

Pressure Dependent Lineshift Measurements on OCS

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A computer-controlled, frequency offset-locked spectrometer using a tunable diode laser is described and new measurements on carbonyl sulfide (OCS) are given to illustrate its use. Two OCS absorption lines, $R(3)$ and $P(30)$, have been measured for the $02^0_0-00^0_0$ vibrational transition near $10\ \mu\text{m}$. An average pressure-induced shift coefficient of $-0.37 \pm 0.04\ \text{kHz/Pa}$ ($-49 \pm 5\ \text{kHz/Torr}$) was observed for the two lines. The self-broadening coefficient for each line has also been measured. © 1991 Academic Press, Inc.

INTRODUCTION

Absorption features of gas phase molecules are often used for the calibration of spectroscopic devices in the infrared (1). Since applications sometimes may require higher pressures than were used for the original frequency measurements, it is important that the effects of pressure-induced shifts be known quantitatively. Yet there are very few measurements of the variation with pressure of the frequency of absorption lines in the infrared spectrum of the compounds used for calibration.

Some of the more accurate attempts that have been made to measure the self-induced pressure shifts for calibration molecules involved the OCS (carbonyl sulfide) (2, 3), N_2O (4), CO (5), and HCl (6) molecules. Of those measurements only the work of Pine and Looney (6) could be described as quantitative. For OCS, N_2O , and CO, which all have small dipole moments, there seems to be general agreement that the self-induced pressure shift is negative (to lower frequency with increasing pressure) and on the order of $-1\ \text{kHz/Pa}$ ($-0.1\ \text{MHz/Torr}$). The best measurements on carbonyl sulfide gave a shift coefficient of $-0.4 \pm 1.5\ \text{kHz/Pa}$ (3).

The pressure shift is much less than the width of the absorption lines so it is difficult to measure. We have constructed a computer-controlled, frequency offset-locking system for our tunable diode laser. This system allows us to measure absorption line profiles with a well controlled and linear scanning system. It provides digitized spectra that can be easily manipulated and analyzed. The most important property of this spectrometer is its ability to make accurate frequency measurements since its frequency is referenced to a stabilized CO_2 laser which is accurate in frequency to 30 kHz. We have used this spectrometer to measure the lineshape and center frequencies of two lines of the $2\nu_2$ band of OCS at several different pressures.

EXPERIMENTAL DETAILS

A computer-controlled, frequency offset-locking (CCFOL) scheme was used for the tunable diode laser (TDL) measurements in this paper. Freed *et al.* (7) demonstrated the use of a frequency offset lock combined with a frequency synthesizer to control the output frequency of TDL. We have combined that technique with the scanning and data-logging technology used in this laboratory for other measurements (8-10) to obtain accurate data on $d\nu/dP$, the pressure-induced frequency shifts, in the rovibrational spectrum of OCS.

Figure 1 shows a block diagram of the apparatus used for these measurements. The output beams from a TDL and a CO₂ laser frequency standard were focused with separate lenses and then combined with a ZnSe beam splitter and directed to a HgCdTe heterodyne mixer/detector which produced a beatnote at the difference frequency, ν_B , between the two lasers. The beatnote was amplified in an rf amplifier and displayed on an rf spectrum analyzer. A balanced mixer was used to down-convert the beatnote at frequency ν_B to a nominal 160 MHz, the region of operation of the IF amplifier and discriminator. The beatnote was fed to one input arm of the balanced mixer, and the output of the sweepable frequency generator, at frequency ν_{SW} , was fed to the other input arm (the local oscillator arm). The frequency ν_{SW} was adjusted such that $|\nu_{SW} - \nu_B|$ was nominally 160 MHz, and this resulting output signal was fed to the discriminator which had a sensitivity of 0.1 V/MHz and an 80-MHz bandwidth.

