



# Fourier-Transform Infrared Differential Photoacoustic Spectroscopy (FTIR-DPAS) for Simultaneous Monitoring of Multiple Air Contaminants/Trace Gases

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## Abstract

Air pollutants have severe impact on the global environment and the health of human beings. There is an urgent need for cost-effective devices for trace gas monitoring in ambient conditions. However, water vapor in ambient air is still an obstacle in the trace gas absorption detection field due to its complex and strong infrared absorbing characteristics. In this work, a step-scan Fourier-transform infrared differential photoacoustic spectroscopy (FTIR-DPAS) methodology developed in our laboratory through the introduction of two identical T-resonators for enhancing and resolving the DPA signal from two potentially pollutant gases is extended to multiple ambient gas components: carbon dioxide (CO<sub>2</sub>) and acetylene (C<sub>2</sub>H<sub>2</sub>). A key feature of this technique is the ability to resolve hidden target spectral components in ambient air: Despite the fact that the acetylene absorption peaks lie within the strong water vapor absorption band, the infrared PA absorption spectra of acetylene and carbon dioxide are detected with high sensitivity and selectivity in the presence of significant interference of water vapor in the laboratory ambient air, thereby confirming the superiority and capability of step-scan FTIR-DPAS configuration to effectively and totally suppress often dominant background water signals and simultaneously detect multiple trace gases.

**Keywords** Differential mode · FTIR-DPAS · Water vapor absorption cancelation

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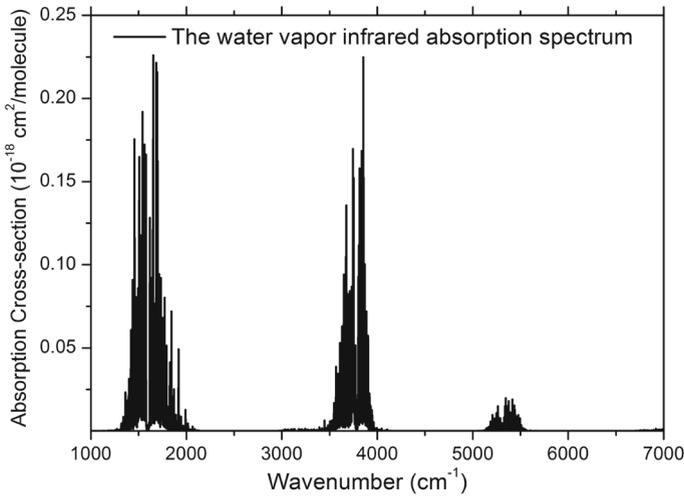
## 1 Introduction

Trace gas detection constitutes an important research topic due to its widespread application potential, e.g., in environmental sensing, industrial monitoring, and biological domains [1–3]. Photoacoustic spectroscopy (PAS) is ideally a zero-background technology and is well known for the virtues of simplicity and robustness of implementation [4] that is widely used in the trace gas detection field. Nevertheless, the complicated absorption features of water vapor background (shown in Fig. 1a, obtained from Hitran data simulation) present a long-term challenge in ambient trace gas infrared absorption spectroscopy analysis. Some publications report using artificially synthetic or pre-dried air as experimental gas samples [5] so as to eliminate the negative influence of water vapor. Numerous gases have absorption peaks in the infrared spectral region as depicted in Fig. 1b (obtained from Hitran data simulation); thus, a step-scan Fourier-transform infrared differential PAS (FTIR-DPAS) method was used in this paper to address the multiple gas analysis and eliminate the overwhelming interference of water vapor. The specially designed compact and robust T-type resonant cell enabled accurate trace gas concentration measurements and considerable system signal-to-noise ratio. This design provides a realistic method for high-performance multiple trace gas detection in ambient air.

