CURRENT STATUS OF FREQUENCY CALIBRATION TABLES (0 TO 3000 CM^{-1})

FOR TUNABLE DIODE LASERS FROM HETERODYNE FREQUENCY MEASUREMENTS

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SUMMARY
     The Time and Frequency Division of the National Institute of
Standards and Technology (NIST), Boulder Laboratories, and the
Molecular   Spectroscopy   Division   of   the   NIST Gaithersburg
Laboratories have collaborated over the past few years in an
effort to provide accurate frequency calibration tables. This
involves the use of heterodyne frequency measurements as. well as
the analysis and fitting of the infrared spectra of selected
molecules. Of major interest are the linear triatomic molecules
OCS and N_2O, which together cover a sizeable portion of the 0 to
3000 cm^{-1} region. Some heterodyne frequency measurements can be
made by locking a tunable diode laser (TDL) to an absorption
feature of OCS, for example, and comparing the TDL frequency
directly against a CO_2 laser frequency standard.   However, most
recent measurements have required a transfer oscillator to relate
a frequency synthesized from CO_2 laser standards to the locked TDL
frequency. The transfer oscillator for many of the measurements
was a liquid-nitrogen-cooled CO laser.   The transfer oscillator
techniques and   calibration tables resulting   from the new
frequency measurements on OCS and CS_2 are presented. Current
status of calibration tables is given for an interim OCS atlas, an
N_2O atlas, and several other molecules of interest.

1. INTRODUCTION
     When the tunable diode laser (TDL) first became commercially
available, the advertised resolution for these devices was orders of
magnitude better than the accuracy of available frequency/wavenumber
calibration standards. In response to the consequent need for improved

calibration standards, the Molecular Spectroscopy Division in the NIST Gaithersburg Laboratories and the Time and Frequency Division in the NIST Boulder Laboratories initiated a joint program to provide calibration standards in the infrared region. The Molecular Spectroscopy Division had the requisite expertise for selection of appropriate molecules as well as for the analysis and fitting of the data. The Time and Frequency Division had a wealth of CO_2 laser standards, frequency measuring apparatus, and expertise remaining from frequency measurements involved in a determination of the speed of light.

Several criteria were established for these standards. First, in order to satisfy the largest number of potential users, it was decided that the most desirable types were <u>absorption standards</u>. A further restriction was made to those molecules that were <u>easily handled</u>. Since many TDLs exhibit a mode hop after tuning about 0.5 cm^{-1}, a <u>fiducial point every 0.5 cm^{-1}</u> was selected as a desirable feature. One of the more important aspects was for the molecule to have a <u>simple spectrum (simple Hamiltonian)</u>; for example, it should display a relatively low line density and freedom from fine structure. The final criterion was a requisite number of <u>transition frequencies good to 3 MHz</u>. The last requirement was to be met by calculations based on constants determined in part from heterodyne frequency measurements traceable to CO_2 laser frequency standards.

Due to the limited number of heterodyne measurements possible, it was desirable to have information from supplementary sources such as microwave measurements. In some cases, TDL spectra which had been calibrated relative to bands determined from prior heterodyne measurements were useful. More recently, the TDL spectra have been supplanted by Fourier transform spectra (FTS) which were calibrated from the heterodyne measurements. The data from all of the various sources were weighted in proportion to the inverse square of the measurement uncertainty in the fitting processes.

Two molecules of major interest and utility have emerged over the last few years: carbonyl sulfide (OCS) and nitrous oxide (N_2O). Both molecules have simple expressions for the energy values, typically (when the vibrational angular momentum is zero),

$$F(v,J) = E_v + B_vJ(J+1) - D_vJ^2(J+1)^2 + H_vJ^3(J+1)^3 - L_vJ^4(J+1)^4, \quad (1)$$

and the observed frequency for a particular transition is

$$\nu_{obs} = F(v',J') - F(v'',J''). \quad (2)$$

When the vibrational angular momentum quantum number, $\ell = 1$, the energy values are given by

$$F(v,J) = E_v + B_vJ(J+1) - D_v[J(J+1) -1]^2 + H_v[J(J+1) -1]^3$$
$$\pm 0.5[q_vJ(J+1) -q_{vJ}J^2(J+1)^2 + q_{vJJ}J^3(J+1)^3]. \quad (3)$$

We refer to papers cited in the references for more complicated cases. In most cases, the number of constants to be fitted for OCS and N_2O is comparatively small. We will describe OCS as a more detailed example and mainly list N_2O results in a companion fashion.

2. HETERODYNE MEASUREMENTS VS. A CO_2 LASER (860 TO 1110 CM^{-1})

In order to make heterodyne frequency measurements on a molecular band of interest, one must first determine which absorption features lie within a specified range (5 GHz, for example) of a CO_2 laser transition. Figure 1 indicates some relevant considerations.
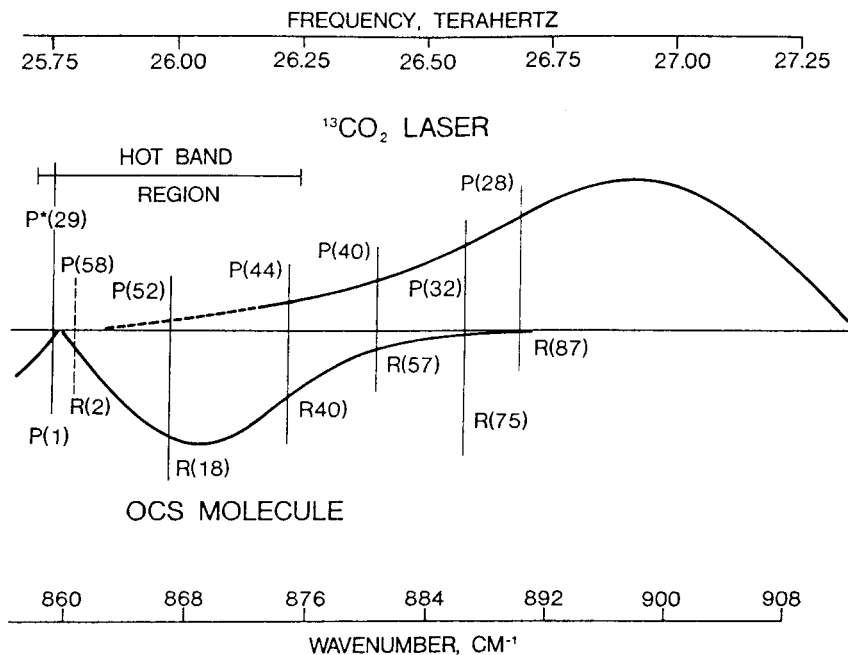

Fig. 1. Sketch of overlap between OCS R-branch and CO_2 laser P-branch.

