Presented at the Third International Symposium on Technology and the Mine Problem, Monterey, California, April 6-9, 1998

Novel Micro-Calorimetric Spectroscopy for Mine Detection

P.G. Datskos[a),b)], S. Rajic [a)], C.M. Egert [a)], and I. Datskou [a)]

[a)] *Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-8039*
[b)] *University of Tennessee, 401 Nielsen Physics Building, Knoxville, TN 37996-1200*

ABSTRACT

We have developed a novel micro-calorimetric spectroscopy technique that can be used in mine detection applications. In this technique target molecules are allowed to adsorb on the surface of sub-femtojoule sensitive micromechanical thermal detectors. The adsorption of molecules on the thermal detector surface causes a differential surface stress resulting in an initial "trigger". By exposing each element in an array of thermal detectors to different photon wavelengths, an extremely sensitive and unique photothermal signature response can be obtained. We will present our results on target chemicals adsorbed on the detector surface at sub-monolayer coverage levels. We will present infrared photothermal spectra for trace concentrations of diisopropyl methylphosphonate (DIMP), 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 the photothermal spectra of DIMP and TNT exhibit a number of peaks and are in excellent agreement with infrared absorption spectra found in the literature. Chemical detectors based on micro-calorimetric spectroscopy can be used to sensitively sense small number of molecules adsorbed on a thermal detector surface. The photothermal signature resulting from photon irradiation can be used for improved chemical characterization.

1. INTRODUCTION

The detection and disposal of unexploded ordnance (UXO) is a complex and difficult problem [1]. Technologies aimed at the detection of surface or near-subsurface UXO are based on sensors that sense either the effects of the mine on its surrounding environment, or the object itself. For example, chemical sensors are based on the detection of the presence of explosive vapors or other chemicals in the vicinity of the buried mine. On the other hand, physical sensors can either sense the mine itself (metal detectors) or as in the case of thermal imaging sensors sense the disturbed thermal signature of the soil where the mine is buried. The fundamental limitation of all presently available technologies is the false alarm rate and the ability to classify targets. Presently, the false alarm rates for sensors detecting UXO are often too high. Understandably, the false alarm issue becomes of primary importance since additional resources need to be expended to determine whether actually a threat is present.

Today, there are a number of available UXO detection technologies. Metal detectors, thermal imaging systems, ground penetrating radar, biological detectors, and trace chemical sensors represent some of the better known technologies [1]. However, all of them posses inherent advantages and, unfortunately, shortcomings. It is widely accepted that no single technology exists which will solve the UXO problem satisfactorily. Although discrete and partial solutions may be adequate for narrowly defined missions, search is still ongoing for UXO detection approaches that do not have the shortcomings that plague presently available technologies.

In this paper we will present a micro-calorimetric spectroscopy technique that has the potential of sensing and identifying extremely small concentrations of target molecules; detection of sub-ppt concentrations may be possible. Chemical detection based on micro-calorimetric spectroscopy is capable of detecting and identifying chemical analytes that have low-vapor pressure (such as explosives, chemical warfare agents, and drugs) or relatively high vapor pressure such as volatile organic compounds (VOCs) [2]. This temperature

based spectroscopy technique employs measurment of minute temperature differences, as a function of wavelength, on micro-structure thermal detector arrays containing adsorbed target molecules. Thus a unique photothermal signature spectrum (signal vs wavelength) can be obtained for submonolayer target chemical coverage. We have applied this technique to the detection of trace quantities of DIMP (a chemical warfare agent simulant), and TNT.

The selection of the infrared (IR) thermal detector plays an important role in the ultimate sensitivity of the micro-calorimetric spectroscopy technique. Presently, there is a number of families of commercially available IR detectors, including thermopiles, bolometers, pyroelectrics, and various solid state detectors [3-12]. In this work, we employed inexpensive micromechanical IR thermal detectors; microcantilever technology is used which is based on the bending of a microcantilever as a result of absorption of IR energy [9-10]. When a microcantilever is exposed to IR radiation, its temperature rises due to absorption of this energy.

