Infrared Microcalorimetric Spectroscopy Using Uncooled Thermal Detectors

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ABSTRACT

We have investigated a novel infrared microcalorimetric spectroscopy technique that can be used to detect the presence of trace amounts of target molecules. The chemical detection is accomplished by obtaining the infrared photothermal spectra of molecules absorbed on the surface of an uncooled thermal detector. Traditional gravimetric based chemical detectors (surface acoustic waves, quartz crystal microbalances) require highly selective coatings to achieve chemical specificity. In contrast, infrared microcalorimetric based detection requires only moderately specific coatings since the specificity is a consequence of the photothermal spectrum. We have obtained infrared photothermal spectra for trace concentrations of chemical analytes including diisopropyl methylphosphonate (DIMP), 2-mercaptoethanol and trinitrotoluene (TNT) over the wavelength region 2.5 to 14.5 μm . We found that in the wavelength region 2.5 to 14.5 μm DIMP exhibits two strong photothermal peaks. The photothermal spectra of 2-mercaptoethanol and TNT exhibit a number of peaks in the wavelength region 2.5 to 14.5 μm and the photothermal peaks for 2-mercaptoethanol are in excellent agreement with infrared absorption peaks present in its IR spectrum. The photothermal response of chemical detectors based on microcalorimetric spectroscopy has been found to vary reproducibly and sensitively as a consequence of adsorption of small number of molecules on a detector surface followed by photon irradiation and can be used for improved chemical characterization.

Keywords: infrared, microcalorimetric spectroscopy, thermal detector, gravimetric sensor

1. INTRODUCTION

The need for improved and more timely control as well as regulation of waste stream composition, product quality and equipment operation has provided a strong driving force for efforts to develop new types of chemical sensors. This has shifted the determination of chemical composition from laboratory-based, off-line methods such as chromatography or fluorescence spectroscopy to new types of rapid, on-line sensors. Present day chemical detection technologies have been based primarily on adaptation of laboratory instruments. For example, a large number of spectroscopic methods have been introduced over the past twenty years that are based upon methods such as optical absorption^{1,4}, laser scattering⁵, luminescence^{6,7}, atomic fluorescence spectroscopy⁸ or refractive index changes⁹. However, these methods rely on performing laboratory chemical analyses on extracted samples, provide no real-time data for operational feedback, and are generally expensive and complicated to use. Successful chemical sensors should be both sensitive and selective, have a fast, real-time response, and should be able to be miniaturized and integrated into other devices. Currently used miniature, real-time chemical sensors such as multi-analyte, single-fiber, optical sensors¹⁰, sol-gel indicator (SGI) composites¹¹, portable acoustic-wave sensors (PAWS)¹², thin film resonators¹³, and surface acoustic wave array detectors¹⁴ have sufficient chemical sensitivity but suffer from lack of chemical specificity.

In this work we have investigated a new chemical detection technique that affords significant opportunities for higher sensitivity and specificity, miniaturization, mass production and customization based on a microcalorimetric spectroscopy shown schematically in Figure 1. Microcalorimetric spectroscopy based detection technique is capable of detecting and identifying chemical analytes that have relatively high vapor pressure such as volatile organic compounds (VOCs) or low-vapor pressure such as explosives, chemical warfare agents, and drugs. The detection of the presence and identity of molecules using microcalorimetric spectroscopy can be broken down into two main steps. In the first step the sample is allowed to interact with the surface of a femtojoule sensitive thermal detector that is

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coated with an appropriate chemical layer selective to the family of the target chemicals. Since the chemical selectivity is primarily a consequence of the photothermal "signature", only moderately selective chemical layers are needed such as those customarily used to coat GC columns. In the second step, a photothermal spectrum is obtained for the molecules adsorbed on the detector surface, by scanning a broadband wavelength region with the aid of a monochromator. For wavelengths, λ , at which the target chemical absorbs incident photons, the minute (but detectable) temperature change of those particular detector pixels will be proportional to the number of photons absorbed which, in turn, is proportional to the number of molecules adsorbed on the detector surface. Because different pixels will be exposed to different wavelengths, a sensitive and unique photothermal signature response can be obtained.

In the present studies we used microcantilevers as thermal detectors. However, currently available state-of-the-art microbolometer thermal detectors¹⁴ are particularly attractive, especially because of their multi-row (two-dimensional) configuration and elegant addressing that allows different rows to be coated with different chemically sensitive coating providing increased selectivity and perhaps multichemical detection.

