



Photoacoustic spectroscopy with mica and graphene micro-mechanical levers for multicomponent analysis of acetic acid, acetone and methanol mixture



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ABSTRACT

Multilayer graphene and mica cantilevers as part of an optical microphone in combination with CO₂ laser emitting in the range of 9–11 μm were employed in a multicomponent analysis of a mixture of acetone, acetic acid and methanol by photoacoustic spectroscopy. Using these elements, the detection limits of mica circle cantilever were 0.54, 0.80 and 24.8 ppm for acetic acid, methanol and acetone, respectively; these limits were approximately 5 times lower than the detection limit of the highest-class microphone used in this study. The multicomponent analysis was performed using five selected CO₂ laser lines and a classical method of least squares. Despite the inaccuracies of our system, very good agreement between the concentration of acetic acid calculated from the photoacoustic signal and from weighing of concentration standards (~3%) was found when measuring the signal in a 10:1:1 mixture of acetone:acetic acid:methanol at five selected laser lines. The absorption coefficient of acetic acid at 10.24 μm was almost 500 times higher than that of acetone, which showed the good ability of this method to detect acetic acid in a high background of acetone, which can be beneficial in the medical analysis of breath.

1. Introduction

The detection and spectroscopic characterization of acetic acid is highly important in many fields, including breath analysis, catalysis, atmospheric monitoring and astrophysical research [1–5]. Acetic acid can be an indicator of gastro-oesophageal reflux disease when it is present in human breath at concentrations above 80 ppb [5]. However, the background concentration of acetone in human breath of a healthy individual can be more than one order of magnitude higher [6]. For breath analysis in a laboratory setting, mass spectroscopy combined with chromatography is typically used. However, these methods are cumbersome and difficult to use. For applications in a medical environment, laser spectroscopy techniques seem to be more suitable as they can be incorporated into a compact analyser and can offer both the required sensitivity and selectivity [7–12]. For example, a breath acetone analyser based on ringdown spectroscopy has been recently introduced (with an estimated detection limit of 0.11 ppm) [13]. For breath methane detection, a spectrometer using a distributed feedback

laser and a fiber acoustic sensor was used [14] and for CO₂ breath monitoring, a low cost MEMS system using non-dispersive infrared source was used [15]. Holthoff et al. [16] developed a microelectromechanical-system-based photoacoustic sensor for the trace detection of several gases, including acetone and acetic acid (with estimated detection limits of 0.555 and 0.518 ppm, respectively) with a tunable quantum cascade laser emitting in the mid infrared (MIR) region (1015–1240 cm⁻¹). The vapours of acetic acid can be distinguished from those of acetone by Fourier transform infrared spectroscopy (FTIR) [1,17–19]. Near infrared (NIR) spectroscopy was used to determine the acetic acid content in vinegars [20]. To monitor gas phase acetic acid, UV–vis spectroscopy has also been used [21]. Kästle and Sigrist applied photoacoustic spectroscopy combined with a CO laser to distinguish the spectra of acetic acid monomers and dimers [22]. Herein, we use a photoacoustic sensor [23,24] combined with a CO₂ laser for a multicomponent analysis of a mixture of acetic acid, acetone and methanol.

When we modulate the radiation passing through an absorbing

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species inside an enclosed cell, photoacoustic pressure waves with the same frequency as the modulation frequency emerge. This is the well-known photoacoustic phenomenon. The essence of this phenomenon is the quick nonradiant dissipation of absorbed energy to the translational energy of the molecules [25]. The resulting pressure p is described by Eq. (1) [26,27]:

$$p = \frac{k}{\omega C_v} n \alpha I_0 \sin \omega t \quad (1)$$

where k is the Boltzmann constant, ω is the modulation frequency, C_v is the specific heat at constant volume, n is the concentration of the absorbing gas, α is absorption coefficient and I_0 is the incident radiation. Unlike classical absorption spectroscopy, this is a zero background method in that the detected pressure (i.e., photoacoustic signal) is directly proportional to the intensity of incident radiation and the absorption coefficient of the absorbing gas.

The sensitivity of this method depends on the absorption coefficient of the detected molecule, the laser wavelength, the laser intensity, the sensitivity of the detector to acoustic pressure and the arrangement of the photoacoustic cell. The last topic was the subject of a literature review [28]. Kauppinen et al. [29] showed that the sensitivity of conventional (i.e., electret and condenser) microphones can be surpassed by using an optical microphone, where the movement of a pressure sensitive element, i.e., a silicon cantilever, is monitored by a laser beam that is reflected from that element onto a position sensitive detector.

We envisioned that the low-dimensional materials prepared from layered precursors could have suitable mechanical properties, such as pressure sensitive elements [30]. For photoacoustic detection, a micro-mechanical detector with cantilevers prepared from layered materials, i.e., highly ordered pyrolytic graphite (HOPG) and muscovite (mica), was used. We compare three different elements: a mica circular cantilever, a mica rectangular cantilever, and a multilayer graphene (MLG) cantilever of low thickness (as low as 100 nm).

