

Quantum Cascade Laser Spectrometer for Carbonyl Sulfide Isotopomer Analysis

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Abstract

A compact absorption spectrometer using a mid-infrared tunable quantum cascade laser operating at $4.86\ \mu\text{m}$ ($2054\ \text{cm}^{-1}$) was utilized to measure low concentrations of carbonyl sulfide (COS) in air. Selectivity of two stable isotopes, $^{12}\text{C}^{16}\text{O}^{32}\text{S}$ and $^{12}\text{C}^{16}\text{O}^{34}\text{S}$, was demonstrated.

Introduction

Recently it has been demonstrated that infrared absorption spectroscopy is an effective tool, which can complement mass spectrometry in isotopomer analyses. In absorption spectroscopy high selectivity between isotopic species can be achieved even for species of equal or nearly equal masses whose discrimination in a mass spectrometer is difficult. Moreover, the in situ or real-time measuring capability is especially favorable for environmental and medical applications. In particular, quantum cascade lasers have the advantage over other mid-infrared sources in that a compact and a user-friendly measurement system can be assembled.

In this report we describe a newly developed quantum cascade laser spectrometer suitable for abundance ratio measurements of carbonyl sulfide isotopomers, $^{12}\text{C}^{16}\text{O}^{32}\text{S}$ and $^{12}\text{C}^{16}\text{O}^{34}\text{S}$. The carbonyl sulfide molecule is known to play an important role in aerosol particulate formation in the stratosphere [Crutzen, 1976]. Hence its isotopomer abundance measurements will bring important information to identify sources and sinks of this molecule. Furthermore, it has been observed that patients suffering from liver disease show elevated COS concentrations in exhaled breath as well as lung transplant patients experiencing acute allograft rejection [Studer, 2001]. There is a possibility that the COS isotopomer ratio contains additional information that will prove to be useful in medical diagnostics.

Isotopic COS Line Selection

Line selection was performed by comparing the tuning range of the QC laser with available $^{12}\text{C}^{16}\text{O}^{32}\text{S}$ and $^{12}\text{C}^{16}\text{O}^{34}\text{S}$ absorption features from approximately 2052.0 to 2054.5 cm^{-1} . The criteria of the absorption lines suited for isotopomer analyses are: (i) there is no overlapping with each other and with potential contaminants, (ii) they are as strong as possible, and (iii) the lower-state energies of the relevant transitions are nearly the same so that the effect of the change in sample temperature is small.

The line pair at 2054.078 to 2053.960 cm^{-1} was chosen for CO^{32}S and CO^{34}S , respectively, because of adequate frequency spacing and sufficient line intensities. To verify

adequate spectral separation, changes in pressure were examined to assess the effect of overlapping lines on the isotopic precision. Figures 1(a) and 1(b) shows simulated CO^{32}S P(19) and CO^{34}S P(18) Voigt absorption profiles at cell pressures ranging from 40 to 200 Torr. Preliminary assessments suggest that a pressure stability of ~ 4 Torr is required to achieved an isotopic precision of 1 ‰ (1 per-mil) for cell pressures between 10 and 60 Torr.

