Frequency measurements of saturated-fluorescence-stabilized CO$_2$ laser lines: comparison with an OsO$_4$-stabilized CO$_2$ laser standard

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Abstract. We have used the Villetaneuse saturated absorption spectrometer working in the 10 µm region, referenced to the OsO$_4$ frequency grid, to test the performance of the saturated fluorescence method for CO$_2$ laser frequency stabilization. The Allan variance for the saturated-fluorescence-stabilized CO$_2$ laser reached 60 Hz for an integration time of 300 s. We also performed three absolute measurements of CO$_2$ laser frequencies stabilized by the saturated fluorescence method, with a sub-kHz accuracy. We obtained a 1.7 kHz redshift of the CO$_2$ saturated fluorescence lines, which we attribute essentially to pressure. This is in contradiction with the previous observation of a blueshift [K.L. SooHoo, C. Freed, J.E. Thomas, H.A. Haus: Phys. Rev. Lett. **53**, 1437 (1984)]. Furthermore, significant deviations of the measured frequencies from the data of Maki et al. [A.G. Maki, C.-C. Chou, K. Evenson, L.R. Zink, J.T. Shy: J. Mol. Spec. **167**, 211 (1994)] demonstrate the need for a new calibration of the CO$_2$ frequency grid.

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CO$_2$ lasers stabilized on narrow sub-Doppler molecular resonances are widely used as secondary frequency standards in the 9–12 µm spectral region. By use of different CO$_2$ isotopic species they provide a dense grid of reference frequencies with accuracies of a few kHz in the IR region. This accuracy can be transferred to other spectral regions by generation of the sum or the difference of two CO$_2$ laser frequencies, which allows the estimation of virtually any frequency between some GHz and 150 THz [1]. Following the first stabilization on the Lamb dip [2], the saturated fluorescence technique developed by Freed and Javan [3] is now commonly used for stabilization because it is not expensive and gives easy access to all laser lines. With this technique, Bradley et al. [4] established in 1986 a CO$_2$ frequency grid with accuracies of 3 to 10 kHz. This grid was recently updated and extended by Maki et al. [5]; it includes now 568 laser line frequencies of the different CO$_2$ isotopic species covering a spectral range from 25.5 to 33.6 THz, with published accuracies 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.

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$_4$. This grid provides higher accuracies between 50 Hz and 1 kHz due to the intense and narrow absorption resonances of OsO$_4$ at low pressure [6–8]. However, this grid is in coincidence with a relatively small number (23) of laser lines, in the 10 µm branch of the normal CO$_2$ isotopomer laser. In 1986, Chardonnet et al. [9] were able to observe for the first time the saturation signal of CO$_2$ lines in an external cell at very low pressure of about 10^{-2} Pa at room temperature with a resolution of 2 kHz. An absolute accuracy of 50 Hz was then achieved on the R(10) line by connection to the OsO$_4$ grid [10].

This opened the way to a significant improvement of the CO$_2$ frequency grid. A linear pressure shift of -480 Hz/Pa was measured on the saturated absorption signal of the R(22) laser line [10], in agreement with theory [11], but in contradiction with the anomalous blueshift of the saturated fluorescence signal reported in [12].

Our group in Villetaneuse recently developed a new stabilization scheme for our CO$_2$ lasers based on the detection of molecular absorption lines in transmission of an external Fabry–Pérot cavity [13, 14]. In addition, we demonstrated the possibility of using the CO$_2$ lines for laser stabilization. Thus, by measuring the beat note of two CO$_2$ lasers, one stabilized on a CO$_2$ line and the other on the closest reference line belonging to the OsO$_4$ frequency grid, we were able to determine twenty absolute frequencies of ^{12}C^{16}O$_2$ laser lines with accuracies between 100 Hz and 1 kHz [15]. This set of measurements revealed some discrepancies of several kHz with the data published by Bradley et al. [4] and Maki et al. [5], larger than the claimed uncertainties. Thus, we pointed out that these uncertainties were perhaps underestimated because no systematic error of the experimental data was taken into account.

