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# HCOOH high resolution spectroscopy in the 9.18 $\mu$ m region

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(Dated: today)

We report on highly accurate absolute frequency measurement against a femtosecond frequency comb of 6 saturated absorption lines of formic acid (HCOOH) with an accuracy of 1 kHz. We also report the frequency measurement of 17 other lines with an accuracy of 2 kHz. Those lines are in quasi coincidence with the 9R(36) to 9R(42) CO<sub>2</sub> laser emission lines and are probed either by a CO<sub>2</sub> or a widely tunable quantum cascade laser phase locked to a master CO<sub>2</sub> laser. The stability of HCOOH stabilized lasers is characterized by a fractional Allan deviation of  $3.1 \cdot 10^{-12} \tau^{-1/2}$ . They give suitable frequency references for H<sub>2</sub><sup>+</sup> Doppler free two-photon spectroscopy.

**Keywords:** CO<sub>2</sub> laser, quantum cascade laser, formic acid, saturated absorption, frequency measurement.

## I. INTRODUCTION

Electron to proton mass ratio is a fundamental constant that is determined with a relative accuracy of  $4.6 \cdot 10^{-10}$  [1] from separate electron and proton mass measurements [2, 3]. Molecular hydrogen ion (H<sub>2</sub><sup>+</sup> or HD<sup>+</sup>) vibrational spectroscopy has recently been proposed as a new tool for very accurate direct optical determination of the electron to proton mass ratio with an improved accuracy [4–6]. H<sub>2</sub><sup>+</sup> high resolution vibrational spectroscopy is feasible using Doppler free two-photon transitions in the 9.1-9.2  $\mu$ m range ( $1087\text{--}1099 \text{ cm}^{-1}$ ), corresponding to the 9R(34)–9R(52) CO<sub>2</sub> laser emission lines. There is no close coincidence between CO<sub>2</sub> laser lines and H<sub>2</sub><sup>+</sup> two-photon lines. However, we have shown that the recently developed quantum cascade laser sources (QCL) are suitable for H<sub>2</sub><sup>+</sup> spectroscopy. The relative accuracy level of interest on the vibrational frequency determination for mass ratio metrology purposes is  $2 \cdot 10^{-10}$ , that corresponds to  $2 \cdot 10^{-7} \text{ cm}^{-1}$  (6 kHz), hence the need for highly accurate molecular frequency references in the 9.1-9.2  $\mu$ m range.

Recently, the 9  $\mu$ m band <sup>12</sup>C<sup>16</sup>O<sub>2</sub> absolute frequencies have been measured with an accuracy better than 1 kHz up to the 9R(36) line [7] using a CO<sub>2</sub> saturated absorption stabilized CO<sub>2</sub> laser. Because the 9  $\mu$ m band is a hot band and because the molecular population dramatically decrease with the angular quantum number, CO<sub>2</sub> saturated absorption signal to noise ratio becomes too low for laser stabilisation purposes beyond the 9R(36) line. Among the large variety of molecules (SF<sub>6</sub>, OsO<sub>4</sub>, NH<sub>3</sub>, CO<sub>2</sub>, HCOOH) which are well known to provide frequency references for CO<sub>2</sub> lasers, formic acid  $\nu_6$  band is the only one that presents intense lines in the 9.1-9.2  $\mu$ m range [8]. As an example, Fig. 1 shows the ( $v=0, L=2$ ) $\rightarrow$ ( $v=1, L=2$ ) H<sub>2</sub><sup>+</sup> two-photon excitation spectrum and formic acid lines close to the 9R(42) CO<sub>2</sub> emission line. Through the paper, CO<sub>2</sub> and HCOOH denote the standard isotopes. At 300 K, HCOOH is in the *trans* conformation, the *cis* one representing only 0.1% of the molecules [9].

