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Step-scan differential Fourier transform infrared photoacoustic spectroscopy (DFTIR-PAS): a spectral deconvolution method for weak absorber detection in the presence of strongly overlapping background absorptions

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The determination of small absorption coefficients of trace gases in the atmosphere constitutes a challenge for analytical air contaminant measurements, especially in the presence of strongly absorbing backgrounds. A step-scan differential Fourier transform infrared photoacoustic spectroscopy (DFTIR-PAS) method was developed to suppress the coherent external noise and spurious photoacoustic (PA) signals caused by strongly absorbing backgrounds. The infrared absorption spectra of acetylene (C_2H_2) and local air were used to verify the performance of the step-scan DFTIR-PAS method. A linear amplitude response to C_2H_2 concentrations from 100 to 5000 ppmv was observed, leading to a theoretical detection limit of 5 ppmv. The differential mode was capable of eliminating the coherent noise and dominant background gas signals, thereby revealing the presence of the otherwise hidden C_2H_2 weak absorption. Thus, the step-scan DFTIR-PAS modality was demonstrated to be an effective approach for monitoring weakly absorbing gases with absorption bands overlapped by strongly absorbing background species.   © 2017 Optical Society of America

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Gas phase photoacoustic spectroscopy (PAS) is widely applied for trace contaminant monitoring, due to its high resolution, large dynamic range, and simple experimental setup [1]. The sensitivity of the PAS method has been improved by acoustic signal amplification produced by different resonant cells [2,3] and high incident intensity laser sources [4]. Nevertheless,

problems persist with the methodologies in the presence of strongly absorbing background gases which tend to mask overlapping spectrum signals from weakly absorbing trace gases and vapors such as ambient air contaminants. In this Letter, we present a highly selective broadband detection configuration: a DFTIR-PAS system capable of deconvolving spectra of such weakly absorbing components within an overwhelming strongly absorbing background. We chose C_2H_2 as the case study target gas because its detection is of importance in environmental monitoring and industrial safety operations [5]; some C_2H_2 absorption peaks (around 1360 cm^{-1}) are hidden behind the usually much stronger ambient water vapor absorption bands.

The step-scan DFTIR-PAS configuration based on a FTIR spectrometer (Bruker, Vertex 70) is shown in Fig. 1. A chopper with a homemade one-side-coated high-reflectivity blade was used to maximize the incident light energy utilization efficiency, avoiding the need for a beam splitter. Two identical T-resonators [6,7] were introduced to suppress coherent noise and cancel background gas signals by means of out-of-phase
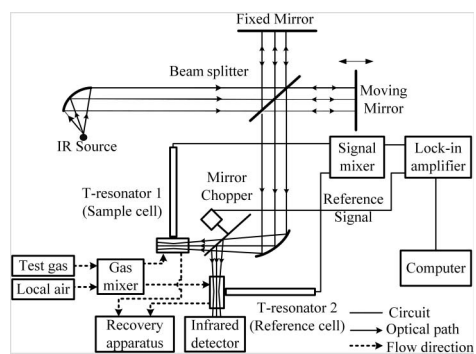

Fig. 1. Schematic of the step-scan DFTIR-PAS configuration.

light modulation [8]. A series of C_2H_2 concentrations was pre-mixed with local air in the gas mixer before being admitted into the resonators. The incident light intensity at the target wavenumber was approximately 30 μW, as calculated from the intensity distribution of the broadband globar source (total infrared intensity: 30 mW).

Figure 2(a) shows the single and differential mode step-scan FTIR-PA spectra acquired when the two cells were filled with local laboratory air (relative humidity [RH] about 45%). Both spectra are normalized by the globar source light intensity distribution in the same wavenumber range. The absorption bands (ranges of 1260–2000 and 3420–3900 cm^{-1}) of the water vapor and the peaks (2349 cm^{-1}) due to the carbon dioxide are clearly observed in the single mode. These spectral features were significantly suppressed in the differential mode verifying equations (9)–(11) in [8], shown here simplified as Eq. (1):

$$B_D(\sigma_m) = \left[I(0) + 2\sum_{j=1}^{N-1} I(jh)\cos(2\pi\sigma_m jh)\right] R_{mic}(\omega_1)CN_{tot}$$
$$\times \left[E_k(\nu)\sum_{k=1}^{T} c(k) + \sum_{k'=1}^{T'} c(k')E_{k'}(\nu)(1+e^{i\varphi})\right]$$
$$j:1,2,3...N-1, m:1,2,3...M. \quad \textbf{(1)}$$

