

Sub-Doppler Frequency Measurements on OCS near 1689 and 1885 cm^{-1}

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We have used an optical polarization heterodyne technique to measure the frequencies of two OCS lines, one near 5.3 μm and the other near 5.9 μm . These sub-Doppler measurements gave 56 533 766.125 \pm 0.035 MHz for the $2\nu_2 + \nu_3$ $P(16)$ transition and 50 627 632.013 \pm 0.100 MHz for the $2\nu_3$ $P(48)$ line. The $P(16)$ measurement is in excellent agreement (20 kHz) with a new result obtained with an alternate technique by a group at the University of Bonn. The $2\nu_3$ measurement was combined with other frequency measurements to produce an improved calibration table for the $2\nu_3$ OCS band near 1700 cm^{-1} . These and other sub-Doppler frequency measurements in different spectral regions give improved frequencies for a number of OCS bands. These new frequencies will soon be incorporated into calibration data that will be available over the Internet.

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INTRODUCTION

The first phase of a joint NBS/NASA program (which began in 1979 (1)) to generate infrared frequency standards for the users of tunable lasers culminated in 1991 with the publication of a calibration atlas, NIST SP 821 (2). Although other new atlases (with some complementarity in frequency coverage) have recently been published (3, 4), the NIST atlas is the only one in the mid-infrared based primarily on infrared frequency measurements. The NIST atlas has a spectral map/facing table format, and the facing table information is also available in the form of computer diskettes in NIST Reference Data Base 39 (5). About four times as many other frequencies (of transitions too weak and numerous to be included in the atlas proper) are included in the diskettes. A text (6), intended as a companion to Data Base 39, contains references and other relevant information that also appears in the atlas. The frequency measurements used for the generation of tables in this atlas were based primarily on Doppler-limited spectra. The frequency measurements were based on CO_2 lasers used as frequency standards.

Phase two of this on-going effort features three new developments, an ever increasing number of sub-Doppler frequency measurements, a revision of CO_2 laser frequencies, and the dissemination of the atlas material on the new information superhighway.

Sub-Doppler frequency measurements on OCS include contributions in the 9- μm region by Fayt *et al.* (7). More recently Urban's group at the Institut für Angewandte Physik in Bonn have extended their CO frequency measurement techniques at 5 μm (8) to include OCS (9). The first NIST sub-Doppler measurements on OCS were made at 3.3 μm (10). The initial measurements at 5 and 3.3 μm relied on accidental coincidences between OCS and CO laser lines (both $\Delta v = 1$ and $\Delta v = 2$ transitions)

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or on coincidences that were possible after shifting the CO frequency with an acousto-optic modulator (AOM).

The number of such accidental coincidences is rather small and the revolutionary development of a new frequency measurement system featuring tunable sidebands on a CO laser at the Institut für Angewandte Physik (Bonn) eliminates the need for coincidences. Many high quality new measurements are pending publication (11, 12) and others are being planned.

The precision of these sub-Doppler frequency measurements is quite high (uncertainties down to tens of kilohertz), and a new set of more accurate CO₂ transition frequencies makes possible absolute frequency measurements with accuracies commensurate with this precision. This new set of CO₂ laser frequencies was determined by a refit of all the frequency measurements for CO₂ and its isotopomers by Maki *et al.* (13). It is based on the most accurate frequency measurements currently available. These new CO₂ frequency values have been used in the sub-Doppler OCS frequency measurements on OCS. While the new OCS results are within the uncertainties of the frequencies listed in SP 821, they represent improved frequency values with much smaller uncertainties.

The results of new measurements are continually being added to the data bases used to calculate frequencies of transitions in the atlas, and the development of the information superhighway will permit the dissemination of the newly calculated frequencies to everyone in a more timely fashion. This first update of the calibration atlas will be available in 1995 on the Internet.

In the following, we describe two new sub-Doppler frequency measurements of OCS absorption lines, one at 5.3 μm the other at 5.9 μm .

EXPERIMENTAL DETAILS

These 5–6 μm experiments were an extension of experiments at 3.3 μm (10). Again, we have used the optical heterodyne polarization technique invented by Wieman and Hänsch (14). The essence of this technique is that a strong pump/saturation beam introduces anisotropy in a sample; that is, the sample becomes dichroic and birefringent when the pump beam frequency is near a molecular resonance. A counterpropagating probe beam will undergo a change in polarization orientation as the laser frequency approaches the vicinity of a molecular resonance. Under appropriate conditions one can detect the orientation changes in polarization and use the resulting dispersion signal as a discriminant for locking a laser frequency to the absorption frequency of a molecule of interest. One can divide a laser beam into several portions and use them for saturation and probing of a sample, and have a third portion for frequency measurement.