Line frequency measurements in the HCOOH  $\nu_6$  band have been performed using Fourier transform, diode laser, CO<sub>2</sub> laser, and laser-radiofrequency double resonance and microwave spectroscopy [10–15]. Among them, the most accurate ones were obtained by CO<sub>2</sub> laser spectroscopy with accuracies in the 50-250 kHz range [11] for a small number of lines. When compared to theoretical models, those measurements lead to the determination of effective hamiltonian parameters and to the prediction of HCOOH line positions and intensities. The HITRAN 2004 database [8] gives the HCOOH line positions with a  $10^{-2}$  to  $10^{-3} \text{ cm}^{-1}$  uncertainty. Recently, simultaneous analysis of rotational and rovibrational data [16] was performed, allowing the  $\nu_6$  band line assignment with a  $2.4 \cdot 10^{-4} \text{ cm}^{-1}$  root mean square deviation (7.2 MHz). Last year, absolute line intensities in the  $\nu_6$  and  $\nu_8$  bands have been measured [9], resulting in new intensity predictions, the line strength of the  $\nu_6$  band lines being corrected by nearly a factor of 2 [17]. New line positions are also given in [17].

The aim of this work is the measurement at the kHz accuracy level of molecular reference frequencies in quasi coincidence with the 9R(36) to 9R(42) CO<sub>2</sub> laser lines. We first describe the CO<sub>2</sub>/HCOOH reference laser and the widely tunable QCL we have implemented. We then describe the frequency measurements and give the absolute

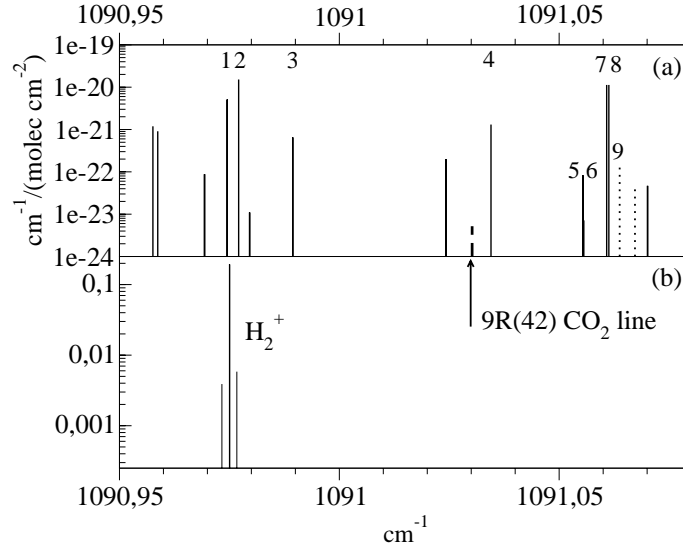


FIG. 1: (a) Full lines : HCOOH lines of intensity larger than  $10^{-23} \text{ cm}^{-1}/(\text{molec cm}^{-2})$  from HITRAN 2004 database [8]. Dotted lines : additional lines predicted by A. Perrin [17]. The numbering of the HCOOH lines corresponds to that given in the last column of Table I. When operated on the 9R(42)  $\text{CO}_2$  line, the  $\text{CO}_2/\text{HCOOH}$  reference laser is stabilized on line n°4. (b)  $(v=0, L=2) \rightarrow (v=1, L=2)$   $\text{H}_2^+$  two-photon transition spectrum in atomic units, see ref. [4]. The central peak is a 6.5 MHz wide doublet.

frequencies of 23 HCOOH lines. Finally, we analyse the relative stability of two independant lasers locked to two different HCOOH lines.

## II. THE LASER SOURCES

The experimental setup consists in a HCOOH stabilised  $\text{CO}_2$  reference laser (see Fig. 2) and in a tunable QCL (see Fig. 3).

