

HETERODYNE FREQUENCY MEASUREMENTS ON THE 12^00-00^00 BAND OF OCS

A. G. Maki

*Molecular Spectroscopy Division
National Bureau of Standards
Gaithersburg, Maryland 20899*

and

J. S. Wells

*Time and Frequency Division
National Bureau of Standards
Boulder, Colorado 80303*

and

A. Hinz

*Institut Für Angewandte Physik
der Universität Bonn
Wegelerstrasse 8 D-5300
Bonn 1, West Germany*

Received February 9, 1986

Abstract

Heterodyne frequency measurements have been made on the 12^00-00^00 band of carbonyl sulfide in the wavenumber range from 1866 to 1915 cm^{-1} . Frequency measurement techniques reported earlier are used to measure the OCS absorption lines by means of a tunable diode laser, a CO laser local oscillator, and two CO_2 lasers used as secondary frequency standards. A table of calculated absorption frequencies is given for OCS from 1866 to 1919 cm^{-1} .

heterodyne frequency measurements, OCS calibration frequencies, carbonyl sulfide constants

Introduction

We have been making heterodyne frequency measurements on OCS (1) and N₂O (2) in order to provide accurate frequency values for absorption features which can be used for frequency calibration in the infrared. In this paper we report the first direct heterodyne frequency measurements on the 12⁰₀-00⁰₀ band of OCS between 1915 and 1866 cm⁻¹.

Earlier measurements of this band were reported by Maki et al. (3), Butcher et al. (4) and Buckley et al. (5), but those earlier measurements used calibration techniques that were one or two orders of magnitude less accurate than the present measurements. Quite good measurements were reported by Fayt et al. (6) based on grating spectrometer measurements which are not as reliable as frequency measurements.

Sattler et al. (7) reported three heterodyne measurements on the 12⁰₀-10⁰₀ vibrational transition and other less accurate measurements of the 12⁰₀-10⁰₀ and 12⁰₀-02⁰₀ transitions. Sattler's data, in combination with the heterodyne measurements on the 10⁰₀-00⁰₀ and 02⁰₀-00⁰₀ transitions given in refs. (1 and 7) can be used to determine the frequencies of the 12⁰₀-00⁰₀ band transitions, but the uncertainties in the frequencies thus determined are rather large. In this paper we have combined these earlier measurements by Sattler with the present measurements to get a much improved set of frequency values for the entire band.

Experimental Techniques

Heterodyne frequency measurements on OCS with respect to a single CO₂ laser are relatively straightforward, as a HgCdTe detector can easily generate the difference frequency between the tunable diode laser (TDL) and the gas laser (8,9). Since the HgCdTe detector cannot generate harmonics of CO₂ lasers and our attempts to compare a TDL generated frequency with that of a synthesized frequency in a metal-insulator-metal (MIM) diode have yet to be successful, we rely on a transfer oscillator scheme

for measurements at 5 μm , see for example Refs. (1,10). This technique uses both the HgCdTe detector and the MIM diode in two simultaneous measurements. A block diagram of this scheme is shown in Fig. 1. In one measurement, the frequency of a CO laser is measured with respect to a frequency generated from

