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Quartz-enhanced photoacoustic spectroscopy of HCN from 6433 to 6613 cm^{-1}

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ABSTRACT

We developed a spectrometer based on quartz-enhanced photoacoustic spectroscopy. A widely and continuously tunable fiber-coupled telecom-grade external cavity diode laser was used as a spectroscopic source. The hydrogen cyanide (HCN) absorption spectrum in the near-infrared spectral region from 6433 to 6613 cm^{-1} was measured. The spectrum of P branch of (20^00)–(00^00) band of HCN was analyzed. The analyzed results are in excellent agreement with published reference absorption spectra and given by the GEISA03 database.

1. Introduction

Recently, toxic chemical species quantification and monitoring has become increasingly important due to the widening interest in environmental and health problems. Hydrogen cyanide (HCN) is one of an extremely toxic chemical species (colorless gas or bluish white liquid at ambient temperatures). The toxicity of HCN is a function of the product of concentration and exposure time, rather than just a function of concentration alone. The National Institute for Occupational Safety and Health (NIOSH) recommended short-term exposure limits for hydrogen cyanide is 4.7 ppmv averaged over 15 min and not to be exceeded at any time in the workday [1]. HCN was fatal to humans at concentrations ranging from 135 ppmv to 270 ppmv. Many plants and microorganisms can produce HCN through their metabolic processes which may be released when the organism decomposes. However, most of the HCN released into the environment is from anthropogenic sources including: exhaust emissions, electroplating, metal mining, metallurgy, and metal cleaning processes. It can also be released during its use in a variety of chemical processes, such as the manufacture of adiponitrile (for nylon), plastics, sodium cyanide, cyanuric chloride, pharmaceuticals, and other specialty chemicals as well as its use in the fumigation of ships, buildings, and various foods [2].

As HCN is a highly toxic chemical species and it is also considered as a warfare chemical agent, it is very important and interest to study the spectra of HCN. Therefore, the development of a compact HCN sensor capable of detecting sub-ppmv concentration levels and operating in harsh environments is very important [3]. A number of techniques have been developed to measure HCN [4–7]. However, most of these methods demonstrated in the laboratory are unsuitable for real world applications because of the sensor size, weight, cost, power consumption, time-consuming, and some lack selectivity or sensitivity. Laser photoacoustic spectroscopy (PAS) is a well established method that widely used in trace gas sensing applications, providing high chemical selectivity and sensitivity [8–13]. A novel alternative approach to PAS, named quartz-enhanced photoacoustic spectroscopy (QEPAS) has been introduced in 2002, by the Rice group, in which a quartz tuning fork (QTF) was used as a resonant acoustic transducer [14]. Compared to conventional resonant PAS, QEPAS sensor accumulates the absorbed energy not in the gas but in the sensitive element of QTF, which offers several advantages: immune to environmental acoustic noise, inexpensive, compact with the capability to analyze extremely small gas samples [15].

In the present work, we describe the development of a near-infrared spectrometer based on QEPAS and its application to the measurements of HCN absorption spectrum in the spectral region of 6433–6613 cm^{-1} by using a widely tunable external cavity

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laser. In the present work, we mainly focus on measurement of absorption spectra of HCN molecules, the detection sensitivity and other impact factors on sensitivity were not considered at this stage. So the absorption detection module of QEPAS based spectrometer was made in simplest configuration, micro-resonator was not added which usually used in QEPAS based sensor for increasing sensitivity [15,16]. Of course, further work will be carried out in the future, to characterize the impact factors on the QEPAS-based detection performance and improve the detection sensitivity by adding a micro-resonator in absorption detection module.

2. Fundamentals of QEPAS

When the laser radiation is absorbed by a sample, the absorbed energy will transfer to heat energy by non-radiate processes, which results in increase of local temperature and pressure change in the closed volume of the photoacoustic cell. Therefore, by using modulated laser radiation at an audio frequency, an acoustic wave is produced. The acoustic wave can be detected by using a sensitive microphone. The intensity of this optically generated sound wave is proportional to laser radiation power, absorbing sample concentration and its absorption coefficient. Generally, the photoacoustic signal S in acoustic resonant cell can be expressed as [9,15]

$$S = C\frac{\alpha PQ}{f} \tag{1}$$

where C is cell constant, α is the absorption coefficient of the target species, P is the optical power, Q is the factor of the acoustic resonator, f is the photoacoustic sound frequency.

