Accurate frequencies of molecular transitions used in laser stabilization: the 3.39-μm transition in CH_4 and the 9.33- and 10.18-μm transitions in CO_2

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The frequencies of three lasers stabilized to molecular absorptions were measured with an infrared-frequency synthesis chain extending upwards from the cesium frequency standard. The measured values are 29.442 483 315 (25) THz for the 10.18-μm $R(30)$ transition in CO_2, 32.134 266 891 (24) THz for the 9.33-μm $R(10)$ transition in CO_2, and 88.376 181 627 (50) THz for the 3.39-μm $P(7)$ transition in CH_4. The frequency of methane, when multiplied by the measured wavelength reported in the following letter, yields 299 792 456.2 (1.1) m/sec for the speed of light.

The direct measurement of frequencies was recently extended to the 88-THz (3.39-μm) He-Ne laser.[1] Prior to this measurement, frequencies of the HCN,[2] H_2O,[3] and CO_2[4] lasers had been measured, completing a chain of frequency measurements extending from the frequency standard. In these previous measurements the lasers were tuned to the peaks of their gain curves; consequently, accuracy was limited to a few parts in 10^7. This letter describes remeasurements of differences between these lasers using CO_2 and He-Ne lasers stabilized with saturated molecular absorption in CO_2[5] and CH_4,[6] and presents results with an increase in accuracy of more than a factor of 100. The wavelength of the same $P(7)$ methane transition used to stabilize the He-Ne laser has been measured,[7] and the product of the new value for frequency and wavelength yields an updated value for the speed of light considerably more accurate than the presently accepted value. The new value of c is limited only by the present length standard.[7]

A block diagram in Fig. 1 illustrates the entire laser frequency chain. The three saturated-absorption-stabilized lasers are shown in the upper right-hand section, and the transfer chain oscillators are in the center column. The He-Ne and CO_2 lasers in the transfer chain were offset locked[8]; that is, they were locked at a frequency a few megahertz different from the stabilized lasers. This offset-locking procedure produced He-Ne and CO_2 transfer oscillators without the frequency modulation used in the molecular-stabilized lasers. The measurements of the frequencies in the entire chain were made in three steps shown on the right-hand side, by using standard heterodyne techniques previously described.[1-4]

Conventional silicon point-contact harmonic generator-mixers were used up to the frequency of the HCN laser. Above this frequency, tungsten-on-nickel diodes were used as harmonic generator-mixers. These metal-metal diodes required 50 or more mW of power from the lasers. The 2-mm-long 25-μm-diam tungsten antenna, with a sharpened tip which lightly contacted the nickel surface, seemed to couple to the radiation in two separate manners. At 0.89 and 10.7 THz it acted like a long wire antenna,[9,10] while at 29—88 THz its conical tip behaved like one-half of a biconical antenna.[10] Conventional detectors were used in the offset-locking steps.

The methane-stabilized He-Ne laser used in these experiments is quite similar in size and construction to the device described by Hall and Barger.[6] The gain tube was dc excited, and slightly higher reflectivity mirrors were employed. The latter resulted in a higher energy density inside the resonator and consequently a somewhat broader saturated absorption. Pressure in the internal methane absorption cell was about 0.01 Torr (1 Torr = 133.3 N/m^2).

The two 1.2-m-long CO_2 lasers used in the experiments contained internal absorption cells and dc-excited sealed gain tubes. A grating was used on one end for line selection, and frequency modulation was achieved by dithering the 4-m—radius-of-curvature mirror on the oppo-

