

Carbonyl sulfide detection with a thermoelectrically cooled midinfrared quantum cascade laser

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A compact absorption spectrometer with a midinfrared tunable quantum cascade laser operating at $4.86\ \mu\text{m}$ ($2054\ \text{cm}^{-1}$) is used to measure lower concentrations of carbonyl sulfide (COS) in air. A detection sensitivity of ~ 30 parts in 10^9 of COS and the selectivity of two stable isotopes, $^{12}\text{C}^{16}\text{O}^{32}\text{S}$ and $^{12}\text{C}^{16}\text{O}^{34}\text{S}$, are demonstrated. Specifically, the feasibility of detecting COS in expired human breath as a potential noninvasive medical diagnostic tool is investigated. © 2003 Optical Society of America

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Sensitive concentration measurements of carbonyl sulfide (COS) have important applications in atmospheric monitoring¹ and medical diagnostics.^{2,3} In regard to medical diagnostics, elevated COS trace gas concentrations in exhaled breath have been observed in patients suffering from liver disease² and in episodes of acute lung rejection in transplant recipients.³ Measurement of expired COS in breath is inherently noninvasive and in some cases could obviate the need for more invasive surgical procedures such as lung biopsies.

Tunable laser absorption spectroscopy (TLAS) is a promising sensor technology for quantifying low levels of COS concentrations because of its molecular selectivity, rapid response times, ease of sample collection, and large absorption line intensities of COS ($>1 \times 10^{-18}\ \text{cm}^{-1}/\text{molecule cm}^{-2}$) in the mid-IR region. High-resolution TLAS with single-frequency mid-IR lasers can resolve COS absorption features in the $4.86\text{-}\mu\text{m}$ (2054-cm^{-1}) spectral region without interference from CO_2 or H_2O , which is important in the development of environmental and medical gas sensors. TLAS with mid-IR lead-salt lasers has been used to perform high-precision COS measurements in the atmosphere at concentrations of ~ 500 parts in 10^{12} with a 117-m optical path length.⁴ However, lead-salt lasers require cryogenic cooling ($<120\ \text{K}$), and the need to maintain cryogenic laser substrate temperatures is burdensome. The introduction of quantum cascade (QC) lasers capable of operating in the mid-IR region without the need for cryogenic cooling has thus provided an alternative to lead-salt lasers in the development of sensitive and compact trace gas sensors based on TLAS.⁵ In this Letter we report the development of a TLAS-based sensor

capable of measuring concentration levels of parts in 10^9 of COS at $4.86\ \mu\text{m}$ with a thermoelectrically cooled QC laser. Both $^{12}\text{C}^{16}\text{O}^{32}\text{S}$ and $^{12}\text{C}^{16}\text{O}^{34}\text{S}$ stable isotopic absorption features were resolved. We also measured COS mixed with exhaled breath to confirm that expired breath constituents do not spectrally interfere with the COS absorption lines of interest.

A schematic of the experimental sensor configuration is shown in Fig. 1. A QC laser was mounted on a two-stage Peltier cooler with a copper heat sink inside an evacuated housing.⁵ The QC laser output was collimated with an antireflection-coated aspheric ZnSe lens. The laser beam exited the housing through a wedged CaF_2 window and entered a multipass gas cell (New Focus Model 5611) of 36-m optical path length

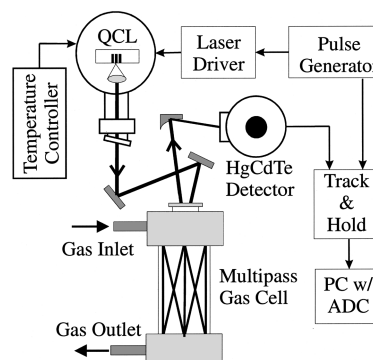


Fig. 1. Schematic of a TLAS sensor consisting of a pulsed thermoelectrically cooled QC laser (QCL), a 36-m optical multipass gas cell, a photovoltaic HgCdTe detector, and an analog-to-digital converter for acquiring data from the output of the track-and-hold circuit.

and 0.3-l volume. After traversing the gas cell, the laser beam was focused onto a liquid-N₂-cooled HgCdTe detector by use of an off-axis parabolic mirror.

The QC laser was excited with 1.96-A peak current pulses of 14-ns width at a 500-kHz repetition rate. To tune the QC laser output frequency, the laser substrate temperature was varied with a standard temperature controller (Wavelength Electronics, Inc., Model LFI-3751). A photovoltaic HgCdTe detector with a 35-ns 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.

