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U. S. DEPARTMENT OF COMMERCE/Technology Administration
National Institute of Standards and Technology

*Standard Reference Materials®*

# Carbon Monoxide Absorption References for 1560 nm to 1630 nm Wavelength Calibration — SRM 2514 ($^{12}C^{16}O$) and SRM 2515 ($^{13}C^{16}O$)

**S. L. Gilbert and W. C. Swann**

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# Carbon Monoxide Absorption References for 1560 nm to 1630 nm Wavelength Calibration – SRM 2514 ($^{12}C^{16}O$) and SRM 2515 ($^{13}C^{16}O$)

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## Abstract

Standard Reference Materials (SRMs) 2514 and 2515 are optical-fiber-coupled wavelength references based on the fundamental absorption lines of carbon monoxide $^{12}C^{16}O$ and $^{13}C^{16}O$ in the 1560 nm to 1630 nm region. The center wavelengths of 41 lines of the 3ν rotational-vibrational band of carbon monoxide $^{12}C^{16}O$ are certified for SRM 2514, and the center wavelengths of 41 lines in the corresponding band of $^{13}C^{16}O$ are certified for SRM 2515. These lines are certified with expanded uncertainties (2σ) ranging from 0.4 to 0.7 pm. This document describes SRMs 2514 and 2515 and details the uncertainty analysis.

Keywords: absorption; carbon monoxide; CO; molecular spectroscopy; optical fiber communications; pressure broadening; pressure shift; Standard Reference Material; wavelength calibration; wavelength division multiplexing; wavelength reference; wavelength standards; WDM

# 1. Introduction

Wavelength division multiplexing (WDM) in optical fiber communication systems increases bandwidth by using many wavelength channels. Current WDM systems typically employ 50 or 100 GHz channel spacing (0.4 or 0.8 nm, respectively) in the 1530–1560 nm WDM C-band, and WDM is expanding into the L-band region (approximately 1565–1625 nm). Wavelength references are needed in these regions to calibrate instruments that are used to characterize components and monitor the wavelengths of the channels. To complement our wavelength calibration references for the WDM C-band (Standard Reference Materials SRM 2517a and SRM 2519) [1,2], we have developed SRMs 2514 and 2515, carbon monoxide $^{12}C^{16}O$ and $^{13}C^{16}O$, respectively. SRM 2514 is for use as a wavelength reference in the 1560–1595 nm region and SRM 2515 is for use in the 1595–1630 nm region. This document describes SRMs 2514 and 2515 and summarizes the results of our uncertainty analysis.

Fundamental atomic or molecular absorption lines provide wavelength references that are very stable under changing environmental conditions, such as temperature and pressure variations or the presence of electromagnetic fields. The carbon monoxide $^{12}C^{16}O$ 3ν rotational-vibrational combination band, shown in Fig. 1a, contains about 40 absorption lines between 1560 nm and 1595 nm. The $^{13}C^{16}O$ isotopic species of carbon monoxide, shown in Fig 1b, has about 40 absorption lines between 1595 nm and 1630 nm

Standard Reference Material 2514 is intended for wavelength calibration in the spectral region from 1560 nm to 1595 nm. The unit contains a 20 cm long borosilicate glass cell filled to a pressure of 133 kPa (1000 Torr) with high purity (99.95 %) $^{12}C^{16}O$ gas. The gas is contained in the cell with all-glass seals at the windows and the fill port. Before filling, the cell window seals are inspected and leak-tested by the manufacturer. To reduce optical loss and interference fringes the cell windows are antireflection coated, wedged by about 1°, and fused to the cell body at an angle of 5°. Light from a singlemode optical fiber is collimated into a free beam, and then passes through the cell in a four-pass configuration, yielding an 80 cm path length. Figure 2 shows a schematic diagram of the fiber-pigtailed SRM cell holder. The cell holder is packaged in a small instrument box (approximately 32 cm long × 12.5 cm wide × 9 cm high) with two FC/PC fiber connectors for the input and output of a user-supplied light source. When measured using a narrowband source, such as a tunable laser, the 80 cm path length provides lines with depths ranging from a few percent to 18 % and widths of 0.04 nm to 0.06 nm. When measured using an optical spectrum analyzer (OSA) set at 0.05 nm resolution bandwidth, the maximum line depth is reduced to about 14 %; this depth is further reduced to about 9 % when measured using an OSA set at 0.1 nm resolution bandwidth. The certificate for SRM 2514 is presented in Appendix A. It includes the certified wavelength values, spectra, and instructions for use.

Standard Reference Material 2515 is intended for wavelength calibration in the spectral region from 1595 nm to 1630 nm. The unit contains a 20 cm long borosilicate glass cell filled to a pressure of 133 kPa (1000 Torr) with high purity (99%) $^{13}C^{16}O$ gas. The optical packaging is identical to that described above for SRM 2514 and provides similar line strengths and widths. The certificate for SRM 2515 is presented in Appendix B.

The vacuum wavelengths of selected $^{12}C^{16}O$ 3ν lines have been measured and tabulated for very low pressure conditions with an uncertainty of about 8 x $10^{-6}$ nm [3]. The HITRAN database [4] values for $^{12}C^{16}O$ agree with those in Ref. [3] to within 0.02 pm. The predicted line centers of $^{13}C^{16}O$ 3ν lines are also reported in the HITRAN database [4]. Our measurements of 18 line centers in the $^{13}C^{16}O$ spectrum [5] show excellent agreement (within 0.14 pm) with the HITRAN data. For a wavelength reference, the stability of the wavelength of each absorption line is a critical characteristic. The largest potential source of line shift is energy level shifts caused by the interaction of the molecules during elastic collisions [6]. Commonly called the pressure shift, this shift depends linearly on the collision frequency. For wavelength calibration of instruments, it is often desirable to use a moderate or high pressure sample in order to pressure-broaden the lines and match the reference bandwidth to the instrumental resolution. This results in the strongest signals for a given resolution bandwidth. To provide maximum sensitivity when used with a 0.05 nm resolution instrument, such as an OSA, we chose a pressure of 133 kPa. Our measurement of the pressure-induced shift and broadening for 14 lines in the 3ν rotational-vibrational band of carbon monoxide $^{12}C^{16}O$ and 18 lines in the corresponding $^{13}C^{16}O$ band is described in Ref. 5 (Appendix C of this document).

The dominant source of uncertainty for SRMs 2514 and 2515 is the pressure shift uncertainty. Other potential sources of uncertainty are negligible at the level of uncertainty quoted for the line centers. For example, a slope or variation in the background level can shift the apparent center of a line. Nearby absorption lines, interference fringes due to reflected laser light, wavelength dependence of the optical components, and variations in the optical source spectrum can cause background variation. We found no evidence of nearby absorption lines in either spectrum. As discussed above, interference fringes were minimized in the SRM design. Each SRM unit is carefully aligned to reduce background slope. For higher accuracy applications, the instructions for use in the SRM Certificate caution the user to divide the SRM output spectrum by the source spectrum.

Section 2 gives the uncertainty analysis for the pressure shift adjustment. We summarize the results in section 3.

## 2. Pressure Shift Adjustment

SRM 2514 uses carbon monoxide $^{12}C^{16}O$ gas at a pressure of 133 ± 27 kPa (1000 ± 200 Torr). We have accurately measured the pressure shift for 14 lines in the 3ν rotational-vibrational band of $^{12}C^{16}O$ [5]. For SRM 2514, we derive the line centers by adding each line's pressure shift (at 133 kPa) to the low-pressure literature values [4]. SRM 2515 uses carbon monoxide $^{13}C^{16}O$ gas at a pressure of 133 ± 27 kPa. We have accurately measured the pressure shift for 18 lines in the 3ν rotational-vibrational band of $^{13}C^{16}O$ [5] and derive the line centers for SRM 2515 by adding each line's pressure shift (at 133 kPa) to the low-pressure literature values [4].

The uncertainties quoted in this document are specified as either *standard uncertainties* (i.e., 1σ values) or *expanded uncertainties* using a coverage factor of 2 (i.e., 2σ values). If no specification is given, the uncertainties quoted are expanded uncertainties.

Figures 3 and 4 show the results of our pressure shift measurements. The pressure shift varies with line number and is largest for lines far from the band center (transitions between states with high rotational quantum number). The two isotopic species showed nearly identical shift behavior, with a shift coefficient of about +0.01 pm/kPa (equivalently, $+1.3\times10^{-3}$ pm/Torr or −0.16 MHz/Torr) near the band center, and about 0.02 pm/kPa (equivalently, $+2.7\times10^{-3}$ pm/Torr or −0.31 MHz/Torr) for lines further from the band center. As discussed in Ref. [5], our shift coefficient values for $^{12}C^{16}O$ have lower uncertainty and are in good agreement with previous measurements [3,7]. To our knowledge, there are no other measurements of the pressure shift of $^{13}C^{16}O$ absorption lines reported in the literature.

For the remainder of the lines in the band, we derive pressure shift coefficient values using linear interpolation between the measured data points. Since we do not have a quantitative theoretical model for the pressure shift of carbon monoxide, we assign a higher uncertainty to these interpolated values. We assume that there is a 95 % probability that the shift coefficient values for the intermediate lines lie between the values bounded by the upper and lower extents of the expanded ($2\sigma$) uncertainties of the bracketing measured values. This yields an interpolation standard uncertainty of $a/2$, where the range bounded by the expanded uncertainties of the bracketing measured values is $2a$ [8]. We combine this (in quadrature) with the uncertainty of the bracketing measured values to obtain the combined standard uncertainty of the pressure shift coefficient for the interpolated values. In the case where the uncertainties for the bracketed measured values are different, we use the larger uncertainty in this calculation. For example, we measured the shift coefficients for lines R21 and R16 in $^{12}C^{16}O$ (see Table 1). We assume that there is a 95 % probability that the shift coefficients for intermediate lines lie between $(0.0157 - 2 \times 0.0009)$ and $(0.0188 + 2 \times 0.0010)$ pm/kPa, and assign an interpolation standard uncertainty of $[0.0188 + 2 \times 0.0010 - (0.0157 - 2 \times 0.0009)]/4 = 0.0017$ pm/kPa. This is then combined in quadrature with the larger of the bracketing measured value's standard uncertainty (0.0010 pm/kPa) to yield a shift coefficient standard uncertainty of 0.0020 pm/kPa for lines R17, R18, R19, and R20. We compared our interpolated pressure shift coefficient values for $^{12}C^{16}O$ with previous measurements [3,7] and find that they agree within the quoted uncertainties.

There are two components of the pressure shift uncertainty for the SRMs: the component arising from the pressure shift coefficient uncertainty (described above) and the component arising from the uncertainty of the pressure within the absorption cell ($P = 133 \pm 27$ kPa). We add these two components in quadrature to obtain the pressure shift uncertainty for each certified line. The pressure shift coefficient values, the pressure shift at the SRM pressure of 133 ± 27 kPa, and the respective uncertainties are tabulated in Tables 1 and 2.

## 3. Sensitivity to Other Environmental Conditions

We evaluated molecular absorption line center sensitivity to temperature changes and electromagnetic fields in Ref. [9] and concluded that these effects are small compared with the pressure shift. Due to the fact that the pressure shift depends on the molecular collision rate, there is a small dependence of the pressure shift on temperature:

$$\Delta l\,(T) = \Delta l\,(T_m)\sqrt{\frac{T}{T_m}}\,,$$

where $\Delta\lambda(T)$ is the pressure shift at temperature T, $\Delta\lambda(T_m)$ is the pressure shift measured at temperature $T_m$, and the temperatures T and $T_m$ are in degrees Kelvin. From the above equation it can be seen that a line center is fairly insensitive to temperature changes; a 50 °C increase from room temperature would increase the pressure shift by only 8 %. This corresponds to a maximum shift change of only 0.2 pm. To avoid thermal stress of the optical packaging, we recommend that the SRM units be used and stored near ambient room temperature (22 ± 5 ºC).

## 4. NIST Certification Procedure

The purpose of the SRM certification procedure is to verify that the unit (a) contains the correct pressure of the appropriate isotopic species of carbon monoxide gas, (b) has no significant contaminants, and (c) shows no evidence of cell leakage. Measurements of the spectral band, similar to those shown in Figure 1 of the certificates (Appendices A and B), are made using a broadband source and an optical spectrum analyzer. Higher resolution measurements are made using a tunable diode laser (~1 MHz linewidth) and a calibrated wavelength meter; spectra similar to those shown in Figure 3 of the certificates are taken of each SRM unit, and one or more lines are accurately fit to verify the line's center and width using the procedure described in Ref. [5]. To test for cell leakage, the higher resolution measurements described above are repeated after a minimum waiting period of one month, and the results are compared to the earlier data. Any differences between the two data sets, particularly the linewidth values, may indicate cell leakage. This test is repeated on any suspicious unit, and the unit is rejected if it continues to change or does not meet the line center specifications.

## 5. Summary

Tables 3 and 4 give the SRM certified wavelengths for 41 lines of the 3ν rotational-vibrational band of $^{12}C^{16}O$ (Table 3; SRM 2514) and 41 lines of the 3ν rotational-vibrational band of $^{13}C^{16}O$ (Table 4; SRM 2515). The lines are certified with expanded uncertainties (2σ) ranging from 0.4 pm to 0.7 pm.

Sample certificates for SRMs 2514 and 2515 are presented in Appendices A and B. The certificates include the certified wavelength values, spectra, and instructions for use. Appendix C gives details of our pressure shift and pressure broadening measurements.

