

Heterodyne Measurements on OCS near 1372 cm^{-1}

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Heterodyne frequency measurements are given for the 01^11-00^00 and 02^01-01^10 bands of OCS between 1363 and 1398 cm^{-1} . These measurements were combined with heterodyne measurements on the 01^11-01^10 and 02^01-00^00 bands to obtain frequencies for the 01^10-00^00 transitions by two independent paths. A table of wavenumbers is given for the ν_2 band of OCS from 488 to 557 cm^{-1} . © 1989 Academic Press, Inc.

Heterodyne frequency measurements have been used to provide accurate wavenumber calibrations in the infrared based on carbonyl sulfide (OCS) absorption features (1, 2). The OCS bending fundamental, ν_2 , near 520 cm^{-1} would be a useful calibration band, but direct frequency measurements in our laboratory are restricted to the region 860 to 1110 cm^{-1} (CO_2 laser coverage) and the region 1220 to 1945 cm^{-1} (CO laser coverage). As an alternative we can use frequency measurement techniques to locate the energy levels involved in the ν_2 transitions. This paper reports heterodyne frequency measurements in the region 1372 cm^{-1} on two bands, 01^11-00^00 and 02^01-01^10 . These measurements were combined with earlier frequency measurements of the 01^11-01^10 and 02^01-00^00 bands² to determine the molecular constants necessary to calculate the ν_2 band, 01^10-00^00 . Fourier transform measurements have already been used to provide wavenumbers for the ν_2 band (4), but heterodyne frequency measurements are less prone to unknown systematic errors.

The present measurements used the same heterodyne measurement techniques described in earlier papers on OCS (5) and N_2O (6). Since the 01^11-00^00 band is quite weak, a multireflection, long-path absorption cell was used for the measurements. A pressure of 1.2 kPa (9 Torr) was used for all measurements, and the path length ranged from 20 to 40 m .

¹ Formerly National Bureau of Standards.

² The vibrational numbering system adopted by the IAU-IUPAP joint commission on spectroscopy (3) is used throughout this paper. Most other authors use a notation that interchanges ν_1 and ν_3 .

TABLE I
Heterodyne Measurements on OCS near 1372 cm⁻¹

Transfer Oscillator	Carbonyl Sulfide		
	CO Trans. Pv" (J")	Trans. ^a	Frequency, ^b MHz
P29(14)	P(20)B	40880607.3(200)	15.7
P29(14)	P(21)A	40885958.5(150)	1.6
P29(13)	P(13)A	40985706.8(150)	-9.5
P29(10)	R(9)A	41265881.6(50)	-0.1
P29(10)	R(11)B	41271214.9(350)	3.9
P29(9)	R(17)A	41360969.2(80)	-2.7
P29(9)	R(19)B	41367444.2(400)	-2.2
P28(15)	R(30)B	41898893.7(100)	-8.8
P28(15)	R(29)A	41501244.6(50)	0.7
P28(13)	R(46)A	41694907.5(50)	1.9
P28(13)	R(47)B	41700480.9(200)	2.6
P28(12)	R(55)A	41794911.1(50)	-0.8
P28(11)	R(64)A	41893079.4(100)	-3.6

^aThe A denotes the 01¹1-00⁰0 band and the B denotes the 02⁰1-01¹0 band.

^bThe estimated uncertainty in the last digits is given in parentheses.

The measured transitions are given in Table I. In most of our previous papers on measurements of this kind, we have also included our measured values for the CO laser transition involved in the transfer oscillator measurement process (5, 6). We are discontinuing this practice since a complete listing of CO laser transitions derived from frequency measurements is now available (7, 8).