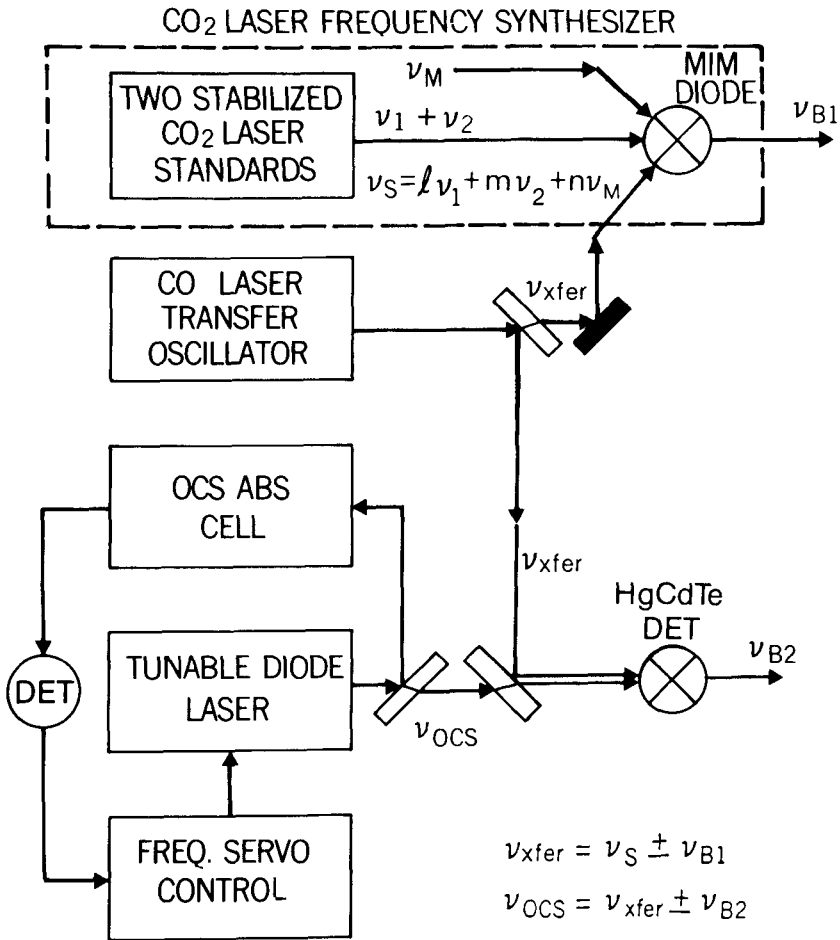


Figure 1. Block diagram of scheme used for OCS frequency measurements described in this paper. The synthesized frequency, ν_S , is given by the equation, where l , m , and n are positive or negative intergers.

CO₂ laser frequency standards. The other measurement consists of a difference frequency determination between the CO laser and a TDL which is locked to the OCS frequency of interest. (The latter measurement is contingent upon a frequency overlap of 10 GHz or less between the OCS feature and the CO laser transition.) The two measurements are algebraically combined to give the measured frequency for the carbonyl sulfide transition.

The basis for the heterodyne measurements are two stabilized CO₂ laser frequency standards which have been stabilized by the Freed-Javan scheme (11) and whose frequencies are known to one part in 10⁹ with respect to the cesium standard (12,13). By irradiating a MIM diode with the output from two such gas lasers and a microwave source, one can synthesize any of the CO laser frequencies; however in practice it is more convenient to synthesize a frequency that is just close, say in the 100 to 1200 MHz range. This practice allows the observation of a beatnote, ν_{B1} , whose value is adjusted to some particular value, and marked by an oscillator at frequency, ν_m . Then various combinations below will synthesize the frequency of any of the CO laser transitions used in these measurements;

$$\nu_{CO} = \nu_{xfer} = \nu_1 + \nu_2 \pm \nu_M(\text{or } 0) \pm \nu_m \quad (1)$$

or

$$\nu_{CO} = \nu_{xfer} = 3\nu_1 - \nu_2 \pm \nu_M(\text{or } 0) \pm \nu_m, \quad (2)$$

where ν_1 and ν_2 are the frequencies of the CO₂ lasers, and ν_M is a microwave frequency. The main utility of the CO laser is as a transfer oscillator. Nevertheless, we tune the CO laser through its lasing bandwidth and measure the center of the corresponding excursion of the beatnote, ν_{B1} , by adjusting the marker frequency, ν_m . This also gives a new value for the CO transition. We estimate that we can determine the CO transition frequency to within ± 3 MHz. Our results for the transitions in Table I are an average of 6.6 MHz lower than the values calculated from the best available constants in the literature. The frequency of the transfer oscilla-

tor, ν_{Xfer} , is known to an estimated ± 0.2 MHz, however, and it is this smaller uncertainty that is carried forward to the next phase of the measurement.

