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Improved Molecular Constants and Frequencies for the CO_2 Laser from New High-*J* Regular and Hot-Band Frequency Measurements

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We dedicate this paper to the memory of F. R. Petersen, a pioneer in the field of laser frequency measurements. His meticulous attention to detail in the design and operation of the CO_2 laser and subsequent precise measurement of its transition frequencies led to his outstanding examples of stabilized laser frequency tables (*1–3*), which were the essential foundation for the present work.

New frequencies are given for the $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{18}O_2$, and $^{13}C^{18}O_2$ regular band laser transitions and for the hot-band transitions of $^{12}C^{16}O_2$. These frequencies are based on a new least-squares analysis of all the frequency measurements of these four molecular species including new high-*J* measurements reported here and recent absolute frequency measurements. Fourteen new high-*J* transitions of the regular $^{12}C^{16}O_2$ laser bands have been observed, the lasers have been stabilized with sub-Doppler saturated 4.3-μm fluorescence, and their frequencies have been measured. Nine of these transitions fill the gap between the 9.4- and 10.4-μm bands. Saturated 4.3-μm fluorescence also has been used to stabilize the $01^11\text{–}[11^10,03^10]_{\rm I}$ and $01^11\text{–}[11^10,03^10]_{\rm II}$ hot-band laser lines. New frequency measurements are reported for 84 hot-band lines, which were also included in the reanalysis of the CO_2 laser transitions.

INTRODUCTION

The CO_2 laser is a very useful source of infrared radiation of well-defined frequencies because it can be easily and reproducibly stabilized by means of the saturated 4.3-μm fluorescence locking technique (*4*). With its many isotopic variations it provides a convenient grid of secondary frequency standards in the infrared. By means of techniques for generating sum and difference frequencies, those frequency standards can be propagated throughout much of the infrared (*5, 6*). Because of its power, the CO_2 laser has also been instrumental in generating several thousand far-infrared (FIR) laser lines through optical pumping (*7*) of polar molecules. We have now used the saturated 4.3-μm fluorescence locking technique to stabilize the laser on linecenters of the two regular bands ($00^01\text{–}[10^00,02^00]_{\rm I,II}$) and their two hot bands ($01^11\text{–}[11^10,03^10]_{\rm I,II}$), including lines of the newly discovered 9-μm hot band (*8*). We measured the frequencies of the regular CO_2 laser transitions to higher-*J* values and have also applied those techniques to the measurement of the hot-band transitions, $01^11\text{–}[11^10,03^10]_{\rm I,II}$. These new measurements close the gap between the 9-μm *P* branch and the 10-μm *R* branch and also provide a broader and denser grid of well-measured

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transitions for use as secondary frequency standards and for optically pumping new FIR laser lines.

Before the present work the best $^{12}C^{16}O_2$ laser transition frequencies were based on the rovibrational constants given by Petersen *et al.* (*1*). The best constants for the other isotopomers were presented by Bradley *et al.* (*9*). Those constants were determined from a least-squares analysis of the frequency measurements given by Petersen *et al.* (*1*), Evenson *et al.* (*10*), and Petersen *et al.* (*2*), as well as measurements on many isotopically substituted species by Bradley *et al.* (*9*). At that time the frequency measurements were limited to transitions below $J = 58$; consequently, the higher-J transition frequencies were not very well determined. That left a gap of about 16 cm^{-1} between the 10- and 9-μm regular bands where lines did not lase and no accurate frequency measurements had been made. We have now developed a more efficient laser that oscillates on lines that fill that gap (*8*). That laser has been stabilized with saturated 4.3-μm laser-fluorescence techniques, and frequency measurements have been made on the $R(56)$ to $R(62)$ transitions of the 10-μm regular laser band and the $P(58)$ to $P(66)$ transitions of the 9-μm band. We have also measured the $P(50)$ to $P(60)$ transitions of the 10-μm regular laser band.

Recent more accurate measurements (*11–13*) of the frequency of the methane line require that the $R(30)_I$ CO_2 laser line frequency (*1*) be corrected by −2.9 kHz. New absolute frequency measurements of the $P(12)_I$, $P(14)_I$, $R(10)_I$, $R(30)_I$, and $R(12)_{II}$ lines have also been reported (*14–17*). We have calculated new tables of laser frequencies for the CO_2 laser transitions by taking into account these new absolute frequency measurements as well as our own new high-J measurements.

In this paper we also report the frequency measurements of 84 laser transitions of the hot band 01^11–$[11^10,03^10]_I$ and the newly observed hot band 01^11–$[11^10,03^10]_{II}$. For the main isotopomer, $^{12}C^{16}O_2$, the frequencies of the low-frequency band, 01^11–$[11^10,03^10]_I$, were first measured by Whitford *et al.* (*18*) and were more accurately measured by Petersen *et al.* (*19*). On the other hand, the high-frequency band, 01^11–$[11^10,03^10]_{II}$, has been discovered only recently and was measured with sufficient accuracy to verify the identification (*8*). For our new measurements, the hot-band laser was locked to the linecenter by using the saturated 4.3-μm fluorescence technique of Freed and Javan (*4*) with a longitudinal hot cell developed recently by Chou *et al.* (*20*).

EXPERIMENTAL DETAILS

The CO_2 laser used for this work consists of a ribbed laser tube with a cavity length of 1.5 m and an active discharge length of 1.34 m (*8, 21*). The zeroth-order beam of the laser grating was used as the laser output. A 171 line/mm grating, 2.5 cm long, was used for the 9-μm hot-band lines, and another 8-cm-long 171 line/mm grating was used for the 10-μm hot-band lines. We used a 100 line/mm grating for the 10-μm hot-band lines with $J > 35$ and for the high-J regular band lines.

We measured the frequency difference between the new laser lines and the laser lines of another fluorescence stabilized CO_2 laser, used as a frequency standard. The frequency difference was determined by using a spectrum analyzer to measure the beat frequency between the two lasers and the desired harmonic of a microwave source. A single MIM diode was used as a harmonic generator and mixer. Each beat frequency was measured several times, and the scatter of the measurements was used as a guide in estimating the uncertainty of the measurement. The uncertainty assigned to each

TABLE I

Measured $^{12}C^{16}O_2$–$^{13}C^{16}O_2$ Laser Frequency Differences in MHz

$^{12}CO_2$	$^{13}CO_2$[a]	Beat Freq.[b] (unc.)	obs.-calc.
10*P*(60)	10*P*(12)	-16 128.142 (0.016)	-0.007
10*P*(58)	10*P*(10)	2 864.342 (0.015)	0.014
10*P*(54)	10*P*(4)	-7 857.706 (0.010)	0.009
10*P*(52)	10*P*(4)	58 541.766 (0.063)	-0.064
10*P*(50)	10*R*(2)	-39 413.022 (0.020)	0.024
10*R*(56)	9*P*(26)	2 720.760 (0.004)	-0.004
10*R*(58)	9*P*(26)	26 946.274 (0.004)	-0.006
10*R*(60)	9*P*(24)	-7 097.086 (0.020)	0.025
10*R*(62)	9*P*(24)	15 420.540 (0.007)	0.012
9*P*(66)	9*P*(22)	-9 704.556 (0.008)	-0.002
9*P*(64)	9*P*(20)	5 294.201 (0.006)	-0.001
9*P*(62)	9*P*(18)	20 498.182 (0.009)	-0.003
9*P*(60)	9*P*(14)	-17 263.907 (0.007)	-0.009
9*P*(58)	9*P*(12)	-802.484 (0.005)	0.005

[a] The 10 designation before the laser transition indicates the 10 μm $00^01-[10^00,02^00]_I$ laser transition and the 9 designation indicates the 9 μm $00^01-[10^00,02^00]_{II}$ laser transition.

[b] The beat frequency is the difference given by subtracting the $^{13}CO_2$ laser frequency from the $^{12}CO_2$ laser frequency.

measurement was increased whenever necessary to ensure that the deviation obtained from the fit was not much greater than the uncertainty.

