

# Explosive Vapor Detection Using Microcantilever Sensors

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## I. INTRODUCTION

In recent years, microcantilever sensors have attracted much attention due to their potential as a platform for the development of many novel physical, chemical, and biological sensors [1-11]. Microcantilevers are the simplest micro-electro-mechanical systems (MEMS) device that can be micromachined and mass-produced. Microcantilever sensors offer improved dynamic response, greatly reduced size, high precision, and increased reliability. In addition, microcantilever sensors also offer many advantages including fabrication of multi-element sensor arrays and integration of micromechanical components with on-chip electronic circuitry.

The basic microcantilever operation is quite simple. When molecular adsorption is confined to one surface of a microcantilever, it undergoes bending due to adsorption-induced stress. It is known from the literature that molecular adsorption changes surface forces (surface stress) [10,12,13]. If the two surfaces of the cantilevers are different (bi-material), molecular adsorption will result in a differential stress between the top and bottom surfaces of the cantilever. Molecular adsorption-induced surface stress on a microcantilever can be observed as changes in cantilever deflections. Using this concept, we have demonstrated the feasibility of chemical detection of a number of vapor phase analytes with high sensitivity; see, for example [1,2,6].

The radius of curvature of adsorption-induced surface stress of the microcantilever can be found using Stoney's formula [12,13]. The radius of curvature of the bending of the cantilever can be calculated using the physical parameters of the cantilever and can be written as:

$$z = \left( \frac{3(1-\nu)L^2}{t^2 E} \right) \delta s \quad (1)$$

where  $z$  is the cantilever's radius of curvature,  $E$  is Young's modulus for the substrate,  $t$  is the thickness of the cantilever,  $L$  is the length,  $\nu$  is the Poisson's ratio, and  $\delta s$  is the differential stress on the cantilever. The bending of a cantilever can be measured with sub-angstrom resolution using the techniques

perfected for the atomic force microscope (AFM), such as optical, piezoresistive, capacitive, and piezoelectric detection methods. In the present experiments we use an optical method described below.

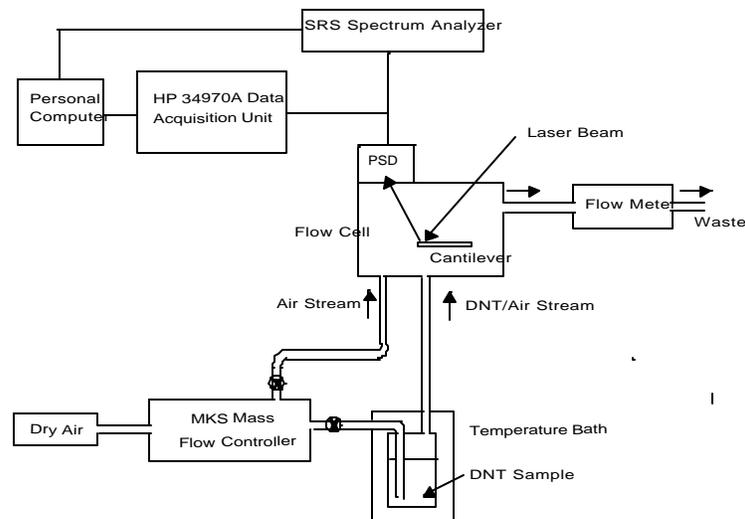
In addition to the standard bending measurements, we have also conducted experiments where a current is passed through a piezoresistive cantilever, causing a coating of explosive material deposited on its surface to evaporate. Absorption of heat from the cantilever during evaporation causes it to undergo enhanced bending, which can be quantified. The shift in resonance frequency of the cantilever is simultaneously measured which can be used to estimate the amount of explosive that was initially on the cantilever. Furthermore, the temperature at which evaporation occurs may be used to differentiate between different explosives and interferences.

## II. EXPERIMENTS

### A. Bending Measurements

Commercially available “V”-shaped silicon cantilevers of 180  $\mu\text{m}$  length, 38  $\mu\text{m}$  width, and 1  $\mu\text{m}$  thickness from Park Scientific Instruments, Inc. were used in these experiments; the force constant was 0.40 N/m (all these are manufacturer’s specifications). One side of these cantilevers was coated with gold by the manufacturer (thickness of the coating not known), and this side was used to reflect the laser beam for deflection measurements; see below. Some cantilevers were coated on the “silicon” side with SFXA, PIB, FPOL, and PECH polymers at the Naval Research Laboratory (NRL) in order to enhance the adsorption of explosive vapors.

