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Rotational Constants for $^{12}C^{16}O_2$ from Beats between Lamb-Dip–Stabilized Lasers

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New experimental measurements of the frequency separations of 30 pairs of $^{12}C^{16}O_2$ laser lines in the 10.4-μm band and 26 pairs in the 9.4-μm band have been made with Lamb-dip–stabilized lasers. The use of a Josephson junction as the frequency-mixing element simplified the measurements. Uncertainties in existing rotational constants for the laser vibrational levels were reduced 20 to 30 times and an additional rotational constant H_v was determined for the first time.

The determination of rotational constants for excited vibrational states in molecules has undergone dramatic improvement as the experimental methods have changed from wavelength metrology to frequency metrology. Wavelength methods were limited primarily by instrumental linewidths of absorption spectrometers to about 0.1 cm^{-1} or 3 GHz. For CO_2, the first big improvement was by Bridges and Chang,[1] who used laser sources and measured the difference frequencies of pairs of laser transitions. The uncertainties in the rotational constants were reduced 25 to 200 times with the accuracy being primarily limited by how well the laser could be set to the center of the Doppler- and pressure-broadened gain profile of the laser ($\approx$100 MHz wide).

With the discovery of Lamb-dip phenomena in the 4.3-μm fluorescent radiation,[2] the lasers could be servo controlled to a spectral feature 100 times narrower than previously. Thus, it appeared experimentally profitable to redetermine the absolute frequencies and the rotational constants. Further motivation is provided by the fact that the CO_2 laser is an excellent secondary frequency standard[3] in the wavelength band from 9 to 11 μm since the frequency of a line in each of the two laser bands has been accurately measured relative to the primary frequency standard.[4] In addition, it can be used as a highly accurate length standard since the accuracy of the velocity of light is limited mostly by the uncertainty in the primary length standard.[5] A third motivation and the principal reason for using the Josephson junction was to study the Josephson effect at CO_2 frequencies. Results of this investigation will be reported separately.

Beams from two CO_2 lasers oscillating on adjacent rotational lines were focused onto a Josephson junction and mixed with the nth harmonic ($3 \leq n \leq 6$) of an applied X-band frequency. Thus, the junction served both as the microwave harmonic generator and as the infrared mixer. This technique allowed us to measure laser difference frequencies ranging from 32 to 63 GHz with a single microwave oscillator. The nominally 60-MHz beat frequency from the junction was amplified with a narrow-band amplifier and observed on a spectrum analyzer. Because of residual spurious frequency modulation of the lasers, the beat-signal spectrum was digitally averaged for 100 sec to obtain a more accurate beat frequency. The averaged 60-MHz beat frequency F_B was measured relative to simultaneously recorded frequency markers by linear interpolation as illustrated in Fig. 1. The X-band klystron was stabilized by a standard phase-lock technique, and

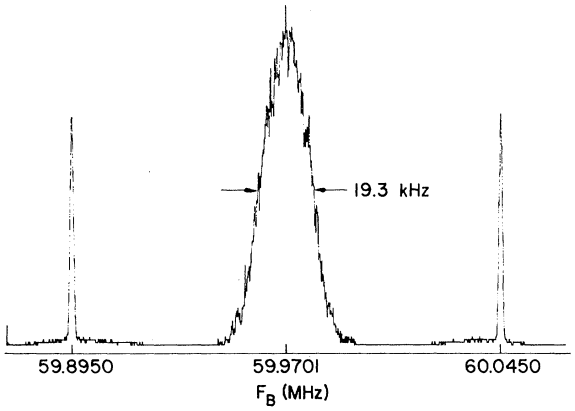

FIG. 1. Signal-averaged beat note between transitions $P(18)$ and $P(20)$ in the 9.4-μm band with frequency markers. The spectrum analyzer was set for linear response with a predetection bandwidth of 1 kHz. The postdetection bandwidth, as determined by the averaging time of the digital averager, was 0.1 sec/channel with 1024 channels for the above spectrum.

its frequency was counted directly by a counter referenced to the AT (National Bureau of Standards) time scale via a quartz-crystal oscillator. The laser difference frequency is then given by $F_D = nF(X \text{ band}) + F_B$.

