Program Manager: Joong H. Kim, ONR 30
Joong.Kim@navy.mil

Final Report

1. Project Title: Determining the Binding Mechanisms of Nitro-Group Containing Explosives on Metal-Oxide Semiconductor Surfaces

2. Performer: Applied Physics Laboratory, University of Washington

3. Contract or Grant Number: N000141612643

4. Principal Investigator: William E Asher

email: asherwe@uw.edu phone: 206-543-5942

5. Progress Narrative:

Work in this project has

1. Completed survey of methodologies to be used including FT-IR spectroscopy (reflection and transmission) and VSFS.

2. Determined that due to low signal intensities, FT-IR will not provide a useful method for studying binding mechanisms of explosives on MOS surfaces.

3. Determined that previous measurements of the sum-frequency response of explosives on MOS and other surfaces were due to the bulk-phase sum-frequency response from microcrystals of explosive rather than the sum-frequency response of surface-adsorbed molecules.

4. Developed methods for producing monolayer, and sub-monolayer, surface coverage densities of explosive molecules adsorbed on solid surfaces.

5. Characterized of the vibrational sum-frequency (VSF) response of two nitro-based explosives, RDX and picric acid, in monolayer-coverage density on the surface of fused silica and titanium dioxide (TiO_2).

6. Developed working hypothesis of the binding mechanisms between a TiO_2 surface and a nitro-based explosive that can be used for data interpretation.

7. Measured the azimuthal angle dependence of the VSF signal of picric acid (PA) at monolayer-coverage mass loadings on single-crystal anatase TiO_2.

8. Published a paper in IEEE Sensors Journal discussing the use of TiO_2 nanowire sensors for detecting nitro-containing explosives.

9. Begun producing a manuscript discussing the VSF results.

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The primary experimental results described in Item 6 above are shown in Figures 1 and 2, which are VSF intensity spectra for RDX and picric acid in the infrared region containing the resonance for the symmetric stretch of the -NO_2 group on the molecule. The top spectra in each figure show the bulk-phase VSF intensity for the pure crystalline explosive. Since the molecules in each organic crystal interact through van der Waals bonding, these spectra should be the simplest of the three. The middle spectra in each figure are the VSF intensity of a monomolecular film of explosive adsorbed on a fused silica window. The surface of fused silica is composed mostly of hydroxyl groups, and should represent a near-ideal surface for hydrogen bonding of the -NO_2 groups on the RDX or picric acid. The lower spectra in each figure show the VSF intensity of a monomolecular film of explosive adsorbed on a single-crystal TiO_2 surface. There are two competing models for the interaction of a -NO_2 group with TiO_2: the standard model where the oxygen atoms interact covalently with separate Ti^{+4} atoms on the semiconductor surface; the hydrogen-bonding model proposed by Antao Chen and Danling Wang, where the oxygen atoms on the semiconductor surface form hydroxyls in the presence of atmospheric water vapor, and these hydroxyls then form hydrogen bonds with the nitro groups.

Comparing the spectra for RDX in bulk crystal form with adsorbed onto fused silica shows the two are very similar, with a strong resonance at 1318 cm^{-1}. This similarity is interesting, because when in a bulk crystal, RDX cannot form hydrogen bonds since there are no hydroxyl groups. However, a fused silica surface contains a high surface density of hydroxyls, which would be available to form hydrogen bonds with RDX. However, there is no difference in the nitro group resonance for RDX going from the bulk crystal to adsorbed on fused silica. Hydrogen bonding generally leads to a red shift of at most 10 cm^{-1}, which would be visible as a shoulder on the peak at 1318 cm^{-1}. The absence of a second resonance for the fused silica spectra implies either the hydrogen-bonded nitro group is not active as a sum-frequency transition or that the nitro groups in RDX do not interact via hydrogen bonds with the fused silica surface.

The spectra for RDX adsorbed on TiO_2 differs from the fused silica and bulk crystal spectra by the appearance of a resonance at 1260 cm^{-1}, with the resonance at 1318 cm^{-1} also present. It is hypothesized that the resonance at 1260 cm^{-1} represents the symmetric stretch of a nitro group that is adsorbed to the TiO_2 surface. The red shift of the symmetric stretch of the nitro group by nearly 60 cm^{-1} is too large to be due to hydrogen bonding, and likely reflects the shift due to the strong bidentate adsorption of the two oxygen atoms of the nitro group to the titanium ions on the semiconductor surface.

