Heterodyne frequency measurements with a tunable diode laser-CO$_2$ laser spectrometer: spectroscopic reference frequencies in the 9.5-µm band of carbonyl sulfide

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The frequencies of twelve carbonyl sulfide absorption lines near 9.5 µm have been measured by means of a heterodyne frequency measuring technique, which uses a frequency stabilized CO$_2$ laser and a tunable diode laser. The diode laser was locked to the peak of each OCS absorption line by means of a first derivative frequency lock procedure. In addition to lines in the 02°0-0000 band, measurements also include some nearby OCS hot band features as well as lines in isotopically enriched samples of OC$_3$S, O$_{13}$CS, and $^{18}$OCS. These measurements are part of an effort to provide frequency standards for the calibration of tunable IR laser devices.

1. Introduction

The advent of tunable diode lasers (TDL) and color center lasers within the last few years has led to a resurgence in IR spectroscopy in the 2-30-µm region. These devices permit one to obtain Doppler limited spectra with relative ease. Complex spectra of heavy molecules have been observed with a resolution that was previously not possible. Presently the accuracy of such measurements has not kept pace with the resolution, and a 0.005-cm$^{-1}$ value for uncertainty in the line position is not uncommon. While standards do exist (for part of the region of interest) in the form of the CO$_2$ and the CO lasers, a vast majority of the laboratories with some 200 TDL spectrometers have neither access to these lasers nor the heterodyne apparatus to use them, as is evident by the relatively small number of laboratories reporting TDL heterodyne measurements. This paper describes our initial effort to satisfy partially an increasing demand for absorption frequency standards by the users of tunable laser devices.

Good frequency calibration standards for tunable laser systems should satisfy the following criteria: (1) absorption lines (rather than laser or emission lines) will be used; (2) the calibration substance must be convenient, i.e., must be easily obtained and easily handled; (3) there must be at least one calibration point every 0.5 cm$^{-1}$ (additionally, several nearby spectral features to help identify the calibration line would be extremely valuable); (4) the lines must be well resolved and free of accuracy limiting fine structure; and (5) each line must either be measured accurately or else calculated reliably and accurately. Although no single calibrant can fulfill these requirements over the entire spectral range, the requirements can be easily fulfilled in selected spectral regions by such linear molecules as OCS and N$_2$O. The present efforts to generate a table of standards involve carbonyl sulfide.

Carbonyl sulfide is easily obtained and can be handled in any gas handling apparatus without special precautions. It does not attack normal IR absorption cells or IR windows. The 02°0-0000 band of interest in this paper has primary features about 0.4 cm$^{-1}$ apart. The spectral lines of OCS are well resolved and do not break up into hyperfine components even when studied with microwave resolution (resolution of 100 kHz). In order to satisfy the fifth criterion, it is necessary to make frequency measurements of sufficient accuracy such that the 0.002-cm$^{-1}$ uncertainty on the OCS line position in the 02°0-0000 band can be reduced to the 0.0003-0.0001-cm$^{-1}$ range.

Realizing a sufficient number of frequency measurements is somewhat simplified due to the existence of a wealth of very accurate microwave measurements of the rotational constants for OCS. For a linear molecule such as OCS (ignoring for the sake of brevity the effect of vibrational angular momentum), the IR frequencies can be accurately predicted using the equation
$v = v_0 + B'(J + 1)(J + 1 + 1) - D'(J + 1)(J + 1 + 1)^2$
- $B''J(J + 1) + D''J(J + 1)^2$,  

where $J$ is the quantum number of rotational angular momentum for the lower state, and the + sign is taken for $\Delta J = +1$ transitions, while the - sign is for $\Delta J = -1$ transitions. Microwave measurements give very accurate values for $B'$ and $B''$, the rotational constants for the upper and lower states, respectively. The ground state centrifugal distortion term $D''$ and certain upper state $D'$ terms have also been determined from microwave measurements, although some improvement would be helpful. In order to determine accurate values for the frequencies of all the calibration lines in a given band, it is necessary in principle to measure accurately only a few lines in order to determine the values of the remaining poorly determined terms in Eq. (1). A measurement of these few lines is the objective of these experiments.

