# Trace Gas Absorption Spectroscopy Using Laser Difference-Frequency Spectrometer for Environmental Application

W. Chen<sup>1</sup>, F. Cazier<sup>1</sup>, D. Boucher<sup>1</sup>, F. K. Tittel<sup>2</sup>, and P. B. Davies<sup>3</sup>

<sup>1</sup> MREID, Université du Littoral, 145 Av. Maurice Schumann, Dunkerque, 59140 France e-mail: chen@univ-littoral.fr

<sup>2</sup> Rice Quantum Institute, MS 366, Rice University, 6100 Main St., Houston, TX 77005 USA

<sup>3</sup> Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW UK

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**Abstract**—A widely tunable infrared spectrometer based on difference frequency generation (DFG) has been developed for organic trace gas detection by laser absorption spectroscopy. On-line measurements of concentration of various hydrocarbons, such as acetylene, benzene, and ethylene, were investigated using high-resolution DFG trace gas spectroscopy for highly sensitive detection.

# INTRODUCTION

The increasing need for rapid, *in situ* characterization and quantification of pollutant species has led to the development of spectroscopic monitoring techniques for stack and open-air environmental sensing, industrial process control, remediation activities, and the support of regulatory activities [1]. In the mid-infrared fingerprint region from 3 to 20  $\mu$ m, most molecular pollutants exhibit characteristic spectroscopic features. This permits sensitive and selective detection of numerous important atmospheric trace gases and toxic organic pollutant species by laser absorption spectroscopy. Laser infrared absorption spectroscopy offers the advantage of highly selective *in situ* and real time measurements with detection sensitivities in the ppm (part in 10<sup>6</sup>) to sub-ppt (part in 10<sup>12</sup>) range.

Infrared laser sources based on nonlinear optical frequency down-conversion have been developed during the past decade. This has led to numerous applications ranging from high-resolution laser spectroscopy to advanced environmental monitoring and control techniques. Various spectrometer designs using infrared coherent light based on difference-frequency generation (DFG) in periodically poled LiNbO<sub>3</sub> (PPLN), RbTiOAsO<sub>4</sub> (PPRTA), KTiOPO<sub>4</sub> (PPKTP), KTiOAsO<sub>4</sub> (PPKTA) for the 3–5  $\mu$ m spectral region [2–5], AgGaS<sub>2</sub> for the 4–12  $\mu$ m region [6–9], and GaSe for longer infrared wavelengths from 8–19  $\mu$ m [10–12] have been reported recently.

In this work we report a laser difference-frequency generation spectrometer developed in Dunkerque for volatile organic compounds (VOCs) analysis. Trace concentration of various hydrocarbons, such as acety-lene ( $C_2H_2$ ), benzene ( $C_6H_6$ ), and ethylene ( $C_2H_4$ ), was measured by means of high-resolution laser absorption

spectroscopy. Pressure-induced linewidth coefficient of the  $v_4 R(6) C_6 H_6$  line was also investigated.

# DFG LASER SPECTROMETER

The DFG based laser spectrometer has been detailed elsewhere [11]. In brief, it is based on laser frequencies mixing in a nonlinear optical crystal to generate infrared light at the difference frequency of the lasers via the second-order optical nonlinearity  $\chi^{(2)}$ . A schematic diagram of the DFG laser spectrometer is shown in Fig. 1. Two Ar<sup>+</sup> laser-pumped continuous-wave (cw) single frequency Ti: Sapphire lasers (700-800 nm, and 800-900 nm respectively, Coherent, Inc.) were mixed in a z-cut gallium selenide (GaSe) crystal, 5 mm thick and 10 mm in diameter. The infrared DFG radiation, with a spectral purity of  $\sim 10^{-4}$  cm<sup>-1</sup>, was continuously tunable from 8 to 19  $\mu$ m (1250–525 cm<sup>-1</sup>) by laser wavelengths tuning and z-axis orientation of the crystal for a type I phase matching condition. The DFG power was ~0.1  $\mu$ W at ~9  $\mu$ m. The absolute accuracy and reproducibility of the frequency measurement, as determined by the wavelength meter (part of one of the Ti: Sapphire pump lasers), are  $7 \times 10^{-3}$  cm<sup>-1</sup> and  $2 \times 10^{-3}$  cm<sup>-1</sup>, respectively.

The wide spectral tunability provides convenient access to infrared probing wavelengths suitable for sensitive and selective trace gas detection [13]. In addition the dynamic range for detection can be enhanced readily by using a strong and weak absorption lines to perform low and high concentration measurements, respectively, of the same absorber with a single instrument.

A high-resolution spectrum of ethylene of the  $v_7$  band was recorded in order to evaluate the spectroscopic performance of this novel type of the infrared



Fig. 1. Experimental setup of a widely tunable infrared spectrometer based on laser difference frequency generation in GaSe crystal.