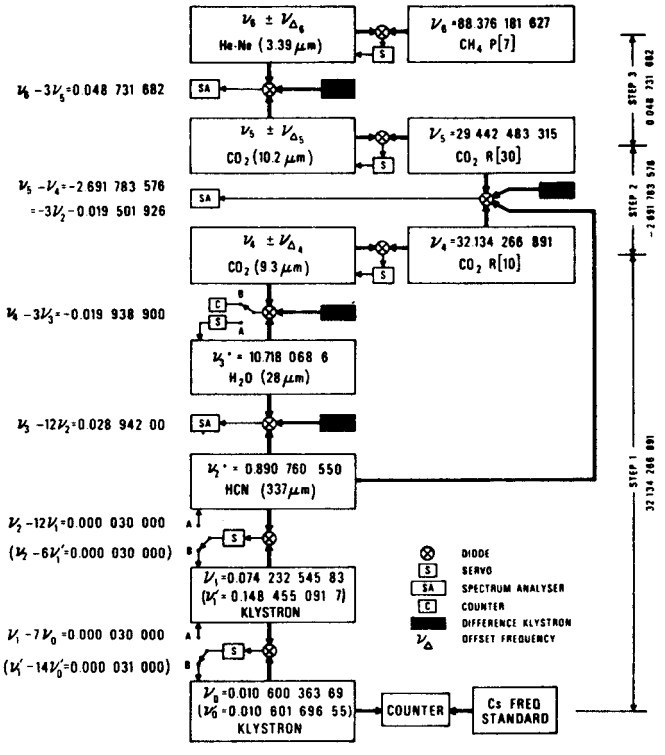

FIG. 1. Stabilized laser frequency synthesis chain. All frequencies are given in THz; those marked with an asterisk were measured with a transfer laser oscillator tuned to approximate line center.

TABLE I. Summary of Measurements. Molecular frequencies (the CO_2 frequencies include a 20-kHz systematic uncertainty combined with previous uncertainties in ν_4 and ν_5): $\nu_4 = 32.134\,266\,891\,(24)$, $\nu_5 = 29.442\,483\,315\,(25)$, $\nu_6 = 88.376\,181\,627\,(50)$.

Run	Step 1 ν_4	Step 2 $\nu_5 - \nu_4$ [a]	Step 3 $\nu_6 - 3\nu_5$ [b]
I	32.134 266 885 (37)	−2.691 783 577 (9)	0.048 731 658 (65)
		−2.691 783 573 (9)	
II	32.134 266 925 (31)	−2.691 783 595 (14)	0.048 731 656 (65)
III	32.134 266 885 (20)	−2.691 783 577 (9)	0.048 731 693 (25)
		−2.691 783 573 (9)	
IV	32.134 266 890 (14)	−2.691 783 574 (9)	0.048 731 680 (20)
		−2.691 783 575 (9)	
Weighted values	32.134 266 891 (14),	−2.691 783 576 (5)	0.048 731 682 (20)

[a]Double entries correspond to interchanging the two CO_2 lasers. [b]Includes a −12-kHz correction to runs III and IV.

site end. CO_2 pressure in the internal absorption cell was 0.020 Torr. The laser frequency was locked to the zero-slope point on the Lamb dip in the 4.3-μm fluorescent radiation.[5] The 0.89-, 10.7-, and 88-THz transfer lasers were 8-m-long linearly polarized cw oscillators with single-mode output power greater than 50 mW. The Michelson HCN laser has been described.[11] The H_2O laser used a double-silicon-disk partially transmitting end mirror and a 0.5-mil polyethylene internal Brewster-angle membrane served to polarize the laser. The 8-m He-Ne laser oscillated in a single mode without any mode selectors because of a 4-Torr pressure with a 7:1 ratio of helium to neon. This resulted in a pressure width approximately equal to the Doppler width, and the high degree of saturation allowed only one mode to oscillate.

Conventional klystrons used to generate the four difference frequencies between the lasers were all stabilized by standard phase-lock techniques, and their frequencies were determined by cycle counting at X band.

An interpolating counter controlled by a cesium clock via the AT (NBS) time scale[12,13] in the NBS Time and Frequency Division counted the 10.6-GHz klystron in the transfer chain. This same standard was used to calibrate the other counters and the spectrum analyzer-tracking generator.

In step 1, a frequency synthesis chain was completed from the cesium standard to the stabilized $R(10)$ CO_2 laser. All difference frequencies in this chain were either measured simultaneously or held constant. Each main chain oscillator had its radiation divided so that all beat notes in the chain could be measured simultaneously. For example, a silicon-disk beam splitter divided the 10.7-THz beam into two parts: one part was focused on the diode which generated the 12th harmonic of the HCN laser frequency, the remaining part irradiated another diode which generated its own third harmonic and mixed with the output from the 9.3-μm CO_2 laser and the 20-GHz klystron.

Figure 1 shows the two different ways in which the experiment was carried out. In the first scheme (output from mixers in position A), the HCN laser was frequency locked to a quartz crystal oscillator via the 148- and 10.6-GHz klystrons, and the frequency of the 10.6-GHz klystron was counted. The H_2O laser was frequency locked to the stabilized CO_2 laser, and the beat frequency between the H_2O and HCN lasers was measured on the spectrum analyzer. In the second scheme (output from mixers in position B) the 10.6-GHz klystron was phase locked to the 74-GHz klystron, which in turn was phase locked to the free-running HCN laser. The 10.6-GHz klystron frequency was again counted. The free-running H_2O laser frequency was monitored relative to the stabilized CO_2 laser frequency. The beat frequency between the H_2O and HCN lasers was measured as before on the spectrum analyzer.