### A. The $\text{CO}_2/\text{HCOOH}$ reference laser

The  $\text{CO}_2$  laser is a sealed-off low pressure (13 Torr) dual-discharge-arm 1m-long laser emitting in a single longitudinal mode. The laser cavity is made of a 90-95% efficiency diffraction grating in the Littrow configuration and of a high reflectivity mirror at  $9.2\mu\text{m}$ . The main output of the laser is the zero<sup>th</sup> order of the grating. Laser oscillation is obtained up to the 9R(48) emission line of  $\text{CO}_2$  at  $9.142\mu\text{m}$  with more than 1W of optical power. The  $\text{CO}_2$  laser frequency is stabilised onto a formic acid saturated absorption signal detected in transmission of a 1m long optical cavity of finesse 100 and beam waist 3.8 mm containing a low pressure HCOOH gaz (0.5-2 mTorr, 66-266 Pa). Both the laser and the cavity mirrors are glued on piezoelectric transducers for sweeping and modulation purposes. The cavity resonance frequency is slightly modulated (frequency:  $f_1=33 \text{ kHz}$ , depth:  $\sim 1 \text{ kHz}$ ) and is locked to the laser frequency using first harmonic phase sensitive detection at  $f_1$  of the transmitted intensity. The intracavity optical power is set at  $400 \mu\text{W}$ . The laser frequency is modulated (frequency  $f_2=5.67 \text{ kHz}$ , depth 100-200 kHz). A third harmonic phase-sensitive detection at  $3f_2$  gives a saturated absorption signal similar to that of Fig. 4, with a high signal to noise ratio of more than 1000 at 1s integration time. This signal is used to stabilise the  $\text{CO}_2$  laser with a loop bandwidth of 100 Hz. In the case of the 9R(42)  $\text{CO}_2$  line, there is no coincidence with intense HCOOH lines, so the  $\text{CO}_2$  laser frequency is up-shifted by 128 MHz using an acousto-optic modulator to reach a HCOOH line.

## B. The QCL system

The QCL is a singlemode cw distributed feedback laser [18] operated in a liquid nitrogen cryostat. The threshold current is 400 mA at 77 K, the maximum current is about 1 A with a 9 V polarisation voltage. It can deliver up to 160mW optical power and is tunable from 9.166  $\mu\text{m}$  to 9.240  $\mu\text{m}$ . The temperature and current tunabilities are respectively 3 GHz/K and 150 MHz/mA. Because the QCL's emission spectrum is several MHz wide and exhibits a jitter over tens of MHz, the free running QCL is not suitable for high resolution infrared spectroscopy. The spectral features of singlemode CO<sub>2</sub> lasers are much better with a linewidth in the kHz range [19]. We have shown that they can be written out on the QCL spectrum with a 300-1500 MHz tunable frequency offset using a fast phase-lock loop [20] with a bandwidth of 6 MHz. The tunability range has been extended to 2 GHz by applying a 3-5 V reverse bias to the HgCdZnTe room temperature detector that monitors the beat note between the CO<sub>2</sub> laser and the QCL, resulting in a better detectivity. The 6 MHz loop bandwidth implies that the CO<sub>2</sub> laser frequency modulation is also written out on the QCL frequency with the same depth. For HCOOH spectroscopy, the QCL beam is injected into a second Fabry-Perot cavity similar to the first one (1.5 m long, finesse 100, beam waist 4.2 mm, intra-cavity optical power 400  $\mu\text{W}$ , HCOOH pressure 0.5-2 mTorr). The cavity resonance frequency is modulated (frequency  $f'_1=50$  kHz, depth  $\approx 1$  kHz) and is locked to the QCL emission frequency. A third harmonic phase-sensitive detection at  $3f_2$  gives the HCOOH saturated absorption signal depicted in Fig. 4.