The spectra for picric acid in Figure 2 are more complicated than for RDX, mostly because picric acid forms an intramolecular hydrogen bond between the hydroxyl at the “1” position on the benzene ring with the nitro group at the “2” position. Furthermore, this intramolecular hydrogen bond is a resonant structure with the aromatic benzene ring, leading to a much larger red shift that usual. FT-IR spectra of the absorption bands for picric acid crystals in the -NO_2 symmetric stretch region show a large peak at approximately 1350 cm^{-1} and a smaller peak at approximately 1325 cm^{-1}. This is consistent with the idea that one of the nitro groups is involved with an intramolecular hydrogen bond and the other two are associated with molecules in the crystal through van der Waals interactions. However, the sum-frequency spectra for picric acid crystals in Figure 2 shows only the main resonance at 1350 cm^{-1}. It is likely that the hydrogen-bonded resonance is not observed in sum-frequency due to symmetry considerations.

The spectra for picric acid on fused silica shows the large main resonance has red-shifted to 1335 cm^{-1}, which would be expected if the nitro groups were hydrogen bonded to the fused silica surface. Furthermore, there is evidence that there is a shoulder at 1315 cm^{-1}, which possibly represents the resonance of the -NO_2 that is intramolecularly hydrogen bonded to the phenolic OH. It is the spectra for picric acid on TiO_2 that is most interesting, and to understand it a discussion of how these nitro compounds bind to TiO_2 is in order.

It has been proposed that nitro-aromatic compounds such as picric acid (i.e., 1-hydroxy-2,4,6-trinitro-benzene) adsorb to a TiO_2 surface through a bidentate interaction of two oxygen atoms of the -NO_2 group at the para position (i.e., the "4" nitro) with two Ti^{4+} at the TiO_2 crystal surface. This binding mechanism forces the picric acid molecules into a preferred orientation, where the planar surfaces of the benzene rings align in parallel with each other. This gives the surface-bonded nitro group a preferred orientation with respect to the crystal surface. (In contrast, the two nitro groups have a more random distribution, and the axis of the C-O bond of the hydroxyl group is symmetric with respect to the surface normal.) Of equal importance is that when adsorbed to TiO_2, there should be three distinct nitro resonances: the -NO_2 group adsorbed to the TiO_2, the -NO_2 group that is part of the intramolecular hydrogen bond, and the -NO_2 group that is unattached to the TiO_2 or the OH (i.e., it is free in space).

Because molecular interactions such as hydrogen bonding or strong surface adsorption weaken bonds (because they reduce electron density in the bonding orbitals), one expects red shifts of the interacting nitro groups. Furthermore, it would be expected the red shift of the surface adsorbed nitro would be larger than the red shift of the hydrogen-bonded nitro, with the free nitro having little to no red shift. The spectra of picric acid on TiO_2 agrees with this hypothesis, with a resonance at 1365 cm^{-1} (free nitro group), 1325 cm^{-1} (intramolecularly bonded nitro group), and a resonance at 1285 cm^{-1} (surface adsorbed nitro group). Interestingly, the red shift for the proposed surface adsorbed nitro group of approximately 50 cm^{-1} is approximately the same between picric acid and RDX, showing that the interaction between TiO_2 and the nitro-containing explosive is similar for both compounds.

Further evidence that the picric acid resonance at 1285 cm^{-1} is the surface-bonded nitro group is provided by Figures 3, 4, and 5. These figure shows the results of SF measurements of picric acid monolayers adsorbed on a single crystal sample of anatase TiO_2. The data in the figure was collected by mounting the TiO_2 sample on a rotational stage, allowing the SF intensity to be measured as a function of azimuthal angle with respect to the polarization of the incoming laser beams. The data in Figure 1 were collected using PPP polarization, meaning the incoming 532 nm beam, the incoming infrared beam, and the outgoing SF photons, were all polarized parallel to scattering plane defined by the incoming and outgoing photons with respect to the TiO_2 crystal.

