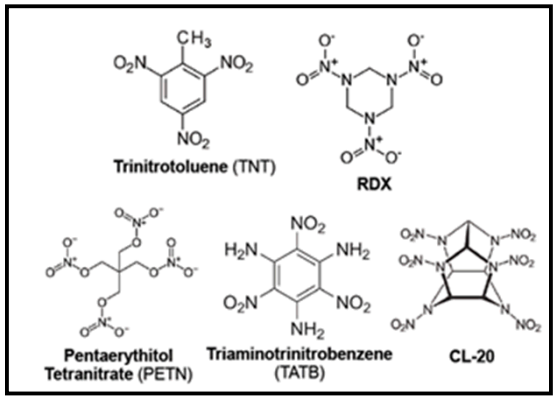
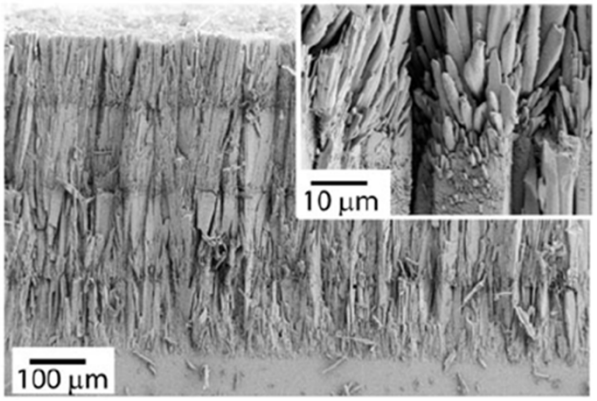
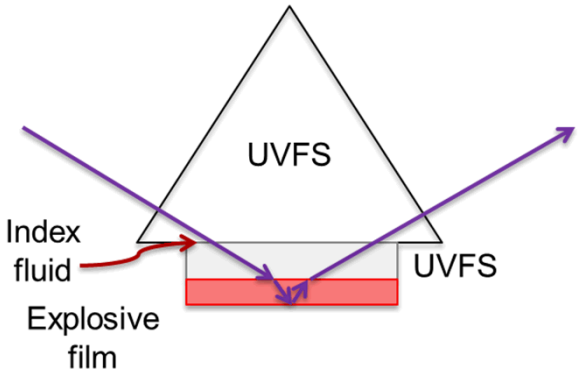
Exceptional service in the national interest

SAND2016-2038C

Sandia National Laboratories







Measuring HOMO/LUMO gap of explosive film at air interface using ATR spectroscopy

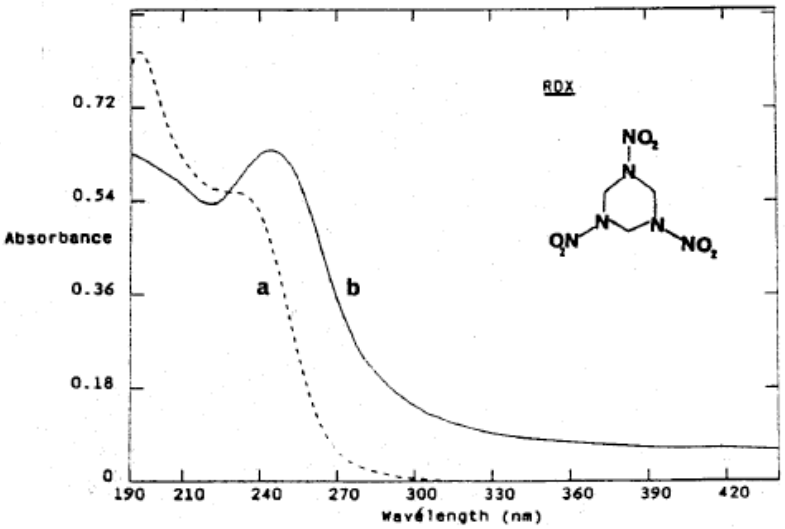
Darcie Farrow, Laura Martin, Stephen Rupper ,Kathy Alam, Ian Kohl,
Sean Kearney, Robert Knepper, Michael Marquez, Jeffrey Kay

U.S. DEPARTMENT OF ENERGY

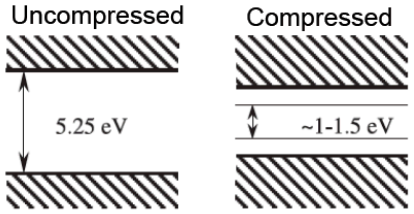
National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND NO. 2011-XXXXP

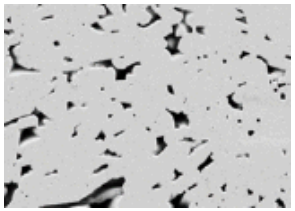
Motivation

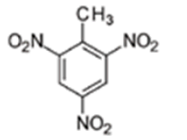


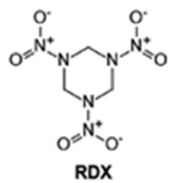
Smit, Journal of Energetic Mat. (1991)

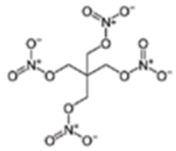


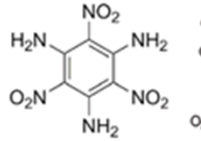
Kuklja *Appl. Phys. A* **76**, 359 (2003)

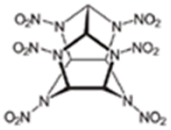






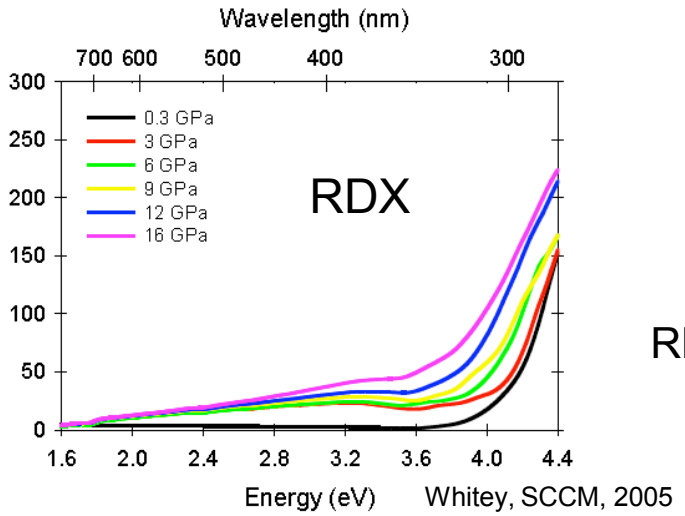




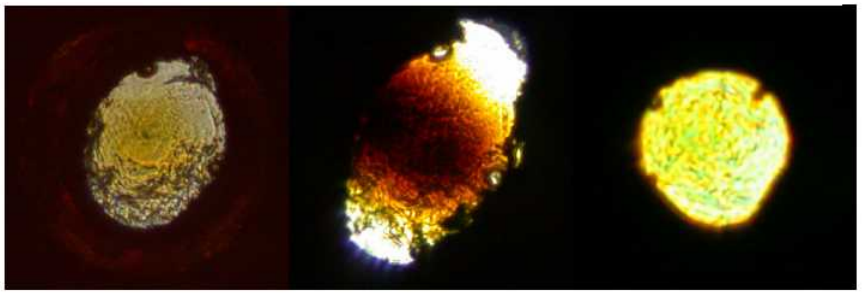


- Secondary explosives are ***stable molecules*** that react rapidly under shock compression.
- Voids and grain boundaries significantly increase the sensitivity and rate of initiation and solid explosives have additional bands extending into visible.
- Band gap and electronic properties can be influenced by the presence of crystalline defects.
- Surface is simplest type of defect to probe – how does electronic structure differ from bulk?

What has been measured:

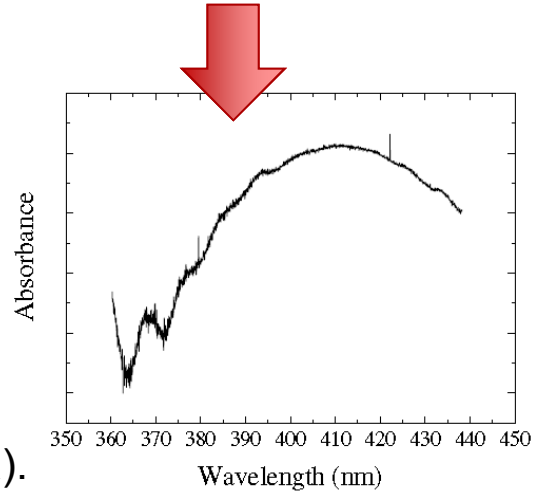


Whitey, SCCM, 2005



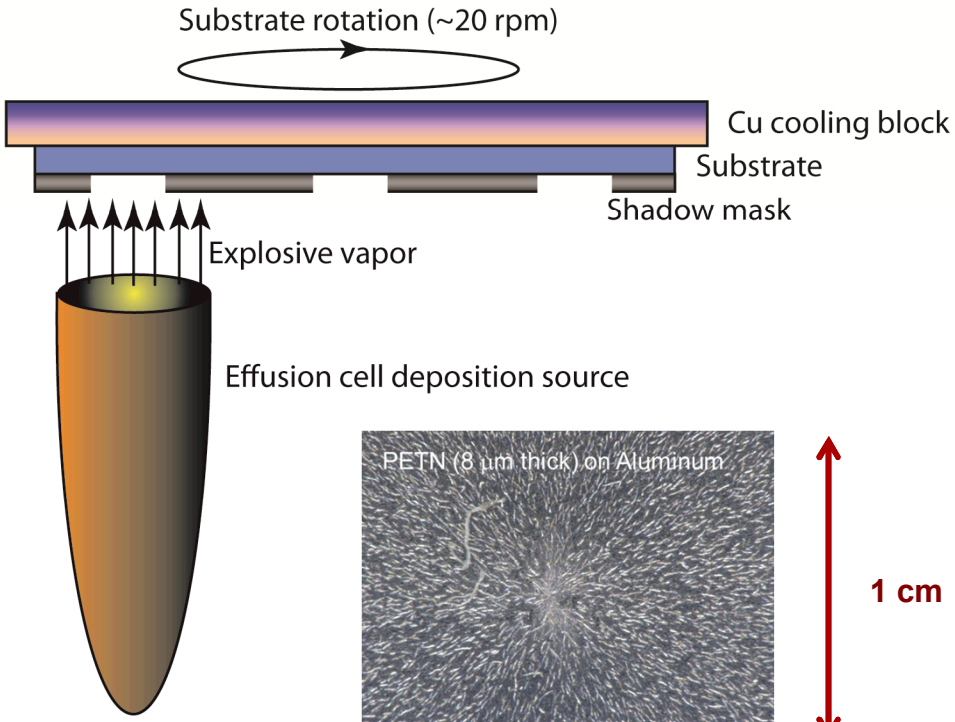
RDX/CsI: 22GPa 48GPa RDX: 65 GPa

Goto et al., Material Science Forum Volumes (2004)



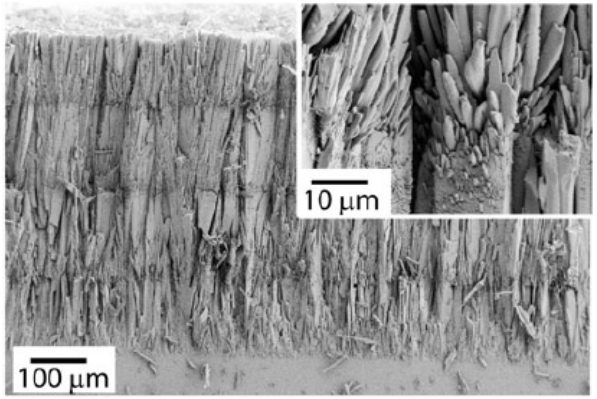
- DAC UV/Vis data on RDX. Significant change in absorption spectrum of RDX around ~50 GPa in single crystals
- Transient absorption measurements (390- 780 nm) of single crystal PETN and RDX show building absorption during compression assigned to reaction or defect formation (< 30 GPa). (McGrane et al. IDS, 2010)
- No direct measurement of electronic absorption at explosive surfaces has been done at ambient or elevated pressure.

UV/Vis of explosive film/air interface: Model for void.



1 cm

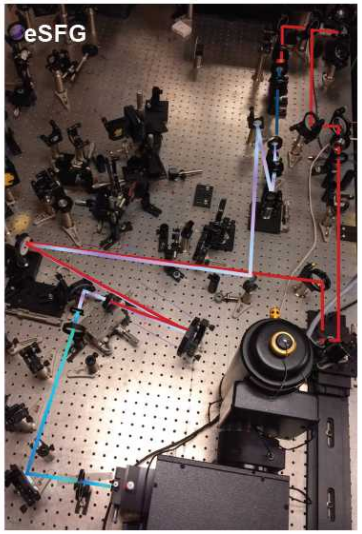
1 cm

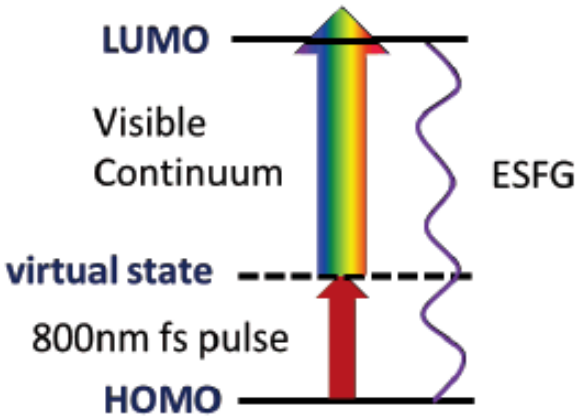


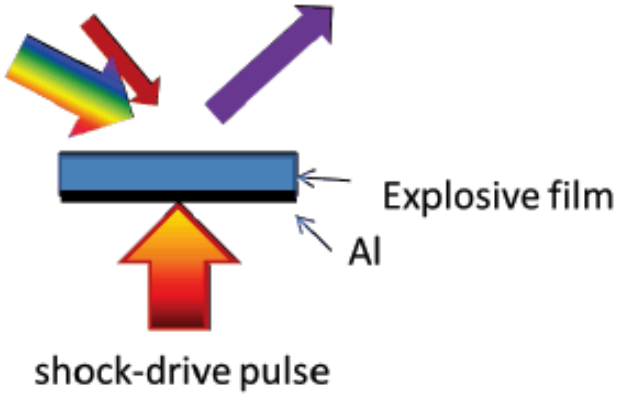
Knepper et al. *J.Mater.Res.* **26** (2011)

2-5 um of PETN, HNS, CL20, HNAB or RDX vapor deposited over Aluminum or UV fused silica.

Surface selectivity: Electronic Sum Frequency Generation.

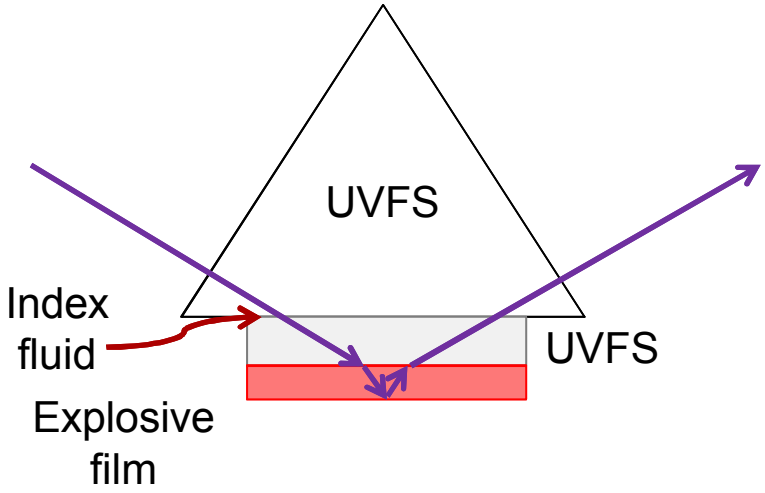


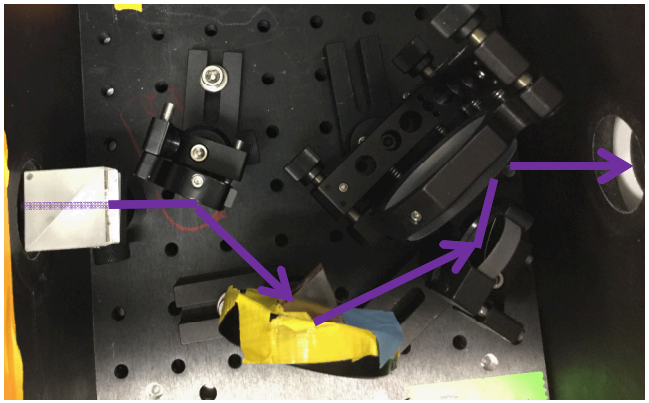




- Previously demonstrated for dye/water samples, semiconductors, and in heterodyne configurations (Yamaguchi, JCP 129, 2008).
- Sum Frequency Generation is not allowed in bulk centrosymmetric materials, enhanced at resonant transitions.
- UV continuum generation did not produce the 1 uJ needed for ESFG. Is there a simpler way?

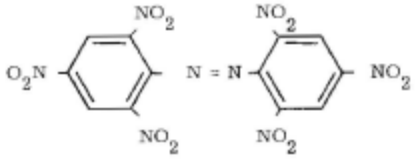
UV/Vis Attenuated Total internal Reflection.

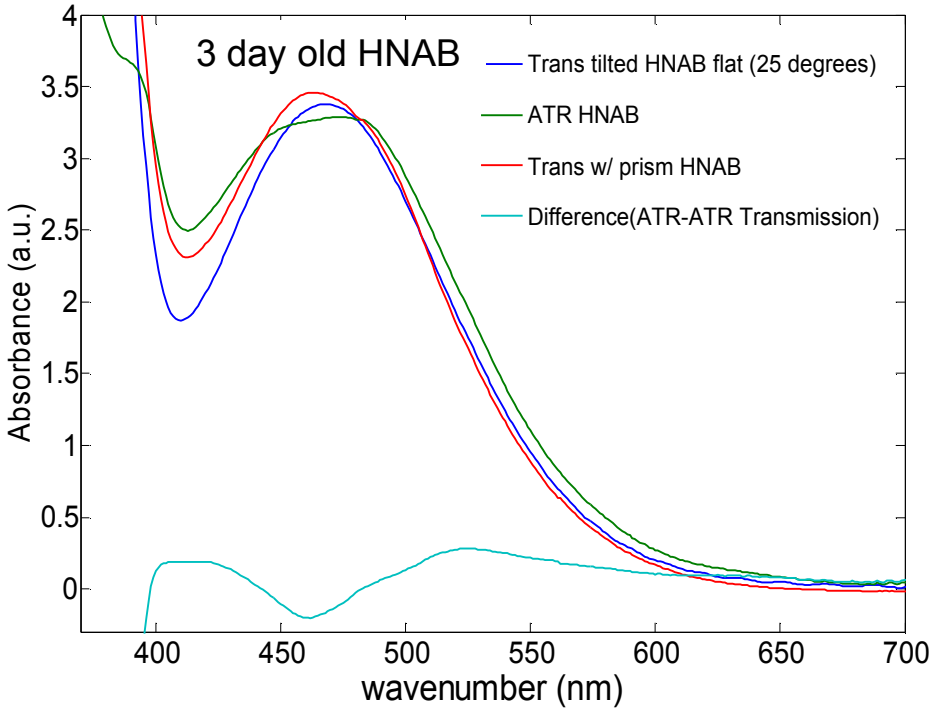


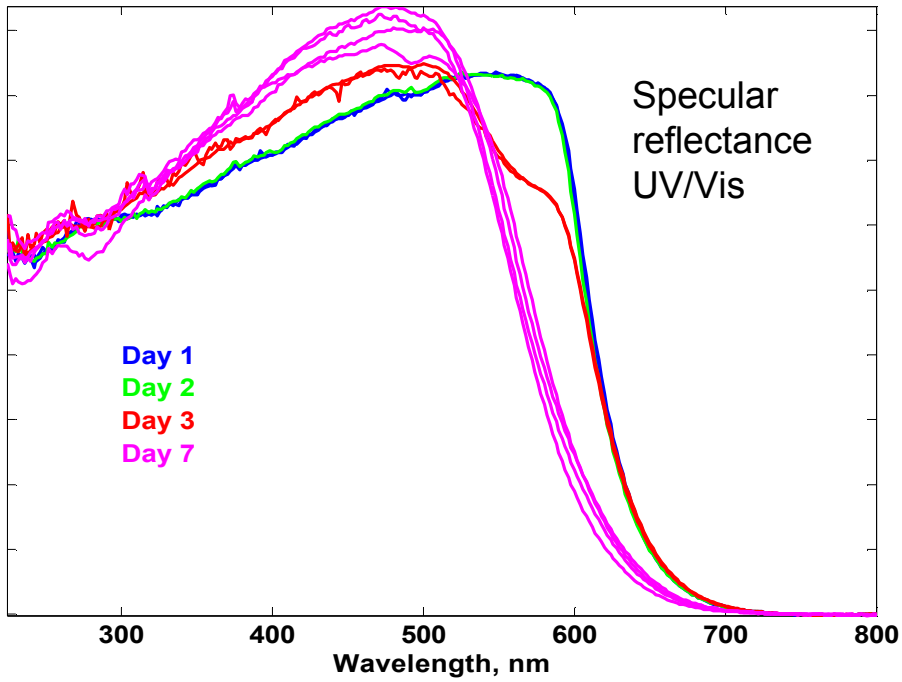


- PerkinElmer Lambda 750 equipped with tungsten-halogen and deuterium sources, with PMT detection.
- Spectra referenced to ATR spectra of identical UVFS plate w/o film. UV absorption from two passes through film will contribute to spectrum.
- Spectra taken of thin film in transmission mode through prism/index fluid and w/o for comparison.

UV/Vis ATR HNAB

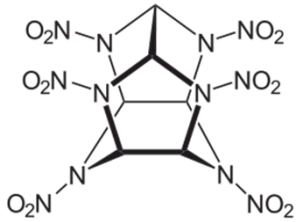


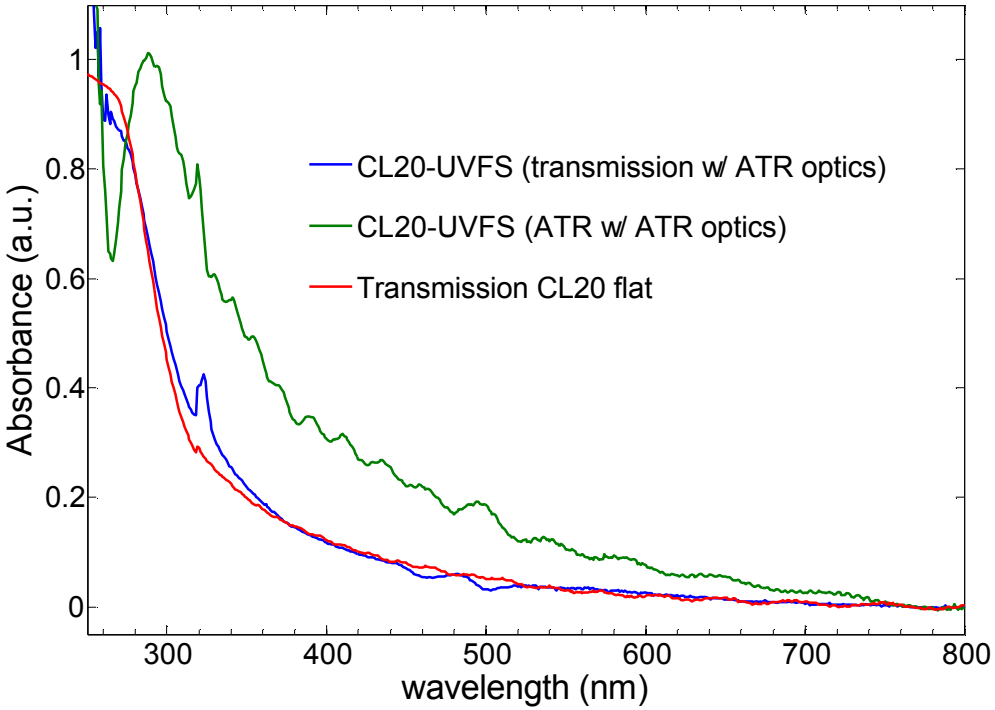


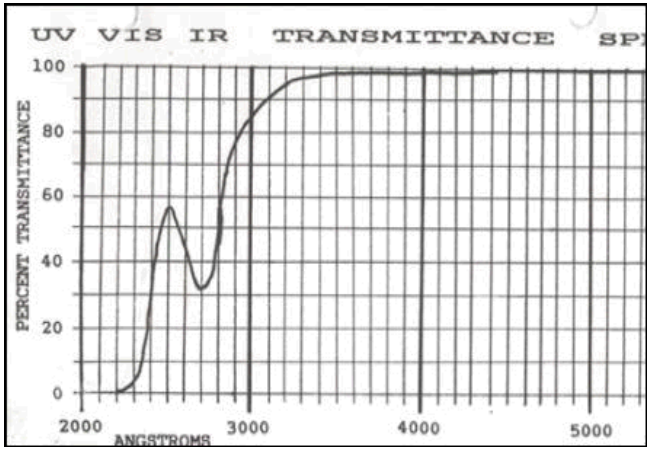


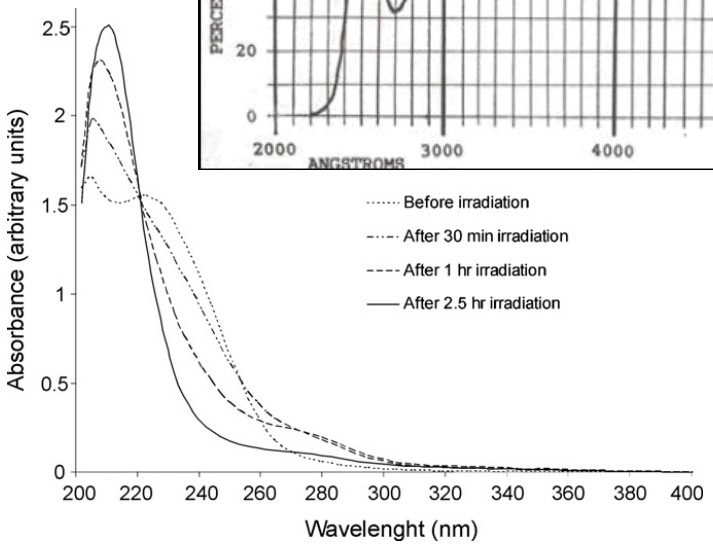
- HNAB vapor deposited film undergoes phase transition from amorphous to HNAB II.
- Broadening and red shift in HNAB spectra that does not match amorphous HNAB spectrum.
- E-wave penetration < 90 nm (worst case FS @ critical angle) @ 550nm

UV/Vis ATR CL20



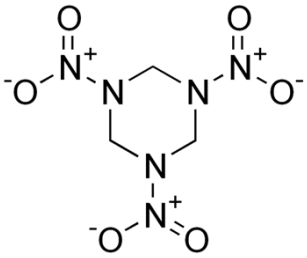


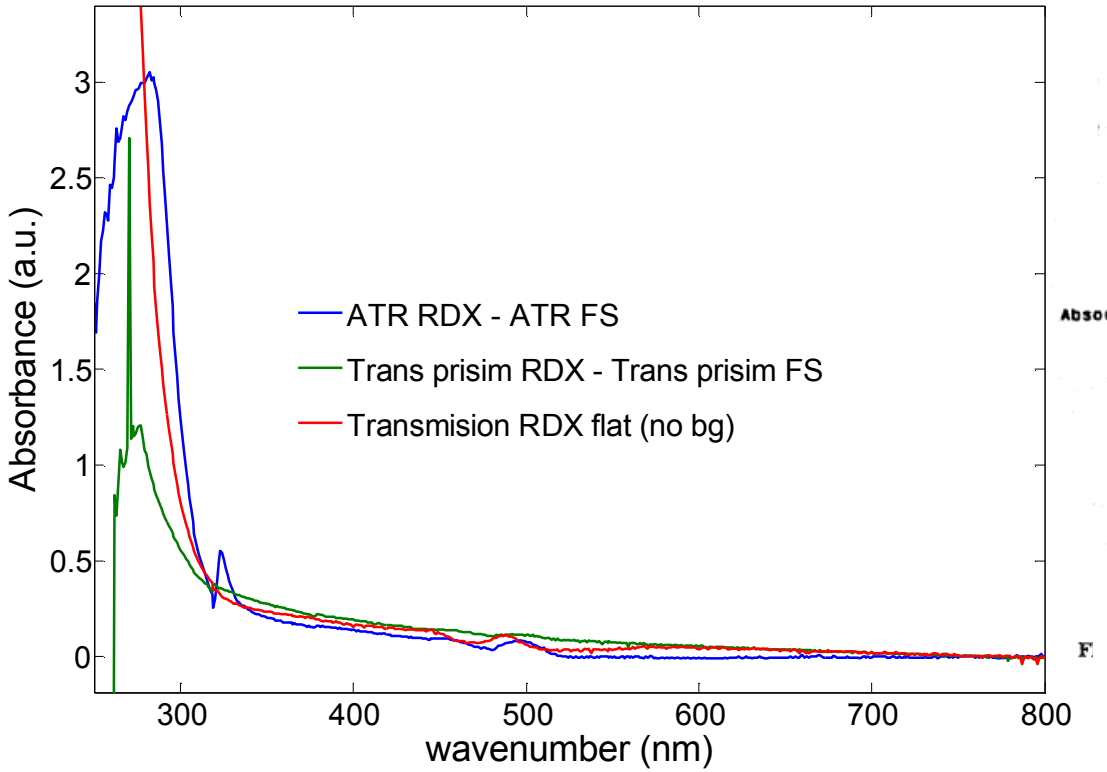


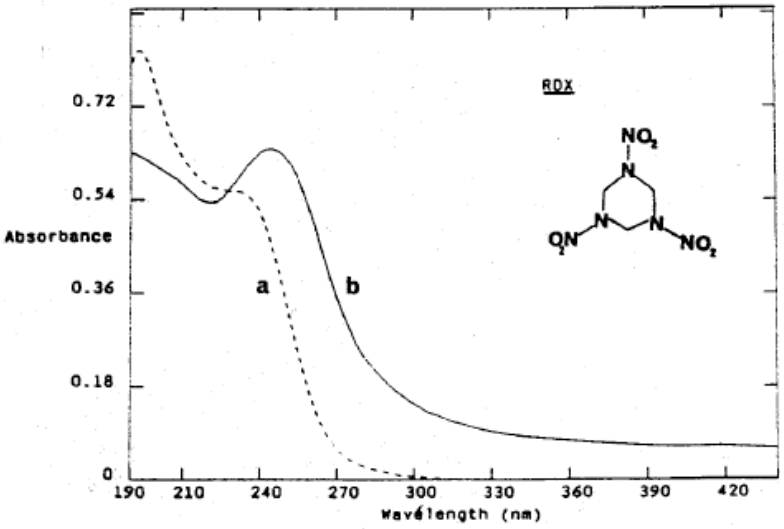


- While index matching fluid is present in CL20 surface, broadening increased in surface spectra from 300-750 nm. (retaking data next week)
- E-wave penetration < 50 nm (worst case FS @ critical angle) @ 300nm

UV/Vis ATR RDX



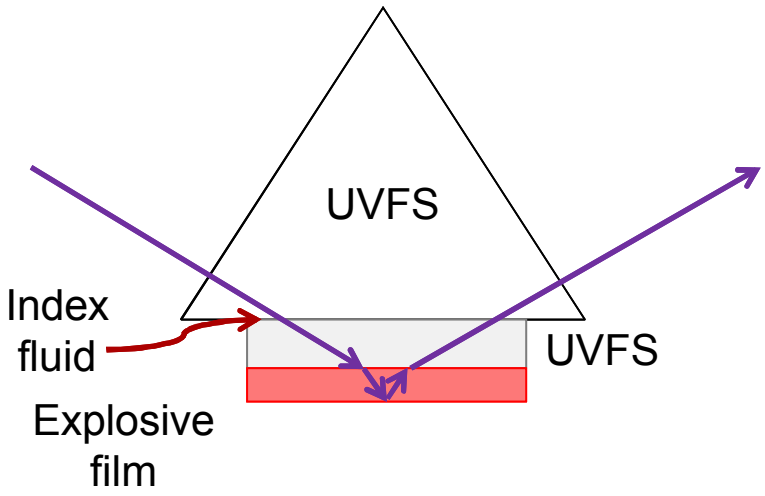


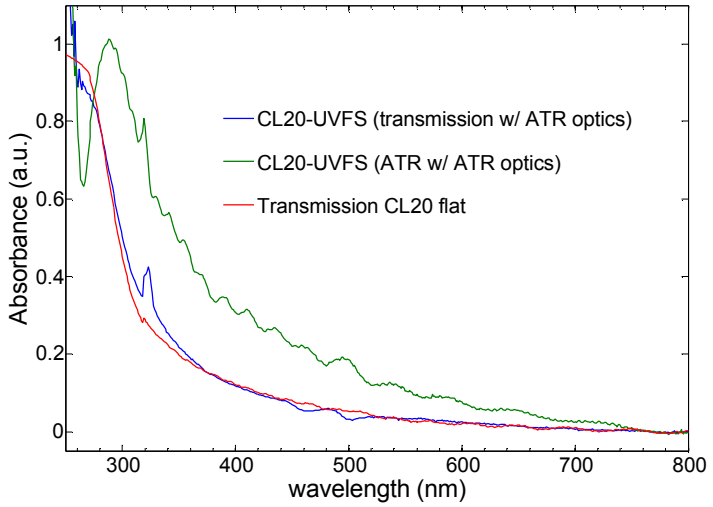


Smit, Journal of Energetic Mat. (1991)

Peak of spectra ~ 280nm is red shifted from UV/Vis transmission data in published spectra in salt.

Conclusions:





- We have characterized UV/Vis spectra of explosive within 50-100 nm of the explosive/air interface.
- UV/Vis absorption at the surface has a qualitatively different shape and is red shifted with respect to bulk UV/Vis absorption.
- Difference between bulk and surface dominated UV/Vis spectra motivate time-resolved surface spectroscopy under dynamic compression (ESFG with probe from TOPAS or ATR TA measurement under laser shock).

Thankyou…

- Laura Martin, Kathy Alam (UV/Vis ATR)
- Stephen Rupper, Ian Kohl (ESFG)
- Robert Knepper, Michael Marquez (explosive samples)
- S. Yamaguchi, P. Dhar, R. Prasankumar for discussions on ESFG/ UV ATR.
- SNL ES LDRD funded work.

… and you for your time.