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Laser-Induced Breakdown Spectroscopy (LIBS) as a Complement to Large-Scale Detonations and Means to Characterize Intermediates STL-05-14, Year 2 of 2

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Challenge

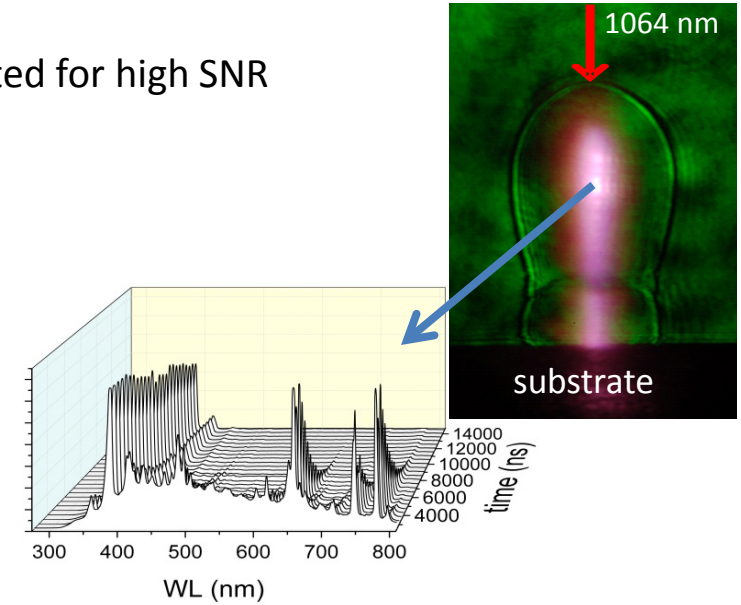
Nuclear forensics, including NCNS, needs accurate models of optical and RF emissions from explosions to validate models

Large-scale, high explosive field tests generate data for such models, but:

- Expensive, subject to weather, and time-consuming
- Difficult to obtain high temporal and spectral resolution
- Difficult to distinguish important factors (e.g., metal [and ions produced], explosive type, chemistry in the ambient atmosphere)

Laser-Induced Breakdown Spectroscopy (LIBS) can mimic aspects of large-scale detonations

- Provides high-resolution, time-resolved spectral signatures at high pressures and temperatures
  - 5–10 Hz repetition rate and shots can be integrated for high SNR
- Is time- and cost-effective
- Permits experiments that are easily modified, yielding more variations on the parameter space
- Can be used to test and validate field diagnostics



Integration of lab and field studies:

- Successful optical field collect at HET (FY14)
- Benchtop LIBS to prepare for HELIOS (FY16)

Innovation: LIBS application to HE testing

Aluminum (Al) Studies:
LIBS applied to survey Al species in vacuum, air ,and argon (Al casing at HET/HELIOS)