As the laser substrate temperature was changing from -15 to -35 °C at a rate of ~ 5 °C/min, 800 laser pulses were sampled every 50 ms. Their averaged energy was recorded as a function of temperature. Figure 2 depicts both measured and simulated COS absorption spectra between 2052.1 and 2054.3 cm^{-1} at a concentration of 13.2 parts in 10^6 and a total gas pressure of 40 Torr. Simulated absorption profiles and identification of $^{12}\text{C}^{16}\text{O}^{32}\text{S}$ and $^{12}\text{C}^{16}\text{O}^{34}\text{S}$ isotopic lines were performed with COS spectral data from the HITRAN 2000 database.⁶ The laser output frequency had a linear relationship with temperature, $\Delta\nu/\Delta T = -0.13$ cm^{-1}/K . The measured COS absorption amplitudes were less than the equivalent simulated absorption amplitudes due to the instrument function (laser linewidth) being convolved with the COS absorption lines.

Pulsed QC lasers, in contrast to continuous-wave QC lasers, produce broader linewidths because of the frequency chirping caused by rapid heating of the laser active region during the pump current pulses. To determine the laser linewidth, the CO^{32}S P19 absorption line (2054.07 cm^{-1}) at a 2-Torr total pressure of a 13.2 parts in 10^6 COS:N₂ mixture was acquired. At this pressure the absorption profile is primarily Doppler broadened and has a FWHM of ~ 0.004 cm^{-1} (106 MHz). The laser linewidth was approximated at ~ 0.018 cm^{-1} (540 MHz) from the measured FWHM of the COS absorption profile and is in good agreement with linewidths of pulsed QC lasers reported in the literature.⁵

COS concentration analysis cannot be performed by a traditional method of line fitting with a Voigt function because of the significant laser linewidth and asymmetric line shape. Instead, spectral data acquired with a sample of known COS concentration were used to fit the data to be analyzed.⁷ Briefly, the COS absorption of the analyzed sample $y(T)$ (T is the laser temperature) is related to the reference absorption data $x(T)$ as $y(T) = Bx(T - \Delta) + c$. Here B yields the ratio of two COS concentrations, Δ represents a possible shift due to imperfect temperature control, and c accounts for baseline compensation. In our experiment a smoothed absorption profile acquired at 0.5 parts in 10^6 COS concentration was used as a reference function.

A key issue in using TLAS for exhaled breath analysis is spectral interference from breath constituents, namely, H₂O and CO₂. Figure 3 shows the acquired absorption spectra of ~ 500 parts in 10^9 of COS. This COS concentration simulates the expected concentration from a patient suffering from an occult occurrence of acute lung rejection.³ Two samples were prepared by adding the same quantity of certified 13.2 parts in 10^6 COS:N₂ mixture to either exhaled breath from a healthy volunteer (upper plot) or pure N₂ (lower plot). It can be seen that the intensity of the CO^{32}S P19 absorption line was not affected by other breath components. Indeed, the quantitative analysis shows a 3% difference in the measured COS concentrations mixed

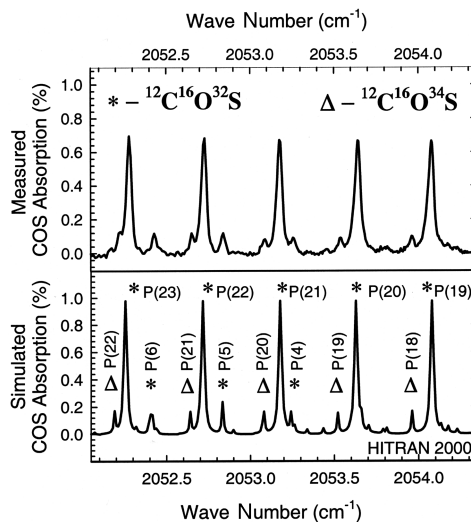


Fig. 2. Measured and simulated COS absorption spectra between 2052.1 and 2054.3 cm^{-1} for a 13.2 parts in 10^6 COS concentration and 40-Torr total cell pressure. Stable COS isotopes, $^{12}\text{C}^{16}\text{O}^{32}\text{S}$ and $^{12}\text{C}^{16}\text{O}^{34}\text{S}$, are denoted as * and Δ , respectively. The series of strong and weak $^{12}\text{C}^{16}\text{O}^{32}\text{S}$ lines belong to the ν_3 and $\nu_2 + \nu_3 - \nu_2$ bands, respectively. The $^{12}\text{C}^{16}\text{O}^{34}\text{S}$ lines belong to the ν_3 band.