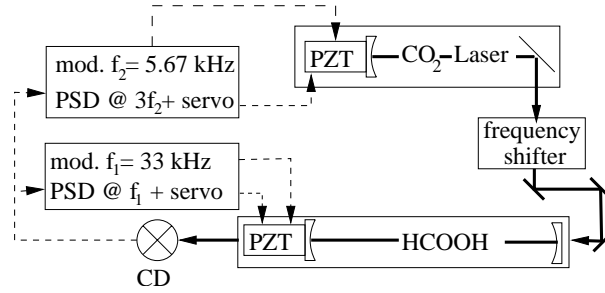


FIG. 2: CO<sub>2</sub>/HCOOH reference laser. The CO<sub>2</sub> laser is stabilised on a HCOOH saturated absorption line. The frequency shifter is an acousto-optic modulator only used when the CO<sub>2</sub> laser is operated on the 9R(42) CO<sub>2</sub> line to up-shift the laser frequency by 128 MHz. CD: Liquid nitrogen cooled HgCdTe detector. PZT: piezo transducer. PSD : phase sensitive detection.

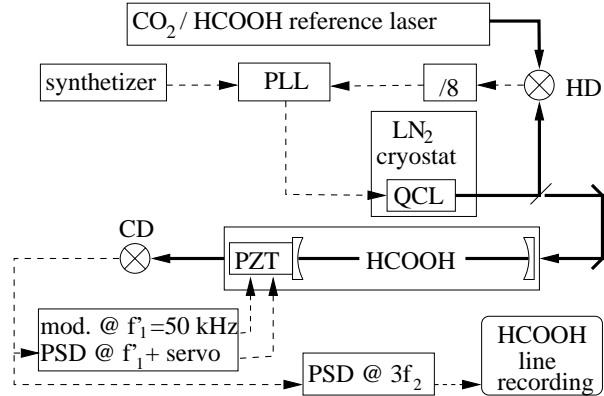


FIG. 3: QCL spectrometer. The QCL and CO<sub>2</sub>/HCOOH reference laser beams are beaten on a fast room temperature HgCdZnTe detector (HD). The beatnote frequency is divided by 8 and phase compared to a RF synthesizer of frequency  $\delta$ . The QCL is phase-locked to the reference laser with a tunable frequency offset  $8\delta$ . Because the frequency modulation of the reference laser is transferred to the QCL by the fast phase-lock loop, the HCOOH saturated absorption line is phase sensitive detected at the third harmonic  $f_2$ , see Fig. 2. PZT: piezo transducer, PLL : phase-lock loop.

### III. RESULTS AND DISCUSSION

We have performed absolute (A) and relative (R) frequency measurements of HCOOH saturated absorption lines. The results are given in Table I and are respectively labelled by A or R in the second column.

#### A. Absolute frequency measurement

For the absolute measurements, the CO<sub>2</sub>/HCOOH reference laser (Fig. 2) has been transported to LPL laboratory where a femtosecond frequency comb infrared frequency measurement facility is implemented [21]. We have measured the absolute frequency of 6 HCOOH lines in quasi coincidence with 9R(36) to 9R(42) CO<sub>2</sub> laser lines for which no accurate molecular reference were known.

The HCOOH/CO<sub>2</sub> reference laser frequency is measured by comparison with a very high-harmonic of the repetition rate of a femto-second (fs) laser [21]. In the frequency domain, the fs laser provides a comb of modes separated by the repetition rate [22]. A second comb is produced by a sum-frequency generation (SFG) of the fs laser comb and the CO<sub>2</sub> laser in a nonlinear crystal. This results in a beat between the low frequency part of the SFG comb and the high frequency part of the initial comb. The infrared frequency is thus compared to the difference between two modes of the comb. The beatnote is finally used to phase-lock the repetition rate to the CO<sub>2</sub> laser frequency. This scheme is independent of the comb offset and does not require any broadening of the comb. To complete the frequency measurement procedure, the repetition rate (about 1 GHz) is detected with a fast photodiode and counted against a local oscillator at 1 GHz. This local oscillator is phase-locked to a reference signal transmitted via a 43-km long optical fiber from the LNE-SYRTE laboratory, located in Paris [23]. This laboratory has developed a high stability oscillator, which is based on a combination of a cryogenic Sapphire oscillator (CSO), an H-Maser and a set of low noise microwave synthesizers [24]. Its frequency is steered by the H-Maser in the long-term, and monitored by the Cs atomic fountain for accuracy [25]. This signal shows a frequency stability slightly below  $10^{-14} \tau^{-1}$  in the range 1-10 s, and  $10^{-15}$  from 10 to 105 s. The transfer through the optical link degrades this stability by less than one order of magnitude, while the phase noise introduced by the link can be efficiently suppressed with an active correction. Finally the resolution of the whole measurement chain is better than 0.3 Hz ( $10^{-14}$  in relative value) and will definitely not be a limitation for the present measurements.