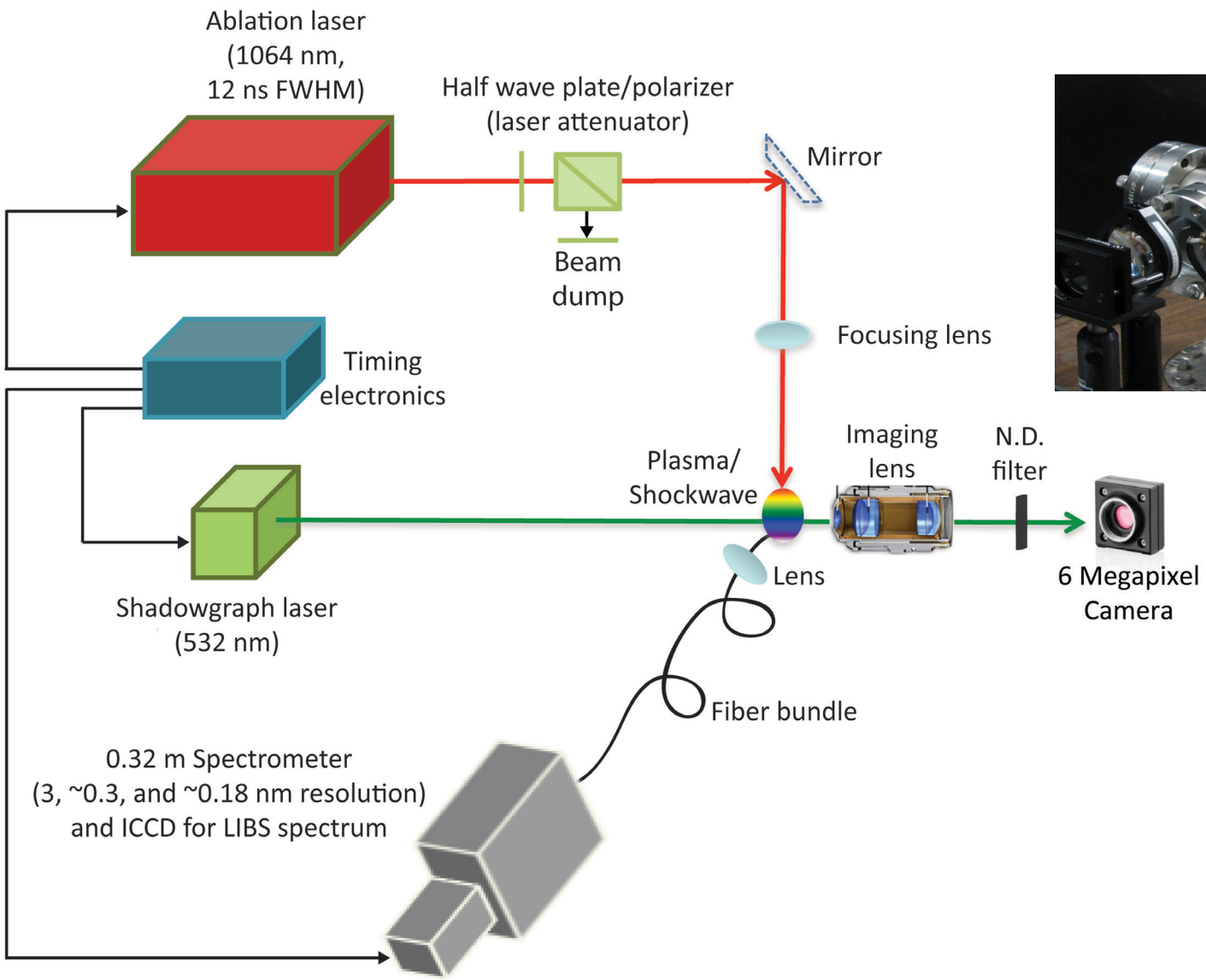
- Select LIBS results compared to bombproof chamber and optical spectra from FY14 HET field tests (2014 HET fielding funded as part of this SDRD)
- Tie to optical field studies focusing on the UV (reduced blackbody) and solar-blind UV
  - impact on filters
  - candidate analytical techniques to determine experimental conditions (e.g., temperature and electron density)

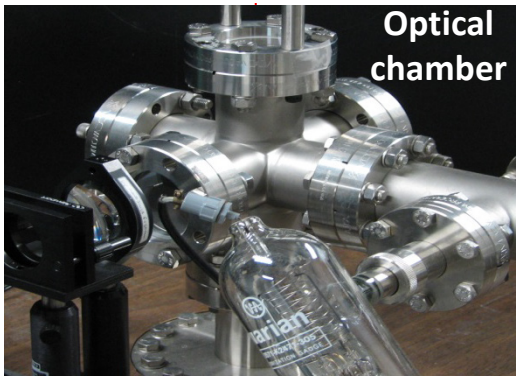
Graphite Studies:
HE modelers are interested in understanding the effect of carbon on temperature as a function of time.

- Time-resolved spectra of graphite in air
  - Temperature with and w/o extraneous carbon source compared at 10 µs (500 ns gate width)
  - Chemistry explored: Formation of atomic and molecular species with laser sparked air

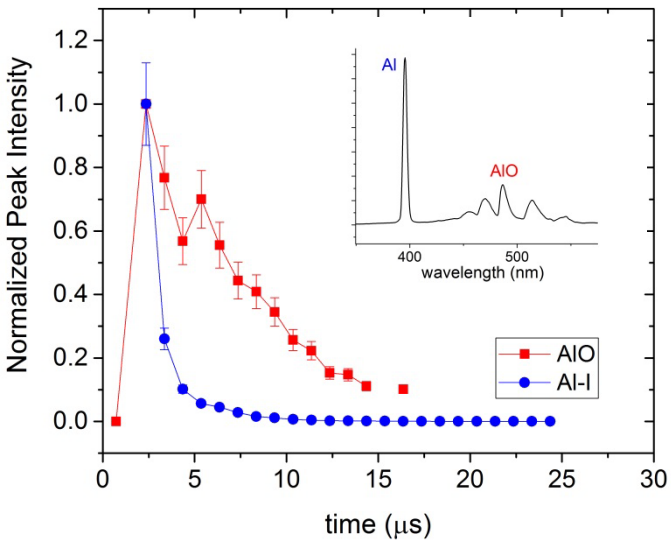
To our knowledge, this has not been done before.