In step 2, the difference between the two CO_2 lines was measured. The HCN laser remained focused on the diode used in step 1, which now also had two CO_2 laser beams focused on it. The sum of the third harmonic of the HCN frequency, plus a microwave frequency, plus the measured rf beat signal is the difference frequency between these two CO_2 lines. The two molecular-absorption-stabilized CO_2 lasers were used directly, and the relative phase and amplitudes of the modulating voltages were adjusted to minimize the width of the beat note. The beat note was again measured on a combination spectrum analyzer and tracking generator-counter. Dual entries in step 2 of Table I arose from interchanging the roles of the CO_2 lasers to detect possible systematic differences in the two laser-stabilization systems.

In step 3, the frequency of the $P[7]$ line in methane was measured relative to the $R(30)$ line (10.4-μm band) of CO_2. Both the 8-m 3.39-μm laser and the CO_2 laser were offset locked from saturated-absorption-stabilized lasers and thereby not modulated. The 10- to 100-MHz beat note was again measured either on a spectrum analyzer and tracking generator, or, in the final measurement when the S/N ratio of the beat note was large enough (about 100), directly on a counter.

The measurements are chronologically divided into four runs, and the results are presented in Table I along with a one-standard-deviation estimation of the uncertainties. Efforts were made to make experimental improvements from one run to the next, and consequently the results from run IV have the smallest experimental uncertainties. Run II contains results of measurements on two days, in which all three steps were accomplished each day. The results were marred, however, by a leaky CO_2 absorption cell, which may account for the differences with respect to runs I, III, and IV. In runs I, III, and IV, the various steps were sometimes per-

TABLE II. Estimated uncertainties in the data of run IV. Parts in 10^{10}.

Term	Measurement	Uncertainty in transfer oscillator frequencies
Step 1		
ν_0	Cs standard	0.7
ν_0	±1 count	0.001
$\nu_0 \rightarrow \nu_1$ lock frequency	SA-TG[a]	1.2
$\nu_1 \rightarrow \nu_2$ lock frequency	SA-TG	0.1
$\nu_2 \rightarrow \nu_3$ beat note	SA-TG	2.0
$\nu_2 \rightarrow \nu_3$ beat note	Possible asymmetry[b]	3.0
$\nu_3 \rightarrow \nu_4$ beat note	Counter (±1 count)	0.3
ν_4 resetability		2.0
$\nu_0 \rightarrow \nu_4$ statistical fluctuations	Standard deviation mean ($N = 25$)	0.7
Step 1: σ_{ν_4}	$(\Sigma_i \sigma_i^2)^{1/2}$ (total of above)	4.4
Step 2		
$\nu_4 \rightarrow \nu_5$ beat note	Possible asymmetry[b]	1.0
$3\nu_2$	First four terms in step 1 divided by 10	0.14
ν_4 resetability		2.0
ν_5 resetability		2.0
$\nu_4 \rightarrow \nu_5$ statistical fluctuations	Standard deviation mean ($N = 20$)	0.3
Step 2: $\sigma_{\nu_4 - \nu_5}$	$(\Sigma_i \sigma_i^2)^{1/2}$	3.0
Step 3		
$\nu_5 \rightarrow \nu_6$ beat note	Counter	0.1
ν_5 resetability		2.0
ν_6 resetability		1.0
$\nu_5 \rightarrow \nu_6$ statistical fluctuations	Standard deviation mean ($N = 20$)	0.2
Step 3: $\sigma_{\nu_5 - \nu_6}$	$(\Sigma_i \sigma_i^2)^{1/2}$	2.2

[a]SA-TG, spectrum analyzer-tracking generator.

[b]4% of linewidth.

formed on different days, but all were done within several days of each other. The cumulative changes in experimental techniques led to the improved results in run IV. With configuration B (step 1 in Fig. 1) an improved signal-to-noise ratio facilitated connection of the 74-GHz klystron and the HCN laser with a phase-lock loop and thus decreased the uncertainty in the HCN laser frequency. The accuracy of the H_2O to CO_2 $R(10)$ beat frequency measurement was improved by cycle counting, as was the CO_2 $R(30)$ to He-Ne beat frequency measurement in step 3.

Weighted values for each of the steps and for ν_4, ν_5, and ν_6 were obtained by weighting the results of all runs inversely as the square of the standard deviations.