2. Materials and methods

2.1. Photoacoustic spectroscopy setup

A scheme of the experimental setup is depicted in Fig. 1. A continuous wave CO₂ laser (Edinburgh Instruments WL-8-GT, Livingstone, Scotland) emitting in a spectral range of 9–11 μm was used as an excitation source. This laser has typically 60 laser lines and it was tuned to

fixed wavelength by a diffraction grating [31]. The full-width at half maximum of the laser lines is typically in the order of 10⁻⁴ μm at 300 K (estimated using Spectraplot software [32]). For the multicomponent analysis, five CO₂ laser lines were selected (9.24, 9.5, 9.58, 10.2 and 10.24 μm). The power of the laser ranged from 170 mW to 1 W on various laser lines used for the analysis. The laser beam was periodically interrupted by a chopper placed in front of the window of a photoacoustic cell. The frequency of the chopper was tuned at the resonance for each element (166 Hz for the microphone, 252 Hz for multilayer graphene cantilever, 275 Hz for mica circle cantilever and 581 Hz for rectangular mica cantilever). The custom-made photoacoustic cell was made from brass (145 mm in length, 6 mm inner diameter, Fig. 2) and was equipped with the microphone (Brüel and Kjaer, condenser microphone, type 4144, sensitivity 50 mV/Pa). The Q factor of the cell is approximately 11, which was estimated from the width of the resonance peak of the longitudinal photoacoustic mode. The cantilever was glued to a glass substrate placed inside photoacoustic cell. This arrangement allowed easy change of the cantilevers. A beamsplitter was placed in front of the chopper to monitor the intensity of the CO₂ laser by using a powermeter (Coherent Field Max II, Santa Clara, California, USA).

A He-Ne laser together with a four-quadrant detector (a red enhanced quad-cell silicon photodiode, SD 085-23-21-021, Laser Components, Olching, Germany) were used to detect the cantilever's movement. The signal from the quadrant detector was monitored by an oscilloscope (LeCroy 9361, New York, USA).

Quantitative measurements were performed using a phase sensitive lock-in amplifier with 300 ms time constant/0.53 Hz bandwidth. (Stanford Research Systems SR530, Sunnyvale, USA). The reference signal from the chopper, i.e., the frequency of interruptions of the laser beam, served as a reference signal for the lock-in amplifier. The signal from the lock-in was converted by an AD converter (BNC 2110, National Instruments, Austin, USA) with 1 s sampling rate and processed by a PC. The resulting signal was an average of 100 traces. Details can be found elsewhere [30].

2.2. FTIR spectra

Reference FTIR spectra were obtained using a Bruker IFS 125 HR spectrometer (Bruker GmbH, Germany). Measured samples of pure acetic acid (Lachema, Brno, Czech Republic), methanol and acetone (Sigma Aldrich, USA) were separately evaporated into a White cell with

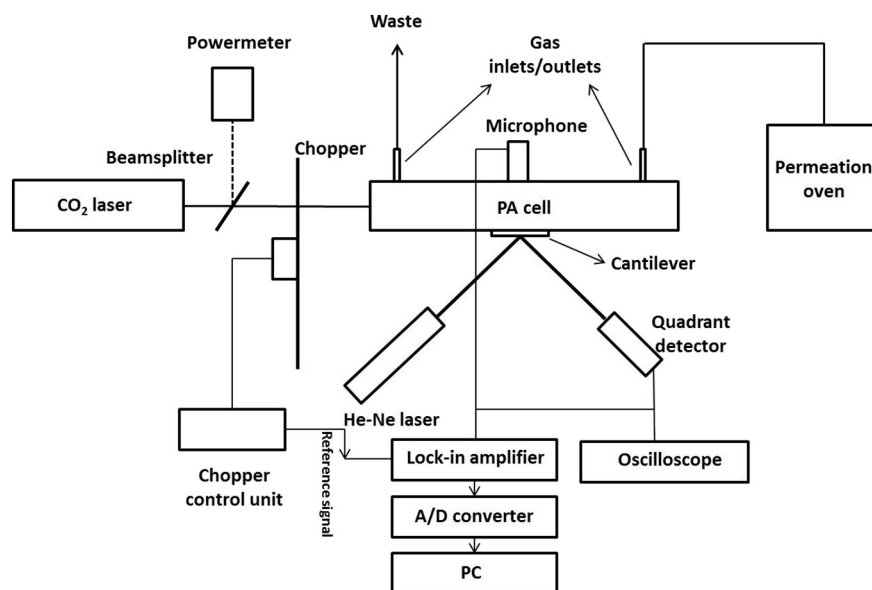


Fig. 1. Experimental setup.

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