Two different apparatus were used to deliver explosive vapors to the cantilever. A vapor generator for DNT was constructed (see Fig. 1) based on the design of Dionne et al [14]; a detailed description of the apparatus and the results will be published later [15]. Briefly, dry air was passed over a sample of DNT in a glass impinger in a temperature-controlled bath at 20<sup>o</sup>C. A gas flow rate of 120 sccm was controlled by a MKS mass flow controller. Since DNT sticks to most surfaces, the vapor generator was constructed and run for three weeks to condition the Silcosteel tubing (i.e., glass lined stainless steel tubing) from the generator to the microcantilever cell. The concentration of DNT was measured by trapping a known volume of gas in a Tenax trap (Tenax TA 60-80 mesh) and thermally desorbing it into a gas chromatograph/mass spectrometer (GC-MS). The concentration of DNT was determined from a calibration curve (from 10 –100 ng,  $R^2 = 0.993$ ) constructed by thermally desorbing known quantities of DNT into the GC-MS and the volume of the gas sample. During the three week conditioning period, the concentration of DNT measured at the end of the tubing increased from 72 ppb (5-days) to 131 ppb (3 weeks). The final concentration of DNT at the inlet to the cell was  $107 \pm 14$  ppb. The DNT concentration at the exit of the cantilever cell was  $\approx 1$  ppb to  $\approx 0.7$  ppb. Therefore, for estimation purposes we will take the DNT concentration in the cantilever cell to be 50 ppb.



**Figure 1. A schematic diagram of the home-made 2,4 DNT generator.**

In these measurements, a mass flow controller (MKS) was used to provide two separate streams of air at the flow rate of 120 sccm on demand. One air stream was sent through the DNT generator which provided the DNT/air mixture for the measurements, and the other stream of air was used as a control. The Silcosteel tubing outlet from DNT vapor generator and the stainless-steel tubing carrying the air flow were connected to the measurement cell. The flow rate at the exit of the cell was periodically monitored to verify that there were no leaks. The cantilever was subjected to 120 sccm flow of either the DNT/air mixture or the air stream at all times, i.e., when the DNT/air mixture was turned off, the air flow was turned on simultaneously. This was done in order to avoid the cantilever response to the change of flow. No significant deflection was observed in the changing of the gas flow.

Explosive vapor detection can be hindered by the tendency of these vapors to be adsorbed on cold surfaces [16]. With the DNT vapor generator described above, the delivery lines needed to “conditioned” by exposure to DNT vapor for several weeks before reasonably constant vapor pressure could be detected at the exit. The cantilever cell cannot be “conditioned” letting a thin coating to deposit on its walls, since this will lead to the exposure of the cantilever to DNT vapor at all times. (Also, this will interfere with the optical measurements). Due to this reason, the DNT concentration of 107 ppb mentioned above gives only an upper bound to the concentration actually seen by the cantilever. Furthermore, the above mentioned apparatus can be used only for measurements on DNT.

In order to deliver a variety of explosive vapors and to better control the amount of vapor delivered to the cantilever cell, we recently assembled an apparatus where a GC is used to deliver the explosive vapors to the cantilever cell [17]. A Hewlett-Packard 5890 gas chromatograph equipped with a HT-5 column (5% phenyl polycarborane siloxane 0.22 mm i.d., 12 m in length, 0.1  $\mu\text{m}$  film thickness, Scientific Gas Engineering, Inc., Austin, TX) was used. The methodology described here was derived

from previously reported desorption explosives analytical methods [18-21]. The injected sample was split into two after going through the column: one half was fed into a Flame Ionization Detector (FID), and the other half was fed to the cell containing the microcantilever as described below. Therefore, the response of the FID and the microcantilever could be monitored simultaneously. After the measurements, a calibration experiment was conducted where samples were collected at the outlet of the chromatography column directed into the cantilever cell using Tenax TA sorbent traps. The samples collected on Tenax TA were analyzed using a second HP 5989B mass spectrometer operating in the negative ion chemical ionization (NICI) mode [18-21]. Additional experimental details will be reported elsewhere [17].