Above the line is an envelope of the P branch of the $^{13}CO_2$ laser; below is the R branch of the $00^01 - 00^00$ band of OCS. At the very least, it is desirable to measure low-J P and R branch lines to determine the band center, mid-J lines for B-values, and a few high-J lines for centrifugal distortion constants. More generally, we aim for lines separated by about $\Delta J = 10$; however some of these are not accessible due to holes in the TDL coverage. The vertical lines show overlaps for potential measurements, but the P(58) line would not lase. Fortunately, some hot-band transitions (indicated by the horizontal bar) lased, were subsequently measured, and then were used to measure the low -J OCS lines.

The heterodyne frequency measurements made against the CO_2 laser were straightforward. The TDL was locked to the OCS line of interest by a simple first derivative lock. In cases where the TDL mode did not have zero slope background, the lock was compensated to hold the midpoint of the derivative signal. The TDL and CO_2 laser outputs were heterodyned in a HgCdTe detector, and the resulting beatnote was measured by means of a spectrum analyzer and marker oscillator whose frequency was counted. The uncertainty in the measurement was taken as one-half the Doppler width divided by the signal-to-noise ratio of the lock signal plus one-tenth of the beat note linewidth on the spectrum

analyzer. Table I indicates partial results from some measurements on the 00^01 - 00^00, $01^{1e,f}1$ - $01^{1e,f}0$ and 00^02 - 00^01 bands of the most abundant isotope of OCS[1].

Table I. Heterodyne Frequency Measurements on OCS near 860 cm^{-1}.

$^{13}CO_2$ Laser[a] Transition	OCS^b Trans.	Diff. Freq. MHz	OCS Frequency[c] MHz	O. - C. MHz
P(28)	R(87)A	73.0	26674291.6(60)	0.4
P(32)	R(75)A	2773.8	26566226.9(30)	-0.1
P(38)	R(57)A	395.6	26393239.6(20)	-0.1
P(44)	R(40)A	1362.7	26218193.2(30)	0.0
P(52)	R(18)A	1733.6	25975344.4(20)	-1.8
P(25)*	R(7)A	-1668.0	25847177.1(20)	1.5
P(29)	P(1)A	-1277.5	25739018.1(20)	0.8
P(36)	R(84)B	174.0	26450485.5(30)	0.3
P(50)	R(42)B	-628.4	26034711.5(60)	0.2
P(25)*	R(25)B	-707.3	25848137.8(20)	-0.7
P(26)*	R(22)B	-1400.2	25814164.2(20)	1.1
P(50)	R(42)C	820.7	26036160.6(60)	-1.0
P(25)*	R(25)C	-34.5	25848810.6(40)	-0.2
P(26)*	R(22)C	-841.4	25814723.0(40)	-1.9
P(36)	R(86)D	600.4	26450911.4(30)	0.1
P(40)	R(73)D	-439.6	26334336.9(30)	-0.3
P(15)*	R(50)	810.7	26111131.5(40)	1.2
P(19)*	R(40)	85.0	26007511.5(40)	0.0
P(54)	R(31)	-329.0	25910930.4(60)	2.3
P(29)*	R(16)	2772.1	26743067.7(30)	-0.7

[a]Transitions marked by an asterisk are from the 01^11 - $[11^0, 03^10]_I$ hot band. The others are the P_I branch (lower frequency CO_2 band).
[b]In the IAU-UPAP convention used here, A refers to the 00^01 - 00^00 band, B,C correspond to the $01^{1e,f}1$ - $01^{1e,f}0$ bands and D denotes the 00^02 - 00^01 band.
[c]The estimated uncertainty in the last digits is given in parentheses.

Measurements have also been made on other isotopic species of OCS. The natural abundance in un-enriched species is given in Table II. The observation of OCS lines in the TDL spectra (due to some of these isotopes) were not listed in our earliest calibration tables. We later obtained enriched samples for $OC^{34}S$, $O^{13}CS$, and ^{18}OCS and now have made measurements on the 00^01 - 00^00 bands of all six isotopic species listed in Table II as well as some hot bands[2,3]. The energy level diagram shown in Fig. 2 summarizes the measurements in the 860 cm^{-1} region and gives the key to the band notation used in our pending OCS calibration atlas. Not all of the bands shown in the sample page of the atlas (Display I) are defined in Fig. 2. Additional band definitions will be supplied to any interested user requesting portions of the OCS atlas.

Table II. Natural Abundances of Isotopic Carbonyl Sulfide.

Species	Abundance (%)
OCS	93.7
$OC^{34}S$	4.2
$O^{13}CS$	1.1
$OC^{33}S$	0.75
^{18}OCS	0.2
$O^{13}C^{34}S$	0.05

(Note: We are now using the IAU-IUPAP notation in which the ν_1 and ν_3 bands are interchanged relative to the notation used by most workers. Even though we did not use this notation for some of our earlier papers, we adhere to the IAU-IUPAP notation in our current description of that earlier work.)

