Measurements of benzene concentration by difference-frequency laser absorption spectroscopy

Weidong Chen, Fabrice Cazier, Frank Tittel, and Daniel Boucher

Measurements of benzene concentration based on high-resolution laser absorption spectroscopy by use of the $R(6)$ transition in the ν_4 fundamental vibrational band near 14.8 μm (676.6 cm^{-1}) are reported. These measurements were performed with a tunable continuous-wave, mid-infrared spectroscopic light source that employs difference-frequency mixing of two Ti:sapphire lasers in a GaSe nonlinear optical crystal. A minimum benzene concentration detection of ~11.5 parts in 10^6 was realized at a reduced pressure of 40 mbars. © 2000 Optical Society of America

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1. Introduction

There is considerable interest in the detection of volatile organic compounds (VOC's) in the atmosphere. The most important VOC's that are present in ambient air include benzene and 1,3-butadiene, as potential leukemia-inducing agents; formaldehyde, as a potential nasal carcinogen; polynuclear aromatic hydrocarbons, as potential lung cancer–inducing agents; polychlorinated biphenyl compounds and polychlorinated terphenyl compounds; and dioxins and furans.

The need to identify and quantify VOC levels in the atmosphere and for industrial process control has led to the development of VOC measurement techniques. VOC measurements are usually performed by means of chromatography and mass spectrometry[1] or by Fourier-transform infrared (FTIR) spectroscopy.[2] Chromatography, coupled with mass spectrometry, offers both excellent sensitivity and selectivity, but in certain cases it may require conveniently realized and rapid response air sampling for *in situ*, real-time, continuous trace-gas monitoring. In the mid-infrared fingerprint region of 3–20 μm, most molecular pollutants exhibit strong rotational–vibrational absorption with characteristic features. This property permits sensitive and selective detection of numerous important atmospheric trace gases and pollutant species by laser-based absorption spectroscopy. Measurement techniques that are available include tunable diode laser absorption spectroscopy[3] and difference-frequency laser absorption spectroscopy (DFLAS). Although nonaromatic hydrocarbons have strong absorption bands in the 2.8–3-μm region because of the CH stretching vibrations, they also have lower-frequency vibrational bands in the 8–20-μm region. The number and wavelength range of these bands depend on the number of carbon atoms and also on whether they contain aliphatic rings. Frequently these lower-frequency bands are stronger than those near 3 μm. FTIR spectroscopy permits *in situ*, on-line analysis over a broad mid-infrared frequency range, but obtaining a spectral resolution of better than 0.1 cm^{-1} increases the complexity, size, and cost of the instrumentation. The minimum detectable absorbance level is approximately 10^{-3}–10^{-4}.

Laser infrared absorption spectroscopy offers the advantage of highly selective *in situ* (in particular when direct sampling is not possible) and real-time measurements with detection sensitivities in the parts-in-10^6 (ppm) to parts in 10^{12} range. Based on measurement of the absorption line(s), one determines gas concentrations either by fitting a characteristic spectral absorption profile to a theoretical model using molecular line parameters or by using a validated calibration standard.

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In this paper we report the feasibility of measuring concentrations of benzene (C_6H_6) by using mid-infrared DFLAS near 14.8 μm (676.6 cm^{-1}). This spectral region was selected because it provides the least congested fundamental absorption spectrum for performing sensitive and selective C_6H_6 concentration measurements in ambient air. Benzene is an important organic solvent that is widely used as an additive gasoline that is emitted into the atmosphere by engine exhausts. The maximum limit of benzene concentration in terms of toxicity has been set in Europe at 5 ppm.[4] Monitoring of benzene with tunable Pb-salt diode laser absorption spectroscopy near 14 μm was previously reported in Ref. 5. A minimum detectable concentration of 80 ppm of benzene with a 3.46-m path-length Herriott multipass cell was reported. A benzene spectrum in the ν_{14} band near 9.78 μm (1023 cm^{-1}) measured by pulsed tunable diode laser absorption spectroscopy was reported.[6] Benzene detection with a path-integrated concentration sensitivity of 2 ppm/m in the ultraviolet from 235 to 270 nm by use of an open-path Fourier-transform ultraviolet spectrometer was described in Ref. 7.

