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Extension of Heterodyne Frequency Measurements on OCS to 87 THz (2900 cm^{-1})

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Heterodyne frequency measurements have been extended to 87 THz by using the CO overtone laser as a transfer oscillator. Measurements were made on the 11^11–01^10 band of OCS at 2900 cm^{-1}. Frequency differences were measured between a tunable diode laser (TDL) which was locked to OCS absorption lines and a stabilized overtone laser which was referenced to stabilized CO_2 lasers. These measurements have been combined with earlier Fourier transform (FT) measurements and a comprehensive set of data from frequency and FT measurements on lower lying transitions in OCS. This permits obtaining accurate values of transition frequencies for calibration of spectra in the 3.4-μm region.

INTRODUCTION

During the last decade a number of infrared heterodyne frequency measurements have been made on OCS at wavenumbers below 2200 cm^{-1} (*1–5*). These measurements have been combined with Fourier transform measurements, other infrared frequency measurements, and microwave measurements in a least-squares fit to produce a reliable set of molecular constants. This has made it possible to calculate transition frequencies for the regions 2550–2600 cm^{-1} (11^10–00^00),[3] 2695–2762 cm^{-1} (02^00–00^00), and 2915–2963 cm^{-1} (04^01–00^00), which are outside the region of the heterodyne frequency measurements (*3, 5*). It would be considerably more difficult to provide additional frequency calibration for the regions up to 3500 cm^{-1} and above unless heterodyne measurements can be made at higher frequencies.

The invention of a broadband CO overtone laser in 1988 (*7*) now enables us to make heterodyne frequency measurements with the transfer oscillator technique, a tunable diode laser (TDL) vs CO overtone laser, between 2500 and 3750 cm^{-1}. This paper presents the first practical demonstration of such heterodyne frequency measurements on OCS. By combining new heterodyne measurements between 2898 and 2913 cm^{-1} with recent FTS measurements, we have determined new values for the molecular constants of the 11^11 state. In addition to providing calibration frequencies

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[3] The vibrational numbering system adopted by the IAU–IUPAP joint commission on spectroscopy (*6*) is used throughout this paper. Some other authors use a notation that interchanges ν_1 and ν_3.

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for the 2900-cm^{-1} region, these measurements also can be used to provide frequencies for the 11^11–00^00 band near 3424 cm^{-1}. That band, however, may be too weak for practical use as a source of calibration.

EXPERIMENTAL DETAILS

The technique and experimental design for this type of measurement was described at the beginning of our program for determining frequency absorption standards in the low-lying vibration–rotational levels of OCS (*1*). It was also described in a recent book on heterodyne frequency measurements for frequency calibration data (*8*). The variation of the scheme for the present experiment is shown in Fig. 1. A TDL is locked on the first derivative of the OCS absorption line of interest. Part of the TDL beam is transferred to a broadband HgCdTe detector to heterodyne it against a local oscillator, which is a stabilized laser whose frequency is measured against a frequency standard by a separate heterodyne measurement. The frequency difference, ν_{B1}, between the local oscillator, ν_{CO}, and the TDL is then either added to or subtracted from the local oscillator frequency to determine the frequency of the OCS transition. We used a USA manufacturer's lead-salt diode laser covering the range 2700 to 2930 cm^{-1} with a typical output power of 0.5 mW. A disadvantage of the apparatus used here was the lack of an appropriate monochromator to provide a single-mode TDL beam. Therefore we carefully matched all possible parameters of the diode laser to achieve single mode or nearly single-mode[4] operation. Despite that effort, we rejected some measurements where the diode laser was running multimode.

The local oscillator was a liquid nitrogen-cooled, flowing-gas, CO-overtone laser similar in design to that described in Ref. (*7*). In order to cover the 2891 to 2913 cm^{-1} region required for these measurements, we operated the laser on the $v = 28 \rightarrow 26$ band, where we obtained a maximum output power of about 20 mW. The laser was stabilized by locking it to the maximum of its gain profile.

The frequency of the overtone laser was determined in a second (nearly simultaneous) heterodyne experiment by the usual technique of using an MIM diode and two CO_2 laser frequency standards. Both CO_2 lasers were stabilized by the Freed–Javan technique (*10*), and in this case extracavity fluorescence cells were used. Even though the overtone laser was locked, it was susceptible to feedback from the MIM diode. This feedback was manifested in the form of a frequency pulling at a low rate (estimated to be about 100 to 200 kHz/sec) starting after the diverting mirror had directed the beam to the MIM diode. It was therefore necessary to make the frequency measurement of ν_{B2} within a few seconds after placing the mirror in the beam. The procedure was to measure the beatnote between the CO overtone laser and the TDL and then immediately measure the frequency of the CO laser. The frequency relations were

$$\nu_{OCS} = \nu_{TDL} = \nu_{CO} \pm \nu_{B1},$$

and

$$\nu_{CO} = 2\nu_1 + \nu_2 \pm \nu_{B2},$$

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[4] We define nearly single mode as that condition where at least 90% of all the power is in one mode. Proper current and temperature values were found with the help of a mode chart (*9*).

