Simultaneous Multi-Gas Detection Using ICL Photoacoustic Spectroscopy

ABSTRACT

Researchers from China have developed and demonstrated a simultaneous, multi-component gas detection system based on differential Helmholtz resonance spectroscopy with a mid-infrared, tunable, interband cascade laser (ICL). The first harmonic demodulation method was used under ambient pressure to detect three light carbon gases: CH_4, C_2H_4, and C_2H_6. Using this photoacoustic system, the detection limits reached 98.8 ppb, 252 ppb, and 33 ppb for methane, ethylene, and ethane, respectively. Multi-wavelength linear regression was implemented to reduce the effects of cross-interference of the three gases, maintaining the accuracy of the gas concentration measurements. This new method, using an ICL with a Helmholtz resonator, provides a simple and fast multiple gas detection technique for atmospheric research, medicine, the food industry, pollutant monitoring, and the power industry.

PHOTOACOUSTIC SPECTROSCOPY

Photoacoustic spectroscopy (PAS) is a common technique for trace gas detection, reaching concentration levels as low as part-per-billion and part-per-trillion levels. Instead of using scattered light or absorption spectrum from molecules, PAS uses acoustic detection to measure the effect of light on a sample. These designs include microphones or tuning forks in the acoustic detection module or near the resonator chamber to transduce the acoustic signal into an electrical signal. Multiple wavelengths of light will produce a photoacoustic spectrum and can be used to identify the components in a sample.

PAS, as an indirect detection method, can be advantageous with high detection sensitivity, good selectivity, fast detection speed, and long service life.[1] These benefits are critical for reaching part-per-billion detection levels of trace gases in the atmosphere or lab environment. PAS has been widely used in atmospheric research, medicine, the food industry, pollutant monitoring, and the power industry.[1] However, most systems are designed to detect only a single gas, not multiple components simultaneously. A single device that can measure multiple gases in real-time can provide safety, environmental, and economic benefits in research laboratories, field experiments, or even residential applications.

The light source to generate the photoacoustic effect has recently improved with the invention of tunable lasers and, specifically, quantum cascade lasers (QCLs) with narrow linewidths for higher sensitivity. Along with the laser, the photoacoustic cell and pressure sensor are critical factors affecting the detection performance of PAS.[1]

PROBLEMS AND GOALS

Simple mid-infrared lamps and single-wavelength laser arrays have achieved multiple gas detection, but they require mechanical or optical accessories to accomplish wavelength switching. To achieve multiple component detection with a single laser, tunable lasers, such as CO_2 gas lasers and QCLs, can be used to cover a wide range of wavelengths. Wider wavelength ranges provide a better selection of absorption signal wavelengths of specific gases. Although QCLs have advanced the PAS capabilities with extremely narrow linewidths and large tuning ranges, they require a large threshold current to operate. Interband cascade lasers (ICLs) allow each injected electron to be reused at a forward bias to emit multiple photons and decrease this threshold current and total required electrical input power.[1]

A major issue with multiple gas detection when compared to single gas detection is cross-interference. Some absorption peaks of different gases may be relatively close in wavelength, and this may cause the pressure sensor to decrease in accuracy in detecting concentrations of multiple gases. The photoacoustic cell and pressure sensor directly correlate to cross-interference.

Some PAS designs utilize quartz tuning forks and cantilever beams to detect pressure changes due to sample absorption of light with high sensitivity. A high-pressure cell may be required to contain these devices, increasing frequency noise and cross-interference and leading to frequent inaccurate measurements. Temperature and high cost can also deter researchers from using these systems. A better, more efficient, lower cost, and highly sensitive design is needed for simultaneous multi-gas detection with PAS designs.

METHOD

Researchers from the College of Chemistry and Molecular Engineering, Nanjing Tech University, China have developed a photoacoustic cell to detect traces of CH_4, C_2H_4, and C_2H_6 using an ICL source and a differential Helmholtz resonance cell under ambient pressure. The setup, including the laser, photoacoustic cell, and gas flow, can be seen in **Figure 1**.

