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Higher Time-Resolution LASEM, Part II: Influence of Plasma Chemistry on the Laser- Induced Shock Waves of Explosives

by Jennifer L Gottfried and Brian C Barnes

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Higher Time-Resolution LASEM, Part II: Influence of Plasma Chemistry on the Laser-Induced Shock Waves of Explosives

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14. ABSTRACT The laser-induced shock waves and emission from five different military explosives were measured with an improved laser-induced air shock from energetic materials (LASEM) setup. The new system has a higher time-resolution than the original LASEM configuration and more advanced diagnostic capabilities to track the plasma and combustion chemistry for the excited materials. The materials investigated include trinitrotoluene (TNT), triaminotrinitrobenzene (TATB), cyclotrimethylene trinitramine (RDX), cyclotetramethylene tetranitramine (HMX), and hexanitrohexaazaisowurtzitane (CL-20). The laser-induced shock velocities strongly correlated to the measured detonation velocities of the explosives, enabling estimation of detonation performance with milligram quantities of material. Fewer laser shots were required to obtain comparable confidence intervals to those obtained with the original LASEM configuration. For the first time, automation of the shock wave position measurements with sufficient accuracy to enable discrimination of energetic materials was demonstrated. Alternative methods for fitting the propagation of the laser-induced shock wave were also investigated. Application of blast-wave models to the LASEM data provided new insights into the effect of the laser-induced plasma generated by energetic materials on the surrounding air and plume expansion. Time-resolved temperatures and near-infrared emission spectra have been reported for the excited explosive samples for the first time, providing insight into the reaction chemistry.					
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1. Introduction

This report is a continuation of Part I,¹ which discussed the experimental upgrades to the laser-induced air shock from energetic materials (LASEM) system and the influence of aluminum (Al) morphology on the laser-induced shock waves and chemistry. In that work, we confirmed that more Al nanoparticles (nano-Al) react on the microsecond timescale than micrometer-sized Al particles (micron-Al), and presented detailed spectroscopic information about the emission from the high-temperature chemical reactions of the excited Al samples (bulk Al, nano-Al, and micron-Al).

In addition to measuring the energy release rates of metallic (or metal-containing) samples,²⁻¹⁰ LASEM has been used extensively to estimate the detonation performance of conventional carbon, hydrogen, nitrogen, and oxygen (CHNO)-type explosives¹¹⁻¹⁶ and novel disruptive energetic materials.¹⁷⁻¹⁹ Here, we investigate the influence of higher time-resolution LASEM measurements on the correlation between the laser-induced shock wave velocities and reported detonation velocities of conventional military explosives. We also present new spectroscopic data on five explosives: trinitrotoluene (TNT), triaminotrinitrobenzene (TATB), cyclotrimethylene trinitramine (RDX), cyclotetramethylene tetranitramine (HMX), and hexanitrohexaazaisowurtzitane (CL-20). The molecular structures and formulas for the explosives are shown in Fig. 1, along with the number/types of chemical bonds, the average experimental detonation velocities reported in Gottfried¹² (corrected to the theoretical maximum density, or TMD), and the calculated detonation temperatures and heats of detonation from the thermochemical code CHEETAH.²⁰

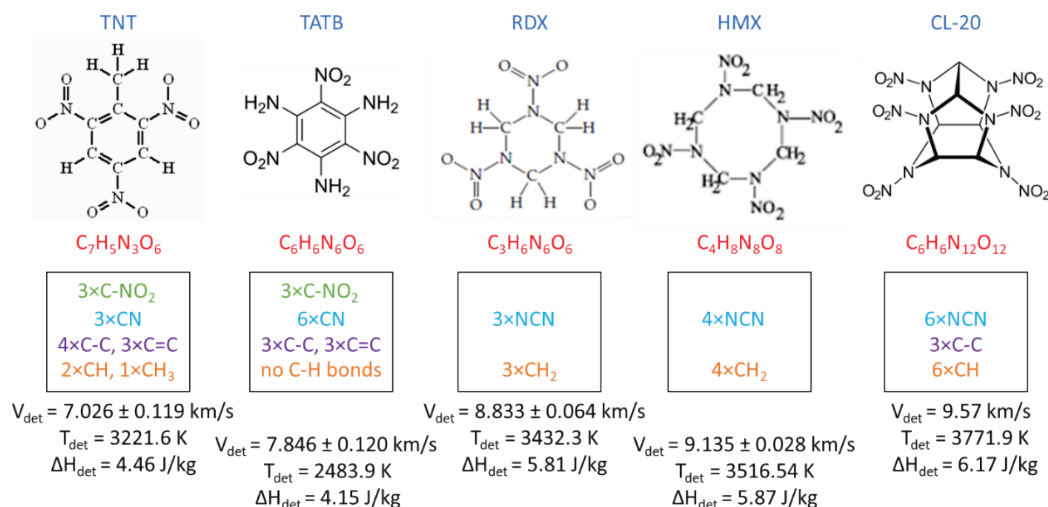


Fig. 1 Molecular structures and formulas for the five explosives used in this study (TNT, TATB, RDX, HMX, and CL-20). The number and type of chemical bonds are shown in the boxes; the average detonation velocities measured from large-scale testing (corrected to the TMD)¹² and calculated detonation temperatures and heats of detonation²⁰ are also shown.

2. Experimental

2.1 Sample Preparation

The samples were prepared as previously described for other LASEM experiments.^{11,12} The TNT, TATB, RDX, HMX, and CL-20 were obtained from colleagues at the US Army Combat Capabilities Development Command (CCDC) Army Research Laboratory (ARL). Each explosive was spread onto double-sided tape affixed to a 75- × 25-mm glass microscope slide (Fig. 2). Table 1 lists the amount of material added to each slide and the approximate surface coverage prior to data collection. Excess material not bound to the tape was ejected off the slide after each laser shot; the size of the blow-off region depended on the explosive's properties (Fig. 2). Multiple slides were required to obtain 20 laser shots for the samples with the largest blow-off regions. All of the samples showed evidence of combustion following laser ignition (e.g., scorch marks), although sustained combustion reactions above the sample surface were only observed for some of the explosives (Section 3.2.4).

Table 1 Sample slide surface coverage for the explosive materials

Sample	Material mass (mg)	Est. slide coverage (mg/cm²)
TNT	20.0	2.5
TATB	11.3	1.6
RDX (Class 1) [slide 1]	28.5	4.5
RDX [slide 2]	16.9	2.6
HMX (Grade B, Class 1) [slide 1]	14.5	1.9
HMX [slide 2]	10.9	1.4
CL-20 [slide 1]	13.6	1.6
CL-20 [slide 2]	12.6	1.5

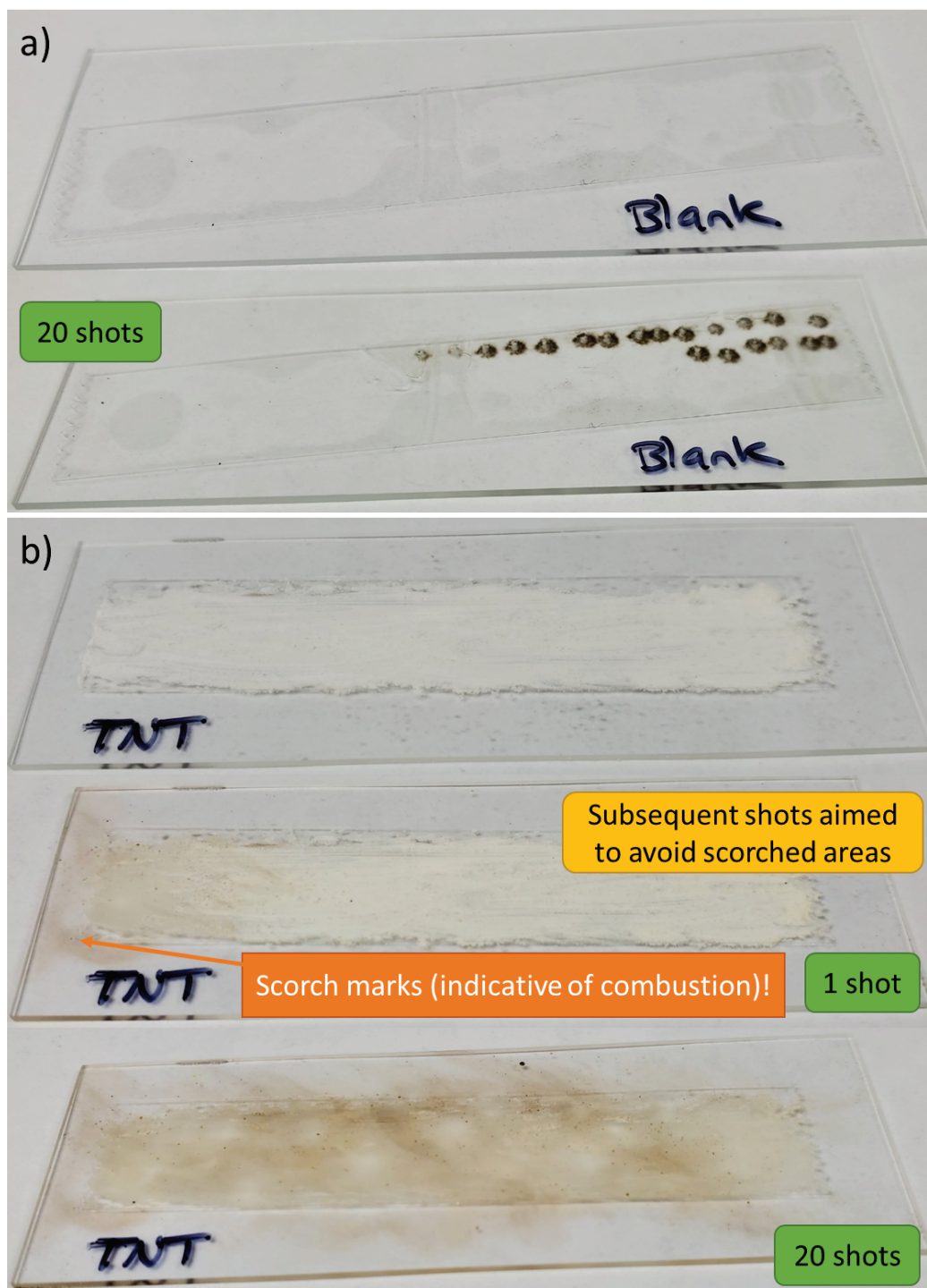


Fig. 2 Prepared sample slides including a) the blank tape substrate, b) TNT, c) TATB, d) RDX, e) HMX, and f) CL-20. The first slide in each series consists of the as-prepared slide; subsequent images in each series show the slide after one or more laser shots.

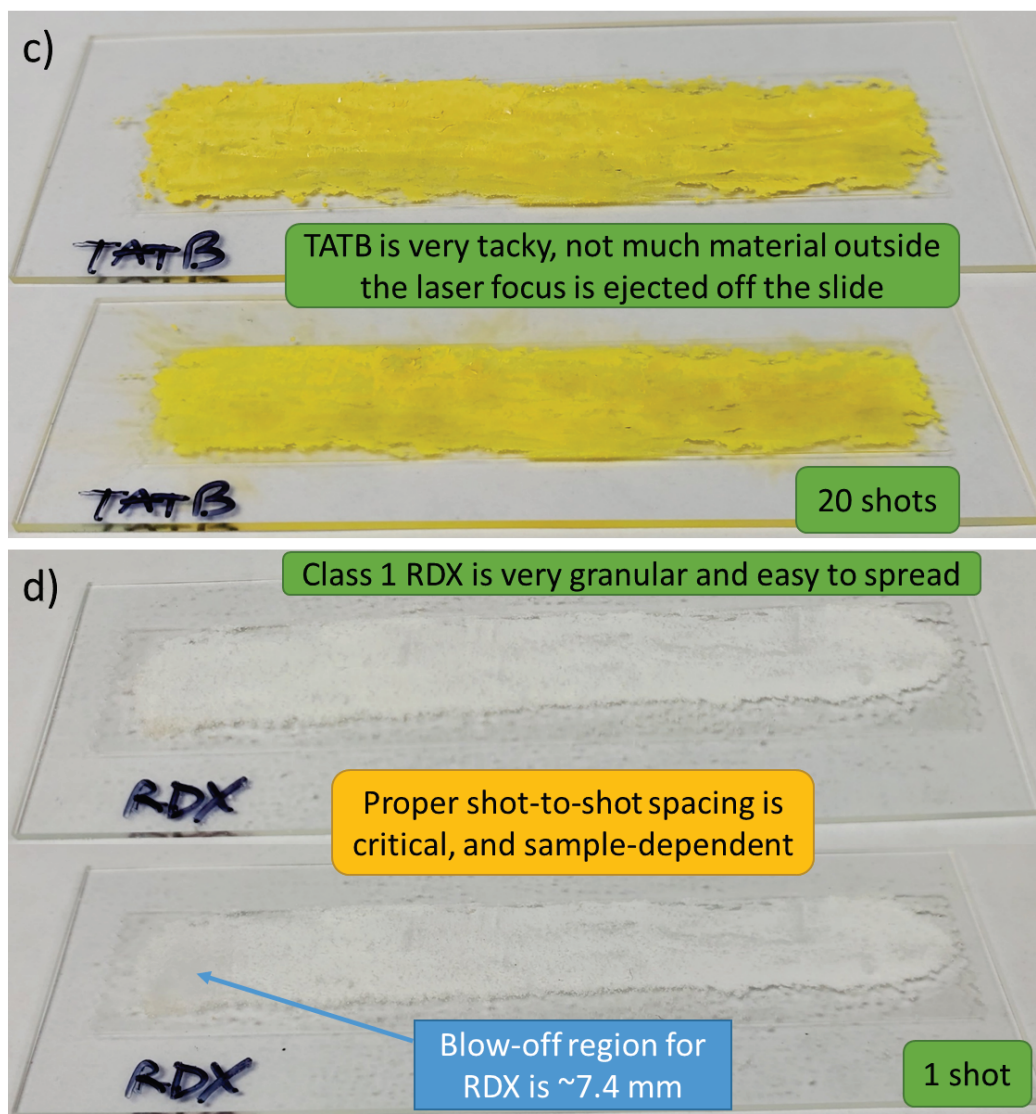


Fig. 2 Prepared sample slides including a) the blank tape substrate, b) TNT, c) TATB, d) RDX, e) HMX, and f) CL-20. The first slide in each series consists of the as-prepared slide; subsequent images in each series show the slide after one or more laser shots. (continued)



Fig. 2 Prepared sample slides, including a) the blank tape substrate, b) TNT, c) TATB, d) RDX, e) HMX, and f) CL-20. The first slide in each series consists of the as-prepared slide; subsequent images in each series show the slide after one or more laser shots. (continued)

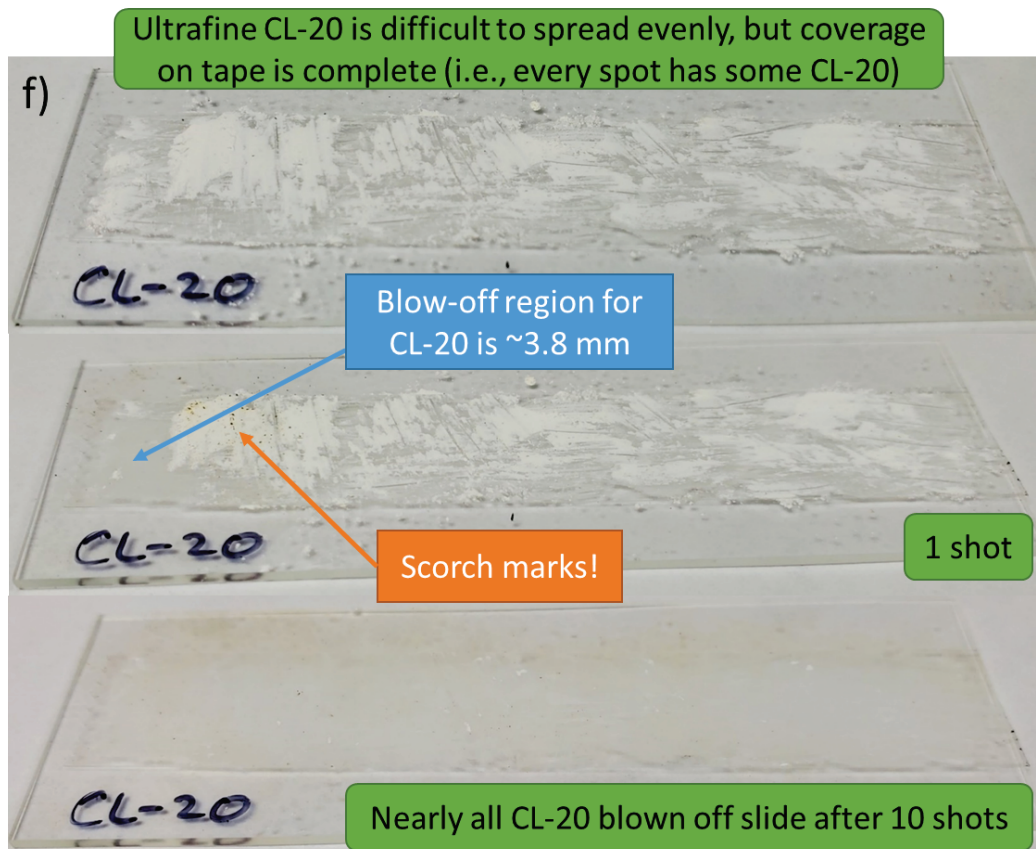


Fig. 2 Prepared sample slides, including a) the blank tape substrate, b) TNT, c) TATB, d) RDX, e) HMX, and f) CL-20. The first slide in each series consists of the as-prepared slide; subsequent images in each series show the slide after one or more laser shots. (continued)

2.2 LASEM Configuration

The experimental setup used to collect the sample data was described in Part I of this report series.¹ Following pulsed laser excitation of the prepared samples (20 laser shots each), numerous diagnostic data were collected for each sample to understand the influence of the high-temperature chemistry on the laser-induced plasma properties and the resulting material reactions. Table 2 summarizes the diagnostic methods and instrument settings used for this work.

Table 2 Experimental diagnostics, measured data, and instrument settings for the current study

Diagnostic method	Data collected	Instrument settings
High-speed schlieren imaging	Laser-induced shock wave propagation into air above sample	420,000 frames per second; 369-ns shutter; image size 832×16 pixels
High-resolution gated plasma emission spectroscopy	Laser-induced plasma emission in the 200–1000 nm range (0.02-nm resolution)	1.5- μ s delay, 10- μ s gate width; gain = 900
Time-resolved emission detection with two monochromator/photomultiplier tubes (PMTs)	Emission at 486.58 ± 0.02 nm and 656.100 ± 0.004 nm	Relative intensities calibrated with a Tungsten-Halogen light source; PMT gains = 1
Combustion emission spectroscopy	Combustion emission in the 230–900 nm range (0.25-nm resolution)	200- μ s delay, 4-ms gate width
Sequential emission spectroscopy	100 sequential spectra obtained using two linked spectrometers, from 200 to 1100 nm (1.4-nm resolution) and from 1000 to 2500 nm (8.9-nm resolution)	1.5- μ s delay, 1.050-ms gate width from 200 to 1100 nm and 500- μ s gate width from 1000 to 2500 nm
Time-resolved infrared emission detection	Integrated infrared emission (900–1700 nm)	Gain = 3×10^3 (Blank, CL-20, TATB, RDX, HMX); gain = 3×10^2 (TNT)

2.3 Shock Wave Detection Algorithm

Shock wave detection is performed using a Python script that executes both image preprocessing and a set of custom heuristics for shock front location. Initial work developed a one-dimensional (1-D) convolutional neural network (CNN) with supervised learning for front detection. While that model identified trends correctly, it was not precise enough for regular use. Building upon the basic idea of how the 1-D CNN works, the final model described in this section works to analyze intensity gradients within moving windows and constrain detection of the shock front by relevant physics: the shock front must move forward over time. To both simplify analysis and reduce noise, the image analysis is performed on a 1-D reduction of the raw camera image, averaging pixel values across the narrow (16 pixel) dimension. In the following subsections we describe the process in detail.