STL Shadowgraph/LIBS System Design





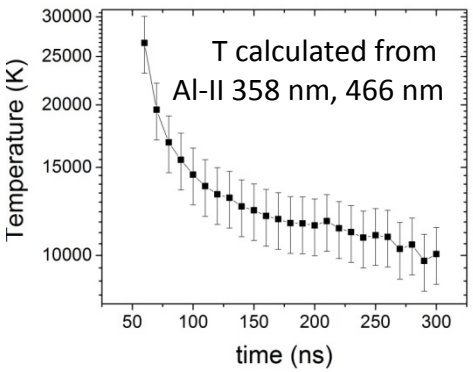
Al LIBS vs. Aluminized Explosive: Al-I and AlO



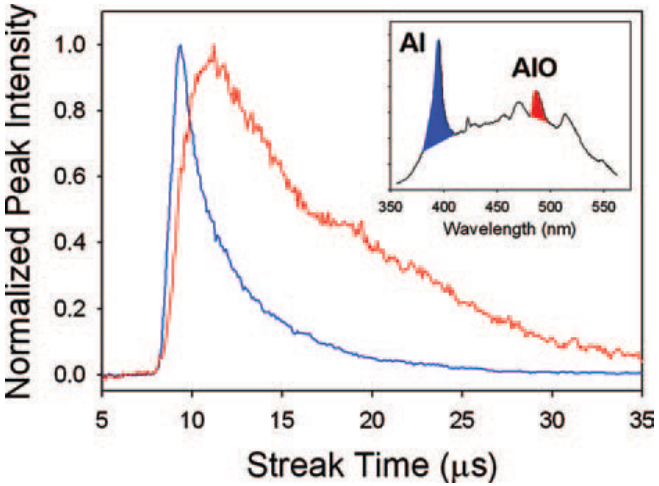
Intensity vs. time—Very similar, a few differences:

- AlO first appears ~2 μs with LIBS and 2 μs after first light with aluminized explosive (PBXN-113)
- Al-I (394, 396 nm, $3s^24s \rightarrow 3s^23p$) intensity decreases exponentially with LIBS and PBXN-113

LIBS temperatures (T) are on the order of 30,000 K at ~ 50 ns



Compare above data (LIBS) to confined 20 g charge of PBXN-113 in bomb-proof chamber. Qualitatively the same.



Carney, et al., *Rev. Sci. Instrum.*, 2006

$Al(g) + O_2 = AlO + O$ (1)

$Al(g) + O + M = AlO + M$ (2)

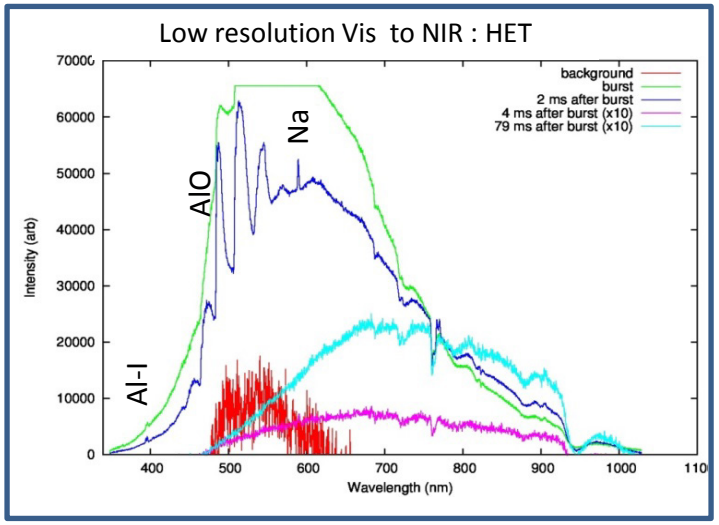
Reactions are in cooperation or competition with O recombination:

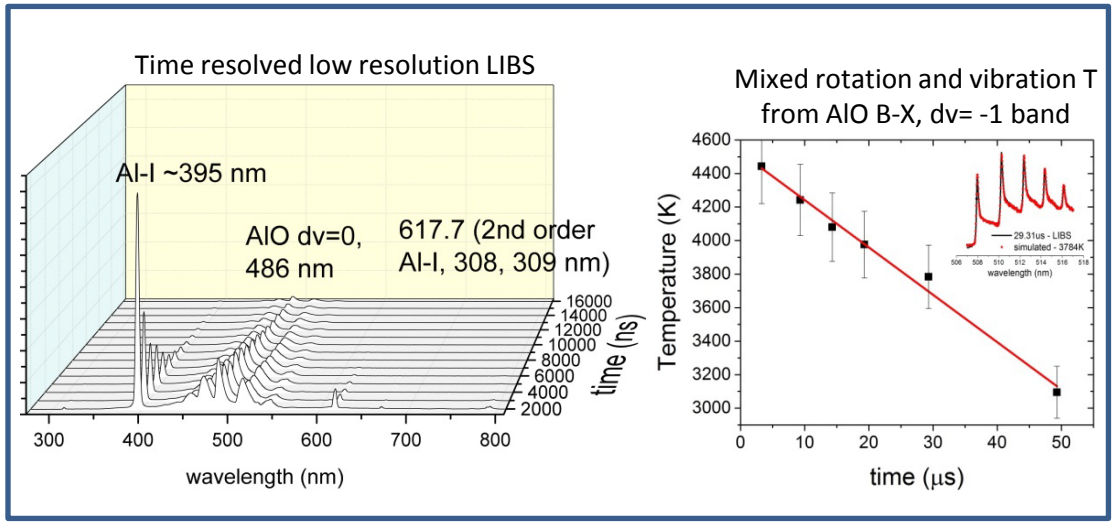
$O + O + M = O_2 + M$

AlO is formed from Al neutral and high T dissociates AlO.

As T drops to ~4300 K, eqns 1 and 2 both favor AlO formation.

LIBS vs. HET Comparison: Timing and AlO Temperature





Al-I: 394, 396 nm lines ($3s^24s \rightarrow 3s^23p$) and 308, 309 nm ($3s^23d \rightarrow 3s^23p$)

HET: 394, 396 nm—during burst and 2 ms later, strongest at 5 ms; gone by 10 ms

308, 309 nm—seen at 5 ms with UV spectrometer

LIBS: All observed in the ns to multiple μs range

Ionic emissions: Not observed at HET, but dominate at early times with LIBS (up to Al^{2+} in vacuum)

Al combustion:

HET: Apparent within 2 ms of initial explosive burst. AlO simulation temperature (T) ~6000 K.

Blackbody Ts initially ~6000+ K range, followed by T ~4500 K.

LIBS: AlO observed from ~2–16 μs. AlO simulation from high-resolution spectra: T ~4400 K initially.

Blackbody is absent.

Perhaps different time scales are due to oxygen throttling in the explosions, and smaller Al particles formed with LIBS.

Note: imaged spectra from ASI demonstrate spatial dependence on AlO density and temperature.

LIBS as complement to HE field diagnostic specifications, calibration, and analysis

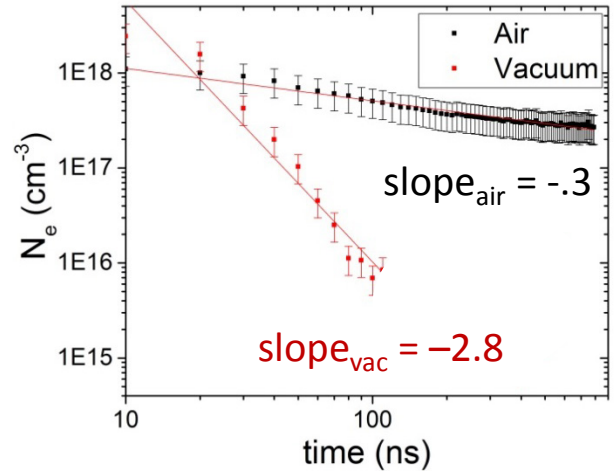
STL to field spectrometers and high-speed camera at FY16 HELIOS: UV and UV–solar blind emphasis for reduced blackbody and solar influence

- LIBS to inform camera filter selection and for field diagnostic calibration before fielding
- LIBS of Al as benchmark for other metals—to quickly determine relative lifetimes and emission strengths

