

Heterodyne Frequency Measurements of CO and OCS Beyond 2100 cm⁻¹

A. G. MAKI

Dept. of Chemistry, University of Washington, Seattle, Washington 98195

AND

J. S. WELLS AND D. A. JENNINGS

Time and Frequency Division, National Institute of Standards and Technology, Boulder, Colorado 80303

Infrared heterodyne frequency measurements are given for absorption lines of the 04⁰0-00⁰0 band of OCS and the fundamental band of CO. Transition frequencies of several isotopomers of CO are given. The frequency measurements were based on doubled CO₂ laser radiation used as a local oscillator and as a frequency standard. Tables of wavenumber standards based on both OCS and CO absorption lines are given. © 1990 Academic Press, Inc.

INTRODUCTION

In an earlier paper (1), heterodyne measurements of the frequency difference between a diode laser and a CO laser were used to determine the frequencies of infrared absorption lines in the 2000 cm⁻¹ region. Such measurements were limited to wavenumbers smaller than 2086 cm⁻¹ which was the upper limit of the CO laser transitions. By using doubled CO₂ laser radiation, a technique we first used in 1984 (2), we have now been able to obtain heterodyne frequency measurements for carbon monoxide (CO) and carbonyl sulfide (OCS) absorption lines at wavenumbers up to 2155 cm⁻¹.

The present heterodyne measurements have been combined with earlier frequency measurements reported for OCS and CO to provide improved calibration tables based on the 04⁰0-00⁰0 band of OCS and the CO fundamental band.

EXPERIMENTAL DETAILS

All of the OCS measurements given in this paper and most of the new CO absorption measurements were made by using heterodyne techniques to measure the frequency of a tunable diode laser with respect to doubled CO₂ laser radiation. The tunable diode laser was locked to the absorption maximum of the line to be measured. The experimental setup was more or less the same as described in an earlier paper (2). The frequencies of the doubled CO₂ laser radiation were taken as twice the frequencies given in the tables by Petersen *et al.* (3) and by Bradley *et al.* (4).

As indicated in Table I, some CO lines were measured by means of a CO laser used as a local oscillator. The CO laser frequency was simultaneously determined by mea-

TABLE I

Heterodyne Frequency Measurements Involving the $v = 1$ State of CO

CO Transition $P_{v''}(J'')$	Observed ^a Frequency [MHz]	Calculated Frequency [MHz]	Obs.-Calc. [MHz]
¹² C ¹⁶ O			
$P_0(31)$	60 214 084.9(100)	60 214 077.99	6.91
$P_0(31)^b$	60 214 073.8(50)	60 214 077.99	-4.19
$P_0(18)^b$	62 022 472.1(40)	62 022 472.18	-0.08
$R_0(2)$	64 593 150.8(30)	64 593 152.06	-1.26
$P_1(13)^b$	61 894 667.4(30)	61 894 667.32	0.08
$P_1(12)^b$	62 021 140.6(30)	62 021 138.10	2.50
$P_1(11)^b$	62 146 613.4(30)	62 146 612.34	1.06
$P_1(10)^b$	62 271 086.6(30)	62 271 085.62	0.98
$P_1(9)^b$	62 394 555.0(30)	62 394 553.57	1.43
¹³ C ¹⁶ O			
$P_0(18)^c$	60 708 713.5(40)		
$P_0(7)$	62 046 719.4(100)		
¹² C ¹⁸ O			
$P_0(21)$	60 216 141.4(150)		
$P_0(6)$	62 047 042.9(150)		
¹³ C ¹⁸ O			
$R_0(6)$	61 975 673.9(150)		

- a. The uncertainty in the frequency measurements is given in parentheses.
 b. Measurements reported in Ref. (5).
 c. Measured against the $P_3(10)$ CO laser transition.

asuring the frequency difference between it and combinations of CO₂ laser frequencies generated in a MIM diode, a technique also described by Wells *et al.* (2).

The OCS lines were all measured with an absorption path length of 1.7 m and most of the lines were measured at pressures of 130 Pa (1 Torr) or less. The weakest OCS line, $R(67)$, required a pressure of 270 Pa.