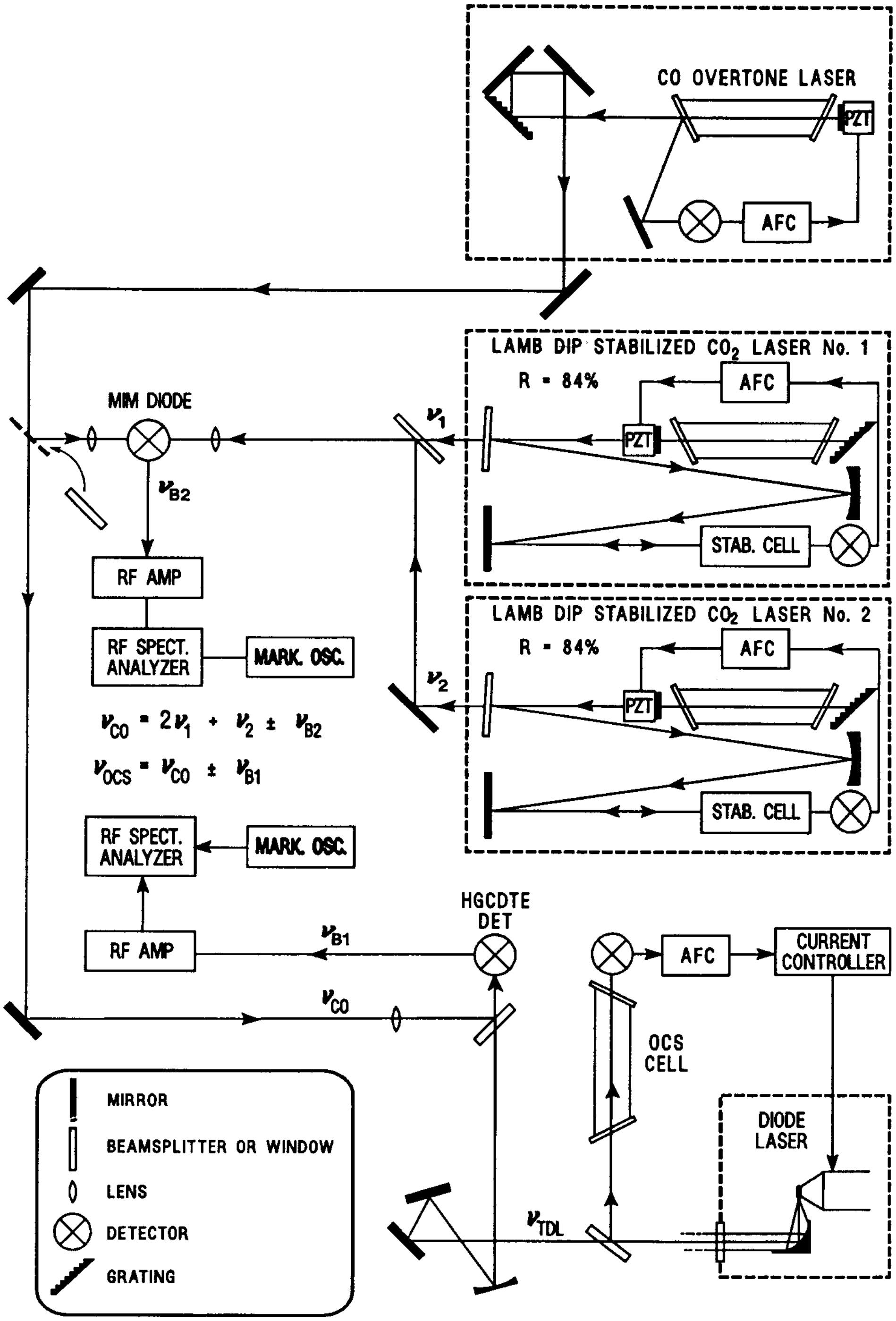

FIG. 1. Block diagram of the experimental setup for measurements at 3.4 μm.