LIBS indicates where to look spectrally. Better time and spectral resolution in the field may permit extraction of relevant parameters. UV examples:

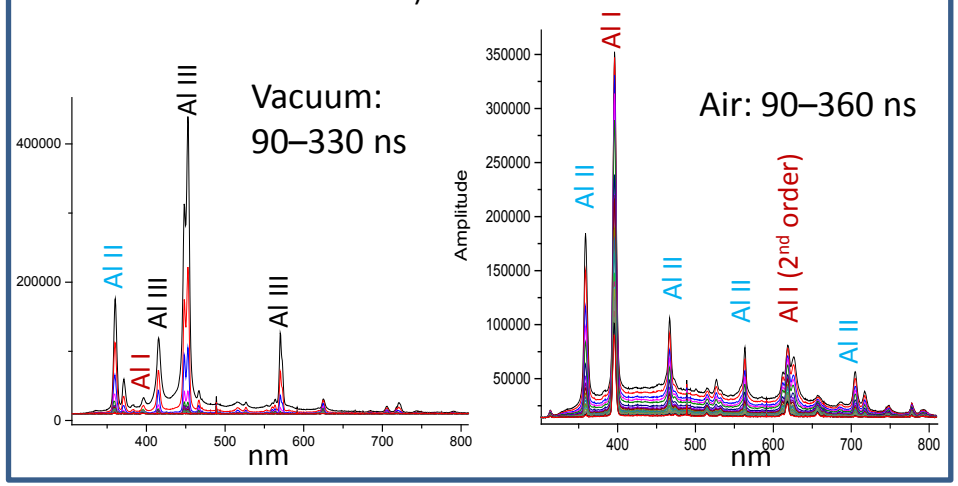
1. Electron density via Stark broadening (ex. Al-II at 281 nm)
2. Observation of ionic Al species of interest to RF modelers.
3. Temperature from pairs of species:
   - Al-I: 308.215 and 396.152 nm
   - Al-II: 263 and 281 nm
4. Temperature from molecular emissions:
   - CN (B-X ~388 nm); N_2^+ (B-X ~380 nm)

INFLUENCE OF PRESSURE ON ELECTRON DENSITY: Al-II 281 nm



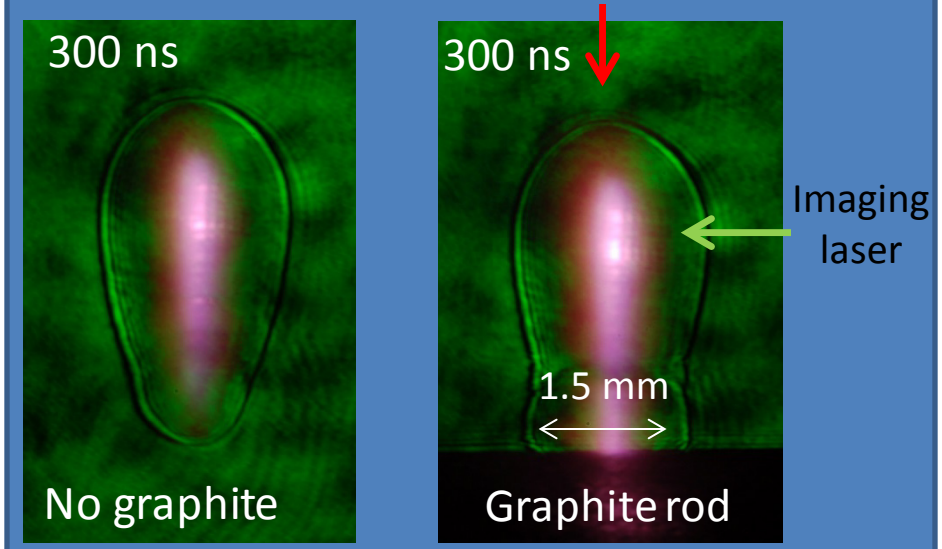
Free expansion in vacuum vs. plasma confinement in air

LIBS PERMITS HIGH RESOLUTION, HIGH SNR (5–10 "EXPLOSIONS" PER SECOND). IONS ID'D MAY INFORM RF MODELS



Graphite Studies

- Modelers want to know how graphite affects the temperature (T) of shocked air
- LLNL TNT model finds graphite is a dominant detonation product
- LIBS can ablate graphite while monitoring T and produces high-T air sparks