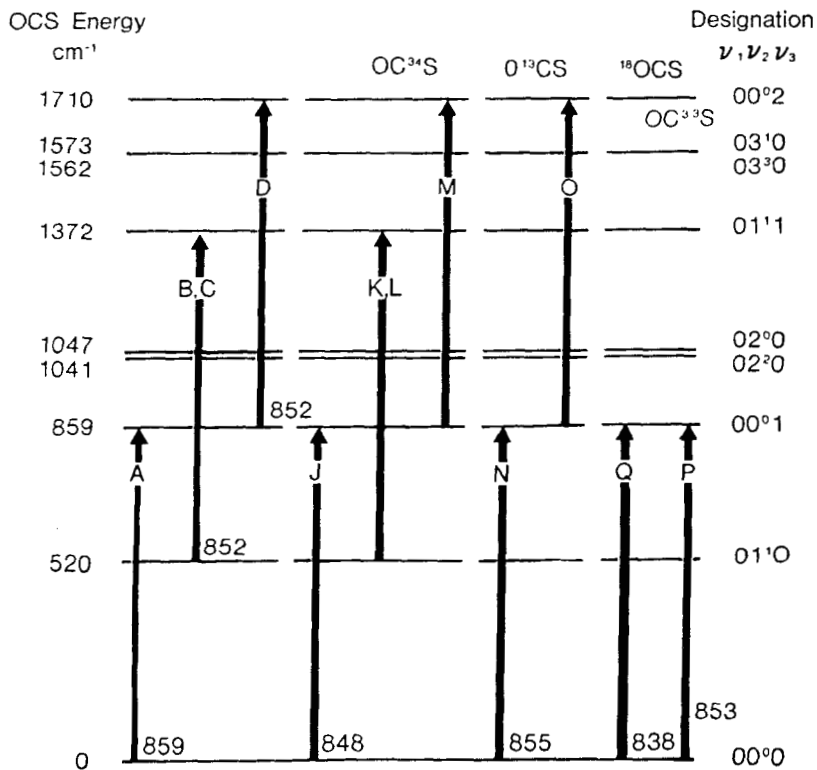## ENERGY LEVELS FOR CARBONYL SULFIDE
(IAU-IUPAP Convention)

Fig. 2. Transitions in calibration tables in the 797-893 cm^{-1} region.

The accuracy and number of measurements for the A band were sufficient to generate a calibration table for the 815 to 892 cm^{-1} region. This table was then used to calibrate about 85 supplementary TDL measurements for the B,C and D hot bands[2]. Display I shows a sample page from a multiband table covering the 797 to 893 cm^{-1} region.

ATLAS OF INFRARED ABSORPTION LINES FOR OCS NEAR THE 860 CM(-1) BAND

1/CM (UNC)	MHZ (UNC)	ROT.	BAND	ENERGY	INT
854.45408(5)S	25615888.9(14)	R(5)	C	526.51	0.491-021
854.56673(18)	25619266.1(54)	R(22)	H	1474.92	0.382-022
854.58610(18)	25619846.7(53)	R(22)	I	1475.04	0.382-022
854.63052(6)	25621178.3(19)	R(35)	K	769.05	0.402-022
854.63773(15)	25621394.6(46)	R(23)	G	1159.35	0.936-022
854.65317(6)	25621857.5(17)	R(46)	Q	411.24	0.132-022
854.66086(4)S	25622088.1(11)	R(17)	J	60.55	0.630-021
854.66406(12)	25622184.0(36)	R(35)	L	769.31	0.402-022
854.73308(17)	25624253.2(52)	R(22)	E	1144.08	0.958-022
854.73405(17)	25624282.2(52)	R(22)	F	1144.09	0.958-022
854.75017(5)S	25624765.5(14)	R(18)	O	923.41	0.510-023
854.76286(6)S	25625145.9(18)	R(36)	M	1110.48	0.157-022
854.79130(8)	25625998.6(24)	R(3)	P	2.40	0.335-022
854.80633(5)S	25626449.0(16)	R(6)	D	867.46	0.224-021
854.84917(5)S	25627733.5(14)	R(6)	B	528.94	0.571-021
854.85306(5)S	25627850.1(14)	R(6)	C	528.95	0.571-021
854.85551(2)S	25627923.3(6)	P(10)	A	22.31	0.976-020
854.87161(3)S	25628406.2(10)	R(0)	N	.00	0.120-022
854.94391(18)	25630573.6(54)	R(23)	H	1484.24	0.381-022
854.96450(18)	25631191.0(53)	R(23)	I	1484.36	0.381-022
854.98053(5)	25631671.5(16)	R(47)	Q	429.11	0.124-022
854.98521(6)	25631811.9(19)	R(36)	K	783.31	0.386-022
855.01810(15)	25632797.9(46)	R(24)	G	1169.12	0.930-022
855.02019(11)	25632860.5(34)	R(36)	L	783.58	0.386-022
855.03405(4)S	25633276.0(11)	R(18)	J	67.68	0.643-021
855.11089(6)S	25635579.5(18)	R(37)	M	1125.07	0.150-022
855.11513(17)	25635706.7(52)	R(23)	E	1153.45	0.956-022
855.11626(17)	25635740.5(52)	R(23)	F	1153.45	0.956-022
855.12872(4)S	25636114.2(13)	R(19)	O	931.07	0.518-023
855.18592(8)	25637829.0(24)	R(4)	P	4.01	0.415-022
855.20093(5)S	25638279.0(15)	R(7)	D	870.29	0.253-021
855.24637(5)S	25639641.2(14)	R(7)	B	531.78	0.647-021
855.25095(5)S	25639778.4(14)	R(7)	C	531.80	0.647-021
855.27206(2)S	25640411.4(6)	P(9)	A	18.26	0.897-020
855.27362(3)S	25640458.1(10)	R(1)	N	.40	0.239-022
855.30674(5)	25641451.1(16)	R(48)	Q	447.36	0.116-022
855.31991(18)	25641845.7(54)	R(24)	H	1493.96	0.379-022
855.33876(6)	25642410.9(19)	R(37)	K	797.96	0.369-022
855.34175(17)	25642500.6(52)	R(24)	I	1494.09	0.379-022
855.37519(11)	25643503.0(32)	R(37)	L	798.25	0.369-022
855.39740(15)	25644169.0(45)	R(25)	G	1179.29	0.921-022
855.40603(3)S	25644427.8(10)	R(19)	J	75.19	0.653-021
855.45766(6)S	25645975.6(18)	R(38)	M	1140.06	0.143-022
855.49610(17)	25647128.0(52)	R(24)	E	1163.21	0.951-022
855.49741(17)	25647167.1(52)	R(24)	F	1163.22	0.951-022
855.50602(4)S	25647425.4(13)	R(20)	O	939.13	0.523-023
855.57935(8)	25649623.5(24)	R(5)	P	6.01	0.494-022
855.59430(5)S	25650071.8(15)	R(8)	D	873.53	0.280-021
855.63181(5)	25651196.4(16)	R(49)	Q	465.99	0.108-022
855.64244(5)S	25651515.0(13)	R(8)	B	535.03	0.719-021
855.64774(5)S	25651673.8(14)	R(8)	C	535.05	0.719-021
855.67442(3)S	25652473.9(10)	R(2)	N	1.21	0.358-022
855.68742(2)S	25652863.4(6)	P(8)	A	14.60	0.812-020