In both experiments, the microcantilever bending response was measured using a modified atomic force microscope head. The microcantilever was held in place in a vacuum-tight quartz cell using a spring-loaded wire. We utilized an optical beam deflection technique to measure the cantilever bending: In this investigation, the light from a laser diode was focused at the apex of the cantilever (the gold-coated side). The reflected laser beam was allowed to fall on a position sensitive detector (PSD). The output from the PSD was analyzed using a home-made electronics box and fed to a Hewlett Packard model 34970A data logger for cantilever bending measurements. The flow rate of gas around the cantilever was kept constant to minimize the bending due to gas flow. Since the bimetallic cantilevers can also respond to temperature, all the experiments were done at constant temperature. In the case of the home-made DNT generator, the whole apparatus was kept at room temperature. In the case of the GC experiment, the base plate of the AFM head had to be kept at  $\approx 97^{\circ}$  C in order to maintain the elevated temperature of the GC delivery line; see Section III. This led to heating the AFM head to  $\approx 50^{\circ}$  C.

## **B. Evaporation Measurements**

The apparatus [22] used for these measurements is shown in Fig. 2. A homemade “oven” was used in conjunction with a shutter (not shown) to generate a vapor of the explosive material and to deposit a small amount on the piezoresistive cantilever. By controlling the oven temperature and the exposure time, the amount deposited can be varied. A voltage pulse of (5-10 V; 25 mA) was sent through the cantilever thereby heating it. The bending of the cantilever due to this voltage pulse was monitored using an optical detection scheme described in the previous section; the photodetector signal was sent to a Nicolet 450 digitizer (to monitor cantilever bending) and a SRS 760 Spectrum Analyzer (to monitor the resonance frequency of the cantilever). The same voltage pulse was sent through the cantilever before and after depositing the explosive vapor, so that the changes due to the explosive vapor adsorbed on the cantilever surface can be recorded. Piezoresistive cantilevers were purchased from Park Scientific Instruments and were machined to a thickness of 2  $\mu$ m for the data shown in this paper.

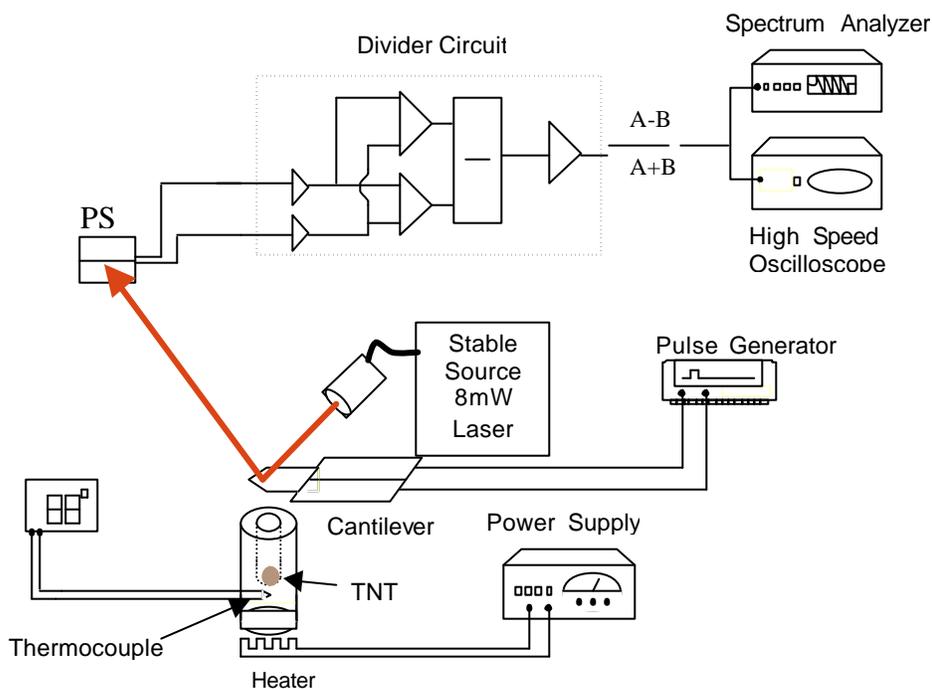


Figure 2. A schematic diagram of the apparatus used for the evaporation measurements.