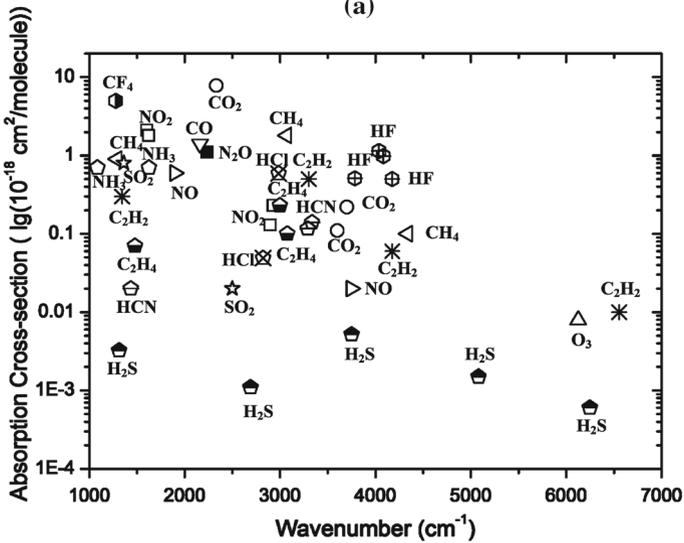
## 2 Instrumentation and Experiments

The step-scan FTIR-DPAS system based on a FTIR spectrometer is depicted in Fig. 2. The configuration involves two identical T-resonators, the resonant frequency of which is 342 Hz in the spectrometer compartment. A T-resonator consists of three parts: the absorption, buffer, and resonance cylinders [6, 7]. The resonant frequency of a T-resonator is mainly determined by the geometry of the resonance cylinder which is perpendicular to the absorption cylinder, providing a realistic approach to the often conflicting requirements for low frequency and limited space available in the FTIR spectrometer sample compartment. The incident light into the two cells is modulated using a laboratory-made one-side-coated high-reflectivity chopper which alternatively transmits and reflects the beam to avoid splitting the optical power, thereby maximizing the light utilization efficiency [8]. One resonator labeled the sample cell which is filled up with a mixture of target gas(es) and ambient air. The other resonator, known as the reference cell, only contains ambient air. The FTIR-PA signals from the two cells are combined and stored in the signal processing unit.

Due to the fact that some prominent absorption peaks ( $1320$  and  $1360\text{ cm}^{-1}$ ) of acetylene are within the water absorption band as shown in Fig. 1, the mixture of acetylene and ambient air (relative humidity is 45%) was used as the gas sample to test the capability of resolving trace absorber information. Also, the mixture of carbon dioxide and ambient air was used for illustration of multiple trace gas detection ability. The two preferred gases were supplied by Linde<sup>®</sup> Gas/AGA. Several designed concentrations of gas sample were premixed in the “gas mixer.” All the exhaust products were collected in the recovery apparatus after the experiments.



(a)



(b)

**Fig. 1** (a) Infrared absorption spectrum of water vapor; (b) absorption information of typical contaminant gases

The premixing device adopted was based on a flowmeter (Model 7300, Matheson<sup>®</sup>), which was incapable of mixing more than two gases. The spectra of the two kinds of samples (air-carbon dioxide and air-acetylene mixtures) were collected separately and combined together as multiple target gas spectra. The background noise was suppressed by subtracting the data collected with the incident light off. All the raw spectra were normalized with the incident light intensity distribution.

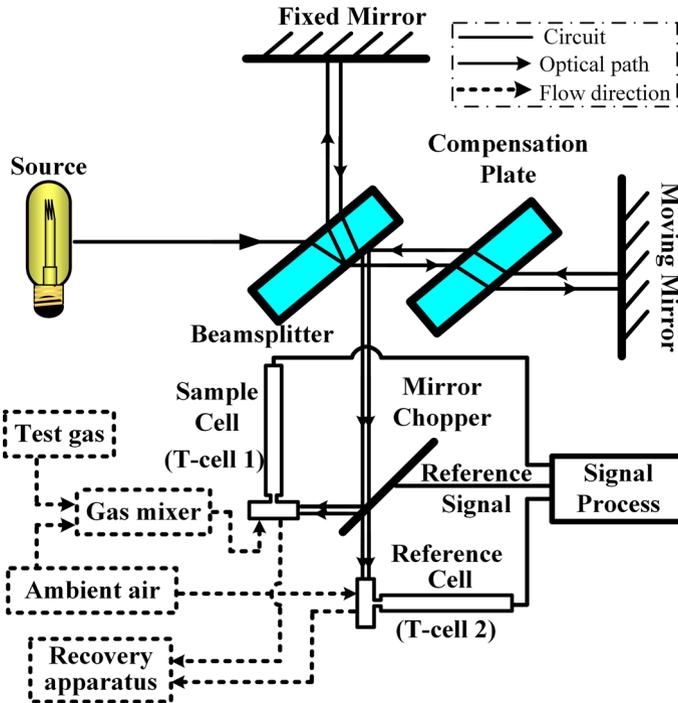
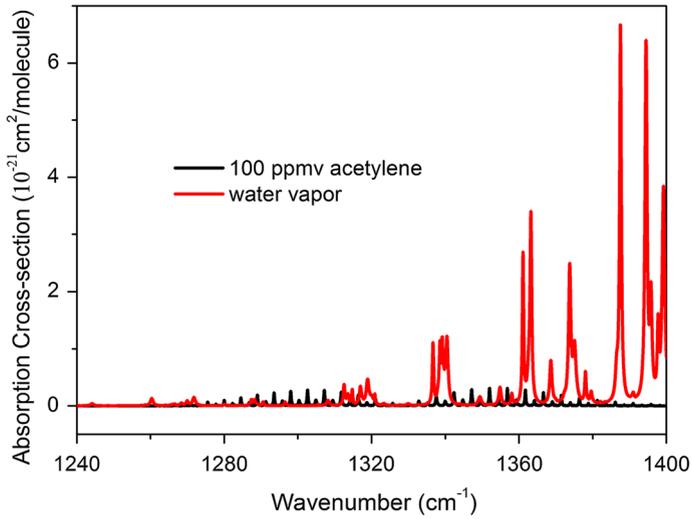