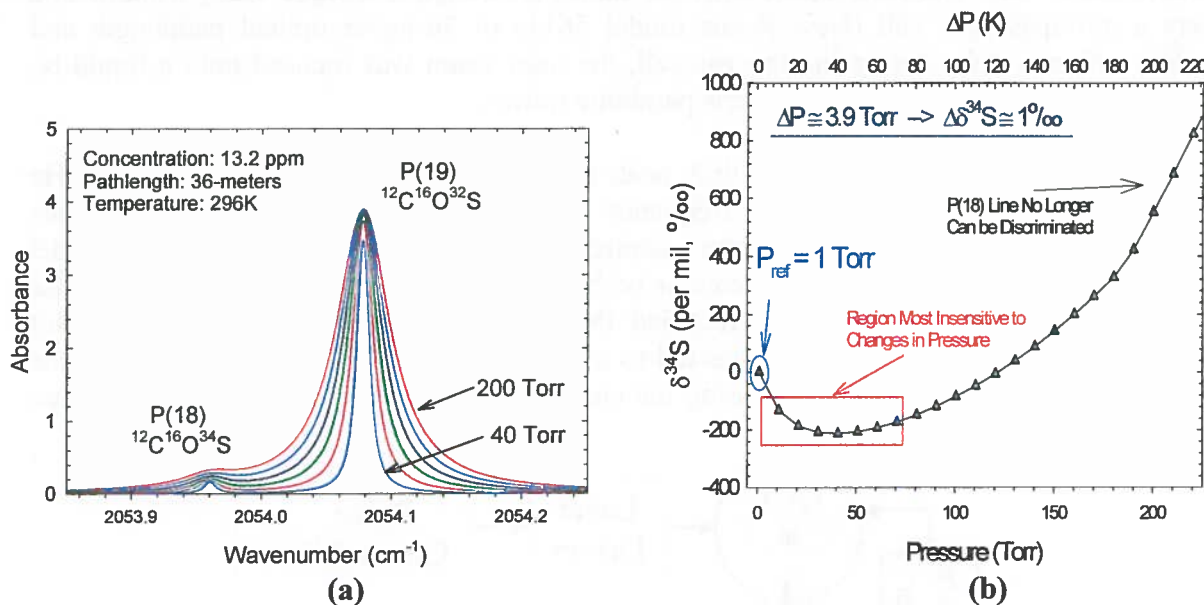


Figure 1. (a) Simulation of COS isotopic absorption lines of interest as the cell pressure increases from 40 to 200 Torr. (b) Plot of the per-mil precision as a function of pressure with the pressure reference set to 1-Torr.

In addition to spectral spacing and line intensities of the isotopic COS lines, the lower state energies are also examined to determine the affect of temperature instabilities on isotopic measure precision. Figure 2 shows per-mil change in peak absorbances for cell temperatures of 275 to 320 K at cell pressures of 10, 30, and 50 Torr. A change in cell temperature of 1.8 K is expected to result in a 0.23 ‰ when measuring peak absorbances at 10 Torr.

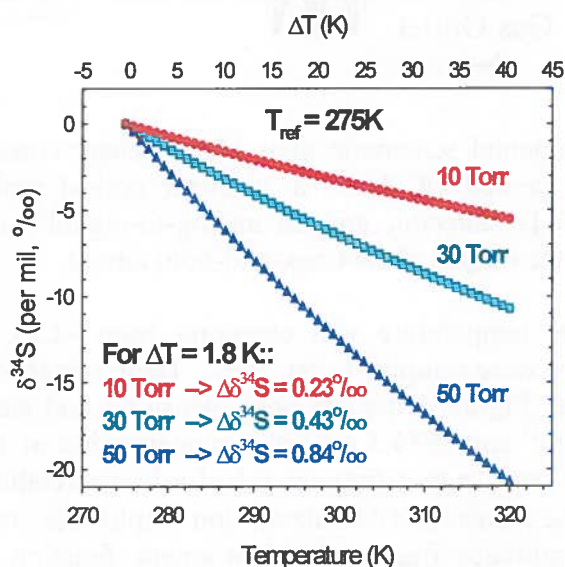


Figure 2. Effects of temperature changes on the per-mil precision of CO^{32}S P(19) and CO^{34}S P(18) lines at cell pressures of 10, 30, and 50 Torr.

Experimental Setup and Results

A schematic of the experimental sensor configuration is shown in Figure 3. A QC laser was mounted on a two-stage Peltier cooler with a copper heat sink inside an evacuated housing [Roller, 2003]. The QC laser output was collimated with an anti-reflection coated aspheric ZnSe lens. The laser beam exits the housing through a wedged CaF₂ window and enters a multipass gas cell (New Focus model 5611) of 36-meter optical pathlength and 0.3 liter volume. After traversing the gas cell, the laser beam was focused onto a liquid-N₂ cooled HgCdTe detector using an off-axis parabolic mirror.

The QC laser was excited with 1.96A peak current pulses of 14ns widths at a 500kHz repetition rate. The QC laser output frequency was tuned by varying the laser substrate temperature using a standard temperature controller (Wavelength Electronics, Inc., Model LFI-3751). A photovoltaic HgCdTe detector with a 35ns response time resolved each pulse and a track-and-hold (T&H) circuit rectified the peak detector output voltage. A 12-bit analog-to-digital converter (ADC) connected to a laptop computer sampled and digitized the output of the T&H circuit, thus measuring the energy of each laser pulse after the multipass gas cell.

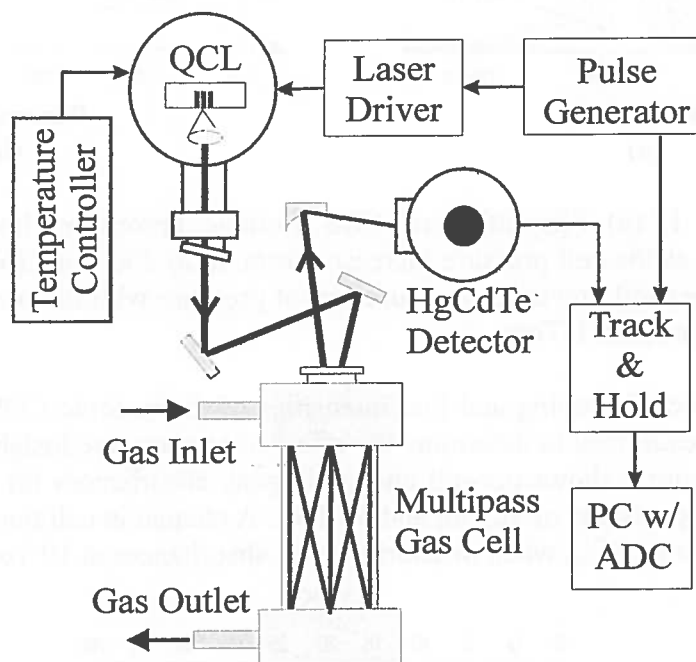


Figure 3. Experimental schematic of a TLAS sensor consisting of a pulsed thermoelectrically cooled QC laser, a 36-meter optical multipass gas cell, a photovoltaic HgCdTe detector, and an analog-to-digital converter (ADC) to acquire data from the output of the track-and-hold circuit.