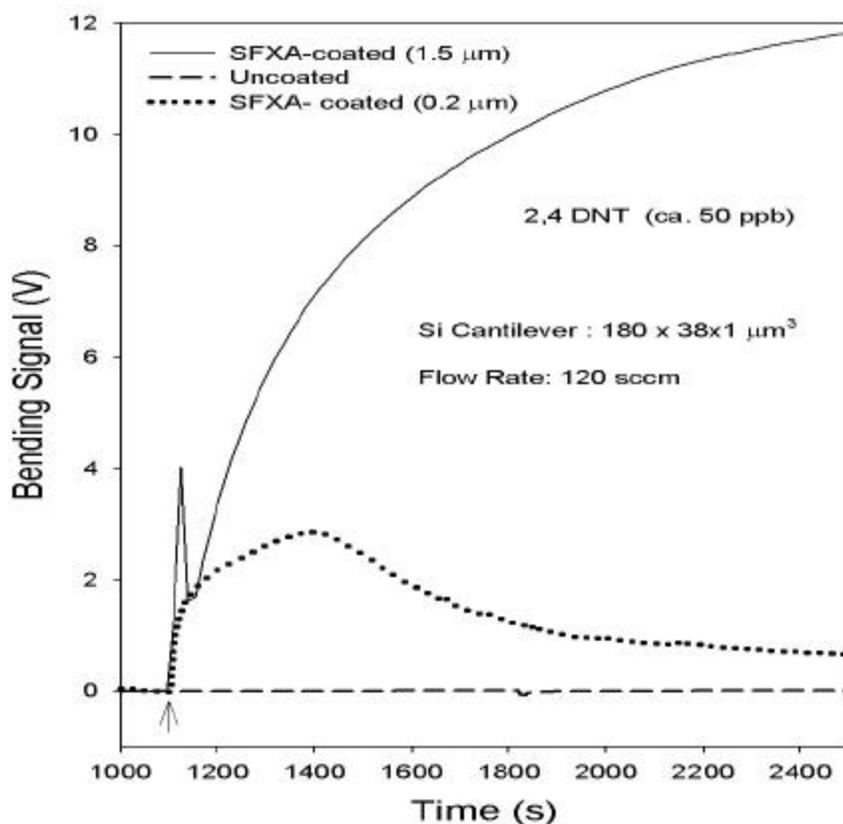
### III. RESULTS AND DISCUSSION

#### A. Bending Measurements

Most of the experiments up to now have been conducted on the detection of DNT using the apparatus shown in Fig. 1. Of the polymer coatings that we have tested so far, the response decreases from SFXA, PIB, PECH, to FPOL for DNT. Here we will discuss the results obtained with the SFXA-coated cantilevers. It appears that the response of the coated cantilever is drastically different depending on whether the coating thickness is above or below a value located between  $0.2 \mu\text{m}$  and  $0.5 \mu\text{m}$ .

The response of an uncoated Si cantilever exposed to DNT (ca. 50 ppb) compared to those from SFXA-polymer-coated cantilevers with estimated film thicknesses of  $0.2 \mu\text{m}$  and  $1.5 \mu\text{m}$  is shown in Fig. 3; The cantilevers were initially exposed to an air stream, and the air stream was turned off and the DNT stream was simultaneously turned on at the time indicated by the arrow. The signal from the cantilever with the  $0.2 \mu\text{m}$ -coating increased to  $\approx 3 \text{ V}$ , and then started decreasing even though it was still exposed