The day to day repeatability of the measurements is 100 Hz for controlled experimental conditions. No significant frequency shifts are observed by varying the intracavity optical power between 400  $\mu$ W and 2mW, varying the laser modulation depth by more than a factor eight and introducing significant but small error signal offsets. We have observed a positive pressure shift smaller than 2 kHz by varying the HCOOH pressure up to 4 mTorr. At the 0.5 mTorr level, formic acid pressure cannot be precisely controlled in our setup, probably because of adsorption effects on the vacuum chamber walls. We therefore give a conservative uncertainty of 1 kHz or  $3.3 \cdot 10^{-8} \text{ cm}^{-1}$  on the absolute frequency measurements.

#### B. HCOOH spectroscopy

We have measured the HCOOH lines that are red or blue detuned by 300-1600 MHz with respect to the closest CO<sub>2</sub>/HCOOH reference laser line using the widely tunable phase-locked QCL. The QCL frequency is swept by 1.6 kHz increments and the saturated absorption profile is recorded and fitted by the third derivative of a lorentzian shape to determine the line center and width (see Fig 4). We are easily able to detect lines with a signal to noise ratio between 3 and 1000 in a 1s integration time, the former corresponding to normalized intensities down to  $1.6 \cdot 10^{-22} \text{ cm}^{-1}/(\text{molec cm}^{-2})$ , (taking into account the recent corrections of the line intensities by a factor of two [9]). With optimized intracavity power and gas pressure, the sensitivity of the spectrometer is high enough to detect the CO<sub>2</sub> 9R(42) saturated absorption line that have a  $5 \cdot 10^{-24} \text{ cm}^{-1}/(\text{molec cm}^{-2})$  normalized intensity. Nevertheless, absolute HCOOH line intensities cannot be determined precisely from the line profile because of the large uncertainty on the actual pressure in the cavity.

The HCOOH fitted linewidths are between 160 and 220 kHz and are dominated by modulation broadening. Indeed, the transit time broadening is 26 kHz, the pressure broadening is  $0.32 \text{ cm}^{-1}/\text{atm}$  [9] i.e. 12.8 kHz/mTorr and the natural width and power broadening are negligible.

Thanks to the high signal to noise ratio of the lines, the fitted line centers are determined with uncertainties better than 1 kHz. Nevertheless, taking into account the independant uncertainties on the reference line frequency (1 kHz), the line position (1 kHz) and the HCOOH pressure determination (1 kHz), we give a conservative uncertainty of 2 kHz or  $6.6 \cdot 10^{-8} \text{ cm}^{-1}$  on the HCOOH line frequency determined with the QCL spectrometer.

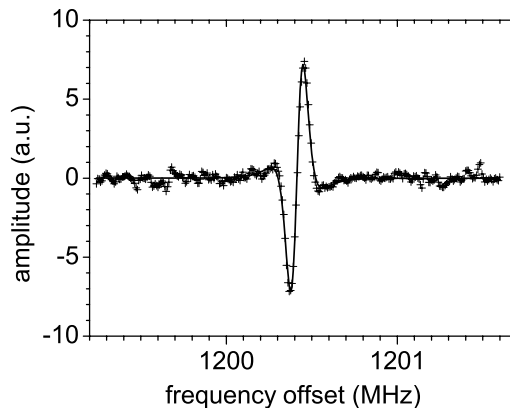


FIG. 4: Third harmonic phase sensitive saturated absorption signal of HCOOH at 32 707 063 566.1 kHz, labelled 3 in the last column of Table I versus the frequency offset  $8\delta$  between the reference laser and the phase locked QCL (see Fig. 3). The integration time is 1 s per point. Full line: adjustment by a third Lorentzian derivative. The full width at half maximum is 220 kHz.