Of the three sum-frequency resonances observed from the picric acid/TiO_2 system in the region from 1250 cm^{-1} to 1400 cm^{-1}, the peak at 1285 cm^{-1} is the -NO_2 group that is adsorbed to the TiO_2 surface. The peak at 1365 cm^{-1} is the free -NO_2 group, and the resonance at 1325 cm^{-1} is the intramolecularly bonded nitro group. If picric acid is bound to the semiconductor surface through a bidentate adsorption, then the sum frequency intensity from the resonance at 1285 cm^{-1} will depend on the azimuthal angle of the crystal with respect to the polarization of the laser beams. This happens because the symmetry axis of the bond's dipole will rotate in and

out of phase with the polarization axis of the laser beams. In contrast, there should be little to no rotational dependence of the resonances at 1325 cm^{-1} and 1365 cm^{-1} since these dipoles are aligned in a vertical direction and there is no rotational dependence with respect to the polarization axis.

Figure 3 shows the normalized sum frequency intensities for the three resonances plotted as a function of azimuthal rotation angle of the TiO_2 crystal. The resonances at 1325 cm^{-1} and 1365 cm^{-1} show a nearly circular symmetry on rotation whereas the resonance at 1285 cm^{-1} is elliptical. This suggests that there is a fixed orientation to the resonance at 1285 cm^{-1}, which is consistent that this is the nitro group that is adsorbed to the TiO_2 surface. The circular symmetry of the other two resonances is also consistent with the hypothesis that they represent the free nitro group and the intramolecularly bonded nitro group.

The plot of the ratio of the SF intensity at 1320 cm^{-1} to the SF intensity at 1285 cm^{-1} as a function of azimuthal angle shown in Figure 4 is also elliptical, which would be expected if the lower wavenumber is the resonance from a bond that has a fixed orientation to the crystal surface and the high wavenumber represents a resonance with no angular dependence. In contrast, a plot of ratio of the SF intensity at 1320 cm^{-1} to the SF intensity at 1365 cm^{-1} as a function of azimuthal angle shown in Figure 5 shows a nearly circular symmetry, which is consistent with the hypothesis that these two resonances have no azimuthal dependence.

Taken together, these sum frequency data provide evidence that nitro-containing explosives bind to TiO_2 surfaces through a bidentate adsorption, and not through hydrogen bonding. In fact, the bidentate adsorption is so strong (as evidenced by the large red-shift in the sum-frequency resonance) it is difficult to imagine how the chemiresistive response of TiO_2 with respect to explosives could be improved upon by coating the surface with an organic layer. It is likely, based on these data, that TiO_2 represents the maximum chemiresistive signal possible for detecting explosives. However, because the bidentate adsorption is so strong, these results also demonstrate that care must be taken with TiO_2 sensors to prevent buildup of explosives.

6. Risk and Issues associated with cost

No risks or issues associated with cost

7. Additional notes to program manager

No additional notes.