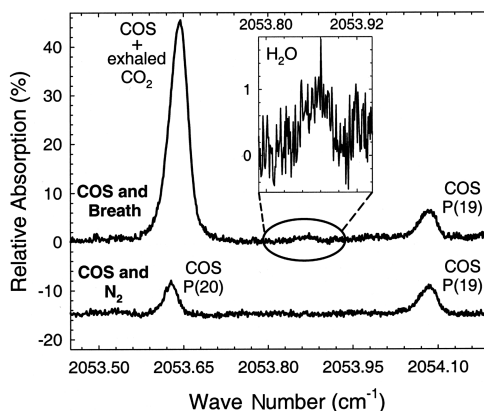


Fig. 3. Measured absorption spectra for 500 parts in 10^9 COS mixed with breath (upper plot) and with purified N₂ (lower plot). The upper plot has discernible CO₂, H₂O, and COS absorption features at 2053.63, 2053.86, and 2054.07 cm^{-1} , respectively. The COS absorption profiles at 2054.07 cm^{-1} are not significantly affected by the molecular constituents in breath.

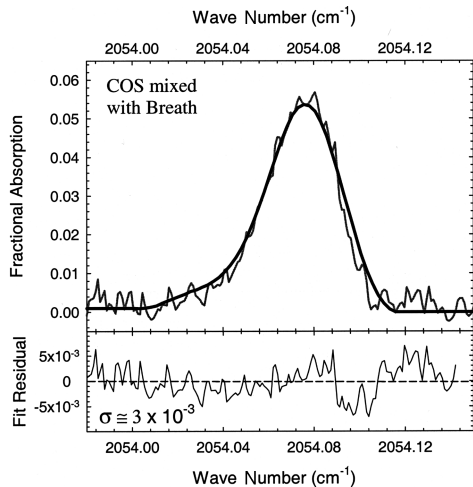


Fig. 4. Absorption spectrum of COS at 2054.078 cm^{-1} and a fitted absorption profile for exhaled breath mixed with COS. The COS concentration level was estimated to be 573 ± 5 parts in 10^9 (1σ). The lower plot is the fit residual.

with N_2 (557 parts in 10^9) or with breath (574 parts in 10^9).

An absorption line of CO_2 at 2053.629 cm^{-1} overlaps the P_{20} line of CO^{32}S . However, the CO_2 concentration can be readily calculated if the COS concentration defined from the interference-free P_{19} line is taken into account. According to HITRAN, the integrated line intensity of the P_{20} line at 296 K is 1% higher than the line intensity of P_{19} . When the corrected area of P_{19} from the data presented in Fig. 3 (upper plot) was subtracted from the area of the absorption feature at 2053.63 cm^{-1} , a comparison of the resulting number with the HITRAN data yielded a CO_2 concentration of $\sim 4.20\%$. The ability to measure exhaled CO_2 simultaneously with COS could prove useful in standardizing the collection and analysis of expired breath.⁸

The equation $\delta A = \sigma[\Delta\nu/\int g^2(\nu)\delta\nu]^{1/2}$ derived in Ref. 9 was used to estimate the measurement precision. In this equation δA is the standard deviation of the absorption line area A , σ is the standard deviation of the fit residual, $\Delta\nu$ is the average spectral separation of the acquired data points ($7.3 \times 10^{-4}\text{ cm}^{-1}$ for our data), and $g(\nu)$ is the absorption line profile normalized by the condition $\int g(\nu)d\nu = 1$. Spectral data for the P_{19} absorption line presented in Fig. 3 (upper plot), fitted by the reference function as shown in Fig. 4, were used to calculate the parameters for this equation. It was found that $\sigma = 2.8 \times 10^{-3}$ and $\int g^2(\nu) - d\nu = 15.7\text{ cm}$, which yields $\delta A = 1.9 \times 10^{-5}\text{ cm}^{-2}$, or ~ 5 parts in 10^9 COS concentration (0.072% peak absorption). This corresponds to a detection limit of ~ 15 parts in 10^9 at $3\delta A$ levels (0.16% peak absorption). The equation used here to determine the detection limit does not take into account the line position uncertainty and baseline modulation; therefore the practical detection limit may be somewhat higher. A weak H_2O absorp-

tion line at 2053.86 cm^{-1} (Fig. 3, upper plot) provides another way to estimate sensitivity. This line is clearly observed with a peak absorption of 0.6% and is within the detection limit of 0.16% estimated above. A compromise between the ascribed detection limit for the analytical analysis and the observed fractional absorption of H_2O yields a conservative detection limit of $\sim 0.3\%$ (30 parts in 10^9 COS concentration).

In conclusion, we demonstrated a TLAS sensor based on a thermoelectrically cooled QC laser that is capable of measuring low levels of COS in parts in 10^9 . The pulsed QC laser exhibited a sufficiently narrow laser linewidth of $\sim 0.018\text{ cm}^{-1}$ to resolve COS lines near $4.86\text{ }\mu\text{m}$. CO_2 and H_2O in expired breath do not significantly interfere with the strong COS line at 2054.078 cm^{-1} . Further improvement of COS detection sensitivity can be realized with fast wavelength modulation techniques, as described in Ref. 5. Finally, isotopic selectivity for CO^{32}S and CO^{34}S may prove useful in identifying the chemical pathways that produce COS in biological tissue and the environment.

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