The basic scheme for the 5.3- μm experiment is shown in Fig. 1. The starting point is a liquid-nitrogen-cooled, flowing-gas CO laser which has been converted from 3.3 μm ($\Delta v = 2$) operation to $\Delta v = 1$ operation by substituting a 240 line/mm grating and appropriate coupler for those used earlier. About 400 mW were available from the $P_9(6)$ transition, and polarization purity of the output beam was about 2000:1 as it left the laser. The beam from the CO laser was directed to an uncoated ZnSe beam splitter, and the transmitted beam as well as two reflected beams were used in the experiment.

The transmitted beam was passed through a novel two-stage device (equivalent to a quarterwave plate) which produced the circularly polarized saturating beam. This reflective device has a throughput of about 60% and produced a circularly polarized

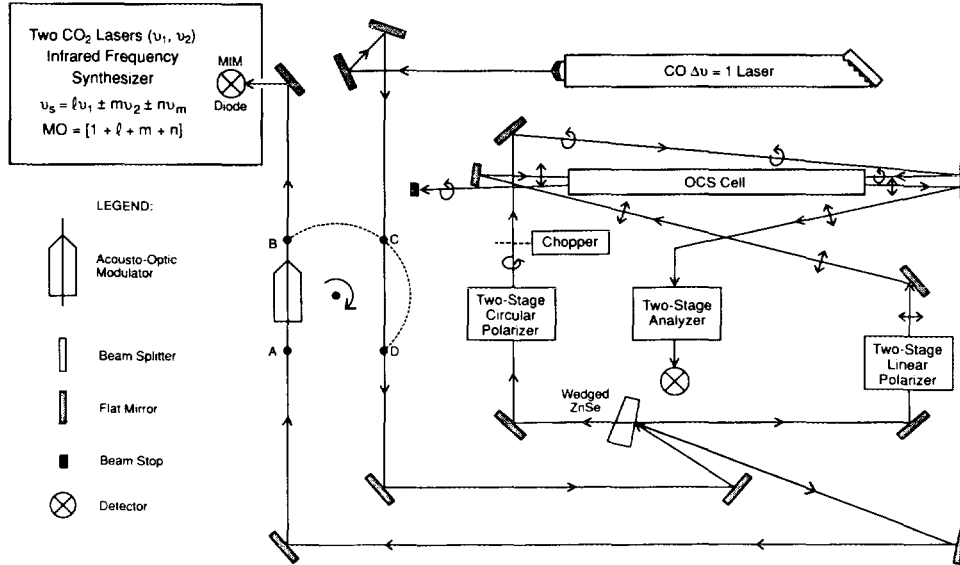


FIG. 1. Functional diagram for the optical polarization heterodyne spectroscopic experiment in the 5–6 μm region. The diagram has been stylized to a certain extent in the interest of simplicity.

beam with about 99.5:1 polarization purity as measured with a Rochon polarizer. The power transmitted through the beam splitter and polarizer was about 165 mW at the cell entrance. The saturating beam was chopped and the modulation transferred to the probe beam provided the signal at the detector.

The beam reflected from the first surface was used for the probe beam after passing through a two-stage device (with about 78% throughput) which increased its polarization purity to about 200 000:1, again with the use of reflective elements. The details of both of these two-stage polarization devices appear elsewhere (10, 15). The power of the probe beam was about 50 mW at the absorption cell.

The reflected beam from the second surface was directed to the CO_2 laser frequency synthesizer through an AOM in order to prevent feedback from the MIM diode to the CO laser. The AOM was coated for 3.3 μm , and this reduced power in the vicinity of the MIM to about 25 mW.

Since details of the synthesizer appear in several places (2, 6, 16, 17); we briefly state that the synthesized frequency ν_s is given by

$$\nu_s = l\nu_1 \pm m\nu_2 \pm n\nu_m, \quad (1)$$

where we define l , m , and n to be positive integers. A microwave frequency is represented by ν_m , and ν_1 and ν_2 are the new frequencies of the CO_2 laser frequency standards. The CO_2 lasers are now stabilized ($1 - f$ detection) by means of 4.3- μm fluorescence in an external absorption cell using the latest recommendations of Freed and co-workers (18). In general, it becomes more difficult (more stringent requirements on the impedance of the MIM and the sharpness of the antenna point) to synthesize a useful reference signal in the MIM diode as the mixing order increases. With the above definition of l , m , and n , the mixing order, MO, is defined as