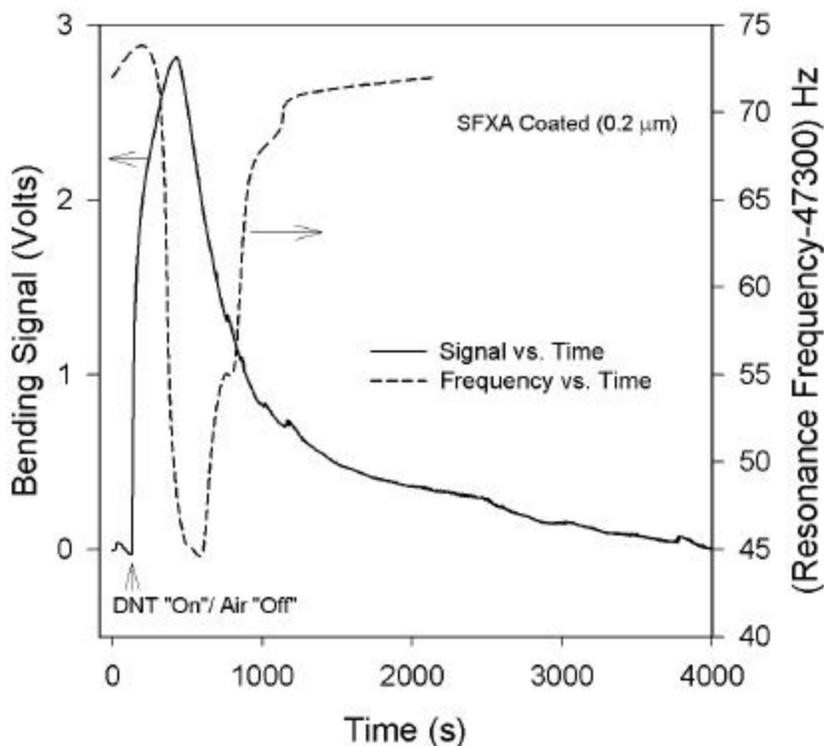
to the DNT vapor stream; i.e., the cantilever started bending due to the adsorption of DNT vapor, but after about 300s, the bending started to relax apparently due to desorption. We conducted an additional experiment to monitor the adsorption/desorption of vapors from the cantilever by monitoring its resonance frequency simultaneous with the bending measurement. The results are shown in Fig. 4: it is clear that the resonance frequency of the cantilever shifts to lower values as the mass of the cantilever increased due to adsorption; when the bending relaxed, the resonance frequency increased back to the original value confirming the desorption process. At present it is not possible to explain why the DNT is desorbed while being exposed to the DNT vapor for the cantilevers with the 0.2  $\mu\text{m}$ -coating; all cantilevers from that particular batch responded in the same manner.



**Figure 3.** Comparison of the bending response of an uncoated cantilever to that of cantilevers coated with SFXA with film thicknesses of 0.2 and 1.5 micrometers.

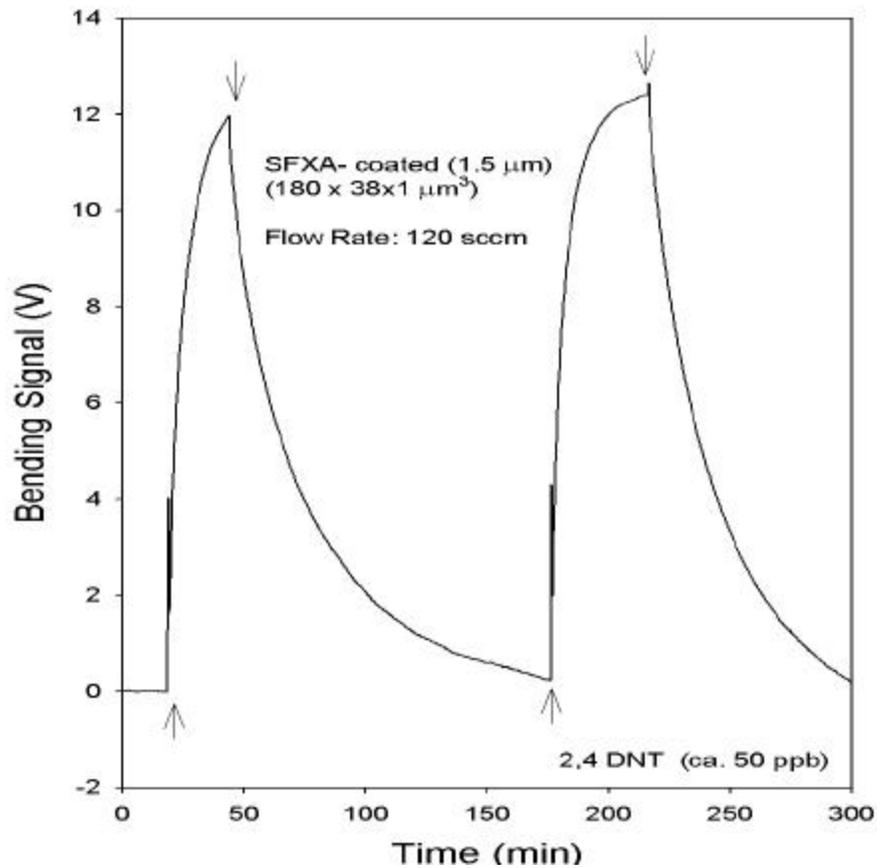
The cantilever coated with the 1.5  $\mu\text{m}$  film increased gradually until reaching a level of  $\approx 12$  V (maximum signal from the photodetector); when the DNT stream was turned off (and the air stream was simultaneously turned on), the cantilever gradually relaxed. Figure 5 shows the response of a cantilever with the 1.5  $\mu\text{m}$ -coating subjected to this “ON/OFF” cycle; In Fig. 4, turning “ON” of the DNT stream is indicated by the arrows pointing up, and turning “OFF” of the DNT stream is indicated by the arrows pointing down. The signals from the cantilevers coated with 0.5  $\mu\text{m}$  and 1.0  $\mu\text{m}$  were similar to that from