At Bonn University we have developed, during the last few years, CO$_2$ lasers stabilized on saturated fluorescence signals, in order to provide a calibration of our CO lasers in the 3 and 5 µm region by summing or doubling CO$_2$ laser

frequencies on MIM diodes and performing beat note experiments [16–18]. In order to check the accuracy of our system, we measured some frequency differences of CO_2 laser lines that can be compared to the data provided by [5]. Strong discrepancies were found [17]. As an example, the deviation from Maki's values reached 17 kHz for the $^{12}C^{16}O_2$ P(34) - $^{13}C^{16}O_2$ R(22) frequency difference, despite the reproducibility of our system being better than 1 kHz.

These sets of measurements in Villetaneuse and Bonn suggested the need for a careful comparison of the frequency standards obtained by saturated fluorescence and by saturated absorption. For this purpose our two groups decided to perform frequency difference measurements between CO_2 lasers stabilized, respectively, on a saturated fluorescence signal of CO_2 and on a saturated absorption signal of OsO_4. The latter is expected to have significantly better performance. The saturated fluorescence stabilization system was brought from the Institut für Angewandte Physik, University of Bonn, and combined with the saturated absorption spectrometer in the Laboratoire de Physique des Lasers, Université Paris 13.

1 Experimental details

The experimental setup is shown in Fig. 1. The two CO_2 lasers, which emit on the same laser line, are stabilized on OsO_4 and CO_2 respectively and are heterodyned on a HgCdTe detector.

The OsO_4 frequency stabilization system is already described in [14]. It consists of a CO_2 laser stabilized onto a saturation signal of OsO_4 placed in a Fabry–Pérot cavity. A crucial component of the stabilization scheme is a broadband CdTe electro-optic modulator (EOM). This EOM generates sidebands and one of them is tuned into resonance with the molecular line. Thus, efficient and clean frequency modulations can be applied to the sidebands simply by modulating the frequency of the synthesizer which drives the EOM. The cavity resonance is first locked to the sideband frequency using 1-f detection of the cavity signal at 90 kHz and a feedback loop of about 100 Hz bandwidth. The corrections are applied to a piezoelectric transducer (PZT) of the external cavity. A second servoloop then locks the EOM sideband to the molecular line with a 3-f detection of the 4.9 kHz modulation frequency; slow and fast corrections are respectively applied to a PZT of the CO_2 and an acousto-optic modulator. Standard conditions for the detection of the OsO_4 saturated absorption signal are a pressure of 0.04 Pa and a laser power of $50\,\mu$W inside the cavity. In this regime, the 3-f molecular signal has a peak-to-peak linewidth of about 20 kHz and the signal-to-noise ratio is 500 at $\tau = 1$ ms. The metrological performances of such a system are the following: by stabilizing both lasers onto the same strong $P(46)A_1^2(-)OsO_4$ line in coincidence with the $P(14)CO_2$ laser line we obtained a laser linewidth of 6 Hz (FWHM) and an Allan variance of 0.1 Hz ($\Delta\nu/\nu = 3.5 \times 10^{-15}$) for a time constant of 100 s. The reproducibility of the OsO_4 frequencies was estimated to be 10 Hz.