II. Experimental Method

The spectrometer used for the measurement of the OCS frequencies is diagramed in Fig. 1. The PbSnTe tunable diode laser is housed in a liquid helium Dewar that can accommodate three such lasers. A translatable stage facilitates positioning of one of the three lasers on the optic axis. A laser control module (LCM), which supplies current to the laser, has capabilities for slow sweep, several internal modulation options, and an external modulation capability from dc to 10 kHz. The Dewar, laser, and laser control module are all commercially available. The radiation from the diode was collimated by a 5-cm f/1 ZnS polycrystalline lens. Off-axis parabolic mirrors were used to focus the TDL radiation on the entrance slit ($S_1$) of the monochromator and recollimate the beam after it emerged from the exit slit ($S_2$). The 0.8-m monochromator was an f/10.7 Ebert-Fastie with a 150-line/mm grating. Removable 150-μm slits were used in line identification measurements. For general use, the entrance slit was replaced with an aperture (which was blackened and shaped to reduce fringes due to slit reflections feeding back to the TDL), and another slit, typically 500 μm or greater, was used on the output. Isolators, consisting of 20-cm long attenuator cells (0-30 dB) with variable pressure of ethyl ether, were also inserted to ameliorate the troublesome fringe problem resulting from feedback to the TDL. Isolation (3 dB) in the alternate leg was added by the OCS cell when the TDL frequency coincided with a strong OCS transition.

A ZnSe beam splitter was used to divide the post monochromator collimated radiation. One beam was directed through a 50-cm long cell containing OCS that can accommodate three such lasers. A translatable stage facilitates positioning of one of the three lasers on the optic axis. A laser control module (LCM), which supplies current to the laser, has capabilities for slow sweep, several internal modulation options, and an external modulation capability from dc to 10 kHz. The Dewar, laser, and laser control module are all commercially available. The radiation from the diode was collimated by a 5-cm f/1 ZnS polycrystalline lens. Off-axis parabolic mirrors were used to focus the TDL radiation on the entrance slit ($S_1$) of the monochromator and recollimate the beam after it emerged from the exit slit ($S_2$). The 0.8-m monochromator was an f/10.7 Ebert-Fastie with a 150-line/mm grating. Removable 150-μm slits were used in line identification measurements. For general use, the entrance slit was replaced with an aperture (which was blackened and shaped to reduce fringes due to slit reflections feeding back to the TDL), and another slit, typically 500 μm or greater, was used on the output. Isolators, consisting of 20-cm long attenuator cells (0-30 dB) with variable pressure of ethyl ether, were also inserted to ameliorate the troublesome fringe problem resulting from feedback to the TDL. Isolation (3 dB) in the alternate leg was added by the OCS cell when the TDL frequency coincided with a strong OCS transition.

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length several meters past the NaCl beam splitter. The CO₂ laser was focused onto the detector with a 40-cm focal length lens positioned to produce a beam waist at the mixer element. We estimate the CO₂ laser power at the detector to be about 1 mW. Figure 2(a) shows the rectified signals from both the CO₂ laser and TDL radiation. These levels, along with a negative 0.6-V bias on the detector, give rise to the beat note shown in Fig. 2(b), which has a width of about 2 MHz. The width of the beat note increased considerably at higher TDL currents, thereby limiting the range over which useful measurements could be made.

Fig. 2. (a) Rectified signals from tunable diode laser and CO₂ laser radiation. The detector was connected directly to the scope, which was adjusted to a 10-mV/division display. The lower frequency 40-mV chopped signal is due to the CO₂ laser. Detector nonlinearity is evidenced by the TDL signal, which drops from nearly 5 mV with the CO₂ laser off to about 1 mV with the CO₂ laser on. (b) Beat note between TDL [near P(41) of the OCS molecule] and the P(36) line of the CO₂ laser. The TDL current was about -0.69 A, just slightly above threshold. The center frequency is 530 MHz, and the dispersion is 10 MHz/cm. Other spectrum analyzer parameters are linear display, 300-kHz bandwidth, and 10-msec/cm sweep rate.

A set procedure for the measurements started with a real-time display of the spectrum on the oscilloscope. After identifying the OCS line to be measured, the monochromator was then roughly adjusted to shape the transmitted signal on the oscilloscope such that it was nearly flat over the region of the transition. A chopper was inserted in front of S₁, and the signal was phase detected and displayed on the recorder as the current was slowly swept. The monochromator was then finely adjusted to flatten the transmitted signal on both sides of the OCS transition. (This procedure and a first derivative lock were used in lieu of a third derivative lock.)
The chopper was then removed, and the spectral feature was again observed on the scope. The \( f/1 \) lens in front of the diode was readjusted (and the ethyl ether pressure in the cells increased if necessary) to minimize any feedback fringe distortion on or near the line. Recorder display was resumed, and a phase sensitive detector reference signal was used to frequency modulate the TDL as the current was slowly swept. This 10-mV 3.5-kHz signal produced a 10-MHz frequency modulation for our particular TDL at currents a few hundred mA above threshold. The 10 MHz was chosen as a trade off of beat frequency linewidth (narrowness) for fringe discrimination and lock stability.

