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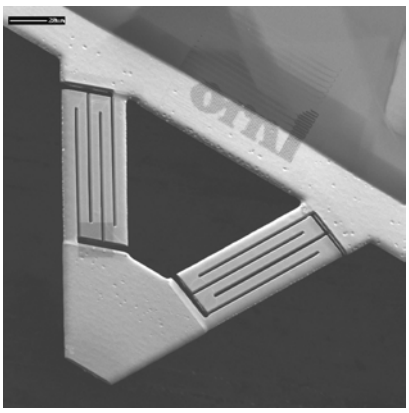
MEMS Based Calorimetric Spectroscopy (CalSpec)

{Chemical And Biological Detection}

CalSpec Concept And Background

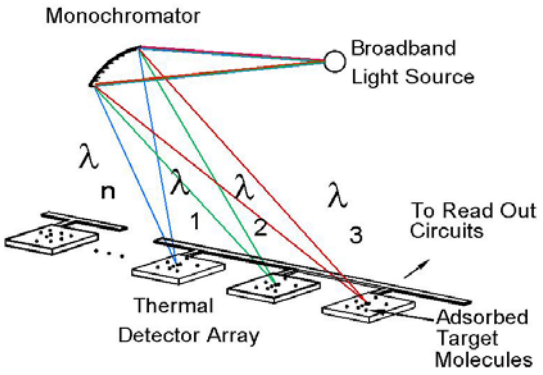
We have developed a novel micro_calorimetric spectroscopy technique that can be used for chemical and biological detection applications. This is a micro-electro-mechanical-systems (MEMS) based technique that provides detailed spectral information about the target species. However, since it is MEMS based, the device volume can be extremely small. Single chip versions have been envisioned and the components for such a detector are presently being developed. In the CalSpec approach target molecules interact with sub-femtojoule sensitive micro-mechanical thermal detectors. Thus a temperature spectrum is measured along the detector array, as a function of wavelength, for the target species. Since we are using extremely sensitive thermal detectors, a substantially smaller target sample is required compared to traditional absorption spectroscopy. Both chemical and biological species have routinely been detected. An example of a typical bi-material MEMS thermal detector that can be used for CalSpec is shown in the figure on the right. This technology has received both a US patent and an R&D 100 award.



Detailed CalSpec Detection Approach

- **Target molecules adsorb onto thermal detector surfaces.**
- **Detector surfaces illuminated with discrete wavelengths**
- **Photons are absorbed and excite target molecules on selected detector elements**
- **Preferential detector element heating produces unique photothermal spectrum.**

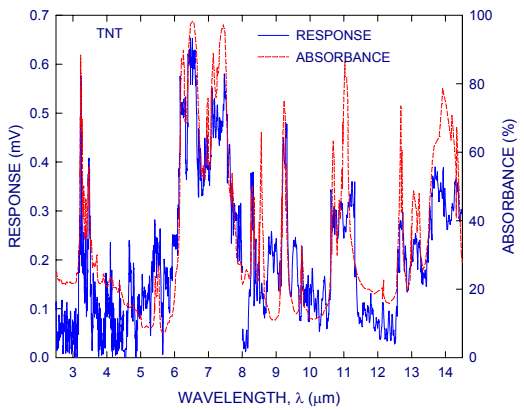
The detection of the presence and identity of target species using CalSpec can be broken down into simple steps. In the first step the sample is allowed to interact with the surface of a femtojoule sensitive thermal detector that can be coated with an appropriate chemical layer selective to the family 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 selectivity in our approach is primarily a consequence of the photothermal "signature", and therefore only moderately selective chemical layers may be needed such as those customarily used to coat GC columns. In the next step, a photothermal spectrum is obtained for the molecules adsorbed on the detector surface, by scanning a broadband wavelength region across the detector array such that a narrow part of the spectrum illuminates each individual thermal detector. The

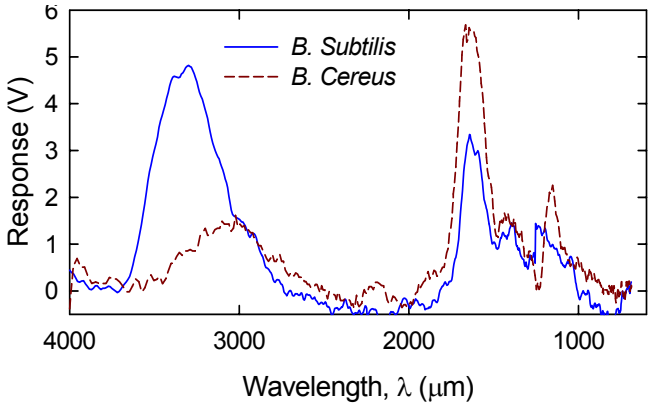


temperature changes of those particular detector elements is proportional to the number of photons absorbed which, in turn, is proportional to the number of molecules adsorbed on the detector surface. Because different detector elements will be exposed to different wavelengths, a sensitive photothermal signature response can be obtained. Photothermal spectra are very similar to conventional infrared spectra and can be used to uniquely identify the adsorbed molecules. The figure above illustrates this unique detection technique.

Representative Data

Shown below are two photo-thermal spectra taken with the CalSpec technique. Both TNT chemical and anthrax simulants biological data is presented. The typical wavelength range that we have spanned is from 2.5 to 14.5 um. The TNT data represents less than one mono-layer of chemical coverage on the thermal detector surface. The biological data shows that two similar species can be differentiated with this technique. In fact this data was reproduced in two different sampling approaches. Both evaporation and direct application of the target bacteria onto the detector surface produced similar data. Only several hundred bacteria were applied to the MEMS thermal detector to produce the data shown





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Chemical Sensors Based on Nanomechanical Resonators

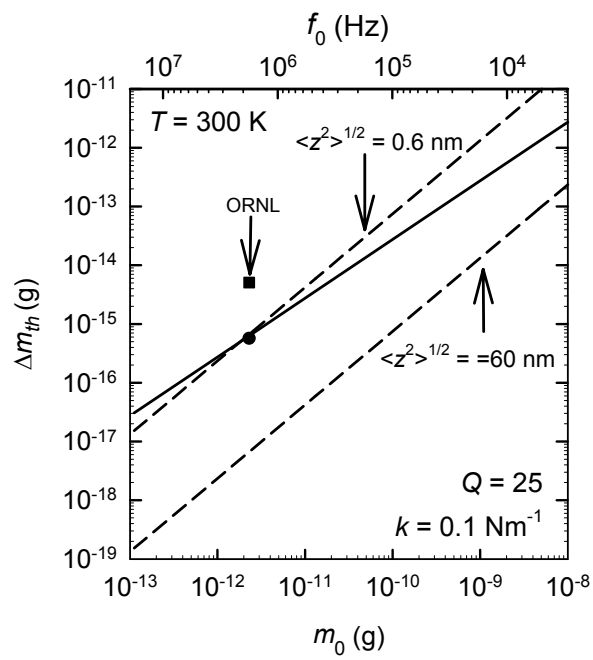
Low-cost, high performance nanosensor arrays

During the past decade, nanoscience and nanotechnology have been recognized as important research topics for the 21st century. Anticipated applications of nanotechnology are vast and they include a possibility to address many challenges of chemical, environmental, and biological analysis. One of the approaches to implement this possibility is associated with the use of nanomechanical resonators which may function as ultra sensitive transducers. Micromechanical and electromechanical resonators, such as flexural plates (FPs), quartz crystal microbalances (QCMs) and surface acoustic wave (SAW) devices have already found numerous applications as mass sensitive transducers in chemical and biological sensors. It is important to note that sensor designs based on QCM and SAW devices have been thoroughly refined over several decades and the demonstrated figures of merit closely approach their theoretical limitations. In the case of cantilever resonators, however, dramatic improvements in analytical figures of merit can be achieved merely by scaling their sizes down to the nanoscale.

Development of low-cost, high performnce chemical nanomechanical sensors

Our overall goal is to develop a low-cost, high performnce chemical nanomechanical sensor. Cantilever respond to stimuli by changes in their radius of curvature (bending), shifts in resonance frequency, changes in the amplitude and qualuty factor Q of their vibration. We have developed optical readouts that can sense positional changes of the cantilever. Resonating nanomechanical devices with very small mass and size have the potential for mass sensing at the level of individual molecules. We have demonstrated operation of nanomechanical resonators as mass sensors under ambient pressure and temperature and achieved femtogram level mass sensitivity. Our nanomechanical resonators were gold coated silicon cantilevers with resonance frequencies in the range of 1-10MHz, characteristic thicknesses of 50-100 nm and force constants of about 0.1 N/m. We used cantilevers as nanomechanical resonators with resonance frequency of 2.2 MHz which was excited photothermally and measured a mass change of 5.5 fg upon chemisorption of 11-mercaptoundecanoic acid.

In Figure 1 we show a comparison of mass detection thresholds for a resonating rectangular Si cantilever with $k = 0.1$ N/m defined by a fixed frequency instability of 10^{-4} (solid line) and by the cantilever intrinsic thermal noise (dashed lines). Thermally limited mass detection thresholds



Comparison of mass detection thresholds for a resonating rectangular Si cantilever with $k = 0.1$ N/m defined by a fixed frequency instability of 10^{-4} (solid line) and by the cantilever intrinsic thermal noise (dashed lines).

are calculated for the two cases: (i) z_{max} ($=\langle z^2\rangle^{1/2}$) = 0.6 nm, Q = 25, *i.e.* weakly excited resonator (upper dashed line) and (ii) strongly excited resonator with z_{max} = 60 nm, Q =25 (lower dashed curve). The experimentally measured mass change (solid square) is approximately 10 times larger than the mass detection threshold (solid circle) calculated for the cantilever with f_0 = 2.25 MHz used in our experiments.