### C. Discussion

In Table I, the measured frequencies are compared to the HITRAN 2004 database predicted values [8] that are given in a normalized format with a  $10^{-6} \text{ cm}^{-1}$  resolution, but with an uncertainty in the  $10^{-3}$ - $10^{-2} \text{ cm}^{-1}$  range (uncertainty code of 3). The HITRAN 2004 predictions are in excellent agreement with our measurements since the discrepancy is below  $2 \cdot 10^{-4} \text{ cm}^{-1}$  for most of the lines excepted one for which a  $8 \cdot 10^{-4} \text{ cm}^{-1}$  (24 MHz) offset is observed. The agreement with the line positions predicted by O. I. Baskakov [16] and by A. Perrin [17] are of comparable quality. The root mean square of the deviations is of the order of  $2 \cdot 10^{-4} \text{ cm}^{-1}$ , in agreement with the uncertainty level claimed by the authors,  $2.4 \cdot 10^{-4}$  and  $5 \cdot 10^{-4} \text{ cm}^{-1}$  respectively.

Two doublets predicted by A. Perrin [17] at 1089.040400 and 1089.998920  $\text{cm}^{-1}$  with the intensities  $1.85 \cdot 10^{-22}$  and  $5.72 \cdot 10^{-22} \text{ cm}^{-1}/(\text{molec cm}^{-2})$  have not been observed in a frequency interval of  $\pm 8 \text{ MHz}$  ( $2.6 \cdot 10^{-4} \text{ cm}^{-1}$ ) around the predicted values, and with a sensitivity of  $1.6 \cdot 10^{-22} \text{ cm}^{-1}/(\text{molec cm}^{-2})$ .

In Table II, we compare the present frequency measurements with previously published ones. There is a good agreement with the measurements obtained by  $\text{CO}_2$  laser saturation spectroscopy and reported in [11], the accuracy being improved by at least one order of magnitude.

### D. Reference frequency stability

The aim of this work is to build a reliable and stable frequency reference to probe two-photon vibrational transitions in  $\text{H}_2^+$  with a resolution of the order of 1 kHz. We have measured the relative frequency stability of two independent systems. The first one is the  $\text{CO}_2/\text{HCOOH}$  reference laser stabilized on the HCOOH line n°4 of Table I. The second system involves the QCL and a master  $\text{CO}_2$  laser similar to the first one. The QCL is phase locked to the  $\text{CO}_2$  laser with a fixed frequency offset. The QCL beam probes HCOOH line n°7 of Table I. The saturated absorption signal is used to lock the master  $\text{CO}_2$  laser frequency. To characterize the relative stability of the two laser systems, the beatnote frequency is counted with 1 s gate time during a few tenth of minutes. The Allan deviation shown in Fig. 5 exhibits a white frequency noise behaviour of  $146 \text{ Hz } \tau^{-1/2}$ , that corresponds to a  $4.5 \cdot 10^{-12} \tau^{-1/2}$  fractional stability, i.e. when divided by the laser frequency. The relative stability reaches the 10 Hz level for 200 s integration time. Both lasers are locked independently using saturated absorption signal having similar signal to noise ratios, so individual stabilities are expected to be comparable. They are given by  $146/\sqrt{2} \approx 100 \text{ Hz } \tau^{-1/2}$ , corresponding to a  $3.1 \cdot 10^{-12} \tau^{-1/2}$  fractional stability.