Program Manager: Joong H. Kim, ONR 30
Joong.Kim@navy.mil

8. Graphics.

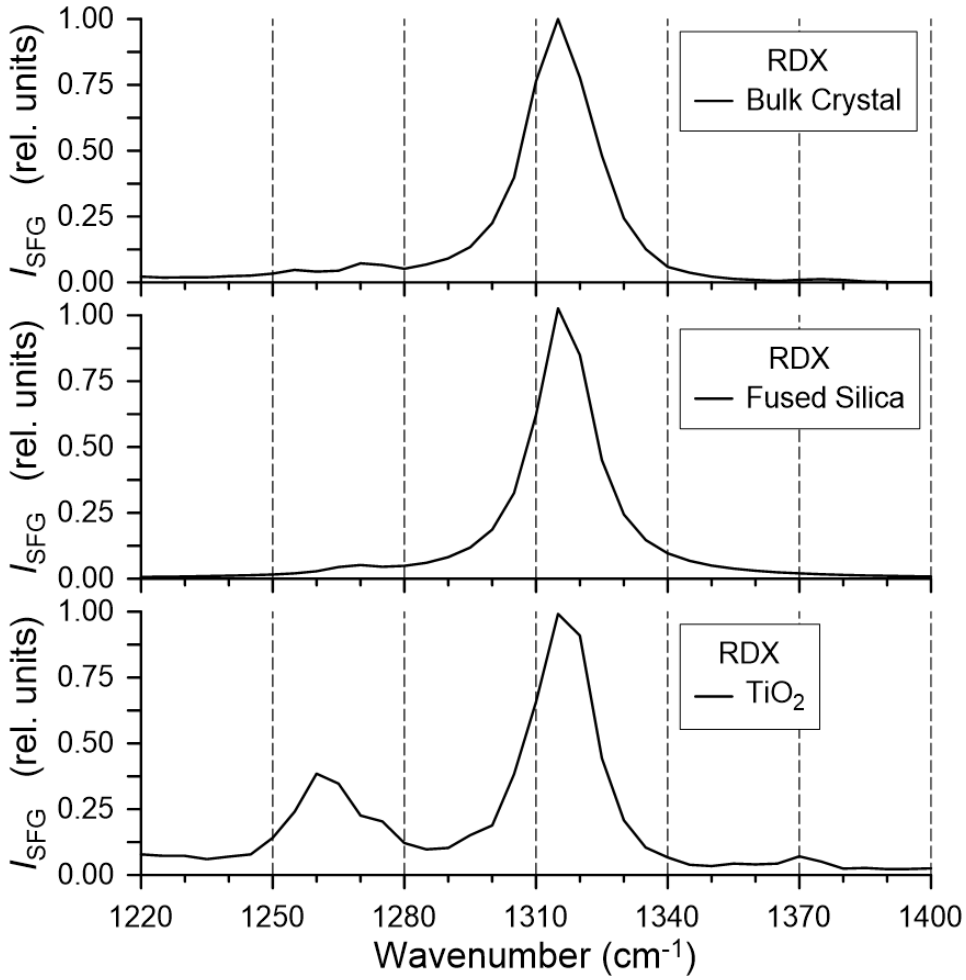

Figure 1: Spectra of normalized vibrational sum-frequency intensity, I_{SFG}, of RDX as a function of infrared wavenumber in the region where the resonance of the symmetric stretch of the nitro group ($-NO_2$) occurs. The top spectra shows the bulk response of RDX crystals where there is no hydrogen bonding of the $-NO_2$ groups. The middle spectra shows the response of a monomolecular film of RDX adsorbed on a fused silica surface. The bottom spectra shows the response of a monomolecular film of RDX adsorbed on a single-crystal surface of titanium dioxide (TiO_2). The large peak at 1315 cm^{-1} in all three spectra is the symmetric stretch of the $-NO_2$ groups in the absence of strong intermolecular/surface interactions (i.e., no hydrogen bonding or dipole-dipole interactions). The weak peak at 1270 cm^{-1} in all three spectra (seen as a shoulder on the larger peak at 1260 cm^{-1} in the TiO_2 spectra) is a resonance of the RDX molecule not associated with the $-NO_2$ group (i.e., possible a ring mode or non-aromatic C-N bond).