Features

- **Nanomechanical detection – Can approach single molecule detection**
- **Can operate in vacuum, ambient air or liquid environment**

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Detection of Chemical, Biological and Radiological Stimuli Using Nanosensor Arrays

Technical Concept

Nanomechanical systems were found to exhibit very high sensitivity to physical, chemical and biological stimuli. Both the resonance frequency and bending of nanocantilevers change when exposed such stimuli. This is similar to what has been demonstrated for microcantilevers but with orders of magnitude better sensitivity. In fact, cantilevers respond to stimuli by changes in their radius of curvature (bending), shifts in resonance frequency, changes in the amplitude and quality factor *Q* of their vibration.

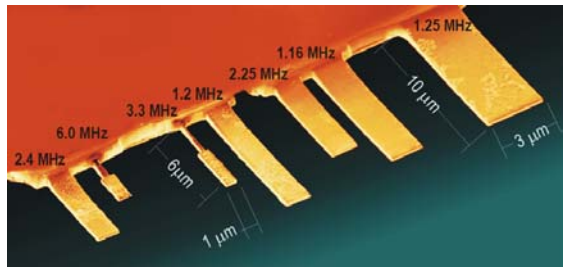

Figure 1. Nanosensor arrays made from nanocantilevers with different resonance frequencies. The bending, resonance frequency and *Q*-factor change when exposed to target stimuli.

We have fabricated arrays of nanocantilevers (such as the ones shown in Figure 1) with an optical readout that can be used sense small positional changes providing high sensitivity to target stimuli. These devices are made from Si and they are 2 – 9 µm in length, 1 to 4 µm in width and 50 to 100 nm in thickness. Resonating nanomechanical devices with very small mass and size have the potential for mass sensing at the level of individual molecules. We have demonstrated operation of nanomechanical resonators as mass sensors under ambient pressure and temperature and achieved femtogram (10^{-15} g) level mass sensitivity. To date we have demonstrated that mass changes of 5.5×10^{-15} g can be detected.

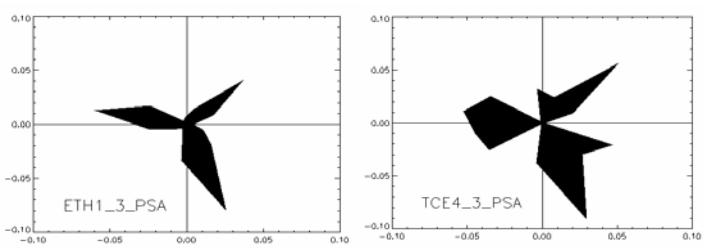

Figure 2. Patterns resulting from the differential response of an array of four differentially coated cantilevers to ethyl alcohol and trichloroethane (TCE). The resulting pattern is

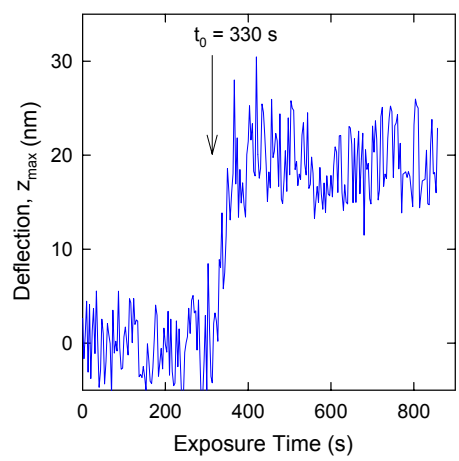

Figure 3. Response of a nano-mechanical device to electric charge produced by alpha particles.

Chemical and biological specificity is achieved using nanosensor arrays. We found that the each element in the array can be made to respond differently to chemical or biological stimuli by moderately specific coatings. This pattern can be represented visually by properly plotting the response of each element in the nanosensor array (see Figure 2).

We found that these nanomechanical sensors are sensitive to the presence of electric charge. This sensitivity can be used to passively detect ionizing radiation. Because of their small dimension (thickness of 50 to 100 nm) they are mostly "transparent" to ionizing radiation. But as alphas, betas or gammas interact with matter they create electron-ion (or electron hole) pairs in the vicinity of the nanosensor array thereby casing a response due to the generated charge. In Figure 3 we show the response of a nanomechanical device to the presence of electric charge produced by the interaction with an alpha particle.

Current Prototype Abilities

- Handheld lab prototype chemical and biological sensors
- Low weight and power consumption – candidate for Unmanned Air Vehicles and other remote platforms
- Low-cost, high performance nanosensor arrays
- Can operate in ambient, liquid or vacuum environment
- Multiparameter stimuli response (chemical, biological, radiological)
- High sensitivity using nanomechanical detection - Can approach detection of single molecule
- High selectivity utilizing differentiated response – each chem./bio stimuli produces unique patterns in the array

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