CO <sub>2</sub> line		f (kHz)	$\delta f$ (kHz)	$\sigma_m$ (cm <sup>-1</sup> )	$\delta_H$ (cm <sup>-1</sup> )	$\delta_B$ (cm <sup>-1</sup> )	$\delta_P$ (cm <sup>-1</sup> )	J' K <sub>a</sub> ' K <sub>c</sub> ' J'' K <sub>a</sub> '' K <sub>c</sub> ''		
9R(36)	A	32 615 874 282.1	1.0	1087.948 459 40			-0.000601	26 21 5 27 21 6 26 21 6 27 21 7	*	
9R(38)	R	32 645 920 103.8	2.0	1088.950 680 13	-0.000030	0.000157	0.000040	17 3 15 17 4 14		
	R	32 646 482 873.7	2.0	1088.969 452 12	0.000022	-0.000030	0.000072	19 3 16 20 3 17		
	R	32 646 774 027.4	2.0	1088.979 163 96	-0.000216	-0.000038	-0.000096	21 11 10 22 11 11 21 11 11 22 11 12	*	
	A	32 647 442 530.0	1.0	1089.001 462 80	-0.000247	-0.000208	-0.000117	30 1 29 30 2 28		
	A	32 647 451 806.2	1.0	1089.001 772 23			-0.000408	52 6 46 53 5 49		
	R	32 648 078 880.7	2.0	1089.022 689 18	-0.000031	-0.000074	-0.000051	16 3 14 16 4 13		
	R	32 648 797 827.9	2.0	1089.046 670 68	0.000101	-0.000047	-0.000019	20 0 20 21 0 21		
9R(40)	R	32 677 093 109.1	2.0	1089.990 499 66	0.00007	0.000028	-0.000010	29 1 28 29 2 27		
	R	32 677 848 146.1	2.0	1090.015 684 99	0.000105	-0.000028	-0.000255	19 1 19 20 0 20		
	A	32 678 207 409.6	1.0	1090.027 668 73	-0.000021	-0.000041	-0.000021	18 3 16 19 3 17		
	A	32 678 247 320.7	1.0	1090.029 000 02			-0.000070	22 0 22 22 2 21		
	R	32 679 212 591.0	2.0	1090.061 197 97	0.000018	0.000447	0.000088	4 2 3 5 3 2		
	R	32 679 681 163.9	2.0	1090.076 827 88	0.000018		-0.000012	4 2 2 5 3 3		
9R(42)	R	32 706 583 453.5	2.0	1090.974 191 67	-0.000338	0.000412	0.000082	18 9 9 19 9 10 18 9 10 19 9 11	*	1
	R	32 706 672 889.5	2.0	1090.977 174 93	0.000025	-0.000536	-0.000035	17 2 16 18 2 17		2
	R	32 707 063 566.1	2.0	1090.990 206 50	0.000797	-0.000028	0.000077	20 15 5 21 15 6 20 15 6 21 15 7	*	3
	A	32 708 391 980.5	1.0	1091.034 517 64	-0.000038	-0.000045	-0.000032	21 2 20 21 3 19		4
	R	32 709 015 560.0	2.0	1091.055 318 01	-0.000042		-0.000112	8 4 5 7 5 2		5
	R	32 709 017 250.3	2.0	1091.055 374 39	-0.000036		-0.000116	8 4 4 7 5 3		6
	R	32 709 175 798.5	2.0	1091.060 662 99	-0.000147		-0.000023	17 5 12 18 5 13		7
	R	32 709 189 841.6	2.0	1091.061 131 42	-0.000149		0.000081	17 5 13 18 5 14		8
	R	32 709 274 924.5	2.0	1091.063 969 48			-0.000091	22 20 3 23 20 4 22 20 2 23 20 3	*	9
RMS					0.000221	0.000230	0.000173			