**Fig. 2.** Comparison of an experimentally observed spectrum of  $C_2H_4$  (top), obtained at a pressure of ~3 mbar and room temperature filled in a 10-cm long single pass absorption cell, with the assigned simulation (bottom) using the HITRAN96 database [14].

laser spectrometer. Figure 2 shows a spectral comparison of the experimental spectrum, obtained at a pressure of  $\sim$ 3 mbar filled in a 10-cm long single pass absorption cell at room temperature, with a simulated spectrum using the HITRAN database [14].

# SPECTROSCOPIC INVESTIGATION ON TRACE CONSTITUENT MEASUREMENTS

Based on a measurement of an absorption line(s), gas concentration can be determined either by fitting a

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Fig. 3. Voigt line-shape fit (solid line) to an absorption spectrum of  $\sim$ 77 ppm C<sub>2</sub>H<sub>2</sub> (dots) and the accompanying residuals.

characteristic spectral absorption profile to a theoretical model using molecular line parameters (e.g., absorption transition frequency, line strength, and pressurebroadening linewidth coefficient). A Voigt fit (solid line) to an absorption spectrum of  $\sim$ 77 ppm C<sub>2</sub>H<sub>2</sub> around 730 cm<sup>-1</sup> is depicted in Fig. 3; or by using a validated calibration standard. A comparison of pure (a) and 1% calibration (b)  $v_7$ -C<sub>2</sub>H<sub>4</sub> absorption spectra near 950 cm<sup>-1</sup> is shown in Fig. 4. In this case, the measurement of trace concentration is typically carried out by comparing the observed spectrum ("sample") with a calibrated spectrum ("ref") using a least-squares fit method:

$$C_{\text{sample}} = \frac{C_{\text{ref}} \times L_{\text{ref}} \times P_{\text{ref}} \times T_{\text{sample}} \times S_{\text{sample}}}{L_{\text{sample}} \times P_{\text{sample}} \times T_{\text{ref}} \times S_{\text{ref}}}$$

where C is the concentration, P and T the pressure and temperature, L the optical absorption path length, and S is the area under the molecular absorption line(s).

In the former case, the quantitative analysis of the trace gas concentration is performed by nonlinear least-squares fit of the absorption spectrum A(v) based on the Beer–Lambert law:

$$A(\mathbf{v}) = 1 - \exp\left[-\sum g_i(\mathbf{v}_{0_i}, \gamma_{D_i}, \gamma_{L_i}) \times S_i \times C \times L\right],$$

where  $S_i$  is the line strength of the *i*th absorption line, *C* is the concentration, and *L* is the optical path length. The absorption line shape  $g_i$  is considered by a Voigt profile, in function of the absorption line position  $v_{0_i}$ , the Doppler and pressure broadened line widths  $\gamma_{D_i}$ ,  $\gamma_{L_i}$  respectively. Hence a detailed and precise knowledge of the line parameters is required. A convenient spectroscopic database is not available for many of the heavy toxic organic molecules, which exhibit very dense vibrational spectra in the infrared. Figure 5 depicts a spectrum of benzene vapor of the  $v_4 R$  branch



**Fig. 4.** Comparison of pure (a) and 1% calibration (b)  $C_2H_4$  absorption spectra near 950 cm<sup>-1</sup>.



Fig. 5. Doppler limited resolution DFG spectrum of benzene vapor of the  $v_4 R$  branch recorded at a pressure of ~1 mbar and room temperature.

obtained using our DFG laser spectrometer. The benzene spectrum is characterized by resolved J structure, whereas the K structure is completely smeared out even for a Doppler limited spectral resolution at ~1 mbar of pressure.

In the present work, the absorption cell used was a 10-cm single pass stainless steel cell fitted with ZnSe windows. A lock-in amplifier was tuned at 2 kHz with a time constant of 1 s. The  $C_2H_2$  and  $C_2H_4$  concentrations were determined both by using line parameters fitting and standard gas calibration methods. The  $C_6H_6$  concentration was measured with a calibration standard via gas chromatography, because of the lack of an available benzene database.

# Air-Broadening Linewidth Coefficient

In order to determine the air broadened linewidth coefficient  $\gamma_{air}$ , air was added incrementally in one series of measurements and the absorption linewidths were measured for different pressures. The pressures were measured with a capacitance manometer (Model 600 Barocel, EDWARDS) with an accuracy of 0.15%. The pressure-dependent linewidth was determined by fitting a Voigt line-shape function to the experimental absorption line, and the air-broadening coefficient  $\gamma_{air}$  was deduced from the regression slope.