After the switch in the loop filter was closed, the discriminator-based locking loop

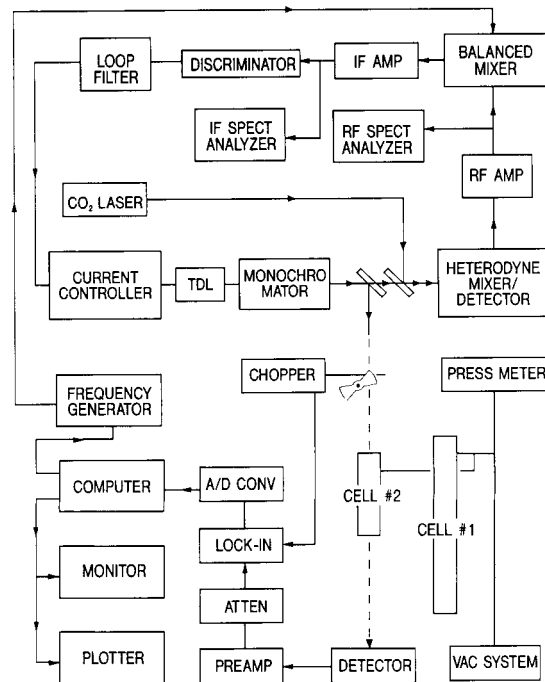


FIG. 1. Block diagram of the computer-controlled frequency swept TDL system.

adjusted the TDL frequency to ensure that the beatnote ν_B was locked at a frequency ν_{DO} away from ν_{SW} . That is,

$$\nu_{DO} = |\nu_{SW} - \nu_B|,$$

where ν_{DO} is close but (due to the presence of various zero offsets in the locking loop) not necessarily equal to 160 MHz. For frequency shift and lineshape measurements, the important point is that the frequency ν_{DO} must remain fixed, whatever value it assumes. If a frequency measurement is the objective, it becomes necessary to measure ν_{DO} . The frequency of the CCFOL TDL is then given by

$$\nu_{TDL} = \nu_{CO_2} \pm \nu_{SW} \pm \nu_{DO}.$$

The choice of signs in the above equation is most readily illustrated by Fig. 2, which shows how measurements were made either above or below the CO_2 laser frequency.

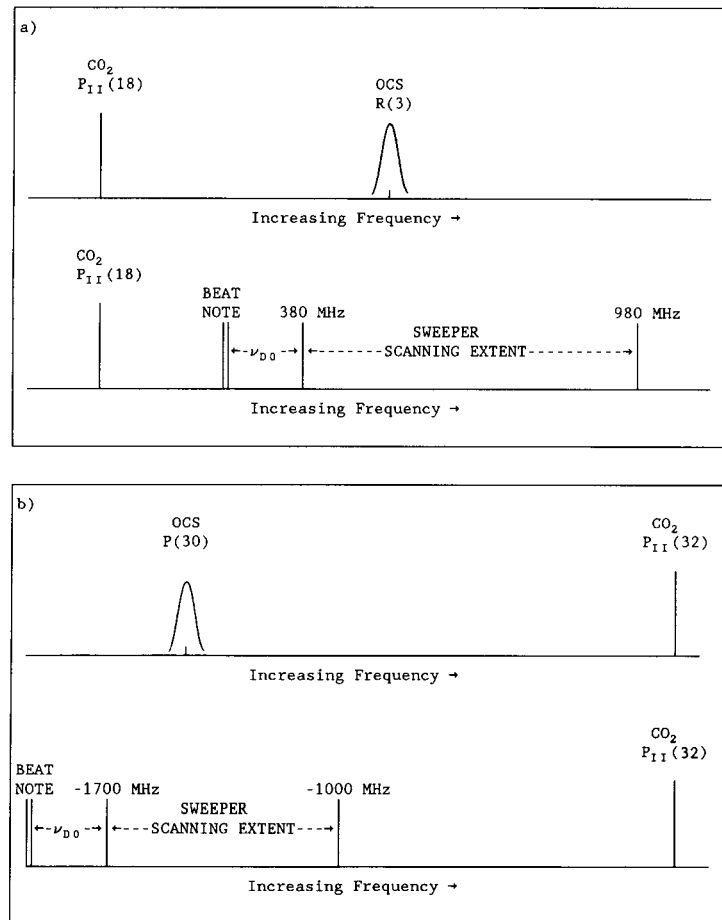


FIG. 2. Diagram of the frequencies involved in (a) the $R(3)$ measurement and (b) the $P(30)$ measurement. The positions of the beatnotes shown are for the start of each scan.