In the analysis of the transitions for which $v_2 \leq 1$ the term values were given by

$$T(v, l, J) = G(v, l) + B_v J(J+1) - D_v [J(J+1) - l^2]^2 + H_v [J(J+1) - l^2]^3, \quad (1)$$

TABLE II
Band Centers Determined from Heterodyne Measurements on OCS

Transition	Wavenumber (cm ⁻¹)	Frequency (MHz)
01 ⁰ 0-00 ⁰ 0	520.42207(17) ^a	15601861.1(49)
01 ¹ 1-01 ¹ 0	852.03716(8)	25543431.5(24)
01 ¹ 1-00 ⁰ 0	1372.45923(16)	41145292.6(48)
02 ⁰ 1-01 ¹ 0	1371.80849(19)	41125783.9(56)
02 ⁰ 1-00 ⁰ 0 ^b	1892.23056(10)	56727645.0(29)

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

b) The separation 02⁰1-02²1 = 5.282976 cm⁻¹ was used in the l-type resonance calculation.

TABLE III

 Rovibrational Constants in Wavenumbers (cm^{-1}) Determined for OCS

vib. state	E_v	$D_v \times 10^8$	$H_v \times 10^{15}$
00 ⁰ 0	0.2028567415(10) ^a	4.341064(374)	-2.38(63)
01 ¹ 0	0.2032098316(31)	4.411467(409)	[-2.38]
01 ¹ 1	0.2026570765(437)	4.54206(159)	[-2.38]
02 ⁰ 1	0.2029534877(229)	4.5552(94)	[-2.38] ^b
02 ² 1	0.2030482225(165)	4.6351(95)	[-2.38]
	$q_v \times 10^4$	$q_{vJ} \times 10^{10}$	$q_{vJJ} \times 10^5$
01 ¹ 0	2.12193973(109)	1.4353(116)	0.82(51)
01 ¹ 1	2.284961(903)	2.968(780)	-12.3(114)
02 ⁰ 1	2.2238(110)	2.010(169)	---

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

b) The H_v constants were all set equal to the ground state constant.

and the transition band center was given by

$$\nu_0 = G(v', l') - G(v'', l''). \quad (2)$$

When $l = 1$ the l -type doubling was taken into account by substituting for B_v the expression

$$B_v \pm 0.5[q_v - q_{vJ}J(J+1) + q_{vJJ}J^2(J+1)^2],$$

where the value of q_v is assumed to be positive. For OCS, the positive sign is needed for the f levels and the negative sign is needed for the e levels (that is, the f levels are higher in energy than the e levels).

For those levels for which $v_2 > 1$ there is an l -type resonance that couples (v_1, v_2, v_3, l, J) levels with $(v_1, v_2, v_3, l \pm 2, J)$ levels. This was taken into account by using the treatment described in Ref. (2). There is also a weak Fermi resonance that couples the levels (v_1, v_2, v_3, l, J) and $(v_1, v_2 + 2, v_3 - 1, l, J)$, but it was ignored in this treatment.

The measurements given in Table I were combined in a large least-squares fit with all other heterodyne, microwave, and infrared data pertinent to the analysis of the present heterodyne measurements. In fact, the least-squares fit included all infrared and microwave data on OCS available to us. Only heterodyne frequency measurements were used to determine the band centers given in Table II, but all the data contributed to determining the rotational constants given in Table III. Data that were particularly useful in this analysis were taken from Refs. (1, 2, 4, 5, 9-14).

The constants given by this least-squares fit, and reported in Tables II and III, were used to calculate the transitions for the 01¹0-00⁰0 band reported in Table IV. The variance-covariance matrix given by the least-squares fit was used to determine the uncertainties given in Table IV.