For the purpose of spectroscopic analysis of VOC's by mid-infrared absorption laser spectroscopy, particularly in the 14.8-μm region, a continuous-wave spectrometer based on difference-frequency generation (DFG) in GaSe that is widely tunable from 8 to 19 μm was developed.[8,9] Continuous-wave DFG in GaSe was reported by Eckhoff *et al.*[10] for the mid-infrared region of 8.8–15 μm. More recently, an automated spectrometer based on diode laser–pumped DFG in GaSe (Ref. 11) and a DFG laser spectrometer that uses $AgGaS_2$ tunable from 6.8 to 12.5 μm (Ref. 12) were reported. All DFG spectrometers that have been reported to date are laboratory instruments. However, with the rapid recent advances of optical telecommunication technology (i.e., single-frequency telecom diode lasers and fiber amplifiers) and new quasi-phase-matched materials, such as orientation patterned epitaxially grown GaAs crystals,[13] a compact and fieldable DFG trace-gas sensor in the 8–15-μm spectral region that is suitable for detection and quantification of VOC's should be realizable.

2. Spectroscopic Considerations for Measurements of Gas Concentration by DFLAS

The relevant factors involved in the selection of a specific absorption line for precise measurements of benzene concentration include the choice of a strong spectral line for high sensitivity that at the same time should be isolated from interfering lines that result from other gas species or from the same species (which is particularly important in the case of large VOC molecules).

Initially, a FTIR survey absorption spectrum of benzene vapor was recorded with a Fourier-transform spectrometer (Perkin-Elmer System 2000 FT-IR) in the infrared region from 500 to 2500 cm^{-1}. Figure 1 shows a FTIR spectrum of benzene (lower trace). The spectrum was obtained with ~50-mbar benzene in a 12-cm-long single-pass cell. The resolution of the FTIR spectrometer was limited to 0.2 cm^{-1}. The ν_4-fundamental A_{2u} band (Herzberg notation[14]) near 14.8 μm exhibits the strongest absorption in the infrared, which results from an out-of-plane hydrogen motion. For the band and molecular constants of high-resolution benzene spectra, see Refs. 15–17. The line strength of the ν_4 band is ~1 order of magnitude higher than that of the ν_{14} band near 10 μm. Moreover, as the only parallel band of all four infrared fundamental bands, the ν_4 band has the simplest rotational structure, and no strong Fermi or Coriolis resonance perturbs the ν_4 state.[15] This band is therefore favorable for highly sensitive measurements of benzene concentration. However, as shown in Fig. 1 (upper trace) the atmospheric CO_2 absorption interferes with the ν_4 band of C_6H_6, whereas the ν_{14} band is almost completely free of interference from atmospheric absorption, as mentioned above. Hence a high-resolution spectroscopic measurement is necessary for the discrimination of benzene absorption from CO_2 interference.

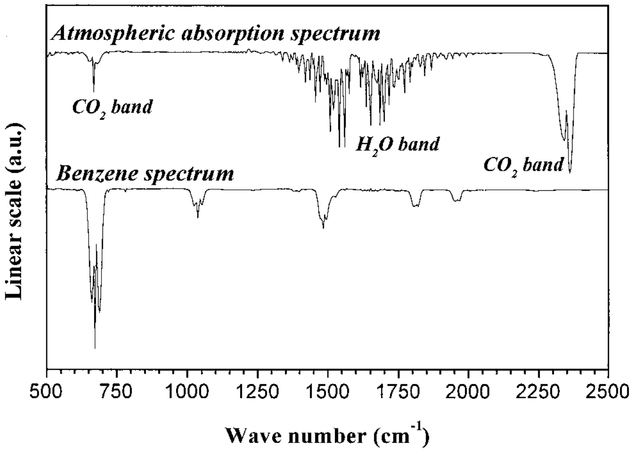

Fig. 1. FTIR absorption spectrum of benzene vapor in the 500–2500-cm^{-1} spectral region. The absorption spectrum of atmospheric CO_2 and H_2O vapor is shown for comparison.