2.3.1 Preprocessing

The raw images associated with a single shot are accumulated in pandas Series within a DataFrame, using the imageio library. Images are read in as numpy arrays composed of signed 32-bit integers, as unsigned integers may cause problems for

background subtraction in a later preprocessing step. The images include a range of pixels near the sample stage and laser-induced plasma that will never be relevant for automated shock front detection and have exceptionally high intensity (100 pixels). They also include an area at the far end that is generally irrelevant to the shock-fitting methodology (60 pixels). For all images (or “frames”), those front 100 and tailing 60 pixels are removed by slicing the numpy arrays. The last five frames of a shot are also discarded. After the frames are thus collected, a background (pre-shot) frame is subtracted from all the other frames. This serves to reduce noise associated with static errors (e.g., per-pixel differences in the camera). After background subtraction, the image is averaged along the short dimension, resulting in a 1-D object. All traces for a shot are collected in a new array for analysis. As analysis will operate on intensity gradients, we rescale data using a `MinMaxScaler()` from `scikit-learn` to ensure uniform dynamic range among traces.

2.3.2 Analysis

A rolling window function is constructed with user-defined window. For convenience in reproduction, this function is shown in the following:

```
def rolling_window(a, window):
    shape = a.shape[:-1] + (a.shape[-1] - window + 1,
window)
    strides = a.strides + (a.strides[-1],)
    return np.lib.stride_tricks.as_strided(a, shape=shape,
strides=strides)
```

During analysis, we discovered that only the first 470 elements of the previously preprocessed traces were necessary for analysis (depending on the frame, far fewer may be needed), so the preprocessed traces are further sliced. Analysis is performed on each trace with a rolling window of five pixels. Within each window, a first-degree polynomial fit (i.e., a linear fit) is performed. If the slope of that line is less than 0.1 (a user-adjustable parameter), a “hit” is recorded as a possible shock front location. If multiple shock front locations are recorded for a single trace, then the location most forward in the frame (farthest possible travel) is selected. This ensures the primary shock front location is identified instead of a secondary shock or the plasma bloom border. If no shock front location is recorded in a trace, that frame is not used for subsequent analysis of shock wave velocity. For analysis and conversion to metric, unit conversions are performed through accounting for a sample stage base height of 86.9555 pixels and a conversion factor of 0.082090764 mm/pixel. For each shot, the per-trace shock front locations may then be fit to whatever functional form desired for estimating shock front velocity.

For quick inspection of algorithm performance during development, we also visualized the shock front position detections overlaid on sequences of trace data

using the Python Imaging Library. An example is given in Fig. 3 for the first 424 pixels of 66 traces within a shot.

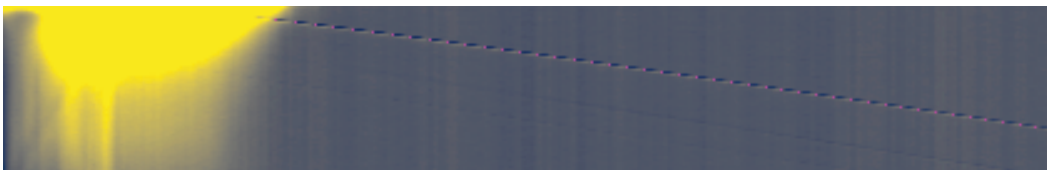


Fig. 3 424×66 pixel image (125% magnified) of aggregated 1-D trace data colorized by intensity for a shot. Pink pixels show automated shock front detection. “Time” goes from top (first trace) to bottom. The shock front travels from left to right.

While the shock front detection is robust at most early and all later times, it may miss the detection of a shock front at very early times when the plasma bloom is still extremely intense. For those initial frames, manual human labeling of shock front location (if it is indeed possible to detect) is still required. But with a high-speed camera, automated shock front detection may remove 95+% of human work for shock front labeling.

3. Results

3.1 High-Speed Imaging of Laser-Induced Shock Waves

3.1.1 High-Speed Video Snapshots

Figure 4a shows the first three images from high-speed video of the blank tape substrate and five explosives. The images are cropped and the ones with the green background had the brightness increased 60% to make it easier to see the laser-induced shock wave once it exited the plasma region. Note the camera focus is placed in front of the plasma, which enhances the visualization of the shock wave but defocuses the plasma emission. For higher-performing explosives such as RDX and CL-20, the reacting material being ejected away from the surface can catch up to the laser-induced shock wave, significantly distorting the shock wave, as shown in Fig. 4b. This typically only occurs for less than 10% of the laser shots from materials that exhibit this phenomenon, but does make it more challenging to measure the shock positions for those shots. More commonly, a small bubble or distortion in the expanding shock wave near the laser-beam path can be observed in the earliest frames (Fig. 5). For these shots, micro-plumes of reacting material can sometimes be observed in this region.

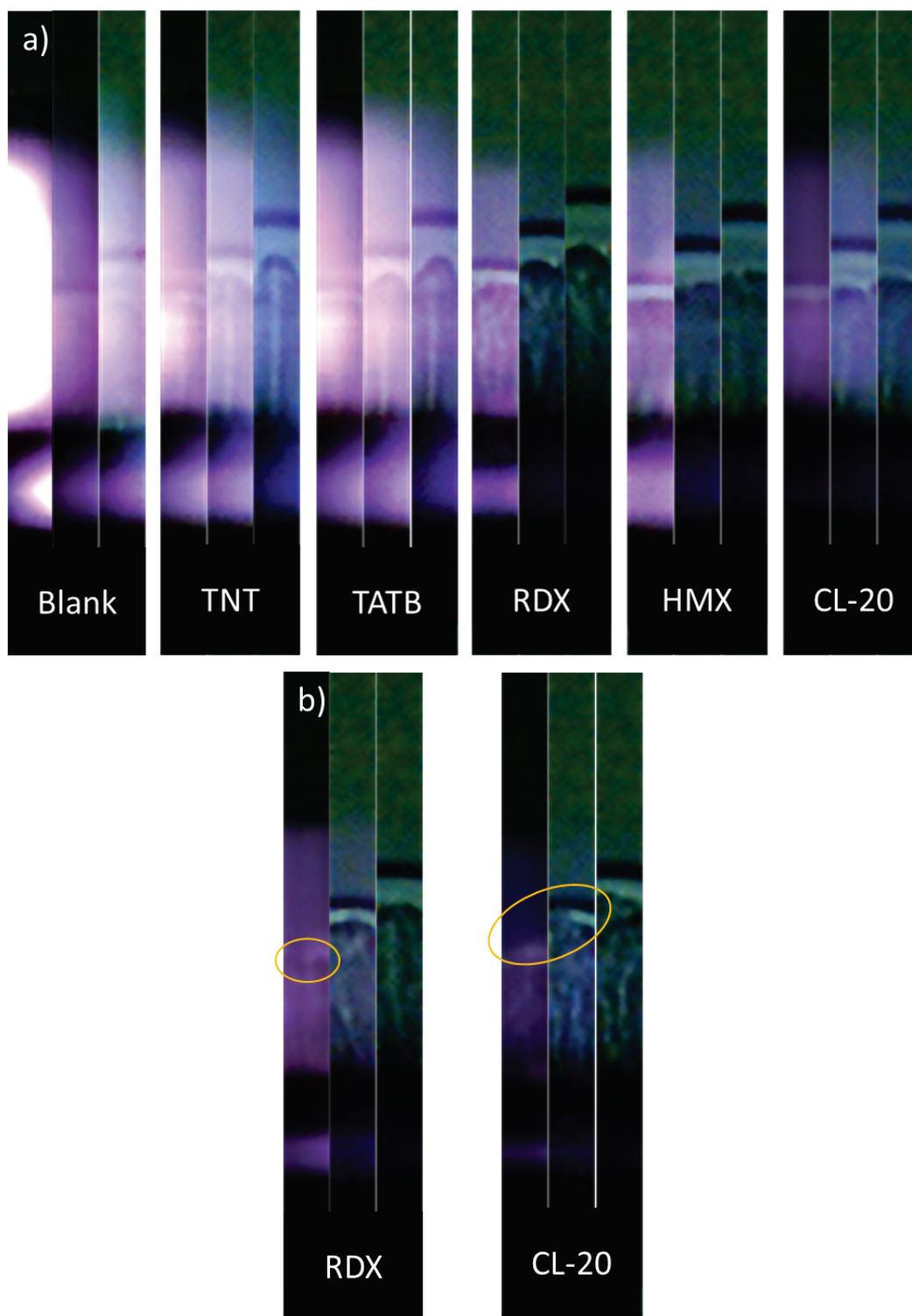


Fig. 4 High-speed video snapshots of the laser-excited blank tape substrate, TNT, TATB, RDX, HMX, and CL-20 showing the first three frames (0, 2.38, 4.76 μ s) for a) representative laser shots and b) examples of laser shots resulting in a distorted laser-induced shock wave.

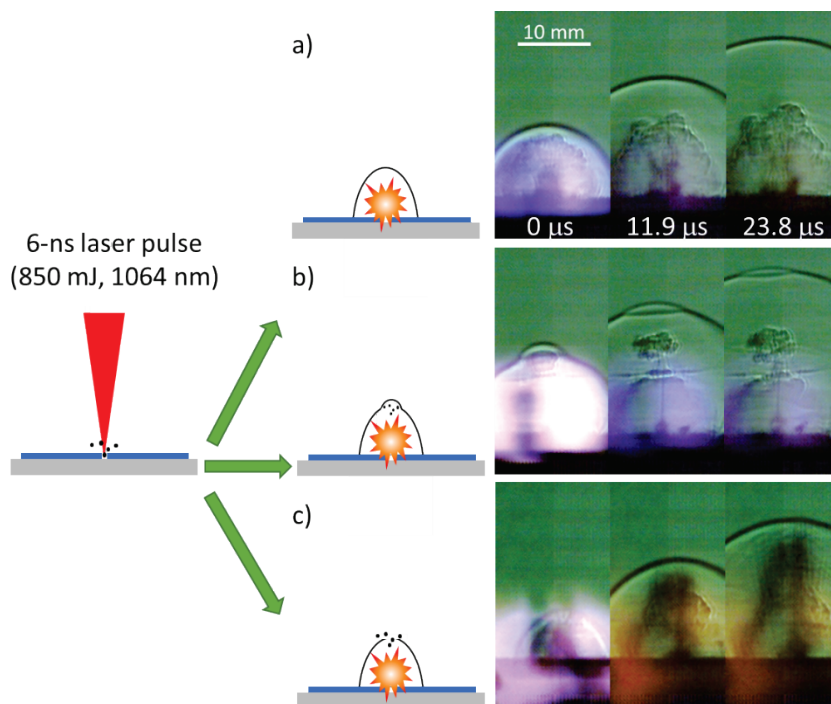


Fig. 5 Examples of laser-induced shock wave propagation following pulsed laser excitation and plasma formation: a) typical hemi-spherical shock wave expansion (which is elongated in the direction of the laser beam at very early times before becoming more symmetrical), b) shock wave bubble caused by micro-plume of reacting material in the path of the laser beam, and c) distortion or breakup of the shock wave at early times due to ejected particles catching up to the shock wave. Snapshots are from previous studies of the novel explosives a) BTNPM,¹⁴ b) and MAD-X1,¹⁴ and c) PETN drop-cast on a nanoporous silicon wafer.³

As previously observed,¹¹ the more energetic CHNO explosives produce less-intense, shorter-lived plasma emission (Fig. 4). McMullan²¹ determined that because the more energetic plasmas reach higher temperatures, heat loss to the surrounding environment is accelerated—resulting in shorter plasma lifetimes. Another possible contribution to this phenomenon is that the faster-reacting energetic materials generate detonation products such as CO, CO₂, H₂O, NO, and NO₂ more rapidly. These species do not emit light in the ultraviolet (UV) or visible (VIS) wavelength regions, unlike the excited atoms, ions, and small molecular species such as diatomic carbon (C₂) or cyano radical (CN) (see Section 3.2.1).

3.1.2 Comparison of Manual and Automated Shock Wave Positions

Figure 6 compares the distance traveled by the laser-induced shock wave into the air above the sample surface as a function of time, as measured for TNT using the original LASEM setup¹¹ and the current, higher time-resolution configuration. The number of data points increases significantly with the higher frame rate setting on the camera, so many more images (Fig. 4) have to be analyzed for each laser shot. For the first time, we were able to use an automated edge-detection algorithm as

described in Section 2.3 to measure the position of the laser-induced shock wave for the majority of the frames in the high-speed video. Unfortunately, at early times the emission from the laser-induced plasma obscures the shock wave such that the algorithm is not able to determine the shock position. However, by carefully adjusting the brightness and contrast, the shock position in these frames can be measured manually as long as the camera sensor was not saturated (e.g., as in the first frame of the blank video in Fig. 4a).

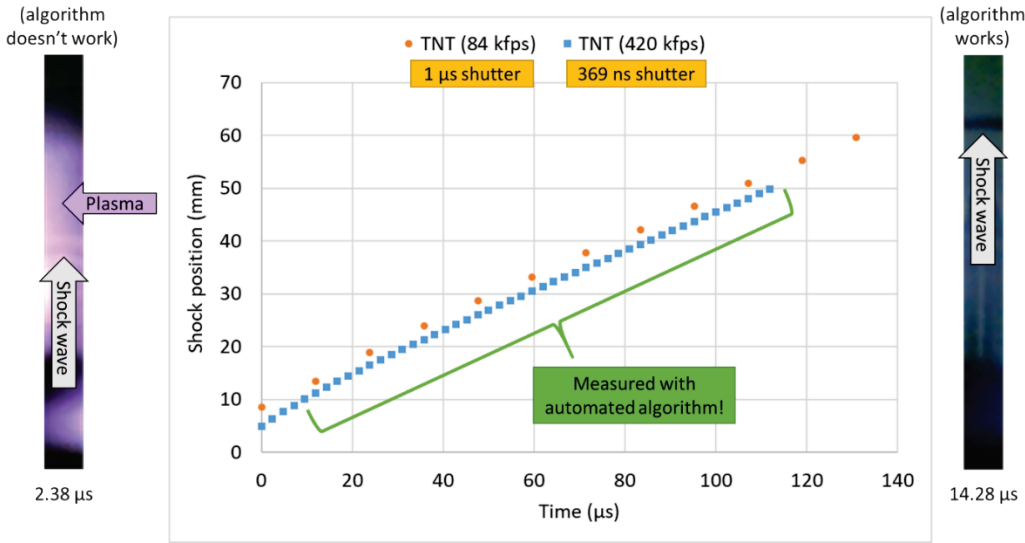


Fig. 6 Comparison of the laser-induced shock wave position above the sample surface vs. the time after the laser pulse for the original LASEM calibration (orange circles) and the current, higher time-resolution study (blue squares). An edge-detection algorithm was used to determine the shock wave position once the shock wave exited the plasma region.

While we previously attempted to use various edge-detection algorithms to automate the shock wave analysis, we found their accuracy was not sufficient for discrimination of energetic materials based on their laser-induced shock velocities; that is, the measurement error was too large. Figure 7 compares the measured laser-induced shock wave position in the air above the sample versus the time after the laser pulse for the blank tape substrate (a) and CL-20 (b). The manually measured shock wave positions are denoted by the diamond markers, while the positions determined by the edge-detection algorithm are denoted by the triangles. Note that the shock wave positions were manually measured out to only 28.6 μs for the CL-20. For most laser shots, the difference in manually and automatically measured shock wave positions (where the overlap occurred) was less than $\pm 1.5\%$ and was highest for the earliest shock positions (i.e., closest to the plasma emission). The manually measured shock position was typically slightly lower than the automatically measured shock position. For both the manual measurements and the edge-detection algorithm, the shock position was determined by the part of the

shock wave closest to the sample surface, that is, at the interface of the white and black bands (Fig. 4). We hypothesize that this very small difference between manual and automated shock front locations is due to the choice of intensity gradient threshold in the automated algorithm, and may be resolved through adjustment of that parameter or normalizing intensities per-window during the automated analysis. As the difference is very small and generally systematic, this is deferred to future work.

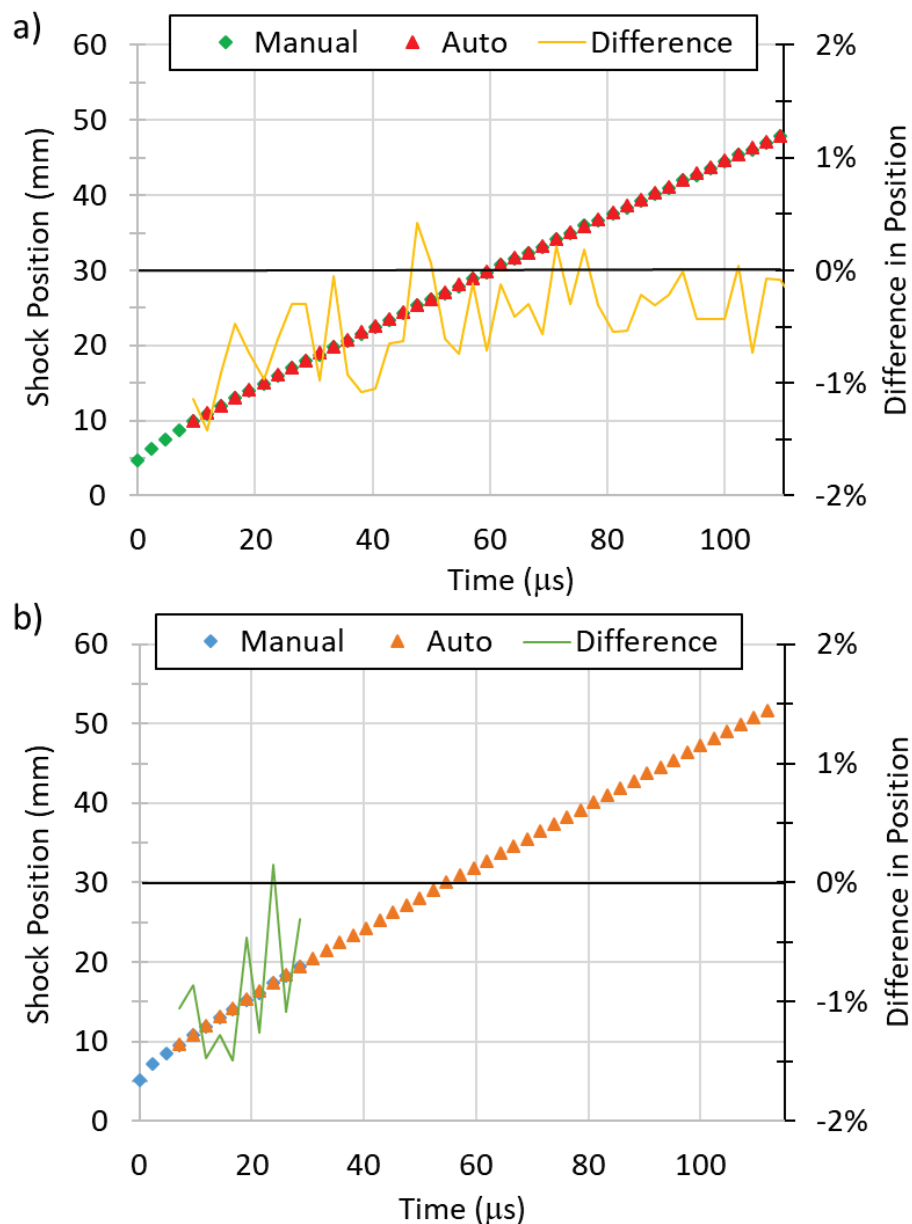


Fig. 7 Comparison of the laser-induced shock wave position in the air above the sample vs. time, based on the manually measured shock wave positions (diamonds) and those determined by the automatic edge-detection algorithm (triangles) for a) the blank tape substrate and b) CL-20. The percent difference in shock positions is also shown where the data overlap.

3.1.3 Comparison of Shock Wave Positions for Each Sample

The laser-induced shock wave positions determined by the edge-detection algorithm for each laser shot were combined with the manually measured positions at early times. Figure 8 shows the average laser-induced shock position for each sample along with the 95% confidence intervals. At full scale, the error bars are too small to see and the samples appear nearly indistinguishable. During the first 10 μs , however, it is clear the laser-induced shock wave for the blank tape substrate expands into the air more slowly than the shock waves for the explosives. Depending on the sample (and laser parameters, which are constant here), it takes approximately 8 μs for the laser-induced shock wave to pass through the plasma region. During this time, the shock wave is influenced by the chemical reactions in the plasma.