the cantilever with the 1.5  $\mu\text{m}$ . The signal from the uncoated cantilever was in the mV range, and thus was insignificant.



**Figure 4.** The response of a microcantilever coated with a 0.2 micrometer film of SFXA. The bending signal and the resonance frequency of the cantilever were simultaneously measured. The DNT flow was initiated around time =0 and was left on.

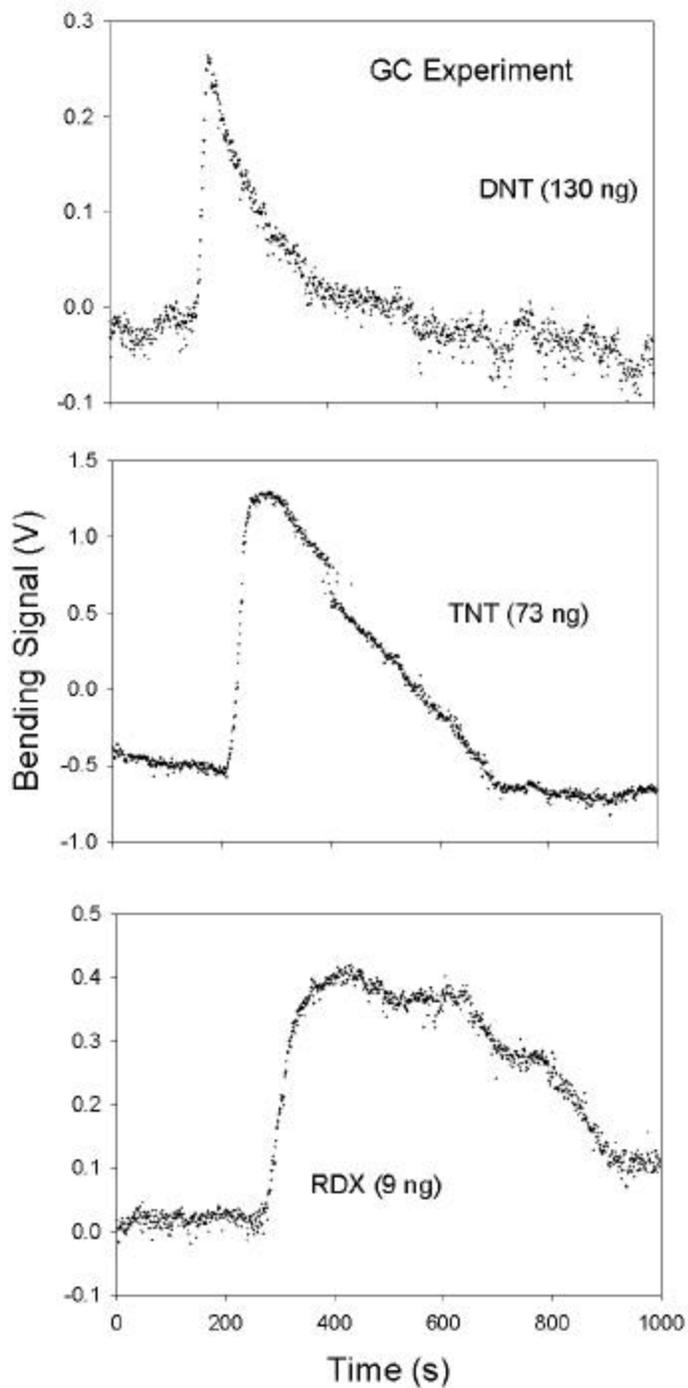
A signal of 1 V corresponds to a cantilever bending of  $\approx 100$  nm. If we use the DNT concentration of 100 ppb at the entrance to the cantilever cell, a sensitivity of 24 nm/ppb DNT exposure is calculated for the cantilever with the 1.5  $\mu\text{m}$ -thick coating. Since the noise level in the signal is less than 1 nm, the polymer-coated microcantilever can detect  $< 0.1$  ppb of DNT. Through optimization of the cell design, polymer coating and cantilever design, we should be able to improve the detection limit.