The frequency of the second laser is stabilized by means of the saturated fluorescence technique in an external cell [16]. The 22-cm-long cell is filled with pure CO_2
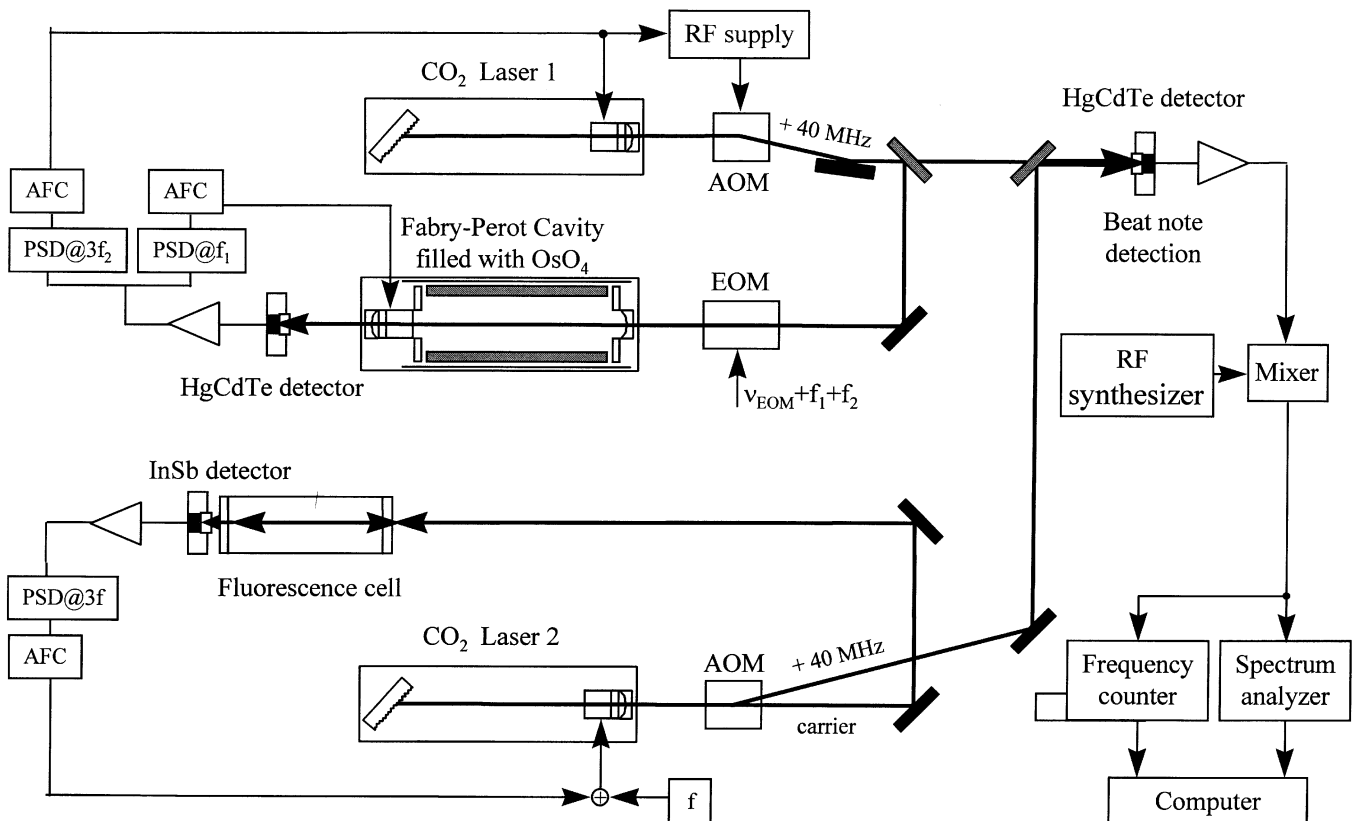

Fig. 1. Experimental scheme. Frequency modulations at $f_1 = 90$ kHz, $f_2 = 4.9$ kHz, and $f = 160$ Hz are applied to the EOM and the laser piezo tube, respectively. AOM: acousto-optic modulator, AFC: automatic frequency control, PSD: phase-sensitive detector

at a pressure of 5.3 Pa and sealed by two dichroic mirrors. The laser beam passes through the first mirror of the cell and is reflected by the second one whereas the 4.3 μm CO_2 fluorescence radiation is reflected by the first mirror and passes through the second one towards the detector, which is a liquid-nitrogen-cooled InSb photodiode. The waist of the laser beam, with a radius of 5 mm in the cell, is located on the backward reflecting mirror. To prevent any feedback to the laser, the fluorescence cell is tilted at an angle of 0.1° relative to the incoming laser beam. The rather high pressure inside the cell leads to a pressure broadening of about 1 MHz and a small pressure shift of the Lamb dip transition frequencies, but is necessary in order to produce a signal which is strong enough for the stabilization. For this purpose, the laser frequency is modulated at 160 Hz with an excursion of ±600 kHz via a piezoelectric transducer carrying the outcoupling mirror of the laser. The fluorescence signal is phase-sensitive processed with a lock-in amplifier and a time constant of 100 ms (Fig. 2). This low bandwidth is imposed by the long lifetime of a few milliseconds of the excited CO_2 molecules inside the cell. We use a third-harmonic detection which reduces strongly the baseline fluctuations and improves the long-term stability, as is well known. This is the main difference from the experiments performed by Bradley [4] and Maki [5]. Because of the low bandwidth of the automatic frequency control system of only a few Hz it is not possible to effectively narrow the free-running laser linewidth of 700 Hz. Nevertheless a long-term stabilization to the central frequency of the Lamb dip is ensured.