Fig. 2 Step-scan FTIR-DPAS configuration

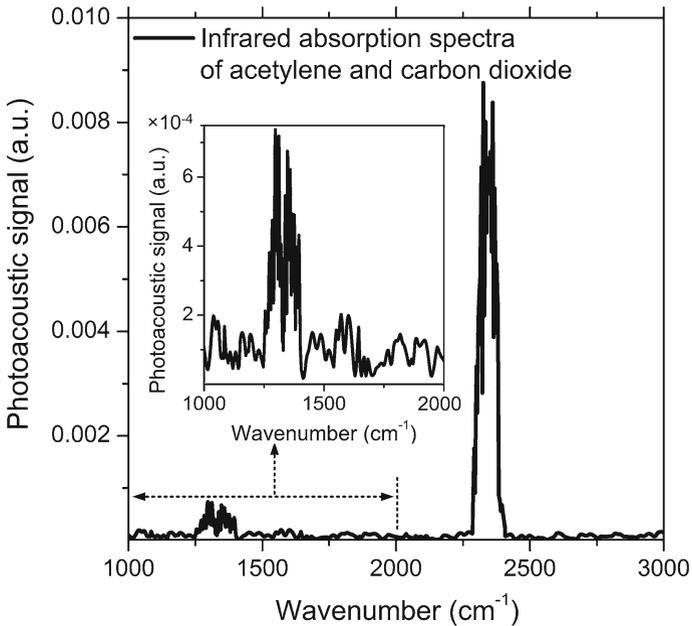
### 3 Results and Analysis

The adverse effect of water vapor in the infrared trace gas detection cannot be neglected as there is a very high water vapor concentration in ambient air [9]. It is impossible or difficult for the single cell (single mode) to observe the trace target gas contribution to the signal, especially when its absorption peaks are overlapped with water-absorbing bands. The 100 ppmv acetylene absorption information (at 1320 and 1360  $\text{cm}^{-1}$ ) was masked in the overwhelming water-absorbing background shown in Fig. 3 obtained by Hitran data simulation [10]. The water vapor concentration in this Hitran simulation was set to be equivalent to the laboratory air humidity. Therefore, the single cell was not able to reveal the low-concentration acetylene in its mixture with ambient air.

However, the “hidden” trace acetylene effective absorption information could be clearly observed by the differential mode system as demonstrated in the inset of Fig. 4. The quality factor of the T cell was 85.5, and the FTIR resolution was 6  $\text{cm}^{-1}$ . One cell was filled with the mixture of 100 ppmv acetylene and laboratory air, and the other cell contained only laboratory air. The two acetylene infrared absorption peaks are obviously distinguishable in the presence of significant water interference. The results demonstrate that the step-scan T-cell-based FTIR-DPAS modality is an effective approach for eliminating the strong water absorption background and revealing “hidden” gases, the absorption peaks of which are concealed due to an overlap with water vapor.



**Fig. 3** Absorption cross section of acetylene and water vapor (simulations from Hitran spectra)



**Fig. 4** Infrared FTIR-DPAS spectra of 100 ppmv acetylene and 500 ppmv carbon dioxide

Figure 4 shows the combined spectra of 100 ppmv acetylene and 500 ppmv carbon dioxide mixed with ambient laboratory air. The absorption peaks of both acetylene and carbon dioxide (near  $2349\text{ cm}^{-1}$ ) are observed, which is convincing evidence of the good sensitivity and selectivity of the differential mode. The results demonstrate

that the step-scan T-cell-based FTIR-DPAS system has inherent multicomponent gas detection capability under the strong interference of water vapor in ambient air.

From a practical viewpoint, the proposed gas detection system can be utilized for two kinds of applications: (1) gas detection with suppression of water absorbance and (2) time-dependent gas concentration change monitoring. For the first case, the reference cell will be filled with a water vapor mixture of known concentrations. The exact concentration of water inside the sample cell can be determined by comparing the water vapor absorption peaks in both cells and adjusting the reference water vapor concentration for matching the spectral peaks of the measurement cell. Differential detection will follow to enhance the presence of “hidden” absorptions behind the water vapor peaks. The second case does not have to quantify the precise concentration of trace gases in every test. By filling the two cells with ambient air at two different instants, the differential mode can reveal the evolution of spectral differences which can work as a good monitor of time-dependent evolution of specific gas concentrations over the testing period.

## 4 Conclusions

A step-scan T-cell-based FTIR-DPAS system with a homemade mirror chopper was tested in this work for enhanced infrared absorption spectral analysis of multiple ambient pollutant trace gases in the presence of ambient air. It was demonstrated that the differential system is capable of totally suppressing the strong absorbing background of water vapor and resolve weak overlapping absorptions, a challenging problem in the infrared gas detection research field. By virtue of its broadband wavelength range and differential spectra cancelation, the FTIR-DPAS method was shown to be an effective enhanced spectroscopic technique for multiple ambient trace gas simultaneous detection.

To further improve the detectivity of the system, a laser source could be adopted for highly sensitive detection within a narrow spectral range. Compared with the non-coherent source in the FTIR system, a laser diode can provide ultra-narrow emission at an absorption peak and sufficiently enhance the sensitivity, provided the absorbing gas spectral peak(s) is (are) known a priori for the appropriate laser line to be selected.

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