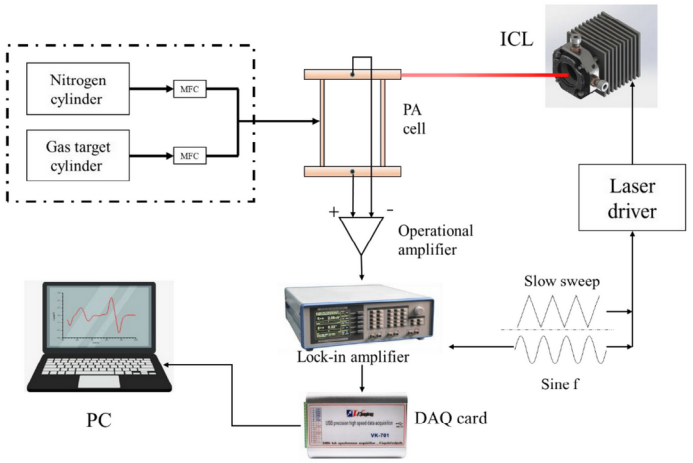

Figure 1. Schematic of the experimental workflow. (MFC: Mass flow controller; ICL: Interband cascade laser; PA cell: Photoacoustic cell; DAQ card: Data acquisition card; PC: Personal computer)[1]

One of the main changes to the PAS design is the addition of the differential Helmholtz resonance (DHR) cell. The simple and low-cost technique is acoustically similar to a mechanical oscillator composed of two mass blocks and springs.[1] The gas cell contains two identical channels with gas moving like a piston: compressing gas in one channel and releasing it in the other channel. Only one channel is irradiated by the laser, but both gas channels produce acoustic signals of the same size and opposite phase because of the laser's Helmholtz resonance frequency.[1] The two channels, and the DHR cell, can be seen in **Figure 2**.

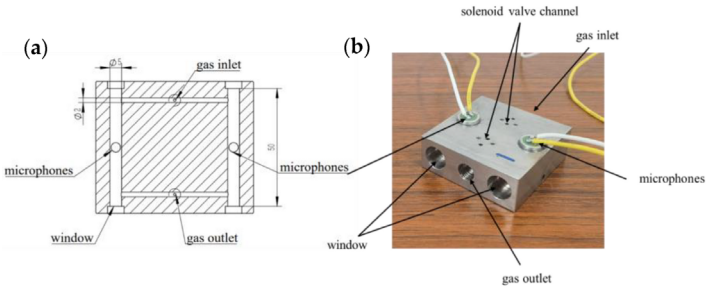

Figure 2. (a) Schematic and (b) photo of the DHR photoacoustic cell.[1]

The DHR is equipped with condenser microphones instead of tuning forks or cantilever beams to detect molecular light absorption. Quartz tuning forks with enhanced photoacoustic spectrum work at lower pressure, but they can be difficult for beam collimation. The condenser microphones, although not as sensitive as cantilever sensors, avoid much of the temperature and vibration-sensitivity issues found in tuning fork and cantilever beam interferometers.

Figure 3 shows the line strengths of the three gases to measure: methane, ethylene, and ethane. A single ICL can cover this wavelength range of absorption signals in 3344-3350 nm. Each gas has absorption peaks at different wavelengths, but minimizing cross-interference will be important.

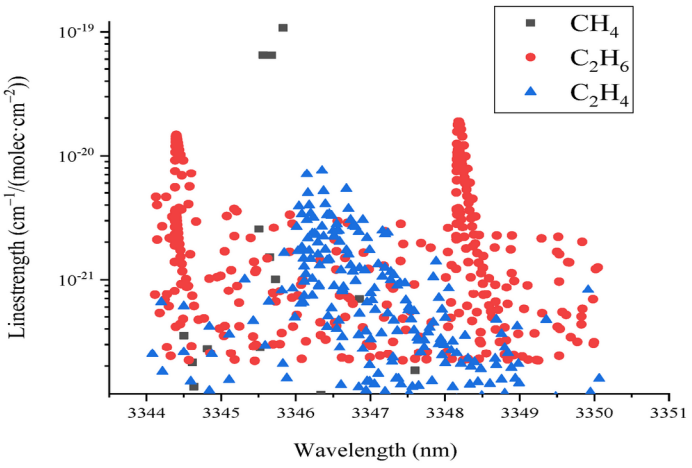

Figure 3. The line strengths of methane, ethylene, and ethane in 3344-3350 nm simulated using the HITRAN database.[1]

The commercial ICL used for the multi-component detection has a center wavelength of 3345 nm and a dynamic current range of 20-100 mA, corresponding to a wavelength range of 3344-3355 nm. Researchers used Wavelength Electronics' WTC3293 temperature controller to regulate and maintain the laser temperature at 20ºC with high precision. The typical output power of the laser is 17.2 mW. Because the system uses microphones instead of tuning forks and cantilever sensors, a collimating lens is used to create a beam 3 mm in diameter with a Gaussian power distribution. The microphones have a sensitivity of -26 ± 3 dB. The main gas tubes are only 50 mm in length, and the photoacoustic cell holds approximately 2.5 mL in volume.

The photoacoustic cell is filled with sample gas for gas detection measurements and is controlled to ambient pressure. The output of the ICL is modulated to cover the

absorption wavelengths of all three sample gases. The signals from the two microphones from both channels were differentially amplified by a preamplifier and passed onto a lock-in amplifier. These devices are seen in **Figure 1**.

Test conditions, such as laser modulation frequency, laser modulation depth, phase angle, and demodulation method are all optimized to meet the best measurement conditions of the three different gases.[1] the resonance frequency was determined to be at 710 Hz, and the photoacoustic signal at different modulation depths is measured at this resonance frequency for methane to find sufficient signal intensities. To avoid spectral line broadening and wavelength shift, a modulation depth of 10 mA is selected.

To determine the detection current of the three gases, the absorption lines are observed over the full dynamic range of the ICL.[1] The laser's injection current is scanned from 50 to 100 mA to create a full profile of the gases' absorption spectra with the DHR signals demodulated at the first (1f) and second (2f) harmonic frequencies. These DHR signals can be seen in **Figure 4**. The 2f demodulation method is undesirable for multi-component detection as the response signals of ethylene and methane are almost in reverse phases and will cancel each other out. These are the blue and violet highlighted regions in **Figure 4**b. A similar situation arises with the 1f signal in the blue and violet highlighted regions in **Figure 4**a, but a detection window is presented for ethylene at a higher injection current in the range of 73.35 to 79.83 mA. Because of this detection window, the demodulation method with the first harmonic signal is chosen for signal acquisition.

The lock-in amplifier and the phase angle play an important role in extracting weak signals from noisy backgrounds to measure them accurately. The reference signal and the detected signal will have some phase difference due to the relaxation of exited gas molecules, energy loss from friction of the photoacoustic cell wall, and the hysteresis of the electronic circuit. To maximize the signal of all three gases, a detection phase angle is set at 12.1° throughout the scanning process.

RESULTS

Due to the cross-interference of the gas absorption signals, each gas absorption signal will correspond to different laser injection currents, and, therefore, emission wavelengths: CH_4 - 62.35 mA, C_2H_4 - 73.88 mA, and C_2H_6 - 88.23 mA. Detecting the gases at different wavelengths will help increase signal intensity without signals canceling each other.

Methane, ethylene, and ethane sample gases with varying concentrations (2-95 ppm) were prepared for absorption detection in the photoacoustic cell. At each selected laser injection current, each concentration was measured to generate a spectra curve. At these current levels, each gas signal has a good linear relationship, but each has unique responsivity levels derived from the linear fit. From the first harmonic signals of each of the three gases (**Figure 5**), an Allan bias analysis can give the detection limits for the appropriate integration time. This detection limit can be compared to detection limits obtained in a separate experiment.

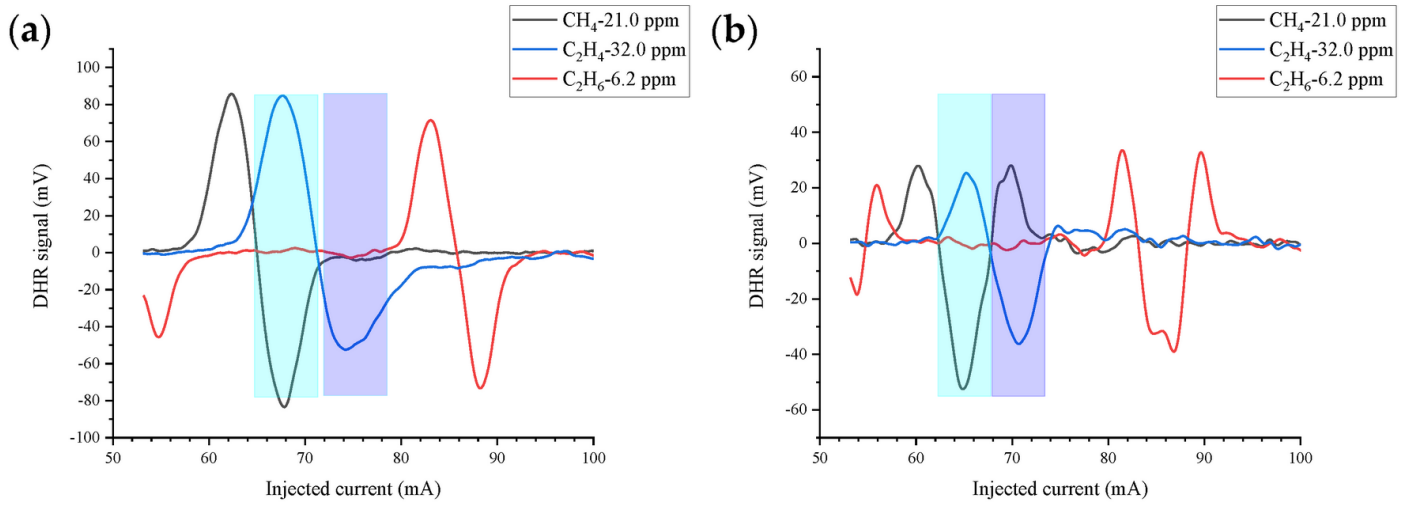

Figure 4. (a) 1f and (b) 2f signals of the three analytes in the full dynamic range of the ICL current (50 to 100 mA).[1]

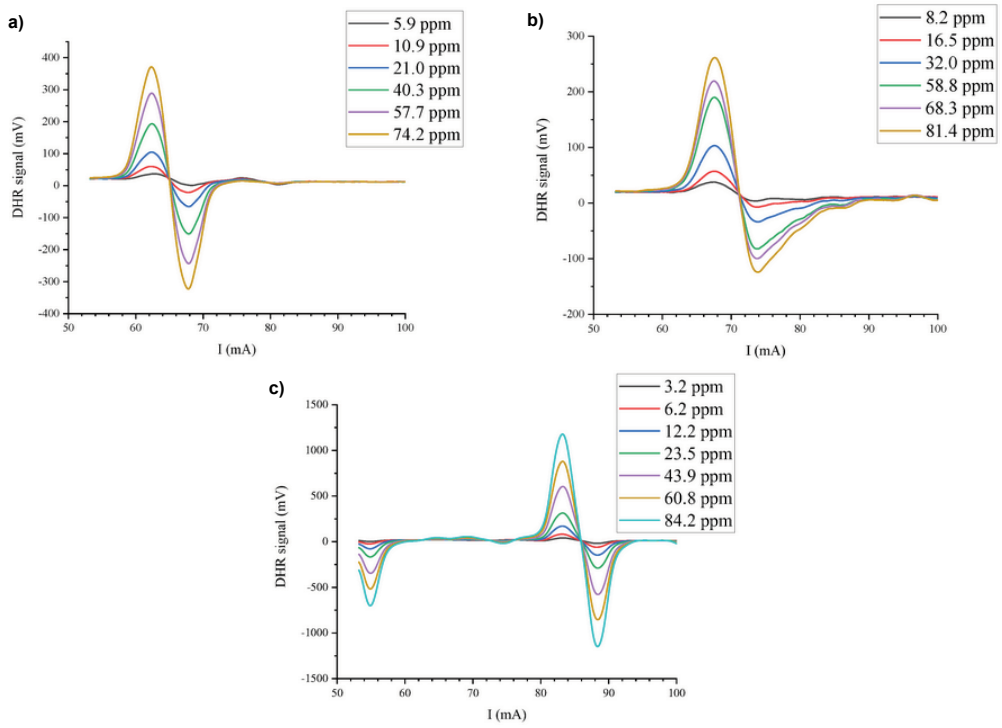

Figure 5. First harmonics signals of a) methane (5 to 80 ppm), b) ethylene (5 to 85 ppm), and c) ethane (2 to 90 ppm) with injection laser current in the range of 53 to 100 mA.[1]

As is seen in **Figure 5**, an increased gas concentration of any sample gas directly correlates to an increased DHR signal. The detection limits for each sample gas are as follows: 98.9 ppb for methane, 252 ppb for ethylene, and 33 ppb for ethane with each having an integration time of 2 seconds. Ethane is detected at a longer wavelength, making the laser power higher than either of the other gases and making it have the highest responsivity. On the other side of the laser power range, ethylene had the lowest absorption strength and did not have any sharp absorption peak shapes. Thus, the responsivity of ethylene is the lowest, leading to the higher detection limit. Although methane may have a stronger absorption intensity, the absorption cross-section is much lower than that of ethane.