The CO_2 lasers have been described previously.[4] The pressure in the internal absorption cells was the same for both lasers in every measurement (either 0.030 or 0.040 Torr) and no difference in the beat frequency was measurable over this pressure range. The laser frequency was locked to the zero-slope point on the Lamb dip in the 4.3-μm fluorescent radiation. Typical saturated absorption lines were approximately 1 MHz full width at half-maximum. Mirror dither produced an FM envelope linewidth of approximately 400 kHz for a single laser, but proper phase and amplitude adjustment of the dither voltage on the two lasers reduced the beat-signal linewidth to the range of 20 to 30 kHz (full width at half-maximum). On certain weak laser lines, the width increased and was probably related to feedback coming from the vicinity of the junction. For most of the measurements, however, feedback was not an appreciable problem.[6]

Various types of effects—such as pressure shifts, power shifts, base-line slope of saturated absorption line, and servo-electronic offsets —can shift the stabilized laser frequency from the unperturbed molecular frequency. These effects, although not at present investigated in great detail, are small and in this experiment were assumed to affect adjacent lines by identical amounts. Hence, no correction was applied. The two lasers when stabilized to the same saturated line normally differed in frequency by less than 2.5 kHz. Consequently, a 2.5-kHz uncertainty is included in the estimate of experimental error for this effect. Other inputs to the estimated experimental error include uncertainty in the X-band frequency, nonlinearity in the spectrum analyzer and data recording system, and uncertainty in determining the center frequency of the averaged beat note including small line asymmetry effects.

Table I gives the measured linewidths, beat frequencies, and estimated experimental uncertainties for each of the 30 lines observed in the 10.4-μm band and 26 lines observed in the 9.4-μm band. Our observations agree well with the frequency differences predicted with the aid of Bridges and Chang's rotational constants except at the higher rotational numbers. The large shifts from the predicted beat frequencies for certain lines[1] were not observed.

The term values for the vibrational-rotational energy levels in CO_2 are given by[7]

$$T(v, J) = G(v) + B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 - L_v J^4(J+1)^4 + \cdots, \quad (1)$$

where the quantities involved are defined in their usual sense. Expressions for the beat frequencies in terms of the rotational constants and quantum numbers are derived by taking appropriate differences with the aid of Eq. (1). Data reduction can then be done with equations which in matrix notation have the form

$$F = X\beta + \epsilon. \quad (2)$$

The elements f_i of F are the measured beat frequencies, and the elements ϵ_i of ϵ are the unknown measurement errors, which are assumed to be uncorrelated and to have a zero mean and a common variance. The elements x_{ij} of X are the exactly known functions of J, and the β_j are sums and differences of upper and lower rotational constants.[1] The method of least squares[8] was used to estimate β and its uncertainty and to propagate the uncertainties in forming linear combinations of β_j.

Data analysis was performed on a digital computer which maintained 25 significant figures throughout the calculations. The input data were not weighted since the experimental uncertainties were of comparable magnitude. It was estimated

TABLE I. Observed and calculated laser difference frequencies. ΔF_B is the full width at half-intensity of the 60-MHz beat frequency, f_i is the experimental measurement of the laser difference frequency, δf_i is the estimated experimental uncertainty in f_i, and r_i is the residual, i.e., the observed minus the predicted frequency. All frequencies are in MHz.