## 6. References

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**Table 1.** Pressure Shift of $^{12}C^{16}O$ Lines
Pressure shift coefficients and pressure shifts at SRM 2514 pressure of 133 ± 27 kPa for lines in the 3ν band of $^{12}C^{16}O$. The lines measured at NIST [5] are indicated in bold. The other line values are interpolated from the measured values. The pressure shift uncertainty is the quadrature combination of the contribution from the pressure shift coefficient uncertainty and the contribution from the cell pressure uncertainty.

| line | pressure shift coefficient pm/kPa | coefficient standard uncertainty (1σ) pm/kPa | pressure shift at 133 kPa pm | shift expanded uncertainty (2σ) pm |
|---|---|---|---|---|
| **R21** | **0.0188** | **0.0010** | **2.50** | **0.57** |
| R20 | 0.0182 | 0.0020 | 2.42 | 0.72 |
| R19 | 0.0176 | 0.0020 | 2.34 | 0.71 |
| R18 | 0.0169 | 0.0020 | 2.25 | 0.70 |
| R17 | 0.0163 | 0.0020 | 2.17 | 0.69 |
| **R16** | **0.0157** | **0.0009** | **2.09** | **0.48** |
| R15 | 0.0156 | 0.0012 | 2.08 | 0.52 |
| R14 | 0.0156 | 0.0012 | 2.07 | 0.52 |
| R13 | 0.0155 | 0.0012 | 2.06 | 0.51 |
| **R12** | **0.0154** | **0.0004** | **2.05** | **0.42** |
| R11 | 0.0153 | 0.0007 | 2.03 | 0.44 |
| R10 | 0.0151 | 0.0007 | 2.01 | 0.44 |
| R9 | 0.0150 | 0.0007 | 1.99 | 0.44 |
| R8 | 0.0148 | 0.0007 | 1.97 | 0.43 |
| **R7** | **0.0147** | **0.0003** | **1.96** | **0.40** |
| R6 | 0.0142 | 0.0009 | 1.88 | 0.45 |
| R5 | 0.0136 | 0.0009 | 1.81 | 0.44 |
| **R4** | **0.0131** | **0.0005** | **1.74** | **0.37** |
| R3 | 0.0124 | 0.0014 | 1.64 | 0.51 |
| R2 | 0.0116 | 0.0014 | 1.55 | 0.49 |
| **R1** | **0.0109** | **0.0008** | **1.45** | **0.36** |
| **R0** | **0.0097** | **0.0010** | **1.29** | **0.37** |
| **P1** | **0.0112** | **0.0010** | **1.49** | **0.40** |
| **P2** | **0.0115** | **0.0009** | **1.53** | **0.39** |
| P3 | 0.0127 | 0.0017 | 1.69 | 0.56 |
| **P4** | **0.0139** | **0.0007** | **1.85** | **0.41** |
| P5 | 0.0146 | 0.0013 | 1.94 | 0.52 |
| P6 | 0.0152 | 0.0013 | 2.03 | 0.53 |
| **P7** | **0.0159** | **0.0005** | **2.11** | **0.44** |
| P8 | 0.0162 | 0.0012 | 2.16 | 0.53 |
| P9 | 0.0166 | 0.0012 | 2.20 | 0.54 |
| P10 | 0.0169 | 0.0012 | 2.24 | 0.54 |
| **P11** | **0.0172** | **0.0007** | **2.29** | **0.49** |
| P12 | 0.0174 | 0.0014 | 2.32 | 0.59 |
| P13 | 0.0177 | 0.0014 | 2.35 | 0.59 |
| P14 | 0.0179 | 0.0014 | 2.38 | 0.60 |
| **P15** | **0.0181** | **0.0009** | **2.41** | **0.54** |
| P16 | 0.0184 | 0.0016 | 2.44 | 0.64 |
| P17 | 0.0186 | 0.0016 | 2.47 | 0.65 |
| P18 | 0.0189 | 0.0016 | 2.51 | 0.65 |
| **P19** | **0.0191** | **0.0010** | **2.54** | **0.57** |

**Table 2.** Pressure Shift of $^{13}C^{16}O$ Lines
Pressure shift coefficients and pressure shifts at SRM 2515 pressure of 133 ± 27 kPa for lines in the 3ν band of $^{13}C^{16}O$. The lines measured at NIST [5] are indicated in bold. The other line values are interpolated from the measured values. The pressure shift uncertainty is the quadrature combination of the contribution from the pressure shift coefficient uncertainty and the contribution from the cell pressure uncertainty.

| line | pressure shift coefficient pm/kPa | coefficient standard uncertainty (1σ) pm/kPa | pressure shift at 133 kPa pm | shift expanded uncertainty (2σ) pm |
|---|---|---|---|---|
| **R21** | **0.0200** | **0.0010** | **2.66** | **0.59** |
| R20 | 0.0196 | 0.0012 | 2.60 | 0.68 |
| R19 | 0.0191 | 0.0012 | 2.54 | 0.67 |
| **R18** | **0.0187** | **0.0010** | **2.49** | **0.56** |
| R17 | 0.0178 | 0.0017 | 2.37 | 0.69 |
| R16 | 0.0169 | 0.0017 | 2.25 | 0.68 |
| **R15** | **0.0160** | **0.0009** | **2.13** | **0.49** |
| R14 | 0.0160 | 0.0009 | 2.13 | 0.53 |
| R13 | 0.0160 | 0.0009 | 2.13 | 0.53 |
| **R12** | **0.0160** | **0.0006** | **2.13** | **0.45** |
| R11 | 0.0156 | 0.0007 | 2.07 | 0.49 |
| **R10** | **0.0152** | **0.0006** | **2.02** | **0.43** |
| R9 | 0.0152 | 0.0006 | 2.02 | 0.45 |
| R8 | 0.0152 | 0.0006 | 2.02 | 0.45 |
| **R7** | **0.0152** | **0.0004** | **2.02** | **0.42** |
| R6 | 0.0146 | 0.0011 | 1.94 | 0.49 |
| R5 | 0.0140 | 0.0011 | 1.86 | 0.48 |
| **R4** | **0.0134** | **0.0006** | **1.78** | **0.39** |
| R3 | 0.0125 | 0.0015 | 1.66 | 0.58 |
| R2 | 0.0115 | 0.0015 | 1.53 | 0.57 |
| **R1** | **0.0106** | **0.0010** | **1.41** | **0.39** |
| **R0** | **0.0101** | **0.0010** | **1.34** | **0.38** |
| **P1** | **0.0111** | **0.0010** | **1.48** | **0.40** |
| **P2** | **0.0118** | **0.0010** | **1.57** | **0.41** |
| P3 | 0.0127 | 0.0013 | 1.69 | 0.56 |
| **P4** | **0.0136** | **0.0008** | **1.81** | **0.42** |
| P5 | 0.0146 | 0.0017 | 1.95 | 0.60 |
| P6 | 0.0157 | 0.0017 | 2.08 | 0.62 |
| **P7** | **0.0167** | **0.0007** | **2.22** | **0.48** |
| P8 | 0.0169 | 0.0007 | 2.25 | 0.53 |
| **P9** | **0.0171** | **0.0007** | **2.27** | **0.49** |
| P10 | 0.0178 | 0.0010 | 2.36 | 0.58 |
| **P11** | **0.0184** | **0.0007** | **2.45** | **0.52** |
| P12 | 0.0180 | 0.0009 | 2.39 | 0.58 |
| **P13** | **0.0175** | **0.0008** | **2.33** | **0.51** |
| P14 | 0.0180 | 0.0013 | 2.40 | 0.65 |
| P15 | 0.0186 | 0.0013 | 2.47 | 0.66 |
| **P16** | **0.0191** | **0.0010** | **2.54** | **0.57** |
| P17 | 0.0197 | 0.0013 | 2.62 | 0.70 |
| P18 | 0.0203 | 0.0013 | 2.70 | 0.71 |
| **P19** | **0.0209** | **0.0010** | **2.78** | **0.62** |

**Table 3. Certified Wavelengths for SRM 2514 ($^{12}C^{16}O$)**
Literature values from Ref. [4] adjusted for the pressure shift listed in Table 1 due to the 133 kPa (1000 Torr) cell pressure. These vacuum wavelengths of the 3ν band of $^{12}C^{16}O$ are certified with the uncertainty indicated in parentheses for the last digits. The uncertainties quoted are the expanded uncertainty using a coverage factor $k = 2$ (i.e., our quoted uncertainty is $\pm 2\sigma$).

| R Branch | Wavelength (nm) | P Branch | Wavelength (nm) |
|---|---|---|---|
| 21 | 1560.5025(6) | 1 | 1575.6498(4) |
| 20 | 1560.8680(7) | 2 | 1576.6311(4) |
| 19 | 1561.2600(7) | 3 | 1577.6397(6) |
| 18 | 1561.6786(7) | 4 | 1578.6758(4) |
| 17 | 1562.1237(7) | 5 | 1579.7392(5) |
| 16 | 1562.5953(5) | 6 | 1580.8300(5) |
| 15 | 1563.0935(5) | 7 | 1581.9485(4) |
| 14 | 1563.6183(5) | 8 | 1583.0945(5) |
| 13 | 1564.1697(5) | 9 | 1584.2683(5) |
| 12 | 1564.7477(4) | 10 | 1585.4698(5) |
| 11 | 1565.3523(4) | 11 | 1586.6993(5) |
| 10 | 1565.9835(4) | 12 | 1587.9567(6) |
| 9 | 1566.6414(4) | 13 | 1589.2422(6) |
| 8 | 1567.3261(4) | 14 | 1590.5559(6) |
| 7 | 1568.0375(4) | 15 | 1591.8978(5) |
| 6 | 1568.7756(5) | 16 | 1593.2681(6) |
| 5 | 1569.5405(4) | 17 | 1594.6669(6) |
| 4 | 1570.3323(4) | 18 | 1596.0942(7) |
| 3 | 1571.1509(5) | 19 | 1597.5502(6) |
| 2 | 1571.9965(5) | | |
| 1 | 1572.8691(4) | | |
| 0 | 1573.7687(4) | | |

**Table 4. Certified Wavelengths for SRM 2515 ($^{13}C^{16}O$)**
Literature values from Ref. [4] adjusted for the pressure shift listed in Table 2 due to the 133 kPa (1000 Torr) cell pressure. These vacuum wavelengths of the 3ν band of $^{13}C^{16}O$ are certified with the uncertainty indicated in parentheses for the last digits. The uncertainties quoted are the expanded uncertainty using a coverage factor $k = 2$ (i.e., our quoted uncertainty is $\pm 2\sigma$).

| R Branch | Wavelength (nm) | P Branch | Wavelength (nm) |
|---|---|---|---|
| 21 | 1595.3772(6) | 1 | 1610.6596(4) |
| 20 | 1595.7554(7) | 2 | 1611.6393(4) |
| 19 | 1596.1595(7) | 3 | 1612.6457(6) |
| 18 | 1596.5895(6) | 4 | 1613.6788(4) |
| 17 | 1597.0454(7) | 5 | 1614.7388(6) |
| 16 | 1597.5271(7) | 6 | 1615.8255(6) |
| 15 | 1598.0349(5) | 7 | 1616.9392(5) |
| 14 | 1598.5686(5) | 8 | 1618.0797(5) |
| 13 | 1599.1284(5) | 9 | 1619.2473(5) |
| 12 | 1599.7141(5) | 10 | 1620.4420(6) |
| 11 | 1600.3258(5) | 11 | 1621.6641(5) |
| 10 | 1600.9636(4) | 12 | 1622.9132(6) |
| 9 | 1601.6274(5) | 13 | 1624.1898(5) |
| 8 | 1602.3174(5) | 14 | 1625.4940(6) |
| 7 | 1603.0334(4) | 15 | 1626.8257(7) |
| 6 | 1603.7756(5) | 16 | 1628.1851(6) |
| 5 | 1604.5439(5) | 17 | 1629.5723(7) |
| 4 | 1605.3385(4) | 18 | 1630.9873(7) |
| 3 | 1606.1593(6) | 19 | 1632.4303(6) |
| 2 | 1607.0064(6) | | |
| 1 | 1607.8799(4) | | |
| 0 | 1608.7799(4) | | |

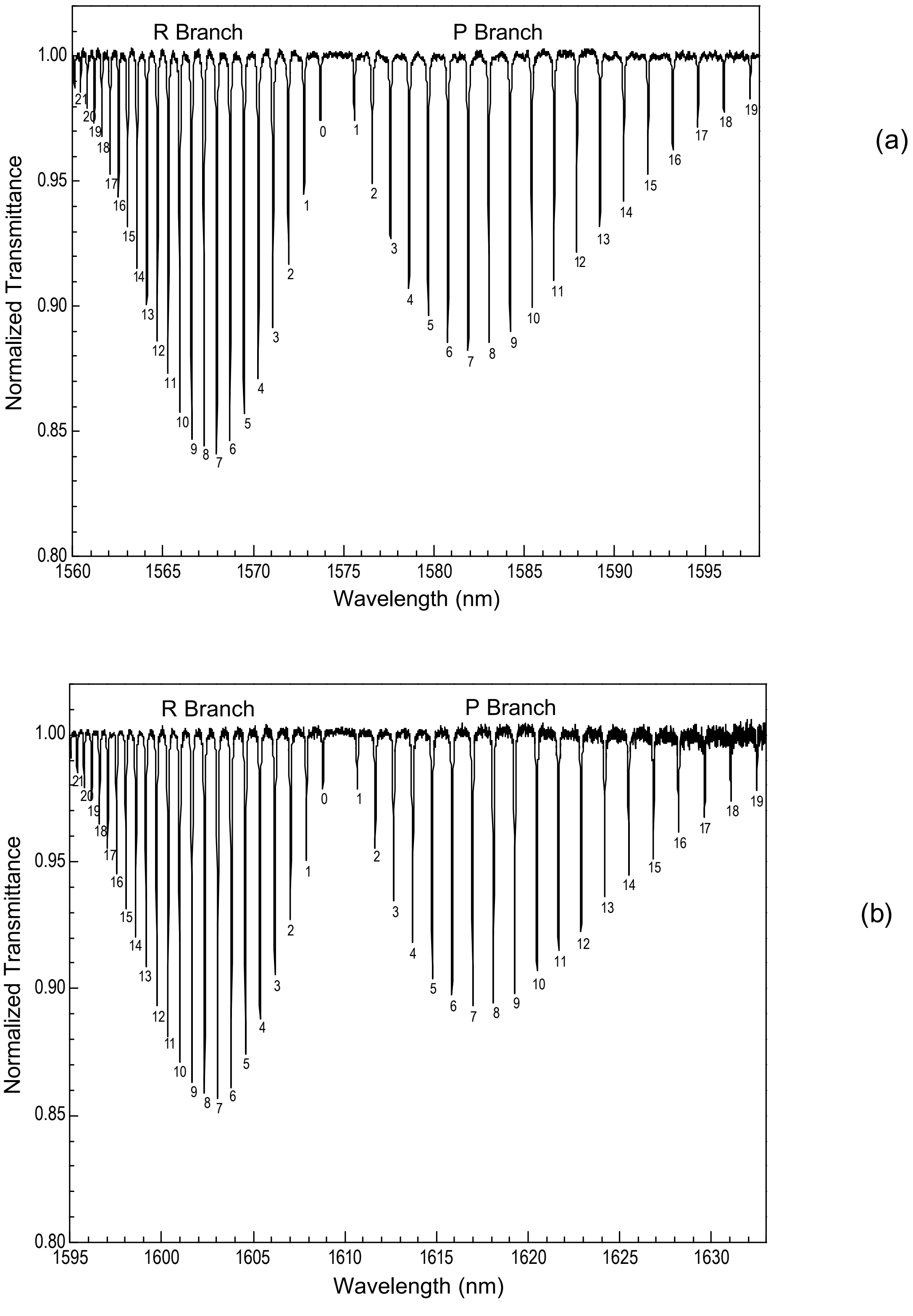

**Figure 1.** Carbon monoxide 3ν rotational-vibrational spectra; (a) $^{12}C^{16}O$ spectrum, (b) $^{13}C^{16}O$ spectrum. Data were taken by passing LED light through an absorption cell and recording the spectrum of the transmitted light using an optical spectrum analyzer set to a resolution bandwidth of 0.05 nm. The figure shows the recorded spectrum divided by the LED spectrum. The CO gas pressure is 133 kPa (1000 Torr); light makes four passes through the cell for a total optical path length of 80 cm.