The high-*J* transitions of the regular laser bands were measured using $^{13}C^{16}O_2$ laser lines, and the hot-band transition lines were measured using either $^{12}C^{16}O_2$ or $^{13}C^{16}O_2$ laser lines as reference frequencies. All of the lasers, including the hot-band lasers, were stabilized on the saturation dip of the fluorescence in the 4.3-μm region by the technique developed by Freed and Javan (*4*). Here we used a conventional fluorescence cell external to the laser cavity for frequency stabilization of the reference CO_2 laser. The reference CO_2 gas pressure used was 5.3 Pa (40 mTorr). However, the population of the lower levels of the hot-band laser and high-*J* regular band laser transitions was too small to give a sufficient signal-to-noise ratio for the saturated 4.3-μm fluorescence locking technique using a conventional cell. Recently Chou *et al.* (*20*) used a longitudinal fluorescence cell external to the laser to lock the sequence-band CO_2 lasers, instead of using the conventional transverse cell (*4*). We have used the same longitudinal cell for the frequency stabilization of the high-*J* regular laser transitions and hot-band lines. For locking the high-*J* transitions the fluorescence cell was heated to ~150°C and filled with 9.3 Pa (70 mTorr) of CO_2 gas. For locking the hot-band transitions it was heated to ~200 C and filled with 10 Pa (75 mTorr) of CO_2 gas.

ANALYSIS OF THE MEASUREMENTS

The $00^01-[10^00, 02^00]_I$ *and* $00^01-[10^00, 02^00]_{II}$ *Bands*

The new measurements of transitions in these bands are given in Table I. Since these measurements were based on the lower-*J* transitions of $^{13}C^{16}O_2$ and since there have been new measurements that affect those frequencies, it was necessary to reevaluate all the CO_2 laser frequencies.

TABLE II

Molecular Constants (in MHz) for the 00^01–$[10^00,02^00]_{\mathrm{I}}$ and 00^01–$[10^00,02^00]_{\mathrm{II}}$ Laser Transitions of $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$

Molecular Constants	$^{12}C^{16}O_2$	$^{13}C^{16}O_2$
$B(00^01)$	11 606.206 933 0(121)[a]	11 610.164 865 8(564)
$D(00^01)\times 10^3$	3.988 023 9(163)	3.984 471 9(489)
$H(00^01)\times 10^9$	0.423 45(763)	0.397 47(1471)
$L(00^01)\times 10^{14}$	0.207(115)	0.207(115)[b]
$\nu_0(00^01\text{-}[10^00,02^00]_{\mathrm{I}})$	28 808 813.821 6(4)	27 383 792.574 2(22)
$B([10^00,02^00]_{\mathrm{I}})$	11 697.569 430 4(130)	11 683.441 646 6(605)
$D([10^00,02^00]_{\mathrm{I}})\times 10^3$	3.445 896 3(179)	3.604 391 8(639)
$H([10^00,02^00]_{\mathrm{I}})\times 10^9$	5.594 20(870)	6.251 5(284)
$L([10^00,02^00]_{\mathrm{I}})\times 10^{14}$	1.695 8(1353)	7.891(413)
$\nu_0(00^01\text{-}[10^00,02^00]_{\mathrm{II}})$	31 889 960.171 4(17)	30 508 659.227 4(28)
$B([10^00,02^00]_{\mathrm{II}})$	11 706.364 616 2(132)	11 719.364 887 7(620)
$D([10^00,02^00]_{\mathrm{II}})\times 10^3$	4.711 450 8(178)	4.747 139 7(649)
$H([10^00,02^00]_{\mathrm{II}})\times 10^9$	6.997 27(785)	8.120 0(302)
$L([10^00,02^00]_{\mathrm{II}})\times 10^{14}$	-2.978 0(1111)	-5.830(556)

[a] The uncertainty (one standard deviation) in the last digits is given in parentheses.
[b] The value of $L(00^01)$ was constrained to be the same for $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$.

Most workers use the CO_2 laser frequencies given by Bradley *et al.* (*9*). Those frequencies were based on a single absolute frequency measurement of the $R(30)$ transition of the 10.6-μm band, which we designate as the $R(30)_{\mathrm{I}}$ line. The frequency difference between the third harmonic of the $R(30)_{\mathrm{I}}$ CO_2 laser line and the 3.39-μm $P(7)$ transition of methane was measured by Evenson *et al.* (*10*). Petersen *et al.* (*1*) discussed the relation of the $R(30)_{\mathrm{I}}$ line to the frequency of the methane line in the light of new measurements of the methane line that were available at that time. Since the work of Petersen *et al.* (*1*) there have been several new and much more accurate measurements of the methane line frequency (*11–13*) which change the frequency of the $R(30)_{\mathrm{I}}$ transition to 29 442 483.3168 ± 0.0009 MHz. That new value has been included in the present fit. Clairon *et al.* (*15*) have made a new measurement of the $R(30)_{\mathrm{I}}$ transition that is independent of the methane line frequency. They also measured the frequency of the $P(28)_{\mathrm{II}}$ transition of $^{13}CO_2$. We have also included in the present fit the measurement of the $R(12)_{\mathrm{II}}$ transition by Blaney *et al.* (*14*). The most important new additions to the data base for the CO_2 laser transitions have been the very accurate new measurements of the $P(12)_{\mathrm{I}}$, $P(14)_{\mathrm{I}}$, and $R(10)_{\mathrm{I}}$ transitions by Chardonnet *et al.* (*16*) and the even more recent remeasurement of the $R(10)_{\mathrm{I}}$ transition (*17*). These measurements were included in a new least-squares fit that also included all the transitions listed in the paper by Bradley *et al.* (*9*) that applied to the laser transitions of $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{18}O_2$, $^{13}C^{18}O_2$, and $^{12}C^{17}O_2$. The uncertainties used in the fit were those given by Bradley *et al.* or by the other papers. The term expressions used for the least-squares fit were

$$E(v, J) = G_v + B_v[J(J+1)] - D_v[J(J+1)]^2 + H_v[J(J+1)]^3 + L_v[J(J+1)]^4$$

and

$$\nu_0 = G'_v - G''_v.$$

One of the goals of the present work was to improve the accuracy of the frequencies of the high-J laser transitions. Consequently, we have included in the analysis the

TABLE III

Molecular Constants (in MHz) for the 00^01–$[10^00,02^00]_I$ and 00^01–$[10^00,02^00]_{II}$ Laser Transitions of $^{12}C^{18}O_2$ and $^{13}C^{18}O_2$

Molecular Constants	$^{12}C^{18}O_2$	$^{13}C^{18}O_2$
$B(00^01)$	10 315.559 498 3(219)[a]	10 319.095 780 8(340)
$D(00^01)\times10^3$	3.150 444 0(302)	3.148 055 7(417)
$H(00^01)\times10^9$	0.211 11(1692)	0.248 41(2184)
$L(00^01)\times10^{14}$	1.252(389)	1.252(389)[b]
$\nu_0(00^01\text{-}[10^00,02^00]_I)$	28 988 597.063 8(52)	27 838 551.136 5(18)
$B([10^00,02^00]_I)$	10 414.894 182 7(205)	10 403.473 582 4(362)
$D([10^00,02^00]_I)\times10^3$	2.767 911 0(277)	2.717 855 1(449)
$H([10^00,02^00]_I)\times10^9$	2.439 33(1504)	3.067 3(241)
$L([10^00,02^00]_I)\times10^{14}$	0.598(332)	1.212(445)
$\nu_0(00^01\text{-}[10^00,02^00]_{II})$	32 489 192.951 1(20)	30 785 884.362 5(22)
$B([10^00,02^00]_{II})$	10 388.527 700 0(218)	10 398.982 431 1(351)
$D([10^00,02^00]_{II})\times10^3$	3.518 141 9(294)	3.656 991 9(426)
$H([10^00,02^00]_{II})\times10^9$	4.697 65(1628)	5.129 17(2146)
$L([10^00,02^00]_{II})\times10^{14}$	-2.645(360)	-1.065(362)

[a] The uncertainty (one standard deviation) in the last digits is given in parentheses.
[b] The value of $L(00^01)$ was constrained to be the same for $^{12}C^{18}O_2$ and $^{13}C^{18}O_2$.

absorption measurements of the 00^01–00^00 transitions given in Refs. (*22–24*). For the 00^01 state, those measurements extended to $J = 141$ for $^{12}C^{16}O_2$, to $J = 123$ for $^{13}C^{16}O_2$, and to $J = 127$ for $^{12}C^{18}O_2$. Those transitions were given weights inversely proportional to the square of their uncertainties, much smaller weights than the sub-Doppler frequency measurements. Including those absorption measurements did not appear to make a significant change in the values of the constants, but rather changed the high-J transition frequencies calculated from those constants and reduced the uncertainties of those calculated transition frequencies.