3. Experimental Details

A. Description of the Spectrometer

A schematic diagram of the DFG-based spectrometer is shown in Fig. 2. The DFG-based spectroscopic source was pumped by two Ar^+ laser–pumped cw single-frequency Ti:sapphire lasers that were tunable from 700 to 800 nm and from 800 to 900 nm, respectively. The laser beams, orthogonally polarized, were mixed in a GaSe crystal to generate tunable infrared radiation at the difference frequency of the two pump lasers by a $\chi^{(2)}$ nonlinear optical parametric frequency-conversion process. The infrared emission was continuously tunable from 8 to 19 μm by pump laser wavelength and angle tuning of the z axis crystal orientation for type I phase matching. The infrared generated power was ~0.1 μW, with a spectral purity of ~1 MHz. Therefore instrumental

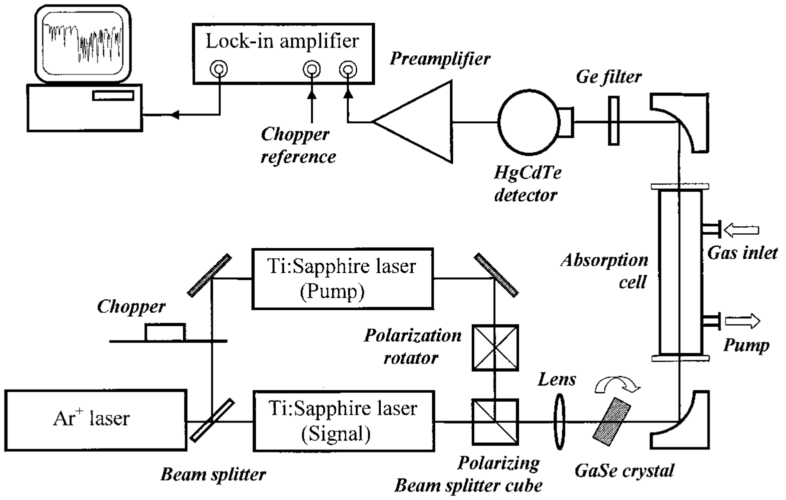

Fig. 2. Schematic of a high-resolution infrared spectrometer based on laser difference-frequency generation in a GaSe crystal tunable from 8 to 19 μm.

contributions to the experimental linewidth are negligible. The absolute accuracy and reproducibility of frequency measurements of the DFG-based spectrometer were 200 and 50 MHz, respectively.

The infrared beam was collimated into an ~10-mm-diameter beam with a parabolic mirror and directed toward a 10-cm-long absorption cell fitted with plane-parallel ZnSe windows. The infrared light that emerged from the cell was collected by a 90° off-axis parabolic mirror and focused onto a liquid-nitrogen-cooled HgCdTe photoconductive detector with a 1-mm^2 active area.

B. Selection of Absorption Lines

C_6H_6 vibrational spectra are dense, as benzene is a heavy molecule. The optimum sampling pressure is a compromise between sensitivity (best at high pressure) and selectivity (best at low pressure) for rotationally resolved infrared spectroscopy. To select a suitable line for spectroscopic trace detection we recorded a high-resolution spectrum of benzene near 667 cm^{-1} with the DFG-based infrared spectrometer. The DFLAS spectrum was obtained from a lock-in amplifier with a time constant of 1 s in a 0–30-kHz bandwidth. The chopping frequency was set at 2 kHz.