The preceding steps were taken in order to insure an acceptable lock of the TDL to an OCS line frequency. One goal, which was not always met, was to have a ratio of OCS line derivative amplitude (signal) to fringe derivative amplitude (noise) of 50:1. A SNR of 50:1 of OCS line derivative amplitude (signal) to fringe derivative amplitude (noise) of 50:1 should permit the location of the center of the 50-MHz Doppler-broadened line to within 1 MHz. A second goal was to have the average of the derivative signal on either side of the OCS line coinde with zero volts. Both goals were satisfied by the derivative of the OCS line displayed in Fig. 3(a). The derivative signal in proper phase was then applied to the modulation input along with the 3.5-kHz signal, and the TDL was locked to the line center to within the limits of our present capabilities. Figure 3(b) shows a beat note between the locked TDL and the CO\(_2\) reference laser.

After verifying the CO\(_2\) laser lock, a marker oscillator was tuned to the center of the beat note and simultaneously fed to a frequency counter in order to measure the TDL–CO\(_2\) laser difference frequency. The last step is needed because the beat notes observed thus far do not have sufficient SNR reliably to drive a frequency counter.

The measurements were made with pressures between 40 Pa and 133 Pa (0.3 Torr and 1.0 Torr) in a 50-cm absorption cell. In addition to an isotopically normal sample of carbonyl sulfide, three isotopically enriched samples were used containing 86% OC\(_3\)S, 64% O\(_{13}\)CS, and 98% \(^{18}\)OCS, respectively. Many lines of the isotopically rare species could be seen in the spectrum of the isotopically normal sample at higher pressures, but the enriched samples were needed to make accurate measurements.

### III. Results and Discussion

Table I gives the measurements obtained in this work. The transitions were identified in the following way. Diode laser spectra were measured from about 0.1 cm\(^{-1}\) below the CO\(_2\) laser transition to about 0.1 cm\(^{-1}\) above it. The observed spectra were then compared with the spectrum calculated from the ro-vibronic constants given in various references. Although there were at first a few uncertainties in the assignments, the uncertainties were usually resolved by observing the relative intensities of the lines, by scanning the diode laser even farther from the CO\(_2\) laser line, or by less ambiguous assignments made elsewhere in the band. In all cases a refit of the present heterodyne measurements with other diode measurements made in our laboratory and with data reported in the appropriate references resulted in an internally consistent fit and yielded ro-vibronic constants close to previously determined values.

Most of the measurements were made with beat frequency widths of 10 MHz (determined by the amplitude of the frequency modulation needed to lock the diode laser to the peak of the absorption line). In such cases repeated measurements (sometimes made by different observers) gave results that always had an rms deviation of less than 1 MHz and often less than 0.5 MHz. Such measurements were assigned an uncertainty of \( \pm 2 \) MHz to allow for possible systematic errors. Possible sources of error that could affect the TDL lock to the OCS line include a small slope of the absorption line background, the pulling effect of feedback fringes, and a residual zero offset from the phase sensitive detector. A nonuniform amplitude vs frequency response of the detector/mixer altered the shape of the beat note and caused measurements to be discarded in two instances. Possible asymmetries in the beat note due to nonlinear tuning of the TDGCo\(_2\) laser have also been considered. As indicated...
The new data indicate the band centers need to be shifted to errors in the band centers determined in that position. The data indicates, however, that the discrepancies are not due to errors in the band centers determined in that work. The new data indicate the band centers need to be shifted by less than 12 MHz from the previous values. A more complete analysis containing results of additional diode laser measurements will be given in a later communication.