2. MICRO-CALORIMETRIC SPECTROSCOPY DETECTION

The detection of the presence and identity of molecules using micro-calorimetric 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 coated with an appropriate chemical layer selective to the family of the target chemicals. Depending on the choice of thermal detector, the initial molecular adsorption can induce surface stress changes that provide a kind of "trigger". However, the chemical selectivity is primarily a consequence of the photothermal "signature", and therefore 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. The temperature changes of those particular detector elements is proportional to the number of photons

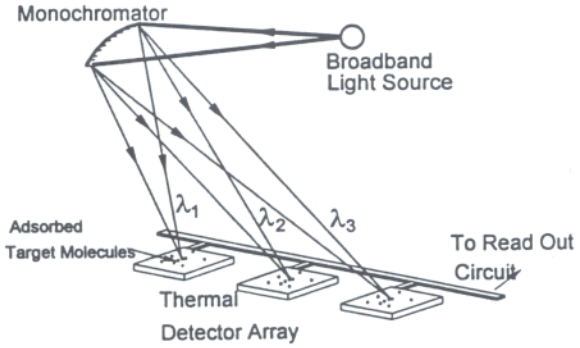

Figure 1. Schematic representation of the principle of microcalorimetric spectroscopy technique. Photons of different wavelength irradiate different thermal detectors configured as a linear array. Molecules adsorbed on the surface of thermal detector elements absorb photons and a photothermal spectrum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

absorbed which, in turn, is proportional to the number of molecules adsorbed on the detector surface. Because different detector elements will be exposed to different wavelengths, a sensitive photothermal signature response can be obtained. Photothermal spectra are very similar to conventional infrared spectra and can be used to uniquely identify the adsorbed molecules.

3. MICROCANTILEVER THERMAL DETECTOR

Bimaterial microcantilevers are constructed from materials exhibiting dissimilar thermal expansion properties; for example, microcantilevers made from silicon nitride (or silicon) coated with a thin film of gold or platinum can be used. The bimaterial effect causes the microcantilever to bend in response to this temperature variation. The extent of bending is directly proportional to the radiation intensity. Previous work has shown that microcantilever bending can be detected with extremely high sensitivity [9-16]. For example, metal-coated microcantilevers that are commonly employed in atomic force microscopy (AFM) allow sub-Angstrom ($< 10^{-10}$ m) sensitivity to be routinely obtained. Recent studies have reported [13-16] the use of microcantilever bending for calorimetric detection of chemical reactions with energies as low as a few pJ. It was demonstrated [16] that a similar

microcantilever thermal detector had an observed sensitivity of 100 pW corresponding to an energy of 150 fJ and use of the sensor as a femtojoule calorimeter was proposed. An estimate of the minimum detectable power level was on the order of 10 pW, corresponding to a detectable energy of 10 fJ and a temperature sensitivity 10^{-5} K. However, using an optimally designed microcantilever, the sensitivity may be improved even further. Hence, in chemical detection based on micro-calorimetric spectroscopy, microcantilevers can be coated with an appropriate layer providing the bimaterial effect, and a moderate chemical selectivity.

The bending of a rectangular bimaterial microcantilever is proportional to the absorbed energy. The maximum deflection, z_{max}, due to differential stress is given by [9,13]
where l and w are, the length and width of the

$$z_{max} = \frac{5}{4}\frac{(t_1+t_2)l^3}{(\kappa_1 t_1 + \kappa_2 t_2)wt_2^2} \times \frac{(\alpha_1-\alpha_2)}{4+6\frac{t_1}{t_2}+4\frac{t_1^2}{t_2^2}+\frac{E_1}{E_2}\frac{t_1^3}{t_2^3}+\frac{E_2}{E_1}} \cdot \eta\left(\frac{dQ}{dt}\right) \quad (1)$$

$\Delta T = \eta \frac{dQ}{dt} / G$

microcantilever, respectively, t_1 and t_2 are the thicknesses of the two layers, κ_1, κ_2; α_1, α_2; E_1, E_2 are the thermal conductivities; thermal expansion coefficients and Young's moduli of elasticity of the two layers; $\eta dQ/dT$ is the fraction of the IR radiation power absorbed. In order to increase the IR detection sensitivity of a microcantilever, z_{max} should be maximized and is is strongly dependent on the geometry and thermal properties of the two layers.

4. EXPERIMENTAL

The chemical detection technique investigated in the present work relies on the adsorption of analytes on the surface of a sensitive thermal

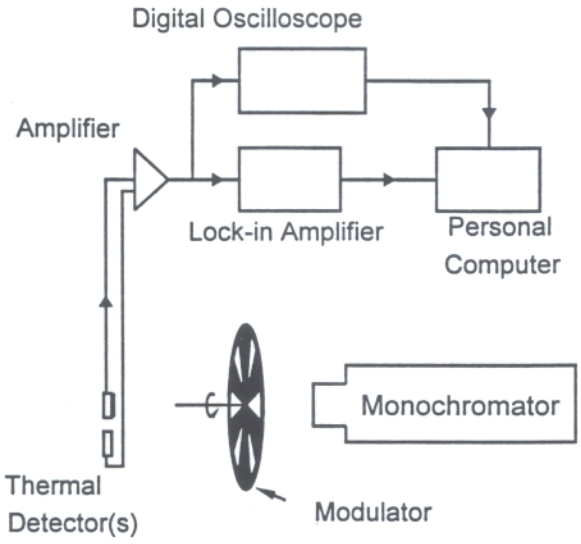

Figure 2. Schematic of the experimental setup used in the present studies.

detector. The IR detector used in our studies was a microcantilever thermal detector [9-16]. The bending of microcantilevers 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 diode laser (delivering 1 mW at 670 nm) was focused onto the tip of the microcantilever using a 20× 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 (A,B,C,D) photodiode detector was used to collect the reflected probe beam. The current output ($i_{A,B,C,D}$) of the photodiode depends linearly on the bending of the microcantilever. A high narrow bandpass optical filter is placed in front of the photodiode allowing the 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 (TDS 780, Tektronix) or sent to a lock-in amplifier (SR850, Stanford Research Systems)

for signal extraction and averaging.

The experimental setup used in the present studies is shown schematically in Figure 2. The microcantilevers used were triangular silicon nitride or silicon microcantilevers. Each was 0.6 μm thick and had either a 50 nm thick gold/chromium film(for DIMP) or a 50 nm platinum film (for TNT) uniformly covering one side. Optical read-out was used to measure the bending of the microcantilever thermal detector due to photothermal response of molecules adsorbed on its surface. Since the quad element photodiode was blind to IR no additional filtering was needed for the read-out circuit.

For the micro-calorimetric studies, the microcantilever thermal detectors were exposed to IR radiation from the spectrometer prior to any exposure to chemicals and their thermal response was recorded as a function of photon wavelength. The wavelength region (2.5 to 14.5 μm) attainable with our spectrometer (Foxboro Miran-80 IR spectrometer) was divided into three regions: (i) 2.5 to 4.5 m, (ii) 4.5 to 8.0 μm, and (iii) 8.0 to 14.5 μm. 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. All measurements were conducted at ambient temperature and atmospheric conditions.

5. RESULTS

5.1 Thermal Detector Measurements

In order to optimize the thermal detectors used in our micro-calorimetric technique, we investigated the response of microcantilevers to IR radiation. A HeNe laser was used to thermally excite gold coated microcantilevers. The bending of the microcantilever was determined using an optical read-out scheme as described earlier. The signal was digitized and stored, or sent to a lock-in amplifier. Assuming a uniform heat dissipation over the entire length, l, of the microcantilever (of thickness t) the change in temperature at the tip, ΔT ($\approx l^2/2\lambda t \; dQ/dt$), depends on geometrical factors

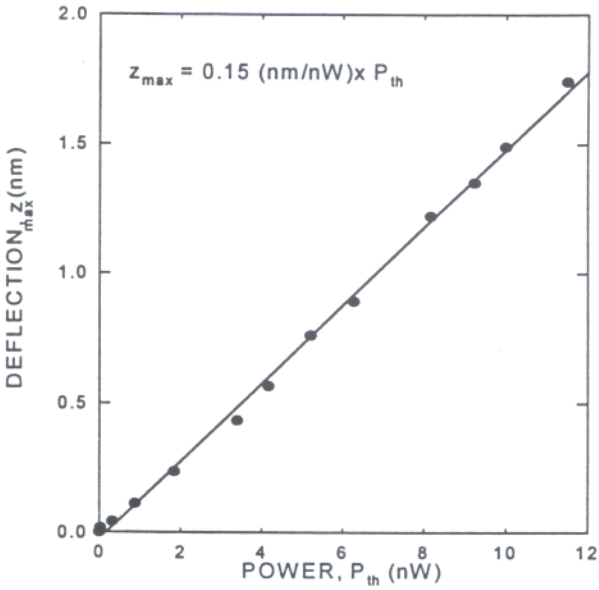

Figure 3. Deflection, z_{max}, of the microcantilever thermal detector as function of the absorbed thermal power.

such as l and t. A temperature change of $\Delta T = 10^{-4}$ K leads to deflections of ~1 nm.

Assuming a spatially uniform incident power, dQ/dt, onto a bimaterial microcantilever the maximum deflection, z_{max}, depends on the temperature rise [17] and is proportional to the incident power [10]. The thermally induced deflection of the microcantilever is caused by the bimaterial effect which arises due to the difference in the thermal properties of the metal layer, and the native body of the microcantilever. In Figure 3 we plotted the maximum bending z_{max} as a function of the absorbed power P_{th} and it can be seen that it increases linearly with increasing power; the reflectivity of the gold film is >0.99. From the slope of the line in Figure 3 we obtained a deflection sensitivity of ~0.15 nm/nW. Using a Stanford Research Systems SR 540 chopper to modulate the IR radiation at a frequency of 30 Hz, we calculated a noise equivalent power (*NEP*) of ~ 520 pW/Hz$^{1/2}$.

The microcantilever thermal detector was found to exhibit two thermally distinct response times due to the incoming IR radiation; a time $\tau_{th}^1 < 1$ ms and a time τ_{th}^2 that is somewhat longer (~10 ms). The fast thermal response is attributed to thermal equilibrium between the top (exposed to the IR

radiation) and the bottom surfaces, while the longer thermal response results from the heat flow (along the body of the microcantilever) to the supporting base.

5.2 Chemical Detection Measurements

Our chemical detection studies were performed by using micro-calorimetric spectroscopy to obtain photothermal spectra of molecules adsorbed on a micromechanical thermal detector surface. In order to determine an upper limit on the number of the adsorbed molecules we measured the resonance frequency shift of the microcantilever before and after exposure to chemicals.

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

$$\frac{\Delta f}{f_0} = \frac{\Delta m}{m_c} \qquad (2)$$

where f_0 is the resonance frequency and m_c is the microcantilever mass and m is the additional mass deposited. Measurement of the resonance frequency shift Δf allowed us to estimate the surface coverage due to molecular adsorption [18-20].

5.2.1 DIMP

Diisopropyl methylphosphonate (DIMP) is a phosphorous containing organic chemical and is used as 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 study [18] has used a SAW device with self-assembled monolayers to derive selectivity and reversibility. 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 direct heating of the substrate. In Figure 4 we plotted the thermal response of a microcantilever thermal detector from 8.0 to 14.5

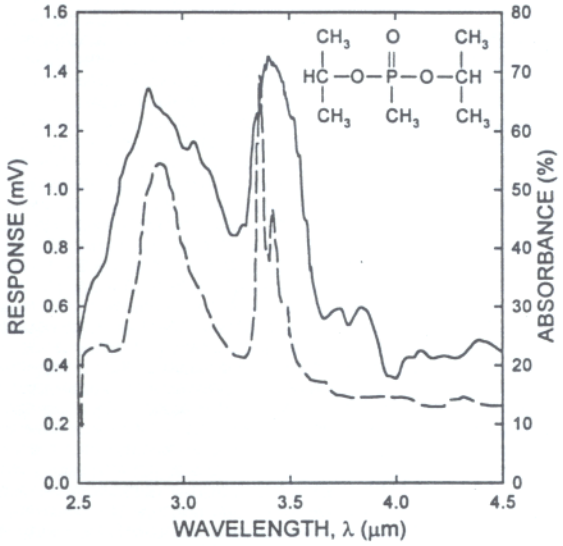

Figure 4. Photothermal response of a microcantilever thermal detector exposed to DIMP as a function of photon wavelength (solid curve). The dashed curve represents the infrared absorption spectrum of DIMP [19]. Less than one monolayers coverage was present on the thermal detector surface.

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 4 is the infrared absorption spectrum [19] of DIMP between 8.0 and 14.5 μm (dashed curve). The peaks in the photothermal spectrum of DIMP shown in Figure 4 correspond well with the absorption peaks in the IR spectrum of DIMP (Figure 4, dashed curve). The change in the resonance frequency of the microcantilever was < 0.1 Hz and therefore the adsorbed upper limit on the mass of DIMP was < 2×10^{-15} g which corresponds to roughly less than 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 to the gold substrate. It is the heat of 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 micro-calorimetric spectroscopy. In addition, the photothermal spectrum can provide a unique identification "fingerprint" of DIMP adsorbed on the thermal detector surface.

5.2.2 TNT

TNT is solid at room temperature, has very low vapor pressure (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 platinum 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 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. We found that initially the resonance frequency was f_0 = 7.521 kHz. After TNT molecules adsorbed on the microcantilever surface the resonance frequency shift was < 0.1 Hz. This places an upper limit on the adsorbed mass of TNT of less than 10^{-15} g or fewer than 3×10^{7} molecules.

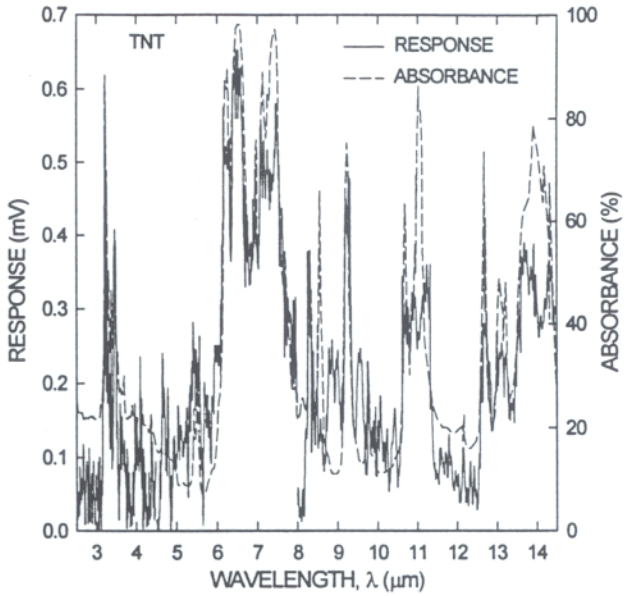

Figure 5. Photothermal response of a microcantilever thermal detector exposed to TNT as a function of wavelength (solid curve). The dashed curve represents the adsorption spectrum TNT [19]. Less than one monolayer coverage was present on the thermal detector.

6. DISCUSSION

The results of the present study demonstrate that micro-calorimetric spectroscopy can provide a powerful analytical tool that can be used to develop multichemical sensors that exhibit both increased sensitivity and selectivity. Using micro-calorimetric spectroscopy it is 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 of micro-calorimetric spectroscopy is not a consequence of a highly selective coating but comes from the unique photothermal signature for each target chemical [20-26]. 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.

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 also rapid identification as well. 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 achieved [27].

It may also be possible to use micro-calorimetric spectroscopy in conjunction with other trace chemical detection technologies. For example, gravimetric, photo-induced stress and resonance frequency changes can all provide complementary information.

It is well known that canines are excellent trace chemical detector and can sense sub ppt concentrations. Although their ability stems from millions of years of evolution and they use a sophisticated "pattern recognition," the fact remains that trace chemical detectors can detect the extremely small chemical concentrations near and around burried UXO. Therefore, drawing from nature, sub-ppt detection limits should be attainable with bio-mimetic based detection or even with trace chemical detection approaches.

7. CONCLUSIONS

The results presented in this paper demonstrate that micro-calorimetric spectroscopy can detect the presence of small number of molecules on the surface of sensitive micromechanical thermal detectors. In addition, the photothermal spectra obtained can be used to uniquely identify the chemical analytes. Micro-calorimetric spectroscopy represents is a form of spectroscopic technique, and therefore the effect of unwanted contaminant or interfering substances can be eliminated or minimized.

8. ACKNOWLEDGEMENTS

This work was supported by the Laboratory Director's Research and Development Program of Oak Ridge National Laboratory. Oak Ridge National Laboratory is operated for the U.S. Department of Energy by Lockheed Martin Energy Research Corporation under contract DE-AC05-96OR22464.

9. REFERENCES

[1] Unexploded Ordnance Clearance, Report to Congress, Office of the Under Secretary of Defense (acquisition and Technology), 25 March (1997).

[2] P.G. Datskos, S. Rajic, I. Datskou, and C.E. Egert "Infrared Micro-calorimetric Spectroscopy Using Uncooled Thermal Detectors." *Imaging Spectroscopy III* [Proc. SPIE **3118**, 280 (1997)].

[3] A. Rogalski, "New Trends in Infrared Detector Technology," Infrared Physics and Technology, **35**, 1 (1994).

[4] J. L. Miller, *Principles of Infrared Technology* (Van Nostram Reinhold, New York, 1994).

[5] E. L. Dereniak and G. D. Boreman, *Infrared Detectors and Systems* (Wiley and Sons, New York, 1996).

[6] R. A. Wood and N. A. Foss, "Micromechanical Bolometer Arrays Achieve Low-Cost Imaging," Laser Focus World; June, 101 (1993).

[7] R. A. Wood, "Uncooled Thermal Imaging with Monolithic Silicon Focal Planes," Infrared Technology XXI, SPIE, **2020,** 322 (1993).