Benzene vapor was obtained from vaporization of liquid benzene. A direct absorption spectrum of ~1-mbar quasi-pure benzene vapor is shown in Fig. 3(a) (lower line). We recorded the spectrum by fixing the signal laser frequency and the external crystal angle at 11 911 cm^{-1} and ~45°, respectively, and scanning the pump laser frequency starting at 12 586.5 cm^{-1} in 20-MHz steps. The wave-number calibration was checked with the atmospheric CO_2 $R(10)$-01(1E)0-00(0)0 line at reduced pressure.[18] The upper spectrum in Fig. 3(a) is a background spectrum of air that shows the presence of CO_2 absorption. Sensitive measurements of C_6H_6 concentration can be made with the strong absorption lines between two adjacent strong CO_2 absorption lines [with line strengths of $\sim 10^{-19}$ cm molecule^{-1} (Ref. 19)] separated by ~1.5 cm^{-1}. In this manner benzene absorption lines of the $\nu_4 R(6)$ and $\nu_4 + \nu_{20}$–ν_{20} $R(9)$ near 676.62 cm^{-1} were selected, as shown in Fig. 3(b). These lines exhibit an absorption intensity of $\sim 10^{-21}$ cm molecule^{-1}. Unfortunately, the much stronger Q-branch lines ($S \sim 10^{-19}$ cm molecule^{-1}) at 673–674 cm^{-1} could not be used for spectroscopic concentration measurements because of strong CO_2 interference. The benzene spectrum exhibited the resolved J but not the K structure with Doppler-limited resolution. For air monitoring applications, the spectroscopic resolution is usually limited by pressure broadening. The line parameters of most VOC's are not available in either the GEISA[19] or the HITRAN[20] spectroscopic database; hence original spectroscopic laboratory studies are necessary.

C. Benzene Trace-Gas Measurements

A 10-l glass flask was used for the preparation of benzene trace-gas samples. The flask was filled with ambient air at a pressure of ~250 mbars, and an accurately weighed sample of the liquid benzene contained in a microsyringe was injected into the flask. Sufficient time was allowed to ensure complete vaporization of the sample. This benzene gas mixture was then introduced into the absorption cell at a reduced pressure in the range of some tens of millibars to reduce the pressure effects of broadening and spectral interference. The pressure was measured with a capacitance manometer (Barocel Model 600) designed for the 0–1000-mbar range, with a resolution of 0.1 mbar and a reading accuracy of 0.15%. The C_6H_6 concentration was determined by gas chromatography (Varian Saturn 4D). For calibration of the chromatography-based measurement we employed a 99.4-ppm (±2% calibration) benzene-in-air mixture (Scott Specialty Gases Scotty IV). The calibration curve depicted in Fig. 4 shows that the ratio

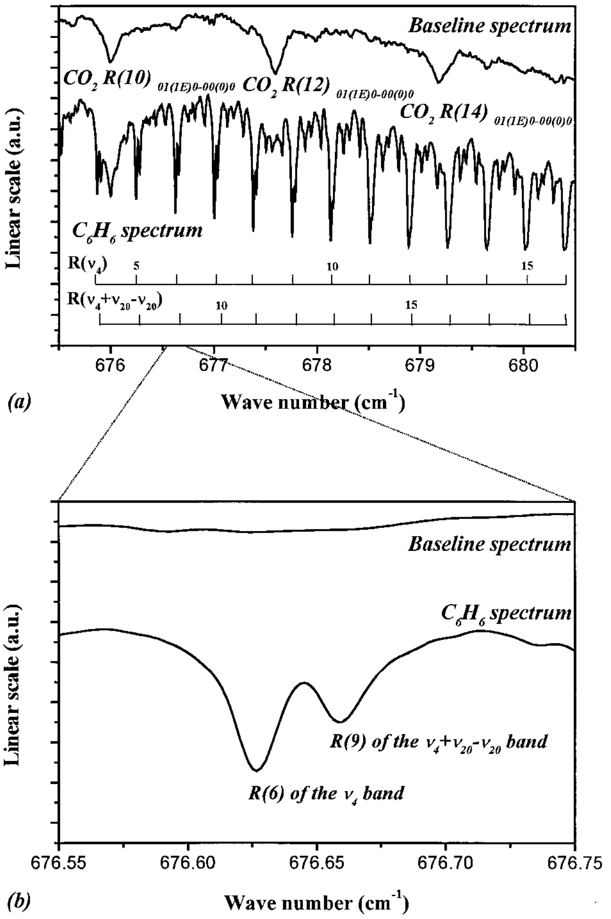

Fig. 3. High-resolution C_6H_6 spectrum recorded with the laser difference-frequency-based spectrometer. (a) Background baseline spectrum, indicating the presence of CO_2 absorption in ambient air, and experimental spectrum of ~1-mbar quasi-pure benzene with interfering CO_2 absorption lines. (b) Selected C_6H_6 lines for measurements of concentration by laser absorption spectroscopy.