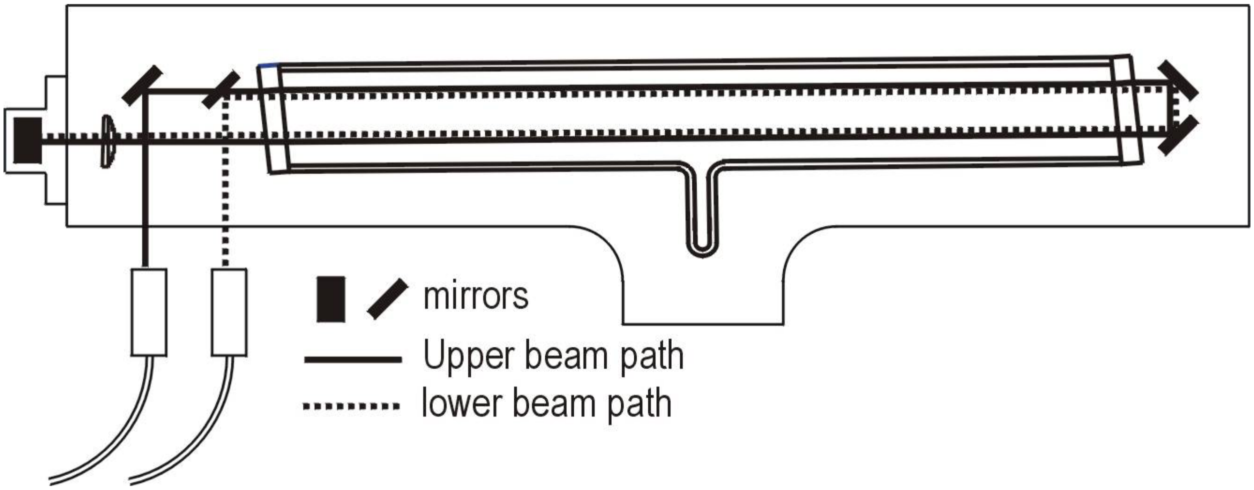

**Figure 2.** Schematic diagram of the fiber-pigtailed SRM cell holder. The light beam path is shown in solid and dashed lines; the mirror on the left end directs the beam down to the lower beam path. The absorption cell length is 20 cm and the light makes four passes through the cell for a total optical beam path of 80 cm.

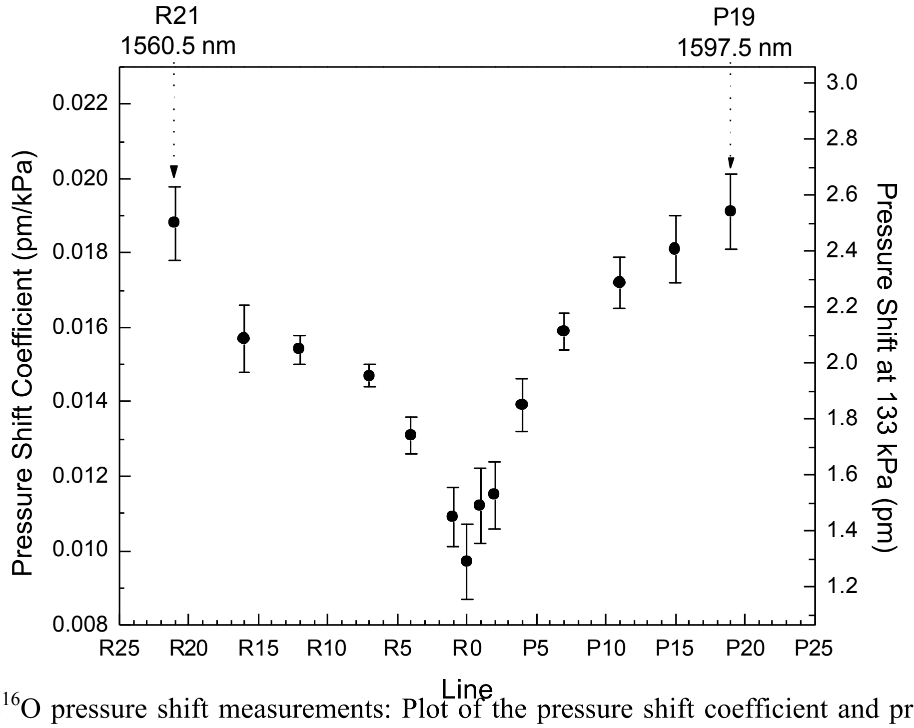

**Figure 3.** $^{12}C^{16}O$ pressure shift measurements: Plot of the pressure shift coefficient and pressure shift at the SRM pressure of 133 kPa versus line number for the R and P branches of the 3ν band. Data are from Ref. [5].

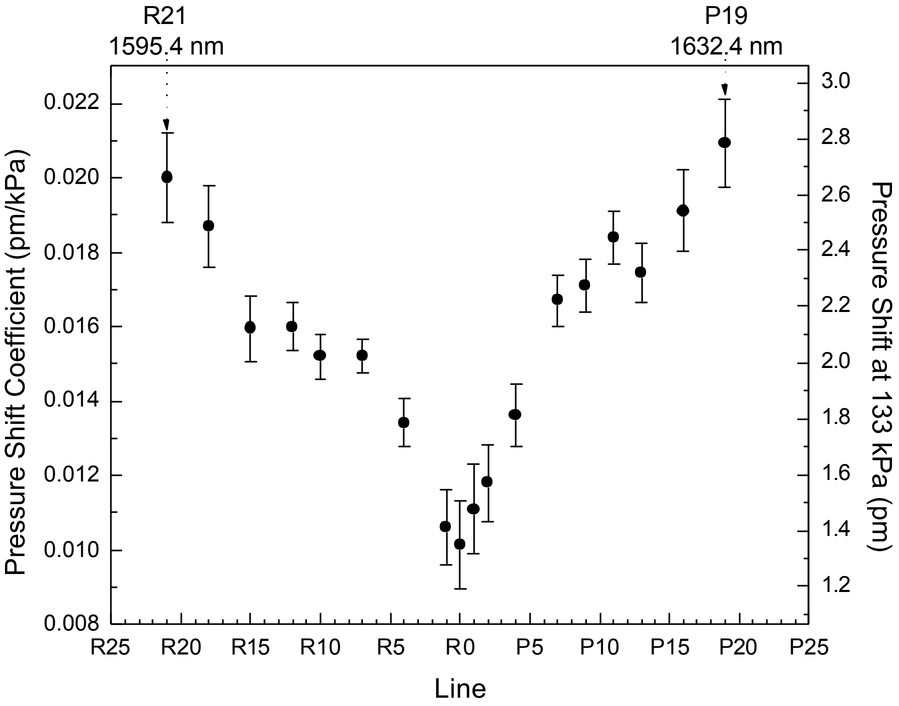

**Figure 4.** $^{13}C^{16}O$ pressure shift measurements: Plot of the pressure shift coefficient and pressure shift at the SRM pressure of 133 kPa versus line number for the R and P branches of the 3ν band. Data are from Ref. [5].

## Appendix A

SRM 2514 Certificate

## Appendix B

SRM 2515 Certificate

## Appendix C

Journal Article:
W.C. Swann and S.L. Gilbert, “Pressure-induced shift and broadening of 1560–1630-nm carbon monoxide wavelength-calibration lines,” J. Opt. Soc. Am. B **19**, 2461-2467 (2002).

National Institute of Standards & Technology

# Certificate of Analysis

## Standard Reference Material® 2514

## Wavelength Calibration Reference for 1560 nm to 1595 nm (Carbon Monoxide $^{12}C^{16}O$)

Serial No.:

This Standard Reference Material (SRM) is intended for wavelength calibration in the spectral region from 1560 nm to 1595 nm. SRM 2514 is a single-mode optical-fiber-coupled absorption cell containing carbon monoxide ($^{12}C^{16}O$) gas at a pressure of 133 kPa (1000 Torr). The absorption path length is 80 cm and the absorption lines are about 50 pm wide. The cell is packaged in a small instrument box (approximately 32 cm long x 12.5 cm wide x 9 cm high) with two FC/PC fiber connectors for the input and output of a user-supplied light source. This SRM can be used for calibrating a variety of wavelength-measuring instruments, such as optical spectrum analyzers, tunable lasers, and wavelength meters. Carbon monoxide $^{12}C^{16}O$ has about 40 accurately measured absorption lines in the 1560 nm to 1595 nm wavelength region.

**Certified Wavelength Values:** The vacuum wavelengths of absorption lines in the R and P branches of the 3ν rotational-vibrational band of $^{12}C^{16}O$ have been determined previously to high accuracy and are tabulated in the HITRAN database [1]. These literature values for the vacuum wavelengths were adjusted for the pressure shift due to the collisions between carbon monoxide molecules at the 133 kPa (1000 Torr) pressure within the SRM cell to obtain the certified wavelength values for this SRM. Details of the measurement procedure and data analysis for the determination of the pressure shift can be found in Reference 2, and the uncertainty analysis for the SRM is documented in Reference 3. A spectrum of the absorption band is shown in Figure 1 and certified wavelength values are given in Table 1. Figure 2 shows an expanded scan near lines R6, R7, and R8. Figure 3 shows a high resolution scan of line R7. The center wavelengths of the lines listed in Table 1 are certified with uncertainties ranging from 0.4 pm to 0.7 pm. These uncertainties are the expanded uncertainties using a coverage factor $k = 2$, i.e., our quoted uncertainty is $\pm 2\sigma$.

**Expiration of Certification:** The certification of this SRM is valid indefinitely within the measurement uncertainties specified, provided the SRM is handled, stored, and used in accordance with the instructions given in this certificate (see Instructions for Use). The gas is contained in a glass cell with all-glass seals at the windows and the fill port. In the unlikely event of cell leakage, the linewidths and the small pressure shift of the line centers will change. Contact NIST if the linewidths or depths differ significantly from those shown in Figures 1 through 3, when measured using comparable resolution (see specific criteria in the section Suggested Procedure for High-*Accuracy Requirements*).

Development of this SRM and supporting measurements were performed by W.C. Swann and S.L. Gilbert of the NIST Optoelectronics Division.

Statistical consultation was provided by C.M. Wang of the NIST Statistical Engineering Division.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by J.W.L. Thomas.

Gordon W. Day, Chief
Optoelectronics Division

Gaithersburg, MD 20899
Certificate Issue Date: 17 May 2002

John Rumble, Jr., Acting Chief
Standard Reference Materials Program

Table 1. Certified Wavelengths for SRM 2514

Literature values from Reference 1 adjusted for the pressure shift due to the 133 kPa (1000 Torr) cell pressure. These vacuum wavelengths of the 3ν band of $^{12}C^{16}O$ are certified with the uncertainty indicated in parenthesis for the last digits. The uncertainties quoted are the expanded uncertainty using a coverage factor *k* = 2, i.e., our quoted uncertainty is ± 2σ.

| R Branch | Wavelength (nm) | P Branch | Wavelength (nm) |
|---|---|---|---|
| 21 | 1560.5025(6) | 1 | 1575.6498(4) |
| 20 | 1560.8680(7) | 2 | 1576.6311(4) |
| 19 | 1561.2600(7) | 3 | 1577.6397(6) |
| 18 | 1561.6786(7) | 4 | 1578.6758(4) |
| 17 | 1562.1237(7) | 5 | 1579.7392(5) |
| 16 | 1562.5953(5) | 6 | 1580.8300(5) |
| 15 | 1563.0935(5) | 7 | 1581.9485(4) |
| 14 | 1563.6183(5) | 8 | 1583.0945(5) |
| 13 | 1564.1697(5) | 9 | 1584.2683(5) |
| 12 | 1564.7477(4) | 10 | 1585.4698(5) |
| 11 | 1565.3523(4) | 11 | 1586.6993(5) |
| 10 | 1565.9835(4) | 12 | 1587.9567(6) |
| 9 | 1566.6414(4) | 13 | 1589.2422(6) |
| 8 | 1567.3261(4) | 14 | 1590.5559(6) |
| 7 | 1568.0375(4) | 15 | 1591.8978(5) |
| 6 | 1568.7756(5) | 16 | 1593.2681(6) |
| 5 | 1569.5405(4) | 17 | 1594.6669(6) |
| 4 | 1570.3323(4) | 18 | 1596.0942(7) |
| 3 | 1571.1509(5) | 19 | 1597.5502(6) |
| 2 | 1571.9965(5) | | |
| 1 | 1572.8691(4) | | |
| 0 | 1573.7687(4) | | |

**Storage and Handling:** The protective caps provided for the FC/PC fiber connectors should be replaced when the SRM is not in use. This SRM is intended to be used in a laboratory environment near ambient room temperature (22 °C ± 5 °C). The user should avoid exposing the unit to large temperature variations, temperature cycling, or mechanical shock, as these may cause the optical alignment to degrade. Such optical misalignment affects the throughput of the SRM but will not shift the centers of the absorption lines.

**Certification Measurement Conditions and Procedure:** The long term stability of carbon monoxide and the use of fundamental molecular absorption lines render the SRM insensitive to changes in environmental conditions. The purpose of the certification procedure is to verify that the unit contains the correct pressure of $^{12}C^{16}O$ gas, has no significant contaminants, and shows no evidence of cell leakage. Measurements of the spectral band, similar to that shown in Figure 1, are made using a broadband source and an optical spectrum analyzer. Higher resolution measurements are made using a tunable diode laser (~1 MHz linewidth) and a calibrated wavelength meter; spectra similar to that shown in Figure 3 are taken of each SRM unit and one or more lines are accurately fit to verify the line's center and width using the procedure described in Reference 2.

## INSTRUCTIONS FOR USE

**General Considerations:** The SRM can be used to calibrate a laser or wavelength measuring instrument in the 1560 nm to 1595 nm region. The values in Table 1 are vacuum wavelengths; if the user requires the wavelength in air, the appropriate correction for the index of refraction of air must be applied (see Reference 4). Depending on what type of instrument is being calibrated, a user-supplied broadband source or a tunable narrowband source may be used. Typical optical connections are shown in Figure 4. The unit is bi-directional (has no preferred input/output port); connections to the unit should be made using single-mode optical fibers terminated with clean FC/PC connectors.

**Use With a Broadband Source:** A broadband source in the 1560 nm to 1595 nm region such as a light emitting diode, white light, or amplified spontaneous emission source is useful when calibrating an instrument, such as a diffraction grating based optical spectrum analyzer. A schematic for this type of calibration is shown in Figure 4(a). Light from the broadband source is coupled into the SRM and the output (transmission through the SRM) is connected to the instrument that is being calibrated. The absorption lines of carbon monoxide appear as dips in the spectrum of the light source.

**Use With a Tunable Source:** The SRM can be used to calibrate the wavelength scale of a tunable source in the 1560 nm to 1595 nm region (such as a diode laser, a fiber laser, or a source filtered by a tunable filter). A schematic for this type of calibration is shown in Figure 4(b). The laser is tuned over one or more of the carbon monoxide absorption lines. The transmission through the SRM is monitored by a detector; the transmitted power passes through a minimum at the center of an absorption line. Alternatively, a tunable laser source and the SRM can be used to check the calibration of a wavelength meter by measuring the wavelength of the laser (using the wavelength meter) as the laser is tuned through an absorption line.

**Suggested Procedure for Low-Accuracy Requirements; Calibration Uncertainty > 30 pm:** If calibrating an instrument using a broadband source, use an instrument resolution of ≤ 0.1 nm. If using a tunable source, use a data point density of at least one point every 0.005 nm (5 pm). After identifying a particular absorption line by comparing to the spectrum in Figure 1, find the center or minimum point of the line. Calibrate the instrument to the center wavelength of this line (from Table 1) using the calibration procedure specified by the instrument manufacturer. The instrument's linearity can be checked by repeating the procedure for a different absorption line and comparing it to the value listed in Table 1.

**Suggested Procedure for Moderate-Accuracy Requirements; Calibration Uncertainty in the Approximate Range of 3 pm to 30 pm:** If the source power varies significantly with wavelength, divide the SRM transmission spectrum by the source spectrum to obtain a normalized trace. After identifying a particular absorption line by comparing to the spectrum in Figure 1, make a high resolution scan of the line. If calibrating an instrument using a broadband source, use an instrument resolution of ≤ 0.05 nm. If using a tunable source, use a data point density of at least one point every 0.002 nm (2 pm). Find the wavelength readings on both sides of the line where the absorption is 50 % of the maximum; the line center is half-way between these two wavelength readings. For higher accuracy results, repeat this procedure five times and take the average of the measurements. Alternatively, the line center can be determined by fitting the central portion using a fourth order polynomial function. Calibrate the instrument to the center wavelength of this line (from Table 1) using the calibration procedure specified by the instrument manufacturer. The instrument's linearity can be checked by repeating the procedure for a different absorption line and comparing it to the value listed in Table 1.

**NOTE:** Highly reproducible *relative* wavelength measurements can be made using the procedure described for moderate-accuracy requirements. However, the procedure described in the following section is recommended to achieve high-accuracy *absolute* wavelength calibration.

**Suggested Procedure for High-Accuracy Requirements; Calibration Uncertainty < 3 pm:** Connect a narrowband tunable light source (source bandwidth ≤ 1 pm) to one of the fiber connectors on the SRM unit. After identifying a particular absorption line by comparing to the spectrum in Figure 1, make a high resolution scan of the line. Use a data point density of at least one point every 1 pm and divide the SRM transmission spectrum by the source spectrum to obtain a normalized trace. Using a fitting technique such as the least squares technique, fit the absorption data to a Lorentzian or Voigt lineshape. Details of a line fitting procedure and potential errors sources can be found in Reference 2, which is also included as an appendix in Reference 3. Calibrate the instrument to the center wavelength of this line (from Table 1) using the calibration procedure specified by the instrument manufacturer. The instrument's linearity can be checked by repeating the procedure for a different absorption line and comparing it to the value listed in Table 1. Contact NIST if the width of line R7 differs by more than 25 % from the width shown in Figure 3. A large change in linewidth could indicate cell leakage.

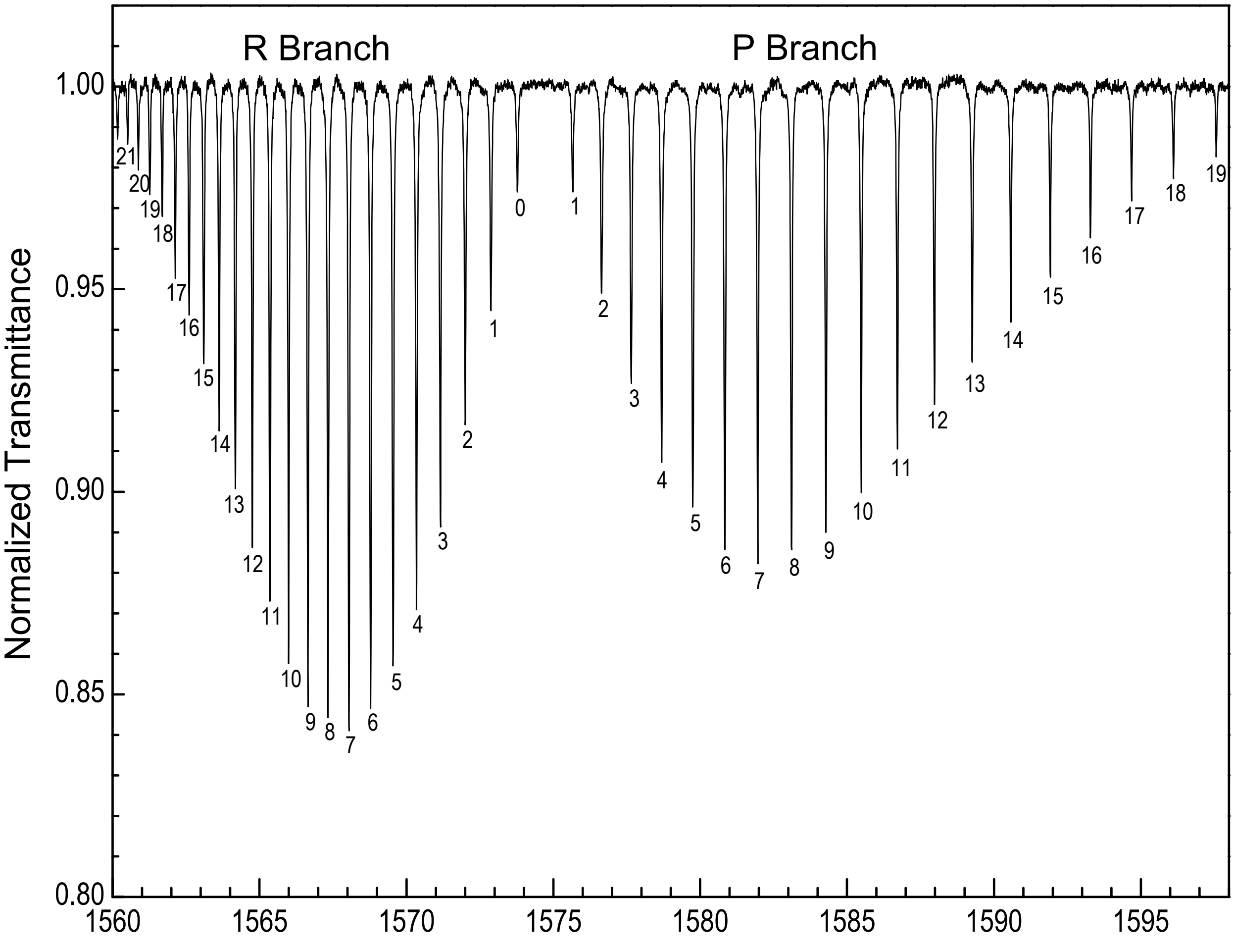

Figure 1. Normalized spectrum of the 3ν band of $^{12}C^{16}O$ obtained by passing LED light through an SRM 2514 unit and recording the spectrum of the transmitted light using an optical spectrum analyzer set to a resolution bandwidth of 0.05 nm. The figure shows the recorded spectrum divided by the LED spectrum. The $^{12}C^{16}O$ gas pressure is 133 kPa (1000 Torr); light makes four passes through a 20 cm long cell for a total optical path length of 80 cm.

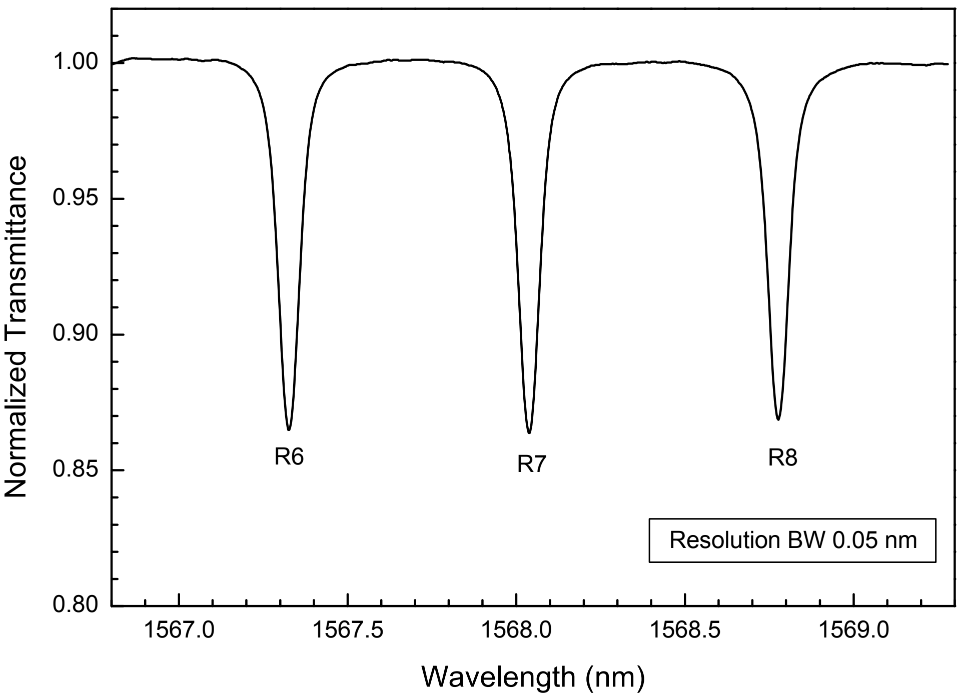

Figure 2. Spectrum of the R6, R7, and R8 lines obtained by passing LED light through an SRM 2514 unit and recording the spectrum using an optical spectrum analyzer set to a resolution bandwidth of 0.05 nm.

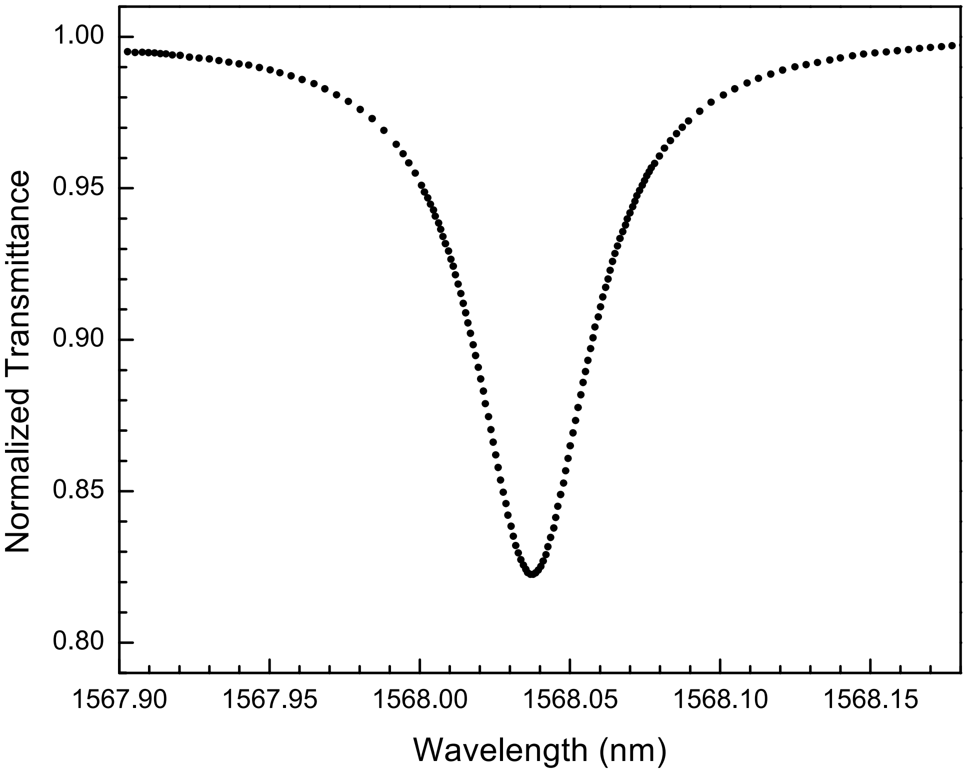

Figure 3. High resolution spectrum of line R7 obtained by passing tunable diode laser light through an SRM 2514 unit and recording the transmittance as the laser is scanned.

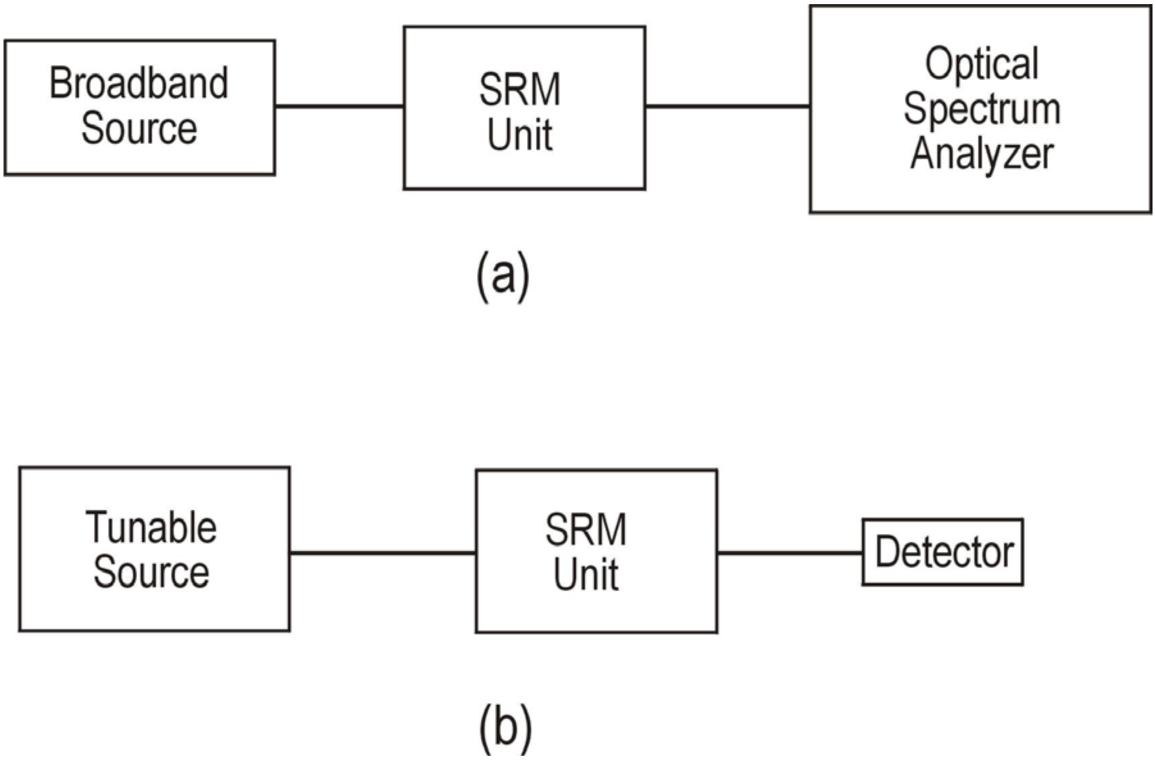

Figure 4. (a) Schematic of technique when using the SRM and a broadband source to calibrate an optical spectrum analyzer. (b) Schematic of technique when using the SRM to calibrate a tunable source. A wavelength meter can be calibrated by using a tunable laser in the configuration shown in (b) and measuring its wavelength using the wavelength meter.

## REFERENCES

[1] Rothman, L.S. et al.; *The HITRAN Molecular Spectroscopic Database and HAWKS (HITRAN atmospheric workstation): 1996 Edition*; J. Quant. Spectrosc. Rad. Transf. Vol. 60, pp. 665-710 (1998); available at http://www.hitran.com/.

[2] Swann, W.C.; Gilbert, S.L.; *Pressure-Induced Shift and Broadening of 1560–1630 nm Carbon Monoxide Wavelength Calibration Lines*; J. Opt. Soc. Am. B **19**, pp. 2461-2467 (2002). Note: This paper is included as an appendix in Reference 3 (below).

[3] Gilbert, S.L.; Swann, W.C.; *Carbon Monoxide Absorption References for 1560 nm to 1630 nm Wavelength Calibration – SRM 2514 ($^{12}C^{16}O$) and SRM 2515 ($^{13}C^{16}O$)*; NIST Special Publication 260-146.

[4] Edlen, B.; *The Refractive Index of Air, Metrologia;* Vol. 2, p. 12 (1966); CRC Handbook of Chemistry and Physics 77th Ed., pp. 10-266 (1996).

*Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.*

DEPARTMENT OF COMMERCE
UNITED STATES OF AMERICA

# National Institute of Standards & Technology

# Certificate of Analysis

## Standard Reference Material® 2515

### Wavelength Calibration Reference for 1595 nm to 1630 nm
### (Carbon Monoxide $^{13}C^{16}O$)

Serial No.:

This Standard Reference Material (SRM) is intended for wavelength calibration in the spectral region from 1595 nm to 1630 nm. SRM 2515 is a single-mode optical-fiber-coupled absorption cell containing carbon monoxide ($^{13}C^{16}O$) gas at a pressure of 133 kPa (1000 Torr). The absorption path length is 80 cm and the absorption lines are about 50 pm wide. The cell is packaged in a small instrument box (approximately 32 cm long x 12.5 cm wide x 9 cm high) with two FC/PC fiber connectors for the input and output of a user-supplied light source. This SRM can be used for calibrating a variety of wavelength-measuring instruments, such as optical spectrum analyzers, tunable lasers, and wavelength meters. Carbon monoxide $^{13}C^{16}O$ has about 40 accurately measured absorption lines in the 1595 nm to 1630 nm wavelength region.

**Certified Wavelength Values:** The vacuum wavelengths of absorption lines in the R and P branches of the $3\nu$ rotational-vibrational band of $^{13}C^{16}O$ have been determined previously to high accuracy and are tabulated in the HITRAN database [1]. These literature values for the vacuum wavelengths were adjusted for the pressure shift due to the collisions between carbon monoxide molecules at the 133 kPa (1000 Torr) pressure within the SRM cell to obtain the certified wavelength values for this SRM. Details of the measurement procedure and data analysis for the determination of the pressure shift can be found in Reference 2, and the uncertainty analysis for the SRM is documented in Reference 3. A spectrum of the absorption band is shown in Figure 1 and certified wavelength values are given in Table 1. Figure 2 shows an expanded scan near lines R6, R7, and R8. Figure 3 shows a high resolution scan of line R7. The center wavelengths of the lines listed in Table 1 are certified with uncertainties ranging from 0.4 pm to 0.7 pm. These uncertainties are the expanded uncertainties using a coverage factor $k = 2$, i.e., our quoted uncertainty is $\pm 2\sigma$.

**Expiration of Certification:** The certification of this SRM is valid indefinitely within the measurement uncertainties specified, provided the SRM is handled, stored, and used in accordance with the instructions given in this certificate (see Instructions for Use). The gas is contained in a glass cell with all-glass seals at the windows and the fill port. In the unlikely event of cell leakage, the linewidths and the small pressure shift of the line centers will change. Contact NIST if the linewidths or depths differ significantly from those shown in Figures 1 through 3, when measured using comparable resolution (see specific criteria in the section Suggested Procedure for High-Accuracy Requirements).

Development of this SRM and supporting measurements were performed by W.C. Swann and S.L. Gilbert of the NIST Optoelectronics Division.

Statistical consultation was provided by C.M. Wang of the NIST Statistical Engineering Division.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by J.W.L. Thomas.

Gordon W. Day, Chief
Optoelectronics Division

Gaithersburg, MD 20899
Certificate Issue Date: 17 May 2002

John Rumble, Jr., Acting Chief
Standard Reference Materials Program

Table 1. Certified Wavelengths for SRM 2515

Literature values from Reference 1 adjusted for the pressure shift due to the 133 kPa (1000 Torr) cell pressure. These vacuum wavelengths of the 3ν band of $^{13}C^{16}O$ are certified with the uncertainty indicated in parenthesis for the last digits. The uncertainties quoted are the expanded uncertainty using a coverage factor $k = 2$, i.e., our quoted uncertainty is $\pm 2\sigma$.

| R Branch | Wavelength (nm) | P Branch | Wavelength (nm) |
|---|---|---|---|
| 21 | 1595.3772(6) | 1 | 1610.6596(4) |
| 20 | 1595.7554(7) | 2 | 1611.6393(4) |
| 19 | 1596.1595(7) | 3 | 1612.6457(6) |
| 18 | 1596.5895(6) | 4 | 1613.6788(4) |
| 17 | 1597.0454(7) | 5 | 1614.7388(6) |
| 16 | 1597.5271(7) | 6 | 1615.8255(6) |
| 15 | 1598.0349(5) | 7 | 1616.9392(5) |
| 14 | 1598.5686(5) | 8 | 1618.0797(5) |
| 13 | 1599.1284(5) | 9 | 1619.2473(5) |
| 12 | 1599.7141(5) | 10 | 1620.4420(6) |
| 11 | 1600.3258(5) | 11 | 1621.6641(5) |
| 10 | 1600.9636(4) | 12 | 1622.9132(6) |
| 9 | 1601.6274(5) | 13 | 1624.1898(5) |
| 8 | 1602.3174(5) | 14 | 1625.4940(6) |
| 7 | 1603.0334(4) | 15 | 1626.8257(7) |
| 6 | 1603.7756(5) | 16 | 1628.1851(6) |
| 5 | 1604.5439(5) | 17 | 1629.5723(7) |
| 4 | 1605.3385(4) | 18 | 1630.9873(7) |
| 3 | 1606.1593(6) | 19 | 1632.4303(6) |
| 2 | 1607.0064(6) | | |
| 1 | 1607.8799(4) | | |
| 0 | 1608.7799(4) | | |

**Storage and Handling:** The protective caps provided for the FC/PC fiber connectors should be replaced when the SRM is not in use. This SRM is intended to be used in a laboratory environment near ambient room temperature (22 °C ± 5 °C). The user should avoid exposing the unit to large temperature variations, temperature cycling, or mechanical shock, as these may cause the optical alignment to degrade. Such optical misalignment affects the throughput of the SRM but will not shift the centers of the absorption lines.

**Certification Measurement Conditions and Procedure:** The long term stability of carbon monoxide and the use of fundamental molecular absorption lines render the SRM insensitive to changes in environmental conditions. The purpose of the certification procedure is to verify that the unit contains the correct pressure of $^{13}C^{16}O$ gas, has no significant contaminants, and shows no evidence of cell leakage. Measurements of the spectral band, similar to that shown in Figure 1, are made using a broadband source and an optical spectrum analyzer. Higher resolution measurements are made using a tunable diode laser (~1 MHz linewidth) and a calibrated wavelength meter; spectra similar to that shown in Figure 3 are taken of each SRM unit and one or more lines are accurately fit to verify the line's center and width using the procedure described in Reference 2.

## INSTRUCTIONS FOR USE

**General Considerations:** The SRM can be used to calibrate a laser or wavelength measuring instrument in the 1595 nm to 1630 nm region. The values in Table 1 are vacuum wavelengths; if the user requires the wavelength in air, the appropriate correction for the index of refraction of air must be applied (see Reference 4). Depending on what type of instrument is being calibrated, a user-supplied broadband source or a tunable narrowband source may be used. Typical optical connections are shown in Figure 4. The unit is bi-directional (has no preferred input/output port); connections to the unit should be made using single-mode optical fibers terminated with clean FC/PC connectors.

**Use With a Broadband Source:** A broadband source in the 1595 nm to 1630 nm region, such as a light emitting diode, white light, or amplified spontaneous emission source is useful when calibrating an instrument, such as a diffraction grating based optical spectrum analyzer. A schematic for this type of calibration is shown in Figure 4(a). Light from the broadband source is coupled into the SRM and the output (transmission through the SRM) is connected to the instrument that is being calibrated. The absorption lines of carbon monoxide appear as dips in the spectrum of the light source.

**Use With a Tunable Source:** The SRM can be used to calibrate the wavelength scale of a tunable source in the 1595 nm to 1630 nm region (such as a diode laser, a fiber laser, or a source filtered by a tunable filter). A schematic for this type of calibration is shown in Figure 4(b). The laser is tuned over one or more of the carbon monoxide absorption lines. The transmission through the SRM is monitored by a detector; the transmitted power passes through a minimum at the center of an absorption line. Alternatively, a tunable laser source and the SRM can be used to check the calibration of a wavelength meter by measuring the wavelength of the laser (using the wavelength meter) as the laser is tuned through an absorption line.

**Suggested Procedure for Low-Accuracy Requirements; Calibration Uncertainty > 30 pm:** If calibrating an instrument using a broadband source, use an instrument resolution of ≤ 0.1 nm. If using a tunable source, use a data point density of at least one point every 0.005 nm (5 pm). After identifying a particular absorption line by comparing to the spectrum in Figure 1, find the center or minimum point of the line. Calibrate the instrument to the center wavelength of this line (from Table 1) using the calibration procedure specified by the instrument manufacturer. The instrument's linearity can be checked by repeating the procedure for a different absorption line and comparing it to the value listed in Table 1.

**Suggested Procedure for Moderate-Accuracy Requirements; Calibration Uncertainty in the Approximate Range of 3 pm to 30 pm:** If the source power varies significantly with wavelength, divide the SRM transmission spectrum by the source spectrum to obtain a normalized trace. After identifying a particular absorption line by comparing to the spectrum in Figure 1, make a high resolution scan of the line. If calibrating an instrument using a broadband source, use an instrument resolution of ≤ 0.05 nm. If using a tunable source, use a data point density of at least one point every 0.002 nm (2 pm). Find the wavelength readings on both sides of the line where the absorption is 50 % of the maximum; the line center is half-way between these two wavelength readings. For higher accuracy results, repeat this procedure five times and take the average of the measurements. Alternatively, the line center can be determined by fitting the central portion using a fourth order polynomial function. Calibrate the instrument to the center wavelength of this line (from Table 1) using the calibration procedure specified by the instrument manufacturer. The instrument's linearity can be checked by repeating the procedure for a different absorption line and comparing it to the value listed in Table 1.

**NOTE:** Highly reproducible *relative* wavelength measurements can be made using the procedure described for moderate-accuracy requirements. However, the procedure described in the following section is recommended to achieve high-accuracy *absolute* wavelength calibration.

**Suggested Procedure for High-Accuracy Requirements; Calibration Uncertainty < 3 pm:** Connect a narrowband tunable light source (source bandwidth ≤ 1 pm) to one of the fiber connectors on the SRM unit. After identifying a particular absorption line by comparing to the spectrum in Figure 1, make a high resolution scan of the line. Use a data point density of at least one point every 1 pm and divide the SRM transmission spectrum by the source spectrum to obtain a normalized trace. Using a fitting technique such as the least squares technique, fit the absorption data to a Lorentzian or Voigt lineshape. Details of a line fitting procedure and potential errors sources can be found in Reference 2, which is also included as an appendix in Reference 3. Calibrate the instrument to the center wavelength of this line (from Table 1) using the calibration procedure specified by the instrument manufacturer. The instrument's linearity can be checked by repeating the procedure for a different absorption line and comparing it to the value listed in Table 1. Contact NIST if the width of line R7 differs by more than 25 % from the width shown in Figure 3. A large change in linewidth could indicate cell leakage.

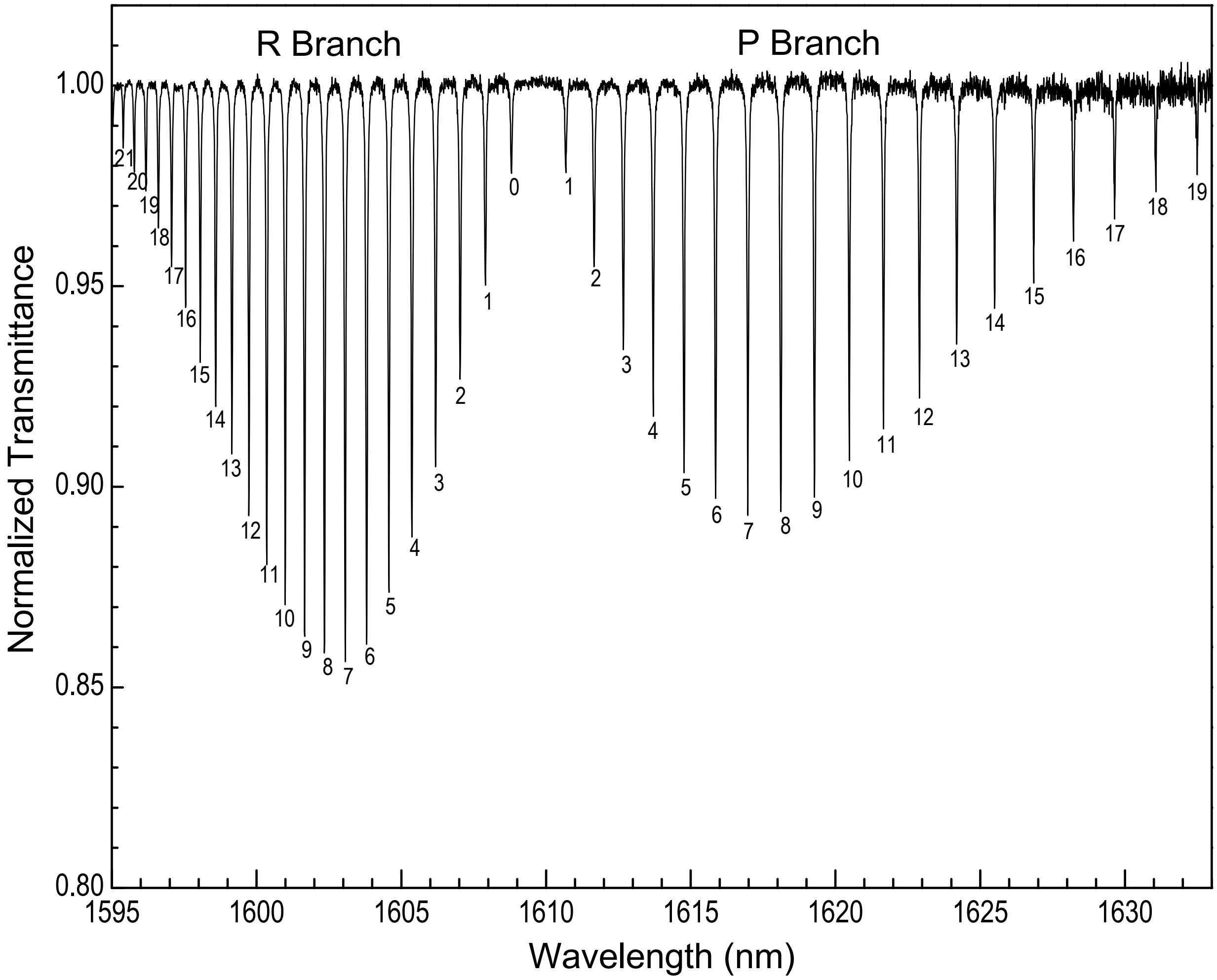

Figure 1. Normalized spectrum of the 3ν band of $^{13}C^{16}O$ obtained by passing LED light through an SRM 2515 unit and recording the spectrum of the transmitted light using an optical spectrum analyzer set to a resolution bandwidth of 0.05 nm. The figure shows the recorded spectrum divided by the LED spectrum. The $^{13}C^{16}O$ gas pressure is 133 kPa (1000 Torr); light makes four passes through a 20 cm long cell for a total optical path length of 80 cm.