The second part of the measurement was a determination of the difference frequency between the transfer oscillator and the tunable diode laser which was locked to the OCS absorption feature of interest. The measurement consisted of averaging the beatnote ν_{B2} on a spectrum analyzer with storage capability. The center of the beatnote was marked with an oscillator whose frequency was counted. There were two components of uncertainty in this measurement; one was taken to be one tenth the width of the averaged beatnote width. A smaller contribution came from the uncertainty in locking the TDL to the OCS line center with a first derivative lock (offset from zero in a case when background slope was nonzero). We define this part as one half the frequency corresponding to the derivative extrema signal divided by the signal to noise ratio of the derivative signal.

The path length used for these measurements was 1.7 m and typical fill pressures ranged from 30 to 500 Pa (0.25 to 3.7 Torr). The cell was elevated to higher temperatures for some of the high J measurements.

Analysis of the Measurements

The measurements are given in Table I. These measurements were combined in a least-squares analysis with the measurements involving the same upper state vibrational level given by Sattler et al. (7). Since the Sattler measurements were hot band measurements, the appropriate lower state constants were taken from refs. (1 and 7) and used in the least-squares fit. Also used in the fit were the two microwave measurements on the 12^{00} level given by Morino and Matsumura (14).

Table I. Frequency Measurements of the $12^0_0-00^0_0$ Band of OCS with Respect to CO_2 Laser Frequencies via a CO Laser Transfer Oscillator

$^{12}\text{C}^{16}\text{O}$ Laser		OCS Molecule		
Transition	Frequency MHz	Transition	Frequency ^a MHz	Obs-Calc. ^b MHz
P ₉ (11)	55 963 509.4	P(64)	55 965 945.3(40)	-0.8
P ₉ (10)	56 079 579.6	P(54)	56 081 803.3(100)	-0.3
P ₈ (15)	56 250 164.1	P(40)	56 246 523.7(60)	-1.7
P ₇ (20)	56 387 993.7	P(28)	56 389 513.8(60)	-1.3
P ₈ (12)	56 610 485.9	P(10)	56 606 278.8(100)	-5.5
P ₇ (17)	56 766 141.6	R(2)	56 764 171.2(40)	1.3
P ₇ (15)	57 013 382.2	R(22)	57 009 004.1(90)	5.2
P ₆ (20)	57 148 228.4	R(33)	57 144 743.6(60)	-4.2
P ₆ (19)	57 276 295.5	R(43)	57 268 989.4(70)	-1.6
P ₆ (18)	57 403 402.3	R(54)	57 406 810.3(80)	2.0

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

b) The rms deviation was 3.0 MHz.

The least-squares analysis was based on the usual equations, namely:

$$\nu_{\text{obs}} = \nu_0 + F'(J') - F''(J'') \quad (3)$$

and

$$F(J) = B_V J(J+1) - D_V J^2(J+1)^2 + H_V J^3(J+1)^3. \quad (4)$$

The ground state constants were taken from ref. (1). The constants resulting from this fit are given in Table II. The constants are all within two standard deviations of the values given by Sattler et al. The largest change is the band center, which is found to be 8 MHz lower in the present work.

The constants given in Table II were combined with the variance-covariance matrix from the least-squares fit to obtain the calculated transition wavenumbers and their uncertainties as given in Table III.

Table II. Constants for the $12^0_0-00^0_0$ Band of OCS

Constant	Frequency ^a (MHz)
$\nu_0(12^0_0-00^0_0)$	56 727 646.4(22) ^b
B (12^0_0)	6084.3895(46)
D(12^0_0)	$1.07894(298) \times 10^{-3}$
H(12^0_0)	$0.942(510) \times 10^{-9}$
B(00^0_0)	[6081.492117(10)] ^c
D(00^0_0)	[$1.3014398(421) \times 10^{-3}$]
H(00^0_0)	[$-0.07197(684) \times 10^{-9}$]

a) to convert to wavenumbers (cm^{-1}) divide by 29979.2458

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

c) values enclosed in square brackets were taken from Ref. (1).