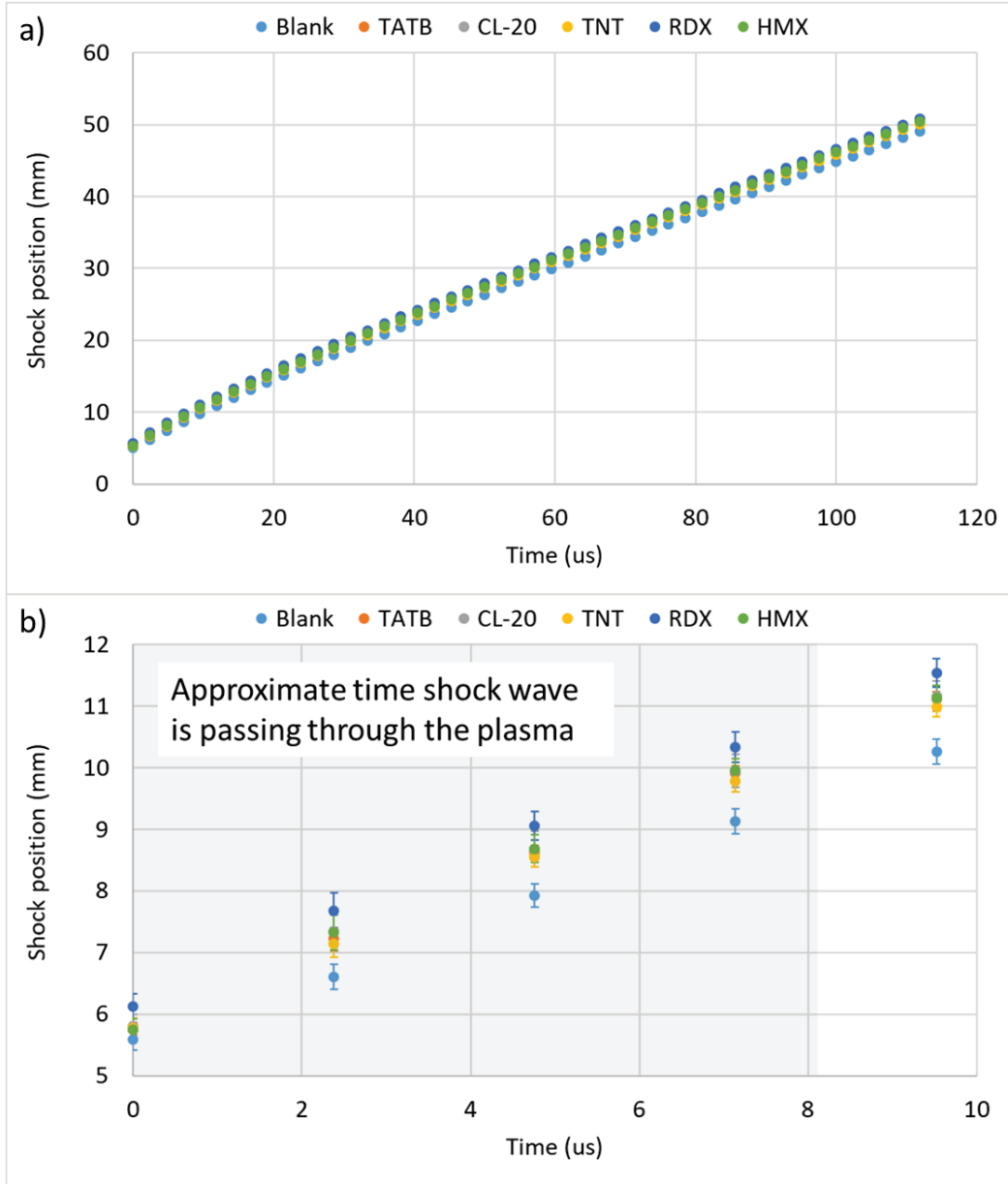


Fig. 8 Laser-induced shock wave position as a function of time for the blank tape substrate and five explosives at a) full-scale and b) the first 10 μ s. The shock wave takes approximately 8 μ s to pass through the plasma region, depending on the sample. Error bars are 95% confidence intervals.

The first shock wave position for the RDX sample started consistently higher than for the other samples (which were not statistically different), although the reason is not clear. Interestingly, the distribution of shock positions for RDX was Gaussian, while the histogram for all other samples had the highest frequency for the smallest shock positions (Fig. 9). Possible causes for the scatter in the first shock wave position include:

- jitter in the camera timing (the camera continuously buffers until the trigger signal is received),
- shock position measurement errors (increased by shock distortion or strong plasma emission),
- differences in the laser–material interaction (stochastic),
- differences in the amount of material ablated into the plasma (previously determined to be independent of residue thickness, within the measurement error⁴), or
- differences in the chemical reaction kinetics of the ablated sample (would matter the most for the fastest-reacting materials).

The latter two contributions are the most likely explanation for the difference in the RDX shock wave behavior, since the other contributions should be similar for all materials. We note that the morphology and molecular structure of RDX and HMX are quite similar.

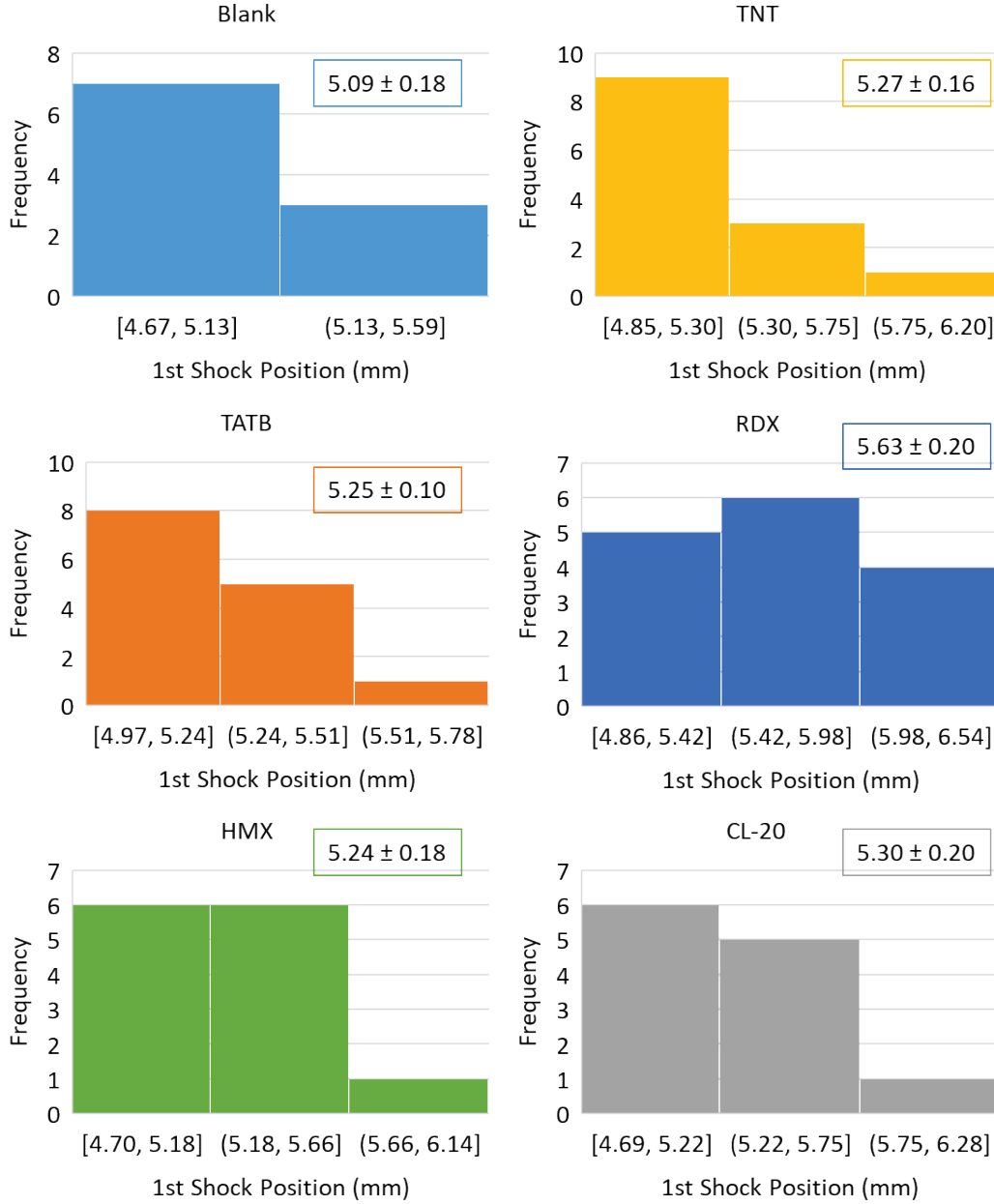


Fig. 9 Histograms for the first laser-induced shock wave position measured for each sample (20 laser shots). The average position and 95% confidence intervals are also given.

Figure 10 shows a closer look at the laser-induced shock wave positions during the passage of the shock wave through the plasma region. RDX was excluded from this plot since the shock wave position in the first frame is not comparable to the other materials. Although the error bars overlap for the samples, comparison of the shock positions shows that in the first frame the average TNT shock wave position is below only that of CL-20. But by the second frame, it is lower than TATB, HMX, and CL-20. This order stays the same after $4.76 \mu\text{s}$, but by $7.14 \mu\text{s}$ the HMX shock

wave has caught up to that of CL-20. In all cases, the shock wave position for the blank tape substrate is much lower than that of the explosives, and this separation increases with time as the chemical reactions of the explosives affect the shock wave propagation. These results support the hypothesis that the relevant chemical reactions that enable differentiation of energetic materials occur on the microsecond timescale, after the laser-induced plasma has started cooling and recombination reactions begin. Additional evidence was provided in Part I¹ of this report series, where the aluminum monoxide emission from oxidation of the nano-Al sample was significantly higher than that of micron-Al on this timescale—resulting in higher laser-induced shock velocities for the nano-Al due to the faster exothermic chemistry of the more reactive nanoparticles.

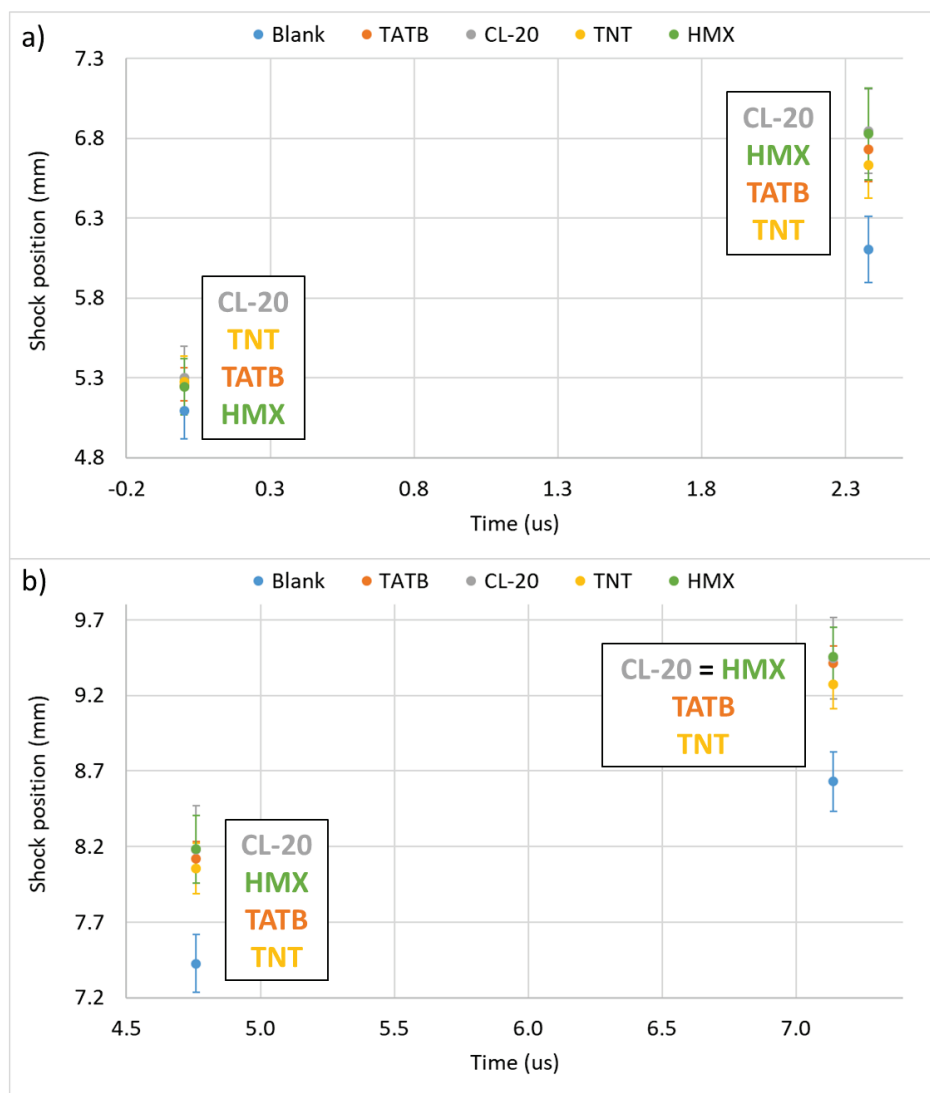


Fig. 10 Laser-induced shock positions as a function of time over a) 0–2.38 μs and b) 4.76–7.14 μs . The text boxes sort the TNT, TATB, RDX, and CL-20 in order of decreasing average shock wave position above the sample surface (from top to bottom).

In the original LASEM calibration,¹¹ we found that fitting the laser-induced shock velocities as a function of time rather than the laser-induced shock positions resulted in improved calibration results. The assumption was that effects such as the jitter in the camera timing and the propagation of error caused by taking the derivative of an imperfect fit to the shock position data (to determine velocity) were minimized by this approach. Figure 11 shows that the relative standard deviation (RSD) in the shot-to-shot measurement error is much lower for the laser-induced shock velocities (determined by the difference between the two previous shock positions at each time step) than the laser-induced shock positions. Lower RSDs make it easier to differentiate between energetic samples based on their calculated laser-induced shock velocities.

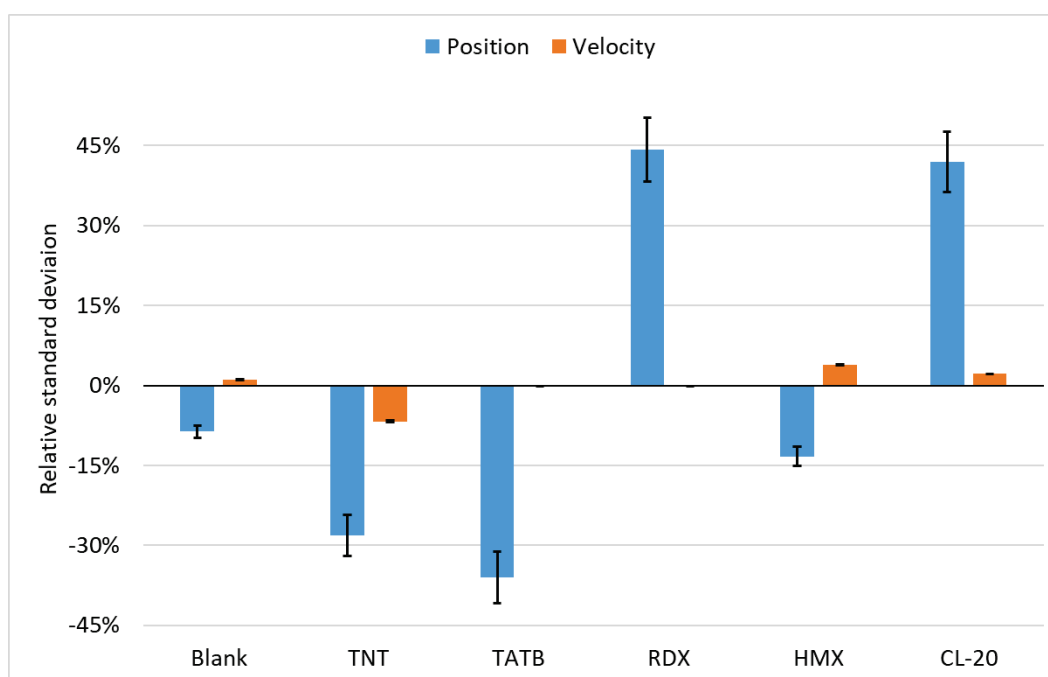


Fig. 11 RSDs of the average 95% confidence intervals for the position and velocity measurements for each sample over 20 laser shots (compared to the average values for the entire sample set). The RSDs for the average TATB and RDX laser-induced shock velocity confidence intervals are -0.1% and -0.2% , respectively.

We considered several methods for calculating the shock velocities directly from the measured laser-induced shock wave positions (Table 3). The “backward difference” method was used for the original LASEM calibration.¹² While the “central difference” method reduces the data scatter and increases the R-squared value (R^2) for the polynomial fit closer to the optimal value of 1 (Fig. 12), it also has the effect of significantly decreasing the first calculated shock velocity. For inert materials like the blank tape substrate (Fig. 12a), the difference in the resulting y-intercept (i.e., characteristic laser-induced shock velocity) is minimal. Energetic

materials like CL-20, on the other hand, have significantly smaller y-intercepts using the central difference method (Fig. 12b) and would be nearly impossible to distinguish from inert materials. While both the “backward difference” and “central difference” velocities are plotted with the “frame time” as the y-axis, the “midpoint difference” is plotted with the “midpoint time” as the y-axis. Thus, when the time between camera frames is constant (as in this work), there is little difference between the backward difference method and the “midpoint difference” method other than a shift to earlier times for the latter. This slight shift results in smaller y-intercepts, which could make distinguishing energetic materials more challenging. Based on these results, we once again used the backward difference method for calculating laser-induced shock velocities.

Table 3 Methods for calculating the laser-induced shock velocity

Frame time	Shock position	Backward difference	Central difference	Midpoint time	Midpoint difference
t₁	d ₁	...	...	...	...
t₂	d ₂	$(d_2 - d_1)/(t_2 - t_1)$	$(d_3 - d_1)/(t_3 - t_1)$	$(t_2 - t_1)/2$	$(d_2 - d_1)/(t_2 - t_1)$
t₃	d ₃	$(d_3 - d_2)/(t_3 - t_2)$	$(d_4 - d_2)/(t_4 - t_2)$	$(t_3 - t_2)/2$	$(d_3 - d_2)/(t_3 - t_2)$

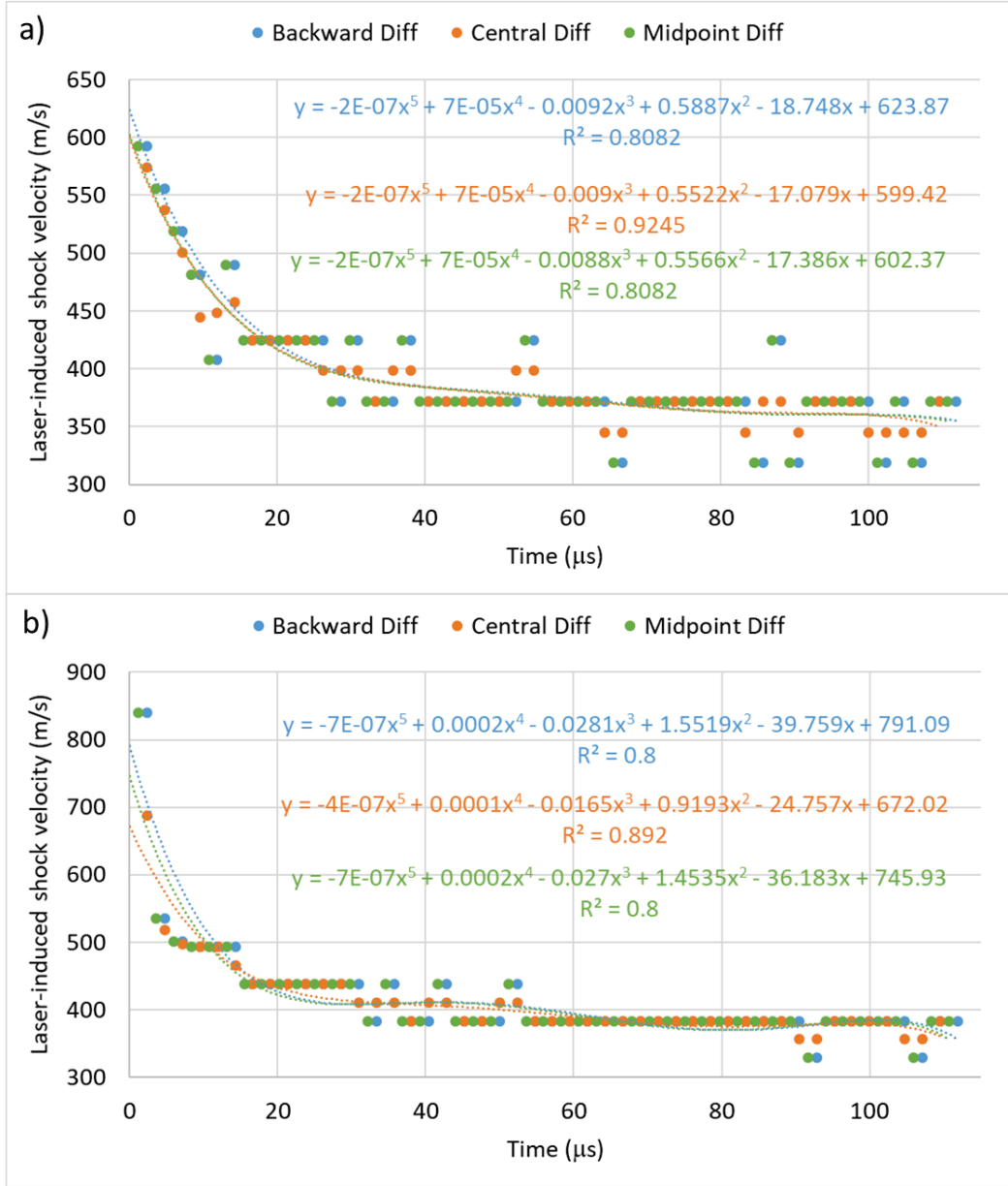


Fig. 12 Comparison of different methods for calculating the laser-induced shock wave velocity at each time step for the a) blank tape substrate and b) CL-20

3.1.4 Comparison of Shock Wave Velocities for Each Sample

Figure 13 shows the measured laser-induced shock velocities as a function of time for the blank tape and five explosives using either the original LASEM setup at 84 kfps or the current setup at 420 kfps. The higher time-resolution data show the increase in available data points to improve the fifth-order polynomial fit. However, the earlier time data at higher shock wave velocities increases the prominence of Runge's phenomenon of polynomial interpolation at later times—where the fit oscillates around the speed of sound in air. This effect is most severe for the more

powerful explosives, which have higher characteristic laser-induced shock velocities. It was not noticeable at the lower frame rates, or for inert materials such as the blank substrate, even at 420 kfps. In addition, the right side of Fig. 13 demonstrates that the fifth-order polynomial fit underpredicts the first data point for all samples at 420 kfps. Thus, it is clear that the curve-fitting procedure used for the original LASEM setup is not necessarily ideal for the higher time-resolution data; alternative fitting methods based on the current experimental settings will be explored in Section 3.1.5.