As the laser substrate temperature was changing from -15°C to -35°C at a rate of $\sim 5^{\circ}\text{C}/\text{min}$, 800 laser pulses were sampled every 50ms. Their averaged energy was recorded as a function of temperature. Figure 4 depicts both measured and simulated COS absorption spectra between 2052.1 cm^{-1} and 2054.3 cm^{-1} at a concentration of 13.2 ppm and a total gas pressure of 40 Torr. The laser output frequency had a linear relationship with temperature, $\Delta\nu/\Delta T = -0.13\text{ cm}^{-1}/\text{K}$. The measured COS absorption amplitudes are less than the equivalent simulated absorption amplitudes due to the instrument function (laser linewidth) being convolved with the COS absorption lines.

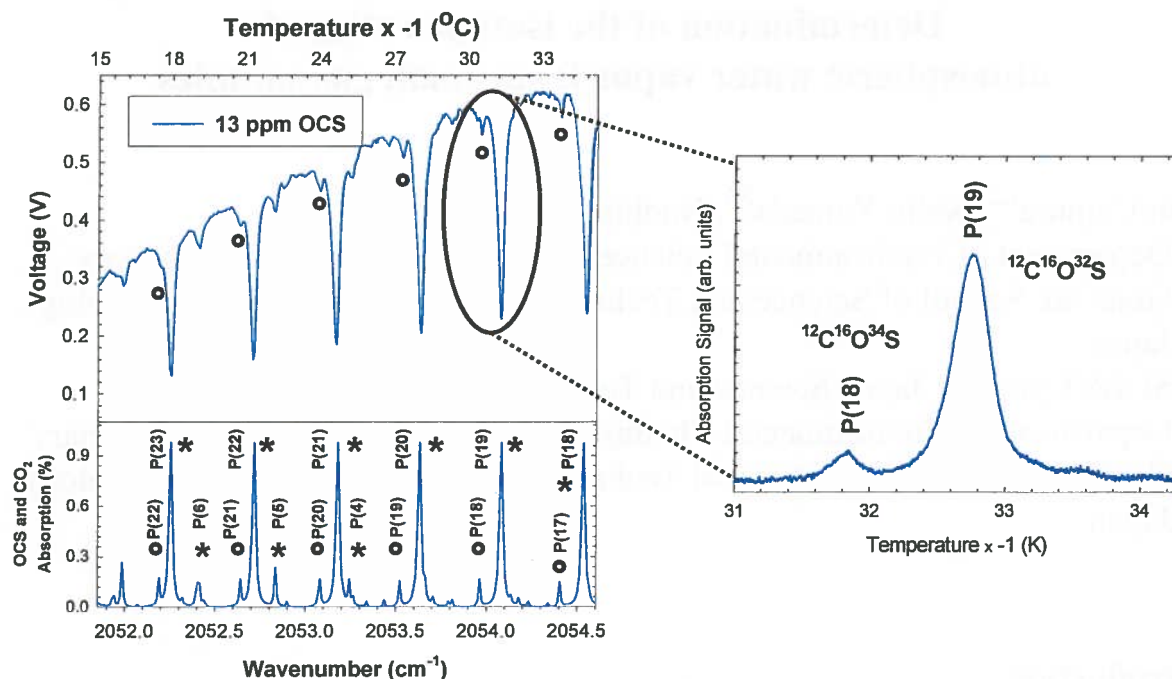


Figure 4. Measured and simulated COS absorption spectra between 2052.1 cm⁻¹ and 2054.3 cm⁻¹ for a 13.2 ppm COS concentration and 40 Torr total cell pressure. Stable COS isotopes, ¹²C¹⁶O³²S and ¹²C¹⁶O³⁴S, are denoted as * and o, respectively. The series of strong and weak ¹²C¹⁶O³²S lines belong to the ν_3 and $\nu_2+\nu_3-\nu_2$ bands, respectively. The ¹²C¹⁶O³⁴S lines belong to the ν_3 band.

The estimated precision for CO³⁴S/CO³²S isotopic ratios at a concentration of 150 ppm is ~2.5 ‰ based on the measurement uncertainty of CO³²S P(19) and CO³⁴S P(18) absorption lines at 2054.078 and 2053.960 cm⁻¹, respectively [Roller, 2003].

References:

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