Photoacoustic detection of gases using microcantilevers

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(Received 24 July 2009; accepted 9 November 2009; published online 14 December 2009)

We describe a new technique for measuring the infrared absorption spectra of gases using atomic force microscope microcantilevers. This photoacoustic system is demonstrated for a dilute acetylene/helium mixture by recording the acetylene $v_1 + v_3$ infrared overtone transitions using a wavelength modulated tunable diode laser as the infrared light source. The technique presents significant advantages over existing methods in terms of size, simplicity, speed and insensitivity to ambient vibrations. The maximum achievable signal-to-noise for resonant and non-resonant photoacoustic excitation of the microcantilever is examined and is found to be limited by the microcantilever’s Brownian noise. © 2009 American Institute of Physics. [doi:10.1063/1.3271157]

I. INTRODUCTION

Sensitive detection and quantification of gas-phase molecules is crucial in a wide range of applications. These include studies of tropospheric pollution,1 monitoring and optimization of industrial processes,2 investigating plant and insect respiration,3,4 and diagnosis of medical conditions.5 A particularly sensitive technique for measuring trace gas concentrations in these different situations is photoacoustic spectroscopy, a method that relies upon detecting acoustic disturbances caused by the infrared absorptions by gaseous molecules.

In this article, we demonstrate that the capabilities of photoacoustic spectroscopy can be significantly extended through use of microcantilevers. We employ standard atomic force microscope (AFM) microcantilevers to serve as sensitive microscale detectors for photoacoustic signals generated through molecular infrared absorptions. The new approach is demonstrated by recording the $v_1 + v_3$ near-infrared overtone transitions of acetylene gas using a tunable diode laser as the light source. The AFM microcantilever photoacoustic method has several advantages compared with existing methods: the microcantilevers are readily available, inexpensive, and have a relatively high resonance frequency, making them resistant to interference from ambient vibrations. Moreover, the detection scheme can easily be implemented in a commercial AFM apparatus to sense low concentrations of infrared active gases over extremely small volumes.

Several modifications have been previously devised to optimize the photoacoustic technique, including the use of sensitive microphones, resonant acoustic cavities, multipass cells, and lock-in detection.5 Recently, there have been attempts to replace microphones with more sensitive acoustic detectors including a piezoelectric cantilever microphone6 and a quartz crystal oscillator (QCO).7 Currently, the best sensitivity has been demonstrated using a specially fabricated miniature Si cantilevers whose movement is sensed interferometrically.8–10 These cantilevers require custom manufacture and typically have active areas of several mm$^2$ and resonant frequencies of several hundred hertz. They are much larger than the commercially available AFM microcantilever employed in our study which has a $5 \times 10^4 \mu$m$^2$ area and resonant frequency $f_0 \approx 5$ kHz. By employing a microcantilever with a high resonant frequency, the noise is thermomechanically limited and independent of the usual $1/f$ noise encountered in previous realizations.

More generally, various laser based schemes have previously been deployed to provoke oscillations in an AFM cantilever, usually through direct interaction between the laser beam and the cantilever. For example, Ratcliff et al.11 used photothermal excitation to resonantly excite a metal-coated SiN cantilever and Song et al.12 used photoelastic modulation to vibrationally excite silicon cantilevers. To our knowledge, this is the first time photoacoustic excitation of a surrounding gas has been used to induce vibrations in a standard AFM microcantilever.

II. EXPERIMENTAL SETUP

The strategy for photoacoustic excitation of an AFM microcantilever is illustrated in Fig. 1. The technique relies on the fact that vibrational energy deposited into a molecule is rapidly converted into translational energy causing localized heating. If the wavelength of the excitation laser is dithered at a frequency $f_{\text{mod}}$, so that it tunes on and off the molecular absorption line, it causes a periodic acoustic disturbance provoking oscillation of the AFM microcantilever. When $f_{\text{mod}}$ is set to the cantilever resonance frequency $f_0$, there is a substantial increase in oscillation amplitude of the cantilever compared with off-resonance excitation. The relative benefits of on- and off-resonance excitation for detection of photoacoustic signals are discussed below.