The band center for ν_2 determined by these measurements is slightly lower than the "corrected value" given by Jolma *et al.* (4) but the difference is only 2.4 MHz and is within the uncertainty of our measurements. Our estimate of the band center for the

TABLE IV
Wavenumbers (cm^{-1}) Calculated for the $01\ ^{1}0\text{--}00^0$ Band of OCS

P-Branch	J''	R-Branch	P-Branch	J''	R-Branch
---	0	520.82828(17) ^a	503.43436(17)	43	538.74541(17)
---	1	521.23498(17)	503.05068(17)	44	539.17210(17)
519.61114(17)	2	521.64217(17)	502.66753(17)	45	539.59922(17)
519.20642(17)	3	522.04985(17)	502.28490(17)	46	540.02677(17)
518.80219(17)	4	522.45803(17)	501.90280(17)	47	540.45474(17)
518.39847(17)	5	522.86669(17)	501.52122(17)	48	540.88315(17)
517.99524(17)	6	523.27584(17)	501.14018(17)	49	541.31197(17)
517.59251(17)	7	523.68548(17)	500.75965(17)	50	541.74122(17)
517.19029(17)	8	524.09560(17)	500.37966(17)	51	542.17090(17)
516.78856(17)	9	524.50620(17)	500.00020(17)	52	542.60099(17)
516.38734(17)	10	524.91729(17)	499.62126(17)	53	543.03149(17)
515.98662(17)	11	525.32886(17)	499.24285(17)	54	543.46242(17)
515.58641(17)	12	525.74091(17)	498.86497(17)	55	543.89375(17)
515.18671(17)	13	526.15344(17)	498.48762(17)	56	544.32550(17)
514.78751(17)	14	526.56645(17)	498.11080(17)	57	544.75766(17)
514.38881(17)	15	526.97993(17)	497.73450(17)	58	545.19022(17)
513.99063(17)	16	527.39389(17)	497.35874(17)	59	545.62319(17)
513.59295(17)	17	527.80833(17)	496.98351(17)	60	546.05656(17)
513.19579(17)	18	528.22324(17)	496.60880(17)	61	546.49034(17)
512.79913(17)	19	528.63861(17)	496.23463(17)	62	546.92451(17)
512.40299(17)	20	529.05446(17)	495.86098(17)	63	547.35909(17)
512.00736(17)	21	529.47078(17)	495.48787(17)	64	547.79405(17)
511.61224(17)	22	529.88756(17)	495.11528(17)	65	548.22942(17)
511.21763(17)	23	530.30481(17)	494.74323(17)	66	548.66517(17)
510.82354(17)	24	530.72253(17)	494.37171(17)	67	549.10131(17)
510.42997(17)	25	531.14071(17)	494.00071(17)	68	549.53784(17)
510.03691(17)	26	531.55935(17)	493.63025(17)	69	549.97476(17)
509.64436(17)	27	531.97845(17)	493.26032(17)	70	550.41206(17)
509.25234(17)	28	532.39801(17)	492.89091(17)	71	550.84973(17)
508.86083(17)	29	532.81802(17)	492.52204(17)	72	551.28779(17)
508.46984(17)	30	533.23850(17)	492.15370(17)	73	551.72623(17)
508.07936(17)	31	533.65942(17)	491.78589(17)	74	552.16504(17)
507.68941(17)	32	534.08080(17)	491.41860(17)	75	552.60422(17)
507.29998(17)	33	534.50263(17)	491.05185(17)	76	553.04377(17)
506.91107(17)	34	534.92491(17)	490.68563(17)	77	553.48369(17)
506.52268(17)	35	535.34764(17)	490.31994(17)	78	553.92397(17)
506.13481(17)	36	535.77082(17)	489.95477(17)	79	554.36462(17)
505.74746(17)	37	536.19444(17)	489.59014(17)	80	554.80563(18)
505.36063(17)	38	536.61850(17)	489.22603(17)	81	555.24700(18)
504.97433(17)	39	537.04301(17)	488.86246(18)	82	555.68872(18)
504.58855(17)	40	537.46795(17)	488.49941(18)	83	556.13080(18)
504.20330(17)	41	537.89333(17)	488.13689(18)	84	556.57323(18)
503.81857(17)	42	538.31915(17)	487.77490(18)	85	557.01601(18)

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

$02^0\text{--}01^10$ hot band is slightly higher than that given by Ref. (4) but again agreement is within our uncertainty. The band centers are also in excellent agreement with those given by Fayt *et al.* (15).

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