$$\text{MO} = [1 + l + m + n]. \quad (2)$$

After traversing the cell, the probe beam is processed with the aid of a two-element analyzer, which is also discussed in Ref. (10). We have shown that the relevant part of the signal through the two-stage analyzer which reaches the detector is proportional to $\phi_1 E_0 (E_0 \Delta n k_0 L)$, where ϕ_1 is the deviation of the crossing angle of the first analyzer, E_0 represents the field of the probe beam, Δn describes the birefringence and has a dispersion characteristic, $k_0 = 2\pi/\lambda$, and L is the estimated overlap length of the slightly crossed beams within the cell. The signal amplitude is the term in parentheses, and the term $\phi_1 E_0$ is the local oscillator amplitude. The main advantage of this heterodyne technique is that a weak signal can be enhanced a great deal by heterodyning it with a much stronger local oscillator. For the $P(16)$ measurement a comparatively large local oscillator power helped produce the dispersion signal shown in Fig. 2. The signal-to-noise ratio shown here is about 10 000:1. The OCS pressure in the cell was 1.3 Pa (10 mTorr), and the effective beam overlap length in the OCS absorption cell was estimated to be 1 m. This discriminant was used for locking the CO laser for the $P(16)$ frequency measurement.

The measurement of the $P(48)$ OCS line at $5.9 \mu\text{m}$ was considerably more difficult, and the measurement uncertainty was increased. For this experiment, a direct overlap between CO and OCS did not exist and it was necessary to shift the frequency of the working beam 90.000 MHz below the frequency of the $P_{15}(18)$ transition by first passing it through the AOM (path changed from A-B to C-D in Fig. 1). The $3.3\text{-}\mu\text{m}$ AR coating on the AOM permitted an even smaller portion of the beam power to be transmitted than was the case at $5.3 \mu\text{m}$. About 30 mW total was available for the three beams departing from our uncoated, wedged beam splitter. The power levels at the cell were about 13 and 4 mW for the saturation and probe beams, respectively, and 4 mW was available for generating the beatnote with the CO_2 synthesizer. As a result of the lower power and a more than an order of magnitude reduction in detector sensitivity in going from 5.3 to $5.9 \mu\text{m}$, the dispersion signal was not nearly as good as that for the $P(16)$ transition. A second difficulty was associated with the higher mixing order (8 in this case). The harmonic numbers were 4, 2, and 1: the need for

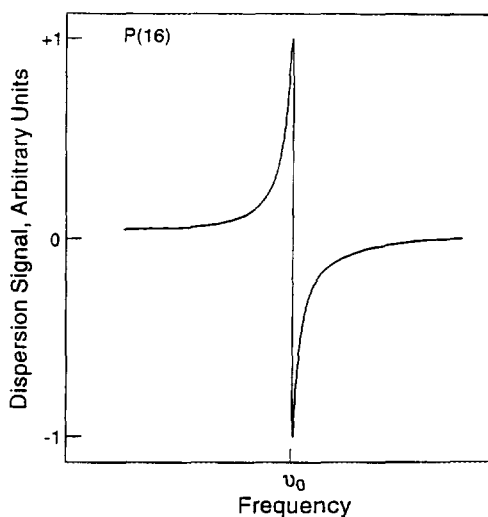


FIG. 2. Dispersion signal for the OCS $P(16)$ transition of the $02^0_1-00^0_0$ band. The peak-to-peak linewidth was about 600 kHz, and the width of the scan shown in the figure was estimated to be about 60 MHz.

higher harmonics also contributed to a larger uncertainty than we had for the $P(16)$ measurement. For the $P(48)$ measurement, the pressure and effective pathlength were also 1.3 Pa and 1 m.

In both instances, the frequency of the radiation in the cell was locked to a sub-Doppler feature of the molecular transition of interest, and a signal was generated in the CO_2 synthesizer that was close to that transition frequency. A difference frequency beatnote, ν_{if} (between the synthesized frequency and the transition frequency) was measured on a spectrum analyzer. The OCS transition frequency was then

$$\nu_{\text{OCS}} = \nu_s \pm \nu_{\text{if}}. \quad (3)$$

Both the Bonn measurement and our measurement of $P(16)$ used CO_2 reference lasers of similar design which are not as accurate as the CO_2 laser system used by Chardonnet *et al.* (19) for their very accurate measurements. Even though these two measurements agree to within 20 kHz, that does not mean that the absolute accuracy is that good. We believe that the uncertainties given here and in Ref. (9) are good estimates of the true uncertainties, regardless of how close the agreement may be. The uncertainty in the $P(48)$ measurement has a larger uncertainty for the reasons already discussed. The results of $P(16)$ and $P(48)$ measurements are shown in Table I.