Table II lists the individual uncertainties in various parts of the frequency synthesis chain as it was used during the final set of measurements (run IV). One notes that the largest uncertainty is a possible asymmetry in the ν_2-to-ν_3 beat note. The error listed for this factor is two-thirds of the estimated limit of detectability of such an asymmetry. This asymmetry might arise, for example, from a nonsymmetrical excursion of the H_2O and HCN laser mirrors.

The uncertainties in the weighted values for steps 1 and 3 were taken to be the same as those of run IV; this was done because of the uncertainties, such as the possible asymmetry in the beat note between ν_2 and ν_3, might be of the same sign from run to run. In step 2, however, the major uncertainties were independent, and the final uncertainty was obtained in the normal fashion.

Numerous other possible errors were considered; however, they were all negligible compared with those listed. Some of those considered were drift of the HCN and H_2O lasers during the measurement, frequencies of difference klystrons, and asymmetries in other beat notes (these were eliminated by direct counting). No frequency shifts are known to result from the multiplication process in the metal-metal diodes.

The saturated-methane line shape and resetability (which can be associated with various kinds of frequency shifts, such as pressure, power, and base line slope) of the stabilized He-Ne laser have been studied in some detail by Hall and Barger.[6] Since the characteristics of our device were not known as well, a comparison was made with a Hall-Barger laser via a transfer laser. A 12-kHz difference, which remained after a base line slope correction had been made, probably resulted from an asymmetric line in our laser caused by too much power inside the resonator. This difference was applied as a correction to the results and appears in Table I. The 1×10^{-10} resetability error assigned to ν_6 (Table II) occurs largely because of the uncertainties involved in transferring the accuracy of the Hall-Barger laser to our laboratory. No corrections were applied for pressure or shifts other than those mentioned, which are believed to be small compared to the assigned resetability error.

Corresponding information for the stabilized CO_2 laser is currently being investigated in our laboratory and will be reported in a future publication.[14] Some, if not all, of the factors which affect the symmetry and frequency of the methane line also affect the saturated CO_2 lines. No

correction for sloping base line, pressure, power, or other shifts was made in the CO_2 frequencies in Table I. From preliminary measurements, it is estimated that base line and power shifts are less than 20 kHz. The pressure shift is believed to be negative and less than 100 Hz/mTorr.

The accuracy of the methane measurement depends on the stability and resetability of the CO_2 lasers rather than on the absolute accuracy of their frequencies since the CO_2 lasers served as transfer oscillators. The fractional frequency variation is $3\times10^{-11}\tau^{-1/2}$ for $10^{-2}\leq\tau\leq10$ sec. It is estimated that the resetability of each CO_2 laser is about 2×10^{-10} (Table II). The stability characteristic is reflected in the statistical fluctuations in Table II.

Since the shifts affecting the true molecular CO_2 frequencies have not been measured, an additional uncertainty of about 20 kHz has been included for these frequencies, as shown in Table I.

Frequencies are currently measurable to parts in 10^{13}, and hence the over-all error of about six parts in 10^{10} represents a result which can be improved upon. The experiment was done fairly quickly to obtain frequency measurements of better accuracy than the wavelength measurements; this was easily done. It should be possible to obtain 50–100 times more accuracy by using tighter locks on the lasers (such as phase locking the HCN laser[15,16]) and by using counting techniques at all beat notes.

The relative ease with which these laser harmonic signals were obtained in this second round of frequency measurements indicates that the measurement of the frequencies of visible radiation now appears very near at hand. Such measurements should greatly facilitate one's ability to accurately utilize the visible and infrared portion of the electromagnetic spectrum.

A measurement of the wavelength of methane reported in the following letter[7] yields a value of 33 922.313 76 (12) Å ($\delta\lambda/\lambda=\pm3.5\times10^{-9}$) when referenced to the center of gravity of the krypton length standard. This value multiplied by the measured frequency, 88.376 181 627 (50) THz ($\delta f/f=\pm5.6\times10^{-10}$), yields a definitive value for the speed of light of $c=299\,792\,456.2$ (1.1) m/sec ($\delta c/c=3.5\times10^{-9}$). This number is in agreement with the previously accepted value[17] of 299 792 500 (100) m/sec and is about 100 times more accurate. A recent differential measurement of the speed of light has been made by Bay, Luther, and White[18]; their value is 299 792 462 (18) m/sec, which also is in agreement with the presently determined value.

The uncertainty in our value for the speed of light essentially arises from the interferometric measurements with the incoherent krypton radiation which operationally defines the international meter. Some various alternatives to the present length standard are discussed elsewhere.[19]

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