	$00^01 - [10^00, 02^00]_I$ Band (10.4 μm)				$00^01 - [10^00, 02^00]_{II}$ Band (9.4 μm)			
	ΔF_B	f_i	δf_i	r_i	ΔF_B	f_i	δf_i	r_i
P(42)-P(44)	0.1610	62511.8642	0.0029	0.0006				
P(40)-P(42)	0.0983	61747.9649	0.0039	-0.0015				
P(38)-P(40)	0.0881	60987.9862	0.0050	0.0027				
P(36)-P(38)	0.0627	60231.6550	0.0035	-0.0024				
P(34)-P(36)	0.0499	59478.7329	0.0039	-0.0021	0.0332	60275.3251	0.0027	0.0010
P(32)-P(34)	0.0365	58728.9700	0.0027	0.0020	0.0227	59527.3102	0.0026	-0.0021
P(30)-P(32)	0.0268	57982.1158	0.0026	0.0036	0.0281	58774.1189	0.0029	0.0009
P(28)-P(30)	0.0375	57237.9238	0.0030	-0.0037	0.0210	58015.9809	0.0028	0.0014
P(26)-P(28)	0.0316	56496.1807	0.0032	0.0031	0.0197	57253.1375	0.0029	-0.0022
P(24)-P(26)	0.0308	55756.6255	0.0027	-0.0043	0.0217	56485.8477	0.0027	0.0020
P(22)-P(24)	0.0293	55019.0548	0.0026	0.0002	0.0217	55714.3462	0.0027	-0.0028
P(20)-P(22)	0.0286	54283.2255	0.0028	-0.0001	0.0256	54938.9063	0.0033	0.0016
P(18)-P(20)	0.0287	53548.9212	0.0030	0.0018	0.0193	54159.7720	0.0027	0.0003
P(16)-P(18)	0.0220	52815.9168	0.0027	0.0019	0.0288	53377.2118	0.0029	0.0000
P(14)-P(16)	0.0220	52083.9924	0.0028	-0.0012	0.0230	52591.4887	0.0028	-0.0011
P(12)-P(14)	0.0247	51352.9398	0.0027	0.0008	0.0249	51802.8745	0.0027	0.0012
P(10)-P(12)	0.0239	50622.5349	0.0029	-0.0016	0.0286	51011.6321	0.0027	0.0001
R(12)-R(10)	0.0280	42201.6916	0.0026	-0.0014	0.0197	41812.5978	0.0029	-0.0005
R(14)-R(12)	0.0333	41461.7219	0.0027	0.0022	0.0253	41011.7838	0.0030	-0.0024
R(16)-R(14)	0.0259	40719.5614	0.0026	-0.0019	0.0223	40212.0685	0.0029	0.0006
R(18)-R(16)	0.0248	39975.0115	0.0031	0.0021	0.0197	39413.7140	0.0032	0.0006
R(20)-R(18)	0.0328	39227.8396	0.0027	-0.0022	0.0207	38616.9922	0.0027	0.0019
R(22)-R(20)	0.0246	38477.8438	0.0027	0.0017	0.0213	37822.1630	0.0030	-0.0007
R(24)-R(22)	0.0227	37724.7889	0.0026	-0.0007	0.0243	37029.4931	0.0031	-0.0027
R(26)-R(24)	0.0354	36968.4624	0.0027	0.0014	0.0236	36239.2524	0.0027	0.0070
R(28)-R(26)	0.0395	36208.6288	0.0031	-0.0015	0.0191	35451.6679	0.0029	-0.0003
R(30)-R(28)	0.0294	35445.0688	0.0034	0.0004	0.0247	34667.0134	0.0026	-0.0023
R(32)-R(30)	0.0248	34677.5481	0.0026	0.0053	0.0208	33885.5331	0.0026	-0.0025
R(34)-R(32)	0.0381	33905.8081	0.0029	-0.0095	0.0254	33107.4698	0.0026	-0.0013
R(36)-R(34)	0.0416	33129.6573	0.0034	0.0043	0.0346	32333.0632	0.0026	0.0024
	Std. Dev. of Residuals = 0.0033 MHz. Degrees of Freedom = 24				Std. Dev. of Residuals = 0.0024 MHz. Degrees of Freedom = 20			

that at the higher J-value terms involving rotational constants through L_v (constants β_6 and β_7) would be significant compared to the 3-kHz estimated experimental uncertainty in the measured beat frequencies. Therefore, various numbers of constants were tried to test the goodness of the fit. Figure 2 shows a plot of the residuals for both bands with two constants (B_v, D_v) and with three constants (B_v, D_v, H_v) used in the analysis. The systematic trend of the residuals with two constants is greatly reduced by the addition of H_v. The addition of L_v increased the uncertainties in the other coefficients without significantly reducing the residuals, and the estimated uncertainty in L_v was comparable to L_v itself. An F-type confidence test[8] indicated that H_v was highly significant while L_v was not statistically different from zero.

Results for the coefficients are given in Table II, and the residuals along with their standard deviations are given in Table I. The 3-kHz standard deviation of the residuals is comparable to the estimated experimental error and is about 100 times smaller than the previous best results

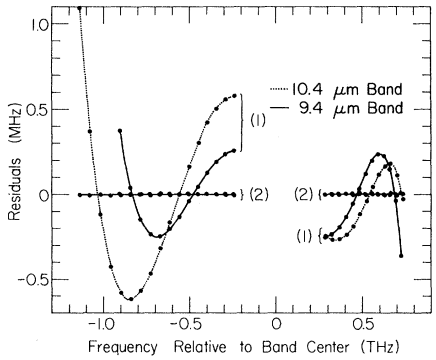

FIG. 2. Residuals plotted relative to the band center with (1) B_v and D_v and (2) B_v, D_v, and H_v used in the analysis. Standard deviations of the residuals in the type-(1) analysis are 416 and 214 kHz for the 10.4- and 9.4-μm bands, respectively, versus 3.3 and 2.4 kHz, respectively, for the type-(2) analysis.