ANALYSIS AND RESULTS

The present results were combined with earlier measurements in a least-squares fit. Earlier heterodyne measurements that involved the $2\nu_3$ state are given in Refs. (20–22), and those involving the $2\nu_2 + \nu_3$ state are given in Ref. (23). In addition, measurements that involve rotational transitions for these vibrational states were given by Vanek *et al.* (24).

The fit used the same Hamiltonian as that described by Maki *et al.* (23). For the 02^01-00^00 transition the effect of l -type resonance was taken into account, but that resonance was not present for the 00^02-00^00 transition.

The present new measurements are useful for determining much improved absolute frequencies for the levels of OCS that are near the same J values as the measurements.

TABLE I

Measured Transition Frequencies for Carbonyl Sulfide

CO Trans. ^a	OCS Trans. ^b	Obs. Freq. ^c (MHz)	CO_2 Laser ^d Synthesis Scheme ^e	ν_{if} (MHz)
$P_9(6)$	$P(16)$ A	$56\,533\,766.125 \pm 0.035$	$P_1(30) + P_1(12) - \nu_m$	307.596
$P_{15}(18)$	$P(48)$ A	$50\,627\,632.013 \pm 0.100$	$4 \times R_1(6) - 2 \times R_{11}(36) - \nu_m$	-449.840

^a For the CO laser designation the subscript indicates the lower state vibrational quantum number and J'' appears in parentheses.

^b We are using the notations in Ref. (2) for these transitions. Thus for the 57 THz transition, A represents the 02^01-00^00 band. For the 51 THz line, A is the designation for the 00^02-00^00 band.

^c The observed OCS frequency is the sum of the synthesized frequency and the beatnote frequency.

^d For the CO_2 laser, the designation I indicates the $10\ \mu\text{m}$ band and II indicates the $9\ \mu\text{m}$ band.

^e For the $P(16)$ measurement, ν_m was $10\,000.000$ MHz, for $P(48)$ ν_m was $10\,007.022$ MHz.

This can be seen in the uncertainties shown in Table II. The uncertainties become quite small for the transitions between $J = 20$ and $J = 65$ of $00^0_2-00^0_0$. For other values of J the uncertainties approach the values given in Ref. (2) but are always smaller. Table II gives the calculated wavenumbers determined by the constants given by a least-squares fit of all the measurements available for the upper and lower states of the $00^0_2-00^0_0$ transitions. The constants from that fit are almost identical to those given by Maki and Wells (2), but there are significant changes in the correlation of the constants and in the variance-covariance matrix elements.

The earlier (9) sub-Doppler measurement of the $P(16)$ transition of $2\nu_2 + \nu_3$ has been confirmed by the present measurement, and the agreement can also be considered

TABLE II
Wavenumbers (cm^{-1}) Calculated for the $00^0_2-00^0_0$ Band of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$