Finally, the frequencies of the two stabilized lasers are compared by measuring their beat note on a HgCdTe detector. This beat note exhibits the very deep 600 kHz frequency modulation carried by the second laser which prevents a direct count of its frequency. To circumvent this problem we mixed this signal with a stable radio frequency, itself modulated at the same rate as the beat note. With this method, we obtained a new beat signal with a width of about 1 kHz at −3 dB (Fig. 3). Under these conditions, it was possible to obtain a satisfactory counting of the beat signal, mainly limited by the laser fluctuations.
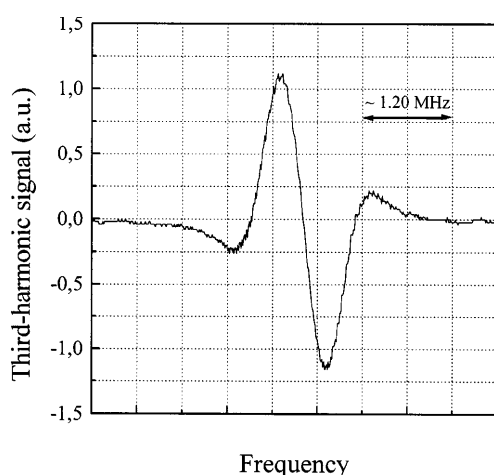

Fig. 3. Beat signal between the laser beat note and the radio frequency modulated at the same rate as the laser 2, for the P(10) laser line. HWHM at −3 dB is about 1 kHz. This demonstrates efficient compensation of frequency modulation, as the width of our free-running lasers is approximately the same

2 Results and discussion

Figure 4 shows the square root of the Allan variance of the beat frequency; it reaches 60 Hz ($\Delta\nu/\nu = 2.1 \times 10^{-12}$) for averaging times of $\tau = 300$ s. With the same saturated fluorescence setup, a value of 130 Hz was obtained in Bonn [17]. This difference is certainly explained by the better linewidth of the free-running lasers in Villetaneuse, mainly due to the very rigid superinvar resonator of the laser and its effective acoustical isolation. The performance of our stabilization scheme is also illustrated in Fig. 5, which displays the drift of the beat frequency during a 1000 s period, with a standard deviation of 503 Hz. Figure 6 displays a histogram of 11 beat note frequencies using an averaging time of 1 s and obtained with different optical alignments. The standard deviation of

Fig. 2. Saturated fluorescence signal recorded with a lock-in amplifier with third-harmonic detection at a time constant of 100 ms. The peak-to-peak linewidth is about 600 kHz
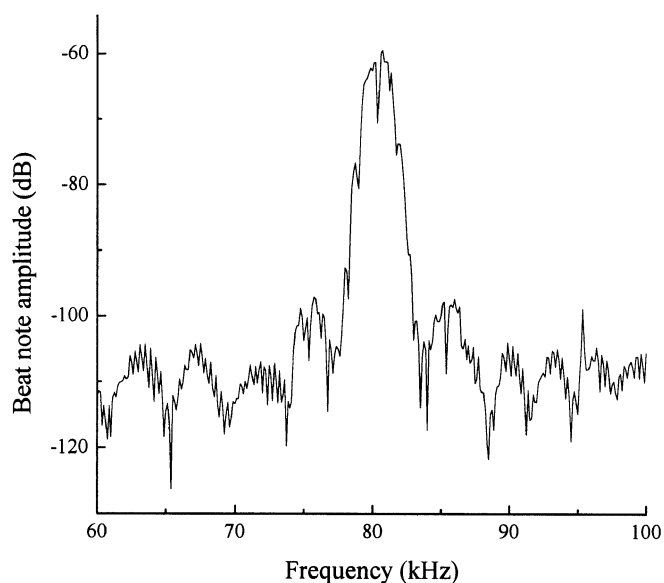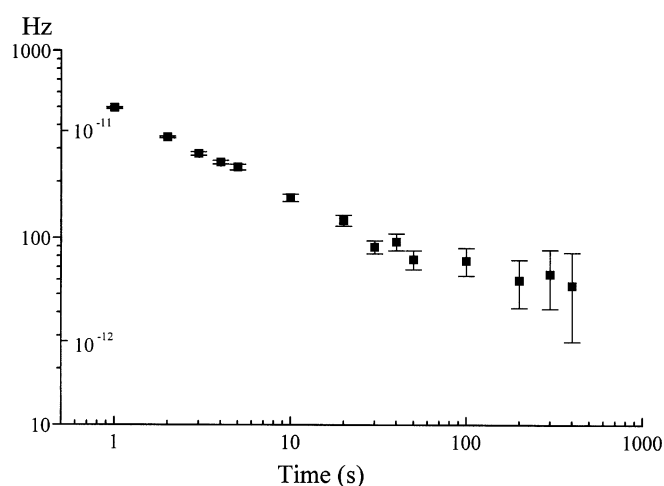