Microcantilever thermal detectors¹⁶⁻¹⁸ have been shown to detect extremely small changes in energy (or temperature) of the order of $\approx 10^{-15}$ J. This unprecedented sensitivity can be utilized to detect target molecules with a sensitivity as low as a few parts per trillion and subsequently identify them through their photothermal spectrum. The chemical detector surface can be regenerated by ohmic heating since the mass of the microcantilever thermal detector element is very small ($\approx 10^{-9}$ g) and therefore, the temperature of the thermal detector can be increased significantly and subsequently cooled within a very short time.

In order to gain some insight about the sensitivity limits of chemical detection using microcalorimetric spectroscopy we assume a typical heat of absorption¹⁹ of ≈ 10 kcal/mole. This is equivalent to an energy of $\approx 7 \times 10^{-20}$ J per absorbed molecule. Using only traditional calorimetry based detection, $\approx 3 \times 10^5$ molecules will need to be adsorbed and cause a temperature change within a time less than the thermal time constant in order to be detected. A typical vibrational mode requires a photon of $\approx 10^{-20}$ J for a molecule to be excited to the first vibrational level. Vibrational excitation of 3×10^5 adsorbed molecules results in $\approx 3 \times 10^{-15}$ J energy increase and the de-excitation that follows leads to heating of the sensitive thermal detector surface producing a measurable signal. Of course, this occurs only for the particular detector pixels illuminated by the appropriate λ , for which the target chemical analyte absorbs the incident photons. Because molecules are adsorbed on the thermal detector surface the measurement can be repeated and averaged.

2. EXPERIMENTAL

The chemical detection technique investigated in the present work relies on the adsorption of analytes on the surface of a sensitive thermal detector. The thermal detector used in our studies was a microcantilever thermal detector¹⁵⁻¹⁸. The bending of microcantilevers due to absorption of photons can be readily determined by a number of means, including optical, capacitive, electron tunneling, and piezoresistive methods. In this work, we used an optical readout technique for observing microcantilever bending due to photothermal heating. A laser was used in a probe configuration to monitor the microcantilever bending. A HeNe laser (delivering 3 mW at 633 nm) was focused onto the tip of the microcantilever using a $30\times$ microscope objective. In order to minimize heating of the tip by the probe laser, optical power was reduced by placing a neutral density filter with an optical density of 1.0 between the probe laser and the objective. A quad-element photodiode displacement detector was used to collect the reflected probe beam. The bending of the microcantilever depends linearly on the current output ($i_{A,B,C,D}$) of the photodiode. A high narrow bandpass optical filter is placed in front of the photodiode allowing the HeNe laser beam to be detected while preventing other wavelengths from reaching the photodiode. The amplified differential current signal from the quad cell photodiode, $i_{A,B,C,D} [= (i_A + i_B) - (i_C + i_D) / (i_A + i_B + i_C + i_D)]$, is monitored and recorded using a digital oscilloscope, or sent to a lock-in amplifier (SR850, Stanford Research Systems) for signal extraction and averaging.

Figure 1. Schematic representation of the principle of microcalorimetric spectroscopy technique. Photons with different wavelengths irradiate different thermal detectors configured as a linear array. Molecules adsorbed on the surface of thermal detector pixel absorb photons and a photothermal spectrum is obtained.

is obtained.

The experimental setup used in the present studies is shown schematically in Figure 2. Microcantilevers typically come from the manufacturer attached to a large rectangular chip (1-mm wide, 3-mm long, 1-mm thick) that is used to facilitate manipulation and mounting, and were used as received. The microcantilevers used were triangular silicon nitride microcantilevers (with a length of 180 μm , a width of 18 μm , and a bending force constant $k = 0.03 \text{ N/m}$, from Park Scientific). Each was 0.6 μm thick and had a gold/chromium film uniformly covering one side. Microcantilevers were mounted in a chip holder and IR radiation from a tunable infrared source (Foxboro Miran-80 infrared spectrometer) was focussed on the surface of the microcantilever thermal detector positioned approximately 50 cm from the source. Optical read-out as described above was used to measure the bending of microcantilever thermal detector in response to absorption of IR photons by the molecules adsorbed on its surface. Since the position sensitive photodiode was blind to infrared no additional filtering was needed for the read-out circuit. The Miran-80 has a 50 Hz internal chopper that provided a reference frequency for lock-in detection. Output wavelength of the Miran-80 was scanned at a rate of 3 nm /s, and the optical bandwidth of the gradient filter used for wavelength selection was approximately 80 nm. Response of the standard detector on the Miran-80 (a lithium tantalate pyroelectric detector with a time constant of 1 s) was used to verify the operation of the spectrometer. All measurements were conducted at ambient temperature and atmospheric conditions.

Figure 2. Schematic of the experimental setup used in the present studies.