To reduce the impact of cross-interference of the three gases on the detection accuracy, researchers carried out broadband multi-wavelength linear regression. This not only reduces cross-interference errors but also accidental errors in the design.[1] A portion of the DHR signal data is extracted throughout the whole range of the laser current, and the selected data with high concentration-signal linearity are further chosen for multi-wavelength fitting. This can help obtain the gas concentrations through linear regression with higher accuracy. Through this process, the error is reduced to less than ±10% for ethylene and methane and less than ±5% for ethane. This helps the designed PAS system meet practical application requirements.[1]

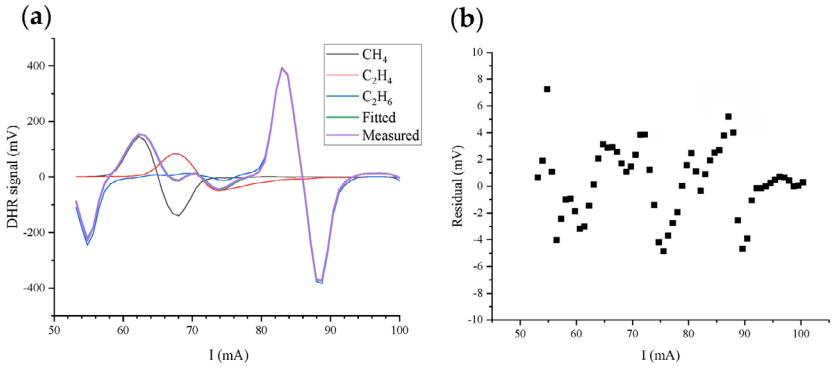

Figure 6. (a) Multi-wavelength fitting profiles of the mixture 3 in Table 2: (b) The fitting residual plot.[1]

Not only did researchers achieve multi-component gas concentration detection, but they also created this system with good stability and relatively low detection limits. At normal pressure, this Helmholtz photoacoustic design can effectively adapt to complex application environments for the power industry, the petroleum industry, agriculture, and other fields.[1] Future studies could look to optimize the fitting process, look at different wavelengths for gas absorption, and use machine learning methods to improve detection performance.

WAVELENGTH'S ROLE

With wavelength stability concerns, the temperature controller is critical in the success of the Helmholtz PAS study. The ICL required high temperature stability since the center frequency shifts with temperature. Because the wavelength is ramped and scanned with varying currents, researchers wanted only the current variable to affect the laser. Precise temperature control of the laser wavelength was crucial with the current ramp changing the laser wavelength only a few nanometers for the full absorption spectrum of the three gases. With a consistent and precise laser temperature, researchers can ensure an accurate and repeatable output from the laser. Researchers used Wavelength Electronics' WTC3243 Temperature Controller with a compact design of 1.3 x 1.28 x 0.313 inches. This ensures efficient space management as well as allowing operation in possible handheld or portable equipment for multiple gas detection.

The WTC3243 can drive up to ±2.2 A of current to a thermoelectric or resistive heater with both heating and cooling current limits. The PI control loop offers maximum stability while maintaining efficiency. The WTC3243 can deliver as low as 0.0009ºC temperature stability over one hour with 0.002ºC stability across ambient.

Researchers also took advantage of the WTC3293 Evaluation Board to rapidly prototype their temperature control system. Onboard switches, connectors, and trimpots make configuration and operation simple. Temperature setpoint, proportional, and integrator time constants can be adjusted via onboard trimpots. This evaluation board enabled researchers to quickly integrate the WTC3243 temperature controller with their Helmholtz resonance spectrometer for multi-component gas detection.

REFERENCES

1. Wu, Zhe; Shi, Yunnxing; Han, Yuwang, Methane, Ethylene, and Ethane Detection by Differential Helmholtz Resonance Spectroscopy Using a 3345 nm Mid-Infrared Tunable Diode Laser Source. *Appl. Sci.* 2023, **13**, 3169. https://doi.org/10.3390/app13053169

USEFUL LINKS

WTC32ND Product Page

WTC32ND-EV Product Page

PERMISSIONS

PRODUCTS USED
WTC3243, WTC3293

KEYWORDS
Photoacoustic spectroscopy, PAS, multicomponent detection, interband cascade laser, ICL, helmholtz resonance, mid-infrared tunable diode laser, methane, ethylene, ethane, WTC3243, WTC3293, temperature controller

REVISION HISTORY

Document Number: CS-TC09

REVISION	DATE	NOTES
A	May 2024	Initial Release