Also indicated are the starting and stopping frequencies of the scans which were programmed for the two measurements reported here.

We have restricted our initial experiments to those OCS transitions which lie within 2000 MHz of a CO₂ laser transition because the lock loop requires a beatnote with a good S/N and the beatnote signal decreases with increasing frequency. This is also the band limit of our most convenient rf amplifier. We chose from the available TDLs those with sufficient power to give a beatnote with a S/N of about 30 dB. For the present measurements a 400-msec integration time was used and 640 points were recorded in each direction. Recording in both directions is a good way to cancel certain types of systematic errors. Generally only one round trip pass was made per measurement but as many passes could be made as required to give a good S/N .

These measurements were made on a commercially produced sample of OCS without further purification. Typically, such a sample contains no more than 3% impurities. The pressure measurements were made with a pressure transducer which was accurate within 1% or less for pressures above 133 Pa (1 Torr). The absorption cells used for the measurements were made of glass and had NaCl windows. The cells had nominal lengths of 3, 30, and 170 cm. Since *absolute* intensity measurements were not the goal of this work, the exact path length and partial pressure of the gas were not important. The measurements were all made at a temperature of about 296 K.

ANALYSIS OF THE DATA

As a test of this technique we have measured the frequency, intensity, and linewidth of two OCS lines near 10 μm , $R(3)$ and $P(30)$, as a function of pressure. The results are summarized in Table I. Initially these two lines were chosen because they seemed to be free of nearby lines that might complicate the analysis. After a preliminary analysis of the $R(3)$ line we concluded that it must hide a weak line about 27 MHz

TABLE I
Parameters Used to Fit the Measurements

line	Press. (Torr)	$\nu_0 - \nu(\text{CO}_2)$ (MHz)	ν_0 (MHz)	$I/P\ell$ ($\text{cm}^{-2}\text{atm}^{-1}$)	γ_G^a (MHz)	γ_L^b (MHz)
R(3)	0.144	497.099(8) ^c	31 438 557.28	0.03440(1)	25.44(1)	[0.88] ^d
P(23) ^e	0.144	524.34(18)	31 438 584.52	[0.002532]	[25.44]	[1.00]
R(3)	20.8	496.008(35)	31 438 556.19	0.03673(1)	[25.44]	127.45(6)
P(23)	20.8	[523.25]	[31 438 583.43]	[0.002702]	[25.44]	[145.]
P(30)	0.144	-1511.54(5)	31 041 206.53	0.09982(19)	25.23(6)	[1.0]
P(30)	4.8 ^f	-1511.72(5)	31 041 206.35	0.1169(1)	[25.23]	34.05(8)
P(30)	10.9 ^f	-1511.95(12)	31 041 206.12	0.1183(2)	[25.23]	71.7(2)
P(30)	20.6	-1512.48(2)	31 041 205.59	0.12336(2)	[25.23]	144.09(4)

- a) γ_G is the half-width at half-height of the Gaussian component of the linewidth.
b) γ_L is the half-width at half-height of the Lorentzian component of the linewidth.
c) The estimated standard error in the last digits is given in parentheses. These are statistically determined numbers that reflect the consistency of the data rather than their absolute accuracy. For the intensities there are significant additional errors due to the uncertainty in the pressure, pathlength, and purity of the gas.
d) Values enclosed in square brackets were fixed during the fit.
e) The P(23) line is for the 04⁰0-02⁰0 transition.
f) Only one set of measurements was made at intermediate pressures so those measurements are less reliable.

higher in frequency. This is the $P(23)$ line of the $04^0_0-02^0_0$ transition, which was calculated to be $27.6 (\pm 3.0)$ MHz higher in frequency and 13.6 times weaker than the $R(3)$ line.

The digitized data were analyzed by means of a nonlinear least-squares fitting program that is similar to that used in the analysis of lineshape data for NO (11). This program fits the spectrum to one or more lines that are assumed to have a Voigt shape. Each line is described by four parameters, the center position, the line intensity, the Doppler (or Gaussian) linewidth, and the pressure-broadened (or Lorentzian) linewidth. Each parameter may be either fixed, constrained, or fitted by the least-squares program. The Voigt lineshape was calculated by means of an algorithm taken from the work of Young (12) although many other equally good algorithms for calculating the Voigt shape are available.