The microcantilever thermal detectors were exposed to IR radiation from the spectrometer prior any exposure to chemicals and their thermal response was recorded as a function of photon wavelength. The wavelength region attainable with the spectrometer used (2.5 to 14.5 μm) was divided into three regions: (i) 2.5 to 4.5 μm , (ii) 4.5 to 8.0 μm , and (iii) 8.0 to 14.5 μm . Subsequently, the thermal detectors were exposed to chemical analytes and a new thermal response was recorded as a function on photon wavelength. The increase in thermal response of the detector at particular wavelengths was attributed to the absorption of photons by the molecules adsorbed on the thermal detector surface.

3. RESULTS AND DISCUSSION

A. DIMP

DIMP is a phosphorous containing organic chemical and is a model for chemical warfare agents. A number of gravimetric based transducers have been used as platforms for detecting phosphorous containing organic compounds. An earlier study²⁰ has used a SAW device with self-assembled monolayers to derive selectivity and reversibility. In those studies a gold-coated substrate was first exposed to 11-mecaptoundecanoic acid forming a self-assembling monolayer on the gold surface. Then, the modified substrate was exposed to $\text{Cu}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ that formed a composite monolayer. This resulted in a Cu^{2+} surface that could reversibly bind DIMP. In the present studies we exposed DIMP directly to gold-coated microcantilevers both for simplicity and because gold reflects most of the incoming IR energy minimizing the heating of the substrate. In future studies we plan to explore such surface modification techniques including the formation of composite self-assembled monolayers.

In Figure 3 we plotted the thermal response of a microcantilever thermal detector from 2.5 to 4.5 μm with DIMP molecules adsorbed on its surface (solid curve). The microcalorimetric (photothermal) spectrum was obtained with about one monolayers of coverage. Also plotted in Figure 3 is the infrared absorption spectrum²¹ of DIMP between 2.5 and 4.5 μm (dashed curve). The two peaks in the photothermal spectrum of DIMP shown in Figure 3 correspond well with the absorption peaks in the IR spectrum of DIMP (Figure 3, dashed curve). Changes in the resonance frequency of microcantilevers can be used to determine the amount of mass deposited²²⁻²⁴. The change in the resonance frequency of the microcantilever was $< 1 \text{ Hz}$ and therefore the adsorbed mass of DIMP was $< 2 \times 10^{-14} \text{ g}$ which corresponds to roughly one monolayer of DIMP.

Since DIMP molecules absorb photons at these wavelengths, their internal energy increases as molecules populated higher vibrational levels. The internal energy of each DIMP molecule is dissipated either by radiation, convection or conduction with the gold substrate. It

is the heat conduction from the "hot" molecules to the gold substrate of the microcantilever that increases the temperature of the microcantilever causing it to bend. Our present results demonstrate that it is possible to detect less than submonolayer of DIMP coverage using microcalorimetric spectroscopy and the photothermal spectrum can provide a unique identification "fingerprint" of DIMP adsorbed on the thermal detector surface.

Figure 3. Response of a microcantilever thermal detector exposed to DIMP as a function of photon wavelength (solid curve). The dashed curve is the infrared absorption spectrum²¹ of DIMP.

B. 2-Mercaptoethanol

2-Mercaptoethanol is a liquid at room temperature, has a vapor pressure of 1 Torr at 20° C, a boiling point of 157.1° C, and possesses a strong unpleasant odor. The odor threshold for mercaptans is between 0.7 and 35 ppb²⁵. 2-Mercaptoethanol has been used as a rust inhibitor in steel, brightening agent in copper deposition, tarnish remover from alloys and metals, ingredient in hair permanent chemicals and hair and wool dyes, mosquito control agent, reagent for diagnostic bioassays, and initiator in polymeric reactions²⁶. About 40,000 workers in the U.S.A. are potentially exposed to 2-mercaptoethanol²⁷.

Because of the effects on biological systems, there is a need for the development of continuous direct reading monitors and personal samplers for 2-mercaptoethanol. Yet, to date no effective sampling method has been identified. While various techniques have been used to collect and analyze airborne mercaptans no information is available in the literature on sampling procedures specific to 2-mercaptoethanol. Sorbent tubes containing Chromosorb 104 is an efficient sampling method for most mercaptans although it has been found unsatisfactory for ethanethiol. Gas chromatographic techniques have been used to detect mercaptans in the ppb range²⁸. A hydrogen flame was used along with a column of 4% carbon 20 M terminated with terephthalic acid on 60-80- mesh hexamethyldisilazane (HMDS) pretreated chromosorb. A column temperature of 73 C was used with N₂ carrier flow set at 63 ml/min, hydrogen flow at 45 ml/min, and air flow at 300 ml/min. The H₂ flame detector temperature was 200° C. A retention time of 3.65 was reported for 2-mercaptoethanol²⁸.