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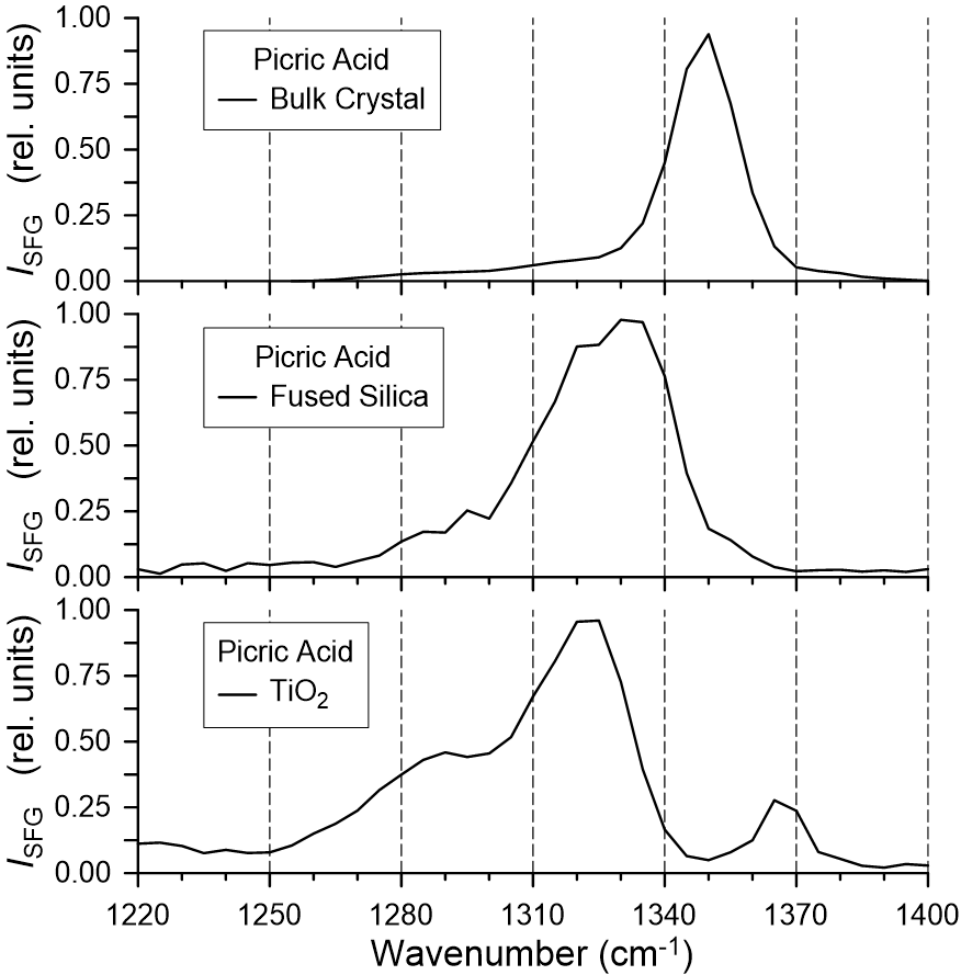

Figure 2: Spectra of normalized vibrational sum-frequency intensity, I_{SFG}, of picric acid as a function of infrared wavenumber in the region where the resonance of the symmetric stretch of the nitro group (-NO_2) occurs. The top spectra shows the bulk response of picric acid crystals where there is no surface bonding of the -NO_2 groups. The middle spectra shows the response of a