

# Detection of explosives based on surface enhanced Raman spectroscopy



L. Gundrum, W. Hüttner, H. Wackerbarth, Laser-Laboratorium Göttingen (June 2010)

## Introduction

The work group “photonic sensor technology” at the Laser-Laboratorium-Göttingen e.V. presents a device based on re-sublimation on a cooled nanostructured surface for the detection of explosives such as TATP and TNT. Because of the wide range of explosives and the many differences in their physical properties, several detection devices detect only certain types of explosives, like explosives made of organic nitro and nitrate compounds, but are not able to find explosives made of inorganic nitrates or non-nitrogenous compounds.

Raman spectroscopy is a vibrational technique which provides specific spectral information about molecules enabling the identification of analytes by their “fingerprint” spectrum. Neat explosives have been extensively studied by Raman spectroscopy. However, the use is so far limited to bulk detection; the detection limits are too high to be practically useful in safety devices. The sensitivity of the inherent weak Raman process can be increased by the SERS (Surface Enhanced Raman Scattering) effect. SERS is a sensitive spectroscopic tool with detection limits down to picogram and femtogram level. This is particularly attractive because it combines high sensitivity with high information content for establishing molecular identity. A further advantage of SERS is the quenching of fluorescence, which is a known obstacle in Raman spectroscopy of explosives.

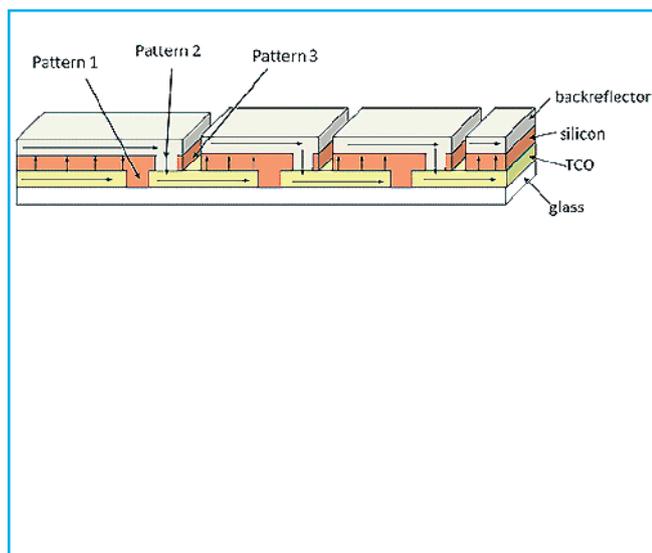


Fig. 1: Design of the constructed vacuum chamber

## Application Note

### Experimental Setup

For the Raman measurements, a standard laser system was used; the excitation wavelength of 785 nm was provided by a GaAlAs diode-laser. The excitation and scattered light were guided by a multimode optical fiber equipped with probe head onto the sample. The scattered light was coupled by a confocal aperture in the optical fiber and transmitted to a spectrograph (Shamrock SR-303i, Andor Technology). The diffracted light was recorded with a CCD camera (iKon-M 934 BR-DD, Andor Technology). All SERS-spectra were recorded using a commercial nanostructured gold surface. The SERS substrate consists of a gold coated periodic square lattice of inverted pyramidal pits with a pitch of 2  $\mu\text{m}$  and a depth of 0.8  $\mu\text{m}$ .

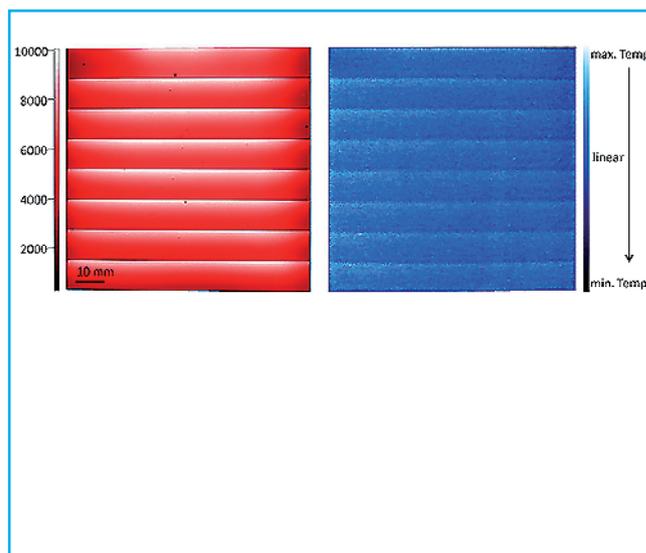


Fig. 2: Schema of the device for the detection of explosives

The modular setup consists of an enrichment, analytical, and detection unit [Fig. 1]. For the evaporation cell and analysis cell, vacuum components are used. The detection unit encompasses the diode laser and the spectrometer system [Fig. 2]. The laser beam is guided by the excitation fiber to the probe. The beam is focused at the end of a Kovar-tube on the nanostructured surface. The scattered light is collected and guided via the collection fiber to the entrance slit of the spectrometer. The explosives are evaporated from the carrier in the enrichment chamber. The explosive which has been released flows into the analysis unit. There, the gaseous analyte re-sublimates on the cooled nanostructured gold substrate.

