†Address after 16 May 1969: IBM Research Laboratory, San Jose, Calif.

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ACCURATE ROTATIONAL CONSTANTS OF $C^{12}O_2^{16}$ FROM MEASUREMENT OF cw BEATS IN BULK GaAs BETWEEN CO_2 VIBRATIONAL-ROTATIONAL LASER LINES

T. J. Bridges and T. Y. Chang
Bell Telephone Laboratories, Holmdel, New Jersey 07733
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A room-temperature bulk GaAs mixer is used to mix frequencies of pairs of cw vibrational-rotational CO_2 laser lines, each stabilized to line center. The beat frequencies, in the millimeter-wave region of 50-80 GHz, are measured for 37 pairs of transitions to better than 1 MHz. The deduced rotational constants for the relevant vibrational levels (00^01, 10^00, 02^00) are 25 to 200 times more accurate than the best previous results (from conventional spectroscopy).

In this Letter we report the cw beating of pairs of CO_2 vibrational-rotational laser lines near 10 μ, in room-temperature bulk GaAs. The beat frequencies (which lie in the 50- to 60- and 70- to 80-GHz millimeter-wave region) were measured for 37 pairs of lines to an accuracy, in most cases, of much better than 1 MHz. From these measurements we have calculated the rotational constants of the 10^00, 02^00, and 00^01 vibrational levels of $C^{12}O_2^{16}$. These constants have 25 to 200 times better accuracy than the best spectroscopic determinations to date. They also have the advantage of being direct frequency measurements rather than the wavelength measurements of conventional spectroscopy and refer to the molecule unperturbed by pressure effects.

Beats between CO_2 laser lines have recently been reported in metal-metal point-contact diodes[1] and in bulk GaAs.[2] The present work is a continuation of that described in Ref. 2 and uses the same bulk GaAs infrared mixer. By using two cw feedback stabilized lasers instead of a single Q-switched laser oscillating simultaneously on two or more lines, we are now able to measure a much larger number of beat frequencies with far greater accuracy than in the previous experiments.

The two lasers used a flowing gas mixture of CO_2, N_2, and He with approximate partial pressures of 1, 2, and 10 Torr, respectively. Each had a diffraction grating as one end mirror and could be tuned to oscillate on at least 43 separate transitions in the P and R branches of the 00^01-10^00 (10.4-μ) and 00^00-02^00 (9.4-μ) bands of CO_2. A piezoceramic mount for the curved dielectric mirror on the other end of the 2-m cavity enabled us to use feedback to stabilize each laser to the center of a chosen line, with a short-term stability of better than 10^5 Hz. The feedback control was obtained by vibrating the curved mirrors of both lasers synchronously at 84 Hz, then demodulating the resulting small amplitude modulation on the laser output with a phase-sensitive detection system, and finally feeding the amplified error signal back to the piezoceramic transducer. On the strongest lines, approximately 2-W single-mode, single-line output was available from the zeroth-order reflection of the grating. The two laser beams were combined by means of a beam splitter. Half of the combined output was sent into a spectrometer for identifying the transitions, while the other half was focused into the GaAs infrared mixer.

The infrared mixer consisted of a GaAs-filled rectangular waveguide with the [111] crystal direction parallel to the narrow dimension. The two infrared beams and their beat signal propagated collinearly along the waveguide axis and were all polarized in the [111] crystal direction. With the waveguide width of 2.77 mm, the coherence length for the difference frequency generation always exceeded the crystal length (13 mm).[2] The beat signal generated in the loaded waveguide was radiated through a tapered transition into standard RG98/U waveguide which was terminated by a silicon-diode microwave mixer.

The detection system was a high-resolution (better than 10^5 Hz), narrow-band spectrum analyzer consisting of a swept-frequency local-oscillator klystron, a microwave mixer, a low-noise i.f. amplifier, and an oscilloscope. The minimum detectable signal was $\approx 10^{-12}$ W and signal-to-noise ratios were greater than 20 for the strongest beats. The frequency was determined by injecting the output of a tunable, X-band (10-GHz) ultrastable signal generator into the microwave mixer and matching one of its harmonics to the laser beat frequency. The X-band frequency was measured directly by an electronic counter to $1{:}10^7$.