monomolecular film of picric acid adsorbed on a fused silica surface. The bottom spectra shows the response of a monomolecular film of picric acid adsorbed on a single-crystal surface of titanium dioxide (TiO_2). Picric acid is more complicated because of intramolecular hydrogen bonding of the hydroxyl group on the 1 carbon of the benzene ring with the -NO_2 group on the 2 carbon of the ring.

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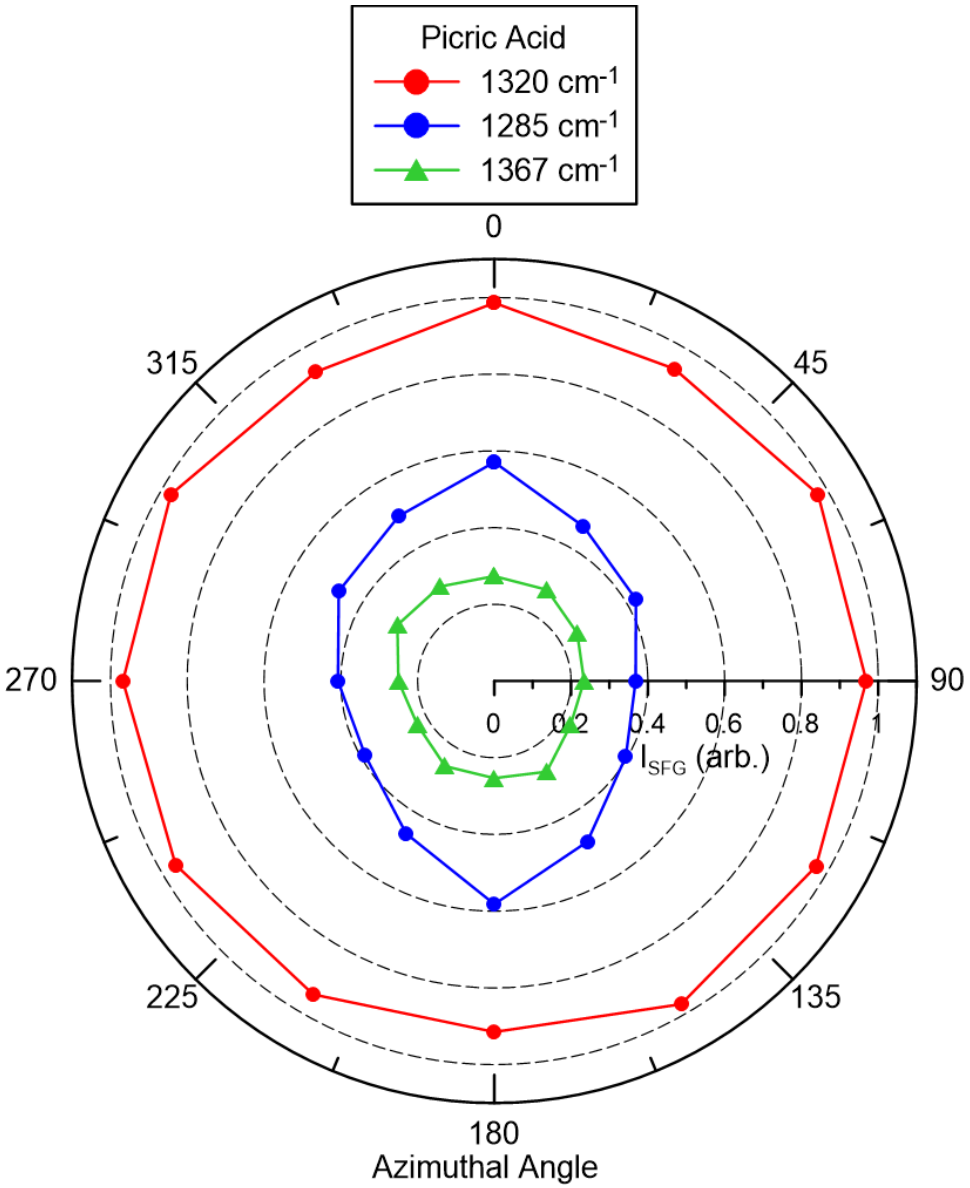