In the present studies 2-mercaptoethanol vapor was allowed to interact and adsorb on a gold coated microcantilever surface. 2-mercaptoethanol adheres well on gold surfaces forming self-assembled monolayers. In Figure 4 we plotted the photothermal response (solid curve) of a microcantilever exposed to 2-mercaptoethanol vapors. Also plotted is the IR absorption spectrum of 2-

Figure 4. Response of a microcantilever thermal detector exposed to 2-mercaptoethanol as a function of photon wavelength (solid curve). The dashed curve represents the absorption spectrum of 2-mercaptoethanol²¹.

mercaptoethanol found in the literature²¹. It can be seen that the photothermal spectrum exhibits peaks that correspond well with the IR absorption peaks. In the present studies the microcantilever (whose photothermal response is shown in Figure 4) exhibited no measurable (< 1 Hz) change in the resonance frequency which corresponds to less than one monolayer of 2-mercaptoethanol coverage.

B. TNT

In recent years, the detection of trinitrotoluene (TNT) has received increased attention by a number of federal agencies in U.S.A. TNT is solid at room temperature, has very low vapor pressure ($\approx 10^{-6}$ Torr) and its detection under ambient conditions presents a challenge. We studied the thermal response of microcantilever thermal detectors with TNT molecules adsorbed on their surface. TNT was placed in a chamber containing a gold coated microcantilever thermal detector allowing TNT molecules to adsorb on the microcantilever surface. TNT was subsequently removed from the chamber and the microcantilever was exposed to IR radiation. In Figure 5 we plotted the thermal response of the microcantilever thermal detector (exposed to TNT vapor) from 4.5 to 14.5 μm with TNT molecules adsorbed on the microcantilever surface. As it can be seen from Figure 5, the photothermal spectrum of the adsorbed TNT exhibits a number of peaks in this wavelength region. These peaks are expected to correspond to infrared absorption peaks of TNT vapor.

In order to estimate the number of TNT molecules adsorbed on the microcantilever surface, we measured its resonance frequency prior to exposure to TNT. For a microcantilever of length l , width w , and thickness t that has analytes uniformly adsorbed on its surface, the fractional change in resonance frequency, $(\Delta f / f_0)$, is given by

$$\frac{\Delta f}{f_0} = \frac{\Delta m}{m_c} \quad (1)$$

where f_0 is the resonance frequency and m_c is the microcantilever mass and Δm is the additional mass deposited. We found that initially the resonance frequency was $f_0^i = 5.251$ kHz. After TNT molecules adsorbed on the microcantilever surface the resonance frequency changed to $f_0^f = 5.206$ kHz corresponding to a $\Delta f / f_0 = 8.6 \times 10^{-3}$. In Figure 6 we plotted the response of the microcantilever to acoustic excitation before and after TNT molecules were allowed to adsorb. Therefore, a change in the resonance frequency of 45 Hz was observed which corresponds to an adsorbed mass of TNT of less than 10^{-12} g or fewer than 3×10^9 molecules.

Figure 5. Photothermal spectrum of TNT adsorbed on a gold coated microcantilever thermal detector surface.

Figure 6. Acoustic response of the microcantilever as a function of frequency before (solid lines) and after (dashed line) exposure to TNT molecules.

4. CONCLUSIONS

The results of the present study demonstrate that microcalorimetric spectroscopy can provide a powerful analytical tool that can be used to develop multichemical sensors that exhibit both increased sensitivity and selectivity. Using microcalorimetric spectroscopy it may be possible to distinguish many target molecules based on their photothermal spectra. Moderately chemically specific (surface modification) coatings can be used to enhance the adsorption of target molecules. However, unlike gravimetric type devices the selectivity is not a consequence of a highly selective coating but comes from the unique photothermal signature for each target chemical. In addition regeneration can also be accomplished. The thermal detector can be easily heated and therefore regenerated with a number of heat cycles, each cycle lasting less than 1 s. In future studies we will employ microbolometer thermal detectors to obtain photothermal spectra of adsorbed molecules. This will also provide a convenient way to regenerate the detector surface using ohmic heating.

A chemical detection approach based on infrared microcalorimetric spectroscopy can provide unique photothermal signatures for the specific target molecule allowing not only its detection but its identification as well. Unlike sensors that rely on highly specific chemical coatings to achieve the desired sensitivity²⁹⁻³², microcalorimetric spectroscopy requires only moderately selective coatings. Moreover, the chemical sensitivity can be further improved (at least an order of magnitude) by increasing the sensitivity of the thermal detector; we have demonstrated that by merely decreasing the thickness of the thermal detector substantially improved response can be achieved³³.

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