TABLE I

Heterodyne Frequency Measurements of Transitions of OCS near 87 THz (2900 cm^{-1})

OCS transition	CO_2 laser[a] 1 transition	CO_2 laser[a] 2 transition	CO laser[a] $\Delta v=2$ trans.	OCS Freq. (MHz)	obs. - calc. (MHz)
P(12) B,C[b]	$R_I(18)$[c]	$P_I(14)$[c]	$P_{26}(11)$[d]	86 898 356.3(90)[e]	-2.1
P(3) B,C[b]	$R_I(28)$	$P_I(24)$	$P_{26}(10)$	87 014 402.9(50)	-4.2
R(24) B	$R_I(16)$	$R_I(6)$	$P_{26}(7)$	87 322 335.8(50)	0.9
R(24) C	$R_I(16)$	$R_I(6)$	$P_{26}(7)$	87 323 138.4(50)	4.0

[a] The OCS cell and the three lasers were filled with the most abundant isotopic species, i.e. $^{16}O^{12}C^{32}S$, $^{12}C^{16}O$, and $^{12}C^{16}O_2$.

[b] The frequency value here is an average of the two (equally intense) unresolved lines. The $11^{1e}1$-$01^{1e}0$ band is denoted by B, and the $11^{1f}1$-$01^{1f}0$ band by C.

[c] The frequency values for the CO_2 laser transitions were taken from Ref. (11).

[d] Both the CO_2 and CO lasers were modulated synchronously. The modulation depths were chosen to minimize the beatnote line width to about 0.5 MHz. The estimated uncertainty in the CO laser frequency was mainly due to the frequency pulling due to feedback and is estimated to be 0.4 MHz. This is included in the OCS measurement uncertainty.

[e] The estimated uncertainty (2σ) in the last digits is given in parentheses.

where ν_1 and ν_2 were the frequencies of the CO_2 laser frequency standards. The CO_2 frequencies used are those given by Bradley *et al.* (*11*). The CO_2 transitions, beatnote frequencies, and measured OCS frequencies are given in Table I.

For the hot band measurements, a 1-m long absorption cell was used with a nominal pressure of about 100 Pa.

RESULTS AND ANALYSIS

The four measurements given in Table I were combined with other data reported in the literature in a least-squares fit to obtain the constants given in Table II. For this fit, the rovibrational constants were defined in the same way as in an earlier paper on heterodyne measurements (*5*). A great many papers give measurements that determine the rovibrational constants for the lower state. To help determine the constants for the upper state, the Fourier transform measurements given by Hunt *et al.* (*12*) and by Maki *et al.* (*13*) were used in the fit. The earlier measurements were used to

TABLE II

Rovibrational Constants in cm^{-1} for OCS

	11^11	01^10
B_v	0.201 515 95(23)[a,b]	0.203 209 834 8(21)
D_v	$0.475\ 74(105)\times10^{-7}$	$0.441\ 148(31)\times10^{-7}$
H_v	$0.878(125)\times10^{-13}$	$-0.260(38)\times10^{-14}$
q_v	$0.237\ 376(132)\times10^{-3}$	$0.212\ 193\ 868(53)\times10^{-3}$
q_{vJ}	$0.858(31)\times10^{-9}$	$0.142\ 413(102)\times10^{-9}$
q_{vJJ}	0.0	$0.574(44)\times10^{-15}$
$\nu_0(11^11$-$01^10) = 2903.71762(18)$		

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

(b) To convert to MHz, multiply by 29 979.2458.

determine the rotational constants, not the band center. We assumed that the band centers for the earlier measurements were different from the true band center. The present heterodyne measurements were the only data used to determine the band center.

The constants given in Table II can be compared with those given by Fayt *et al.* (*14*). Their constants would give a band center at 2903.71811 ± 0.00016 cm^{-1}. The other constants are in equally good agreement. The present constants are also in very good agreement with the ones given earlier by some of the present authors (*13*).

TABLE III

Calculated Wavenumbers (cm^{-1}) for the Vibrational Transition 11^11–01^10

P-Branch			R-Branch	
e - e	*f - f*	J''	*e - e*	*f - f*
---	---	1	2904.519 79(18)[a]	2904.520 79(18)
2902.901 79(18)	2902.900 99(18)	2	2904.915 76(18)	2904.917 33(18)
2902.488 76(18)	2902.487 64(18)	3	2905.308 30(18)	2905.310 51(18)
2902.072 32(18)	2902.070 92(18)	4	2905.697 44(18)	2905.700 31(18)
2901.652 47(18)	2901.650 85(18)	5	2906.083 15(18)	2906.086 75(18)
2901.229 21(18)	2901.227 42(18)	6	2906.465 44(18)	2906.469 82(18)
2900.802 55(18)	2900.800 63(18)	7	2906.844 30(18)	2906.849 51(18)
2900.372 47(18)	2900.370 49(18)	8	2907.219 75(18)	2907.225 83(18)
2899.938 99(18)	2899.936 98(18)	9	2907.591 77(18)	2907.598 77(18)
2899.502 11(18)	2899.500 13(18)	10	2907.960 36(17)	2907.968 34(17)
2899.061 82(18)	2899.059 91(18)	11	2908.325 52(17)	2908.334 52(17)
2898.618 12(17)	2898.616 34(17)	12	2908.687 25(17)	2908.697 32(17)
2898.171 02(17)	2898.169 41(17)	13	2909.045 55(17)	2909.056 74(17)
2897.720 51(17)	2897.719 13(17)	14	2909.400 41(17)	2909.412 77(17)
2897.266 60(17)	2897.265 49(17)	15	2909.751 83(17)	2909.765 41(17)
2896.809 29(17)	2896.808 50(17)	16	2910.099 81(17)	2910.114 66(17)
2896.348 56(17)	2896.348 15(17)	17	2910.444 35(17)	2910.460 52(17)
2895.884 44(17)	2895.884 44(17)	18	2910.785 45(17)	2910.802 98(17)
2895.416 91(17)	2895.417 38(17)	19	2911.123 10(17)	2911.142 04(17)
2894.945 97(17)	2894.946 95(17)	20	2911.457 30(17)	2911.477 69(17)
2894.471 63(17)	2894.473 17(17)	21	2911.788 05(17)	2911.809 94(17)
2893.993 88(17)	2893.996 03(17)	22	2912.115 35(17)	2912.138 78(17)
2893.512 73(17)	2893.515 53(17)	23	2912.439 19(18)	2912.464 22(18)
2893.028 17(17)	2893.031 67(17)	24	2912.759 56(18)	2912.786 23(18)
2892.540 20(18)	2892.544 45(18)	25	2913.076 48(18)	2913.104 83(18)
2892.048 82(18)	2892.053 87(18)	26	2913.389 93(18)	2913.420 01(18)
2891.554 04(18)	2891.559 92(18)	27	2913.699 91(18)	2913.731 76(18)
2891.055 85(18)	2891.062 60(18)	28	2914.006 43(19)	2914.040 09(19)
2890.554 24(18)	2890.561 93(18)	29	2914.309 46(19)	2914.344 98(19)
2890.049 23(19)	2890.057 88(19)	30	2914.609 02(19)	2914.646 44(19)
2889.540 80(19)	2889.550 46(19)	31	2914.905 10(19)	2914.944 46(19)
2889.028 96(19)	2889.039 68(19)	32	2915.197 70(20)	2915.239 04(20)
2888.513 71(19)	2888.525 52(19)	33	2915.486 81(20)	2915.530 17(20)
2887.995 05(20)	2888.007 99(20)	34	2915.772 44(20)	2915.817 86(20)
2887.472 97(20)	2887.487 09(20)	35	2916.054 57(20)	2916.102 09(20)
2886.947 47(20)	2886.962 81(20)	36	2916.333 20(21)	2916.382 87(21)
2886.418 55(20)	2886.435 15(20)	37	2916.608 33(21)	2916.660 18(21)
2885.886 22(21)	2885.904 12(21)	38	2916.879 97(21)	2916.934 03(21)
2885.350 47(21)	2885.369 70(21)	39	2917.148 09(21)	2917.204 41(21)
2884.811 29(21)	2884.831 90(21)	40	2917.412 71(21)	2917.471 32(21)
2884.268 69(21)	2884.290 71(21)	41	2917.673 82(21)	2917.734 75(21)
2883.722 67(21)	2883.746 14(21)	42	2917.931 41(22)	2917.994 69(22)
2883.173 23(21)	2883.198 17(21)	43	2918.185 48(22)	2918.251 16(22)
2882.620 36(22)	2882.646 82(22)	44	2918.436 03(22)	2918.504 13(22)
2882.064 06(22)	2882.092 07(22)	45	2918.683 05(22)	2918.753 61(22)
2881.504 34(22)	2881.533 93(22)	46	2918.926 54(22)	2918.999 60(22)
2880.941 18(22)	2880.972 39(22)	47	2919.166 50(22)	2919.242 08(22)
2880.374 60(22)	2880.407 46(22)	48	2919.402 92(22)	2919.481 05(22)
2879.804 58(22)	2879.839 12(22)	49	2919.635 81(22)	2919.716 52(22)

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

In Table III the $11^{1}1$–$01^{1}0$ transitions are given for the region from 2880 to 2920 cm^{-1}. Those transitions are almost the same as those given in the calibration book by Maki and Wells (*8*) because a preliminary version of these measurements was used in preparing the tables for that book.

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