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### Results and discussion

We have used the explosives TNT and TATP. Both explosives can be identified by their characteristic Raman bands. TNT solved in acetonitrile was dropped on the gold substrate. The acetonitrile was evaporated by heating the substrate to 30 °C for 10 min. The dominant acetonitrile bands in the SERS-spectrum are located at 381 cm<sup>-1</sup> and 920 cm<sup>-1</sup> [Fig. 3a]. These bands disappeared after the evaporation and the TNT bands appeared [Fig. 3b]. Seven bands of the TNT can be attributed to vibrational modes, namely 322 cm<sup>-1</sup> (framework distortion mode), 792 cm<sup>-1</sup> (C-H out-of-plane bend), 824 cm<sup>-1</sup> (nitro-group scissoring mode), 1207 cm<sup>-1</sup> (C<sub>6</sub>H<sub>2</sub>-C vibration), 1355 cm<sup>-1</sup> (NO<sub>2</sub> symmetric stretching vibration), 1542 cm<sup>-1</sup> (NO<sub>2</sub> asymmetric stretching vibration), and 1616 cm<sup>-1</sup> (C=C aromatic stretching vibration). Additionally, the recorded spectrum shows a band at 187 cm<sup>-1</sup>. The SERS spectrum of TNT re-sublimated out of the gas phase is shown in figure 3c. Although, this SERS spectrum shows a bit more noise, most of the TNT bands can be detected. The dominant feature is the band at 1351 cm<sup>-1</sup>. In combination with the bands at 792 cm<sup>-1</sup> and 825 cm<sup>-1</sup>, the TNT can be identified clearly.

The SERS spectrum of TATP was recorded after the re-sublimation at the nanostructured gold surface at 220 K. Due to the high vapor pressure of TATP (4.33 Pa), the concentration in the chamber was 70 ppm. For both spectra in fig. 4 background subtraction was performed. The dominant peak is the sharp intense peak at 866 cm<sup>-1</sup> which is attributed to the peroxide stretching mode. For the first time a SERS spectrum of TATP is analyzed. Generally, most of the characteristic TATP Raman bands are also present in the SERS spectrum [Fig. 4]. The frequencies of the SERS spectrum do not shift more than 2 cm<sup>-1</sup> compared to the Raman spectrum, indicating that the molecular environment has only little influence on the frequencies. This is plausible considering the high volatility and therefore weak intermolecular interactions in solid TATP. The band at 556 cm<sup>-1</sup> dominates the Raman as well as the SERS spectrum. The identification of TATP can be unambiguously done by SERS. The ring torsion and bending bands at 308 and 401 cm<sup>-1</sup>, the prominent

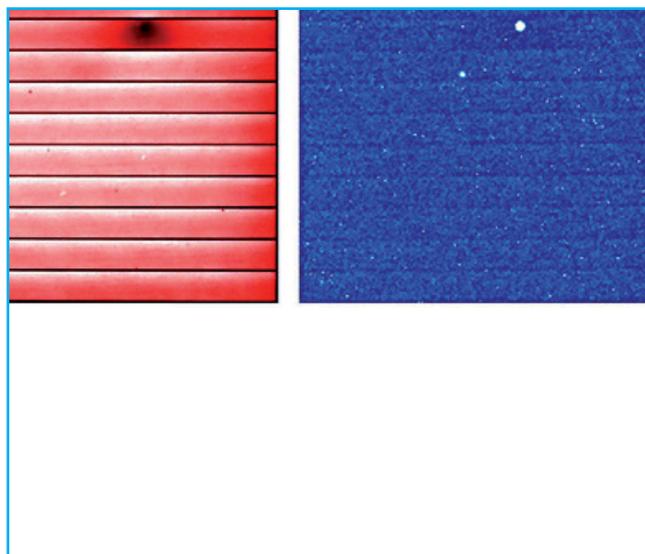


Fig. 3: a.) Raman spectrum acetonitrile

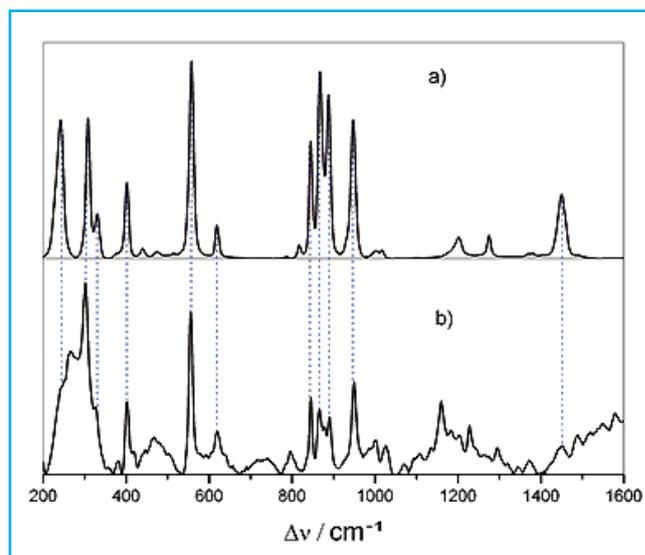
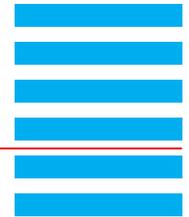


Fig. 3 b.) Raman spectrum TNT, c.) SERS spectrum TNT Fig. 4: a.) Raman spectrum TATP, b.) SERS spectrum TATP

C-O-O-C torsion mode at 558 cm<sup>-1</sup>, and the four bands between 840 and 950 cm<sup>-1</sup> are specific for the peroxide ring structure of TATP.

Raman spectroscopy has been identified as a very useful tool for peroxide and nitro compounds identification. To capture the explosives on the surface, re-sublimation out of the gas phase on a cooled metal surface was used.

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The explosives were detected by Raman spectroscopy. By using a nanostructured gold surface, the signals of the explosives adsorbed at the surface are enhanced due to the SERS effect by several orders of magnitude. The combination of the camera (iKon-M 934 BR-DD) and the usage of the spectrograph (Shamrock SR-303i) allow the obtaining of signals within a very short time and the analysis of high quality data.

### Contact

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