**Figure 5.** The bending response of a SFXA-coated cantilever to two cycles of turning ON/OFF of the DNT stream.

Preliminary data obtained with the second apparatus, where a GC is used to deliver vapors of DNT, TNT, and RDX to the cantilever cell, are shown in Figs. 6. These measurements were obtained using a SFXA-coated cantilever ( $180 \times 38 \times 1 \mu\text{m}^3$ ) with a  $1.5 \mu\text{m}$  film thickness. In these experiments, the temperature of the delivery line that carried the explosive vapors to the cantilever cell was kept at  $230^\circ\text{C}$ . This delivery line was passed through a small hole in the base plate of the AFM head containing the cantilever; in order to avoid condensation of the vapor on this section of the delivery line, the base plate had to kept at an elevated temperature. On the other hand, keeping the AFM head at a high temperature would be detrimental to the laser in the AFM head. As a compromise, we kept the base plate at a temperature of  $\approx 97^\circ\text{C}$ . The amount delivered to the cantilever cell was calibrated by using Tenax TA sorbent traps as described earlier [B17]. These calibration measurements showed that about 50% of the

vapor was delivered to the cell in the case of DNT and TNT, and only about 10% was delivered in the case of RDX.

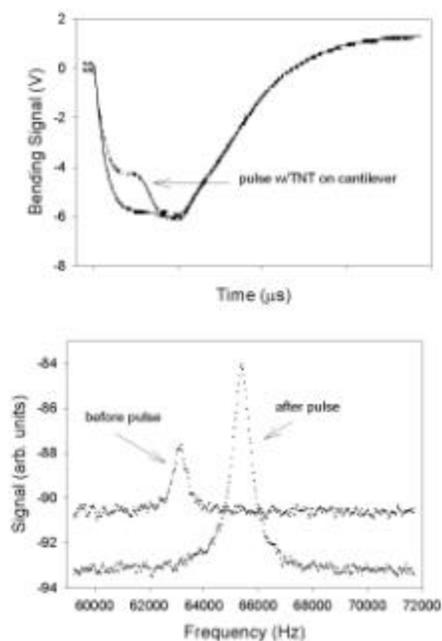


**Figure 6. Bending signals from a SFXA-coated cantilever exposed to DNT, TNT, and RDX vapors delivered using a gas chromatograph.**

We have not yet measured the detection sensitivities for these compounds using this GC apparatus. However, from Fig. 6, it is reasonable to conclude that detection limits for TNT and RDX are better than that for DNT. Since the previous experiment has shown that DNT can be detected with at least ppb range, it should be possible to detect the other two explosive vapors also at parts per billion levels. Further studies are underway to optimize the cantilever size, optimize polymer coatings for different explosive vapors and tagants, and also to measure the response of polymer-coated cantilevers to various interferences.

## B. Evaporation Measurements

Identical voltage pulses were applied to the cantilever before and after it was exposed to the explosive vapor. Figure 7 (a) shows the bending signals of the cantilever resulting from such voltage pulses. The “dip” at the leading edge of the waveform is likely to be due to the cooling of the cantilever by evaporating TNT. If so, the “area under curve” could be expected to be proportional to the mass of TNT deposited on the cantilever. The mass of TNT evaporated by the voltage pulse can be estimated from the shift in resonance frequency of the cantilever, shown in Fig. 7 (b).