TABLE I: HCOOH line frequencies in the  $\nu_6$  band. The first column gives the closest CO<sub>2</sub> laser line and the second one the measurement system (A for absolute frequency measurement and R for relative measurement by QCL spectroscopy). Columns 3 and 4 give the measured frequencies  $f$  (this work) and their uncertainties  $\delta f$ . Column 5 is the corresponding wavenumber  $\sigma_m$ . Columns 6, 7 and 8 give the differences  $\delta_H = \sigma_m - \sigma_H$ ,  $\delta_B = \sigma_m - \sigma_B$  and  $\delta_P = \sigma_m - \sigma_P$  between our measurements and the wavenumbers  $\sigma_H$ ,  $\sigma_B$  and  $\sigma_P$  predicted respectively by the HITRAN 2004 database [8], O. I. Baskakov [16] (supplementary data, file Application\_1.doc) and A. Perrin [17] (supplementary data). The following columns give the usual line nomenclature ( $\nu_6$  band). (\*) denotes predicted doublets. Figures in last column refer to the HCOOH line numbering in Fig. 1(a). The last line (RMS) gives the root mean square deviations of  $\delta_H$ ,  $\delta_B$  and  $\delta_P$ .

	(a)	(b)	(a)-(b)	J' K <sub>a</sub> ' K <sub>c</sub> ' J'' K <sub>a</sub> '' K <sub>c</sub> ''	ref.
	kHz	kHz	kHz		
9R(38)	32 646 774 027.4 (2.0)	32 646 775 100	-1072.6	V6 21 11 10 22 11 11 V6 21 11 11 22 11 12	[14]
	32 647 442 530.0 (1.0)	32 647 442 520 (100)	10.0	V6 30 1 29 30 2 28	[11, 15] *
	32 647 451 806.2 (1.0)	32 647 451 800 (100)	6.2	V6 52 6 46 53 5 49	[11, 15] *
9R(40)	32 678 207 409.6 (1.0)	32 678 207 360	49.6	V6 18 3 16 19 3 17	[11, 15]

TABLE II: Comparison of the present frequency measurements (a) and already published measurements (b). The line assignments are those given in HITRAN 2004 or the recent reference [17]. \*: the line assignment in ref. [11, 15] is different.

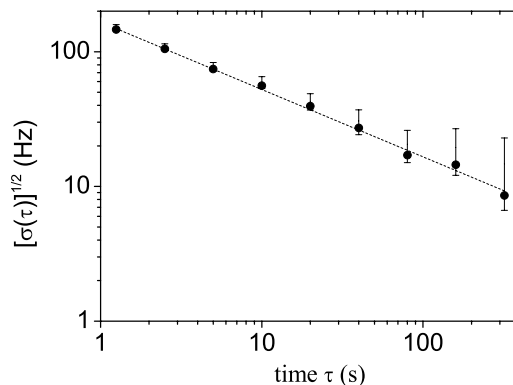


FIG. 5: Square root of the Allan deviation of the two HCOOH stabilized laser beatnote as a function of integration time  $\tau$ , obtained from a record of 633 1s gate time measurements. The dashed curve is a fit giving a  $146 \text{ Hz } \tau^{-1/2}$  behaviour. Dead time between measurements is 0.25 s.

#### IV. CONCLUSION

We have set up a  $\text{CO}_2/\text{HCOOH}$  reference laser that can be operated from the 9R(36) to 9R(42) line and measured the absolute frequency of 6 saturated absorption lines with an accuracy of 1 kHz ( $3.3 \cdot 10^{-8} \text{ cm}^{-1}$ ) improved by two orders of magnitude as compared to previously reported results or predictions. Using a quantum cascade laser phase (QCL) locked to a master  $\text{CO}_2$  laser, we have determined the frequency of 17 additional formic acid lines with an accuracy of 2 kHz. The frequency stability of both the reference laser and the phase locked QCL is characterized by a relative Allan deviation of  $3.1 \cdot 10^{-12} \tau^{-1/2}$ . This performance demonstrates that the  $\text{CO}_2/\text{HCOOH}$  phase locked QCL is a suitable tool for  $\text{H}_2^+$  high resolution spectroscopy at the kHz level.

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