Display I. Page from OCS multiband calibration atlas (855 cm^{-1}).

The table lists the calculated values for the wavenumber and frequency (along with the calculated uncertainties) for each transition. The transitions are designated by the rotational transition and band designation (the more important bands are indicated in Fig. 2). Also given are the intensity and the lower state energy levels to permit the calculation of intensities at temperatures other than 296 K. The intensities have built into them the natural abundance of the isotopes occurring in a normal sample.

The intensity values are not presented as the final word, but are intended to provide relative intensities among the transitions listed. The value listed as A in the equation has units $cm^{-1}/molecules\ cm^{-2}$ to conform to AFGL tapes. The transmission at the absorption peak is given by

$$I = I_o \exp(-KLN_m),$$

where

$$K = [\Pi^{-1}\ln 2]^{1/2} A/b_D.$$

L is path length in cm, N_m is the concentration in molecules per cm^3, and b_D is the Doppler width in cm^{-1}.

The S listed after some of the wavenumber entries indicates transitions that are recommended for possible calibration standards. The spacing and relative intensities of lines in the immediate vicinity are used to identify unambiguously the standard frequencies. In some spectral regions, the OCS patterns are so similar in appearance that it is necessary to use an etalon to identify the line of interest. This provides added motivation to make heterodyne measurements on the hot bands and the isotopic species.

Measurements have also been made on the $2\nu_2$ ($02^00 - 00^00$) OCS band at 1040 cm^{-1} and some hot bands in this same region[4,5]. Our multiband table (available on request) is recommended for the 1008 to 1092 cm^{-1} region. Other direct measurements with a CO_2 laser include the $10^00 - 00^00$ band of N_2O (978 to 1093 cm^{-1})[6] and some high J hot N_2O bands near 1107 cm^{-1}[7].

3. HETERODYNE FREQ. MEASUREMENTS WITH A CO LASER (1220 to 1945 CM^{-1})

The next higher frequency region where we have made measurements was the 1257 to 1340 cm^{-1} region. In this region, we rely on a transfer oscillator technique to relate the N_2O frequencies of interest to the CO_2 laser frequency standards. Each nitrous oxide measurement was a result of two nearly simultaneous measurements. The first measurement was a determination of the frequency of the CO laser relative to CO_2 frequency standards; this could not have been possible without the use of the metal-insulator-metal (MIM) diode. The second was a measurement of the N_2O transition of interest relative to the CO laser frequency. A detailed block diagram of the scheme is shown in Fig. 3.

The CO_2 laser synthesizer consists of two stabilized CO_2 lasers, a phase-locked microwave oscillator and frequency counter, a MIM diode, and rf components (amplifier, spectrum analyzer and synthesizer). First to be outlined is the measurement of the transfer oscillator frequency relative to the standard CO_2 frequencies. By coupling radiation from the two stabilized CO_2 lasers and a microwave oscillator onto the MIM diode, we generated currents in the diode at a synthesized frequency ν_s, given by

$$\nu_s \quad = \quad \ell\nu_1 \quad + \quad m\nu_2 \quad + \quad n\nu_{Mw} \tag{4}$$

where ν_1 and ν_2 were the frequencies of the CO_2 laser standards and ν_{Mw} was a microwave frequency. The quantities ℓ, m, and n are integers which were allowed both positive and negative values. The synthesized ν_s signals generally become weaker as the mixing order, $[1 + |\ell| + |m| + |n|]$, increases. When the radiation from the CO laser, ν_{CO}, was additionally coupled to the MIM diode, a beat note of frequency, ν_{B1}, propagated from the diode, was amplified and then measured on the spectrum analyzer. The measured CO frequency was then

$$\nu_{CO} \quad = \quad \nu_s \quad \pm \quad \nu_{B1} \quad = \quad \nu_{xfer}. \tag{5}$$