The measured difference frequencies are given in Table I. In the P branches, beats between adjacent lines were measured. In the R branches, however, measurements were restricted to beats between every other line because of equipment limitations. The beat frequency was typically stable and readable within $5{:}10^6$. A value for the beat frequency was obtained by averaging ten readings, resulting in a standard error of better than $2{:}10^6$. The group of ten measurements was repeated at least four times for each pair of lines by successively interchanging the frequencies of the two lasers. This procedure indicated any systematic bias in the lasers. It was found that the accuracy of the final result was limited by the reproducibility of the measurement to about $1{:}10^5$. The mean value and the standard deviation of the four repeated measurements are given in Table I. According to Mocker,[3] pressure shifts of the CO_2 emission lines are negligibly small over the operating pressure range of the laser (8-14 Torr total gas pressure). We therefore consider the measured emission frequency to be that of the unperturbed molecule (with two exceptions discussed below).

Table I. Observed and calculated beat frequencies in MHz. $\bar{f}_0$: mean value of the observed beat frequency. s_0: standard deviation of repeated measurements on f_0. f_c: calculated value of the beat frequency (from derived constants). s_{c0}: standard deviation of $f_c - \bar{f}_c$ for each branch. Figures in parentheses are corrected for a perturbation in a line frequency (see text).

Transitions	$\bar{f}_0$	s_0	$(f_c - \bar{f}_0)$
00°1-10°0 Band (10.4μ)			
P(30)-P(32)	57982.12	0.23	-0.15
P(28)-P(30)	57237.96	0.66	-0.01
P(26)-P(28)	56496.06	0.56	+0.23
P(24)-P(26)	55756.70	0.52	+0.08
P(22)-P(24)	55019.05	0.22	+0.14
P(20)-P(22)	54284.33	0.19	-1.01 (-0.01)
P(18)-P(20)	53548.16	0.37	+0.81 (-0.19)
P(16)-P(18)	52816.14	0.49	-0.23
P(14)-P(16)	52084.00	0.42	-0.06
P(12)-P(14)	51352.69	1.17	+0.16
			s_{co} =0.43 (0.15)
R(14)-R(10)	83663.36	0.21	+0.20
R(16)-R(12)	82181.16	0.58	+0.26
R(18)-R(14)	80694.22	0.15	+0.47
R(20)-R(16)	79203.58	0.02	-0.64
R(22)-R(18)	77705.84	0.26	-0.09
R(24)-R(20)	76202.99	0.37	-0.29
R(26)-R(22)	74693.34	0.30	+0.03
R(28)-R(24)	73177.67	0.51	-0.34
R(30)-R(26)	71653.69	0.20	+0.48
			s_{co} =0.36
00°1-02°0 Band (9.4μ)			
P(30)-P(32)	58774.17	0.20	-0.30
P(28)-P(30)	58016.14	0.48	-0.18
P(26)-P(28)	57252.92	0.36	+0.32
P(24)-P(26)	56485.83	0.29	+0.17
P(22)-P(24)	55714.02	0.52	+0.47
P(20)-P(22)	54939.00	0.60	+0.01
P(18)-P(20)	54159.89	0.13	-0.07
P(16)-P(18)	53377.36	0.51	-0.17
P(14)-P(16)	52591.58	0.39	-0.18
P(12)-P(14)	51802.90	0.22	-0.17
			s_{co} =0.24
R(14)-R(10)	82824.49	0.27	-0.06
R(16)-R(12)	81223.38	0.44	+0.55
R(18)-R(14)	79626.01	0.34	-0.14
R(20)-R(16)	78030.92	0.57	-0.11
R(22)-R(18)	76438.87	1.00	+0.45
R(24)-R(20)	74854.28	0.60	-2.38 (-0.38)
R(26)-R(22)	73269.47	0.80	-0.32
R(28)-R(24)	71689.40	0.41	+2.19 (+0.19)
			s_{co} =1.17 (0.32)