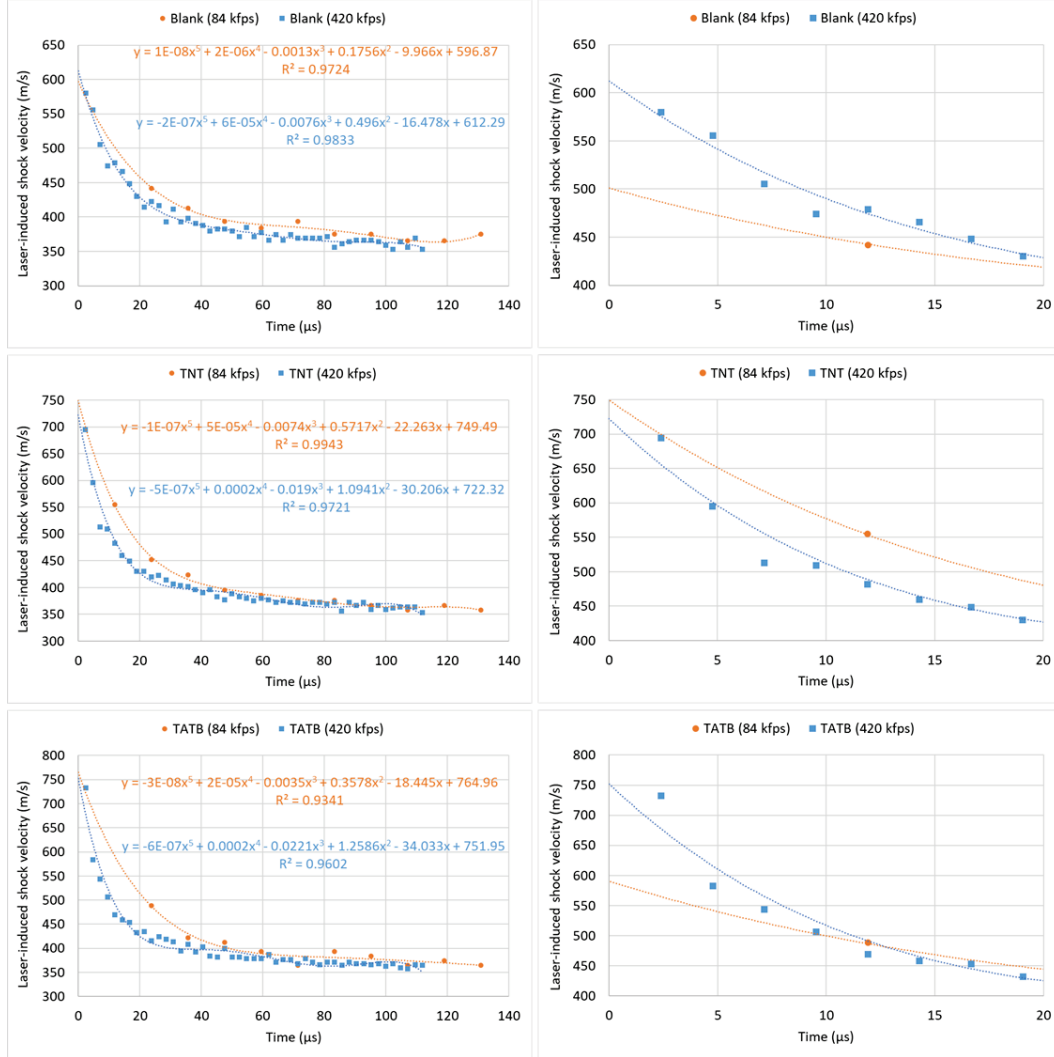


Fig. 13 Comparison of laser-induced shock wave velocities for the blank tape substrate and five explosives measured as a function of time at 84 kfps (original LASEM setup) and 420 kfps (this work). A zoomed-in view of the first 20 μs for each sample is shown on the right side of the figure.

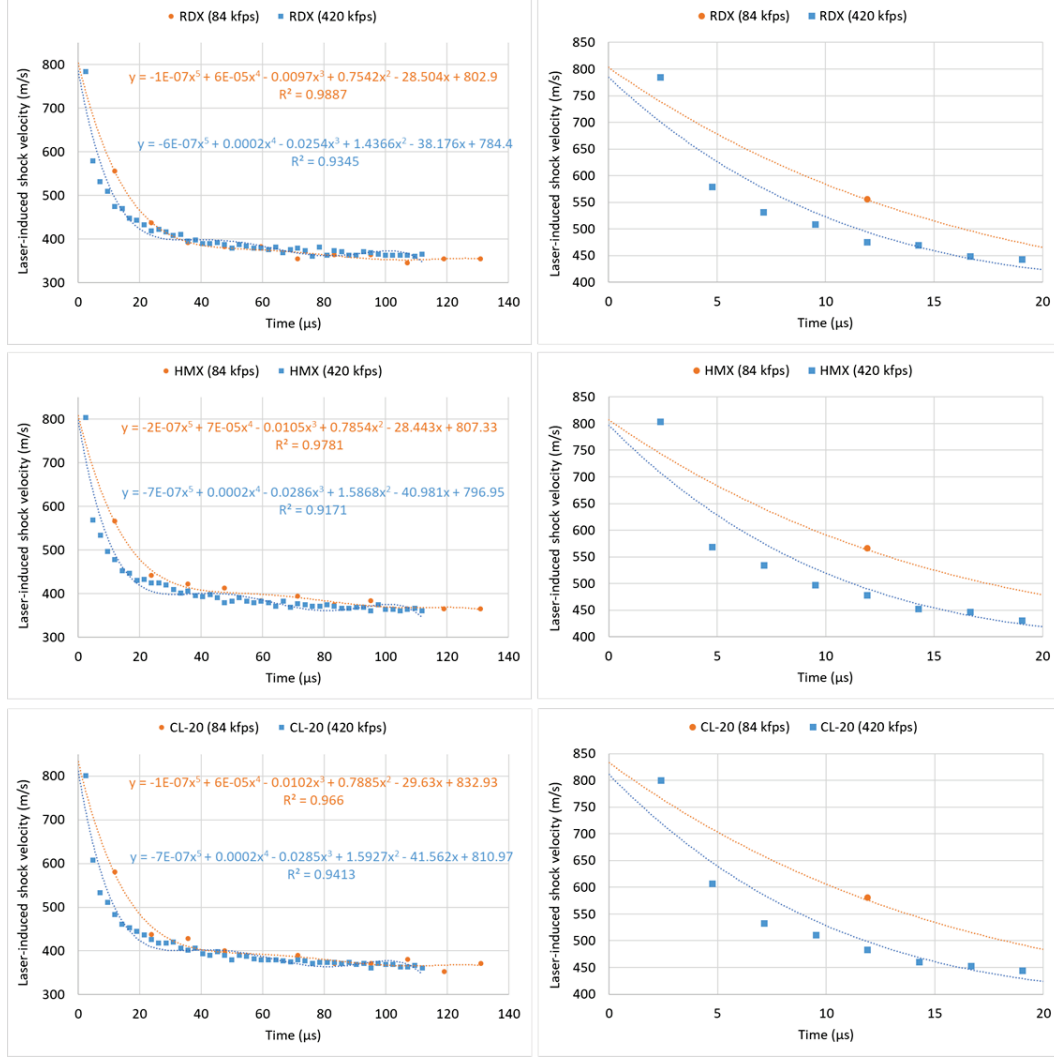


Fig. 13 Comparison of laser-induced shock wave velocities for the blank tape substrate and five explosives measured as a function of time at 84 kfps (original LASEM setup) and 420 kfps (this work). A zoomed-in view of the first 20 μs for each sample is shown on the right side of the figure. (continued)

Although the fifth-order polynomial fit is not as accurate for the higher time-resolution data, we fit the new data using the same procedure as in the original LASEM calibration to directly compare the results. As before, the average y-intercepts of the fits were defined as the characteristic laser-induced shock wave velocity for each sample. These y-intercepts were plotted against the average measured detonation velocities (V_{det}) for the explosives, corrected to the theoretical maximum density (TMD). The resulting linear correlation data are shown in Table 4. Error bars were determined from the 95% confidence intervals (based on 40+ laser shots for the 84 kfps data and 20 laser shots for the 420 kfps data). Comparable confidence intervals were obtained for the two data sets (Table 4), even though less than half the number of laser shots were used for the 420 kfps data—

suggesting a significant improvement in the precision of the data fitting compared to the lower time-resolution data. Although the characteristic laser-induced shock velocities were lower with the higher time-resolution data (except for the blank tape substrate), the linear correlation with the measured V_{det} from large-scale testing was even better than the original LASEM setup (Fig. 14). The difference in laser-induced shock velocities obtained from each of the setups was less than 3%. These data validate the strong correlation between the laser-induced shock velocities and large-scale detonation performance of explosives and confirms that the chemistry in the laser-induced plasma is similar to that which occurs in the chemical-reaction zone behind the detonation wave in bulk explosives.

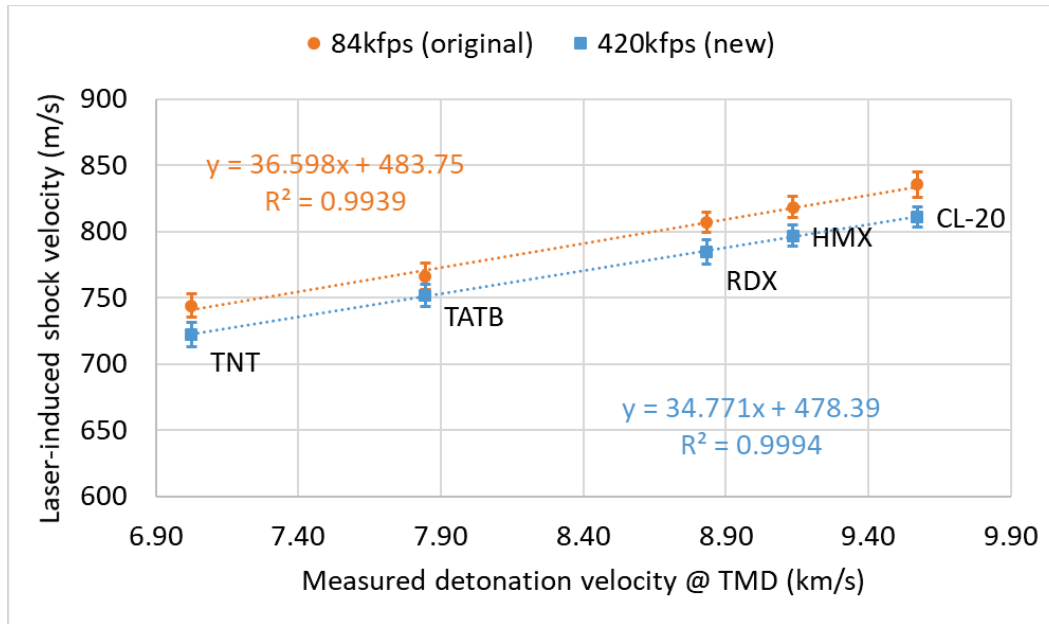


Fig. 14 Comparison of the calibration fit for the original LASEM setup at 84 kfps¹² (orange) and the new, higher time-resolution data (blue). Characteristic laser-induced shock velocities were determined from the y-intercepts of the fifth-order polynomial fits. Error bars are 95% confidence intervals.

Table 4 Characteristic laser-induced shock velocities for the blank tape substrate and five explosives compared to the calculated and measured detonation velocities

Sample	Laser-induced shock velocity @ 420 kfps (m/s)	Calc. V_{det} @ 420 kfps (km/s)	Laser-induced shock velocity @ 84 kfps (m/s)	Calc. V_{det} @ 84 kfps (km/s)	Diff. in laser-induced shock velocities	Ave. V_{det} @ TMD ^a (km/s)
Blank	612.29 ± 6.15	...	595.48 ± 9.46	...	-2.7%	...
TNT	722.32 ± 9.29	7.02 ± 0.27	744.08 ± 8.62	7.11 ± 0.24	2.9%	7.03 ± 0.12
TATB	751.95 ± 8.50	7.87 ± 0.24	766.14 ± 9.75	7.72 ± 0.27	1.9%	7.85 ± 0.12
RDX	784.40 ± 9.12	8.80 ± 0.26	806.83 ± 7.74	8.83 ± 0.21	2.8%	8.83 ± 0.06
HMX	796.95 ± 7.72	9.16 ± 0.22	818.44 ± 8.09	9.15 ± 0.22	2.6%	9.14 ± 0.03
CL-20	810.97 ± 7.34	9.56 ± 0.21	835.41 ± 9.52	9.61 ± 0.26	2.9%	9.57

Note: V_{det} = detonation velocity.

^a Gottfried JL. Laboratory-scale method for estimating explosive performance from laser-induced shock waves. *Propellants Explos Pyrotech.* 2015;40(5):674–681.

In Part I of this report series,¹ we demonstrated that fitting the laser-induced shock velocity data out to only 50 μ s instead of the full 112 μ s increased the quality of the fifth-order polynomial fit for the AI samples. While fitting the reduced data did increase the quality of the fit for the blank tape substrate and explosives (Fig. 15), the correlation between the characteristic laser-induced shock velocities and measured detonation velocities decreased ($R^2 = 0.9708$). Runge's phenomenon was exacerbated for the truncated fits. In addition, the 95% confidence intervals for the individual laser shots increased significantly since the number of early time data points significantly influenced the fit. Using CL-20 as an example, the average characteristic laser-induced shock velocity from individual fits was 1115.94 ± 94.72 m/s—an RSD of 8.5% instead of 0.9% (Table 4).

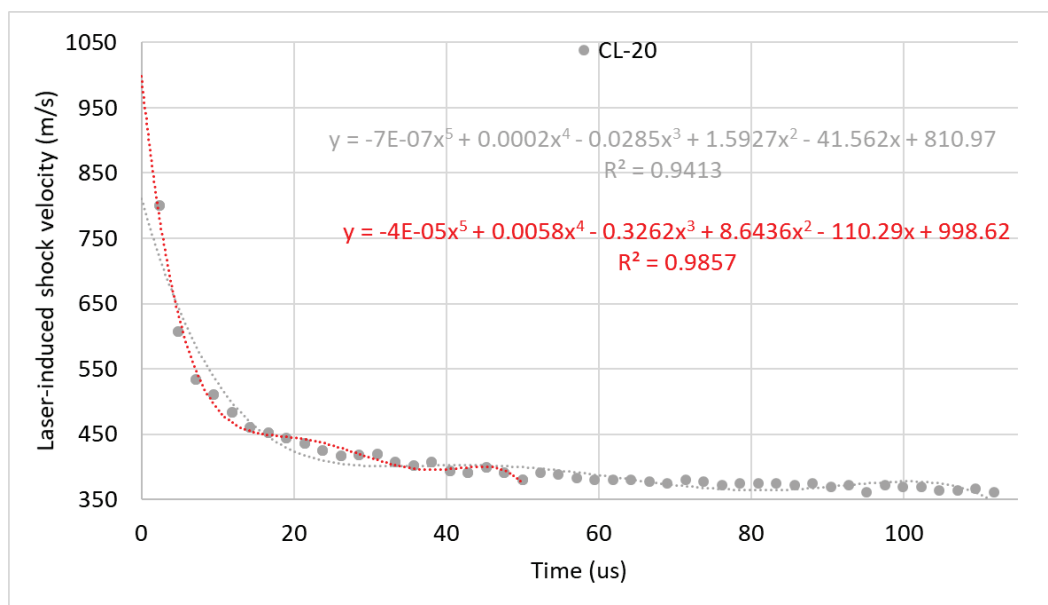


Fig. 15 Fifth-order polynomial fits for CL-20 out to either 50 or 112 μ s

3.1.5 Data Fitting for Optimal Performance Comparison

In this section, we investigate alternative methods for fitting the propagation of the laser-induced shock wave. A similar analysis was performed with the data from the original LASEM setup.¹¹ Because the fifth-order polynomial does not accurately fit the rapid decrease in laser-induced shock velocity at early times, we fit the data to a double exponential fit with an offset using the equation

$$y = y_0 + A_1 e^{\left\{\frac{-(x-x_0)}{\tau_1}\right\}} + A_2 e^{\left\{\frac{-(x-x_0)}{\tau_2}\right\}}, \quad (1)$$

where y_0 is the speed of sound in air, x_0 is the time between data points (2.38 μ s), and A_1 , A_2 , τ_1 , and τ_2 are empirically determined constants (Fig. 16). Unlike the fifth-order polynomial fits, the early data points are accurately captured by the double exponential curve. When y_0 was kept as a fit parameter, an interesting trend was observed—the fitted speed of sound in air increased with increasing energy release (Table 5). The speed of sound in air is a function of the temperature, pressure, and humidity of the air.²² Temperature has a much more significant effect on the speed of sound than either pressure or humidity. We know from the schlieren imaging that the air above the sample surface is heated by the laser-induced plasma. Even after the plasma is gone, the change of refractive index in the air is observed in the high-speed images. The results in Table 5, which include the calculated temperature of the air (T_{air}) based on the speed of sound in air measured for each sample, demonstrate that the more energetic samples heat the surrounding air to higher temperatures. This increase in T_{air} may be useful for quantifying the energy added to the laser-induced plasma by the chemical reactions of the ablated sample. A linear fit of the speed of sound in air versus the measured detonation velocities of the explosives gives a y-intercept of 345.9 m/s ($R^2 = 0.9583$). This speed of sound in air corresponds to 24 °C (75 °F), which is the temperature of our laser laboratory when all the instruments are running.