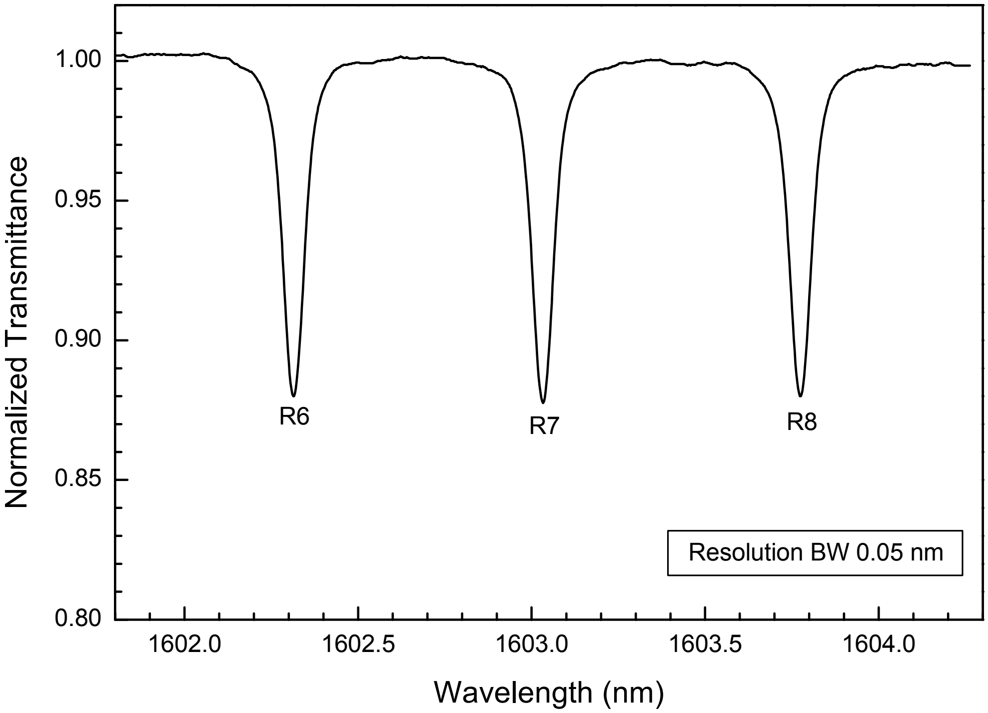

Figure 2. Spectrum of the R6, R7, and R8 lines obtained by passing LED light through an SRM 2515 unit and recording the spectrum using an optical spectrum analyzer set to a resolution bandwidth of 0.05 nm.

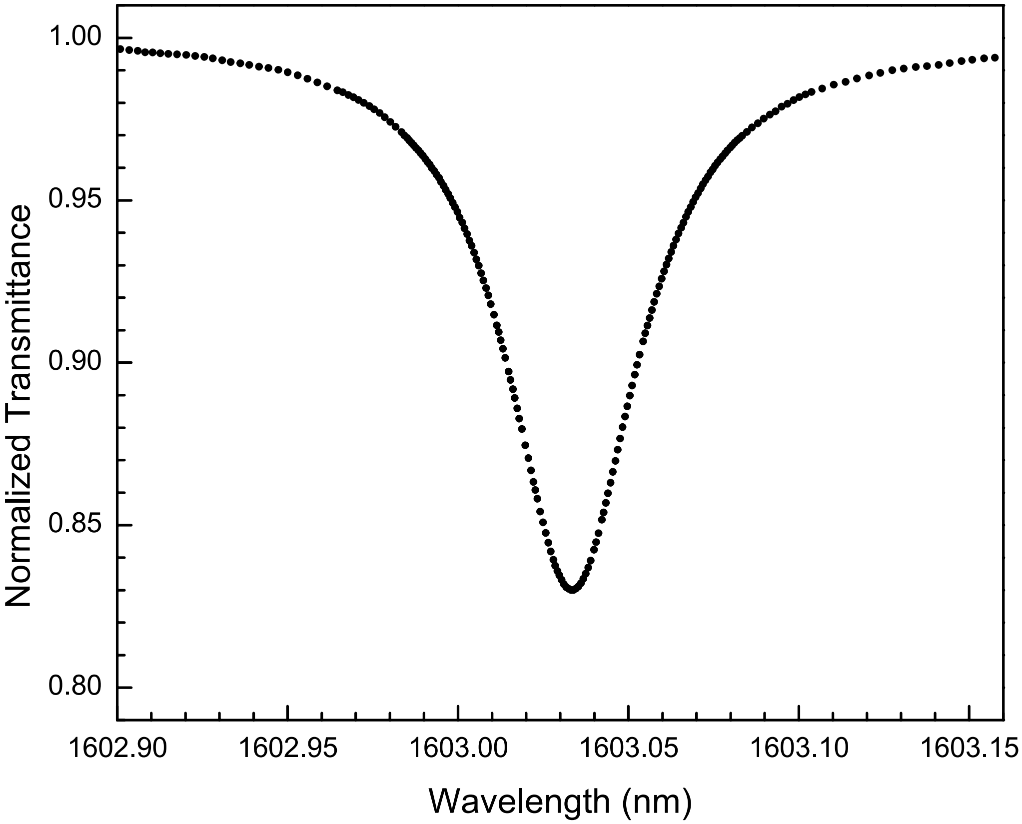

Figure 3. High resolution spectrum of line R7 obtained by passing tunable diode laser light through an SRM 2515 unit and recording the transmittance as the laser is scanned.

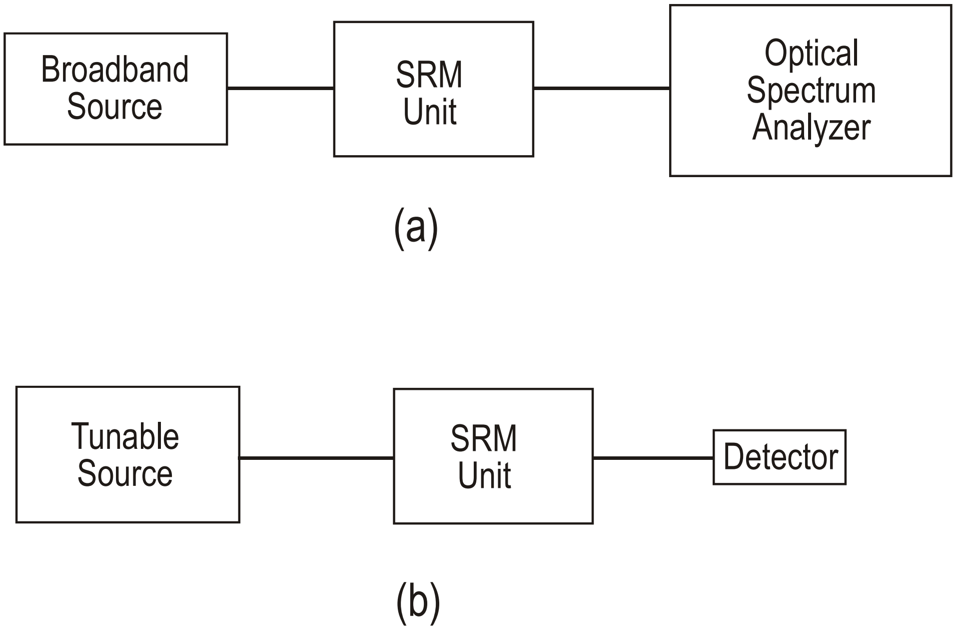

Figure 4. (a) Schematic of technique when using the SRM and a broadband source to calibrate an optical spectrum analyzer. (b) Schematic of technique when using the SRM to calibrate a tunable source. A wavelength meter can be calibrated by using a tunable laser in the configuration shown in (b) and measuring its wavelength using the wavelength meter.

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*Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.*

# Pressure-induced shift and broadening of 1560–1630-nm carbon monoxide wavelength-calibration lines

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We have measured the line centers and the pressure-induced shifts of 14 lines in the $3\nu$ rotational–vibrational band of carbon monoxide, $^{12}C^{16}O$, and 18 lines in the corresponding band of $^{13}C^{16}O$. These lines can be used as wavelength references in the optical fiber communication wavelength-division multiplexing *L* band (approximately 1565–1625 nm). The $^{12}C^{16}O$ spectrum has useful reference lines from 1560 to 1595 nm, and the $^{13}C^{16}O$ spectrum has lines from 1595 to 1630 nm. We observed that, except for a shift of 35 nm toward longer wavelengths for the $^{13}C^{16}O$ spectrum, the behaviors of the two isotopic species are similar. We found that the pressure shift varies with line number, from $\sim$+0.01 to +0.02 pm/kPa ($\sim$0.16 to 0.31 MHz/Torr). In addition, we measured the pressure broadening of these lines; we found that it also varies with line number and is typically 0.3–0.4 pm/kPa (approximately 5–7 MHz/Torr).

*OCIS codes:* 020.3690, 060.2330, 120.3940, 120.4800, 300.0300, 300.6390.

## 1. INTRODUCTION

Wavelength-division multiplexing (WDM) in optical fiber communication systems increases bandwidth by using many wavelength channels. Current WDM systems typically employ 50- or 100-GHz channel spacing (0.4 or 0.8 nm, respectively) in the 1540–1560 nm WDM *C* band. WDM will expand into the *L*-band region (approximately 1565–1625 nm) in the near future, and WDM may be implemented in shorter wavelength regions as well. Wavelength references are needed in these regions for calibration of instruments that are used to characterize components and monitor the wavelengths of the channels.

Fundamental atomic or molecular absorptions provide wavelength references that are stable under changing environmental conditions such as temperature and pressure variations or the presence of electromagnetic fields. The National Institute of Standards and Technology has developed wavelength calibration transfer standards for the 1510–1560-nm region based on acetylene and hydrogen cyanide.[1–3] We examined a number of molecules as potential references for the WDM *L*-band region. Hydrogen and deuterium halides generally have strong lines and simple spectra, but of these only hydrogen iodide[4] has spectral lines in the *L* band. Unfortunately, hydrogen iodide has several drawbacks: the spectrum (lines from 1534 to 1595 nm) only partially covers the *L* band, some of the lines have significant substructure owing to the electric-quadrupole hyperfine interaction, and the gas is difficult to work with because of its reactivity and tendency to decompose. We also investigated various hydrocarbons, halogenated hydrocarbons, and other gases containing one or more C—H bonds, because overtones of the C—H bond's fundamental vibrational frequency have spectra near 1550 nm. Although some of the spectra were in the correct location, we found that they either were too weak or were highly convoluted, containing hundreds of overlapping lines. These are typically not simple linear molecules, and off-axis vibrations cause complicated spectra. The carbon monoxide $3\nu$ rotational–vibrational band has a simple spectrum in this region, but the absorption strength is small; at a pressure of 133 kPa (1000 Torr), a path length of 80 cm produces an absorption of $\sim$15% for the stronger lines.

We decided to develop National Institute of Standards and Technology Standard Reference Material (SRM) transfer standards for the WDM *L* band based on the absorption lines of carbon monoxide ($^{12}C^{16}O$ and $^{13}C^{16}O$). Figure 1 shows the spectra for these two isotopic species; $^{12}C^{16}O$ has $\sim$40 lines from 1560 to 1595 nm, and $^{13}C^{16}O$ has $\sim$40 lines from 1595 to 1630 nm. The vacuum wavelengths of selected $^{12}C^{16}O$ line centers of the $3\nu$ band have been measured and tabulated for low-pressure conditions,[5,6] with one author quoting an uncertainty of $8 \times 10^{-6}$ nm.[5] Similarly accurate measurements of the corresponding band of $^{13}C^{16}O$ have not been made, to our knowledge. However, the predicted low-pressure line centers for $^{13}C^{16}O$, calculated by use of mass-independent Dunham parameters, are reported in the HITRAN database.[7] For wavelength calibration of instruments it is often desirable to use an intermediate- or high-pressure sample to pressure broaden the lines and match the reference bandwidth to the instrument resolution. Doing so results in the strongest signals for a given resolution bandwidth. To provide maximum sensitivity when it is used with a 0.05-nm resolution instrument, such as an optical spectrum analyzer, the gas in the carbon monoxide SRM will be at a pressure of $\sim$133 kPa (1000 Torr). In addition to broadening the lines, the higher pressure also slightly shifts the line centers. This shift, which results from energy-level shifts caused by the interaction of mol-

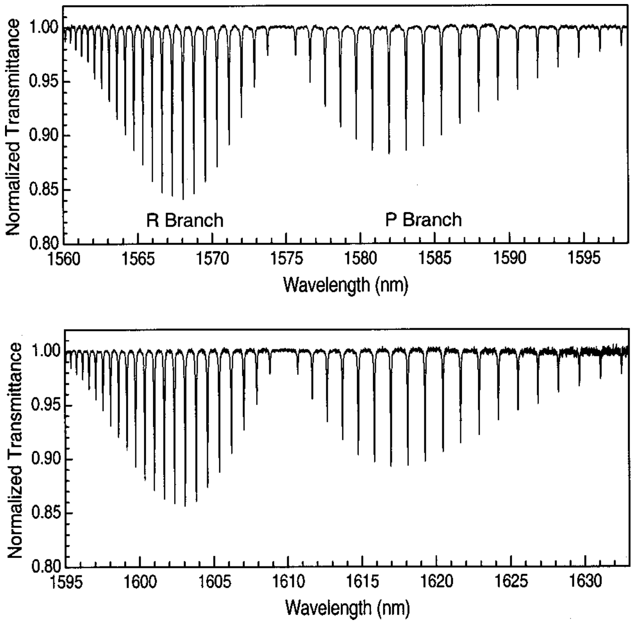

Fig. 1. Carbon monoxide $3\nu$ rotational–vibrational spectra. Top, the $^{12}C^{16}O$ spectrum; bottom, the $^{13}C^{16}O$ spectrum. We took these data by passing LED light through an absorption cell and recording the spectrum of the transmitted light with an optical spectrum analyzer with a 0.05-nm resolution bandwidth. The recorded spectrum divided by the LED spectrum is shown. The CO gas pressure was 133 kPa (1000 Torr); light made four passes through the cell for a total optical path length of 80 cm. The bottom spectrum is noisier because of lower power from the LED.

ecules during collisions,[8] increases linearly with pressure and is often called the pressure shift. Inasmuch as our goal is to certify the SRM references with an uncertainty of less than 1 pm, we need an accurate measurement of the pressure shift for both isotopic species. Picque and Guelachvili[5] measured the pressure shifts of a number of $^{12}C^{16}O$ lines with an uncertainty of $\sim 2.5 \times 10^{-3}$ pm/kPa, and Henningsen *et al.*[6] measured the pressure shift of many lines of the $^{12}C^{16}O$ $R$ branch with an uncertainty of $\sim 1.4 \times 10^{-3}$ pm/kPa (Henningsen did not report values for the $P$ branch). To our knowledge there are no measurements of the pressure shift of $^{13}C^{16}O$ absorption lines reported in the literature.

We measured the line centers, pressure shifts, and pressure broadening of 14 lines in the $^{12}C^{16}O$ spectrum and of 18 lines in the $^{13}C^{16}O$ spectrum. As a check on our measurement accuracy we also extrapolated these line centers to zero pressure and compared those values with the literature values. We describe our measurement procedure in Section 2 and summarize the results in Section 3. Conclusions are presented in Section 4.

## 2. MEASUREMENT DESCRIPTION AND DATA ANALYSIS

A schematic diagram of our pressure-shift measurement apparatus is shown in Fig. 2. Light from a tunable diode laser is sent through two absorption cells simultaneously, and the transmission through each cell is monitored by detectors. One cell contained carbon monoxide gas (either $^{12}C^{16}O$ or $^{13}C^{16}O$) at a relatively low pressure of ~27 kPa (~200 Torr), and the other contained the same isotopic species at a higher pressure of ~133 kPa (~1000 Torr). A third detector monitored the laser power, and a wavelength meter measured the laser's wavelength with an uncertainty of 1 part in $10^7$ (0.16 pm at 1600 nm). A computer controlled the laser wavelength scan and recorded the readings of the three detectors and the wavelength meter.