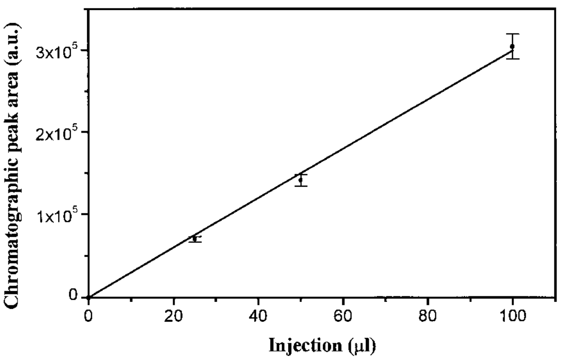

Fig. 4. Chromatographic calibration measurements obtained with a specific benzene-in-air-mixture.

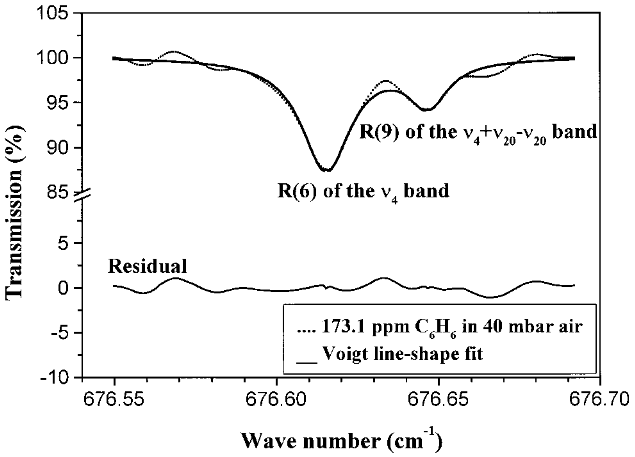

Fig. 5. Measurement of C_6H_6 concentration in ambient air: 173.1-ppm benzene absorption line of $\nu_4 R(6)$ and $\nu_4 + \nu_{20}-\nu_{20} R(9)$ near 676.62 cm^{-1} at 40-mbar pressure and its fit to a Voigt line-shape function and the accompanying residual. The FWHM of the Voigt line-shape fit is 0.0191 cm^{-1} and 0.0144 for the $R(6)$ and $R(9)$ lines, respectively.

of the integrated chromatographic peak area to volume injected by the gas microsyringe is linear, as expected by a fit correlation coefficient $R^2 = 0.996$.

4. Experimental Results

Figure 5 depicts a C_6H_6 trace-absorption spectrum of the $\nu_4 R(6)$ and $\nu_4 + \nu_{20}-\nu_{20}$ $R(9)$ lines near 676.62 cm^{-1} at 40 mbars and room temperature acquired by DFLAS, which we obtained by ratioing the sample spectrum to the empty cell spectrum to make a baseline correction and subtracting the CO_2 absorption. The solid curve is a Voigt profile fitted to the absorption lines (dotted curve). The residual from the Voigt line shape is shown below the C_6H_6 spectrum. A measurement of the benzene concentration in this sample by gas chromatography yielded a benzene concentration of 173.1 ppm. The selected lines are slightly perturbed by the presence of an $^{16}O^{12}C^{16}C$ line at 676.6090 cm^{-1} inside the cell, with $S \sim 3 \times 10^{-23}$ cm molecule^{-1}, as shown in Fig. 3(b). The only way to correct for this absorption would be to record the spectrum of the cell containing ambient air from which benzene is absent and for which the pressure used is identical to that which can contain benzene.

5. Conclusions

Benzene vapor has been successfully detected and quantified with a tunable DFG-based spectrometer in the ν_4 band at ~15 μm. The signal-to-noise ratio of ~15 deduced from this spectroscopic measurement corresponds to a minimum detectable concentration of ~11.5 ppm. Increased sensitivity at ppm levels should be attainable by long-path absorption spectroscopy in combination with software signal filtering and enhanced data-acquisition techniques.

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