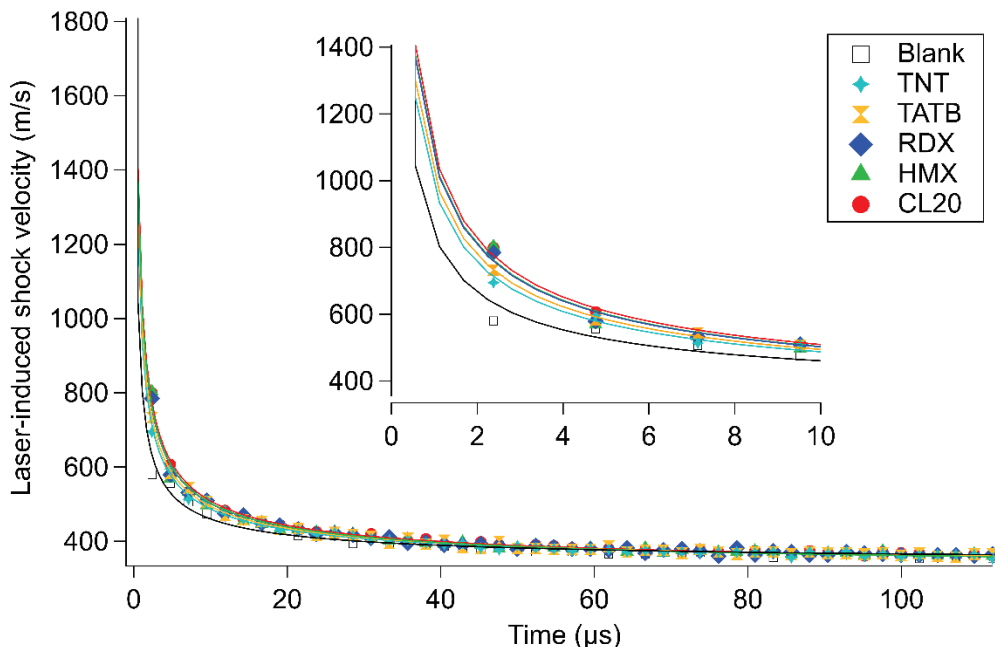


Fig. 16 Double exponential fits for the laser-induced shock velocities of the blank tape substrate and five explosives. The inset shows the first 10 μs of the shock wave propagation.

Table 5 Double exponential fit coefficients and calculated T_{air} for the blank tape substrate and five explosives

Sample	y_0 (m/s)	Calc. T_{air} °C (°F)	A_1	τ_1 (μs)	A_2	τ_2 (μs)
Blank	356.5 ± 6.6	41.7 (107)	132.9 ± 49.2	8.7 ± 2.7	92.8 ± 45.1	33.8 ± 17.5
TNT	361.2 ± 2.3	49.5 (121)	185.0 ± 13.2	3.5 ± 0.4	148.6 ± 11.5	25.0 ± 2.6
TATB	363.6 ± 2.3	53.5 (128)	210.2 ± 13.6	2.9 ± 0.3	155.6 ± 11.5	23.5 ± 2.4
RDX	366.2 ± 1.5	57.8 (136)	230.4 ± 9.8	1.6 ± 0.2	187.2 ± 7.7	19.5 ± 1.2
HMX	366.3 ± 1.7	58.0 (136)	261.9 ± 10.1	1.5 ± 0.1	174.4 ± 7.7	20.6 ± 1.4
CL-20	366.6 ± 1.5	58.5 (137)	268.6 ± 8.4	2.3 ± 0.1	164.1 ± 6.8	22.8 ± 1.4

Although the speed of sound in air correlates strongly to the measured detonation velocities of the ablated samples and produces the expected room temperature, the combination of small differences in y_0 values and relatively large error bars from the fit (Table 5) suggests that this is probably not a practical method for estimating the detonation velocity of unknown samples. Increasing the number of data points at later times or further increasing the time-resolution of the imaging may improve the error bars. The y-intercepts from the double exponential fits (Fig. 16) do not linearly correlate with the measured detonation velocities ($R^2 = 0.5751$). The sum of the A_1 and A_2 constants do correlate reasonably well ($R^2 = 0.9644$), although the correlation is not as strong as that obtained with the y-intercepts from the fifth-order polynomial fits (Fig. 14).

Besides an exponential fit, a power function could potentially be used to describe the shock wave decay. The Sedov-Taylor theory^{23,24} has previously been applied to laser-induced shock waves for nonreactive materials at very short timescales ($<1 \mu\text{s}$). Using the Sedov-Taylor model and approximations by Liberman,²⁵ the shock wave propagation is described by²⁶

$$R(t) = \left(\frac{75}{16\pi} \frac{(\gamma-1)(\gamma+1)^2}{3\gamma-1} \right)^{1/5} \left(\frac{Et^2}{\rho_0} \right)^{1/5}, \quad (2)$$

where R is the radius of the blast wave front as a function of time t , E is the energy of the blast, γ is the specific heat ratio of air (1.40), and ρ_0 is the density of the ambient air. The shock speed (V_s) is then given by

$$V_s(t) = \frac{dR}{dt} = \frac{2}{5} \left(\frac{75}{16\pi} \frac{(\gamma-1)(\gamma+1)^2}{3\gamma-1} \right)^{1/5} \left(\frac{E}{\rho_0 t^3} \right)^{1/5}. \quad (3)$$

We previously demonstrated that classical Sedov-Taylor blast wave theory does not apply to the original LASEM conditions, resulting in an unexpectedly high exponential factor (0.818–0.964 instead of the predicted 0.4).¹¹ The theory assumes the energy from behind the shock wave comes from a point source, and the strength of the blast wave is sufficiently large enough to neglect the ambient gas pressure in comparison with the pressure behind the shock wave. Thus, the effect of exothermic reactions in the laser-induced plasma are not accounted for, and the rapid decay of the shock wave in the microsecond-timescale during which the chemical reactions are happening means that the ambient gas pressure cannot be neglected.

Here, we attempted to fit the higher time-resolution LASEM data using a combination of the Sedov-Taylor theory and the drag model fit²⁷ to describe the shock decay at later times due to atmospheric resistance:

$$V_s(t) = A\alpha t^{(\alpha-1)} + R_0\beta e^{(-\beta t)}, \quad (4)$$

where $\alpha = 2/5$ (0.4) according to the Sedov-Taylor theory, A is a constant incorporating the energy added to the plasma, R_0 is the stopping distance for the shock wave, and β is the slowing coefficient (i.e., drag from air). Although the χ^2 fit coefficients were very high due to the large error bars for the drag model coefficients (Table 6), the fit described the early data points for the explosives reasonably well (Fig. 17). The A coefficients determined by the fits were used to calculate the energy behind the shock wave (E) using the equation²⁶

$$E = A^5 \left(\frac{75}{16\pi} \frac{(\gamma-1)(\gamma+1)^2}{3\gamma-1} \right)^{1/5} \rho_0, \quad (5)$$

where a value of $\rho_0 = 1.17 \text{ kg/m}^3$ was calculated for our laboratory conditions.

Table 6 Fit coefficients and calculated parameters for the combination Sedov-Taylor/drag model ($\alpha = 0.4$)

Sample	A	R_0	β	χ^2	E (mJ)	m_{calc} (g)
Blank	0.315 ± 0.018	$5535 \pm 2e7$	0.06 ± 249	7923	3.38 ± 0.95	...
TNT	0.411 ± 0.009	$5582 \pm 1e7$	0.06 ± 113	1877	12.8 ± 1.3	2.11 ± 0.37
TATB	0.435 ± 0.008	$5564 \pm 9e6$	0.06 ± 91	1461	17.0 ± 1.5	3.27 ± 0.43
RDX	0.467 ± 0.009	$5522 \pm 1e7$	0.06 ± 126	2641	24.2 ± 2.5	3.59 ± 0.46
HMX	0.471 ± 0.014	$5520 \pm 2e7$	0.06 ± 170	4865	25.2 ± 3.3	3.72 ± 0.58
CL-20	0.485 ± 0.009	$5524 \pm 1e7$	0.06 ± 114	2100	29.1 ± 2.7	4.17 ± 0.46

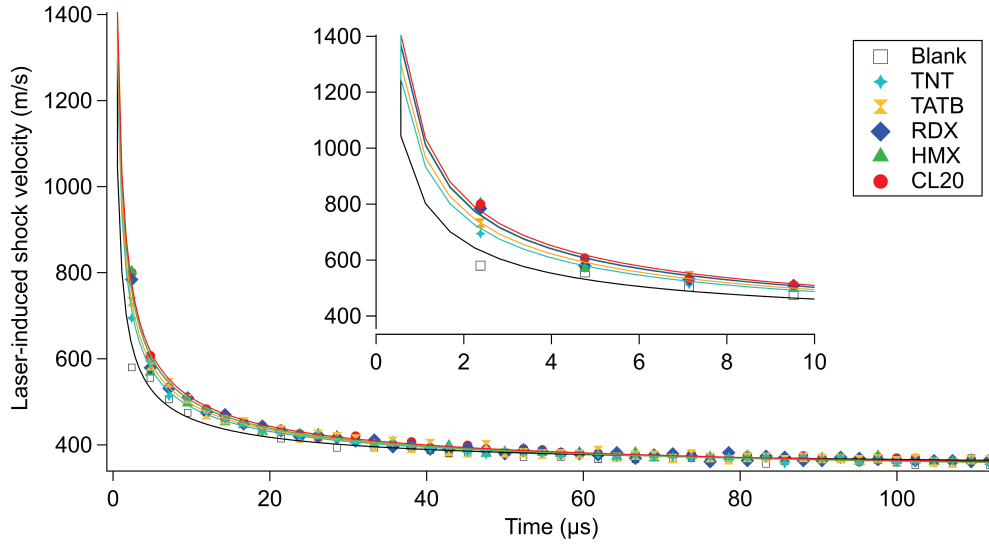


Fig. 17 Combination Sedov-Taylor/drag model fit ($\alpha = 0.4$) for the laser-induced shock velocities of the blank tape substrate and five explosives. The inset shows the first 10 μs of the shock wave propagation.

The differences between the calculated energies for each of the explosives and the blank tape were used in combination with the calculated detonation energies (Fig. 1) to estimate the mass of material that reacted per laser shot (Table 6). Since each sample slide only contained 10–20 mg of material, the calculated values are more than 2 orders of magnitude too high. The absolute magnitudes of the estimated energy release from Sedov-Taylor modelling of laser-induced shock waves were previously shown to be unrealistically high.²⁸ However, the estimated energy values do enable comparison of the relative energy release for each sample. As shown in Fig. 18, these values were strongly correlated to the measured detonation velocities for the explosives.

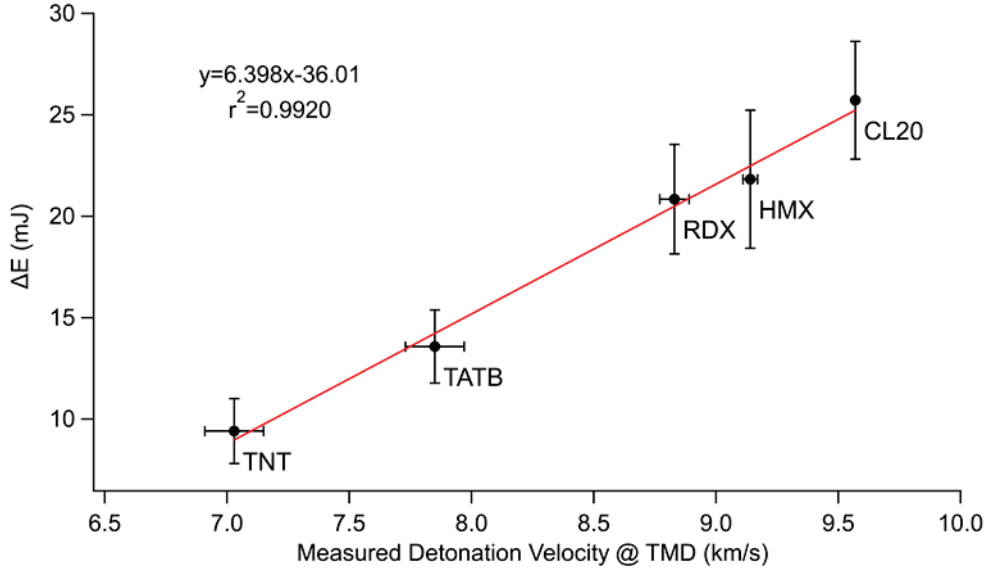


Fig. 18 Correlation between the calculated chemical energy added to the plasma based on Sedov-Taylor theory and the measured detonation velocities of the five explosives

Another type of fit that has been explored for the laser-induced shock waves produced by laser ablation of energetic materials is the Dewey fit,^{29,30} which was originally developed to describe the shock wave from the large-scale detonation of TNT. The radial position of the shock wave is given by

$$R(t) = A + Ba_0t + C\ln(1 + a_0t) + D\sqrt{\ln(1 + a_0t)}, \quad (6)$$

where A represents the initial charge radius, B is the shock wave Mach number as time $t \rightarrow \infty$ (which is equal to 1 as the shock decays to the speed of sound in air a_0); C and D are two additional empirically determined fit coefficients. The corresponding equation for fitting the shock velocity as a function of time is

$$V_s(t) = \frac{dR}{dt} = a_0 \left(B + \frac{C}{(1+a_0t)} + \frac{D}{2(1+a_0t)\sqrt{\ln(1+a_0t)}} \right). \quad (7)$$

When Eq. 7 is used to fit the higher time-resolution LASEM data, nonphysical results are obtained for the values of B (−1.65 for the blank and 15–22 for the explosives) and a_0 (19–46 m/s). Fixing $a_0 = 345.9$ m/s results in values of B of −0.73 for the blank and 1.6–4.2 for the explosives. As shown from the fitting results using Eq. 1 (Table 5), the surrounding air is heated by the laser-induced plasma and chemical reactions—resulting in higher speeds of sound in air for the more energetic materials. For this reason, the values of a_0 in Eq. 7 were fixed to the values of y_0 in Table 5. The results are shown in Fig. 19 and Table 7. The inset in Fig. 19 shows that the Dewey fit misses the early data points for the blank and TNT (too high), accurately fits the TATB, and misses the more energetic materials RDX, HMX, and CL-20 (too low). Since these are the most important data points for

discriminating energetic materials, we confirm our earlier conclusion that the Dewey fit does not appear to be a good model for comparing the laser-induced shock velocities of energetic materials. The correlation between the factor Ba_0 and the measured detonation velocities for the five explosives is $R^2 = 0.9606$, less than other models described previously.

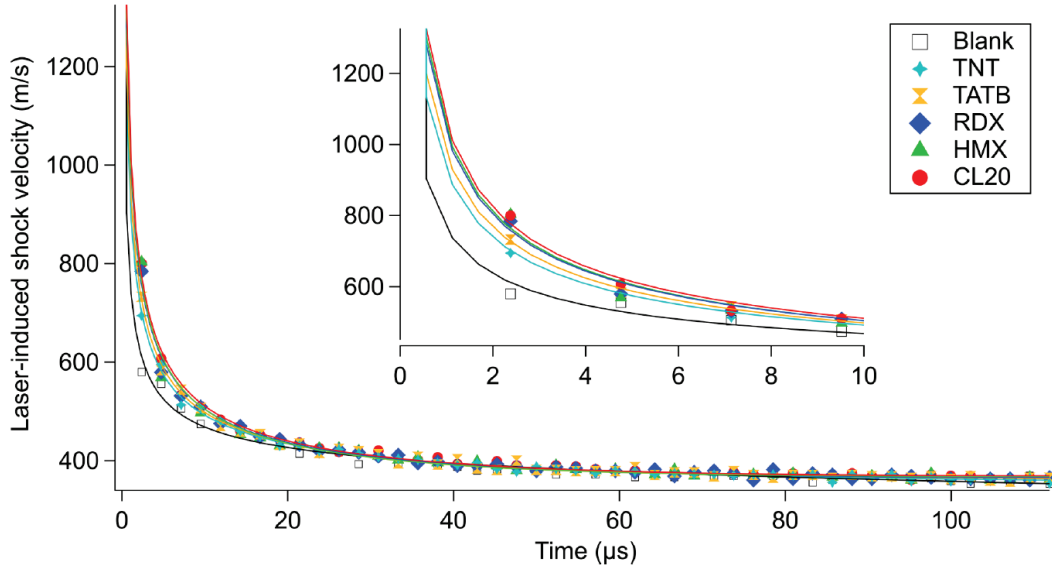


Fig. 19 Dewey fit (with fixed values of a_0) for the laser-induced shock velocities of the blank tape substrate and five explosives. The inset shows the first 10 μs of the shock wave propagation.

Table 7 Fit coefficients and calculated parameters for the Dewey curvefit

Sample	a_0 (fixed)	B	C	D	χ^2
Blank	356.46	-0.66 ± 0.57	1.60 ± 0.59	0.045 ± 0.002	4646
TNT	361.16	1.52 ± 0.30	-0.71 ± 0.30	0.066 ± 0.001	1364
TATB	363.64	2.36 ± 0.31	-1.59 ± 0.33	0.073 ± 0.001	1507
RDX	366.15	3.25 ± 0.45	-2.54 ± 0.46	0.080 ± 0.002	3138
HMX	366.30	3.77 ± 0.59	-3.09 ± 0.61	0.082 ± 0.003	5501
CL-20	366.62	3.64 ± 0.40	-2.94 ± 0.41	0.084 ± 0.002	2471

3.2 Emission data

3.2.1 High-Resolution Plasma Emission Spectroscopy

Atomic, ionic, and molecular emission was observed from the laser-induced plasma following laser excitation (Fig. 20). Spectra from this time regime provides information about the elemental content of the samples (including impurities) and the plasma chemistry. In addition to the expected elemental species carbon (C), hydrogen (H), nitrogen (N) and oxygen (O), common impurities such as

magnesium (Mg), calcium (Ca), sodium (Na), and potassium (K) were present in the samples. C₂ and CN form through either fragmentation of the parent molecule at early times, or through recombination reactions as the plasma cools.^{31–33} We previously used chemometric analysis of the emission spectra (i.e., machine learning) to discriminate between explosives and other hazardous materials.^{34,35} For this study, the spectra were integrated over 10 μ s to compare trends between the plasma emission spectra and properties of the explosives.

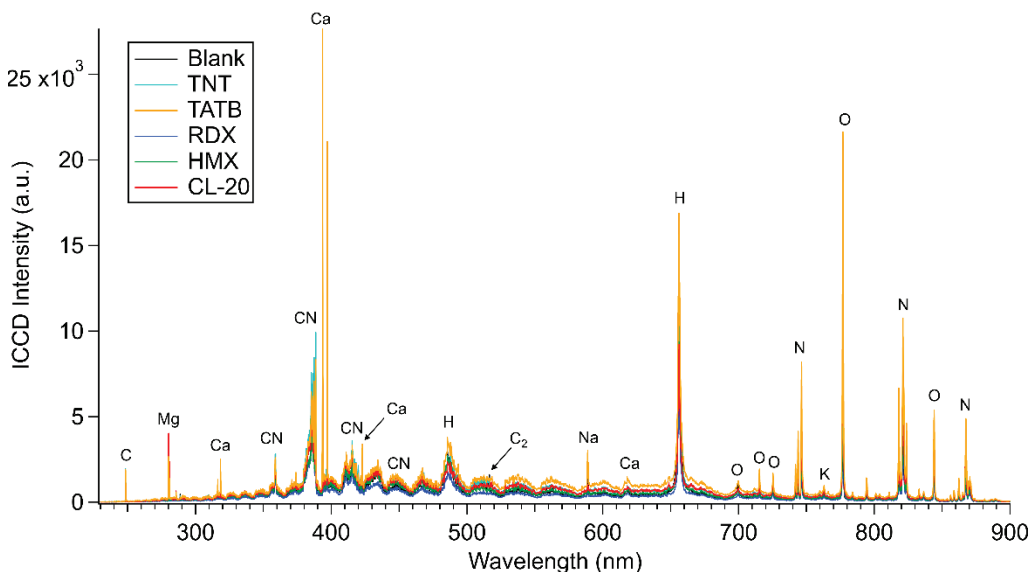


Fig. 20 Laser-induced plasma spectra for the blank tape substrate and five explosives (average of 20 spectra each)

Figure 21 demonstrates that with the exception of C ($R^2 = 0.8316$), the atomic emission intensities integrated over 10 μ s of the laser-induced plasma lifetime do not correlate to the mole fraction of each species in the explosives. This suggests that 1) significant plasma chemistry is occurring during this time regime that affects the relative concentrations of each species, 2) significant differences in the plasma temperatures between samples affect the relative emission intensities of each species, and/or 3) the entrainment of air in the plasma influences the relative concentrations. Although it is likely all three contribute to the poor correlation, we believe the first has the most significant influence on the relative emission intensities. Air is entrained into the plasma and contributed to the O and N emission intensities;^{36–38} however, similar quantities of air should be entrained into each laser-induced plasma since the experimental conditions are kept constant. The influence of the entrained air likely depends on the plasma chemistry and sample properties (e.g., more O from air will react with inherently oxygen-poor explosives such as TNT), although that effect has not been studied in detail. In addition, the high plasma temperatures (exceeding 10,000 K) mean that temperature differences

have less influence on the emission intensities—in contrast to combustion temperature regimes. For example, an increase in 10 K more than doubles the emission intensity at 1000 K, but the increase in intensity at 10,000 K is less than 1%.