Figure 3 shows spectra of line $R7$ of $^{13}C^{16}O$ obtained with the low- and high-pressure cells. The pressure broadening in the high-pressure spectrum is obvious. We are interested primarily in the shift of the high-pressure line center relative to the low-pressure line center. Fourteen lines in the $^{12}C^{16}O$ spectrum and eighteen lines in the $^{13}C^{16}O$ spectrum were scanned with this technique. The measured quantity, transmitted power $I_T$, is related to absorption coefficient $\alpha$ and absorption path length $L$ by

$$I_T = I_0 \exp(-\alpha L), \tag{1}$$

where $I_0$ is the incident power. We first divided the cell transmission curves by the laser power monitor signal to

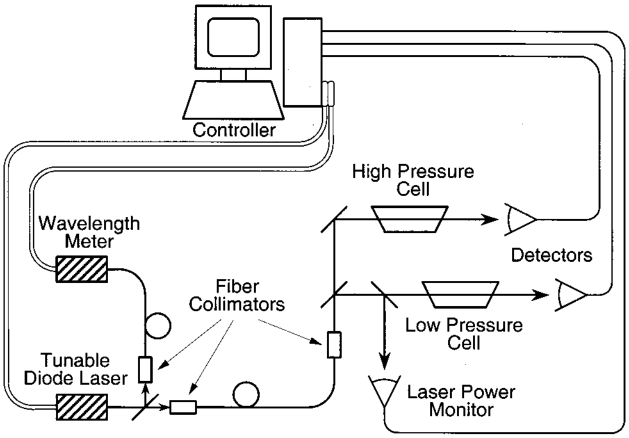

Fig. 2. Diagram of pressure-shift measurement apparatus.

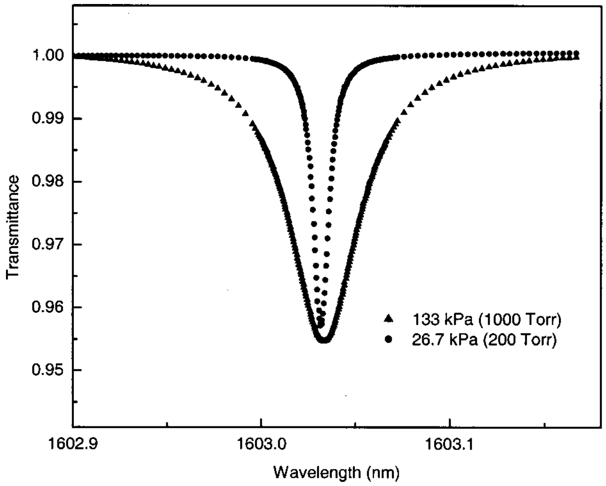

Fig. 3. Tunable diode laser scan of the $^{13}C^{16}O$ $R7$ line showing transmittance through the low-pressure (26.7-kPa) and high-pressure (133-kPa) cells.

remove common-mode intensity variations and normalized the data. We then took the natural logarithm to obtain the absorbance, $\alpha L$.

Individual lines were then fitted to Voigt profiles[8] by use of an orthogonal distance regression algorithm.[9] The orthogonal distance regression, called either error-in-variables or total-least-squares regression, obtains the model parameters by minimizing the sum of squares of the orthogonal distances from the model to the data points. The fitting program was able to account for a background slope and uncertainties in both $x$ (wavelength) and $y$ (transmitted power). A Voigt profile is a convolution of Lorentzian and Gaussian profiles; it results when there is a combination of Gaussian broadening (resulting from Doppler broadening, for example) and Lorentzian line shape (resulting from the natural linewidth or pressure broadening, for example). In our situation, the natural linewidth is small (typically <2 MHz for molecular absorption lines in this region[10]) compared with the Gaussian Doppler broadening (~400 MHz) and the Lorentzian pressure broadening. The pressure-broadened component of the linewidths ranged from 2× to 55× the Doppler-broadened component. We fixed the Doppler linewidth at 3.65 pm (Ref. 8) and allowed other fitting parameters to vary.

The fused-silica absorption cells are 20 cm long, with windows attached to the cells by a glass frit method. To prevent interference fringes in the transmitted signal the windows are mounted at an angle of 11° and also are wedged by ~2°. The cells were first evacuated and leak checked and were then filled with isotopically pure gas (99.95% $^{12}C^{16}O$ or 99% $^{13}C^{16}O$). During the fill process the pressure in the fill manifold (and hence in the cell) was monitored with a capacitance manometer. Once filled, the cells were closed off with a glass valve with O-ring seals. To check a cell's pressure after closing the valve (which changes the cell's pressure as the valve's O ring compresses), and to monitor a cell's pressure over the course of the measurements, we generated a plot of the Lorentzian component of the linewidth (derived from the Voigt line fit) versus pressure for line $R7$. This allowed us to determine a cell's pressure at any time by measuring the width of line $R7$ and comparing it with the plot. To generate the plot we mounted a cell in our pressure-shift measurement apparatus and attached it to our fill manifold with a copper tube. In this way we monitored the cell pressure by using the capacitance manometer while we measured the linewidth and the line center. We conducted these measurements on line $R7$ of both isotopic species for several pressures from 13.3 kPa (100 Torr) to 133 kPa (1000 Torr). Figure 4(a) is a plot of the full width at half-maximum (FWHM) of the Lorentzian component of the $^{13}C^{16}O$ line $R7$ versus pressure and a linear least-squares fit to the data. As can be seen from the figure, the Lorentzian component of the width (pressure broadening) has a linear dependence on pressure. Figure 4(b) shows the line-center wavelength versus pressure of the same line and the corresponding linear least-squares fit; as can be seen from this figure, the pressure shift is also linearly dependent on pressure. Based on our calibration of linewidth versus pressure for line $R7$, the pressures for the low- and high-pressure cell pairs used in the subsequent shift measurements were 26.4 ± 0.5 kPa (198 ± 4 Torr) and 134.5 ± 1.3 kPa (1009 ± 10 Torr) for $^{12}C^{16}O$, and 26.9 ± 0.5 kPa (202 ± 4 Torr) and 133.5 ± 1.3 kPa (1001 ± 10 Torr) for $^{13}C^{16}O$. The pressure uncertainty quoted here is the expanded uncertainty that we obtained by applying a coverage factor $k = 2$ (i.e., our quoted uncertainty is $\pm 2\sigma$).[11]

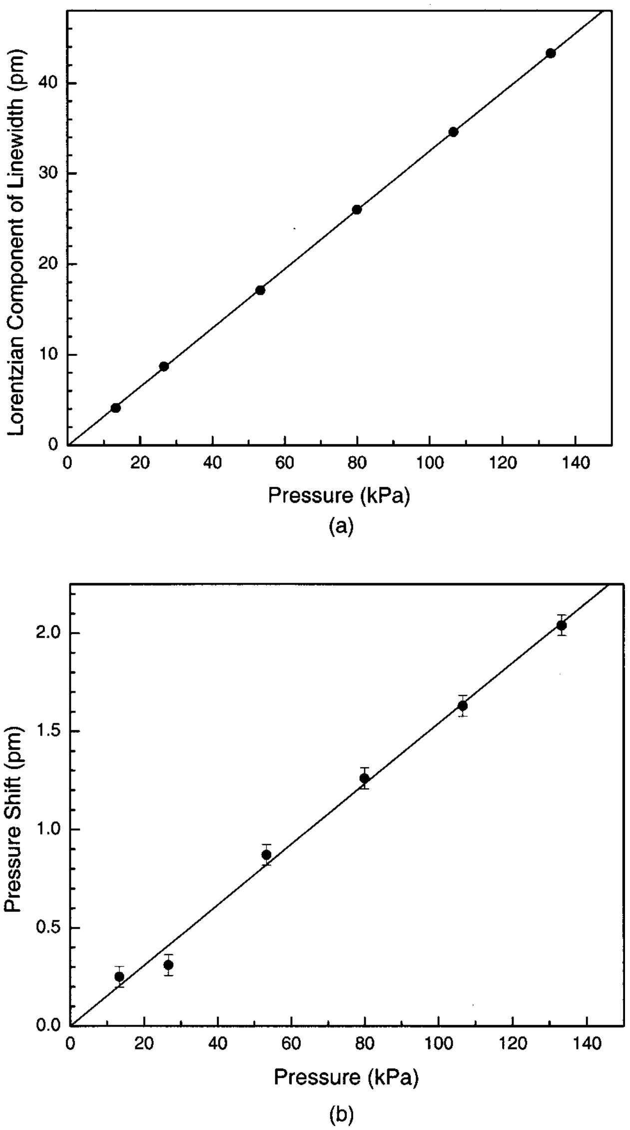

Fig. 4. (a) FWHM of the Lorentzian component of the $^{13}C^{16}O$ $R7$ line versus pressure and the corresponding linear least-squares fit to the data (error bars are smaller than the points). (b) Line $R7$ center wavelength shift from the zero-pressure value versus pressure and the corresponding linear least-squares fit to the data; the error bars are 1 standard uncertainty ($1\sigma$).

Inasmuch as the spectra for the low- and high-pressure cells were measured simultaneously, the absolute accuracy of the wavelength meter was not of critical importance for measurement of the relative pressure shift. However, the short-term statistical variation of the wavelength measurement did add noise to the data. To determine this statistical variation we repeatedly measured a laser that was stabilized to a narrow rubidium line. The statistical variation of repeated measurements yielded a Gaussian distribution with a standard deviation of 0.1

pm. Because of the band coverage of the two carbon monoxide spectra, and the band limitations of our lasers, we needed to use two different lasers through the course of the measurement. We determined the experimental uncertainty in the signal level by measuring the statistical variation of the data within a region of a line wing. The standard deviation of the fluctuations was 3 parts in $10^5$ and 8 parts in $10^6$ of the transmitted power, depending on the laser used.

Each data point was assigned a standard uncertainty of 0.1 pm for the wavelength and a fractional uncertainty of 3 parts in $10^5$ or 8 parts in $10^6$, depending on which laser we used, for the transmitted power. The fitting program determined the line centers and the Lorentzian component of the linewidths, the corresponding uncertainties, and the reduced residual-sum-of-squares ($\chi^2$) value for the fit.

### A. Background Variation

A slope or a variation in the background level can shift the apparent center of a line, particularly for the wide lines of the high-pressure cells. Nearby absorption lines, interference fringes owing to reflected laser light, wavelength dependence of the optical components, beam pointing stability, and variations in the laser power can cause background variation. We found no evidence of nearby absorption lines in either spectrum. As mentioned above, we removed common-mode laser power variations by dividing the cell transmittance data by the power monitor data. Owing to the wavelength dependence of optical fiber couplers (splitters), we used free-space beam splitters to send the laser light to the cells and the power monitor. We minimized interference effects by using wedged cell windows and beam splitters, windowless detectors, and two optical isolators.

Because the remaining background variations were not purely statistical noise, they can potentially add uncertainty to our measurements. We modeled the effect of these variations to determine their contribution to our line-center and linewidth uncertainties. Two model Voigt functions were generated to represent the strongest ($R7$) and the weakest ($P19$) lines that we measured in $^{13}C^{16}O$. We obtained a sample baseline spectrum by scanning a cell transmittance in a spectral region between two absorption lines. Sections of this baseline noise were then added to the model lines, along with modeled wavelength measurement noise. The resultant noisy modeled lines were then fitted by the procedure described above. We then repeated this process approximately 25 times, using a different sample of baseline noise each time; this resulted in a set of fit parameters for the centers and widths of both lines. For the weaker line we found that the standard deviations of the line-fitting parameters were considerably larger than the uncertainties returned by the fitting program for a single line fit (0.09 versus 0.03 pm for the line center and 0.6 versus 0.2 pm for the linewidth of the high-pressure sample). For the stronger line, however, the standard deviations of the modeled line-fitting parameters were approximately the same as the uncertainties returned by the fitting program for a single line fit. This result is not surprising, because we would expect the background noise to have a larger effect for the weaker line. To verify the results of the model we scanned and fitted lines $R7$ and $P19$ eleven times. The standard deviation of the fit parameters agreed with our simulation results. To account for the effect of background variations on the other lines' uncertainties, we interpolated the results that we obtained for lines $P19$ and $R7$ to the other lines based on their line strength.

### B. Wavelength Accuracy

Although the absolute accuracy of the wavelength measurement was not relevant to the pressure-shift measurement, extrapolating our line-center measurements to zero pressure and comparing them with literature values serves as a good verification of our measurements. To determine the line-center accuracy for our measurements we first checked the accuracy of the wavelength meter used in the measurements. We set up a high-accuracy wavelength reference for this purpose.[3] Diode laser light at 1560.5 nm was amplified with an erbium-doped fiber amplifier and was frequency doubled in a periodically poled lithium niobate crystal. The resultant 780-nm light was then used to conduct saturated absorption spectroscopy on the $5S_{1/2} \rightarrow 5P_{3/2}$ transitions of rubidium ($^{85}$Rb and $^{87}$Rb). The line centers of the hyperfine components of these transitions have been measured with an uncertainty of ±0.4 MHz (Ref. 12); a subset of these lines has been measured to higher accuracy.[13] We stabilized the laser to several different hyperfine components of the $^{87}$Rb transition and compared the wavelength meter reading (vacuum wavelength) with the literature values multiplied by 2. As the lines were very narrow (less than 10 MHz), the absolute stability of the laser was much better than the quoted wavelength meter uncertainty of 1 part in $10^7$ (~20 MHz at 1600 nm). From measurements taken before and after our pressure-shift scans we found that the wavelength meter reading was offset by $-0.07 \pm 0.07$ pm ($+9 \pm 9$ MHz). The uncertainty ($2\sigma$) is derived from the standard deviation of multiple wavelength meter calibration measurements made over the course of the pressure-shift measurement. During this time the wavelength meter's offset varied from $+0.03$ pm to $-0.13$ pm.

## 3. PRESSURE SHIFT, LINE CENTER, AND PRESSURE-BROADENING RESULTS

Tables 1 and 2 summarize our line-center, pressure-shift, and pressure-broadening results. To obtain the unperturbed line-center values we adjusted the low- and high-pressure line-center data for the wavelength meter's offset and extrapolated the line centers to zero pressure by use of a Monte Carlo fitting procedure. We also derived the pressure-shift coefficient (change in line-center wavelength versus pressure) from this Monte Carlo fit. The pressure-broadening coefficient for each line was determined by a Monte Carlo fit to the Lorentzian component of the high- and low-pressure linewidths.