The paper by Bradley *et al.* (*9*) included more transitions of the rare isotopic species because they were interested in fitting all of the CO_2 laser measurements for all isotopic species. In our work this did not seem warranted, but we have included all the data linking the isotopic species $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{18}O_2$, $^{13}C^{18}O_2$, and $^{12}C^{17}O_2$. We have only given tables for the first four isotopomers, but the new measurements will lower the frequencies of the laser transitions of the other isotopic species from the frequencies given by Bradley *et al.* by as much as 10 kHz.

Tables II and III give the newly determined constants. Because of correlation among the constants, more digits are needed to reproduce the deviations given by the least-squares fits than would seem to be warranted by their uncertainties. We found that the least-squares analysis was unable to determine a value for the $L(00^01)$ constant for $^{13}C^{16}O_2$, even with the high-J absorption measurements. Because the carbon atom is at the center of mass, the rotational constants for the 00^01 level, which is only very weakly affected by resonances, are nearly the same for both $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$. For comparison, the $D(00^01)$ terms are the same to within 0.1% for both isotopic species. Therefore, we have constrained the least-squares fit to give the same value for the $L(00^01)$ term for both isotopic species. Similarly the $L(00^01)$ term was constrained to be the same for both $^{12}C^{18}O_2$ and $^{13}C^{18}O_2$.

The inclusion of the new measurements gives a significant reduction in the uncertainty of the L_v terms, but, more importantly, gives a greatly improved agreement between the observed and calculated high-J transitions. The value of the L_v terms was

TABLE IV

Calculated Frequencies for the 00^01-$[10^00,02^00]_{\mathrm{I}}$ and 00^01-$[10^00,02^00]_{\mathrm{II}}$ Bands of $^{12}C^{16}O_2$ with Estimated 1σ Uncertainties

Line	10 μm Band Frequency (MHz)	Uncertainty (MHz)	Line	9 μm Band Frequency (MHz)	Uncertainty (MHz)
P(70)	26 721 305.4986	0.0590	P(70)	29 789 856.3816	0.0150
P(68)	26 794 232.6979	0.0419	P(68)	29 861 850.7704	0.0093
P(66)	26 866 318.8281	0.0292	P(66)	29 933 216.1762	0.0059
P(64)	26 937 571.7393	0.0200	P(64)	30 003 944.2856	0.0041
P(62)	27 007 998.9334	0.0135	P(62)	30 074 026.9118	0.0034
P(60)	27 077 607.5730	0.0090	P(60)	30 143 456.0029	0.0032
P(58)	27 146 404.4895	0.0060	P(58)	30 212 223.6494	0.0029
P(56)	27 214 396.1915	0.0042	P(56)	30 280 322.0922	0.0026
P(54)	27 281 588.8723	0.0031	P(54)	30 347 743.7299	0.0024
P(52)	27 347 988.4177	0.0024	P(52)	30 414 481.1268	0.0021
P(50)	27 413 600.4128	0.0020	P(50)	30 480 527.0193	0.0020
P(48)	27 478 430.1491	0.0017	P(48)	30 545 874.3238	0.0019
P(46)	27 542 482.6311	0.0015	P(46)	30 610 516.1428	0.0019
P(44)	27 605 762.5826	0.0014	P(44)	30 674 445.7724	0.0019
P(42)	27 668 274.4524	0.0014	P(42)	30 737 656.7080	0.0019
P(40)	27 730 022.4206	0.0013	P(40)	30 800 142.6511	0.0019
P(38)	27 791 010.4036	0.0013	P(38)	30 861 897.5150	0.0019
P(36)	27 851 242.0595	0.0012	P(36)	30 922 915.4309	0.0018
P(34)	27 910 720.7929	0.0012	P(34)	30 983 190.7533	0.0018
P(32)	27 969 449.7596	0.0011	P(32)	31 042 718.0651	0.0018
P(30)	28 027 431.8712	0.0011	P(30)	31 101 492.1831	0.0018
P(28)	28 084 669.7986	0.0010	P(28)	31 159 508.1628	0.0018
P(26)	28 141 165.9766	0.0009	P(26)	31 216 761.3026	0.0018
P(24)	28 196 922.6071	0.0009	P(24)	31 273 247.1484	0.0018
P(22)	28 251 941.6626	0.0008	P(22)	31 328 961.4975	0.0018
P(20)	28 306 224.8892	0.0008	P(20)	31 383 900.4025	0.0018
P(18)	28 359 773.8093	0.0007	P(18)	31 438 060.1746	0.0018
P(16)	28 412 589.7247	0.0006	P(16)	31 491 437.3869	0.0018
P(14)	28 464 673.7185	0.0005	P(14)	31 544 028.8774	0.0018
P(12)	28 516 026.6574	0.0005	P(12)	31 595 831.7515	0.0017
P(10)	28 566 649.1934	0.0004	P(10)	31 646 843.3842	0.0017
P(8)	28 616 541.7659	0.0004	P(8)	31 697 061.4225	0.0017
P(6)	28 665 704.6025	0.0004	P(6)	31 746 483.7868	0.0017
P(4)	28 714 137.7202	0.0004	P(4)	31 795 108.6725	0.0017
P(2)	28 761 840.9270	0.0004	P(2)	31 842 934.5512	0.0017
R(0)	28 832 026.2195	0.0004	R(0)	31 913 172.5693	0.0017
R(2)	28 877 902.4380	0.0004	R(2)	31 958 996.0623	0.0017
R(4)	28 923 046.4301	0.0003	R(4)	32 004 017.3824	0.0017
R(6)	28 967 457.0656	0.0002	R(6)	32 048 236.2499	0.0017
R(8)	29 011 133.0053	0.0001	R(8)	32 091 652.6619	0.0016
R(10)	29 054 072.7010	0.0001	R(10)	32 134 266.8917	0.0017
R(12)	29 096 274.3936	0.0001	R(12)	32 176 079.4878	0.0017
R(14)	29 137 736.1130	0.0002	R(14)	32 217 091.2720	0.0017
R(16)	29 178 455.6761	0.0003	R(16)	32 257 303.3383	0.0017
R(18)	29 218 430.6854	0.0004	R(18)	32 296 717.0507	0.0018
R(20)	29 257 658.5271	0.0005	R(20)	32 335 334.0404	0.0018
R(22)	29 296 136.3691	0.0005	R(22)	32 373 156.2040	0.0019
R(24)	29 333 861.1585	0.0006	R(24)	32 410 185.6998	0.0020
R(26)	29 370 829.6193	0.0006	R(26)	32 446 424.9454	0.0020
R(28)	29 407 038.2493	0.0005	R(28)	32 481 876.6135	0.0020
R(30)	29 442 483.3169	0.0005	R(30)	32 516 543.6288	0.0020
R(32)	29 477 160.8582	0.0006	R(32)	32 550 429.1636	0.0020
R(34)	29 511 066.6733	0.0006	R(34)	32 583 536.6336	0.0020
R(36)	29 544 196.3220	0.0007	R(36)	32 615 869.6934	0.0020
R(38)	29 576 545.1204	0.0008	R(38)	32 647 432.2318	0.0019
R(40)	29 608 108.1358	0.0009	R(40)	32 678 228.3663	0.0019
R(42)	29 638 880.1829	0.0010	R(42)	32 708 262.4385	0.0019
R(44)	29 668 855.8181	0.0011	R(44)	32 737 539.0079	0.0019
R(46)	29 698 029.3348	0.0013	R(46)	32 766 062.8465	0.0020
R(48)	29 726 394.7580	0.0015	R(48)	32 793 838.9327	0.0021
R(50)	29 753 945.8384	0.0017	R(50)	32 820 872.4450	0.0024
R(52)	29 780 676.0464	0.0019	R(52)	32 847 168.7555	0.0030
R(54)	29 806 578.5659	0.0022	R(54)	32 872 733.4235	0.0038
R(56)	29 831 646.2879	0.0024	R(56)	32 897 572.1885	0.0051
R(58)	29 855 871.8031	0.0027	R(58)	32 921 690.9630	0.0070
R(60)	29 879 247.3957	0.0035	R(60)	32 945 095.8256	0.0097
R(62)	29 901 765.0349	0.0054	R(62)	32 967 793.0133	0.0137
R(64)	29 923 416.3679	0.0088	R(64)	32 989 788.9142	0.0192
R(66)	29 944 192.7116	0.0142	R(66)	33 011 090.0597	0.0267
R(68)	29 964 085.0439	0.0222	R(68)	33 031 703.1165	0.0368
R(70)	29 983 083.9959	0.0335	R(70)	33 051 634.8789	0.0501

TABLE V

Calculated Frequencies for the 00^01–$[10^00,02^00]_{\mathrm{I}}$ and 00^01–$[10^00,02^00]_{\mathrm{II}}$ Bands of $^{13}C^{16}O_2$ with Estimated 1σ Uncertainties