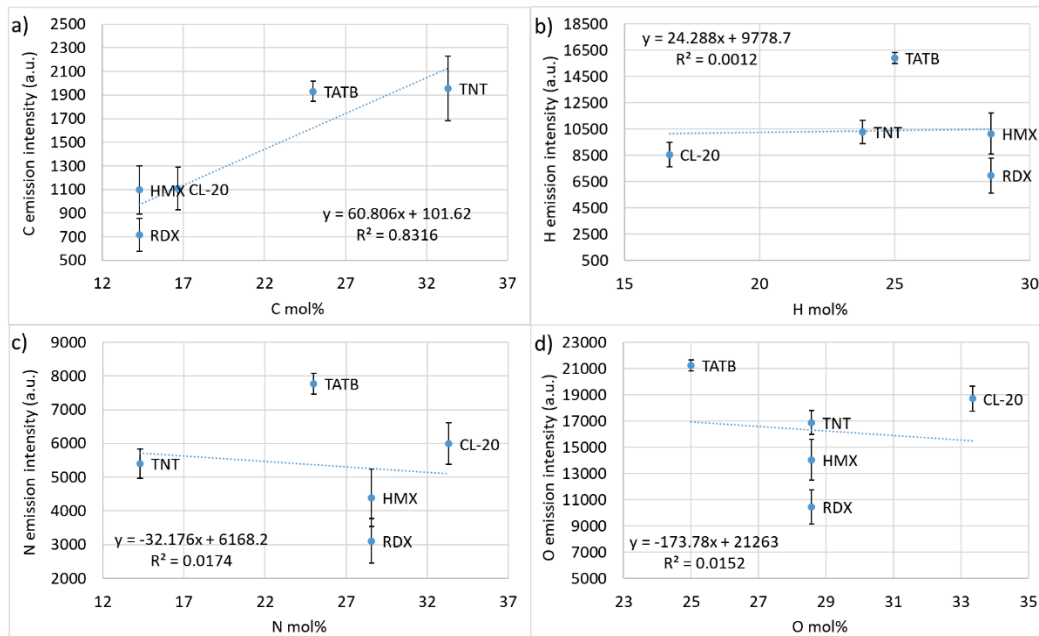


Fig. 21 Correlations between a) C, b) H, c) N, and d) O emission intensities from the five explosives and the mole fraction of each element in the sample

To explore the differences in plasma chemistry for the samples, the correlations between the molecular species CN and C₂ formed through recombination reactions during the spectrometer gate window and the oxygen balances (OBs) of the explosives are shown in Fig. 22. The CN and C₂ emission intensities are strongly correlated to each other ($R^2 = 0.9789$), and appear to be moderately correlated to the OB of the explosive. For CHNO explosives with no added metals, the OB is given by the formula

$$OB\% = \frac{-1600}{MW} \times \left(2C + \frac{H}{2} - O \right), \quad (8)$$

where MW is the molecular weight of the compound, C is the number of carbon atoms, H is the number of hydrogen atoms, and O is the number of oxygen atoms. As the OB increases (i.e., approaches zero), the CN and C₂ intensities decrease. This is because as more O is available, it preferentially reacts with C to form CO and CO₂. In an oxygen-poor environment, the C instead reacts with other C- or N-related species (either from the sample or from air). Similar trends have been observed for the laser-induced plasma emission from other energetic materials under different conditions,³¹ either in the presence of Al or under an argon

atmosphere.^{32,33} The C₂ emission was also observed to decrease with increasing O concentration in graphene oxide samples under LASEM conditions.³⁹

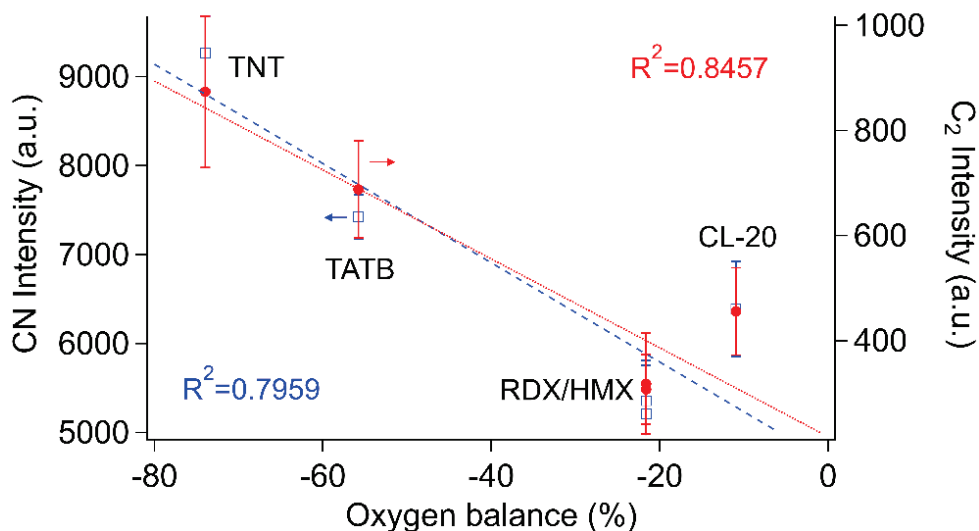


Fig. 22 Correlations between CN (blue) and C₂ (red) emission intensities and OBs for the five explosives

Although other groups have used laser-induced plasma emission intensity ratios (Al/O) to predict the detonation performance of aluminized explosives,^{40,41} we were unable to find a strong correlation between the emission intensities or ratios of pure CHNO explosives and detonation performance. The strongest correlation with the laser-induced shock velocity (i.e., estimated detonation velocity) was with the O/C intensity ratio (Fig. 23). The laser-induced shock velocities were also inversely correlated with the C mol% ($R^2 = 0.8678$) and directly correlated with the N mol% ($R^2 = 0.9153$). They were not correlated with either H mol% ($R^2 = 0.0339$) or O mol% ($R^2 = 0.3605$).

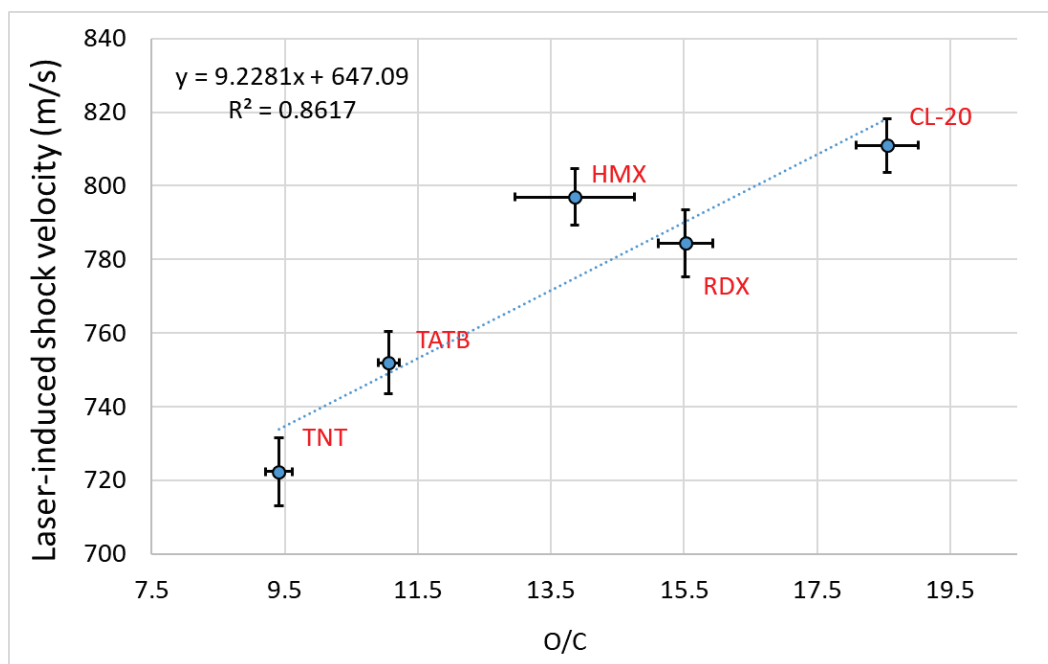


Fig. 23 Correlation between laser-induced shock velocities and O/C emission intensities for the five explosives

The influence of molecular structure on performance was also investigated by correlating the number of different bond types to the emission intensities or laser-induced shock velocities. The C₂ emission intensities were only weakly correlated to the total number of C–C or C=C bonds ($R^2 = 0.7262$) and the CN emission intensity was not correlated with the total number of CN bonds ($R^2 = 0.0020$), indicating the importance of recombination reactions for molecular emission (as well as the availability of O). The laser-induced shock velocities were not correlated to the number of C–C bonds ($R^2 = 0.2672$), and only weakly inversely correlated to the C₂ emission intensities ($R^2 = 0.7756$). Although weakly inversely correlated to the CN emission intensities ($R^2 = 0.7483$), the laser-induced shock velocities appear to be directly correlated to the number of CN bonds in the parent molecule (Fig. 24a). The explosives fell into two separate groupings: 1) the C–N was located in the ring structure of the explosive, or 2) the C in the aromatic ring was bonded to an NO₂ group (ArC–NO₂). A reasonably strong correlation between the laser-induced shock velocities and the number of N–NO₂ groups was also observed (Fig. 24b). More data from different types of explosives are required to confirm these correlations.

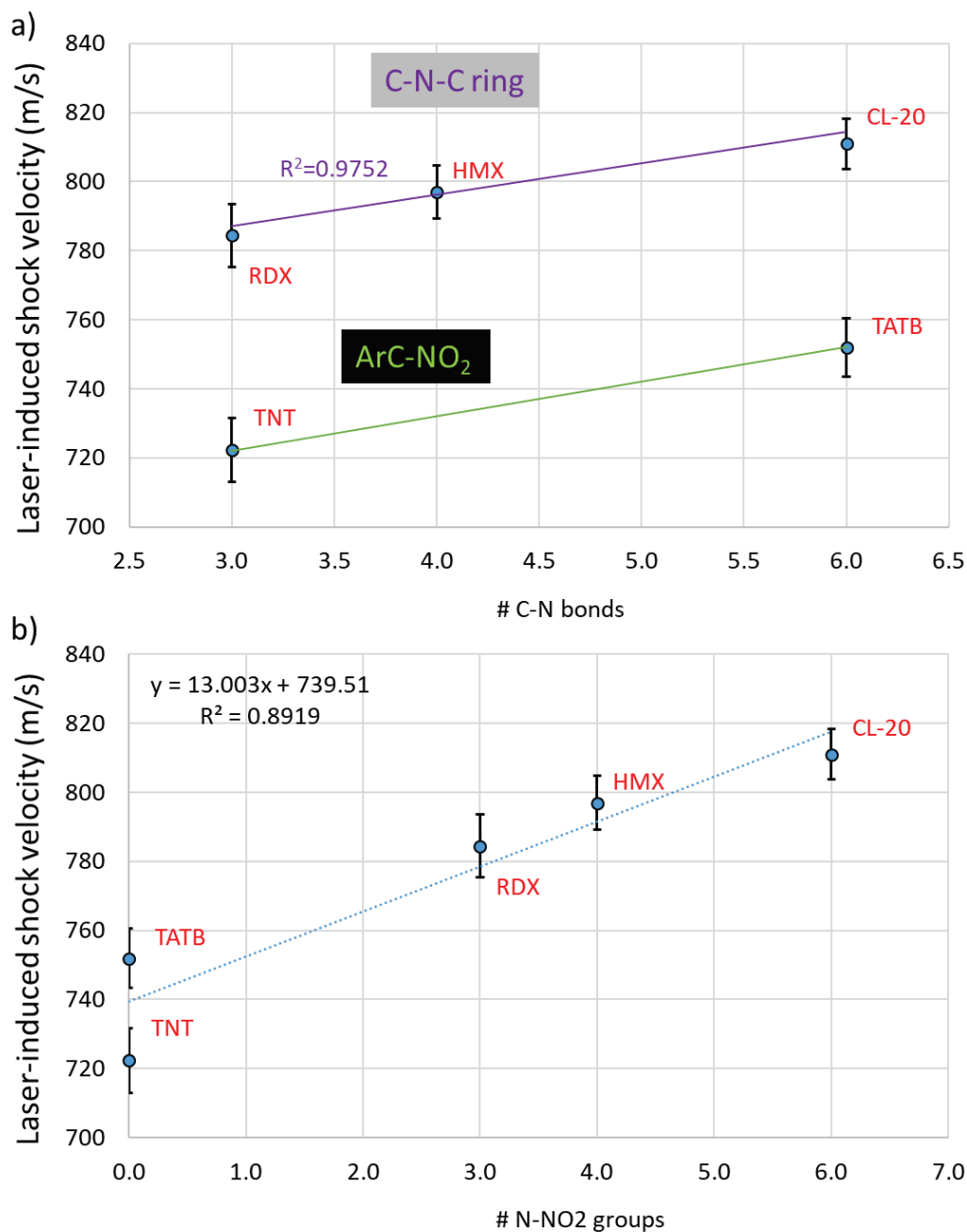


Fig. 24 Correlations between the laser-induced shock velocities and the no. of a) C–N bonds or b) N–NO₂ groups

Compared to the AI data presented in Part I,¹ the shot-to-shot variation in the emission from the organic materials was significantly higher. Figure 25 shows the average RSDs for the emission intensities and ratios for the samples discussed in Part I¹ and this report. The blank tape substrate has a relatively high average RSD because of debris inadvertently affixed to the tape (e.g., fingerprints, dust, etc.). These impurities were visible on the tape, but no effort was made to avoid them for

this study since they do not affect the laser-induced shock velocities. The explosives have higher RSDs than even the Al powders because of the chemical complexity of the samples when excited to high temperatures. In addition to the stochastic laser–material interaction, the laser-induced plasma chemistry affects the resulting emission spectra. Of the explosive samples, the RDX has the largest average RSD and the largest confidence intervals for the laser-induced shock wave positions (Fig. 11). At this time, we do not know why the RSDs are higher for RDX.

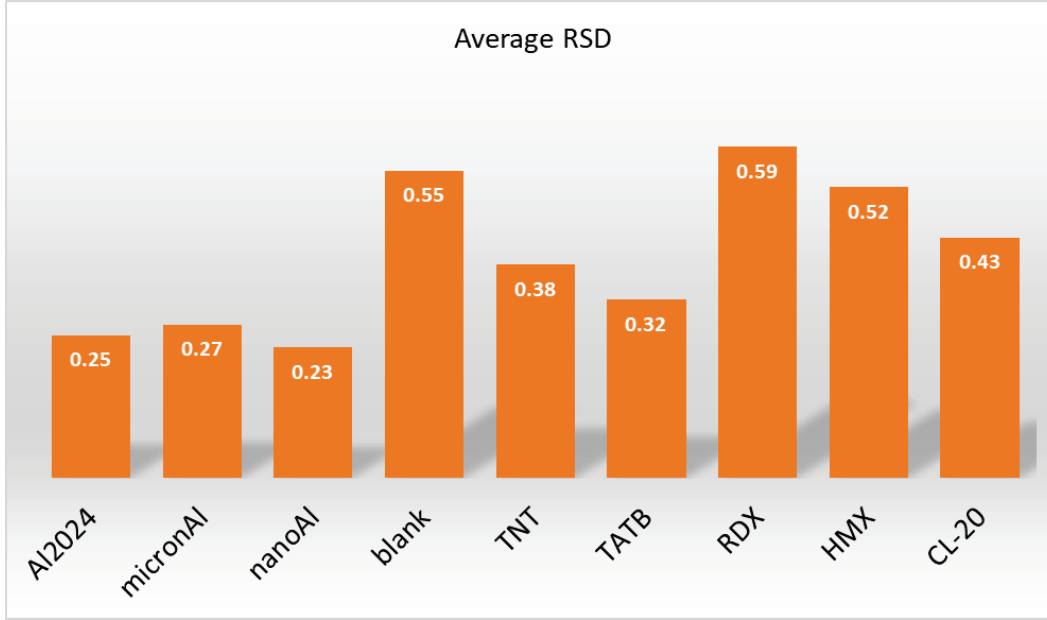


Fig. 25 Average relative standard deviations for 17 emission intensities and 12 emission ratios from the laser-induced plasma spectra of the Al samples from Part I,¹ the blank substrate, and 5 explosives

3.2.2 Temperature and Electron Density Calculations using H Emission

The laser-induced plasma temperatures were calculated using the relative intensities of the H_{α} , H_{β} , and H_{γ} emission lines. Based on previous work showing that organic species such as H were in local thermodynamic equilibrium (LTE) under similar experimental conditions,⁴² we used the Boltzmann plot method to calculate the temperatures:

$$\ln\left(\frac{I\lambda}{gA}\right) = \frac{-E}{kT} + C, \quad (9)$$

where E is the excited state energy level for the transition wavelengths λ , I is the emission intensity (corrected for the response of the detector), A is the transition probability, g is the statistical weight, and C is a constant that includes the partition function. By plotting the left side of Eq. 9 versus E , the slope of the linear fit enables the calculation of the temperature T using the value of the Boltzmann constant k ($0.695 \text{ cm}^{-1}/\text{K}$). The relevant constants were obtained from the National Institute

of Standards and Technology atomic spectra database⁴³ and are given in Table 8. The caveat here is that the electron density in the plasma is much lower without the presence of metal species such as Al, so LTE may not apply under all conditions. In addition, we know that significant plasma cooling and chemical reactions are occurring in the plasma during the spectrometer gate width (10 μ s), so LTE would not strictly apply even if the electron densities were sufficiently high to meet the McWhirter condition. However, LTE is generally reasonable for organic species at the very-high laser energies and relatively short timescales used in the present work. Thus, we provide the plasma temperatures as a relative comparison between samples rather than as absolute values (Table 9). Error bars for the calculated temperatures are 95% confidence intervals based on each laser shot. For comparison, data for the three Al samples from Part I¹ are also shown: a bulk Al alloy plate (Al 2024), micron-Al, and nano-Al. The plasma temperatures for the Al samples are clearly much higher than those of the organic materials.

Table 8 Spectroscopic parameters for emission lines used to calculate plasma temperatures

Transition	λ (nm)	A (10^7 s ⁻¹)	g_u	E_u (cm ⁻¹)
H γ	434.047	0.253	6	105291.657
H β	486.135	0.843	6	102823.904
H α	656.279	4.41	6	97492.304

Table 9 Calculated plasma temperatures and electron densities for the blank tape and five explosives; data for the three Al samples from Part I¹ are included for comparison

Sample	T (K)	N_e (10^{14} cm ⁻³)
Al 2024	5370.09 $\pm$ 103.31	11.72 $\pm$ 3.10
micron-Al	5513.94 $\pm$ 186.53	9.36 $\pm$ 3.99
nano-Al	7314.42 $\pm$ 572.79	10.65 $\pm$ 4.68
Blank	3187.05 $\pm$ 40.49	7.02 $\pm$ 3.46
TNT	3569.42 $\pm$ 46.77	7.09 $\pm$ 3.68
TATB	3269.81 $\pm$ 34.64	8.30 $\pm$ 3.64
RDX	3580.07 $\pm$ 95.75	7.97 $\pm$ 3.46
HMX	3516.54 $\pm$ 56.19	8.18 $\pm$ 3.56
CL-20	3709.12 $\pm$ 53.71	8.04 $\pm$ 3.66

Note: Samples in orange are data from Part I.¹

The electron densities (N_e) were also determined based on the equation

$$N_e = 8.02 \times 10^{12} \left(\frac{\Delta\lambda_{1/2}}{0.0149} \right)^{3/2}, \quad (10)$$

where $\Delta\lambda_{1/2}$ is the full-width at half-maximum (FWHM) of the 656 nm H α line.⁴² The error bars for the electron density were determined by the uncertainty in the

FWHM measurement from a fit of the emission feature to a Voigt line profile. As expected, the electron densities were higher for the Al samples; however, the relatively large uncertainty in the FWHM makes it difficult to determine how significant the observed differences are.

While the electron densities were similar for the blank tape substrate and explosives, the plasma temperatures for the explosives were significantly higher than those for the blank tape. Figure 26 shows there is a strong correlation between the measured laser-induced plasma temperatures (over an integrated timescale from 1.5 to 11.5 μ s) and the calculated detonation temperatures of the explosives. This suggests the plasma temperatures could be used to estimate the detonation temperature of novel explosives.