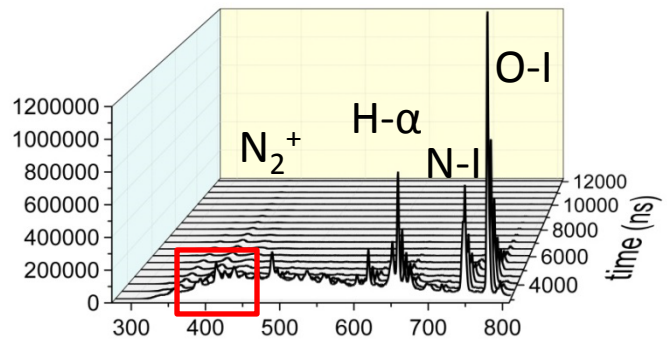


Air spark only

Focus at graphite rod

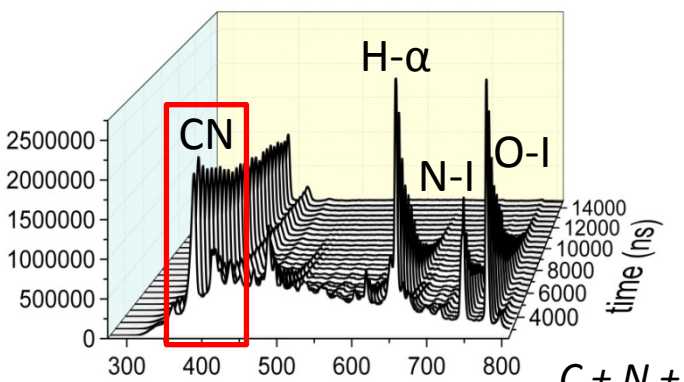
at 10 µs shock wave widths are ~13 mm, velocity ~1km/s

Sparked air—no graphite



majority N_2^+ vs. CN

Focus at surface



majority CN vs. N_2^+

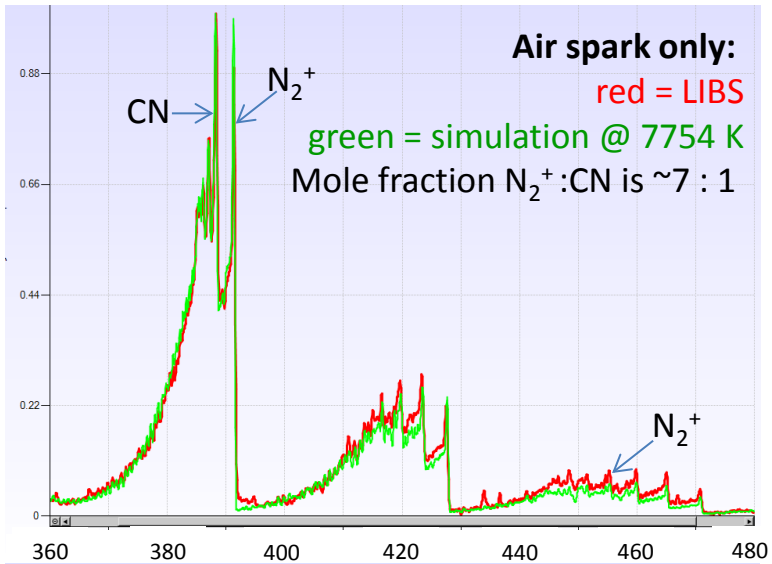
red box: region used for T determination at 10 µs