Fig. 4. Square root of the Allan variance of the beat note frequency for R(10) laser line. The first laser is stabilized directly onto OsO_4, the second one onto CO_2 by means of the saturated fluorescence method

410 Hz illustrates the repeatability of the experiment. Unfortunately, as our collaboration was limited in time, we were not able to perform a larger set of measurements. In particular,
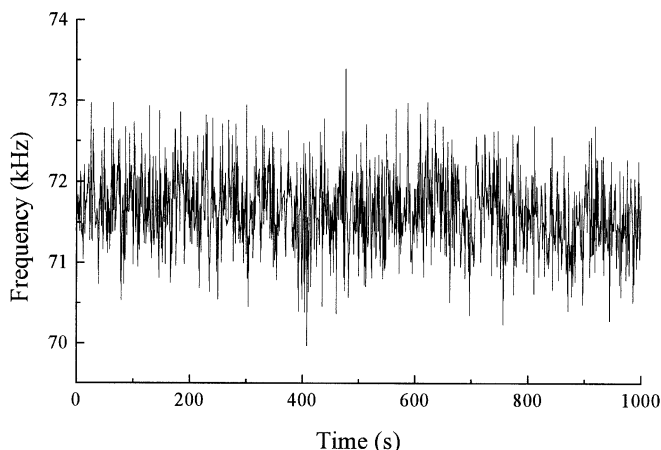

Fig. 5. Drift of the beat note frequency corresponding to Fig. 4. Counting time for a single point is 1 s
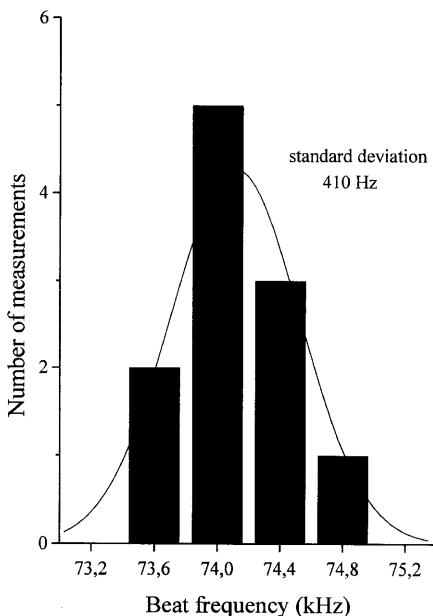

Fig. 6. Histogram of 11 beat frequencies for P(16) laser line counted with an averaging time of 1 s. The associated normal curve with a standard deviation of 410 Hz is superimposed

this histogram was recorded before we carefully controlled the electronic offset of the automatic frequency control system of the second laser, which turned out to drift slightly. We estimate that, with some additional care, this deviation was reduced to less than 300 Hz for the final measurements.