QEPAS is a novel alternative way to detect a photoacoustic signal, which allows quantification, analysis of gas phase species in extremely small sample cell [14,15]. In QEPAS, a QTF with a high Q factor and a resonant frequency close to 32.768 kHz was used as an acoustic transducer, and the acoustic energy was accumulated in the sharply resonant QTF, not in the acoustic cell as in the traditional PAS [14,15]. Such an approach removes the restrictions imposed on the gas cell size by the acoustic resonance conditions, since the resonant frequency is now determined by the QTF. Therefore the gas enclosure is thus optional in QEPAS and serves only to separate the gas sample from the environment and control its pressure. The typical dimension of QTF used in QEPAS is $3\times 8\ \mathrm{mm}^2$, so it is possible to design an absorption detection module (sample cell with QTF) with volume less $1\ \mathrm{cm}^3$.

Wavelength modulation technique and 2f detection was used in most QEPAS studies reported to date [3,14–21], which can effectively suppress the background noise originating from spectrally nonselective absorbers (such as QTF electrodes and the gas cell elements). The laser wavelength was modulated at half the QTF resonant frequency $f_0/2$ in order to generate a modulated optical induced sound wave with a frequency of f_0, where f_0 is QTF resonant frequency, and the laser beam was focused between the two prongs of the QTF by using a focusing lens. The QTF signal was demodulated at QTF resonant frequency f_0 by means of a lock-in amplifier. Spectral data of a sample can be acquired by scanning the laser wavelength.

3. QEPAS spectrometer set-up

A schematic diagram of the QEPAS spectrometer set-up developed in the present work is presented in Fig.1. A fiber-coupled telecom-grade external cavity diode laser was employed as an excitation source. The laser source (Tunics Plus), emitting single mode and single frequency radiation with a maximum optical power of 5 mW, is continuously tunable in the near infrared from 1500 to 1640 nm (C and L bands) with a wavelength resolution of 0.001 nm ($\sim 4\times 10^{-3}\ \mathrm{cm}^{-1}$). The laser emission line width, determined by heterodyne measurements is less than 1 MHz. A QTF with a high Q factor ($Q\sim 1100$ at normal atmospheric pressure) and a resonant frequency f_0 close to 32.768 kHz was used as a photoacoustic transducer. Detection sensitivity was not considered in the present work, as our interesting is to measure absorption spectrum, so micro-resonator was not added. The laser emission was split into two part with a ratio of 10: 90 by means of a fiber beam splitter. The smaller fraction of the laser beam was sent to wave meter for monitoring and measuring the laser wavelength. The remaining laser beam was firstly collimated by a collimator. Subsequently, the collimated laser beam was focused between QTF prongs by use of a focusing lens with a 30 mm focal length. Optical coarse alignment of the diode laser light to the position in the QTF was achieved with the help of a He–Ne laser, whereas the accurate alignment was achieved by monitoring the changing of QEPAS signal with light position, the position that getting maximum QEPAS signal was selected.

The laser current was sinusoidally modulated at half the QTF resonant frequency $f_0/2$ by means of a lock-in amplifier (Stanford Research Systems, Model SR 830 DSP). The QTF signal was amplified by a commercial preamplifier and then demodulated at f_0 by the lock-in amplifier. The lock-in amplifier and the laser were controlled by a GPIB card, where the wave meter was controlled with RS232. The 2nd harmonic signal was acquired by a data acquisition card and sent to a personal computer for signal processing and analysis. All of these were performed by the aid of a home-written program in C language.

4. Results and discussion

4.1. Response property of QEPAS

The most important feature of QEPAS is its highly immunity to ambient noise. This is determined by the QTF. The response curve of QTF fits well to the Lorentz line shape [22]:

$$y = \frac{2A}{\pi}\frac{w}{4(f-f_0)^2 + w^2} \tag{2}$$

where f_0 is the resonant frequency of the QTF, w is the full width at half-maximum (FWHM) of the QTF response curve, A is the area of the line shape. The response curve is schematically shown in Fig. 2, which was acquired by locking the laser wavelength to the absorption line center of target species, and then slowly scanning the modulation frequency. From Fig. 2, we can see that the FWHM of the QTF resonant curve is very narrow, and it decreases with decreasing pressure (see Fig. 3), which result in high immunity to ambient noise since only those frequencies occur into this narrow band can effectively excite the response of the QTF. At the same time, a QTF with a frequency of 32.768 kHz represents an acoustic quadruple [14,15], as a result, the sound waves coming from distant sources tend to apply force in the same direction upon the two QTF prongs positioned at an $\sim$0.3 mm distance, thus resulting in no electrical response. In addition, the resonant frequency of the QTF is about 32768 Hz, therefore, the frequency dependent noise of $1/f$ can be neglected effectively. These factors of the QTF determined that the QEPAS can offer highly immunity to ambient noise.

Analogous to conventional PAS (Eq. (1)) and take into account of the response property of the QTF (Eq. (2)), the photoacoustic signal intensity in QEPAS can be described as: