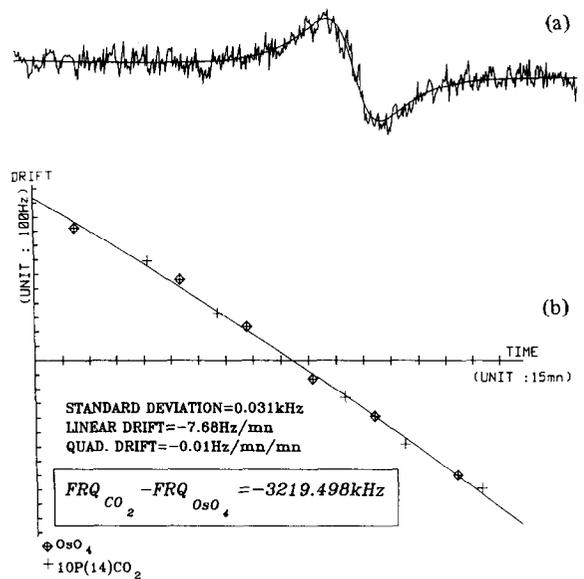
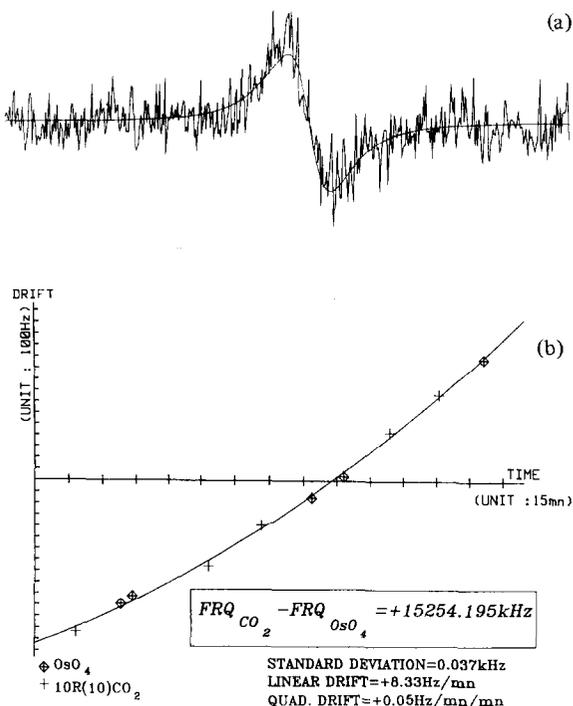


Fig. 2. (a) First derivative of the  $CO_2$  10P(14) saturated absorption line and calculated Lorentzian fit (hwhm = 2.15 kHz). The reference laser was locked to the R(28)  $A_2^0$  line of  $SF_6$  and the time variation of its frequency drift is displayed in (b). The  $^{192}OsO_4$  line to which this  $CO_2$  line is compared, is a hot unidentified line whose absolute frequency has been reported in ref. [13].

P(14) and R(10). The obvious reasons for this choice are: for P(12) the existence of the two strong fundamental lines of the  $\nu_3$  band of  $^{192}OsO_4$  [15] which are easily accessible with a conventional  $CO_2$  laser and for P(14) and R(10) the existence of the unidentified  $^{192}OsO_4$  lines whose absolute frequency has been previously measured directly.

Typical recordings for each one of these three  $CO_2$  lines are shown respectively in figs. 1, 2 and 3. The positions of the line centers have been obtained by using a non-linear regression program which fits the recorded lines with Lorentzian derivatives and a tilted baseline. The results for the three measured frequency intervals between  $CO_2$  and  $OsO_4$  lines are displayed below each of the curves which have been used for the reference frequency drift corrections. These values are not corrected for any other systematic effect (e.g. the second-order Doppler shift, wave-front curvature shift ...) and before any detailed study of these systematic effects has been made, an uncertainty of the order of 200 Hz should be associated with these values. We postpone this detailed discussion of lineshape effects to our next paper.



From these frequency intervals, from our grid of OsO<sub>4</sub> markers [11] and from the two OsO<sub>4</sub> absolute frequencies which have been measured [13,14], new absolute frequencies can be assigned to the CO<sub>2</sub> lines. This new set of frequencies is compared to values reported in the past from saturated fluorescence measurements in table 1. The agreement is within the error bars and the small “blue” shift of our 1980 values can be reasonably explained as a pressure shift [18] corresponding to the typical 40 mTorr pressure used in the external CO<sub>2</sub> cell for the measurements of ref. [9].

◀ Fig. 3. (a) First derivative signal and Lorentzian fit (hwhm = 3.44 kHz) for the CO<sub>2</sub> 10R(10) line and (b) corresponding time dependence of the reference laser frequency shift. The OsO<sub>4</sub> line to which this CO<sub>2</sub> line is connected is an unidentified line corresponding most probably to the isotope 192, located ≈173697.5 kHz below the fundamental R(36) A<sub>1</sub><sup>0</sup> line of the ν<sub>3</sub> band of <sup>192</sup>OsO<sub>4</sub> and whose absolute frequency has been measured with a 50 Hz uncertainty [14]. The reference laser is also locked to an unidentified OsO<sub>4</sub> line.

Table 1  
Absolute frequencies of the three CO<sub>2</sub> lines studied in this work (in kilohertz)

	P(12)	P(14)	R(10)
Saturated fluorescence 1973 [8]	28 516 026 638.2 (28.6)	28 464 673 699.2 (28.9)	29 054 072 693.8 (26.1)
Saturated fluorescence (external cell) and OsO <sub>4</sub> /1980 [9]	28 516 026 661.3 (4.0) b)	28 464 673 723.5 (4.0) b) 28 464 673 723.0 (7.0) a)	
Saturated fluorescence 1983 [12]	28 516 026 657.7 (4.1)	28 464 673 719.0 (4.2)	29 054 072 699.5 (3.8)
Direct absorption and OsO <sub>4</sub> (this work)	28 516 026 658.64 (1.4) b) 28 516 026 657.4 (1.7) c)	28 464 673 719.0 (1.0) b) 28 464 673 717.8 (1.4) c)	29 054 072 700.86 (0.2) c)

a) Direct measurement between R(30) and P(14) [9].  
 b) Using νOsO<sub>4</sub>(P(14)) = 28 464 676 938.5 (1.0) from ref. [13].  
 c) Using νOsO<sub>4</sub>(R(10)) = 29 054 057 446.660 (0.05) from ref. [14].

#### 4. Conclusion and future work

This paper is only a feasibility demonstration that one can obtain CO<sub>2</sub> saturated absorption peaks in the free-flight regime since our 2.1 kHz half-width is essentially dominated by the time of flight across the beam and by modulation broadening. The pressure shift and baseline tilt problems, which limit the accuracy of the saturated fluorescence method at a few kilohertz level, are much less critical with this new approach. One should be able to transfer the 50 Hz absolute frequency accuracy of the OsO<sub>4</sub> line measured in [14] to the R(10) CO<sub>2</sub> line. To achieve this goal a study of systematic effects which are relevant for such a comparison, involving different molecules, has been undertaken in collaboration with the LPTF (Laboratoire Primaire du Temps et des Fréquences in Paris). The result which is already acquired from the present work is a high degree of confidence in the absolute frequency of our OsO<sub>4</sub> and CO<sub>2</sub> reference markers at the kilohertz level. An interesting possibility, which is offered by the resolution that we have reached, is the study of hyperfine structures of the isotopic species of CO<sub>2</sub> with nuclear spin, and which involve either electric quadrupole or magnetic dipole interactions.

Finally we should mention another way of using saturated absorption in CO<sub>2</sub> for metrological applications, which we have also demonstrated recently: we have locked directly the reference laser to CO<sub>2</sub> lines in our auxiliary cells (6 m length) at a much higher pressure (a few tenths of Pascal) giving rise to a much broader saturation resonance (~50 kHz). The time constant of the servo-loop had to be significantly increased (up to ~1 ms). The resulting laser spectral width can be estimated through the corresponding broadening of an OsO<sub>4</sub> resonance in the large cell for which the half-width was found to be 7 kHz (to be compared with the usual 10 Hz spectral width of the same reference laser locked to OsO<sub>4</sub> [17]). As an example of a useful application of this device, the <sup>15</sup>NH<sub>3</sub> ν<sub>2</sub> as R(2.0) hyperfine component of lowest frequency ( $F = 5 \leftrightarrow F = 4$ ) [15] was measured in this way, through a direct beat frequency counting, at 52 790 kHz from the 10 R(42) CO<sub>2</sub> line. The absolute frequency of this ammonia line is therefore 29 638 932 980 ± 15 kHz and can be used to calibrate the Fourier transform spectrum of this molecule.

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