	10 μm Band			9 μm Band	
Line	Frequency (MHz)	Uncertainty (MHz)	Line	Frequency (MHz)	Uncertainty (MHz)
P(66)	25 523 832.2010	0.3838	P(66)	28 512 082.5680	0.6361
P(64)	25 590 013.4838	0.2656	P(64)	28 585 121.9682	0.4535
P(62)	25 655 543.6589	0.1778	P(62)	28 657 449.4381	0.3167
P(60)	25 720 428.2541	0.1146	P(60)	28 729 056.6512	0.2158
P(58)	25 784 672.4872	0.0701	P(58)	28 799 935.4240	0.1429
P(56)	25 848 281.2788	0.0397	P(56)	28 870 077.7247	0.0914
P(54)	25 911 259.2636	0.0198	P(54)	28 939 475.6807	0.0560
P(52)	25 973 610.8011	0.0077	P(52)	29 008 121.5868	0.0325
P(50)	26 035 339.9861	0.0022	P(50)	29 076 007.9121	0.0176
P(48)	26 096 450.6586	0.0039	P(48)	29 143 127.3082	0.0089
P(46)	26 156 946.4128	0.0050	P(46)	29 209 472.6166	0.0045
P(44)	26 216 830.6059	0.0050	P(44)	29 275 036.8754	0.0029
P(42)	26 276 106.3662	0.0044	P(42)	29 339 813.3270	0.0025
P(40)	26 334 776.6010	0.0038	P(40)	29 403 795.4243	0.0022
P(38)	26 392 844.0037	0.0033	P(38)	29 466 976.8383	0.0018
P(36)	26 450 311.0606	0.0031	P(36)	29 529 351.4635	0.0016
P(34)	26 507 180.0571	0.0030	P(34)	29 590 913.4251	0.0014
P(32)	26 563 453.0841	0.0029	P(32)	29 651 657.0844	0.0013
P(30)	26 619 132.0432	0.0027	P(30)	29 711 577.0445	0.0012
P(28)	26 674 218.6518	0.0026	P(28)	29 770 668.1565	0.0013
P(26)	26 728 714.4480	0.0025	P(26)	29 828 925.5236	0.0015
P(24)	26 782 620.7952	0.0025	P(24)	29 886 344.5071	0.0018
P(22)	26 835 938.8857	0.0025	P(22)	29 942 920.7304	0.0021
P(20)	26 888 669.7448	0.0026	P(20)	29 998 650.0833	0.0023
P(18)	26 940 814.2343	0.0026	P(18)	30 053 528.7266	0.0025
P(16)	26 992 373.0551	0.0026	P(16)	30 107 553.0949	0.0026
P(14)	27 043 346.7504	0.0025	P(14)	30 160 719.9011	0.0026
P(12)	27 093 735.7078	0.0025	P(12)	30 213 026.1383	0.0026
P(10)	27 143 540.1619	0.0024	P(10)	30 264 469.0833	0.0026
P(8)	27 192 760.1957	0.0023	P(8)	30 315 046.2989	0.0026
P(6)	27 241 395.7427	0.0023	P(6)	30 364 755.6354	0.0026
P(4)	27 289 446.5876	0.0023	P(4)	30 413 595.2331	0.0027
P(2)	27 336 912.3679	0.0022	P(2)	30 461 563.5228	0.0028
R(0)	27 407 012.8880	0.0022	R(0)	30 531 879.5412	0.0028
R(2)	27 453 013.4587	0.0021	R(2)	30 577 664.6136	0.0027
R(4)	27 498 426.5429	0.0019	R(4)	30 622 575.1884	0.0026
R(6)	27 543 251.1200	0.0018	R(6)	30 666 611.0127	0.0025
R(8)	27 587 486.0225	0.0016	R(8)	30 709 772.1256	0.0023
R(10)	27 631 129.9357	0.0015	R(10)	30 752 058.8571	0.0022
R(12)	27 674 181.3964	0.0014	R(12)	30 793 471.8268	0.0021
R(14)	27 716 638.7918	0.0014	R(14)	30 834 011.9425	0.0021
R(16)	27 758 500.3578	0.0014	R(16)	30 873 680.3976	0.0021
R(18)	27 799 764.1771	0.0014	R(18)	30 912 478.6693	0.0021
R(20)	27 840 428.1774	0.0014	R(20)	30 950 408.5159	0.0021
R(22)	27 880 490.1284	0.0014	R(22)	30 987 471.9731	0.0021
R(24)	27 919 947.6397	0.0014	R(24)	31 023 671.3516	0.0021
R(26)	27 958 798.1569	0.0014	R(26)	31 059 009.2325	0.0020
R(28)	27 997 038.9594	0.0013	R(28)	31 093 488.4640	0.0020
R(30)	28 034 667.1554	0.0013	R(30)	31 127 112.1567	0.0021
R(32)	28 071 679.6788	0.0013	R(32)	31 159 883.6790	0.0022
R(34)	28 108 073.2845	0.0013	R(34)	31 191 806.6525	0.0023
R(36)	28 143 844.5436	0.0013	R(36)	31 222 884.9465	0.0024
R(38)	28 178 989.8381	0.0013	R(38)	31 253 122.6727	0.0026
R(40)	28 213 505.3559	0.0014	R(40)	31 282 524.1792	0.0030
R(42)	28 247 387.0842	0.0016	R(42)	31 311 094.0450	0.0038
R(44)	28 280 630.8039	0.0023	R(44)	31 338 837.0735	0.0053
R(46)	28 313 232.0822	0.0041	R(46)	31 365 758.2860	0.0085
R(48)	28 345 186.2656	0.0079	R(48)	31 391 862.9153	0.0145
R(50)	28 376 488.4724	0.0148	R(50)	31 417 156.3984	0.0249
R(52)	28 407 133.5842	0.0261	R(52)	31 441 644.3699	0.0416
R(54)	28 437 116.2377	0.0437	R(54)	31 465 332.6548	0.0673
R(56)	28 466 430.8148	0.0699	R(56)	31 488 227.2606	0.1054
R(58)	28 495 071.4336	0.1078	R(58)	31 510 334.3704	0.1601
R(60)	28 523 031.9376	0.1611	R(60)	31 531 660.3347	0.2368
R(62)	28 550 305.8850	0.2345	R(62)	31 552 211.6642	0.3420
R(64)	28 576 886.5373	0.3339	R(64)	31 571 995.0217	0.4838
R(66)	28 602 766.8470	0.4661	R(66)	31 591 017.2140	0.6721

TABLE VI

Calculated Frequencies for the $00^01-[10^00,02^00]_I$ and $00^01-[10^00,02^00]_{II}$ Bands of $^{12}C^{18}O_2$ with Estimated 1σ Uncertainties