Figure 3: Normalized sum-frequency intensities, I_{SFG}, measured using PPP polarization of a picric acid monolayer adsorbed on a single crystal anatase TiO_2 surface plotted as a function of azimuthal angle with respect to the polarization plane of the incoming laser beams for the three resonances thought to be due to the three different symmetric stretches of the -NO_2 groups of a picric acid molecule on a TiO_2 surface. The resonance at 1365 cm^{-1} is thought to be due to the unassociated -NO_2 group, the resonance at 1325 cm^{-1} is thought to be the intramolecularly hydrogen-bonded -NO_2 group, and the resonance at 1285 cm^{-1} is believed to be the -NO_2 group that is adsorbed to the TiO_2 surface through the bidentate interaction. When plotted as an azimuthal plot, a circular curve represents a resonance that is randomly aligned with the TiO_2 surface, and an elliptical curve denotes a resonance that has a fixed orientation with respect to the TiO_2 surface. I_{SFG} was normalized by dividing each intensity by the maximum intensity measured for the entire spectra.

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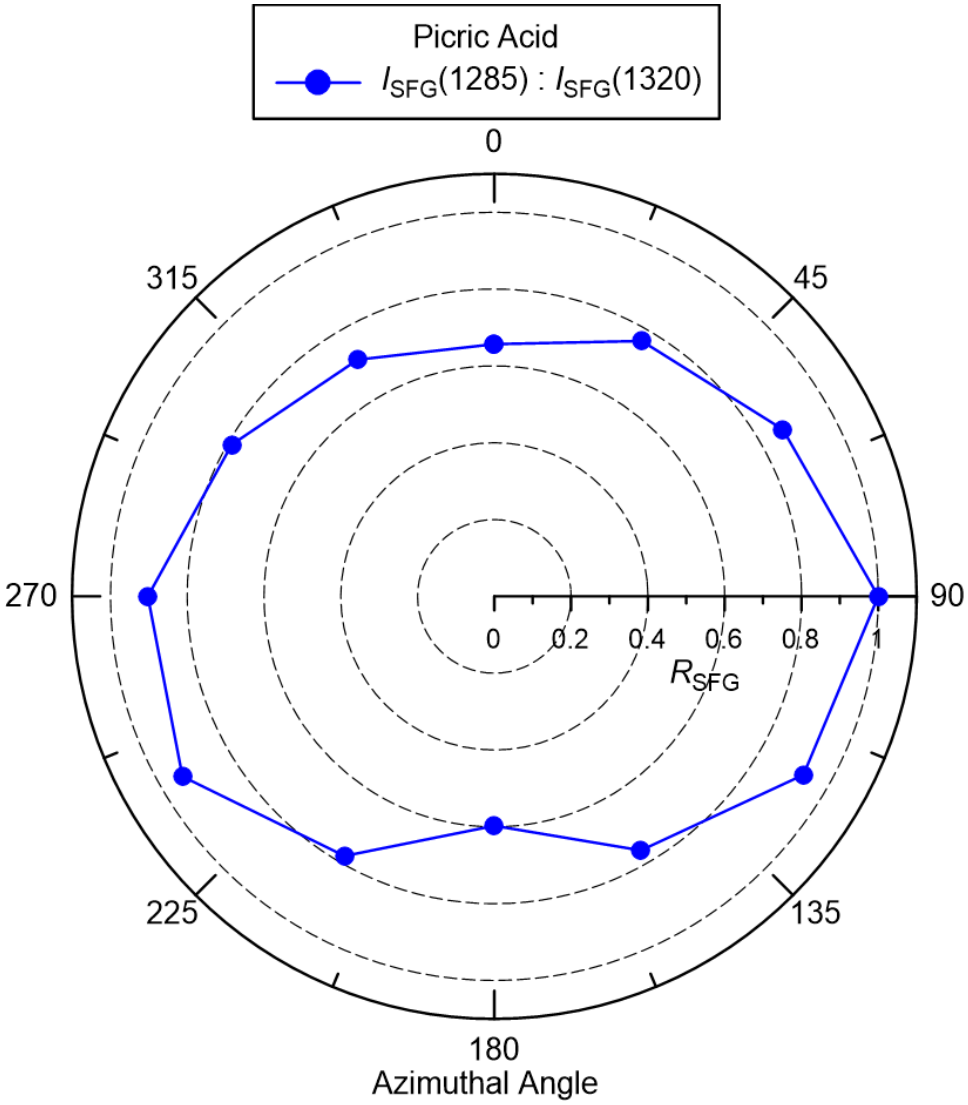

Figure 4: Normalized sum-frequency intensity ratios, R_{SFG}, from measurements of a picric acid monolayer adsorbed on a single crystal anatase TiO_2 surface plotted as a function of azimuthal angle with respect to the polarization plane of the incoming laser beams. For these measurements, PPP polarization was used. R_{SFG} is defined as the SFG intensity at 1320 cm^{-1} divided by the SFG intensity at 1285 cm^{-1}. If one resonance is aligned with a fixed orientation with respect to the TiO_2 surface and one resonance is distributed with more random orientation, the R_{SFG} will plot as an ellipse as the fixed orientation resonance moves in and out of phase with the polarized excitation light.