Acknowledgement

This work was supported in part by the NASA Upper Atmospheric Research Office. We thank our colleague, D. A. Jennings, for the use of his frequency synthesis programs. One of us (A.H.) wishes to thank NBS Time and Frequency Division for the warm hospitality experienced there.

TABLE III. Calculated transition wavenumbers (cm^{-1})^{a)} for the $12^0_0-00^0_0$ band of OCS

R-BRANCH		P-BRANCH	
R(0)	1892.63651(7)		
R(1)	1893.04261(7)	P(1)	1891.82489(7) ^{b)}
R(2)	1893.44890(7)	P(2)	1891.41937(7)
R(3)	1893.85538(7)	P(3)	1891.01405(7)
R(4)	1894.26205(7)	P(4)	1890.60892(7)
R(5)	1894.66892(7)	P(5)	1890.20399(7)
R(6)	1895.07597(7)	P(6)	1889.79926(7)
R(7)	1895.48322(7)	P(7)	1889.39474(7)
R(8)	1895.89065(6)	P(8)	1888.99042(7)
R(9)	1896.29828(6)	P(9)	1888.58630(7)
R(10)	1896.70611(6)	P(10)	1888.18240(6)
R(11)	1897.11412(6)	P(11)	1887.77871(6)
R(12)	1897.52233(6)	P(12)	1887.37523(6)
R(13)	1897.93074(6)	P(13)	1886.97197(6)
R(14)	1898.33934(6)	P(14)	1886.56893(6)
R(15)	1898.74814(5)	P(15)	1886.16611(6)
R(16)	1899.15715(5)	P(16)	1885.76352(6)
R(17)	1899.56635(5)	P(17)	1885.36116(5)
R(18)	1899.97577(5)	P(18)	1884.95904(5)
R(19)	1900.38539(5)	P(19)	1884.55716(5)
R(20)	1900.79521(5)	P(20)	1884.15552(5)
R(21)	1901.20526(5)	P(21)	1883.75413(5)
R(22)	1901.61551(5)	P(22)	1883.35299(5)
R(23)	1902.02599(5)	P(23)	1882.95211(5)
R(24)	1902.43669(5)	P(24)	1882.55149(5)
R(25)	1902.84761(5)	P(25)	1882.15114(5)
R(26)	1903.25877(5)	P(26)	1881.75107(5)
R(27)	1903.67016(5)	P(27)	1881.35127(5)
R(28)	1904.08178(5)	P(28)	1880.95176(5)
R(29)	1904.49364(5)	P(29)	1880.55253(5)
R(30)	1904.90576(5)	P(30)	1880.15361(5)
R(31)	1905.31812(5)	P(31)	1879.75498(5)
R(32)	1905.73073(5)	P(32)	1879.35667(5)
R(33)	1906.14361(5)	P(33)	1878.95867(5)
R(34)	1906.55675(5)	P(34)	1878.56100(5)
R(35)	1906.97016(5)	P(35)	1878.16365(5)
R(36)	1907.38385(5)	P(36)	1877.76664(5)
R(37)	1907.79782(5)	P(37)	1877.36998(5)
R(38)	1908.21208(5)	P(38)	1876.97367(5)
R(39)	1908.62664(5)	P(39)	1876.57772(5)
R(40)	1909.04149(5)	P(40)	1876.18213(5)
R(41)	1909.45665(5)	P(41)	1875.78693(5)
R(42)	1909.87212(5)	P(42)	1875.39211(5)
R(43)	1910.28792(6)	P(43)	1874.99768(5)
R(44)	1910.70404(6)	P(44)	1874.60365(5)
R(45)	1911.12050(6)	P(45)	1874.21004(6)
R(46)	1911.53730(6)	P(46)	1873.81684(6)
R(47)	1911.95445(6)	P(47)	1873.42408(6)
R(48)	1912.37196(7)	P(48)	1873.03176(6)
R(49)	1912.78983(7)	P(49)	1872.63988(6)
R(50)	1913.20808(7)	P(50)	1872.24847(7)
R(51)	1913.62672(7)	P(51)	1871.85752(7)
R(52)	1914.04574(7)	P(52)	1871.46705(7)
R(53)	1914.46517(7)	P(53)	1871.07708(7)
R(54)	1914.88501(7)	P(54)	1870.68761(7)
R(55)	1915.30526(7)	P(55)	1870.29865(7)
R(56)	1915.72595(7)	P(56)	1869.91021(7)
R(57)	1916.14708(7)	P(57)	1869.52231(7)
R(58)	1916.56865(7)	P(58)	1869.13496(7)
R(59)	1916.99069(7)	P(59)	1868.74816(7)
R(60)	1917.41320(7)	P(60)	1868.36194(7)
R(61)	1917.83618(7)	P(61)	1867.97630(7)
R(62)	1918.25966(9)	P(62)	1867.59126(7)
R(63)	1918.68364(10)	P(63)	1867.20683(7)
R(64)	1919.10814(13)	P(64)	1866.82302(9)
R(65)	1919.53316(16)	P(65)	1866.43984(10)