The data have been analyzed by comparing them with theory. An expression for the beat frequencies can be derived from the term values of the vibrational-rotational energy levels, given by[4]

$$T(v,J)=G(v)+B_vJ(J+1)-D_vJ^2(J+1)^2+H_vJ^3(J+1)^3\cdots, \qquad (1)$$

where v denotes the vibrational level, J is the rotational quantum number, and B_v, D_v, etc. are rotational constants slightly dependent on v ($B \gg D \gg H$ etc.). The allowed vibrational-rotational transitions have $J_u-J_l=-1$ for P-branch transitions (upper level is indicated by subscript u, lower by l) and $J_u-J_l=+1$ for R-branch transitions and are customarily labeled by $P(J_l)$ or $R(J_l)$, which symbol also represents the transition frequency. The symmetry properties of the CO_2 levels in question restrict J_l to even integral numbers only.[4] The particular beat frequencies that we have measured can then be expressed as follows (a running odd integer N or M is used to generate the J values of all levels involved in each beat frequency):

$$\begin{aligned}P(N-1)-P(N+1)&=[T(v_u,N-2)-T(v_l,N-1)]-[T(v_u,N)-T(v_l,N+1)]\\&=4B_+-8NB_--8(3N^2+1)D_++8N(2N^2+3)D_-\\&\quad+4(15N^4+33N^2+4)H_+-8N(3N^4+16N^2+9)H_-\cdots \qquad (2)\end{aligned}$$

and

$$\begin{aligned}R(M+1)-R(M-3)&=[T(v_u,M+2)-T(v_l,M+1)]-[T(v_u,M-2)-T(v_l,M-3)]\\&=8B_++16MB_--16(3M^2+4)D_+-16M(2M^2+9)D_-\\&\quad+8(15M^4+123M^2+52)H_++16M(3M^4+46M^2+72)H_-\cdots. \qquad (3)\end{aligned}$$

The constants B_+ and B_- are defined according to the expression

$$B_\pm=\tfrac{1}{2}(B_u\pm B_l),$$

and D_+, D_-, H_+, and H_- are similarly defined.

In the data analysis we treated Eq. (2), and Eq. (3) divided by 2, as a single equation, given by

$$f=4B_++B_-X_1+D_+X_2+D_-X_3+H_+X_4+H_-X_5\cdots, \qquad (4)$$

where f is the beat frequency for the P branch and one-half the beat frequency for the R branch. The values of X_1, X_2, etc. (regarded as independent variables) are known for each N or M from the appropriate coefficients of B_-, D_+, etc. in Eq. (2), or Eq. (3) divided by 2. The best values of the constants B_+, B_-, D_+, D_-, etc. and their standard errors were obtained by a least-squares fit of the data of Table I by this formula. The procedure is equivalent to fitting the experimental data by a straight line in the hyperspace of f, X_1, X_2, etc. and was carried out by a digital computer using a multiple-regression analysis.[5] The values of B_u, B_l, etc. are calculated from B_+, B_-, etc. by addition and subtraction. When this is done for both the 10.4- and 9.4-μ bands, four sets of constants, together with standard error of the constants, result. Since the upper vibrational state is common to both bands, the values for that state should agree, providing a very severe check on the accuracy of the experiment.

The analysis was first performed using constants B, D, and H. The uncertainty in the resulting values of H was at least as large as the values themselves. We deduce that the magnitude of the H_v's is smaller than 10^{-12} cm^{-1} and within the accuracy of our measurements is insignificant. A better fit to the data was obtained by using B's and D's only, and these are the results presented here in Table II. Since the differences of B_v's and D_v's are found to a higher absolute accuracy than the actual values, the actual values are given for the upper 00^01 level only, while the differences are given for the other levels. The error in determination of B_v's is about $2:10^6$ and in D_v's about $3:10^3$, while the absolute error in B_u-B_l and D_u-D_l is at least five times less than that of B_v's and D_v's. The best previous values of these constants obtained from spectroscopic data are also shown in Table II. Our values are 25 to 200 times more accurate.

Table II. Derived rotational constants (limits shown are ± standard error).