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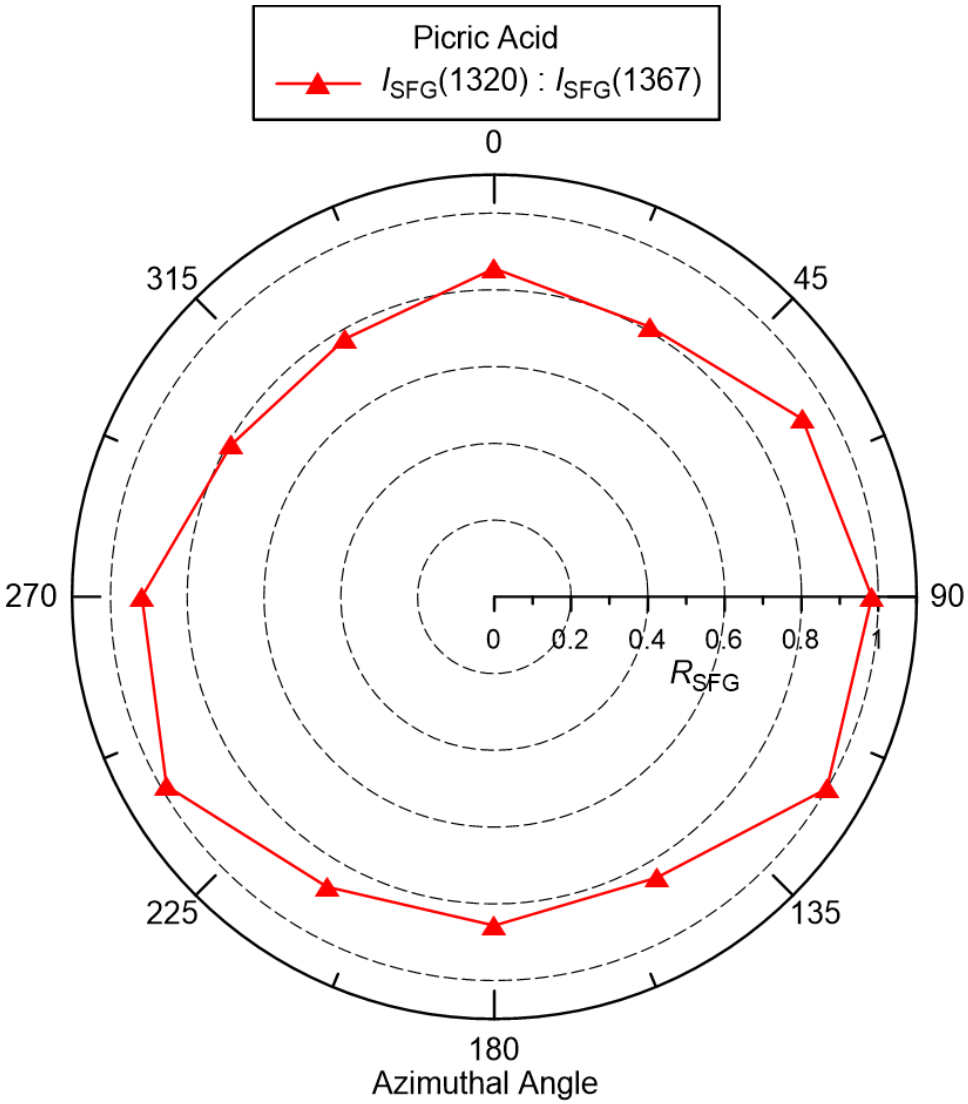

Figure 5: Normalized sum-frequency intensity ratios, R_{SFG}, from measurements of a picric acid monolayer adsorbed on a single crystal anatase TiO_2 surface plotted as a function of azimuthal angle with respect to the polarization plane of the incoming laser beams. For these measurements, PPP polarization was used. R_{SFG} is defined as the SFG intensity at 1320 cm^{-1} divided by the SFG intensity at 1367 cm^{-1}. If one resonance is aligned with a fixed orientation with respect to the TiO_2 surface and one resonance is distributed with more random orientation, the R_{SFG} will plot as an ellipse as the fixed orientation resonance moves in and out of phase with the polarized excitation light. Compared to

Program Manager: Joong H. Kim, ONR 30
Joong.Kim@navy.mil

9. Publication List (Cumulative – Everything under the current grant)

Asher, W., P. Colosimo, E. Thorsos, A. Yao, "On Sensing Nitro-Group Containing Compounds Using Thin Planar Arrays of Titanium Dioxide Nanowires," *IEEE Sensors*, 2018, *in press*.

Colosimo, P., and W. Asher, "Vibration Sum-Frequency Spectroscopy Measurements of Nitro-Containing Compounds on Fused Silica and Titanium Dioxide Surfaces," *Propellants, Explosives, Pyrotechnics*, in preparation, 2018.

10. Others (Media Interest, Awards, Patents, Other Gov't agency interest and funding for the related items, etc.)

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William Asher

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Applied Physics Laboratory
University of Washington
1013 NE 40th Street
Seattle, WA 98105

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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research (ONR Code 30)
875 North Randolph Street
Arlington, VA 22203-1995

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

This project will use nonlinear laser spectroscopic surface analysis techniques to study how nitro-group containing explosives (e.g., TNT, RDX, HMX, PETN) bind to metal oxide semiconductor (MOS) surfaces in the presence of atmospheric water vapor, oxygen, and environmental contaminants. This information can be used to understand which MOS materials would lead to solid-state trace explosive vapor detectors that have low enough detection limits and fast enough response times to be useful for tactical applications.

15. SUBJECT TERMS
Explosives detection, semiconductor trace gas sensors, vibrational sum-frequency spectroscopy

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