Line	10 μm Band Frequency (MHz)	Uncertainty (MHz)	Line	9 μm Band Frequency (MHz)	Uncertainty (MHz)
P(70)	27 045 326.3435	0.2240	P(70)	30 695 237.5749	0.0418
P(68)	27 114 914.1146	0.1640	P(68)	30 755 520.2165	0.0277
P(66)	27 183 635.8101	0.1180	P(66)	30 815 311.4889	0.0178
P(64)	27 251 496.4223	0.0833	P(64)	30 874 607.2063	0.0109
P(62)	27 318 500.7430	0.0575	P(62)	30 933 403.2298	0.0066
P(60)	27 384 653.3660	0.0386	P(60)	30 991 695.4719	0.0036
P(58)	27 449 958.6906	0.0251	P(58)	31 049 479.9006	0.0023
P(56)	27 514 420.9237	0.0157	P(56)	31 106 752.5444	0.0019
P(54)	27 578 044.0835	0.0094	P(54)	31 163 509.4961	0.0019
P(52)	27 640 832.0013	0.0053	P(52)	31 219 746.9179	0.0019
P(50)	27 702 788.3249	0.0029	P(50)	31 275 461.0450	0.0019
P(48)	27 763 916.5207	0.0017	P(48)	31 330 648.1903	0.0019
P(46)	27 824 219.8764	0.0013	P(46)	31 385 304.7485	0.0019
P(44)	27 883 701.5031	0.0013	P(44)	31 439 427.2002	0.0019
P(42)	27 942 364.3382	0.0012	P(42)	31 493 012.1159	0.0019
P(40)	28 000 211.1468	0.0011	P(40)	31 546 056.1603	0.0018
P(38)	28 057 244.5246	0.0011	P(38)	31 598 556.0954	0.0018
P(36)	28 113 466.8996	0.0010	P(36)	31 650 508.7848	0.0018
P(34)	28 168 880.5339	0.0010	P(34)	31 701 911.1972	0.0018
P(32)	28 223 487.5260	0.0009	P(32)	31 752 760.4096	0.0018
P(30)	28 277 289.8121	0.0008	P(30)	31 803 053.6109	0.0018
P(28)	28 330 289.1681	0.0008	P(28)	31 852 788.1048	0.0018
P(26)	28 382 487.2113	0.0007	P(26)	31 901 961.3129	0.0018
P(24)	28 433 885.4012	0.0006	P(24)	31 950 570.7778	0.0018
P(22)	28 484 485.0420	0.0006	P(22)	31 998 614.1653	0.0018
P(20)	28 534 287.2827	0.0005	P(20)	32 046 089.2672	0.0018
P(18)	28 583 293.1192	0.0005	P(18)	32 092 994.0038	0.0018
P(16)	28 631 503.3951	0.0005	P(16)	32 139 326.4255	0.0018
P(14)	28 678 918.8023	0.0005	P(14)	32 185 084.7154	0.0018
P(12)	28 725 539.8828	0.0005	P(12)	32 230 267.1905	0.0018
P(10)	28 771 367.0286	0.0005	P(10)	32 274 872.3038	0.0018
P(8)	28 816 400.4827	0.0005	P(8)	32 318 898.6452	0.0019
P(6)	28 860 640.3401	0.0005	P(6)	32 362 344.9429	0.0019
P(4)	28 904 086.5476	0.0005	P(4)	32 405 210.0647	0.0020
P(2)	28 946 738.9047	0.0005	P(2)	32 447 493.0180	0.0020
R(0)	29 009 228.1702	0.0005	R(0)	32 509 824.0575	0.0020
R(2)	29 049 894.0586	0.0005	R(2)	32 550 648.1719	0.0020
R(4)	29 089 764.2368	0.0004	R(4)	32 590 887.7539	0.0020
R(6)	29 128 837.8427	0.0004	R(6)	32 630 542.4455	0.0020
R(8)	29 167 113.8670	0.0004	R(8)	32 669 612.0294	0.0020
R(10)	29 204 591.1531	0.0004	R(10)	32 708 096.4283	0.0020
R(12)	29 241 268.3966	0.0005	R(12)	32 745 995.7043	0.0019
R(14)	29 277 144.1446	0.0005	R(14)	32 783 310.0577	0.0019
R(16)	29 312 216.7957	0.0006	R(16)	32 820 039.8262	0.0019
R(18)	29 346 484.5986	0.0006	R(18)	32 856 185.4832	0.0019
R(20)	29 379 945.6518	0.0006	R(20)	32 891 747.6364	0.0019
R(22)	29 412 597.9026	0.0006	R(22)	32 926 727.0259	0.0019
R(24)	29 444 439.1459	0.0006	R(24)	32 961 124.5225	0.0019
R(26)	29 475 467.0236	0.0007	R(26)	32 994 941.1253	0.0019
R(28)	29 505 679.0229	0.0007	R(28)	33 028 177.9596	0.0019
R(30)	29 535 072.4754	0.0008	R(30)	33 060 836.2743	0.0020
R(32)	29 563 644.5556	0.0009	R(32)	33 092 917.4392	0.0020
R(34)	29 591 392.2792	0.0010	R(34)	33 124 422.9424	0.0021
R(36)	29 618 312.5020	0.0011	R(36)	33 155 354.3872	0.0022
R(38)	29 644 401.9179	0.0013	R(38)	33 185 713.4886	0.0024
R(40)	29 669 657.0573	0.0018	R(40)	33 215 502.0708	0.0027
R(42)	29 694 074.2852	0.0026	R(42)	33 244 722.0630	0.0033
R(44)	29 717 649.7994	0.0040	R(44)	33 273 375.4964	0.0045
R(46)	29 740 379.6282	0.0063	R(46)	33 301 464.5004	0.0066
R(48)	29 762 259.6288	0.0098	R(48)	33 328 991.2984	0.0098
R(50)	29 783 285.4844	0.0150	R(50)	33 355 958.2046	0.0144
R(52)	29 803 452.7028	0.0226	R(52)	33 382 367.6195	0.0209
R(54)	29 822 756.6133	0.0334	R(54)	33 408 222.0260	0.0298
R(56)	29 841 192.3647	0.0484	R(56)	33 433 523.9854	0.0417
R(58)	29 858 754.9227	0.0689	R(58)	33 458 276.1328	0.0573
R(60)	29 875 439.0673	0.0964	R(60)	33 482 481.1732	0.0775
R(62)	29 891 239.3900	0.1330	R(62)	33 506 141.8769	0.1035
R(64)	29 906 150.2915	0.1808	R(64)	33 529 261.0755	0.1366
R(66)	29 920 165.9784	0.2427	R(66)	33 551 841.6572	0.1783
R(68)	29 933 280.4606	0.3221	R(68)	33 573 886.5626	0.2305
R(70)	29 945 487.5486	0.4227	R(70)	33 595 398.7800	0.2953

TABLE VII

Calculated Frequencies for the $00^01-[10^00,02^00]_{I}$ and $00^01-[10^00,02^00]_{II}$ Bands of $^{13}C^{18}O_2$ with Estimated 1σ Uncertainties