The remainder of the measurement was a determination of the frequency difference, ν_{B2}, between the CO laser frequency and the TDL frequency which was locked to the N_2O transition of interest. The molecular transition frequency, ν_{mol}, was then

$$\nu_{mol} \quad = \quad \nu_{xfer} \quad \pm \quad \nu_{B2} \quad = \quad \nu_{NNO}. \tag{6}$$
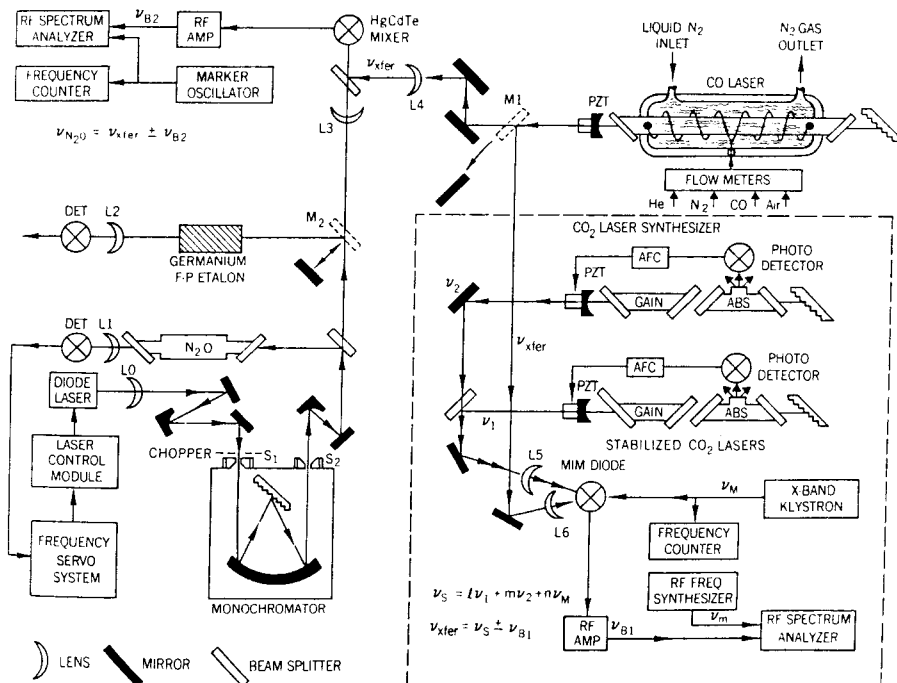
Fig. 3. Diagram of transfer oscillator scheme for CO laser region.

The work in the 1257 to 1340 cm^{-1} region was particularly challenging because it involved operating on the high vibrational levels (v'' ranged from 30 to 34) of a flowing-gas CO laser that was cooled by liquid-nitrogen. For the higher v'' levels, the power levels were so low that it was sometimes difficult to couple usable power to the MIM diode. In spite of this difficulty, 47 N_2O frequency measurements were made in this region[8,9], and a 1600 entry calibration table is available.

In order to indicate the synthesis in some detail, we discuss some measurements of carbon disulfide (CS_2) transitions as an example of the work with the transfer oscillator scheme. Since the region of interest for the CS_2 work was between 1460 and 1550 cm^{-1} the objective of this experiment was to synthesize frequencies in the 43.8 to 46.5 THz region. In an effort to keep the mixing order (more particularly, $[|\ell|+|m|]$) low, we have been constrained to use the highest band of frequencies for the ν_1 laser transition (the R_{II} band of the $^{18}O^{12}C^{18}O$), and the lowest band of frequencies for the ν_2 transitions (the P_I band of $^{16}O^{13}C^{16}O$). While other combinations ($\ell = 4$ and m = -2, for example) will work to synthesize some of the frequencies, a choice of $\ell = 3$ and m = -2 will permit synthesis of most of the frequencies needed without the inconvenience of changing to different CO_2 lasers. The various n values selected were restricted to 0, ± 1, and ± 2, and a single X-band klystron sufficed for the microwave requirements. The difference (between the synthesized frequency and the transfer oscillator frequency) frequency, ν_{B1}, was amplified and then measured with respect to an rf synthesizer. The frequency of the transfer oscillator was then as given by eq. (5) above.

The second part of the procedure was a difference frequency measurement between the CO laser transfer oscillator and a TDL whose frequency was locked to the CS_2 transition of interest. The frequency of the CS_2 transition was then given by eq. (6) where the beat frequency, ν_{B2}, was observed on a microwave spectrum analyzer and measured with a marker oscillator whose frequency was counted. The measurements are given in Table III, which for each carbon disulfide frequency measurement lists the CO_2 laser transitions which oscillate at the frequencies ν_1 and ν_2, the microwave frequency, the two beatnote frequencies, ν_{B1} and ν_{B2}, and the values for the CO and CS_2 frequencies.

A 1.7 m cell was used for the measurements and the pressures were all the order of 10 Pa (0.08 Torr) or less. The carbon disulfide sample was enriched in carbon-13 to provide an equal mixture of both carbon isotopes.

As indicated by the O.- C. (Observed - Calculated) column in Table III, the fit is equal to our best previous work. Two factors permit this result, which is better than some of our other recent work. First, the absorption lines were quite strong and permitted good signal-to-noise ratios for the lock signal. Perhaps even more important was the relatively narrow jitter linewidth of the TDL used for these measurements (compared to TDLs available for much of our work).

The constants derived from this work were used to calculate calibration tables covering the 1460 to 1550 cm^{-1} region[10].

Table III. Heterodyne Frequency Measurements on Carbon Disulfide.

Synthesis Scheme		Transfer Oscillator		Carbon Disulfide		
$\ell \times T(\nu_1)^a + m \times T(\nu_2)^a + n \times \nu_{Hw} +\nu_{B1}$		CO Trans. Pv"(J")	Freq., MHz	Trans. & ν_{B2}	Frequency, MHz	O.- C., MHz
				$^{13}CS_2$		
$3\times^8R_{II}(10) - 2\times^3P_I(10) + 2\times9000$ +725.8		P25(13)	43855934.8 [b]	P(82) +827.9	43856762.7(30) [c]	0.5
$3\times^8R_{II}(16) - 2\times^3P_I(6) - 2\times10500$ +904.4		P25(12)	43957232.4	P(72) -3827.7	43953404.7(30)	-0.1
$3\times^8R_{II}(18) - 2\times^3P_I(12) - 1\times10000$ +966.8		P24(15)	44372051.8	P(22) -3619.8	44375671.6(30)	-2.0
$3\times^8R_{II}(16) - 2\times^3P_I(16) - 0$ +991.8		P24(14)	44476365.2	P(8) -751.6	44475613.6(20)	0.3
$3\times^8R_{II}(16) - 2\times^3P_I(20) - 0$ -746.1		P24(12)	44682033.9	R(24) -2729.7	44679304.2(30)	1.1
$3\times^8R_{II}(20) - 2\times^3P_I(18) - 1\times10000$ -234.5		P24(11)	44783379.9	R(44) -2516.8	44780863.1(30)	1.1
$3\times^8R_{II}(18) - 2\times^3P_I(22) - 1\times12000$ -952.4		P24(10)	44883726.3	R(68) -2917.5	44880808.8(50)	-2.6
$3\times^8R_{II}(20) - 2\times^3P_I(22) - 2\times10000$ -294.1		P24(9)	44983071.0	R(102) -1817.5	44981253.5(30)	0.0
				$^{12}CS_2$		
$3\times^8R_{II}(20) - 2\times^3P_I(22) - 2\times10000$ -294.1		P24(9)	44983071.0	P(116) +3894.3	44986965.3(20)	0.9
$3\times^8R_{II}(22) - 2\times^3P_I(22) - 1\times11500$ -832.7		P23(15)	45095970.6	P(106) +3132.6	45099103.2(50)	2.3
$3\times^8R_{II}(26) - 2\times^3P_I(24) - 1\times10000$ -496.0		P23(12)	45409085.8	P(76) +1282.4	45410368.2(30)	0.1
$3\times^8R_{II}(30) - 2\times^3P_I(28) - 2\times11000$ +563.5		P23(8)	45812635.1	P(30) +1340.7	45813975.8(40)	-2.5
$3\times^8R_{II}(34) - 2\times^3P_I(26) + 1\times12000$ +769.8		P22(14)	45928609.7	P(14) +4723.3	45933333.0(20)	-1.1
$3\times^8R_{II}(30) - 2\times^3P_I(32) - 2\times10500$ -575.5		P22(13)	46034027.1	R(0) +1295.2	46035322.3(30)	0.2
$3\times^3P_I(34) - 1\times^8R_{II}(30) - 2\times9000$ -299.0		P21(16)	46442404.9	R(88) -3407.1	46438997.8(70)	5.2

[a]The left superscript indicates the CO_2 isotope; 8 indicates $^{12}C^{18}O_2$ and 3 is for $^{13}C^{16}O_2$.
[b]We estimate that the CO freq. represents the center of the transition to within 3 MHz. The uncertainty as a transfer oscillator is 0.2 Mhz and is included in the CS_2 uncertainty.
[c]The uncertainty in the last digits is given in parentheses.

The liquid-nitrogen-cooled CO laser was also recently used to measure the $01^11 - 00^00$ and $02^01 - 01^10$ bands of OCS at 1370 cm^{-1}[11], and the $10^00 - 01^10$ band of N_2O at 1635 cm^{-1}[12]. In both instances the bands designated were too weak to be useful for calibration, but were useful for determining bands which were not within our direct measurement capabilities. We will defer discussion of these bands until later.

The $00^02 - 00^00$ band of OCS has been determined by indirect measurements [1], and also by measurements with a sealed-off CO laser which was cooled by a mixture of dry-ice and alcohol [3]. A single band (A band) calibration table covering the 1662 to 1725 cm^{-1} has been published [1], and 45 new measurements in this region have just been completed[13]. One motivation for the new measurements was to improve

the existing calibration table, although the adjustment on the A band is in the 1 MHz range. Most of the measurements are on hot bands and isotopic species and one use will be to upgrade a multiband table in the calibration atlas. The bands involved in the new measurements are shown in Fig. 4, an energy level diagram which indicates the transitions primarily in the 1700 cm^{-1} region.

Earlier measurements that used the sealed-off CO laser included the 01^11 - 00^00 band of N_2O; they provided for a calibration table covering the 1834 to 1918 cm^{-1} region[7]. More recently this system was used to measure the 02^01 -00^00 band of OCS and a single band calibration table covering 1866 to 1919 was published[14]. Subsequently, about 50 isotopic and hot band measurements were made in the same region[15]. These will be used to upgrade a multiband table in the calibration atlas and to provide for tables outside the region described so far.

ENERGY LEVELS FOR CARBONYL SULFIDE
(IAU-IUPAP Convention)

cm^{-1} $\nu_1 \nu_2 \nu_3$

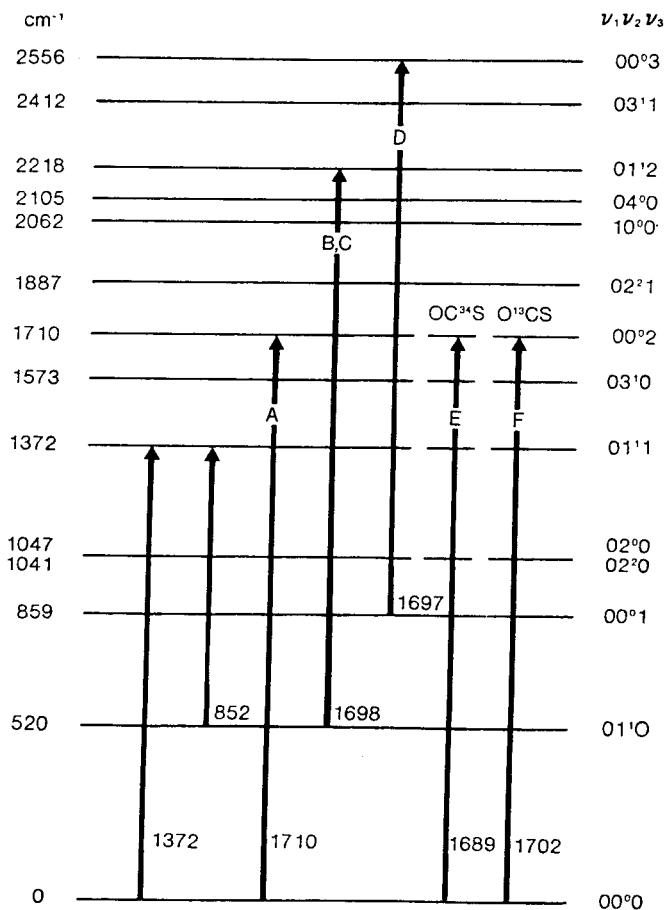| cm^{-1}		$\nu_1\nu_2\nu_3$
2556		00^03
2412	D	03^11
2218		01^12
2105		04^00
2062	B,C	10^00
1887		02^21
	OC^{34}S O^{13}CS	
1710		00^02
1573		03^10
	A E F	
1372		01^11
1047		02^00
1041		02^20
859	1697	00^01
520	852 1698	01^10
	1372 1710 1689 1702	
0		00^00

Fig. 4. Energy levels for OCS transitions in the 1700 cm^{-1} region.

