



# Methane sensing at room temperature using photothermal cantilever deflection spectroscopy



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## ABSTRACT

Detection of methane at room temperature using adsorption-based chemical sensing is a challenge since methane is inert and does not adsorb on surfaces. We demonstrate that nanomechanical photothermal spectroscopy is capable of detecting femtogram level physisorbed methane on a thermally sensitive microcantilever. Even though the residence time of methane is in sub nanoseconds, it is enough for a vibrationally excited methane molecule to transfer its energy to the cantilever through a non-radiative decay process. The variation of cantilever deflection as a function of excitation wavelength shows the characteristic vibrational spectrum of methane. Photothermal cantilever deflection spectroscopy, therefore, offers a powerful technique for chemical characterization of physisorbed molecules which are chemically inert.

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## 1. Introduction

Methane (CH<sub>4</sub>), the main constituent of natural gas, is a colorless, volatile, odorless, flammable gas [1] which can explode at concentrations between 5–15 V/V% [2]. The development of a reliable, low cost methane sensor is thus of great interest, especially for the safe operation of coal mines and factories [3]. However, the detection of methane at room temperature using sorption-based techniques is a challenge due to the inert properties of non-polar methane, which has little tendency to lose or gain electrons at room temperature [4], causing detection approaches based on chemo-selective interfaces to be less effective when used for relatively inert molecules such as methane. Optical detection systems [5–9] for methane detection have attracted attention due to their several advantages; such as the ability to operate in an oxygen free environment, ability to detect a small amount of gas by choosing an appropriate wavelength, as well as the intrinsic safety of the detection system [5]. Stewart et al. [7] have reported the design of a multi-point fiber optic methane sensor using a distributed feedback laser (DFB) source with a branched fiber network and micro-optic cells, Cong et al. [8] have demonstrated using an InGaAsP

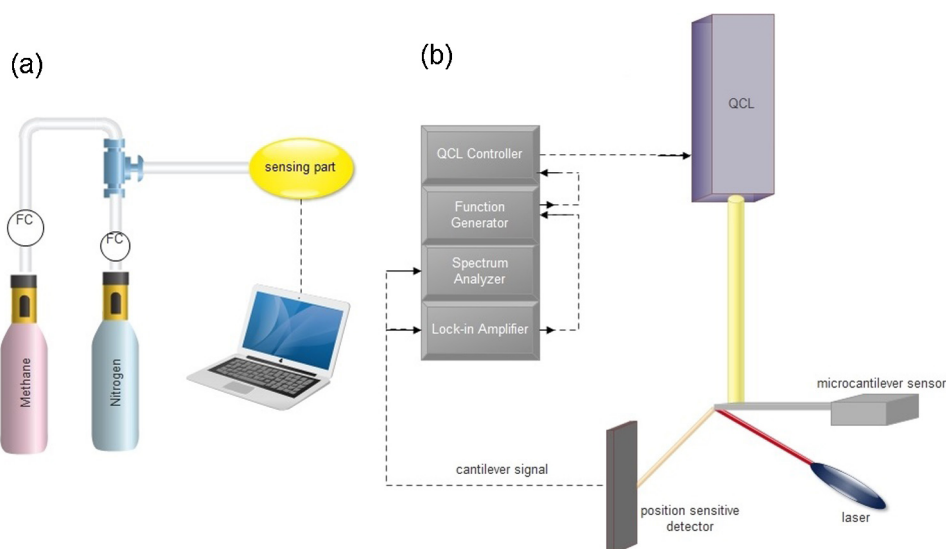
distributed feedback laser for developing a methane detection system, and Massie et al. [6] have designed a sensor based on near-IR LEDs operating around the overtone absorption lines of methane at 1660 nm. The spectrum in the mid infrared (IR) region, however, provides a “molecular finger print” due to the uniqueness of molecular vibrations in the mid infrared range that is free from overtones. Though highly selective, IR spectroscopy is not very sensitive in the mid-IR region [10,11].

Photothermal cantilever deflection spectroscopy (PCDS) combines the high thermal sensitivity of a bimetallic microcantilever with the high selectivity of mid-IR spectroscopy. This technique thus enables obtaining the molecular vibrational signature of trace amounts of adsorbed molecules on the cantilever surface [11–14]. In this technique, the target molecules are first adsorbed on the bimetallic cantilever. In course of the resonant excitation of adsorbed molecules by the IR light source, the cantilever undergoes deflection as a result of the heat generated due to non-radiative decay of excited molecules. The amplitude of cantilever deflection as a function of IR wavelength closely resembles the IR absorption peaks of the molecules. Unlike the detectors used in conventional IR absorption spectroscopy, which require cooled mid-IR detectors, the bimetallic cantilever is uncooled and has temperature sensitivity in 10 mK range. Also, unlike conventional photon detection based sensing, the detection of optical absorption using thermal effects offers a higher signal-to-noise ratio, which increases with incident photon intensity [11]. Therefore, by using recent advances

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**Fig. 1.** Schematics of the gas sensing setup for PCDS experiments. (a) Controlled vapor generation setup. (b) Sensing part consisting of bi-material cantilever deflection setup with IR source for illumination.

in high brightness mid infrared light sources such as quantum cascade lasers (QCL), it is possible to detect extremely small amounts of materials [11].