The silicon AFM microcantilever used as the detector (Nanoworld AG, Arrow TL1Au) was 500 μm long, 100 μm wide, and 1 μm thick, and had a vacuum resonance frequency $f_0=5295$ Hz. Its spring constant ($k = 0.04 \text{ N/m}$) was determined through the method of Sader et al.13 using its resonant frequency and quality factor measured in air ($f_{\text{air}}=5159$ Hz and $Q=23.4$). As supplied, the
cantilever top surface was coated with 5 nm of titanium and 30 nm of gold, although the metal coating is irrelevant for its operation as a photoacoustic detector.

The cantilever assembly was supported on a thin, circular aluminum plate, with the cantilever itself positioned across a 1.5 mm diameter hole in the plate center see Fig. 1). The plate was contained inside a 15 mm diameter gas-tight sample compartment with two glass windows allowing optical access to both sides of the cantilever. The tunable diode laser beam was directed through one window of the cell, traversing ~3 mm of gas before striking the cantilever holder. The cantilever itself was illuminated from the other side at 45° by a HeNe laser beam which was reflected on to the active area of a position sensitive detector (PSD) (PSD; Thorlabs PSDM2). The PSD signal, which is proportional to the cantilever deflection, was sent to a 12 bit DAQ board installed in a PC running LABVIEW software.

For this study, the gas sample consisted of 50 mbar 2% C₂H₂ in He, corresponding to an acetylene density of 2.7 × 10¹⁶ molecules/cm³. Under these conditions Doppler broadening (σD=0.016 cm⁻¹) rather than pressure broadening makes the main contribution to the transition linewidth.

The distributed feedback diode laser used for exciting the acetylene gas produced 14 mW of light over the 6520–6550 cm⁻¹ range and could be scanned over the P₁₁0–P₁₁₂ combination band. The laser wavelength was swept at 5295 Hz, associated with the Brownian motion of the microcantilever, and a sharp peak at fmod resulting from the P₁₁₂ line along with a fitted Gaussian derivative function (σA = 0.026 cm⁻¹). The sample was 50 mbar 2% C₂H₂ in He.

FIG. 1. (Color online) Strategy for photoacoustic excitation of an AFM cantilever. Frequency modulation of the diode laser output across the acetylene absorption line (upper) produces acoustic disturbances that cause periodic deflection of the AFM cantilever (lower), which is surrounded by dilute acetylene gas.

FIG. 2. (Color online) Section of the acetylene ν₁+ν₃ band recorded by lock-in detection of the AFM cantilever deflection signal as the laser wavelength was swept. The laser wavelength dither frequency corresponded to the cantilever resonance frequency (fmod=5295 Hz). Inset is an expansion of the P₇₇ line along with a fitted Gaussian derivative function (σD = 0.026 cm⁻¹). The sample was 50 mbar 2% C₂H₂ in He.

III. RESULTS

To illustrate the performance of the AFM microcantilever sensor, we recorded the acetylene ν₁+ν₃ spectrum by scanning the diode laser wavelength with lock-in detection at the modulation frequency (fmod=5295 Hz). The resulting (unsmoothed) spectrum, shown in Fig. 2, took ~30 min to record, and exhibits a SNR ~ 1000 for the more intense P₇₇ and P₉₉ lines. Optimum microcantilever deflection signal was achieved when the laser was directed on to the cantilever support, although appreciable signal was also detected when the IR beam was intercepted by the cantilever tip or even passed by the cantilever through the hole in the mount. No laser induced signal was observed if the laser wavelength was not tuned to an acetylene absorption line.

The sharp rovibrational lines apparent in Fig. 2 imply that the IR absorption is by gaseous acetylene molecules rather than molecules adsorbed on the cantilever or holder; adsorbed acetylene molecules would exhibit much broader spectral features. The fact that the S/N was around five times higher when the IR laser was directed at the cantilever support rather than passing by the cantilever is presumably because the photoacoustic pressure wave preferentially affects one side of the cantilever, maximizing the deflection. If on the other hand, the laser beam passes by the cantilever, a photoacoustic pulse is generated on both sides of the cantilever resulting in a lower differential pressure.