In order to analyze the data, the intensity measurements were first converted to absorbance units (A) by the usual equation

$$A = \ln(I_0/I_t),$$

where I_t is the observed intensity transmitted by the absorption cell and I_0 is the intensity that would be transmitted by an empty cell.

Determining I_0 is always the hard part of these experiments. Initially I_0 was given by a smooth curve that joined the two ends of the measured spectrum, assuming that each end is far enough from the line center to have zero absorption. For each successive iteration of the fit the I_0 was corrected for the calculated absorption at the ends of the spectrum and the absorbance for the entire spectrum was recalculated.

As Fig. 3 shows, this recalculation of the absorbance at the ends of the spectrum is not necessary for the low-pressure measurements, but as the line gets broader and more absorption is shifted into the wings of the lines at higher pressures the correction becomes important. Two factors contribute to this change. First, for Gaussian lines the intensity drops very quickly with increasing frequency from the line center, whereas for Lorentzian lines the intensity drops very slowly with increasing frequency difference.

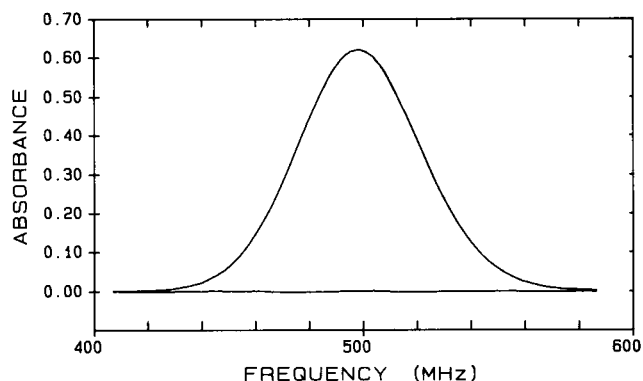


FIG. 3. Observed lineshape for the $R(3)$ line at low pressure 19.2 Pa (0.144 Torr). The lower curve, which looks like a zero absorbance line, is the plot of the difference between the observed spectrum and the calculated Voigt profile given by the constants in Table I.

Second, the spectrometer, as presently constituted, is not capable of scanning very far from the line center. Furthermore, the density of lines in the spectrum of OCS makes it difficult to scan very far from a line without encountering another line. In principle, it is possible to measure I_0 with an empty cell before each measurement, but small changes in the laser intensity can cause residual systematic errors if uncompensated.

A good test of the resolution of the spectrometer was given by the analysis of the low-pressure shapes of the OCS lines. The Gaussian width measured for the $R(3)$ line was 25.44 (± 0.01) MHz while the calculated Doppler width was 25.0 MHz. For the $P(30)$ line the measured width was 25.23 (± 0.06) MHz while the calculated Doppler width was 24.7 MHz. For pressure shift measurements the line center is the parameter of interest and it is not sensitive to errors in the intensity or linewidth parameters.

RESULTS

Pressure Shifts

Table II gives the results of our measurements of the pressure shift coefficients and compares them with values reported by other workers. The pressure shift coefficient for $P(30)$ appears smaller than for $R(3)$, but the uncertainty is too large to draw any conclusions. More measurements are needed to see if there is any rotational dependence.

The coefficients given in Table II were determined for the high- and low-pressure measurements because they were better measurements and were repeated several times. The intermediate-pressure measurements given in Table I for $P(30)$ are only intended to show the approximately linear changes with pressure.

Table II includes values for the shift coefficient that others have measured for rotational transitions within the ground vibrational state. We anticipate that the shift coefficients for transitions within a vibrational state will be smaller or equal to, but

TABLE II
Self-Induced Pressure Shift and Pressure-Broadening Coefficients for OCS

	$\Delta\nu_0/p$ (kHz/Pa)			γ_L/p^a (kHz/Pa)		
	this work	others	[Ref.]	this work	others	[Ref.]
R(3)	-0.40(3) ^b	-0.4(15) {0.00(9) {4.9(7)}	[3] [13] ^d [17]}	46.0(3)	45.9 45.5(26) ^e {45.2(8) ^f }	[21] ^c [20] [22]}
P(30)	-0.34(5)	-0.4(15)	[3]	52.5(3)	48.8 48.1(17) ^g	[21] ^c [20]

a) γ_L is the half-width at half-height of the Lorentzian component of the linewidth.

b) The uncertainties in the last digits (twice the estimated standard error) are given in parentheses.

c) For the OCS band near 860 cm^{-1} .

d) The values enclosed in curly brackets, {}, are for rotational transitions in the ground state.

e) For the R(2) transition.

f) For the J=2+1 transition.

g) for the R(31) transition of 03'0-01'0.

certainly not larger than, the shift for transitions between vibrational states. With this in mind, the results of De Vreede *et al.* (13) are consistent with the present measurements, as are the earlier measurements of MacGillivray (14) and Story *et al.* (15), though none of these were able to measure any significant pressure shift.

Aside from our own earlier work, the only nonzero measurements of a pressure shift for OCS are the works of Hewitt (16) and Lamalle *et al.* (17) and an earlier paper by De Vreede *et al.* (18) that was corrected by the more recent paper from that laboratory (13). Hewitt found a large positive value with an uncertainty that was too close to the measured value to give much confidence. The one large and apparently significant value for the pressure shift is that given by Lamalle *et al.* (17). They found a positive coefficient that is 10 times larger than we measure. Although their measurement was for a different transition than we measured, we think their value must be spurious, and probably results from the uneven background shown in their Fig. 2.

Pressure Broadening

There seem to have been only two earlier measurements of the pressure-broadening coefficient for $\Delta v_2 = 2$ transitions. Within the uncertainties of their measurements, the earlier work of Leavitt and Sattler (19) is in agreement with the more recent and more accurate measurements of Depannemaecker and Lemaire (20). Neither of these papers reports measurements for the same rotational transitions as we have measured, but the change with J is slow so nearby transitions may be compared.

There are only small differences in the pressure-broadening coefficients for different vibrational transitions. Consequently, we can compare measurements made on other vibrational transitions. The most important of the other infrared pressure-broadening measurements are those that Bouanich *et al.* (21) made on the 850-cm^{-1} band. There are also a number of measurements of the pressure broadening of low- J rotational transitions. One of the more accurate studies was that of Creswell *et al.* (22). They give a more complete listing of earlier work.

The uncertainty in the measured line half-width as given in Table I is much smaller than the uncertainty given in Table II for the pressure-broadening coefficient. In Table II we have added the uncertainty in the pressure measurement. While uncertainties in the correct values for I_0 are not important for the frequency shift measurements, they will have a small effect on the half-width measurement. It is not certain how large that source of error may be for these measurements, but it might be as large as 2% of the pressure-broadening coefficient.

The present measurement of the pressure-broadening coefficient for $R(3)$ is in excellent agreement with the earlier values while our value for $P(30)$ is about 7% higher than others have found. We are unable to explain this discrepancy but hope that further measurements of high- J transitions will resolve the matter.

Other Parameters

In Table I we give the absolute values of the center frequency and the intensity for each line. Both of those parameters are subject to sources of error that are less important for the other parameters.

The absolute frequency, for instance, depends on the value of locking-loop frequency,

ν_{DO} . That frequency was measured several times during these measurements, but more work is needed to be certain there are no systematic errors due to frequency pulling. The power of the technique is demonstrated by noting that the weak $P(23)$ line (for $04^0_0-02^0_0$) that is underneath the $R(3)$ line can not be seen in Fig. 3, yet it was measured to be 27.2 ± 0.18 MHz above the $R(3)$ line. This was in excellent agreement with the estimate of 27.6 ± 3.0 MHz based on earlier heterodyne measurements for the 04^0_0 and 02^0_0 levels.

As we noted earlier, these measurements were not intended to give absolute intensity values. For that, more care would have to be used in measuring I_0 , in purifying the sample, and in measuring the pressure and pathlength. The best conditions for making good intensity measurements are at low pressures where the pressure measurement becomes more difficult.

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