	10 μm Band			9 μm Band	
Line	Frequency (MHz)	Uncertainty (MHz)	Line	Frequency (MHz)	Uncertainty (MHz)
P(70)	25 967 863.7013	0.5493	P(70)	28 960 476.2392	0.1999
P(68)	26 033 448.2352	0.4018	P(68)	29 022 326.9655	0.1406
P(66)	26 098 273.8856	0.2889	P(66)	29 083 661.3598	0.0964
P(64)	26 162 346.4614	0.2036	P(64)	29 144 473.5828	0.0641
P(62)	26 225 671.5341	0.1403	P(62)	29 204 757.8781	0.0410
P(60)	26 288 254.4420	0.0941	P(60)	29 264 508.5780	0.0250
P(58)	26 350 100.2945	0.0611	P(58)	29 323 720.1092	0.0143
P(56)	26 411 213.9760	0.0381	P(56)	29 382 386.9991	0.0075
P(54)	26 471 600.1498	0.0227	P(54)	29 440 503.8809	0.0036
P(52)	26 531 263.2619	0.0127	P(52)	29 498 065.4996	0.0019
P(50)	26 590 207.5445	0.0068	P(50)	29 555 066.7171	0.0016
P(48)	26 648 437.0197	0.0037	P(48)	29 611 502.5177	0.0015
P(46)	26 705 955.5028	0.0027	P(46)	29 667 368.0130	0.0015
P(44)	26 762 766.6051	0.0026	P(44)	29 722 658.4473	0.0016
P(42)	26 818 873.7377	0.0026	P(42)	29 777 369.2019	0.0018
P(40)	26 874 280.1140	0.0026	P(40)	29 831 495.8003	0.0020
P(38)	26 928 988.7527	0.0026	P(38)	29 885 033.9121	0.0023
P(36)	26 983 002.4805	0.0026	P(36)	29 937 979.3580	0.0024
P(34)	27 036 323.9347	0.0026	P(34)	29 990 328.1134	0.0025
P(32)	27 088 955.5654	0.0025	P(32)	30 042 076.3126	0.0026
P(30)	27 140 899.6382	0.0024	P(30)	30 093 220.2528	0.0026
P(28)	27 192 158.2361	0.0023	P(28)	30 143 756.3972	0.0026
P(26)	27 242 733.2619	0.0022	P(26)	30 193 681.3787	0.0025
P(24)	27 292 626.4396	0.0021	P(24)	30 242 992.0032	0.0025
P(22)	27 341 839.3166	0.0020	P(22)	30 291 685.2523	0.0024
P(20)	27 390 373.2653	0.0019	P(20)	30 339 758.2865	0.0024
P(18)	27 438 229.4845	0.0018	P(18)	30 387 208.4472	0.0023
P(16)	27 485 409.0010	0.0017	P(16)	30 434 033.2598	0.0022
P(14)	27 531 912.6706	0.0016	P(14)	30 480 230.4352	0.0022
P(12)	27 577 741.1797	0.0015	P(12)	30 525 797.8723	0.0021
P(10)	27 622 895.0456	0.0015	P(10)	30 570 733.6591	0.0021
P(8)	27 667 374.6183	0.0015	P(8)	30 615 036.0749	0.0021
P(6)	27 711 180.0803	0.0016	P(6)	30 658 703.5911	0.0021
P(4)	27 754 311.4481	0.0017	P(4)	30 701 734.8727	0.0022
P(2)	27 796 768.5719	0.0017	P(2)	30 744 128.7785	0.0022
R(0)	27 859 189.3155	0.0018	R(0)	30 806 522.5415	0.0022
R(2)	27 899 959.0889	0.0017	R(2)	30 847 319.2956	0.0022
R(4)	27 940 052.7922	0.0016	R(4)	30 887 476.2168	0.0021
R(6)	27 979 469.5316	0.0015	R(6)	30 926 993.0424	0.0020
R(8)	28 018 208.2480	0.0014	R(8)	30 965 869.7046	0.0020
R(10)	28 056 267.7164	0.0013	R(10)	31 004 106.3298	0.0019
R(12)	28 093 646.5452	0.0012	R(12)	31 041 703.2378	0.0019
R(14)	28 130 343.1761	0.0012	R(14)	31 078 660.9407	0.0019
R(16)	28 166 355.8829	0.0012	R(16)	31 114 980.1418	0.0020
R(18)	28 201 682.7710	0.0012	R(18)	31 150 661.7338	0.0020
R(20)	28 236 321.7761	0.0012	R(20)	31 185 706.7973	0.0021
R(22)	28 270 270.6632	0.0012	R(22)	31 220 116.5989	0.0021
R(24)	28 303 527.0253	0.0012	R(24)	31 253 892.5888	0.0021
R(26)	28 336 088.2820	0.0011	R(26)	31 287 036.3988	0.0021
R(28)	28 367 951.6783	0.0012	R(28)	31 319 549.8393	0.0021
R(30)	28 399 114.2824	0.0012	R(30)	31 351 434.8970	0.0021
R(32)	28 429 572.9843	0.0013	R(32)	31 382 693.7316	0.0021
R(34)	28 459 324.4939	0.0014	R(34)	31 413 328.6726	0.0020
R(36)	28 488 365.3388	0.0014	R(36)	31 443 342.2162	0.0020
R(38)	28 516 691.8623	0.0014	R(38)	31 472 737.0217	0.0019
R(40)	28 544 300.2209	0.0015	R(40)	31 501 515.9072	0.0019
R(42)	28 571 186.3822	0.0016	R(42)	31 529 681.8465	0.0020
R(44)	28 597 346.1222	0.0016	R(44)	31 557 237.9644	0.0021
R(46)	28 622 775.0223	0.0019	R(46)	31 584 187.5326	0.0023
R(48)	28 647 468.4673	0.0035	R(48)	31 610 533.9653	0.0028
R(50)	28 671 421.6417	0.0073	R(50)	31 636 280.8143	0.0043
R(52)	28 694 629.5270	0.0141	R(52)	31 661 431.7647	0.0075
R(54)	28 717 086.8984	0.0251	R(54)	31 685 990.6295	0.0129
R(56)	28 738 788.3217	0.0420	R(56)	31 709 961.3448	0.0214
R(58)	28 759 728.1497	0.0668	R(58)	31 733 347.9645	0.0342
R(60)	28 779 900.5187	0.1023	R(60)	31 756 154.6546	0.0526
R(62)	28 799 299.3446	0.1517	R(62)	31 778 385.6886	0.0785
R(64)	28 817 918.3194	0.2191	R(64)	31 800 045.4408	0.1141
R(66)	28 835 750.9073	0.3096	R(66)	31 821 138.3816	0.1620
R(68)	28 852 790.3403	0.4289	R(68)	31 841 669.0707	0.2255
R(70)	28 869 029.6141	0.5844	R(70)	31 861 642.1520	0.3085

TABLE VIII

Measured Laser Transition Frequency Differences (in MHz) for the $01^{1}1-[11^{1}0,03^{1}0]_{I,II}$ Hot Bands of $^{12}C^{16}O_2$

Transition	Ref.[a]	Beat Freq. (Unc.)	O−C
$01^{1e}1-[11^{1e}0,03^{1e}0]_I$			
P(45)	103*P*(32)	11 704.627(0.010)	0.000
P(43)	103*P*(30)	17 543.393(0.090)	0.096
P(41)	103*P*(26)	-31 205.738(0.010)	-0.002
P(39)	103*P*(24)	-24 961.502(0.120)	-0.115
P(37)	103*P*(22)	-18 810.121(0.120)	-0.121
P(35)	103*P*(20)	-12 751.221(0.050)	0.052
P(33)	103*P*(18)	-6 784.828(0.030)	0.032
P(31)	103*P*(14)	-51 884.087(0.010)	-0.015
P(29)	103*P*(14)	4 872.616(0.020)	0.016
P(27)	103*P*(10)	-39 239.918(0.010)	0.001
P(25)	103*P*(10)	16 165.920(0.010)	-0.011
P(21)	103*P*(6)	27 099.268(0.040)	-0.040
P(19)	10*P*(50)	-91 721.287(0.048)	0.048
P(17)	10*P*(50)	-39 010.514(0.010)	0.000
P(15)	10*P*(50)	13 027.318(0.020)	0.026
P(11)	10*P*(46)	-13 798.149(0.010)	-0.005
P(9)	10*P*(44)	-27 059.254(0.020)	0.017
P(7)	10*P*(44)	22 286.239(0.010)	0.006
R(11)	10*P*(28)	-21 526.996(0.010)	-0.001
R(13)	10*P*(28)	20 708.544(0.010)	-0.004
R(19)	10*P*(22)	-23 963.493(0.010)	-0.006
R(21)	10*P*(22)	15 528.776(0.030)	0.029
R(25)	10*P*(18)	-15 391.419(0.010)	-0.004
R(27)	10*P*(18)	22 024.323(0.010)	0.005
R(33)	10*P*(12)	-26 168.847(0.050)	-0.037
R(39)	10*P*(10)	24 935.613(0.100)	0.110
$01^{1f}1-[11^{1f}0,03^{1f}0]_I$			
P(44)	103*P*(32)	20 938.685(0.140)	0.162
P(42)	103*P*(30)	28 319.066(0.010)	-0.002
P(40)	103*P*(26)	-18 979.942(0.010)	0.000
P(38)	103*P*(24)	-11 376.288(0.110)	-0.117
P(36)	103*P*(20)	-56 685.680(0.030)	-0.042
P(34)	103*P*(18)	-48 858.799(0.040)	0.029
P(32)	103*P*(18)	10 346.562(0.010)	0.002
P(30)	103*P*(14)	-33 744.404(0.010)	-0.011
P(28)	103*P*(14)	23 935.255(0.010)	0.001
P(26)	103*P*(10)	-19 338.710(0.010)	-0.014
P(24)	103*P*(8)	-12 397.930(0.030)	-0.032
P(22)	103*P*(6)	-5 629.855(0.010)	0.008
P(20)	103*P*(6)	49 017.651(0.020)	-0.025
P(18)	10*P*(50)	-69 294.420(0.040)	0.043
P(16)	10*P*(50)	-16 156.058(0.020)	0.018
P(14)	10*P*(48)	-28 600.874(0.010)	0.001
P(12)	10*P*(48)	23 031.156(0.020)	0.022
P(10)	10*P*(46)	9 858.077(0.010)	-0.010
R(8)	10*P*(32)	28 678.021(0.010)	0.000
R(14)	10*P*(26)	-16 452.411(0.010)	-0.002
R(16)	10*P*(26)	24 216.832(0.010)	-0.007
R(24)	10*P*(20)	14 148.103(0.010)	0.011
R(28)	10*P*(16)	-19 369.556(0.040)	-0.034
R(30)	10*P*(16)	15 881.946(0.030)	-0.029
R(36)	10*P*(12)	13 471.042(0.010)	0.006
$01^{1e}1-[11^{1e}0,03^{1e}0]_{II}$			
P(49)	9*P*(42)	20 596.068(0.010)	0.005
P(47)	9*P*(40)	22 306.870(0.020)	-0.026
P(45)	9*P*(38)	24 056.911(0.030)	-0.036
P(43)	9*P*(34)	-34 427.661(0.010)	0.009
P(41)	9*P*(34)	27 680.346(0.010)	-0.012
P(39)	9*P*(30)	-29 217.784(0.010)	0.011
P(37)	9*P*(28)	-26 539.269(0.010)	0.000
P(35)	9*P*(26)	-23 810.546(0.010)	0.002
P(31)	9*P*(22)	-18 199.743(0.030)	-0.024
P(13)	9*P*(4)	9 650.686(0.020)	-0.022
P(11)	9*P*(2)	13 008.096(0.010)	-0.008
P(9)	9*R*(2)	-52 619.071(0.030)	0.033
R(23)	9*R*(36)	13 643.387(0.010)	0.001
R(25)	9*R*(40)	-11 506.892(0.020)	0.018
R(33)	9*R*(44)	70 505.704(0.010)	-0.004
$01^{1f}1-[11^{1f}0,03^{1f}0]_{II}$			
P(48)	9*P*(42)	27 540.722(0.010)	-0.001
P(46)	9*P*(38)	-30 950.072(0.010)	-0.001
P(44)	9*P*(36)	-26 976.931(0.030)	0.034
P(42)	9*P*(34)	-23 026.173(0.010)	0.001
P(40)	9*P*(32)	-19 097.997(0.010)	-0.004
P(38)	9*P*(30)	-15 192.735(0.010)	0.007
P(22)	9*P*(14)	15 175.238(0.060)	-0.054
P(20)	9*P*(12)	18 854.557(0.010)	0.000
P(18)	9*P*(10)	22 505.864(0.020)	-0.003
P(16)	9*P*(6)	-23 293.850(0.010)	0.009
P(14)	9*P*(4)	-18 903.169(0.010)	0.003
P(12)	9*P*(2)	-14 541.198(0.010)	-0.011
P(10)	9*P*(2)	36 816.572(0.020)	-0.023
P(6)	9*R*(2)	20 972.100(0.010)	0.012
R(20)	9*R*(34)	-14 843.677(0.030)	0.036
R(30)	9*R*(44)	10 483.380(0.010)	0.007
R(32)	9*R*(44)	43 866.590(0.010)	-0.012
R(34)	9*R*(44)	76 428.438(0.010)	-0.002