$B_D(\sigma_m)$ is the DFTIR-PAS signal as a function of wavenumber σ_m ($m \in [1, M]$); M stands for the number of wavenumbers (ordinates) considered in one spectrum. $I(jh)$ is the light intensity of the FTIR spectrometer versus optical path difference jh (h is the retardation between adjacent sampling points; there are N sampled points in one interferogram). $I(0)$ stands for the light intensity at zero retardation. R_{mic} is the microphone sensitivity; ω_1 is the angular modulation angular frequency and is equal to the fundamental resonance angular frequency of the T-cells. C is the cell constant. N_{tot} is the total number density of molecules. $c(k)$ and $E_k(\nu)$ are the concentration and the absorption spectrum of the k-th component, respectively. T is the total number of gases to be detected, and T' is the total number of absorbing gaseous species mixed with the residual (background) gas which can generate a spurious photoacoustic signal (e.g., water vapor in ambient air). The phase difference between the outputs of the two cells, φ, is ideally equal to π as a result of the out-of-phase light modulation. Under these conditions, background signals are cancelled, and only the signal from the target gas is present as shown in Eq. (1).
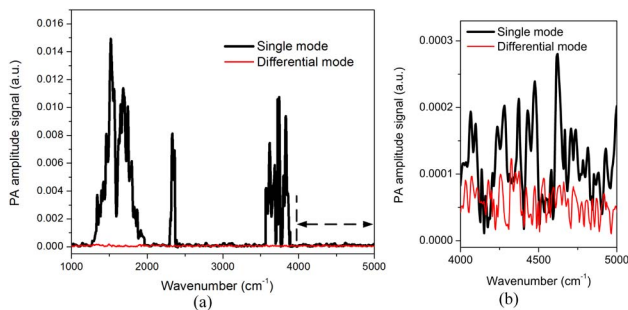
The significant coherent noise attenuation of the differential mode is demonstrated in Fig. 2(b), which is an expanded version of the 4000–5000 cm^{-1} spectrum baseline of Fig. 2(a). It is seen that the single-mode noise level is more than twice as large as that of the differential mode. Figure 2 indicates that the capabilities of the differential mode are twofold: suppression of the coherent noise and cancellation of large background gas/vapor signals. These attributes were found to be the key for the successful deconvolution and emergence of weakly absorbing gas peaks normally "hiding" behind strong absorption spectra of common ambient gases such as water vapor.

Figure 3 shows the step-scan FTIR-PA C_2H_2 spectrum. Three main peaks are prominent at about 1302, 1360, and 3294 cm^{-1}, respectively. The peaks near 3294 cm^{-1} are due to the ν_3 CH stretching vibration, which is in resonance with the $\nu_2 + \nu_4 + \nu_5$ combination band [9]. The other two major peaks can be understood as a strong $\nu_4 + \nu_5$ combination band ($(\nu_4+\nu_5)_+^0$ for 1308 cm^{-1} and $(\nu_4+\nu_5)^2$ for 1360 cm^{-1}) [10].

Figure 4 shows an overlapping region between the C_2H_2 absorption peaks (around 1360 cm^{-1}) and the water absorption spectrum (1300–1500 cm^{-1}) constructed from Hitran data [11]. The water concentration in Fig. 4 was adjusted to be consistent with laboratory air (RH: 45%). The peak intensities of 500 ppmv C_2H_2 are equivalent to those of the laboratory air water concentration (humidity).

The capability of the step-scan DFTIR-PAS configuration to deconvolute a "hidden" target gas from behind the strong water absorption bands was tested with 100 ppmv C_2H_2.