Table II. Rotational constants for $^{12}C^{16}O_2$ derived from a least-squares fit to the measured beat frequencies in Table I. The quoted uncertainties are 1– standard-deviation estimates calculated from the least-squares fit. Differences in rotational constants are presented to preserve the accuracy of the measurement. The subscript l refers to the lower vibrational level.

	$00^01-[10^00,02^00]_I$ (MHz)	$00^01-[10^00,02^00]_{II}$ (MHz)
B_{00^01}	11 606.207 19(53)	11 606.207 27(42)
D_{00^01}	$3.988\,27(30)\times10^{-3}$	$3.988\,23(25)\times10^{-3}$
H_{00^01}	$5.26(83)\times10^{-10}$	$4.93(72)\times10^{-10}$
$B_l-B_{00^01}$	91.362 504(27)	100.157 620(25)
$D_l-D_{00^01}$	$-5.420\,91(33)\times10^{-4}$	$7.233\,04(36)\times10^{-4}$
$H_l-H_{00^01}$	$5.212(12)\times10^{-9}$	$6.469(15)\times10^{-9}$
B_l	11 697.569 70(52)	11 706.364 89(42)
D_l	$3.446\,18(28)\times10^{-3}$	$4.711\,53(25)\times10^{-3}$
H_l	$5.738(74)\times10^{-9}$	$6.961(73)\times10^{-9}$

—an improvement probably best attributed to the factor of 100 reduction in the linewidth. A comparison between the new values and previous best values for the rotational constants shows a 20 to 30 times reduction in estimated standard errors for B_v and D_v and a statistically significant measurement of H_v for the first time. Our two independent measurements of the rotational constants for the 00^01 level agree well within the estimated error.

The authors acknowledge with appreciation many fruitful discussions with Eric Johnson, Daniel Albritton, and Arthur Schmeltekopf concerning statistical analysis of the data and the molecular physics in the experiment. We also thank Matthew Lojko for his advice, patience, and perseverance in producing the computer programs for the data analysis.

[1]T. J. Bridges and T. Y. Chang, Phys. Rev. Lett. 22, 811 (1969).

[2]C. Freed and A. Javan, Appl. Phys. Lett. 17, 53 (1970).

[3]For example, Freed, Ross, and O'Donnell have measured the frequencies of many laser lines in some of the less abundant CO_2 isotopes relative to $^{12}C\ ^{16}O_2$ (C. Freed, A. H. M. Ross, R. G. O'Donnell, to be published).

[4]K. M. Evenson, J. S. Wells, F. R. Petersen, B. L. Danielson, and G. W. Day, Appl. Phys. Lett. 22, 192 (1973).

[5]K. M. Evenson, J. S. Wells, F. R. Petersen, B. L. Danielson, G. W. Day, R. L. Barger, and J. L. Hall, Phys. Rev. Lett. 29, 1346 (1972).

[6]In a separate investigation, radiation was deliberately reflected back into one of the lasers by a vibrating mirror. With low driving frequencies (5 and 50 Hz), the amplitude of the driving voltage was adjusted such that the full width at half-intensity of the beat frequency increased by a factor of 4 to approximately 100 kHz. There was no measurable shift in the center frequency.

[7]G. Herzberg, *Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules* (Van Nostrand, Princeton, N.J., 1950), 2nd ed., and *Molecular Spectra and Molecular Structure: II. Infrared and Raman Spectra* (Van Nostrand, Princeton, N.J., 1945).

[8]*Experimental Statistics*, National Bureau of Standards Handbook 91 (U.S.G.P.O., Washington, D.C., 1963), pp. 6-1 to 6-17.

Measurements of Complex Excitation Amplitudes in Electron-Helium Collisions by Angular Correlations Using a Coincidence Method*

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Angular correlations were measured by delayed coincidences between electrons of incident energy about 80 eV scattered inelastically from helium and photons from excited $3\,^1P$ and $2\,^1P$ states. From the angular correlation in each case we deduce the ratio of the differential cross sections for exciting the magnetic sublevels of the excited state and the phase between the corresponding excitation amplitudes. We compare the atomic radiation patterns with those predicted by the Born approximation.

Valuable information about inelastic electron-atom scattering processes can be obtained from electron-photon angular correlations measured by coincidence techniques.[1,2] This paper reports preliminary measurements of electron-photon coincidences in a crossed electron-helium beam experiment.

The results are significant for several reasons.