The CO measurements were all made at pressures of 130 Pa or less, with the exception of the $R(6)$ line of ¹³C¹⁸O which was measured at a pressure of about 2 kPa (15 Torr). A multireflection White cell with path lengths up to 20 m was used for some of the measurements.

RESULTS OF THE MEASUREMENTS ON CO

Because of a chance mismatch of the diode lasers available to us and the various doubled CO₂ laser transition frequencies, only one measurement of a new ¹²C¹⁶O transition was possible, $R(2)$. In addition, we report here a new frequency measurement of the $P(31)$ fundamental band transition and new frequency measurements of five transitions of different isotopomers of CO.

In Table I the new frequency measurements are given along with earlier measurements involving the $v = 1$ level of CO given by Schneider *et al.* (5). The large uncertainties associated with most of the present measurements are due to the large widths of the beat frequency signal (~ 100 MHz) and some asymmetry observed in the en-

velope of the beat frequency signal. These measurements were combined with the frequency measurements of the overtone band of CO given by Pollock *et al.* (6) and the rotational transitions given by various workers (7-11). For the present analysis, only transitions for the first three vibrational states of CO were included.

The usual Dunham constants were used in the analysis such that the energy levels are given by

$$E(v, J) = \sum_{i,j} Y_{ij} \left(v + \frac{1}{2} \right)^i [J(J+1)]^j.$$

The higher-order constants were taken from the analysis of Schneider *et al.* (5) since those constants could be most reliably estimated from the potential function determined in that paper (from a more complete set of data). Altogether eight lower-order constants were fitted to the limited set of data for the first three energy levels of CO. The complete set of Dunham constants used in or determined by the least-squares fit is given in Table II. These constants are nearly identical to those given by earlier work.

The constants of Table II were used to calculate new calibration tables for the fundamental band of CO, given in Table III. The uncertainties given in Table III are three times the estimated standard error as calculated from the variance-covariance matrix given by the least-squares fit.

There are not enough frequency measurements for the other isotopomers to provide calibration data for transitions of those species. Nevertheless, it is important to note that the new frequency measurements are consistently lower than the measurements given by Guelachvili and Rao (12). In the case of the measurement of the single line of $^{13}\text{C}^{18}\text{O}$ a significant pressure shift may have produced a measurement that is too low by several MHz. The other measurements were all made at pressures low enough to have negligible pressure shifts according to the measurements made by Pollock *et al.* (6).

TABLE II
Dunham Coefficients (in MHz) for $^{12}\text{C}^{16}\text{O}$

$Y_{10} \times 10^{-8}$	0.650 493 535 7(134) ^a
$Y_{20} \times 10^{-6}$	-0.398 363 104(445)
$Y_{30} \times 10^{-3}$	[0.312 265(406)] ^b
$Y_{40} \times 10^{-1}$	[0.211 33(488)]
$Y_{50} \times 10^2$	[0.005(210)]
$Y_{01} \times 10^{-5}$	0.578 983 450 0(359)
$Y_{11} \times 10^{-3}$	-0.524 762 07(358)
$Y_{21} \times 10^1$	0.161 09(1117)
$Y_{31} \times 10^3$	[0.973 6(790)]
Y_{02}	-0.183 522 70(573)
$Y_{12} \times 10^4$	0.302 76(1005)
$Y_{22} \times 10^5$	[-0.533 2(728)]
$Y_{03} \times 10^6$	0.178 47(296)
$Y_{13} \times 10^8$	[-0.436 1(9)]
$Y_{04} \times 10^{11}$	[-0.108 218(6)]
$Y_{14} \times 10^{13}$	[-0.205 2(14)]
$Y_{05} \times 10^{17}$	[-0.141 3(5)]

a. The uncertainty in the last digits (twice the standard error) is given in parentheses.

b. The constants given in square brackets were taken from Schneider, *et al.* (5).

TABLE III

Calibration Wavenumbers (in cm^{-1}) for the Fundamental Band of $^{12}\text{C}^{16}\text{O}$

P-Branch Wavenumber (unc) ^a	J ^{''}	R-Branch Wavenumber (unc)
----	0	2147.081183(22)
2139.426122(22)	1	2150.856057(22)
2135.546230(22)	2	2154.595632(22)
2131.631625(22)	3	2158.299760(22)
2127.682455(22)	4	2161.968295(21)
2123.698867(22)	5	2165.601090(21)
2119.681007(21)	6	2169.197997(20)
2115.629023(21)	7	2172.758871(20)
2111.543061(20)	8	2176.283565(19)
2107.423269(20)	9	2179.771931(18)
2103.269793(19)	10	2183.223824(18)
2099.082780(18)	11	2186.639097(17)
2094.862377(18)	12	2190.017603(17)
2090.608730(17)	13	2193.359197(16)
2086.321987(17)	14	2196.663731(16)
2082.002294(16)	15	2199.931059(16)
2077.649798(16)	16	2203.161036(16)
2073.264645(16)	17	2206.353514(16)
2068.846981(16)	18	2209.508349(16)
2064.396955(16)	19	2212.625393(17)
2059.914710(17)	20	2215.704502(17)
2055.400395(17)	21	2218.745528(18)
2050.854154(18)	22	2221.748327(19)
2046.276135(19)	23	2224.712752(20)
2041.666483(20)	24	2227.638659(22)
2037.025345(21)	25	2230.525901(23)
2032.352865(22)	26	2233.374333(24)
2027.649190(23)	27	2236.183809(26)
2022.914465(25)	28	2238.954185(28)
2018.148835(26)	29	2241.685315(30)
2013.352447(28)	30	2244.377054(33)
2008.525444(30)	31	2247.029256(36)
2003.667973(33)	32	2249.641778(40)
1998.780177(36)	33	2252.214474(44)
1993.862202(39)	34	2254.747200(49)

a. The uncertainty (three times the estimated standard error) in the last digits is given in parentheses.

RESULTS OF THE MEASUREMENTS ON OCS

The new frequency measurements for the $04^0_0-00^0_0$ band of OCS are given in Table IV. The present measurements were combined with earlier infrared frequency measurements involving the $04^0_0-02^0_0$ and $04^2_0-02^2_0$ transitions (13, 14) and measurements that would also determine the separation of the $02^{0,2}_0$ levels with respect

TABLE IV

Heterodyne Frequency Measurements (in MHz) for the $04^0_0-00^0_0$ Transitions of OCS

Rotational Transition	Observed Frequency ^a	Calculated Frequency	Obs.-Calc.
P(10)	62 982 528.8(100)	62 982 525.7	3.1
P(1)	63 088 982.9(30)	63 088 983.2	-0.3
R(43)	63 704 620.0(40)	63 704 620.9	-0.9
R(67)	64 097 977.6(150)	64 097 966.1	11.5

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

TABLE V

Constants in Wavenumbers (cm^{-1}) Needed to Calculate the Transitions for the 04^00-00^00 Band of OCS

vib. state	E_v^a	B_v	$D_v \times 10^8$	$H_v \times 10^{14}$
00^00	---	0.202 856 740 68(88) ^b	4.340 595(276)	-0.3393(336)
04^00	2104.827 67(9)	0.203 968 086 3(178)	4.306 02(1008)	-32.9(85)
04^20	2099.524 62(26)	0.204 051 914 8(241) ^d	4.495 02(860)	[-0.3] ^c
04^40	[2084.378 37]	0.204 248 031 9(632)	4.592 0(308)	[-0.3]

a. E_v is the separation in wavenumbers of the vibrational state from the ground state.

b. The uncertainty (twice the estimated standard error) in the last digits is given in parentheses.

c. The constants enclosed in square brackets were fixed.

d. The ℓ -type resonance constants for the $4v_2$ state were:

$$q_J = 0.201\ 853(424) \times 10^{-3}$$

$$q_{JJ} = -0.125\ 6(358) \times 10^{-8}$$

TABLE VI

Calibration Wavenumbers (in cm^{-1}) for the 04^00-00^00 Band of OCS

P-Branch Wavenumber(unc) ^a	J"	R-Branch Wavenumber(unc)	P-Branch Wavenumber(unc)	J"	R-Branch Wavenumber(unc)
----	0	2105.23561(14)	2091.02936(13)	38	2122.43144(13)
2104.42196(14)	1	2105.64577(14)	2090.71408(13)	39	2122.93131(13)
2104.01847(14)	2	2106.05815(14)	2090.40149(13)	40	2123.43382(13)
2103.61721(14)	3	2106.47275(14)	2090.09160(13)	41	2123.93899(13)
2103.21817(14)	4	2106.88958(14)	2089.78443(13)	42	2124.44686(13)
2102.82136(14)	5	2107.30863(14)	2089.48002(13)	43	2124.95742(13)
2102.42679(14)	6	2107.72991(14)	2089.17838(13)	44	2125.47072(14)
2102.03445(14)	7	2108.15343(14)	2088.87954(13)	45	2125.98677(14)
2101.64436(14)	8	2108.57918(14)	2088.58352(14)	46	2126.50559(14)
2101.25651(14)	9	2109.00716(14)	2088.29035(14)	47	2127.02720(14)
2100.87092(14)	10	2109.43739(14)	2088.00004(14)	48	2127.55163(14)
2100.48758(14)	11	2109.86987(14)	2087.71263(14)	49	2128.07889(14)
2100.10651(14)	12	2110.30460(14)	2087.42813(14)	50	2128.60901(14)
2099.72771(14)	13	2110.74159(14)	2087.14658(14)	51	2129.14202(14)
2099.35119(14)	14	2111.18085(14)	2086.86798(14)	52	2129.67792(14)
2098.97697(14)	15	2111.62239(14)	2086.59238(14)	53	2130.21675(14)
2098.60503(14)	16	2112.06621(14)	2086.31979(14)	54	2130.75852(14)
2098.23541(14)	17	2112.51232(13)	2086.05023(14)	55	2131.30326(14)
2097.86810(14)	18	2112.96073(13)	2085.78373(14)	56	2131.85098(14)
2097.50312(13)	19	2113.41145(13)	2085.52031(14)	57	2132.40171(14)
2097.14048(13)	20	2113.86449(13)	2085.25999(14)	58	2132.95545(14)
2096.78019(13)	21	2114.31987(13)	2085.00279(14)	59	2133.51224(14)
2096.42227(13)	22	2114.77758(13)	2084.74874(14)	60	2134.07209(15)
2096.06672(13)	23	2115.23766(13)	2084.49786(14)	61	2134.63501(15)
2095.71356(13)	24	2115.70010(13)	2084.25015(15)	62	2135.20103(16)
2095.36281(13)	25	2116.16492(13)	2084.00566(15)	63	2135.77015(16)
2095.01448(13)	26	2116.63214(13)	2083.76439(16)	64	2136.34240(17)
2094.66858(13)	27	2117.10177(13)	2083.52635(16)	65	2136.91778(19)
2094.32513(13)	28	2117.57383(13)	2083.29158(17)	66	2137.49631(20)
2093.98415(13)	29	2118.04833(13)	2083.06007(19)	67	2138.07801(22)
2093.64566(13)	30	2118.52528(13)	2082.83186(20)	68	2138.66287(25)
2093.30966(13)	31	2119.00470(13)	2082.60695(22)	69	2139.25092(28)
2092.97619(13)	32	2119.48662(13)	2082.38535(25)	70	2139.84217(31)
2092.64526(13)	33	2119.97105(13)	2082.16709(28)	71	2140.43661(35)
2092.31688(13)	34	2120.45800(13)	2081.95216(31)	72	2141.03426(40)
2091.99109(13)	35	2120.94749(13)	2081.74058(35)	73	2141.63513(46)
2091.66789(13)	36	2121.43955(13)	2081.53237(40)	74	2142.23921(52)
2091.34731(13)	37	2121.93419(13)	2081.32752(46)	75	2142.84652(59)

a. The uncertainty (three times the estimated standard error) in the last digits is given in parentheses.

to the ground state (13-15). In fact, the new measurements were added to a large data base of measurements on OCS (including microwave measurements) in order to obtain the best estimates of the constants, and their uncertainties, for the $04^0_0-00^0_0$ transitions. Table V gives the constants needed to calculate those transitions and Table VI gives the calculated wavenumbers for the transitions of that band.