Temperature changes can slightly modify the pressure shift and pressure broadening of a molecular line by changing the collision frequency.[8] For the measurements reported here, the temperature was 22 ± 2 °C. As discussed in Ref. 1, this temperature range would cause a

**Table 1. $^{12}C^{16}O$ Line-Center, Pressure-Shift, and Pressure-Broadening Results**[a]

| | | Shift Coefficient | | Broadening Coefficient | |
|---|---|---|---|---|---|
| Line | Line Center Extrapolated to Zero Pressure (nm) | pm/kPa | MHz/Torr | pm/kPa | MHz/Torr |
| $R21$ | 1560.50004(24) | 0.0188(20) | −0.309(32) | 0.267(14) | 4.38(22) |
| $R16$ | 1562.59327(20) | 0.0157(18) | −0.257(29) | 0.273(12) | 4.47(20) |
| $R12$ | 1564.74563(14) | 0.0154(8) | −0.251(13) | 0.294(8) | 4.80(14) |
| $R7$ | 1568.03555(10) | 0.0147(6) | −0.239(10) | 0.315(6) | 5.12(10) |
| $R4$ | 1570.33051(14) | 0.0131(10) | −0.212(16) | 0.339(8) | 5.49(12) |
| $R1$ | 1572.86770(20) | 0.0109(16) | −0.176(26) | 0.388(12) | 6.27(20) |
| $R0$ | 1573.76745(24) | 0.0097(20) | −0.157(32) | 0.407(14) | 6.57(22) |
| $P1$ | 1575.64836(24) | 0.0112(20) | −0.180(32) | 0.413(14) | 6.65(22) |
| $P2$ | 1576.62961(20) | 0.0115(18) | −0.185(29) | 0.385(12) | 6.19(20) |
| $P4$ | 1578.67400(16) | 0.0139(14) | −0.223(22) | 0.359(12) | 5.76(20) |
| $P7$ | 1581.94641(16) | 0.0159(10) | −0.254(16) | 0.330(8) | 5.27(12) |
| $P11$ | 1586.69708(16) | 0.0172(14) | −0.273(22) | 0.312(8) | 4.95(12) |
| $P15$ | 1591.89544(20) | 0.0182(18) | −0.285(28) | 0.295(12) | 4.65(18) |
| $P19$ | 1597.54775(24) | 0.0191(20) | −0.299(31) | 0.279(14) | 4.37(22) |

[a] Results for the measured lines of the $3\nu$ band of carbon monoxide $^{12}C^{16}O$ at a temperature of 22 ± 2 °C. Line-center vacuum wavelength results are for low-pressure conditions; our measurements (column 2) are values obtained by extrapolation of the line center to zero pressure. The broadening coefficient is the pressure dependence of the FWHM of the Lorentzian component of the Voigt line profile. The uncertainties in the final digits of the values are indicated in parentheses. The uncertainties quoted are the expanded uncertainties obtained by application of a coverage factor $k = 2$ (i.e., our quoted uncertainty is $\pm 2\sigma$).

**Table 2. $^{13}C^{16}O$ Line-Center, Pressure-Shift, and Pressure-Broadening Results**[a]

| | | Shift Coefficient | | Broadening Coefficient | |
|---|---|---|---|---|---|
| Line | Line Center Extrapolated to Zero Pressure (nm) | pm/kPa | MHz/Torr | pm/kPa | MHz/Torr |
| $R21$ | 1595.37446(20) | 0.0200(20) | −0.314(38) | 0.253(16) | 3.97(26) |
| $R18$ | 1596.58693(20) | 0.0187(20) | −0.293(34) | 0.272(16) | 4.27(25) |
| $R15$ | 1598.03287(18) | 0.0160(18) | −0.250(28) | 0.287(12) | 4.50(20) |
| $R12$ | 1599.71196(16) | 0.0160(12) | −0.250(20) | 0.303(10) | 4.74(15) |
| $R10$ | 1600.96157(16) | 0.0152(12) | −0.237(18) | 0.313(8) | 4.88(13) |
| $R7$ | 1603.03136(12) | 0.0152(8) | −0.237(14) | 0.326(8) | 5.07(12) |
| $R4$ | 1605.33673(16) | 0.0134(12) | −0.208(20) | 0.345(10) | 5.36(16) |
| $R1$ | 1607.87857(20) | 0.0106(20) | −0.164(32) | 0.401(14) | 6.20(22) |
| $R0$ | 1608.77849(20) | 0.0101(20) | −0.157(38) | 0.419(16) | 6.47(26) |
| $P1$ | 1610.65814(20) | 0.0111(20) | −0.171(36) | 0.424(16) | 6.54(24) |
| $P2$ | 1611.63775(20) | 0.0118(20) | −0.182(32) | 0.410(14) | 6.31(22) |
| $P4$ | 1613.67706(18) | 0.0136(16) | −0.209(26) | 0.368(14) | 5.65(21) |
| $P7$ | 1616.93687(16) | 0.0167(14) | −0.255(20) | 0.342(10) | 5.23(16) |
| $P9$ | 1619.24491(16) | 0.0171(14) | −0.261(22) | 0.329(10) | 5.02(16) |
| $P11$ | 1621.66151(18) | 0.0184(14) | −0.280(22) | 0.320(10) | 4.87(15) |
| $P13$ | 1624.18751(18) | 0.0175(16) | −0.265(24) | 0.318(12) | 4.82(18) |
| $P16$ | 1628.18261(20) | 0.0191(20) | −0.288(34) | 0.300(16) | 4.52(22) |
| $P19$ | 1632.42759(20) | 0.0209(20) | −0.314(36) | 0.286(16) | 4.29(24) |

[a] Results for the measured lines of the $3\nu$ band of carbon monoxide $^{13}C^{16}O$ at a temperature of 22 ± 2 °C. Line center-vacuum wavelength results are for low-pressure conditions; our measurements (column 2) are values obtained by extrapolation of the line center to zero pressure. The broadening coefficient is the pressure dependence of the FWHM of the Lorentzian component of the Voigt line profile. The uncertainties in the final digits of the values are indicated in parentheses. The uncertainties quoted are the expanded uncertainties obtained by application of a coverage factor $k = 2$ (i.e., our quoted uncertainty is $\pm 2\sigma$).

±0.3% change in the pressure shift and pressure broadening, which is negligible compared with our pressure-shift and presure-broadening uncertainties.

Figure 5 shows the pressure shift versus line number for $^{13}C^{16}O$. In all cases the wavelength shift was positive with increasing pressure. The $R$ and $P$ branches of both isotopic species showed similar shift-versus-line number behavior, with a shift of approximately 0.01 pm/kPa for lines near the band center, rising to ~0.02 pm/kPa for lines far from the band center (i.e., transitions between states with high rotational quantum numbers).

As discussed above, pressure broadening is responsible for the Lorentzian component of the Voigt line shape. We found that the pressure broadening also varied with line number (Fig. 6). In contrast to the pressure-shift dependence, however, the pressure broadening was largest for lines near the band center (transitions between states with low rotational quantum numbers). The pressure-broadening data for $^{12}C^{16}O$ showed similar trends and magnitudes. Our pressure-broadening analysis does not include the small effect of collisional narrowing that is due to velocity averaging. This effect is negligible at higher pressures, where pressure broadening dominates, but can cause the line shape to deviate from the expected Voigt profile at low pressures.[14] Since we do not observe significant discrepancies between our data and the Voigt function, we conclude that the line-shape modification that is due to collisional narrowing is negligible at the level of our quoted uncertainty.

Figure 7 compares our $^{12}C^{16}O$ pressure-shift results with those of Picque and Guelachvili[5] and Henningsen *et al.*[6] Our pressure-shift standard uncertainty ($1\sigma$) ranges from $3 \times 10^{-4}$ to $1 \times 10^{-3}$ pm/kPa; the uncertainty quoted in Ref. 5 is $2.5 \times 10^{-3}$ pm/kPa, and the uncertainty quoted in Ref. 6 is $\sim 1.4 \times 10^{-3}$ pm/kPa. Our shift values have lower uncertainty and are in good agreement with those of Refs. 5 and 6; the differences between our values and those previous measurements are within the quoted uncertainty for each line. Our pressure-broadening results also agree well with those reported in Ref. 6 for the *R* branch of $^{12}C^{16}O$ (Ref. 6 does not report values in the *P* branch). Figure 8 compares our determinations of the zero-pressure line-center values for $^{12}C^{16}O$ with the more accurate values reported in Ref. 5, which were also extrapolated to zero pressure. Our standard uncertainty ($1\sigma$) is typically near 0.1 pm, whereas the estimated uncertainty given in Ref. 5 is $3 \times 10^{-5}$ cm$^{-1}$ (0.008 pm). All our line-center values are in good agreement with those of Refs. 5 and 7; the differences between the values are within our standard uncertainty for each line center. To date, the only reference that we have found that reports zero-pressure line-center values for $^{13}C^{16}O$ is the HITRAN database.[7] To our knowledge, there are no measurements of the pressure shift of $^{13}C^{16}O$ absorption lines reported in the literature. Our zero-pressure line-center values for $^{13}C^{16}O$ are in good agreement with the HITRAN values; the differences between our values and the HITRAN values are less than 0.15 pm. These comparisons with calculations and previous mea-

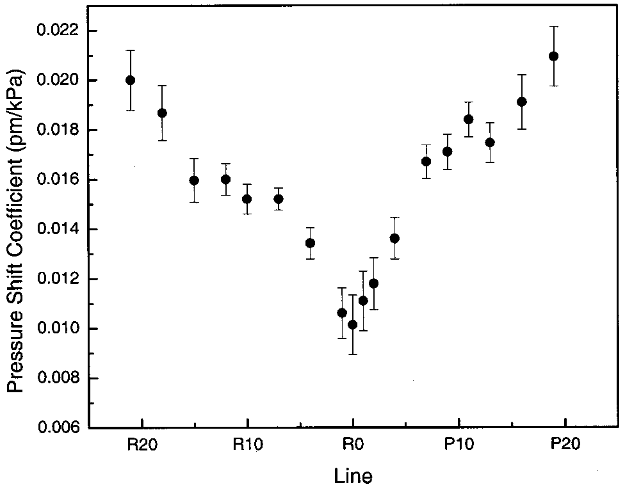

Fig. 5. Pressure-shift coefficient versus line number for $^{13}C^{16}O$.

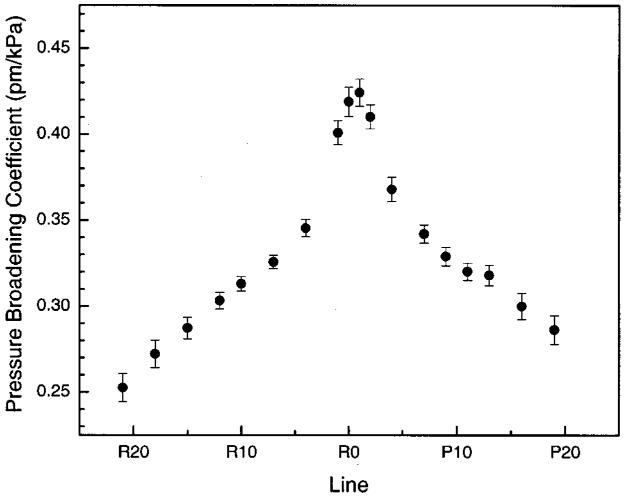

Fig. 6. Pressure dependence of the Lorentzian component (FWHM) of the linewidth versus line number for $^{13}C^{16}O$.

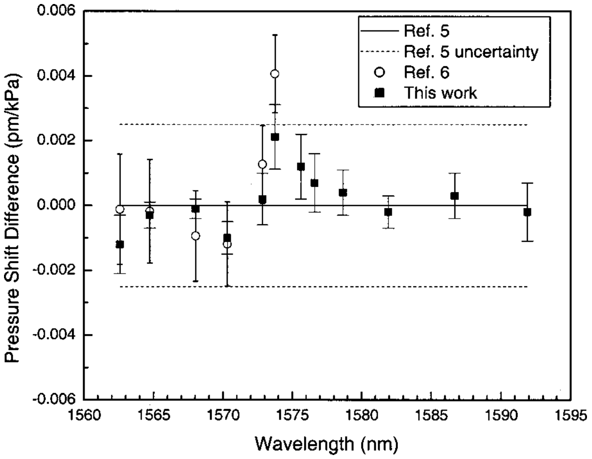

Fig. 7. Comparison of $^{12}C^{16}O$ pressure-shift results. Plotted is the difference between the results of this work, with $1\sigma$ standard uncertainty error bars, and the measurements of Picque and Guelachvili.[5] The difference between the results of Henningsen *et al.*[6] and Ref. 5 are also plotted.

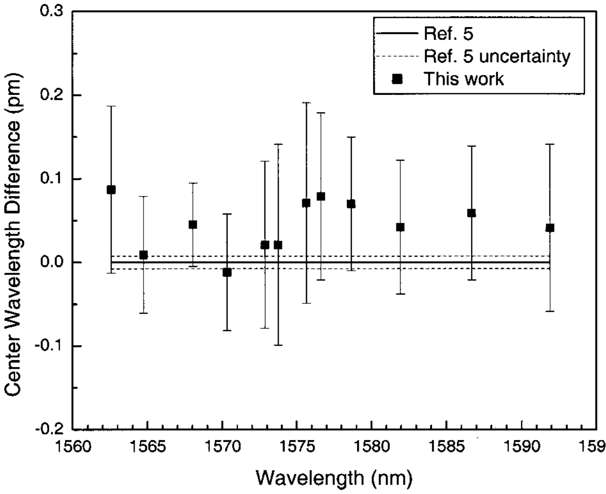

Fig. 8. Comparison of $^{12}C^{16}O$ line-center results. Plotted is the difference between the results of this work, with $1\sigma$ standard uncertainty error bars, and the measurements of Picque and Guelachvili.[5] The HITRAN database values[7] (not shown) are all within 0.02 pm of the Picque–Guelachvili values.

surements give us further confidence in our analysis of the pressure-shift coefficient values and uncertainties for the $^{12}C^{16}O$ and $^{13}C^{16}O$ measurements.

## 4. CONCLUSIONS

We have measured the pressure-shift coefficient for 14 lines of the $^{12}C^{16}O$ isotopic species and 18 lines of the $^{13}C^{16}O$ isotopic species of the $3\nu$ rotational–vibrational band of carbon monoxide. The two isotopic species showed nearly identical shift behavior, with a shift of $\sim$+0.01 pm/kPa (equivalently, $+1.3 \times 10^{-3}$ pm/Torr or $-0.16$ MHz/Torr) near the band center and of $\sim$0.02 pm/kPa (equivalently, $+2.7 \times 10^{-3}$ pm/Torr or $-0.31$ MHz/Torr) for lines farther from the band center. We have also measured the pressure broadening of these lines and found that it also varies with line number, ranging from 0.25 pm/kPa (4 MHz/Torr) to 0.42 pm/kPa (6.5 MHz/Torr). For a pressure of 133 kPa ($\sim$1000 Torr; the conditions of the National Institute of Standards and Technology SRM) the pressure shift is typically near 2 pm but can be as large as 2.8 pm for lines far from the band center and as low as 1.3 pm for lines near the band center. The Lorentzian component of the linewidths at this pressure varies from 34 pm ($\sim$4 GHz) for lines far from the band center to 56 pm ($\sim$7 GHz) near the band center.

Although the pressure shift and the pressure broadening are both due to the interactions between molecules during collisions, they depend on line number rather differently. The pressure shift is largest for lines far from the band center (transitions between states with high rotational quantum number $J$), whereas the pressure broadening is largest for lines near the band center (transitions between states with low $J$). One explanation for the pressure-broadening line dependence is that rotational averaging of the potential during a collision causes states with high rotational angular momentum (high $J$) to be perturbed less than states with low $J$. The pressure shift is more difficult to interpret; it represents the difference between the shift of the excited state and the shift of the ground state. We would need to conduct a more extensive study before drawing any conclusions about the shift of a particular state. Our measurements of pressure broadening and shift of acetylene lines[1] show trends that are similar to those observed in carbon monoxide.

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