The C<sub>6</sub>H<sub>6</sub> R(6) line of the v<sub>4</sub> band was selected for the measurement of the air broadening linewidth coefficient. Figure 6 shows a plot of linear dependence of the linewidths on pressures of the v<sub>4</sub> R(6) line. Benzene

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vapor was buffered by ambient air at room temperature. The pressure-induced linewidths were measured at total pressures varying from 1 to 65 mbars. An airbroadening coefficient  $\gamma_{air}$  (FWHM) of 0.2385 ± 0.0041 cm<sup>-1</sup>/atm was observed at 291 K.

#### **On-Line Measurements of Trace Quantity**

In order to perform sensitive benzene trace detection by laser spectroscopy, the  $v_4$  band was chosen in



**Fig. 6.** Linear dependence of the linewidths of the  $v_4 R(6) C_6 H_6$  line on pressure.

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Summary of sensitive and selective concentration measurements of  $C_2H_2$ ,  $C_2H_4$ , and  $C_6H_6$  using laser difference frequency absorption spectroscopy. The measured concentrations and the minimum detectable concentration (MDC) are normalized in terms of the concentration–path in ppm.m with a confidence level of 99.86% using a 1 s time constant

Molecule	Assignment	Transition frequency (cm <sup>-1</sup> )	Measured concentra- tion-path (ppm.m)	Sampling pressure (mbar)	MDC (ppm.m)
Acetylene (C <sub>2</sub> H <sub>2</sub> )	$v_5 - P(21)$	679.7095	1000	1000	2.5
	$v_5 - Q(11)$	729.7380	7.7	168	0.04
	$v_5 - R(9)$	752.6589	43.2	1000	0.36
Benzene (C <sub>6</sub> H <sub>6</sub> )	$v_4 - R(6)$	676.6258	34.6	65	3.5
Ethylene (C <sub>2</sub> H <sub>4</sub> )	$v_7 - (14_{1.14} - 14_{0.14})$	949.4293	66	250	2.1

the present work, because the absorption intensity is ~10 times higher than that of the  $v_{14}$  band. However the  $v_4$  band is strongly interfered with atmospheric CO<sub>2</sub> absorption lines [15]. Specifically, the  $v_4 R(6)$  line was selected, which is free from spectral interference by atmospheric CO<sub>2</sub> absorption. The measurements of gas-phase benzene concentration were carried out using laser absorption spectroscopy associated with gas chromatography (SATURN 4D, Varian). The concentration calibration was made by use of specified 99.4 ppm (±2%) benzene in air (SCOTTY IV). Figure 7 plots a Voigt fit of 346 ppm C<sub>6</sub>H<sub>6</sub> at 65 mbar and 291 K. A minimum concentration detection of ~23 ppm was obtained for a signal-to-noise ration of ~15.

The advantage of broad tunability was demonstrated in determining optimal condition for detection of  $C_2H_2$ trace quantities using the P(21), Q(11) and R(9) lines of the  $v_5$  band [13]. The  $C_2H_2$  concentrations were deter-



**Fig. 7.** 346 ppm  $C_6H_6$  vapor absorption spectrum at 65 mbars and 291 K.

mined by fitting experimental absorption line(s) to a theoretical line-shape function using the line parameters given in the HITRAN96 database [14]. Sensitive detection of ~1.2 ppm (MDC) was achieved using the Q(11) line near 13.7 µm at a reduced pressure of 168 mbars to avoid pressure-induced line overlap. The R(9) line seems to be a most suitable line in terms of absorption strength and freedom from spectral interference for spectroscopic detection under atmospheric conditions (at room temperature and atmospheric pressure) with a MDC of ~7 ppm.

The measurement of  $C_2H_4$  concentration was implemented using the transition  $(14_{1.14}-14_{0.14})$  of the strong Q branch of the  $v_7$  band. The detection sensitivity was ~22 ppm at a pressure of 250 mbars.

# **SUMMARY**

For the purpose of environmental trace gases analysis by laser absorption spectroscopy, high spectral purity and wide frequency tunability of cw laser source offer the unique advantage of convenient access to wavelengths suitable for high selectivity and sensitivity with a large dynamic range. Spectroscopic analysis of toxic organic trace constituents of acetylene, benzene, and ethylene were carried out using laser difference frequency trace spectroscopy with their relatively isolated high absorption lines in the infrared. The  $C_2H_2$  and C<sub>2</sub>H<sub>4</sub> concentrations were measured by use of molecular line parameters fitting method, which were confirmed with a specified  $C_2H_2$ - $C_2H_4$ -in-nitrogen calibration mixture. The C<sub>6</sub>H<sub>6</sub> concentration measurement was performed using gas chromatography. The preliminary results are summarized in the table. The concentration measurements and the minimum detectable concentration (MDC) are normalized in terms of the concentration-path in ppm.m with a confidence level of 99.86% using a time constant  $\tau = 1$  s. The sensitivity could be further improved by using balanced detection [16], which reduced the excess laser noise by 10 dB, and software signal filtering and enhanced data processing.

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