To explore the ultimate sensitivity of this sensor we measured the frequency response with the diode laser wavelength dithered across the P₇₇ line of the acetylene ν₁+ν₃ combination band. Figure 3 shows two response curves, each of which represents the average of 50 spectra, each taken with a 1 s acquisition time. Both curves contain a broad thermal noise peak centered at the cantilever resonant frequency f₀ =5295 Hz, associated with the Brownian motion of the microcantilever, and a sharp peak at fmod resulting from the photoacoustic excitation.

For the upper response curve [Fig. 3(a)], the diode laser wavelength was dithered at fmod=3500 Hz, well below the broad thermal noise peak centered at the cantilever resonant frequency. For the lower curve [Fig. 3(b)], the dither frequency has been adjusted to the cantilever resonant frequency (fmod=f₀=5295 Hz) leading to a 40-fold increase in the photoacoustically induced cantilever deflection.
match with the measured noise response functions.

The amplitude response of the cantilever due to an acoustic pulse is modeled in the following manner. For simplicity, it is assumed that the generated acoustic pulse propagates as a plane wave. The pressure differential applied between the front and rear faces of the cantilever is then constant. From Euler–Bernoulli beam theory, the displacement response of the cantilever end-tip is

\[
Z(\omega) = \frac{F_{\text{total}}}{k_{\text{end}}} \sum_{k=1}^{\infty} \frac{\left(\sinh \omega_{\text{res},k} \sinh \omega_{\text{res},1} - \sin \omega_{\text{res},k} \sin \omega_{\text{res},1}\right)}{\left(\omega^2 - \omega_{\text{res},k}^2\right)^2 + \frac{\omega^2 \omega_{\text{res},1}^2}{Q^2}},
\]

where \(F_{\text{total}} = P b L\) is the total force applied to the cantilever face, \(P\) is the applied pressure differential, \(b\) is the cantilever width, \(L\) is the length, \(\omega_{\text{res},r}\) is the (radial) resonant frequency of the \(n\)th mode, \(k_{\text{end}}\) is the static spring constant at the end-tip of the cantilever, and \(C_n\) is the \(n\)th root of \(\cos C_n \cosh C_n = -1\).

It then follows from Eq. (4) that the amplitude response at the fundamental resonant frequency \(\omega_{\text{res}} = \omega_{\text{res},1}\) is

\[
Z(\omega_{\text{res}}) = 0.38 \frac{F_{\text{total}}}{k_{\text{end}}} Q.
\]

From Eqs. (2) and (5), the SNR at the fundamental resonant frequency is given by

\[
\text{SNR} = \frac{\left|Z(\omega_{\text{res}})\right|}{\zeta_{\text{noise}}} = 0.19 P b L \sqrt{\frac{Q \omega_{\text{res}}}{k_B T B k_{\text{end}}}},
\]

where the static spring constant \(k_{\text{end}}\) is related to the dynamic spring constant by \(k_{\text{end}} = 12 C_n^2 = 0.97 k\).

Next, we examine how the SNR varies as a function of cantilever geometry. The quality factor due to gas damping is given by

\[
Q = \frac{4 \rho_h h}{\pi p b} + \Gamma_i(\omega_{\text{res}}),
\]

where \(\rho\) is the cantilever density, \(p\) is the gas density, \(h\) is the cantilever thickness, \(\Gamma\) is the (dimensionless) hydrodynamic function, and the subscripts \(r\) and \(i\) refer to the real and imaginary components.

In the high frequency limit, \(\Gamma_I(\omega) \sim O(\omega^{-1/2})\) and \(\Gamma_r(\omega) \sim O(1)\). Consequently, from Eqs. (6) and (7) we find that \(\text{SNR} \sim h^{-1/4} b^{-1/2} L\), at resonance. To maximize the SNR, the cantilever thickness \(h\) should therefore be reduced while both the width \(b\) and length \(L\) should be increased. Insofar as the noise results from Brownian motion of the cantilever, uniformly decreasing the cantilever dimensions always reduces the SNR.