- a) The transition frequencies in MHz may be obtained by multiplying the wavenumbers by 29979.2458.
- b) The estimated uncertainties in the last digits (one standard error) are given in parentheses.

References

1. J. S. Wells, F. R. Petersen, and A. G. Maki, *J. Mol. Spectrosc.* 98, 404-412 (1983).
2. J. S. Wells, D. A. Jennings, A. Hinz, J. S. Murray, and A. G. Maki, *J. Opt. Soc. Am.* 2B, 857-861 (1985).
3. A. G. Maki, E. K. Plyler, and E. D. Tidwell, *J. Res. NBS* 66A, 163-167 (1962).
4. R. J. Butcher, R. B. Dennis, and S. D. Smith, *Proc. Roy. Soc. Lond.* A344, 541-561 (1975).
5. P. G. Buckley, J. H. Carpenter, A. McNeish, J. D. Muse, J. J. Turner, and D. H. Whiffen, *J. Chem. Soc. Faraday Trans II*, 74, 129-135 (1978).
6. A. Fayt, D. Van Lerberghe, J. P. Kupfer, H. Pascher, and H. G. Häfele, *Mol. Phys.* 33, 603-610 (1977).
7. J. P. Sattler, T. L. Worchesky, A. G. Maki, and W. J. Lafferty, *J. Mol. Spectrosc.* 90, 460-466 (1981).
8. J. S. Wells, F. R. Petersen, and A. G. Maki, *Appl. Opt.* 18, 3567-3573 (1979).
9. J. S. Wells, F. R. Petersen, A. G. Maki, and D. J. Sukle, *J. Mol. Spectrosc.* 89, 421-429 (1981).
10. J. S. Wells, D. A. Jennings, and A. G. Maki, *J. Mol. Spectrosc.* 107, 48-61 (1984).
11. C. Freed and A. Javan, *Appl. Phys. Lett.* 17, 53-56 (1970).
12. F. R. Petersen, E. C. Beaty, and C. R. Pollock, *J. Mol. Spectrosc.* 102, 112-122 (1983).
13. K. L. Soohoo, C. Freed, J. E. Thomas, and H. A. Haus, *IEEE J. Quant. Elect.* QE-21, 1159-1171 (1985); Prepublication frequencies by private communication.
14. Y. Morino and C. Matsumura, *Bull. Chem. Soc. Japan*, 40, 1095-1100 (1967).