Here we report the detection of femtogram level adsorbed molecules on a cantilever using photothermal cantilever deflection spectroscopy. Methane molecules are physisorbed on the bimetallic cantilever, which eliminate the need for using any chemoselective interface for detection or its use as a preconcentrator to increase the number of molecules adsorbed on the cantilever. Using the kinetic theory of gases, we have estimated the residence time of the methane molecules on the cantilever as 0.1 ns. At any moment, therefore, there must be some methane molecules physisorbed on the surface long enough to transfer their vibrational energy to the cantilever as heat. Also, resonance frequency measurements conducted on the cantilevers during methane adsorption confirm the femtogram level mass loading due to methane adsorption. Unlike chemoselective interface-based microsensors in which operation life is shortened by degradation of the coating, the PCDS technique offers a robust, selective and sensitive single microstructure without a requisite chemoselective interface [11].

Due to the characteristic vibration frequencies of the chemical bonds (or groups of bonds), infrared spectroscopy can provide detailed information regarding chemical composition at the molecular level. When a material is exposed to IR radiation, the adsorbed radiation excites the molecules to a higher vibrational state. The wavelengths absorbed by the molecule are characteristics of its structure. This technique, therefore, can be used to investigate sample compositions and mixtures. It should be noted that only molecules having a dipole moment can be IR active. Fourier Transform infrared spectroscopy (FTIR) is a routinely used technique based on vibrational spectroscopy which shows the molecular fingerprint of the material being investigated [15]. Both conventional IR spectroscopy and FTIR rely on the Beer–Lambert principle, which relates the absorption of light to the properties of the material through which the light is traveling. It relates the dependence of transmission of light through a material with the product of the distance ( $l$ ) that light travels through the material and the absorption coefficient ( $\alpha$ ) of the material [16]. The transmitted intensity  $I$  scales as  $\exp(-\alpha l)$ . However, signal generation in PCDS does not rely on Beer–Lambert principle. PCDS is based on the heat generated during nonradiative relaxation of vibrationally excited molecules.

Therefore, PCDS provides direct information on vibrational excitation of the molecules.

## 2. Experimental

### 2.1. Microcantilever preparation

We have used commercially available rectangular silicon cantilevers (OCTO 500-S, Micromotive, Germany) in these experiments. The cantilever dimensions were 500  $\mu\text{m}$  in length, 90  $\mu\text{m}$  in width and 1  $\mu\text{m}$  in thickness and had a spring constant of 23 mN/m. The cantilevers were cleaned by rinsing with acetone, ethanol and subjected to UV ozone treatment prior to gold coating. Gold coating was carried out using an evaporator (Ted Pella). A thin layer of chromium (10 nm) was used as an adhesion layer for the 200 nm of deposited gold. Prior to measurements being taken, each cantilever was rinsed several times with acetone and ethanol and dried in a vacuum oven.

### 2.2. PCDS experimental setup

The PCDS setup used in this study is shown in Fig. 1. The microcantilever was mounted on a cantilever holder, which was attached to a Multimode atomic force microscope (AFM) head (Bruker, Santa Barbara, CA). For PCDS experiments, a Quantum Cascade Laser (QCL) (Daylight Solutions, UT-8) was used as the light source. The QCL operated at a 200 kHz pulse rate with a 10% duty cycle and was modulated at 80 Hz using a DS345 function generator (Stanford Research System, Sunnyvale, CA). The IR wavelength was scanned from 7.1  $\mu\text{m}$  to 8.3  $\mu\text{m}$  ( $1408\text{ cm}^{-1}$  to  $1204\text{ cm}^{-1}$  in wavenumber) with a spectral resolution of 5 nm. The nanomechanical IR spectrum was taken using an SR850 lock-in amplifier (Stanford Research System, Sunnyvale, CA) and the resonance frequency of the microcantilevers was measured using an SR760 spectrum analyzer (Stanford Research System, Sunnyvale, CA). Custom developed LabView software was used for data acquisition and processing.

### 2.3. Thermomechanical sensitivity measurements

The thermomechanical sensitivity of a gold-coated silicon cantilever was measured by cycling temperatures between 30  $^{\circ}\text{C}$  and

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