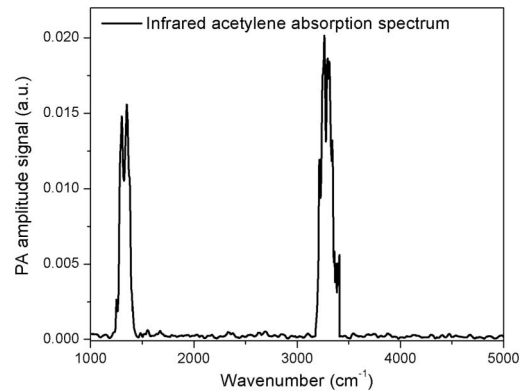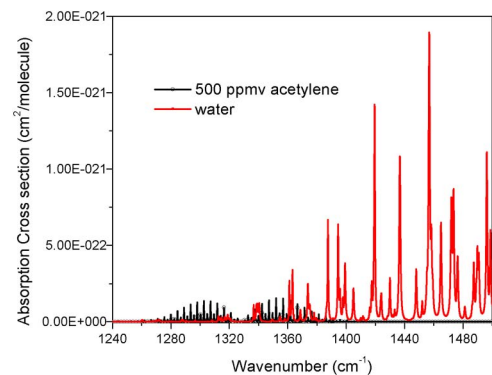**Fig. 3.** Normalized step-scan FTIR-PA C_2H_2 spectrum.

Fig. 2. (a) Normalized two-mode step-scan FTIR-PA spectra of laboratory air. (b) Enlargement of the noise floor of the single and differential FTIR-PAS modalities in a selected wavenumber range of (a).

**Fig. 4.** Absorption cross section of C_2H_2 and water (Hitran data).

The results are shown in Fig. 5. One cell was filled with the mixture of 100 ppmv acetylene and laboratory air, and the other cell contained only laboratory air. The single-mode and differential mode step-scan FTIR-PA spectra of the two cells are shown in Figs. 5(a) and 5(b), respectively. There is no measurable difference between the two spectra in Fig. 5(a) near 1360 cm^{-1}, which leads to the conclusion that it is difficult or impossible for the single mode to detect 100 ppmv acetylene in the presence of other absorbing species. However, the C_2H_2 peaks at 1308 and 1360 cm^{-1} are obviously well distinguished in Fig. 5(b). The differential PA signal strength due to the C_2H_2 peak at 1360 cm^{-1} was 6.75×10^{-4} (arbitrary units, A.U.). The peak signal generated by the target gas is undetectable when it is smaller than the signal fluctuation at baseline (no absorption) which can be taken as the noise floor of the differential mode system. To calculate the fluctuation level, a straight line was fitted to the spectrum in the region where no gas absorption occurs (2800–3050 cm^{-1}). The standard deviation (fluctuation) between the best-fit straight line and the experimental data was found to be 3.06×10^{-5} (A.U.) and was considered to be the noise floor of the DFTIR-PAS system [8]. The quotient of these values yields a signal-to-noise ratio (SNR) of 22.06 for 100 ppmv C_2H_2 by means of DFTIR-PAS, leading to a C_2H_2 detection limit of roughly 5 ppmv (100/22.06). Scaling to equivalent incident light intensity, the DFTIR-PAS revealed better performance and lower C_2H_2 detection limit than several other laser photoacoustic methodologies, as shown in Table 1. Figure 5(c) shows the concentration dependence of the signal amplitudes at the C_2H_2 absorption peaks (1360 cm^{-1}) from 5000 to 100 ppmv measured with the step-scan DFTIR-PAS setup. The lower limit of quantification is 17 ppmv using the criterion of acceptable SNR as 10:1. The experimental data show an excellent linear dependence on concentration, which demonstrates that the DFTIR-PAS modality is an effective approach for revealing the presence of "hidden" gases, the absorption peaks of which are concealed due to an overlap with other strongly absorbing background gases.

The "hidden gas" detection capability of a T-cell resonator-enhanced step-scan DFTIR-PAS system was demonstrated by monitoring C_2H_2 concentrations mixed with local laboratory air, where strong water absorption bands due to the ambient air strongly dominate the gas mixture spectrum. The linear amplitude response to acetylene concentrations is practical and valuable as it obviates the need for complicated nonlinear calibration algorithms.