**Figure 7. (a) Change in cantilever bending due to the adsorbed TNT. (b) Resonance frequency curves before and after the voltage pulse that evaporated the adsorbed TNT.**

A series of measurements were conducted on the cantilever exposed to TNT with different oven temperatures and exposure times. Resulting area shifts are plotted versus the estimated desorbed mass in Fig. 8. It is clear that sub-ng quantities of TNT can be detected.

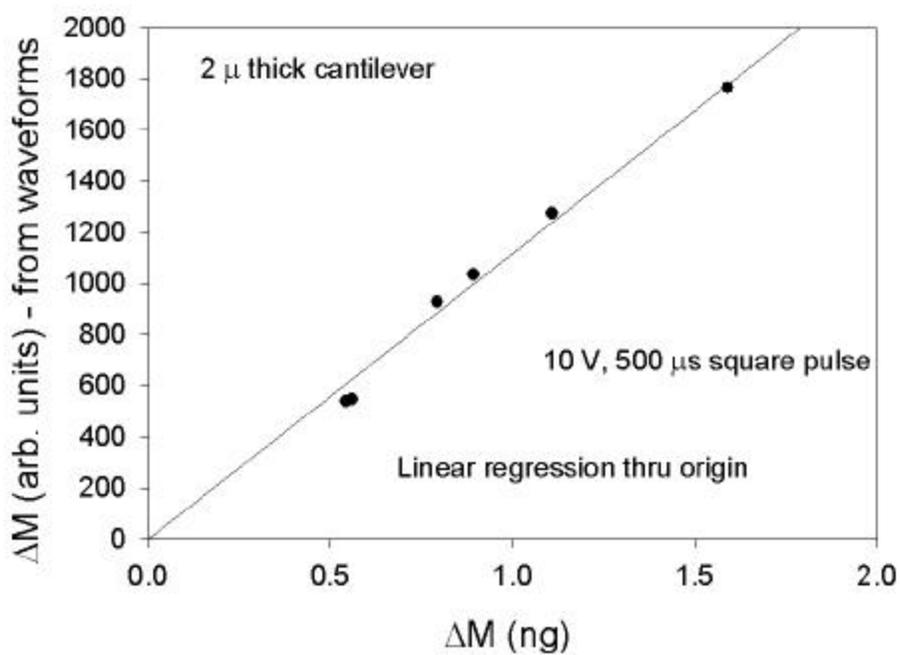


Figure 8. Dependence of the area under the curve as a function of the mass of TNT deposited on the cantilever.

In these measurements, it was observed that as the oven is heated from the room temperature (with exposure time set at a few minutes), the shift in the bending curve becomes noticeable at a specific temperature for a given explosive material. For example, this “transition” occurs around 80<sup>0</sup>C for TNT, around 70<sup>0</sup>C for DNT, and 130-140<sup>0</sup>C for PETN. The melting points for TNT, DNT, and PETN are 80.8<sup>0</sup>C, 70.5<sup>0</sup>C, and 140.3<sup>0</sup>C [23]. Therefore, it is clear that significant vapor generation from the oven occurs when the oven temperature reaches the melting point of the particular explosive. This observation will be helpful in differentiating explosives from interferences. Further experiments are underway on other explosives and possible interferences.

#### IV. CONCLUSIONS

We have conducted experiments to measure the response of polymer-coated cantilevers to the vapors of DNT, TNT, and RDX. Two experimental apparatus were used to deliver the explosive vapors to the flow cell containing the microcantilever: a home-made DNT vapor generator was used in one set experiments; in the other, a gas chromatograph was used to deliver the vapors of DNT, TNT, and RDX. Preliminary experiments conducted with the second apparatus showed that nanogram quantities of DNT, TNT, and RDX vapors can be easily detected by delivering those vapors using a gas chromatograph. These experiments show that SFXA-coated cantilevers have detection sensitivities in excess of parts per billion. The experiments with uncoated piezoresistive cantilevers have shown that it is possible to detect sub-nanogram quantities of TNT and DNT.

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