Table II gives the recommended frequencies (and wave numbers) of the absorption lines of the $02^0-00^0$ band of $^{16}$O$^{12}$C$^{18}$S. This table is designed to be used for the calibration of tunable laser devices in this spectral region. Table III gives the constants used to calculate the transitions given in Table II. The constants were determined by combining the present measurements on $P(41), P(30), P(5),$ and $R(3)$ with the microwave measurements$^{10,18}$ and with the results of the laser Stark resonance measurements.$^{23}$ These data were used in a least-squares fit with each datum weighted by the inverse square of the cited uncertainty. In the case...
of the laser Stark results, the reported band center was used as input to the least-squares fit, but the uncertainty was taken to be ±10 MHz in order to allow for systematic errors, which would not have appeared in the reported statistical analysis of the data. The band center was also lowered to 31 359 542.8 MHz to allow for systematic errors, which would not have appeared in the measurements.

The variance-covariance matrix determined from this least-squares fit was used in calculating the uncertainties given for the frequencies in Table II. The variance-covariance matrix is also given in Table III. The uncertainties determined by the variance-covariance matrix have been doubled because our experience has been that the statistically estimated standard deviation is usually too small. We regard the uncertainties given in Table II as equivalent to one standard deviation. Although the uncertainties were slightly less than 2 MHz from \( P(39) \) to \( R(37) \), a lower limit of ±2 MHz has been set on the uncertainties given in Table II in order to allow for systematic errors in our measurements.

The data were analyzed using the usual equations similar to Eq. (1). The sextic terms \( \nu_0 \) were not used in fitting the data since it has been shown that they cannot be determined with useful accuracy even though the microwave measurements extend to \( J = 67 \) for the ground state. The use of an expansion that goes to higher order than the data warrant will usually result in both extrapolated and interpolated frequencies that are less accurate than those obtained from a lower order expansion.

The last column of Table II gives the estimated intensity of each transition. The intensities were calculated for a temperature of 295 K by using the equation

\[
S = C \nu^2 Q_v Q_o N_i m | \exp(-E^*/kT),
\]

where \( \nu \) is the frequency of the transition (in cm\(^{-1}\)), \( R \) is the transition moment (in debyes), \( Q_v \) and \( Q_o \) are the partition functions for vibration and rotation, respectively, \( N_i \) is the isotopic concentration of the sample (i.e., 0.9325 for \(^{16}\)O\(^{12}\)C\(^{32}\)S in normal abundance), \( E^* \) is the energy of the lower state with respect to the ground state, and \( m = J' \) for \( \Delta J = +1 \) transitions and \( m = -J' \) for \( \Delta J = -1 \) transitions. The constant \( C \) includes Loschmidt's number and several other factors that result in an integrated line intensity given in the usual spectroscopic units of cm\(^{-2}\) atm\(^{-1}\) (i.e., \( C = 10.3546 \) at 295 K).

Foord and Whiffen measured a transition moment of \( |R| = 0.0372 \) D from the integrated intensity of the unresolved \( 2\nu_2 \) band. However, the intensities given in Table II are based on \( |R| = 0.0386 \) D \((0.129 \times 10^{-30} \text{ Cm})\), a value that gives calculated line intensities for \( P(30) \) and \( P(41) \) in better agreement with the intensities observed in the present work.

To calculate the absorption at the peak of a non-pressure broadened line, one must use the usual equations

\[
% \text{transmission} = \frac{I \times 100}{I_0} = 100 \exp(-KLp),
\]

\[
K = S \frac{\sqrt{\Delta f}}{\Delta v},
\]

where \( S \) is the integrated line intensity taken from the last column of Table II, \( \nu_0 \) is the Doppler width (half of the linewidth at half of the intensity, in cm\(^{-1}\)), \( L \) is the absorption path length (in cm), and \( p \) is the partial pressure of the carbonyl sulfide (in atmospheres).

In using Table II one should remember that the absolute intensities are not known very accurately although the relative intensities are quite reliable, at least for lines that are not spectrally far apart.

Plans for similar experiments in the near future include measurements in the \( 10\nu_0 \)-00\( \nu_0 \) band of OCS at 11 μm with respect to the \(^{12}\)C\(^{16}\)O\(^2\)S laser and, then, measurements of the 20\( \nu_0 \)-00\( \nu_0 \) OCS band at 6 μm with respect to a CO laser. It is anticipated that our frequency difference range will be expanded by using the detector in the varactor mode.

We acknowledge useful discussion with W. B. Olson of NASA Upper Atmospheric Research Office.
References
13. H. Flicker, Los Alamos Scientific Laboratories; private communication (LASL is one of the largest users of TDL).