Significantly, the predicted amplitude of the thermal noise peak at resonance \([26 \text{ pm}/\sqrt{\text{Hz}}\text{ from Eq. (2)}]\) sets an absolute scale for the response functions in Fig. 3. For resonant excitation \(f_{\text{mod}} = f_0 = 5295 \text{ Hz}\) the amplitude of the sharp peak arising from the laser-induced cantilever oscilla-
TABLE I. Operating parameters for detection of the acetylene $v_1 + v_3$ P(7) transition in 2% C$_2$H$_2$/He mixture at 50 mbar.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavenumber</td>
<td>6539.457 cm$^{-1}$</td>
</tr>
<tr>
<td>Line-strength (S)</td>
<td>$1.144 \times 10^{-20}$ cm$^{-1}$/molecule cm$^{-2}$</td>
</tr>
<tr>
<td>Doppler width</td>
<td>0.016 cm$^{-1}$</td>
</tr>
<tr>
<td>Peak cross section</td>
<td>$6.8 \times 10^{-19}$ cm$^2$ molecule$^{-1}$</td>
</tr>
<tr>
<td>Laser power</td>
<td>14 mW</td>
</tr>
<tr>
<td>C$_2$H$_2$ number density</td>
<td>$2.7 \times 10^{16}$ molecule cm$^{-3}$</td>
</tr>
<tr>
<td>SNR$^b$</td>
<td>2110</td>
</tr>
<tr>
<td>Min detectable conc.$^b$</td>
<td>$1.3 \times 10^{13}$ molecule cm$^{-3}$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$1.2 \times 10^{-7}$ cm$^{-1}$ W/$\sqrt{\text{Hz}}$</td>
</tr>
</tbody>
</table>

$^a$From Ref. 19.
$^b$For 1 s acquisition time with on-resonance excitation.

tion in Fig. 3(b) is $\sim 56$ nm, the acoustic pressure differential applied to the cantilever is approximately 2 mPa (calculated using Eq. (6)), and the dissipated power is 37 fW. On the other hand, for excitation at $f_{\text{mod}}=3500$ Hz, the oscillation amplitude is $\sim 1.4$ nm.

The measured frequency response data (Fig. 3) and the analysis outlined above confirm that for maximum detector sensitivity it is advantageous to operate on-resonance (SNR = 2110) rather than off-resonance (SNR=830). This is primarily because off-resonance (at 3500 Hz, for example), the white noise detector contribution ($1.5$ pm/$\sqrt{\text{Hz}}$) dominates the cantilever thermal noise ($0.9$ pm$/\sqrt{\text{Hz}}$), whereas on-resonance, the white noise contribution is practically inconsequential compared with the cantilever thermal noise ($26$ pm$/\sqrt{\text{Hz}}$).

The performance characteristics of the AFM cantilever detector for sensing the P(7) transition of the acetylene $v_1 + v_3$ band are summarized in Table I. The estimated normalized sensitivity of the detector, $\alpha=1.2 \times 10^{-7}$ cm$^{-1}$ W/$\sqrt{\text{Hz}}$ in its current configuration, is inferior to specially fabricated larger cantilevers ($1.7 \times 10^{-10}$ cm$^{-1}$ W/$\sqrt{\text{Hz}}$; Ref. 9) and to QCO detectors ($1.0 \times 10^{-8}$ cm$^{-1}$ W/$\sqrt{\text{Hz}}$; Ref. 18). It should be remarked, however, that the absorption path-length for our system (3 nm) is much less than most photoacoustic setups which typically have cells at least 10 cm long.$^7$ Sensitivity could also be improved by incorporating an appropriate acoustic resonator.

V. CONCLUSIONS

In summary, we have demonstrated the feasibility of photoacoustic excitation of a standard AFM microcantilever through absorption of infrared radiation by a surrounding gas and that the AFM microcantilever can be used as a sensor to record molecular infrared spectra. The scheme can in principle be instituted in a standard AFM apparatus to sense low concentrations of various gases over extremely small volumes. Although here we have used excitation of a vibrational combination transitions of C$_2$H$_2$ to modulate the AFM cantilever, alternative combinations of gases, liquids and wavelengths could be used. For example, CH$_4$, NH$_3$, and H$_2$O all possess well known infrared absorptions in the 1.5 $\mu$m region for which appropriate diode lasers are readily available.

ACKNOWLEDGMENTS

The authors are indebted to Dr. Rob Scholten for valuable discussions and for the loan of a diode laser controller and to the Australian Research Council and the University of Melbourne for supporting this research.

19The HITRAN database is available from www.hitran.com.