We conclude the directly measured results with a reference to some measurements made with a color center laser whose frequency was synthesized in the same fashion by combining CO_2 harmonics in a MIM diode. Measured were the 00^02 - 00^00, 20^01 - 00^00, and 12^00 - 00^00 bands of N_2O. These results permitted calibration tables covering the regions; 4341 to 4442, 4573 to 4661, and 4670 to 4755 cm^{-1}[16].

4. CALIBRATION TABLES OUTSIDE THE REGION OF HETERODYNE MEASUREMENTS

All of the TDL measurements described here were made in regions where the CO or CO_2 lasers (with the useful isotopic variations) operate. Some measurements were made to provide information which indirectly determined energy levels required for calibration tables. We refer again to the OCS energy level diagram in Fig 4. The measurements of the OCS 01^11 - 00^00 band at 1373 were combined with
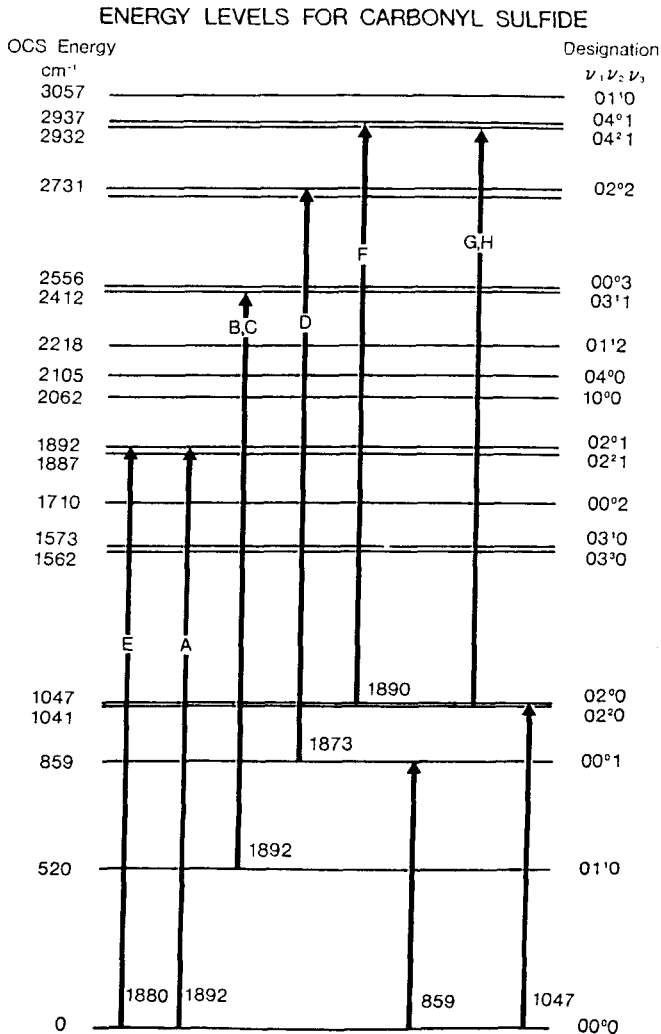
ENERGY LEVELS FOR CARBONYL SULFIDE

Fig. 5. Energy levels for OCS transitions in the 1900 cm^{-1} region.

some hot band measurements of the $01^11 - 01^10$ band at 860 cm^{-1} to provide constants for the 01^10 level at 520 cm^{-1} and a subsequent calibration table covering the 480 to 550 cm^{-1} region. With the constants for the 01^10 level established, B and C hot band measurements at 1700 cm^{-1} permit constants to be determined for the 01^12 level and a calibration band to be calculated for the 2218 cm^{-1} region. The D hot band at 1700 cm^{-1} can be combined with the measured value of the 00^01 level at 859 cm^{-1} to yield constants for the 00^03 level and a subsequent table for the 2556 region.

Similar results are obtained from the 1890 cm^{-1} hot bands shown in OCS energy level diagram in Fig. 5. (The E band refers to the $OC^{34}S$ isotope.) The energy levels at 859 and 1047 cm^{-1} were determined from direct CO_2 laser measurements. With these starting energies determined, the 1873 cm^{-1} D hot band measurements determine the 02^02 level at 2731 cm^{-1}, and the 1890 cm^{-1} F band measurements determine the 04^01 level at 2937 cm^{-1}. Single band tables covering the 2695 to 2762 and 2915 to 2963 cm^{-1} are now available[15].

The same general approach was applied to N_2O. We do not cover the results in detail, but we indicate the measured bands all together in the N_2O energy level diagram (Fig. 6) shown below.