	Derived From Transition		Adopted Value[a]		Previous Best Value
	$00^\circ1$-$02^\circ0$ (MHz)	$00^\circ1$-$10^\circ0$ (MHz)	(MHz)	(cm^{-1})[b]	(cm^{-1})
$B_{00^\circ1}$	11606.167(±.016)	11606.192(±.015)	11606.180(±.011)	$387140.44(\pm.37)\times10^{-6}$	$387132(\pm40)\times10^{-6}$[c]
$D_{00^\circ1}$	$39.641(\pm.117)\times10^{-4}$	$39.764(\pm.076)\times10^{-4}$	$39.728(\pm.063)\times10^{-4}$	$13.252(\pm.021)\times10^{-8}$	$13.45(\pm.50)\times10^{-8}$[d]
$B_{10^\circ0}-B_{00^\circ1}$		91.3584(±.0014)	91.3584(±.0014)	$3047.389(\pm.046)\times10^{-6}$	$3069(\pm10)\times10^{-6}$[e]
$D_{10^\circ0}-D_{00^\circ1}$		$-5.506(\pm.011)\times10^{-4}$	$-5.506(\pm.011)\times10^{-4}$	$-1.8366(\pm.0035)\times10^{-8}$	$-.65(\pm.7)\times10^{-8}$[f]
$B_{02^\circ0}-B_{00^\circ1}$	100.1534(±.0019)		100.1534(±.0019)	$3340.757(\pm.063)\times10^{-6}$	$3344(\pm10)\times10^{-6}$[g]
$D_{02^\circ0}-D_{00^\circ1}$	$7.140(\pm.016)\times10^{-4}$		$7.140(\pm.016)\times10^{-4}$	$2.3816(\pm.0053)\times10^{-8}$	$2.65(\pm1.2)\times10^{-8}$[h]

[a] Weighted average of first two columns, with resultant standard error.

[b] Velocity of light taken as $2.997\,925\times10^8$ m/sec [American Institute of Physics Handbook, edited by D. E. Gray (McGraw-Hill Book Company, Inc., New York 1963), 2nd ed., p. 6-223].

[c] From B_{00^00} [Charles P. Courtoy, Can. J. Phys. 35, 608 (1957)] and $B_{00^01}-B_{00^00}$ [Ralph Oberly and K. Narahari Rao, J. Mol. Spectry. 18, 73 (1965)].

[d] From D_{00^00} [Courtoy (footnote c)] and $D_{00^01}-D_{00^00}$ [Oberly and Rao (footnote c)].

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[f] From $D_{00^01}-D_{00^00}$ [Oberly and Rao (footnote c)] and $D_{10^00}-D_{00^00}$ [derived from Gordon and McCubbin (footnote e)].

[g] From $B_{00^01}-B_{00^00}$ [Oberly and Rao (footnote c)] and $B_{02^00}-B_{00^00}$ [derived from Gordon and McCubbin (footnote e)].

[h] From $D_{00^01}-D_{00^00}$ [Oberly and Rao (footnote c)] and $D_{02^00}-D_{00^00}$ [derived from Gordon and McCubbin (footnote e)].

The differences between the values of beat frequencies calculated from the deduced constants and the observed values are shown in Table I.

The observed beat frequencies, $P(18)-P(20)$ and $P(20)-P(22)$ in the 10.4-μ band and $R(24)-R(20)$ and $R(28)-R(24)$ in the 9.4-μ band, have exceptionally large deviations from the calculated values. These deviations are consistent with a 1-MHz (3×10^{-5} cm^{-1}) upward shift of the 10.59-μ [$P(20)$] line and a 2-MHz upward shift of the 9.249-μ [$R(24)$] line. Perturbation of the energy levels cannot account for these irregularities since other transitions with common levels do not show similar shifts. A pulling of the actual laser oscillation frequency seems to be taking place. We have not yet found a satisfactory explanation of these isolated frequency shifts.

The feedback lasers and spectrum analyzer used in the present experiment were comparatively unsophisticated in design. An improvement of 10 or more in frequency stability[3,6] and measurement accuracy would not be difficult to achieve. The method described here could readily be applied to other CO_2 laser lines,[7] to various isotopic species of CO_2,[8] and also to other molecules that have given cw laser oscillation. These include N_2O,[9] CO,[10] and CS_2.[11]

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