<i>P</i> -Branch	<i>J</i> "	<i>R</i> -Branch	<i>P</i> -Branch	<i>J</i> "	<i>R</i> -Branch
...	0	1711.379 530 (31) ^a	1690.309 118 (05)	45	1726.972 585 (05)
1710.570 547 (31)	1	1711.780 357 (31)	1689.793 863 (05)	46	1727.261 570 (05)
1710.162 392 (31)	2	1712.178 739 (31)	1689.276 166 (05)	47	1727.548 011 (05)
1709.751 796 (31)	3	1712.574 674 (31)	1688.756 026 (05)	48	1727.831 907 (05)
1709.338 760 (31)	4	1712.968 162 (30)	1688.233 443 (05)	49	1728.113 253 (06)
1708.923 286 (31)	5	1713.359 202 (30)	1687.708 414 (05)	50	1728.392 047 (06)
1708.505 373 (30)	6	1713.747 791 (30)	1687.180 940 (05)	51	1728.668 285 (07)
1708.085 023 (30)	7	1714.133 929 (29)	1686.651 018 (06)	52	1728.941 964 (08)
1707.662 237 (30)	8	1714.517 614 (29)	1686.118 647 (07)	53	1729.213 080 (08)
1707.237 015 (29)	9	1714.898 845 (28)	1685.583 827 (07)	54	1729.481 630 (09)
1706.809 358 (29)	10	1715.277 620 (28)	1685.046 556 (08)	55	1729.747 611 (10)
1706.379 267 (28)	11	1715.653 938 (27)	1684.506 833 (09)	56	1730.011 019 (11)
1705.946 741 (28)	12	1716.027 797 (27)	1683.964 656 (10)	57	1730.271 850 (13)
1705.511 782 (27)	13	1716.399 195 (26)	1683.420 024 (11)	58	1730.530 102 (14)
1705.074 391 (27)	14	1716.768 132 (25)	1682.872 936 (13)	59	1730.785 770 (15)
1704.634 567 (26)	15	1717.134 604 (24)	1682.323 389 (14)	60	1731.038 850 (16)
1704.192 311 (25)	16	1717.498 610 (24)	1681.771 383 (15)	61	1731.289 340 (18)
1703.747 623 (24)	17	1717.860 149 (23)	1681.216 917 (16)	62	1731.537 235 (19)
1703.300 504 (24)	18	1718.219 219 (22)	1680.659 987 (18)	63	1731.782 532 (20)
1702.850 954 (23)	19	1718.575 817 (21)	1680.100 594 (19)	64	1732.025 227 (22)
1702.398 973 (22)	20	1718.929 942 (20)	1679.538 734 (20)	65	1732.265 316 (23)
1701.944 561 (21)	21	1719.281 591 (20)	1678.974 407 (22)	66	1732.502 795 (24)
1701.487 719 (20)	22	1719.630 764 (19)	1678.407 611 (23)	67	1732.737 660 (25)
1701.028 446 (20)	23	1719.977 456 (18)	1677.838 344 (24)	68	1732.969 908 (27)
1700.566 743 (19)	24	1720.321 667 (17)	1677.266 604 (25)	69	1733.199 534 (28)
1700.102 609 (18)	25	1720.663 395 (16)	1676.692 389 (27)	70	1733.426 534 (29)
1699.636 045 (17)	26	1721.002 636 (15)	1676.115 698 (28)	71	1733.650 905 (30)
1699.167 050 (16)	27	1721.339 389 (15)	1675.536 528 (29)	72	1733.872 643 (31)
1698.695 624 (15)	28	1721.673 651 (14)	1674.954 878 (30)	73	1734.091 742 (31)
1698.221 767 (15)	29	1722.005 420 (13)	1674.370 746 (31)	74	1734.308 200 (32)
1697.745 479 (14)	30	1722.334 694 (12)	1673.784 129 (31)	75	1734.522 011 (33)
1697.266 760 (13)	31	1722.661 471 (12)	1673.195 026 (32)	76	1734.733 173 (33)
1696.785 608 (12)	32	1722.985 746 (11)	1672.603 435 (33)	77	1734.941 680 (34)
1696.302 025 (12)	33	1723.307 519 (10)	1672.009 353 (33)	78	1735.147 528 (34)
1695.816 009 (11)	34	1723.626 787 (10)	1671.412 778 (34)	79	1735.350 714 (35)
1695.327 559 (10)	35	1723.943 546 (09)	1670.813 709 (34)	80	1735.551 232 (35)
1694.836 677 (10)	36	1724.257 794 (09)	1670.212 143 (35)	81	1735.749 078 (36)
1694.343 360 (09)	37	1724.569 529 (08)	1669.608 078 (36)	82	1735.944 249 (37)
1693.847 608 (08)	38	1724.878 748 (07)	1669.001 512 (37)	83	1736.136 739 (39)
1693.349 421 (08)	39	1725.185 448 (07)	1668.392 441 (38)	84	1736.326 544 (41)
1692.848 798 (07)	40	1725.489 626 (07)	1667.780 865 (40)	85	1736.513 661 (44)
1692.345 739 (07)	41	1725.791 279 (06)	1667.166 781 (42)	86	1736.698 083 (48)
1691.840 242 (06)	42	1726.090 404 (06)	1666.550 186 (45)	87	1736.879 807 (53)
1691.332 307 (06)	43	1726.386 999 (05)	1665.931 078 (49)	88	1737.058 829 (59)
1690.821 932 (06)	44	1726.681 060 (05)	1665.309 454 (54)	89	1737.235 143 (66)

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

as a confirmation of the accuracy of the other sub-Doppler measurement of this paper and of Ref. (10). The present measurements do not make a significant difference to the transition wavenumbers calculated for the $2\nu_2 + \nu_3$ band given as Table IV in the paper by George *et al.* (9).

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