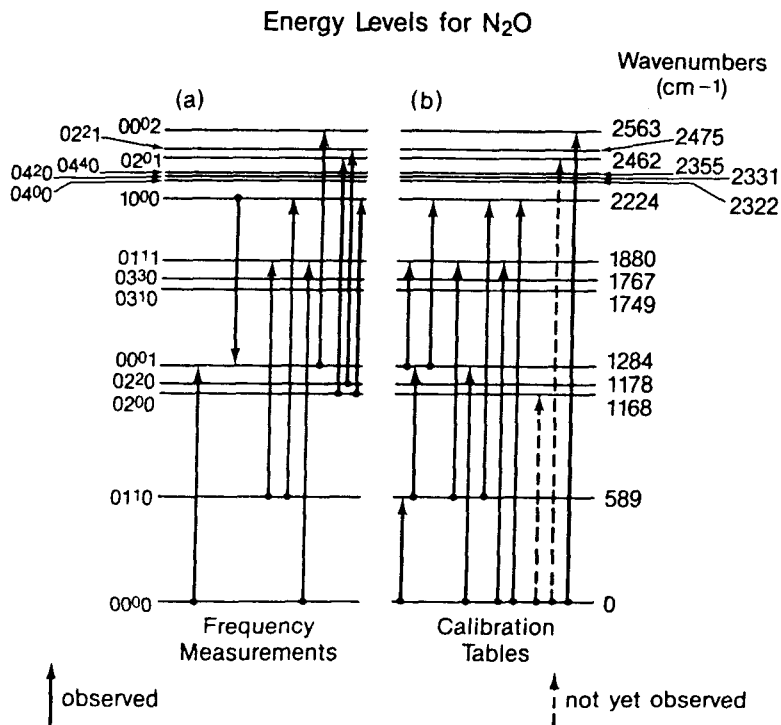## Energy Levels for N$_2$O

Fig. 6. Energy levels and measured transitions for nitrous oxide.

Figure 7 gives a quick indication of the wavenumber regions covered. A summary of availability (Table IV) indicates the extent of calibration standards and points out where coverage for a specific

region may be found. The OCS atlas is not completed at this time, but portions are available from either Maki or Wells on request for specific regions.

Additional work has been done on a few other molecules to fill in some gaps and provide alternate molecules in a few instances. Included in this category are deuterium bromide[17] and nitric oxide[18].

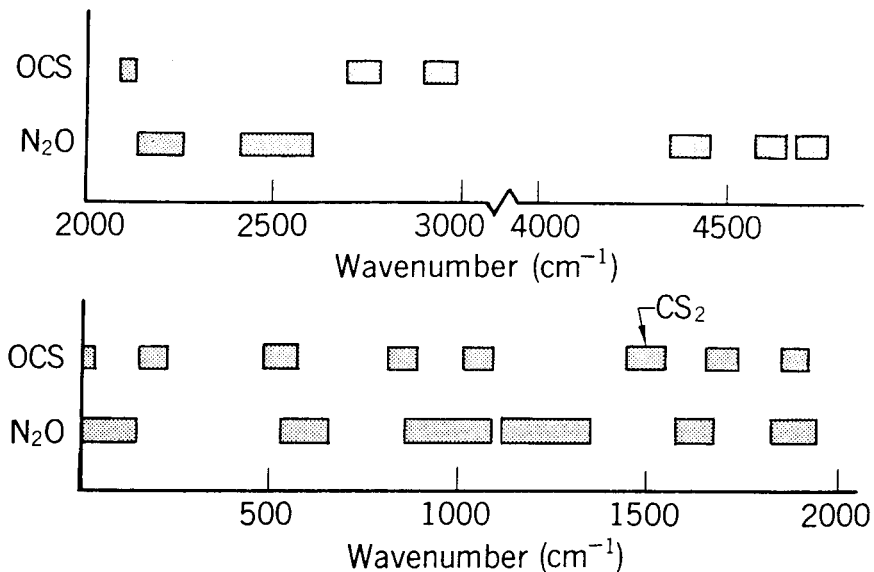## Calibration Standards Available from Frequency Measurements

Fig. 7. Coverage afforded by carbonyl sulfide and nitrous oxide.

6. AVAILABILITY SUMMARY

Table IV. Summary of Bands Available for Calibration.

Wavenumber Region	Molecule	Band	Availability
1 to 207 cm^{-1}	DBr	(rotational)	Ref. [17]
488 to 557	OCS	01^10-00^00	Ref. [11]
520 to 660	N_2O	01^10-00^00	Ref. [12]
797 to 893	OCS	multiband	on request[a]
815 to 892	OCS	00^01-00^00	Ref. [1]
978 to 1093	N_2O	10^00-02^00	Ref. [6]
1008 to 1092	OCS	multiband	on request
1105 to 1238	N_2O	02^00-00^00	Ref. [6]
1207 to 1340	N_2O	00^01-00^00	Ref. [8]
1460 to 1550	$^{13}CS_2,CS_2$	$00^01-0\ 0^00$	Ref. [10]
1594 to 1992[b]	DBr	1-0	Ref. [17]
1649 to 1738	OCS	multiband	on request
1661 to 1738	OCS	00^02-00^00	Ref. [1]
1816 to 1930	N_2O	01^11-00^00	Ref. [8]
1834 to 1918	N_2O	01^11-00^00	Ref. [7]
1845 to 1921	OCS	multiband	on request
1864 to 1920	OCS	03^11-01^10	Ref. [15]
1866 to 1919	OCS	02^01-00^00	Ref. [14]
2013 to 2139[c]	OCS	multiband	on request
2135 to 2268[c]	N_2O	10^00-00^00	Ref. [8]
2409 to 2508	N_2O	02^01-00^00	Ref. [6]
2490 to 2605	N_2O	00^02-00^00	Ref. [9]
2695 to 2762	OCS	02^02-00^00	Ref. [15]
2915 to 2963	OCS	04^01-00^00	Ref. [15]
4341 to 4442	N_2O	20^00-00^00	Ref. [16]
4573 to 4661	N_2O	12^01-00^00	Ref. [16]
4670 to 4755	N_2O	10^02-00^00	Ref. [16]

[a]Available from either A. G. Maki of the Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland 80899 or J. S. Wells, Time and Frequency Division, National Institute of Standards and Technology, Boulder, Colorado 80303.

[b]The spectrum consists of closely spaced pairs (0.5 cm^{-1}) of lines repeated every 11 acm^{-1}.

[c]These bands are not based on heterodyne frequency measurements at this time. We hope to make measurements in the 2000 t0 2300 cm^{-1} region during the coming year.

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