[a] The 9 designation before the reference laser transition indicates that the 9 μm transition of the $^{12}C^{16}O_2$ laser was used, the 103 designation indicates the 10 μm transition of the $^{13}C^{16}O_2$ laser was used, and the 10 designation indicates the 10 μm transition of the $^{12}C^{16}O_2$ laser was used.

changed by more than the uncertainty given by Bradley *et al.* (*9*). As is often the case, the lower-order terms, H_v and D_v, were also affected by the changes in the L_v terms. The addition of the next higher-order term beyond the L_v term gives no improvement in the fit and is not justified.

Since the value of $L(00^01)$ is smaller than three times its uncertainty, by most criteria, it should not be used in the fit. We thought, however, that its inclusion would

TABLE IX

Molecular Constants (in MHz) for the 01^11-$[11^10,03^10]_{I,II}$ Hot-Band Laser Transitions of $^{12}C^{16}O_2$

Molecular Constants	this work	Ref. 19
$B(01^{1e}1)$	11 619.733 802 75(21566)[a]	11 619.728 79(269)
$D(01^{1e}1)\times 10^3$	4.040 499 25(29426)	4.038 345(1925)
$H(01^{1e}1)\times 10^9$	0.370 623(124640)	0.058 4(3147)
$B(01^{1f}1)$	11 637.653 426 68(21559)	11 637.645 55(269)
$D(01^{1f}1)\times 10^3$	4.069 594 36(29446)	4.065 417(1925)
$H(01^{1f}1)\times 10^9$	0.281 145(116342)	0.058 4(3147)
$\nu_0(01^11\text{-}[11^10,03^10]_I)$	27 795 449.875 0(75)	27 795 449.889(46)
$B([11^{1e}0,03^{1e}0]_I)$	11 704.188 968 04(22190)	11 704.184 15(257)
$D([11^{1e}0,03^{1e}0]_I)\times 10^3$	3.772 510 12(30540)	3.770 218(1694)
$H([11^{1e}0,03^{1e}0]_I)\times 10^9$	2.197 670(147081)	1.952 5(2568)
$L([11^{1e}0,03^{1e}0]_I)\times 10^{13}$	0.963 32(23633)	
$B([11^{1f}0,03^{1f}0]_I)$	11 731.899 600 44(21459)	11 731.892 51(257)
$D([11^{1f}0,03^{1f}0]_I)\times 10^3$	3.632 737 73(31056)	3.629 752(1694)
$H([11^{1f}0,03^{1f}0]_I)\times 10^9$	1.382 272(175741)	1.952 5(2568)
$L([11^{1f}0,03^{1f}0]_I)\times 10^{13}$	1.640 31(38987)	
$\nu_0(01^11\text{-}[11^10,03^10]_{II})$	32 124 022.241 1(71)	
$B([11^{1e}0,03^{1e}0]_{II})$	11 714.238 441 98(21651)	
$D([11^{1e}0,03^{1e}0]_{II})\times 10^3$	4.480 426 19(27915)	
$H([11^{1e}0,03^{1e}0]_{II})\times 10^9$	3.135 952(112611)	
$B([11^{1f}0,03^{1f}0]_{II})$	11 742.578 497 25(20681)	
$D([11^{1f}0,03^{1f}0]_{II})\times 10^3$	4.685 890 94(26998)	
$H([11^{1f}0,03^{1f}0]_{II})\times 10^9$	3.004 759(102932)	

[a] The uncertainty in the last digits is given in parentheses.

give a more accurate estimate of the uncertainty in the calculated transitions. Since the L_v term is needed for the lower levels, we decided to use it for all levels. The usual result of including an imperfectly determined higher-order term is to cause the calculation of transitions outside the range of experimental data to be very unreliable. Since absorption measurements beyond $J = 100$ were included in the fit, we believe that this extrapolation problem will not apply to the laser frequency tables given in this paper.

The constants resulting from the present analysis, given in Tables II and III, were used to calculate the frequencies of the laser transitions, given in Tables IV through VII. The relative uncertainties in the frequencies were calculated using the variance–covariance matrix given by the least-squares fit.

The 01^11-$[11^10, 03^10]_I$ and 01^11-$[11^10, 03^10]_{II}$ Bands

Table VIII gives the new frequency measurements of the hot-band laser transitions. As was true for the high-J laser transitions, the measurements consisted of frequency differences between the hot-band transitions and either the $^{12}C^{16}O_2$ or the $^{13}C^{16}O_2$ regular band laser transitions. These measurements were included in the least-squares fit used for the regular laser bands and described above. The *e* and *f* levels of the hot-band transitions were treated as separate states with different values for the rotational and centrifugal distortion constants, but the bandcenters were forced to be the same. The constants resulting from the fit are given in Table IX.

The least-squares fit also included the earlier measurements of frequency differences given by Whitford *et al.* (*18*) and Petersen *et al.* (*19*), along with the un-

TABLE X

Calculated Frequencies for the $01^{1e}1$–$[11^{1e}0,03^{1e}0]_{I}$ and $01^{1e}1$–$[11^{1e}0,03^{1e}0]_{II}$ Hot Bands of $^{12}C^{16}O_2$ with the Estimated 1σ Uncertainties