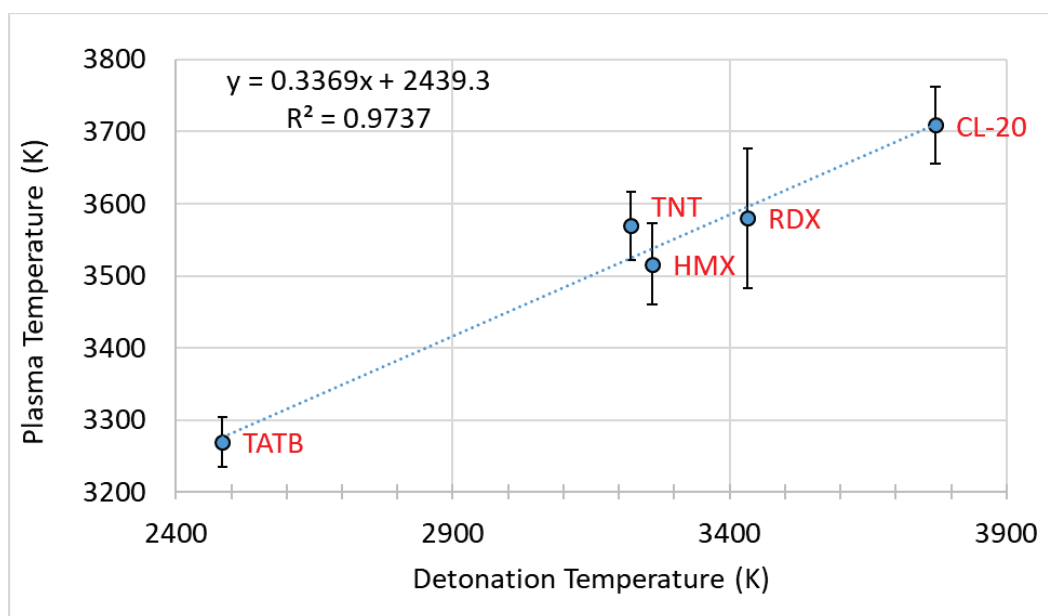


Fig. 26 Correlation between measured laser-induced plasma temperatures and calculated detonation temperatures for the explosives

3.2.3 Time-Resolved H Emission

Two monochromator/photomultiplier tube (PMT) detectors were set up to record the time-resolved emission at 486 and 656 nm, which correspond to the H_{β} and H_{α} transitions for the organic samples. No H emission was observed after approximately 15 μ s, so Fig. 27 shows a zoomed-in timescale for the two signals. At early times the PMTs were saturated by the plasma emission. The PMT signals were corrected for their response using a calibrated lamp and the two signals were used to calculate the plasma temperature using the Boltzmann method (Eq. 9). The results are shown in Fig. 28a. The calculated temperatures are meaningless while the PMTs were saturated (until ~ 2 – 3 μ s), and very noisy at later times when the H

signals become weak. Nevertheless, the temperatures do provide an interesting comparison of the rise in temperature due to chemical reactions of the explosive material as a function of time.

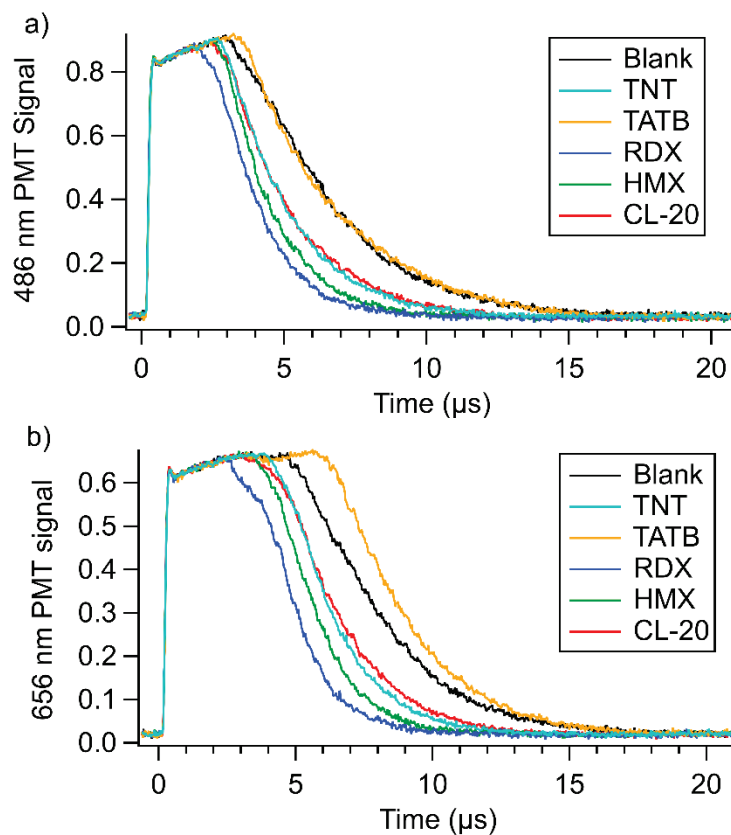


Fig. 27 Time-resolved emission from the a) H_{β} and b) H_{α} transitions for the blank tape substrate and explosives

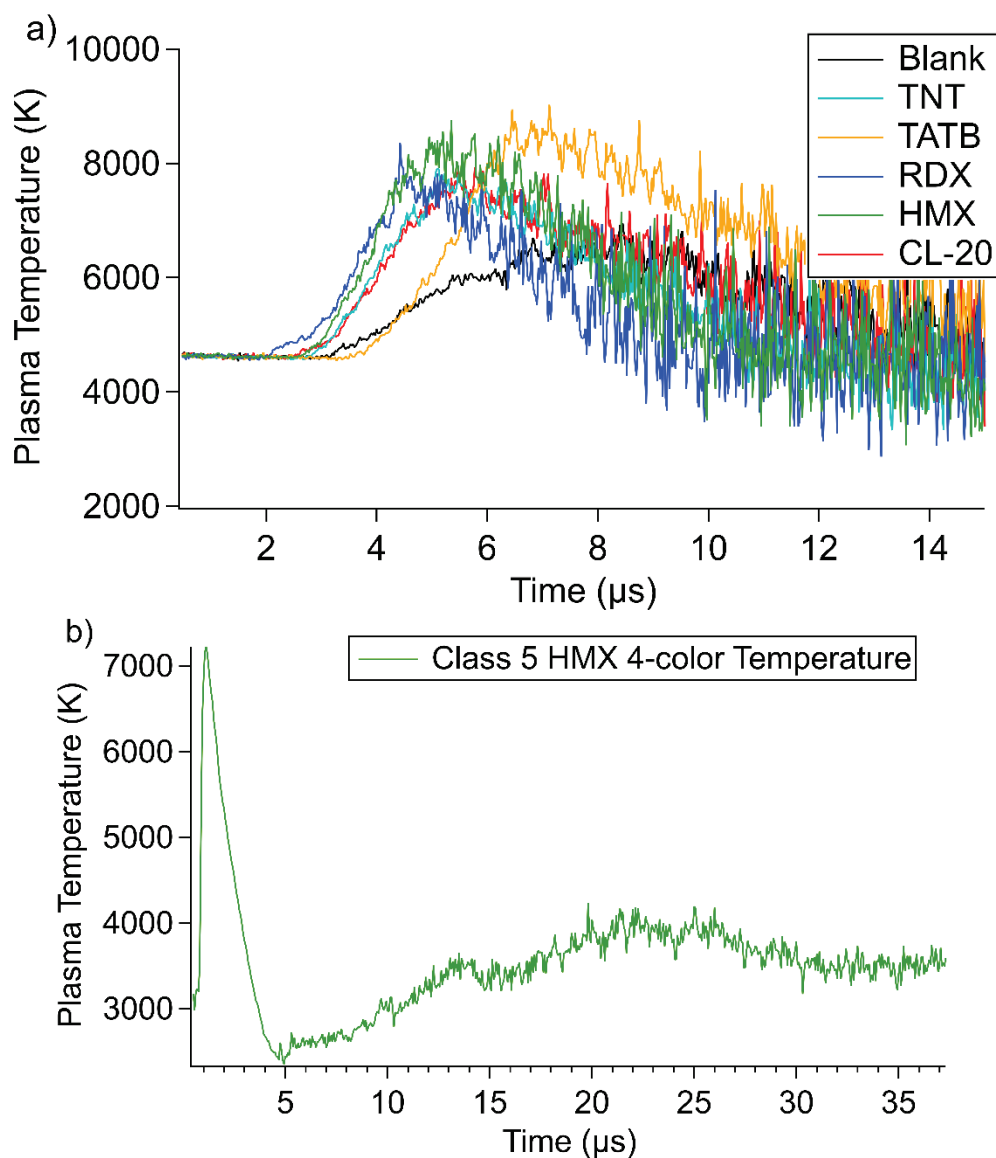


Fig. 28 a) Measured plasma temperatures for the explosives using the time-resolved H_α and H_β emission features; b) for comparison, the time-resolved blackbody temperature for Class 5 HMX measured using a 4-PMT pyrometer system with bandpass filters at 850, 660, 600, and 486 nm is also shown

The calculated temperatures in Fig. 28a are much higher than those calculated using the high-resolution emission spectra (Table 9). TATB takes the longest to reach its peak temperature, which is higher than for the other explosives, surprisingly. The detonation temperature for TATB (Fig. 1) is the lowest of all the explosives, presumably because it takes longer to react and the peak temperature is not reached until after the detonation wave passes through the material. The peak temperature for HMX is slightly higher than for RDX, but also takes more than 1 μs longer to reach. The rises in temperature and peak temperatures are unexpectedly similar for TNT and CL-20. It is possible that the CL-20 reacts earlier, when the PMTs are

saturated. All the explosives have higher peak temperatures and faster reaction rates than the blank tape substrate. For comparison, previous unpublished pyrometry data collected on the LASEM system for Class 5 HMX (smaller particle size than the HMX sample in this study) are shown in Fig. 28b. The temperatures were obtained by calculating the blackbody temperatures using the intensity signals at four wavelengths. A 4-PMT detector with bandpass filters at 850, 660, 600, and 486 nm was used. The Class 5 HMX appears to reach its peak plasma temperature at much earlier times than the Class 1 HMX, but the peak temperatures are similar. Because the 4-PMT system is more sensitive, the temperature can be tracked for much longer periods of time. After the plasma cools, combustion reactions of HMX molecules ejected into the air (and/or ignited on the sample surface) occur and result in increased temperatures at later times. McMullan²¹ showed that the heat from the plasma re-radiates onto the sample surface (resulting in surface temperatures of 900 K for RDX), igniting the material.

3.2.4 Combustion Emission

The combustion emission was studied using a series of sequential emission spectra with wavelength coverage from the UV through the VIS regions and into the near-infrared (NIR). In addition, the time-resolved, integrated infrared (IR) emission was also measured with a photoreceiver.

3.2.4.1 Visible Spectroscopy

A sequential series of UV–VIS emission spectra were acquired following laser excitation of each of the samples. Representative examples of 100 consecutive spectra with 1.050-ms gate widths for each sample are shown in Fig. 29. In the first spectrum of each series, the emission is dominated by atomic, ionic, and molecular species. TATB has relatively strong molecular emission due to the recombination of the Ca impurity to form CaOH. Interestingly, TNT and TATB have the strongest CN emission in the first spectra of the series—they are also the only two explosives in this study with C–NO₂ bonds. Samples that subsequently ignited following the laser-induced plasma cessation radiated gray-body emission (TNT) along with limited atomic emission (Fig. 30). The intense emission features for RDX, HMX, and CL-20 on the millisecond timescale are due to Na (589 nm) and K (766, 769 nm). A second spectrometer with a 200- μ s delay and a 4-ms gate was used to record the temporally integrated combustion emission, which emphasizes the dominance of the gray-body emission from combusting TNT particles and molecular emission from all explosives (Fig. 31). Previous work has shown that when significantly thicker explosive powders are added to the sample slide, strong combustion emission can be observed from all explosives.⁴⁴

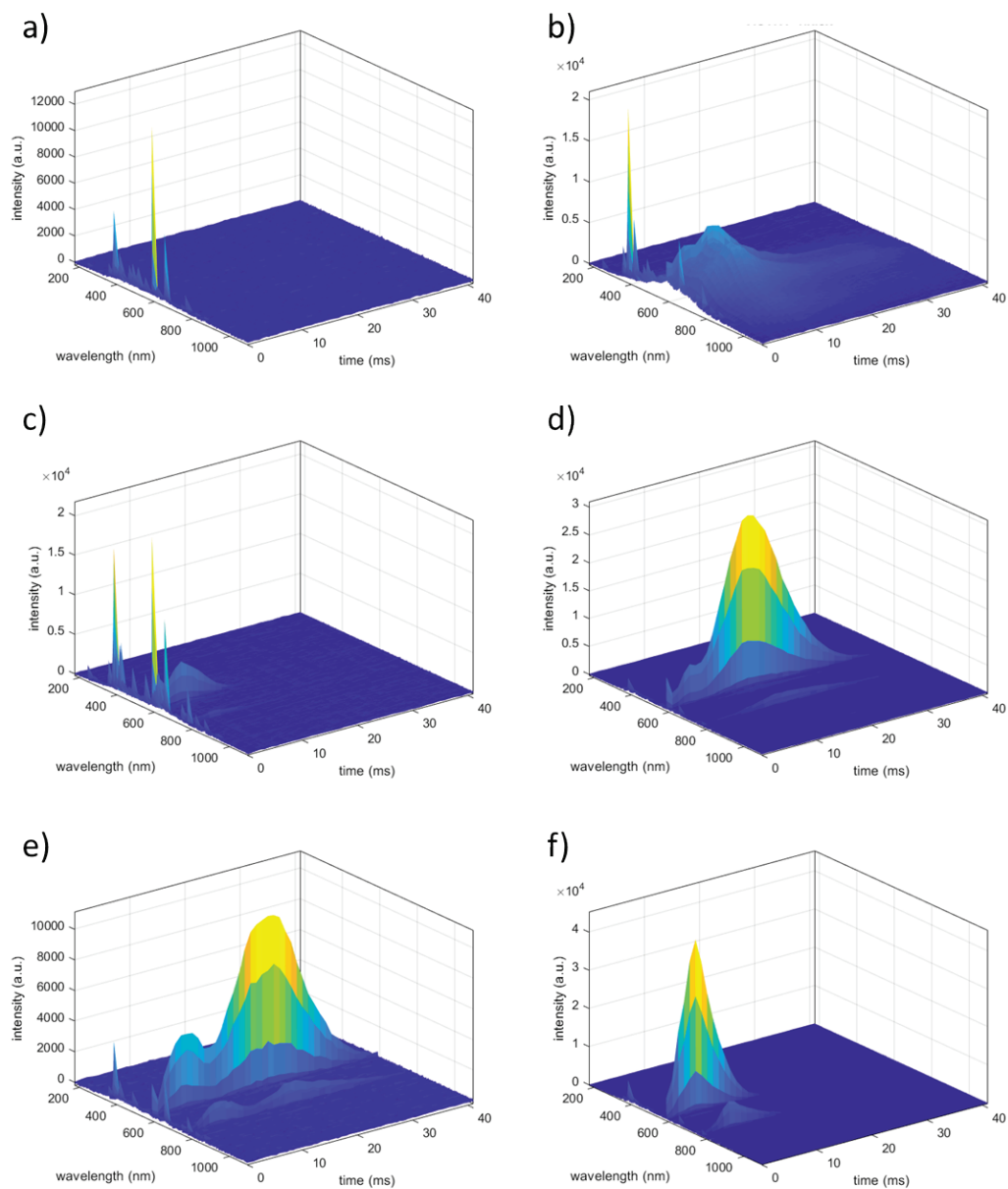


Fig. 29 Sequential visible emission spectra acquired following pulsed laser excitation of the a) blank tape substrate, b) TNT, c) TATB, d) RDX, e) HMX, and f) CL-20 (representative series for each sample shown)

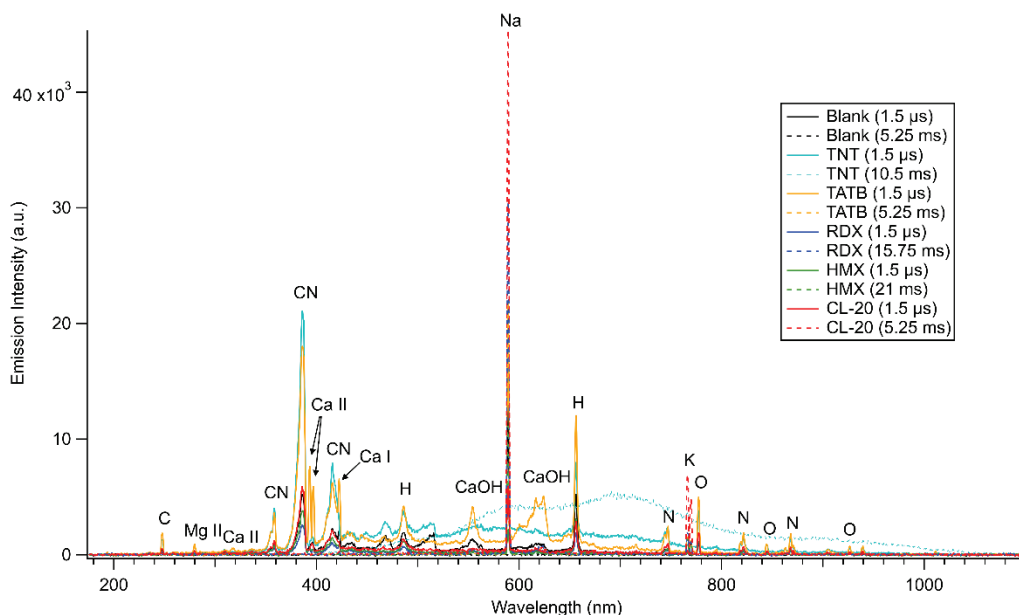


Fig. 30 Selected spectra from the sequentially obtained series of UV-VIS emission spectra for the blank tape substrate and five explosives

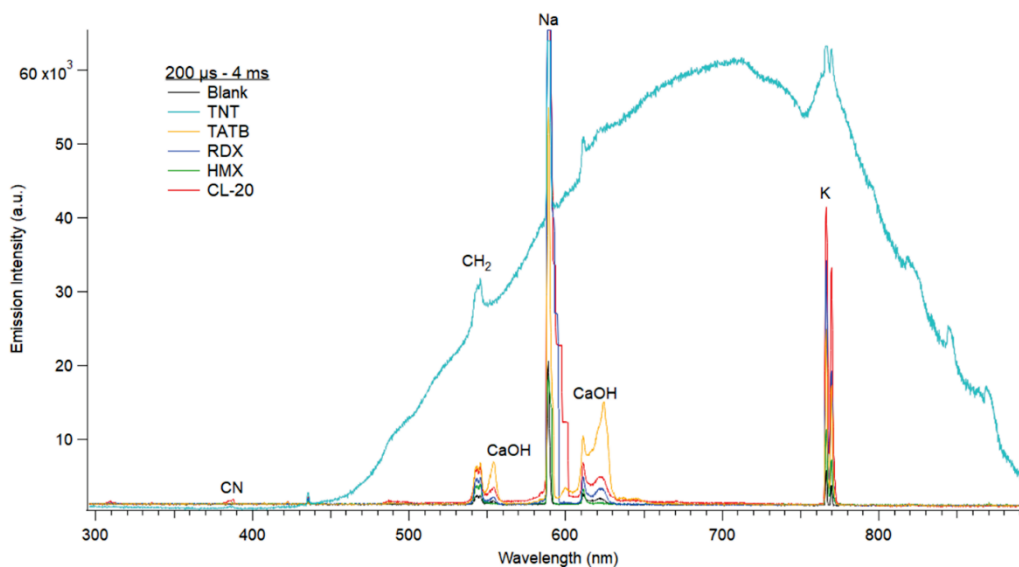


Fig. 31 Combustion emission spectra for the blank tape and explosive samples integrated from 200 μ s to 4 ms after the pulsed laser excitation. Broadband gray-body emission and molecular emission dominate the spectra in this regime, in addition to strong alkali metal emission.