Table 1 shows the results of our frequency measurements and a comparison of these results and the data of Maki [5] to direct absorption measurements [15] for three different CO_2 laser lines. It is immediately apparent that our measured frequencies exhibit a rather constant redshift of $-1.7(0.8)$kHz compared to the direct absorption measurements of [15], which were obtained with a precision better than 150 Hz. Supplementary measurements of other CO_2 frequencies with the same method but higher uncertainties, which are not presented here, show the same redshift. We carefully checked that the electronics of the servo loop contribute less than 300 Hz to this shift because of the use of digital lock-ins and compensation of servo box offsets. In addition, we estimate that the asymmetry of the third derivative (see Fig. 2) cannot induce a systematic shift more than 500 Hz. Thus, we attribute this red frequency shift essentially to the relatively high CO_2 pressure of 5.3 Pa in the fluorescence cell. This view was clearly confirmed by a few other experiments using only half the pressure in the saturated fluorescence cell. This result is quantitatively in agreement with the experimental shift measured on the saturated absorption signal of R(22) [10]. From Fig. 1 of [10], we can extrapolate to a shift of -2.1 kHz at 5.3 Pa. Such a redshift was also theoretically predicted in [11] but is contradictory to the previous observation of a blueshift for the saturated fluorescence signal [12], which is clearly visible on Fig. 5 of [15] but must, in our opinion, be due to instrumental errors.

The frequency values of Maki et al. [5], although they are based mainly on measurements performed with the same saturated fluorescence method, do not show any constant shift relative to the direct absorption measurements. In fact, all the frequencies of [5] result from calculations, using the molecular constants which were derived from a fit of data. These included the very precise R(10) and P(14) saturated absorption measurements [9] which globally redshifted the grid of [5]. In the evaluation of the uncertainty, only statistical errors were considered. However, the present work suggests that two kinds of systematic errors affected the data. First, an instrumental error could explain the blueshift of [5, 12], namely, the saturated fluorescence technique associated with first-harmonic detection suffers sever baseline problems and leads generally to uncertainties of the order of several kHz [4, 11]. Second, there is a pressure shift which, in addition, must vary with the different conditions of the data recordings.

Table 1. Results of our measurements and comparison to direct absorption measurements of CO_2 [15]. All data are given in kHz. Errors in parentheses refer to the last digits quoted for each result. The uncertainty in column 2 results from the sum of two independent errors: first, 300 Hz for the residual offset of the lock box, second 500 Hz for the asymmetry of the recorded saturated fluorescence Lamb dip. In column 3, we also take into account the error due to the OsO_4 frequency standard, whereas the uncertainty due to the CO_2-OsO_4 frequency difference of [15] is negligible for the error of column 4. In column 5, we reproduce the uncertainties given by Maki et al. [5]

CO_2 line	Frequency shift to OsO_4	Absolute frequency of the saturated fluorescence signal	Frequency shift to CO_2 saturated absorption [15]: our data	Maki et al. [5]
P(14)	$-3\,221.1\,(\pm3\pm5)$	$28\,464\,673\,717.8$ (8)	$-1.5\,(\pm3\pm5)$	-0.8 (5)
R(10)	$15\,252.7\,(\pm3\pm5)$	$29\,054\,072\,699.3$ (8)	$-1.7\,(\pm3\pm5)$	0.0 (1)
R(22)	$-9\,988.0\,(\pm3\pm5)$	$29\,296\,136\,370.3$ (12)	$-1.9\,(\pm3\pm5)$	-3.1 (5)

3 Conclusion

We have used our very accurate spectrometer working in the $10\,\mu$m region in connection with the OsO_4 frequency grid to perform three absolute measurements of CO_2 laser frequencies stabilized with the saturated fluorescence method. A systematic redshift of -1.7 kHz at 5.3 Pa, relative to the CO_2 laser frequency stabilized onto CO_2 saturated absorption signals, was obtained. This shift is mainly attributed to a pressure shift, which agrees with that observed at lower pressure in saturated absorption.

This experimental comparison demonstrates also the actual limitations of the CO_2 grid based on the saturated fluorescence method. However, we believe that this technique is reliable in the limit of a very cautious implementation. We showed that the use of a 3-f detection led to at least a 500 Hz repeatability and a strong reduction of instrumental errors. This opens the way to a systematic study of the accuracy, which might be mainly limited by the pressure shift. The extrapolation of CO_2 frequency to zero pressure for a good selection of lines is a valuable goal. This information would then allow calculation of the CO_2 molecular constants with a precision high enough to predict all CO_2 laser transition frequencies at sub-kHz accuracy.

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