In the least-squares fit that gave the constants of Table V, the Hamiltonian included the effects of *l*-type resonance but did not take into account any Fermi (or vibrational) resonance. The matrix elements needed for the *l*-type resonance calculation have been given by Maki *et al.* (16).

As indicated by Fayt and co-workers, (17) there are vibrational potential constants that couple the 04^0_0 levels to the 10^0_0 , 02^0_1 , and 00^0_2 levels (note that we are designating ν_1 as the vibrational state that is 2062 cm^{-1} above the ground state). Since those vibrational couplings have only a very weak rotational dependence, their effect can be accommodated by effective rotational constants that are only slightly different from the unperturbed constants.

ACKNOWLEDGMENT

This work was supported in part by the NASA Upper Atmospheric Research Office.

RECEIVED: July 6, 1990

REFERENCES

1. J. S. WELLS, M. SCHNEIDER, AND A. G. MAKI, *J. Mol. Spectrosc.* **140**, 170-176 (1990).
2. J. S. WELLS, D. A. JENNINGS, AND A. G. MAKI, *J. Mol. Spectrosc.* **107**, 48-61 (1984).
3. F. R. PETERSEN, E. C. BEATY, AND C. R. POLLOCK, *J. Mol. Spectrosc.* **102**, 112-122 (1983).
4. L. C. BRADLEY, K. L. SOOHOO, AND C. FREED, *IEEE J. Quantum Electron.* **QE-22**, 234-267 (1986).
5. M. SCHNEIDER, J. S. WELLS, AND A. G. MAKI, *J. Mol. Spectrosc.* **139**, 432-438 (1990); **141**, 351 (1990).
6. C. R. POLLOCK, F. R. PETERSEN, D. A. JENNINGS, J. S. WELLS, AND A. G. MAKI, *J. Mol. Spectrosc.* **99**, 357-368 (1983).
7. I. G. NOLT, J. V. RADOSTITZ, K. M. EVENSON, D. A. JENNINGS, K. R. LEOPOLD, M. D. VANEK, L. R. ZINK, A. HINZ, AND K. V. CHANCE, *J. Mol. Spectrosc.* **125**, 274-287 (1987).
8. W. GORDY AND M. J. COHEN, *Bull. Amer. Phys. Soc.* **2**, 212 (1957).
9. B. ROSENBLUM, A. H. NETHERCOT, AND C. H. TOWNES, *Phys. Rev. A* **109**, 400-412 (1958).
10. P. HELMINGER, F. C. DELUCIA, AND W. GORDY, *Phys. Rev. Lett.* **25**, 1397-1399 (1970).
11. T. A. DIXON, Ph.D. thesis, University of Wisconsin, 1977.
12. G. GUELACHVILI AND K. NARAHARI RAO, "Handbook of Infrared Standards," Academic Press, San Diego, 1986.
13. J. P. SATTLER, T. L. WORCHESKY, A. G. MAKI, AND W. J. LAFFERTY, *J. Mol. Spectrosc.* **90**, 460-466 (1981).
14. A. FAYT, J. G. LAHAYE, J. LEMAIRE, F. HERLEMONT, AND J. G. BANTEGNIE, *J. Mol. Spectrosc.* **140**, 252-258 (1990).
15. J. S. WELLS, F. R. PETERSEN, AND A. G. MAKI, *Appl. Opt.* **18**, 3567-3573 (1979).
16. A. G. MAKI, WM. B. OLSON, J. S. WELLS, AND M. D. VANEK, *J. Mol. Spectrosc.* **130**, 69-80 (1988).
17. A. FAYT, R. VANDENHAUTE, AND J. G. LAHAYE, *J. Mol. Spectrosc.* **119**, 233-266 (1986).