[8] C. Hanson, "Uncooled Thermal Imaging at Texas Instruments," Infrared Technology XXI, SPIE, **2020,** 330 (1993).

[9] E. A. Wachter, T. Thundat, P. G. Datskos, P. I. Oden, R. J. Warmack, and S. L. Sharp, "Remote Optical Detection Using Microcantilevers," *Rev. Sci. Instrum.* **67** (1996).

[10] P. G. Datskos, P. I. Oden, E. A. Wachter, T. Thundat, and R. J. Warmack, "Remote Infrared Detection Using Piezoresistive Microcantilevers," *Appl. Phys. Lett.* **69**, 2986 (1996).

[11] P. I. Oden, E. A. Wachter, P. G. Datskos, T. Thundat, and R. J. Warmack, "Remote Optical and Infrared Detection Using Microcantilevers," *Infrared Technology and Applications XXII, SPIE* **2744**, 345 (1996).

[12] Amantea, C.M. Knoedler, F.P. Pantuso, V.K. Patel, D.J. Sauer, and J.R Tower, "An Uncooled IR Imager with 5 mK NEDT" SPIE, Orlando, FL.(1997).

[13] J. R. Barnes, R. J. Stephenson, M. E. Welland, C. Gerber, and J. K. Gimzewski, "Photothermal Spectroscopy with Femtojoule Sensitivity Using a Micromechanical Device," Nature, **372,** 79 (1994).

[14] J. K. Gimzewski, C. Gerber, E. Meyer, and R. R. Schlittler, "Observation of a Chemical Reaction Using a Micromechanical Sensor," Chemical Physics Letters, **217,** 589 (1994).

[15] J. K. Gimzewski, C. Gerber, E. Meyer, and R. R. Schlittler, in *Micromechanical Heat Sensor: Observation of a Chemical Reaction, Photon and Electrical Heat Pulses*, 1995 (Kluwer Academic Press), p. 123.

[16] J. R. Barnes, R. J. Stephenson, C. N. Woodburn, S. J. O'Shea, M. E. Welland, T. Rayment, J. K. Gimzewski, and C. Gerber, "Femtojoule Calorimeter Using Micromechanical Sensors," Review of Scientific Instruments, **65**, 3793 (1994).

[17] W. C. Young, *Roark's Formulas for Stress and Strain*, sixth ed. (McGraw Hill, New York, 1989).

[18] L.J. Kepley, J. and R. M. Crooks, "Selective Surface Acoustic Wave-Based Organophosphonate Chemical Sensor Employing a Self-Assembled Composite Monolayer: A paradigm for Sensor Design," *Anal. Chem.* **64** 3191 (1992).

[19] *Sadtler Standard Spectra*: Sadtler Research Laboratories, Inc. (1966).

[20] T. Thundat, P. I. Oden, P. G. Datskos, G. Y. Chen, and R. J. Warmack, "Microcantilever Sensors," presented at the 16th Warner Brandt Workshop on Charged Particle Penetration Phenomena, Oak Ridge Tennessee, 1996.

[21] T. Thundat, G. Y. Chen, R. J. Warmack, D. P. Allison, and E. A. Wachter, "Vapor Detection Using Resonating Microcantilevers," *Anal. Chem.* **67**, 519 (1995).

[22] T. Thundat, E. A. Wachter, S. L. Sharp, and R. J. Warmack, "Detection of Mercury Using Resonating Microcantilevers," *Appl. Phys. Lett.* **66** (1995).

[23] J. Janata, M. Josowicz, and D. M. Devaney, "Chemical Sensors," *Anal. Chem.* **66**, R207 (1994).

[24] J. Janata, *Principles of Chemical Sensors*. New York: Plenum, 1989.

[25] J. W. Grate, S. J. Martin, and R. M. White, "Acoustic Wave Microsensors Part I," *Anal. Chem.* **65**, 940A (1993).

[26] K. D. Schierbaum, A. Gerlach, M. Huag, and W. W. Gopel, "Selective Detection of Organic Molecules with Polymers and Supramolecular Compounds: Application of Capacitance, Quartz Microbalance and Calorimetric Transducers," *Sensors and Actuators A* **31**, 130 (1992).

[27] S. Rajic, B. M. Evans III, P. G. Datskos, P. I. Oden, T. G. Thundat, and C. M. Egert, "Piezoresistive Microcantilever Optimization for Uncooled Infrared Detection Technology," *Infrared Spaceborne Remote Sensing IV,SPIE* **2817**, 179 (1996).