3.2.4.2 NIR Spectroscopy

Fundamental vibrational modes that appear in the mid-IR region (2500–25,000 nm) have overtone and combination bands at lower wavelengths. Highly anharmonic vibrations due to C–H, O–H, and N–H bonds have overtone and combination bands in the NIR region from 1000 to 2500 nm. In Part I we

showed that the NIR spectra of the laser-excited Al samples was dominated by emission from the organic contaminants in the samples.¹ Explosives inherently contain a large number of these NIR-active bonds. An NIR spectrometer was used to obtain 100 sequential spectra with a 500- μ s gate width following a 1.5- μ s delay triggered by the laser pulse. Figure 32 shows representative spectral series for each sample. The blank tape substrate has no detectable NIR emission, most likely due to the relatively long gate width compared to the short reaction time. NIR emission from TNT saturated the spectrometer for many milliseconds during peak combustion. Clear differences in the NIR emission spectra of the explosives were observed. NIR spectra of explosives is extremely rare^{45–47}—and to our knowledge, the NIR spectra of military explosives in this wavelength region following pulsed laser excitation has not been previously observed. Mid-IR emission from the laser-induced plasmas of non-energetic materials has been observed,^{48,49} along with emission signatures for chlorate and nitrate compounds (1–12 μ m).⁵⁰ Long-wave IR emission from explosives including RDX and HMX has also been reported.⁵¹

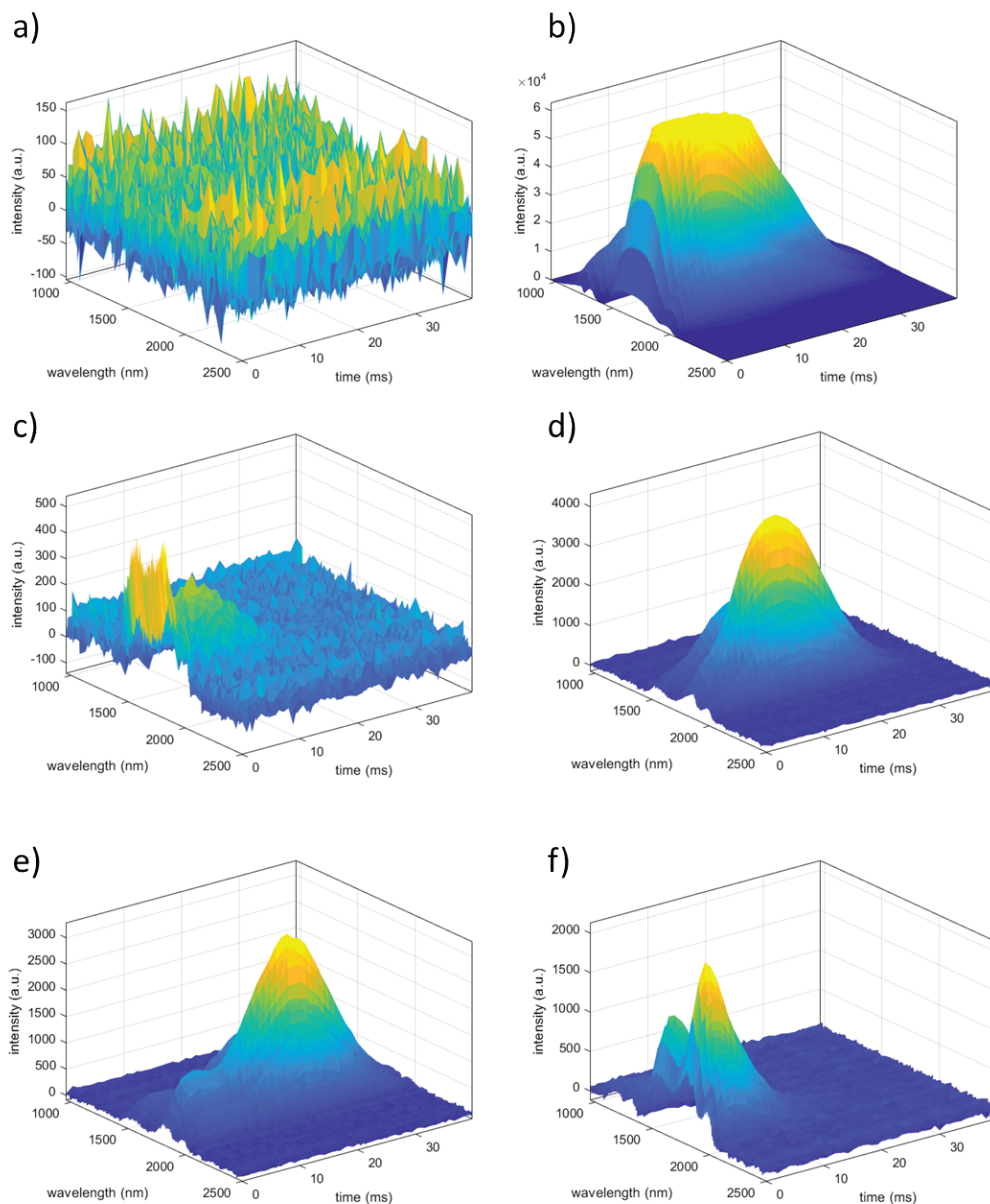


Fig. 32 Sequential NIR emission spectra acquired following pulsed laser excitation of the a) blank tape substrate, b) TNT, c) TATB, d) RDX, e) HMX, and f) CL-20 (representative series for each sample shown)

The NIR spectra were corrected for the spectral response of the detector using a calibrated lamp. Figure 33 shows selected spectra from each sample based on their strongest (unsaturated) emission intensities. The spectral features changed only in intensity with time—their positions and shapes remained constant. Due to their complexity, NIR spectra can be challenging to interpret. The resolution of our spectra (8.9 nm) is also worse than the published absorption spectra of explosives (2 nm).⁴⁷ No emission features were observed beyond 2100 nm in our spectra due

to the drastic decrease in spectral response between 2100–2500 nm. The spectra were also quite noisy from 1000 to 1300 nm due to the intensity corrections. Tentative feature assignments (Table 10) were made based on NIR absorption spectra of explosives published by Zapata et al.⁴⁷ and the general guidelines for NIR interpretation in Workman and Weyer.⁵² However, our emission spectra contain features not present in the published TNT and RDX absorption spectra⁴⁷ (e.g., near 1300, 1800, and 2000 nm) and are missing features that are present in the absorption spectra (e.g., near 1400 nm).

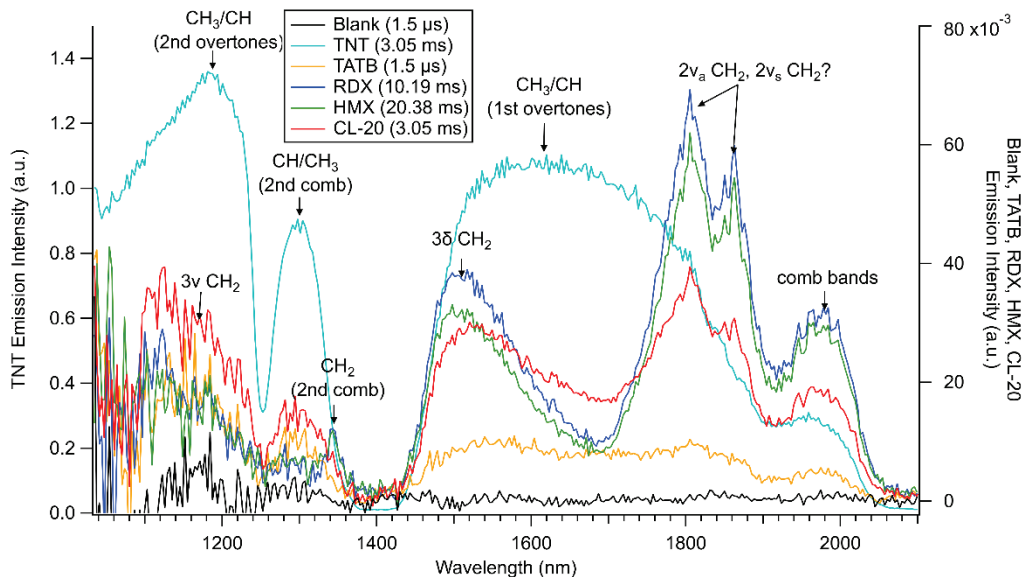


Fig. 33 Selected intensity-corrected spectra from the sequentially obtained series of NIR emission spectra for the blank tape and explosive samples

Table 10 NIR band positions and tentative assignments

Band position (nm)	Band assignment
~1170	3v CH ₂ (2nd overtone)
~1185	3v CH ₃ /CH
~1300	CH ₃ /CH combination bands
~1343	CH ₂ (2nd combination bands)
~1510	3δ CH ₂ (2nd deformation)
~1500–1800	2v CH ₃ /CH (1st overtones)
~1805	2v _a CH ₂ (asymmetric)
~1863	2v _s CH ₂ (symmetric)
~1978	Combination bands

While various overtone and combination bands for CH₃/CH (TNT) and CH₂ (TATB, RDX, HMX, CL-20) have been assigned, no clear evidence for NH or NH₂-related bands was found. There was also no evidence for atomic emission features such as O, Na, or K, which have previously been observed in this

region.^{45,50} Simulated spectra from the HITRAN–HITEMP database⁵³ were calculated at different temperatures to search for evidence of combustion or decomposition products such as NO₂, NO, H₂O, OH, O₂, H₂, CO₂, CO, or CH₄. NO₂ has no transitions in the wavelength region of our spectrometer. Example spectra for the remaining species are shown in Fig. 34. None of the spectra appeared to be a good match with the observed NIR emission spectra in Fig. 33.

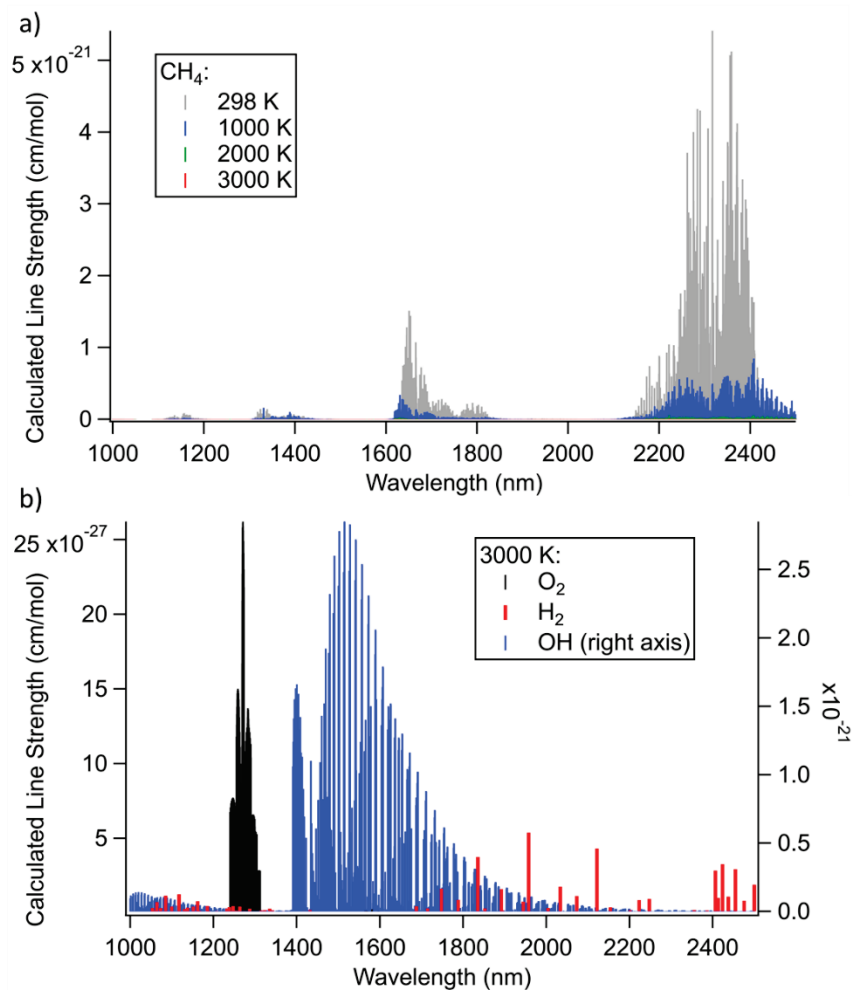


Fig. 34 Simulated spectra for a) CH₄ at different temperatures, b) potential decomposition products, and c) potential combustion products using the HITRAN–HITEMP database⁵³

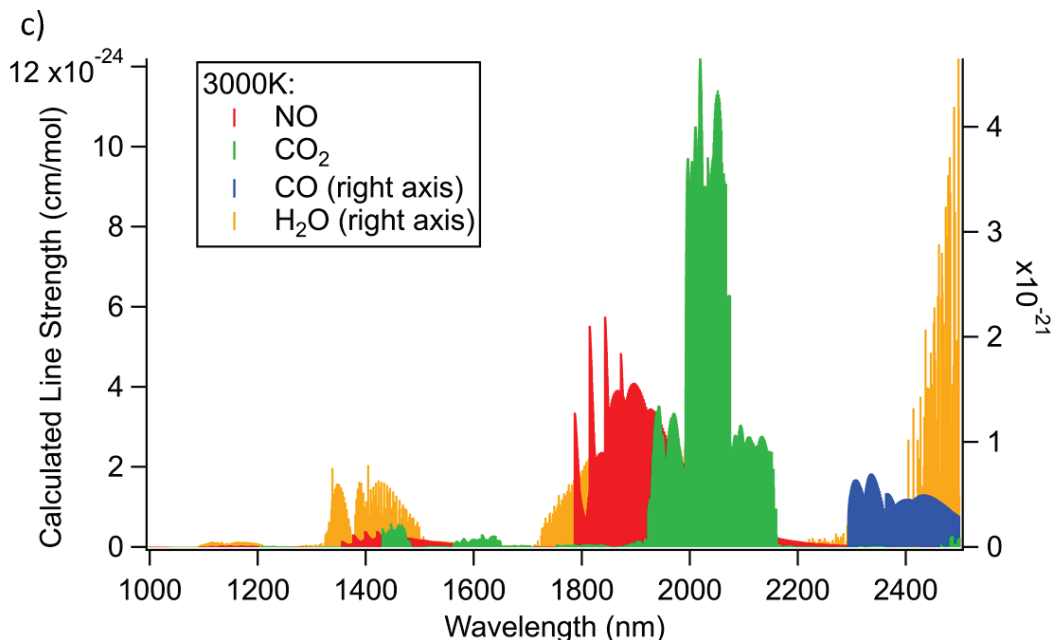


Fig. 34 Simulated spectra for a) CH₄ at different temperatures, b) potential decomposition products, and c) potential combustion products using the HITRAN–HITEMP database (continued)⁵³

3.2.4.3 Integrated Infrared Emission

Even though the sample preparation for the current experiments was not optimized for investigating the deflagration reactions of the explosives,⁴⁴ the time-resolved integrated IR emission provides information about the time to peak combustion and the duration of the combustion reactions. As shown in Fig. 35, CL-20 has the fastest time to peak combustion (2.2 ms), followed by HMX (7.8 ms). Re-ignition of the surrounding material results in a second combustion peak for HMX around 20 ms. TNT and RDX have similar times to peak combustion, while TATB has very weak combustion without a clear peak in intensity. TNT combusts for the longest period of time.

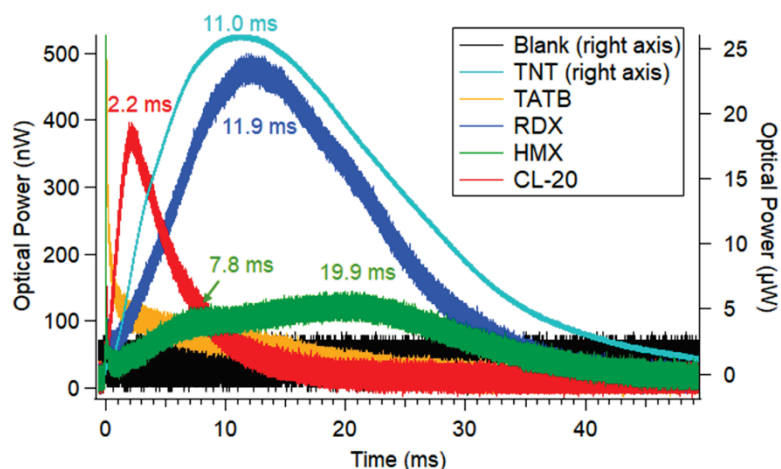


Fig. 35 Time-resolved integrated IR emission for the blank tape and explosive samples. The initial spikes at time zero are due to the laser-induced plasma emission.

4. Conclusions

Higher time-resolution LASEM data obtained for five explosives were used to demonstrate that the timescale for the chemical reactions of the ablated material to influence the plasma chemistry and resulting shock wave is between approximately 1–8 μ s. These data were also used to recalibrate the LASEM technique, resulting in improved correlation between the characteristic laser-induced shock wave velocities and the measured detonation velocities from large-scale testing ($R^2 = 0.9994$ vs. 0.9939). In addition, only 20 individual laser shots were acquired for each sample, compared to the 40+ shots used in the original calibration.

Because the fifth-order polynomial fit previously used to fit the laser-induced shock velocities did not initially appear adequate to describe the higher time-resolution data, alternative fitting methods were investigated. The speed of sound in air determined via a double exponential fit demonstrated that the more powerful explosives heated the surrounding air to higher temperatures. The measured speeds of sound were correlated with the measured detonation velocities of the materials ($R^2 = 0.9583$). A combination fit incorporating both Sedov-Taylor theory and the drag model was used to calculate the energy behind the laser-induced shock wave and estimate the mass of ablated material that reacted in the plasma. Although the values were higher than expected, the calculated energy was strongly correlated to the measured detonation velocities ($R^2 = 0.9920$). Finally, a Dewey fit with the speed of sound in air fixed to the values determined by the double exponential fit was used to fit the data. Although this fit resulted in values for the constants that were not physical, the correlation of Ba_0 with the detonation velocities was

reasonable ($R^2 = 0.9606$). None of the fits described all of the data perfectly (e.g., energetic vs. non-energetic, or early vs. late time).

The high-resolution laser-induced plasma emission spectra were used to understand the chemistry of the reacting material ablated into the plasma during the first 10 μ s. The fact that the emission intensities for C, H, N, and O did not correlate to their mole fraction in each explosive demonstrates the importance of the plasma chemistry during the time the laser-induced shock wave is passing through the plasma region. The CN and C₂ emission was shown to increase with decreasing OB. The O/C intensity ratio was reasonably well correlated to the estimated detonation performance ($R^2 = 0.8617$), despite the significant shot-to-shot variation in the emission intensities for the explosives. The laser-induced shock wave velocities were shown to directly correlate to both the number/type of CN bonds in the explosive and the number of NO₂ groups. The H emission features were used to calculate the plasma temperatures and electron densities for each sample. While the plasma temperatures were lower than those measured for the Al samples, they were strongly correlated to the calculated detonation temperatures for the explosives ($R^2 = 0.9737$). Time-resolved temperatures were also calculated, demonstrating the TATB takes the longest to reach its peak temperature. TATB has the lowest detonation temperature of the explosives. All of the explosives have faster temperature rises and higher peak temperatures than the blank tape substrate.

For the first time, NIR emission spectra of explosives following pulsed laser excitation have been reported. Distinct differences in the spectra, particularly between TNT (which has a CH₃ group on the aromatic ring) and the other explosives (which do not) were observed. Changes in the NIR spectra with the addition of Al (Part III⁵⁴) or other additives may provide insight into the chemistry of the reacting explosive materials.

Future work will look at the high-resolution, time-resolved emission from the laser-induced plasmas of the explosives to compare the chemical kinetics on a microsecond timescale. We also plan to repeat the experiments under argon to account for the influence of air entrained in the plasma. The extensive emission data presented here for conventional military explosives will be used to provide insight into the chemical reactions of novel energetic materials under development.

The edge-detection algorithm described in this report is currently being incorporated into a graphical user interface that will enable manual measurement of the shock wave position at early times, automated measurement of the shock wave position at later times, data fitting, determination of the characteristic laser-induced shock wave velocity, and estimates of detonation performance. This will

enable significant improvements in the time required for data analysis with LASEM.

5. References

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List of Symbols, Abbreviations, and Acronyms

1-D	one-dimensional
Al	aluminum
ARL	Army Research Laboratory
C	carbon
C ₂	diatomic carbon
Ca	calcium
CCDC	US Army Combat Capabilities Development Command
CH	methine group
CH ₂	methylene group
CH ₃	methyl group
CH ₄	methane
CHNO	carbon, hydrogen, nitrogen and oxygen
CL-20	hexanitrohexaazaisowurtzitane
CN	cyano radical
CNN	convolutional neural network
CO	carbon monoxide
CO ₂	carbon dioxide
FWHM	full-width at half-maximum
H	hydrogen
H ₂ O	water
HMX	cyclotetramethylene tetranitramine
IR	infrared
K	potassium
LASEM	laser-induced air shock from energetic materials
LTE	local thermodynamic equilibrium
Mg	magnesium

micron-Al	micrometer-sized Al particles
N	nitrogen
Na	sodium
nano-Al	Al nanoparticles
NH	imidogen
NH ₂	amino group
NIR	near-infrared
NO	nitric oxide
NO ₂	nitrogen dioxide
O	oxygen
OB	oxygen balance
OH	hydroxyl group
PMT	photomultiplier tube
R ²	R-squared value
RDX	cyclotrimethylene trinitramine
RSD	relative standard deviation
T_{air}	temperature of the air
TATB	triaminotrinitrobenzene
TMD	theoretical maximum density
TNT	trinitrotoluene
UV	ultraviolet
V _{det}	detonation velocity
VIS	visible

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