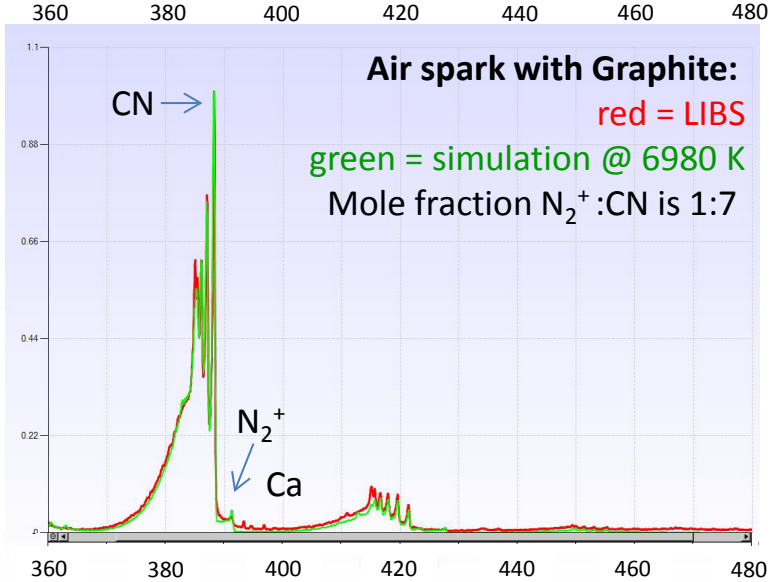
$C + N + M \rightarrow CN + M$

$C + N_2 \rightarrow CN + N$

Temperature Simulations: w/o and with graphite

(1064 nm ablation, ~60 mJ, 10 us delay, 500 ns gate width)





SPECAIR software calculates temperature (T) and concentrations of air plasma species from v-UV to mid-IR

Adding graphite increases CN concentration by ~50x and lowers the plasma temperature by ~700 K (assuming LTE)

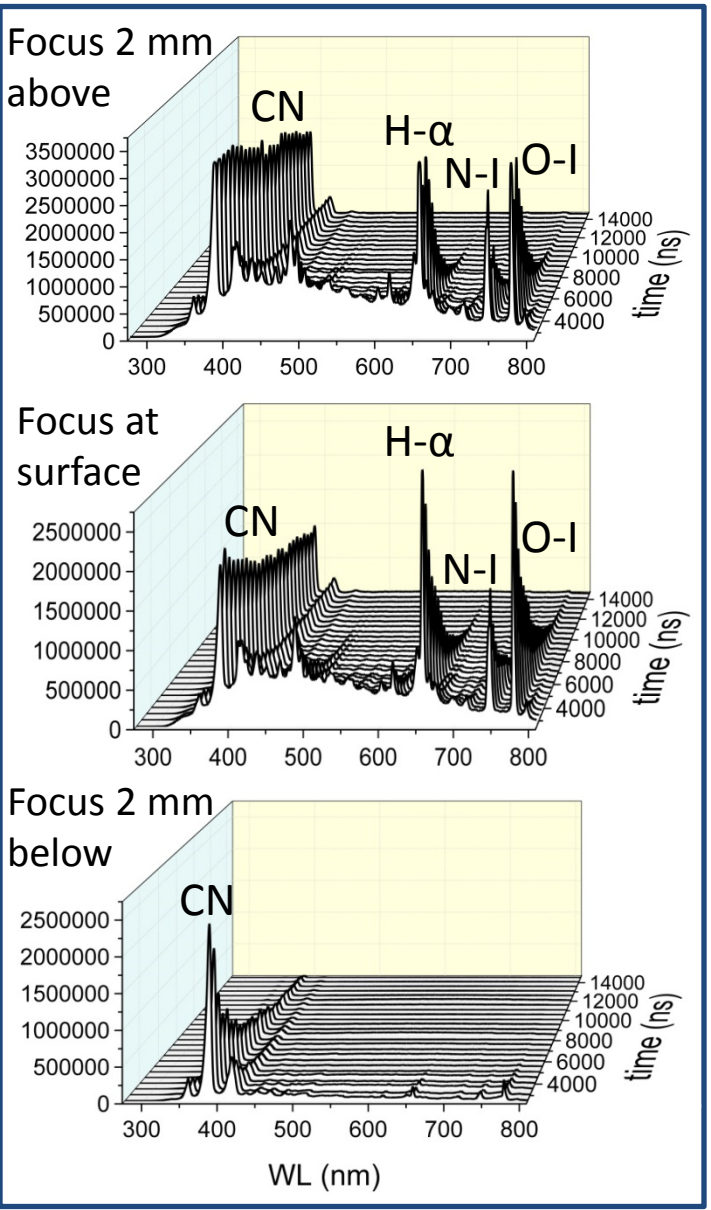
Hypothesis:

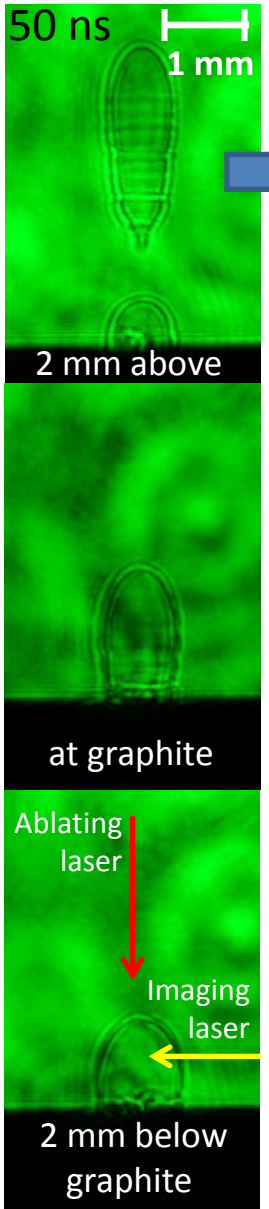
Incandescent emission may be cooling plasma

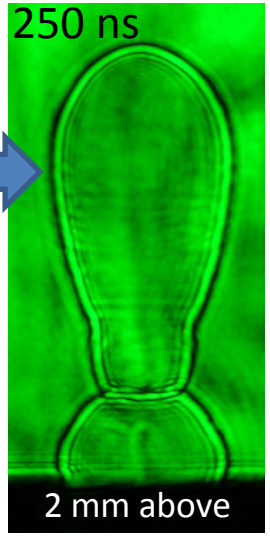
- Delayed firework-like emission—attributed to ejected hot particles or droplets formed by overheating of trapped gases in the layered graphite structure—was observed by ICCD for graphite in vacuum (Harilal, *JAP* **110** [2011])

Air-Graphite Chemistry

Position of the laser focus changes species decay







- Focus 2 mm above—and at—surface: breakdown of air and graphite
  - Significant and fairly steady CN emission
- Focus 2 mm below the surface: less air plasma—less axial elongation in shockwave and less O, N, H in spectra
  - Lower energy density in air and at surface (relative to focus at surface)
  - CN emission decays most quickly
    - CN may be more efficiently scavenged at, or near, the surface

Summary and Further Studies

LIBS complements HE field tests and modeling

- With LIBS of Al: atomic and molecular species are consistent with those observed in bomb-chamber and field
- LIBS can help drive field diagnostic needs and analysis
  - FY14 SDRD UV-Vis field collects positioned us for HELIOS collects in 2016
    - LIBS as a platform for field instrument calibration, and indicator of signatures (intensity and lifetime) likely observable in the field
  - Possible future studies:
    - Collection of shadowgraphs to complement ASI copper studies, and for comparison of Cu emission line intensities to Al
    - With ASI/Sandia, possible laser focus dependence of Al chemistry
- Focused graphite experiment:
  - With graphite we provide information on a question asked by modelers
  - Possible future studies:
    - Explore configuration and spatial dependence of temperature; time dependence as well
    - Mid-IR for CO, CO_2, NO, NO_2
    - Diamond ablation with corresponding chemistry and temperature analysis
    - Chemical kinetic modeling
    - Effect of Al on graphite/diamond air chemistry

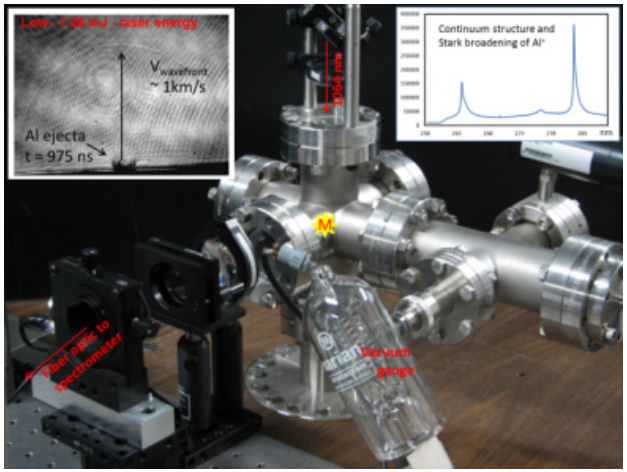
Impact

We showed that LIBS should be incorporated into our explosive testing work

NSTec LIBS capability further developed: increased knowledge regarding collection and analysis techniques

New collaborations started/developed for ongoing work:

- FY16 – HELIOS funding received for optical field work, based on FY14 UV-Vis results
- ASI (Rick Russo, Xianglei Mao), Sandia (Daryl Dagel, Olga Spahn)
  - Proposal requested for potential collaborative funding in FY16, leading to possible venture in FY17
- Allen Kuhl (LLNL modeler)

New interest from outside parties

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