	10 μm Band			9 μm Band	
Line	Frequency (MHz)	Uncertainty (MHz)	Line	Frequency (MHz)	Uncertainty (MHz)
P(55)	26 257 240.777	0.338	P(55)	30 561 557.592	0.043
P(53)	26 322 208.223	0.202	P(53)	30 627 802.034	0.026
P(51)	26 386 481.428	0.113	P(51)	30 693 368.701	0.015
P(49)	26 450 062.678	0.057	P(49)	30 758 252.771	0.009
P(47)	26 512 954.108	0.025	P(47)	30 822 449.547	0.006
P(45)	26 575 157.711	0.009	P(45)	30 885 954.462	0.006
P(43)	26 636 675.341	0.008	P(43)	30 948 763.083	0.005
P(41)	26 697 508.712	0.009	P(41)	31 010 871.112	0.005
P(39)	26 757 659.408	0.009	P(39)	31 072 274.388	0.005
P(37)	26 817 128.885	0.008	P(37)	31 132 968.894	0.005
P(35)	26 875 918.472	0.007	P(35)	31 192 950.754	0.005
P(33)	26 934 029.375	0.006	P(33)	31 252 216.242	0.006
P(31)	26 991 462.678	0.006	P(31)	31 310 761.778	0.007
P(29)	27 048 219.351	0.005	P(29)	31 368 583.933	0.007
P(27)	27 104 300.243	0.005	P(27)	31 425 679.432	0.008
P(25)	27 159 706.092	0.005	P(25)	31 482 045.155	0.008
P(23)	27 214 437.524	0.005	P(23)	31 537 678.136	0.008
P(21)	27 268 495.051	0.005	P(21)	31 592 575.572	0.007
P(19)	27 321 879.077	0.005	P(19)	31 646 734.817	0.007
P(17)	27 374 589.899	0.005	P(17)	31 700 153.387	0.006
P(15)	27 426 627.704	0.005	P(15)	31 752 828.960	0.006
P(13)	27 477 992.575	0.005	P(13)	31 804 759.380	0.006
P(11)	27 528 684.487	0.005	P(11)	31 855 942.655	0.006
P(9)	27 578 703.312	0.005	P(9)	31 906 376.958	0.006
P(7)	27 628 048.815	0.006	P(7)	31 956 060.631	0.006
P(5)	27 676 720.661	0.006	P(5)	32 004 992.180	0.006
P(3)	27 724 718.408	0.007	P(3)	32 053 170.282	0.007
R(1)	27 841 759.770	0.008	R(1)	32 170 312.039	0.007
R(3)	27 887 393.210	0.007	R(3)	32 215 845.085	0.008
R(5)	27 932 349.294	0.007	R(5)	32 260 620.812	0.008
R(7)	27 967 627.011	0.006	R(7)	32 304 638.826	0.008
R(9)	28 020 225.252	0.006	R(9)	32 347 898.899	0.007
R(11)	28 063 142.803	0.005	R(11)	32 390 400.972	0.007
R(13)	28 105 378.346	0.005	R(13)	32 432 145.151	0.007
R(15)	28 146 930.458	0.005	R(15)	32 473 131.714	0.007
R(17)	28 187 797.612	0.005	R(17)	32 513 361.100	0.007
R(19)	28 227 978.176	0.005	R(19)	32 552 833.915	0.007
R(21)	28 267 470.409	0.005	R(21)	32 591 550.931	0.007
R(23)	28 306 272.467	0.005	R(23)	32 629 513.079	0.007
R(25)	28 344 382.394	0.005	R(25)	32 666 721.456	0.007
R(27)	28 381 798.127	0.006	R(27)	32 703 177.316	0.007
R(29)	28 418 517.490	0.007	R(29)	32 738 882.073	0.007
R(31)	28 454 538.197	0.008	R(31)	32 773 837.297	0.007
R(33)	28 489 857.848	0.011	R(33)	32 808 044.715	0.009
R(35)	28 524 473.924	0.015	R(35)	32 841 506.206	0.014
R(37)	28 558 383.792	0.024	R(37)	32 874 223.800	0.023
R(39)	28 591 584.696	0.037	R(39)	32 906 199.676	0.036
R(41)	28 624 073.760	0.056	R(41)	32 937 436.160	0.055
R(43)	28 655 847.981	0.081	R(43)	32 967 935.723	0.080
R(45)	28 686 904.226	0.115	R(45)	32 997 700.977	0.113
R(47)	28 717 239.232	0.160	R(47)	33 026 734.672	0.156
R(49)	28 746 849.601	0.221	R(49)	33 055 039.695	0.209
R(51)	28 775 731.794	0.304	R(51)	33 082 619.066	0.276
R(53)	28 803 882.126	0.418	R(53)	33 109 475.937	0.359
R(55)	28 831 296.767	0.578	R(55)	33 135 613.583	0.461

certainties given by them. Tables X and XI give the calculated laser transition frequencies and their uncertainties for the hot bands as calculated by using the rovibrational constants and the variance–covariance matrix given by the least-squares fit.

TABLE XI

Calculated Frequencies for the $01^{1f}1–[11^{1f}0,03^{1f}0]_{\mathrm{I}}$ and $01^{1f}1–[11^{1f}0,03^{1f}0]_{\mathrm{II}}$ Hot Bands of $^{12}C^{16}O_2$ with the Estimated 1σ Uncertainties

Line	10 μm Band Frequency (MHz)	Uncertainty (MHz)	Line	9 μm Band Frequency (MHz)	Uncertainty (MHz)
P(56)	26 189 552.806	1.013	P(56)	30 494 732.829	0.064
P(54)	26 257 339.574	0.657	P(54)	30 563 455.632	0.041
P(52)	26 324 329.019	0.410	P(52)	30 631 445.107	0.025
P(50)	26 390 525.205	0.242	P(50)	30 698 694.546	0.014
P(48)	26 455 931.978	0.133	P(48)	30 765 197.431	0.008
P(46)	26 520 552.971	0.066	P(46)	30 830 947.444	0.005
P(44)	26 584 391.607	0.027	P(44)	30 895 938.466	0.005
P(42)	26 647 451.111	0.009	P(42)	30 960 164.579	0.005
P(40)	26 709 734.506	0.007	P(40)	31 023 620.072	0.005
P(38)	26 771 244.624	0.009	P(38)	31 086 299.441	0.005
P(36)	26 831 984.107	0.008	P(36)	31 148 197.394	0.006
P(34)	26 891 955.407	0.006	P(34)	31 209 308.851	0.006
P(32)	26 951 160.794	0.005	P(32)	31 269 628.948	0.007
P(30)	27 009 602.357	0.005	P(30)	31 329 153.039	0.007
P(28)	27 067 282.004	0.005	P(28)	31 387 876.699	0.007
P(26)	27 124 201.466	0.004	P(26)	31 445 795.723	0.007
P(24)	27 180 362.298	0.004	P(24)	31 502 906.132	0.007
P(22)	27 235 765.879	0.004	P(22)	31 559 204.169	0.006
P(20)	27 290 413.418	0.005	P(20)	31 614 686.309	0.006
P(18)	27 344 305.950	0.005	P(18)	31 669 349.251	0.005
P(16)	27 397 444.337	0.005	P(16)	31 723 189.928	0.004
P(14)	27 449 829.274	0.005	P(14)	31 776 205.501	0.004
P(12)	27 501 461.283	0.005	P(12)	31 828 393.364	0.004
P(10)	27 552 340.718	0.005	P(10)	31 879 751.146	0.005
P(8)	27 602 467.765	0.006	P(8)	31 930 276.710	0.005
P(6)	27 651 842.440	0.006	P(6)	31 979 968.150	0.006
P(4)	27 700 464.591	0.007	P(4)	32 028 823.800	0.006
P(2)	27 748 333.899	0.007	P(2)	32 076 842.229	0.007
R(2)	27 864 709.863	0.007	R(2)	32 193 218.194	0.007
R(4)	27 909 939.276	0.007	R(4)	32 238 298.486	0.008
R(6)	27 954 412.330	0.006	R(6)	32 282 538.040	0.008
R(8)	27 998 127.780	0.006	R(8)	32 325 936.725	0.008
R(10)	28 041 084.218	0.005	R(10)	32 368 494.646	0.008
R(12)	28 083 280.062	0.005	R(12)	32 410 212.144	0.008
R(14)	28 124 713.567	0.006	R(14)	32 451 089.794	0.008
R(16)	28 165 382.816	0.006	R(16)	32 491 128.406	0.008
R(18)	28 205 285.722	0.006	R(18)	32 530 329.024	0.008
R(20)	28 244 420.031	0.005	R(20)	32 568 692.921	0.007
R(22)	28 282 783.316	0.006	R(22)	32 606 221.606	0.007
R(24)	28 320 372.981	0.006	R(24)	32 642 916.815	0.007
R(26)	28 357 186.258	0.007	R(26)	32 678 780.515	0.007
R(28)	28 393 220.202	0.008	R(28)	32 713 814.897	0.007
R(30)	28 428 471.699	0.009	R(30)	32 748 022.381	0.006
R(32)	28 462 937.456	0.008	R(32)	32 781 405.610	0.005
R(34)	28 496 614.004	0.007	R(34)	32 813 967.448	0.006
R(36)	28 529 497.693	0.008	R(36)	32 845 710.980	0.011
R(38)	28 561 584.694	0.015	R(38)	32 876 639.511	0.019
R(40)	28 592 870.991	0.029	R(40)	32 906 756.557	0.032
R(42)	28 623 352.384	0.052	R(42)	32 936 065.853	0.050
R(44)	28 653 024.482	0.088	R(44)	32 964 571.341	0.075
R(46)	28 681 882.700	0.144	R(46)	32 992 277.174	0.108
R(48)	28 709 922.257	0.229	R(48)	33 019 187.709	0.151
R(50)	28 737 138.166	0.357	R(50)	33 045 307.507	0.205
R(52)	28 763 525.239	0.546	R(52)	33 070 641.328	0.274
R(54)	28 789 078.071	0.817	R(54)	33 095 194.129	0.359

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