In conclusion, by virtue of efficient noise level suppression and differential spectra cancellation, the step-scan T-cell resonator DFTIR-PAS approach was demonstrated to be a sensitive, broadband, quantitative spectroscopic technique for

Table 1.   Summary of Acetylene Detection Limit by Laser Photoacoustic Related Methodologies

Wavelength (nm)	Absorption Coefficient (cm^{-1})	Incident Light Intensity (mW)	Detection Limit
1530.7	2.04×10^{-2}	500	1.56 ppb [12]
1534.099	3.16×10^{-2}	1.71	1.5 ppmv [13]
1513.0–1513.3	5.06×10^{-2}	3.5	10 ppmv [14]
1529.18	1.26×10^{-2}	500	2 ppb [15]

(a)

(b)

(c)
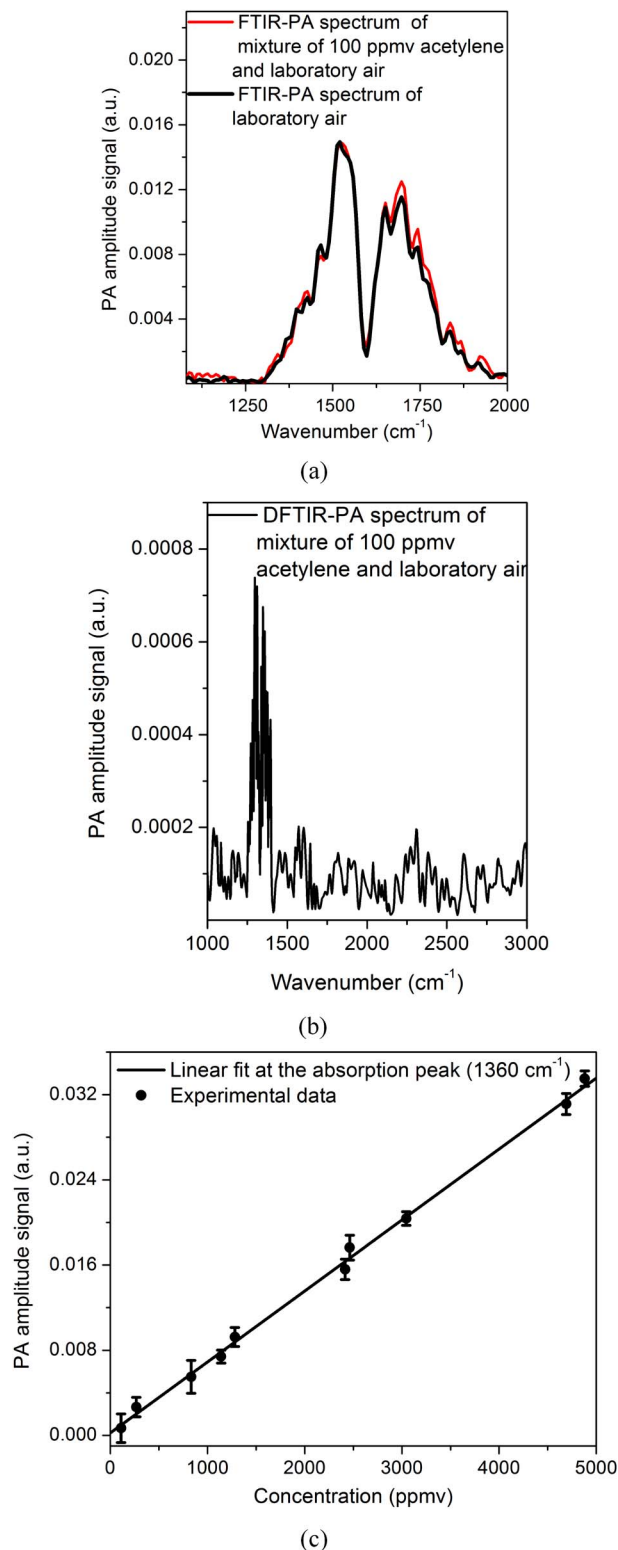
Fig. 5. (a) Single-mode step-scan FTIR-PA spectra of the two cells. (One cell is filled with the mixture of 100 ppmv acetylene and laboratory air; the other cell contained laboratory air only.) (b) Step-scan DFTIR-PA spectrum of 100 ppmv C_2H_2 and laboratory air. (c) Step-scan DFTIR-PAS amplitude responses at the C_2H_2 absorption peak (around 1360 cm^{-1}).

ambient trace gas detection in the presence of strongly overlapping absorption bands.

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