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RPPR Final Report

as of 31-Jan-2019

Agency Code:

Proposal Number: 63120EG

Agreement Number: W911NF-13-1-0217

INVESTIGATOR(S):

Name: Dana Dlott Ph.D.
Email: dlott@illinois.edu
Phone Number: 2173333574
Principal: Y

Organization: **University of Illinois - Urbana - Champaign**

Address: c/o Office of Sponsored Programs, Champaign, IL 618207406

Country: USA

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Final Report for Period Beginning 01-Jul-2013 and Ending 30-Apr-2019

Title: Fundamental Mechanisms of Impact Initiation of Reactive Materials (Research Area 1.4.2 Propellant Combustion Processes)

Begin Performance Period: 01-Jul-2013

End Performance Period: 30-Apr-2019

Report Term: 0-Other

Submitted By: Dana Dlott

Email: dlott@illinois.edu

Phone: (217) 333-3574

Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 2

STEM Participants: 6

Major Goals: The goal of this project is to understand the fundamental mechanisms of shock initiation of reactive materials (RM) or energetic materials (EM) using advanced shock compression instrumentation and diagnostics developed by us.

Accomplishments: We developed the "shock compression microscope" in which cassettes of hundreds of well characterized tiny plastic explosives can be studied upon impact with 0-4.5 km/s laser-launched flyer plates. This microscope has the ability to measure the pressure, density, temperature, composition and microstructure with high time and space resolution. We studied reactive materials consisting of Al and Teflon and nanothermites produced by ball milling. We developed the ability to produce controlled detonations on a tabletop and demonstrated this ability with a model system, liquid nitromethane, and a variety of plastic-bonded explosives. We studied the origin and mechanism of hot spots in shocked explosives.

Training Opportunities: Nothing to Report

Results Dissemination: This is a program of fundamental research and the results were disseminated in the form of 16 peer reviewed journal articles. In addition, the PI, postdocs and graduate students presented this work at national, international and topical meetings. The PI made 17 presentations, including Plenary talks in Nagoya and Beijing.

Honors and Awards: Dana Dlott. • American Chemical Society Physical Chemistry Division Award in Experimental Physical Chemistry, 2013

Dana Dlott. • William H. and Janet G. Lycan Professor of Chemistry

James Christensen NDSEG fellowship 2014

Dana Dlott. Lippincott Award in Vibrational Spectroscopy from the Optical Society of America, 2015.

Will Bassett. Harry G. Drickamer Fellowship

William Shaw. Award to fund attendance at Gordon Research Conference on Energetic materials.

Will P. Bassett. Award to fund attendance at Gordon Research Conference on Energetic materials.

Will P. Bassett. GSCCM Early Career Award from American Physical Society

Protocol Activity Status:

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Technology Transfer: A number of DoD and DOE laboratories have copied aspects of our shock compression microscope, including Sandia, Los Alamos, Livermore, and Army Research Laboratory. Dr. Lara Leininger of the Energetic Materials Center at Livermore Labs hired Will Bassett as a postdoc so he could build our pyrometer at Livermore.

PARTICIPANTS:

Participant Type: PD/PI

Participant: Dana Donald Dlott

Person Months Worked: 1.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: William L. Shaw

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: James M. Christensen

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Will P. Bassett

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Jue Wang

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Alexandr A. Banishev

RPPR Final Report
as of 31-Jan-2019

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Belinda Johnson

Person Months Worked: 2.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Erin Nissen

Person Months Worked: 2.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Lawrence Salvati III

Person Months Worked: 6.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Undergraduate Student

Participant: Hoya Ihara

Person Months Worked: 2.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

ARTICLES:

RPPR Final Report

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Review of Scientific Instruments

Publication Identifier Type: DOI

Publication Identifier: 10.1063/1.4871361

Volume: 85

Issue: 4

First Page #: 43908

Date Submitted:

Date Published:

Publication Location:

Article Title: Laser-driven flyer plates for shock compression science: Launch and target impact probed by photon Doppler velocimetry

Authors:

Keywords: shock wave, laser launch

Abstract: We investigated the launch and target impact of laser-driven Al flyer plates using photon Doppler velocimetry (PDV). We studied different flyer designs launched by laser pulses of different energies, pulse durations and beam diameters, that produced km s⁻¹ impacts with transparent target materials. Laser-launching Al flyers 25–100 μm thick cemented to glass substrates is usually thought to involve laser vaporization of a portion of the flyer, which creates many difficulties associated with loss of integrity and heating of the flyer material. However, in the system used here, the launch mechanism was surprising and unexpected: it involved optical damage at the glass/cement/flyer interface, with very little laser light reaching the flyer itself. In fact the flyers launched in this manner behaved almost identically to multilayer flyers that were optically shielded from the laser pulses and insulated from heat generated by the pulses. Launching flyers with nanosecond laser pulses creates u

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Journal of Physics: Conference Series

Publication Identifier Type: DOI

Publication Identifier: 10.1088/1742-6596/500/19/192002

Volume: 500

Issue: 19

First Page #: 192002

Date Submitted:

Date Published:

Publication Location:

Article Title: Dynamics of shocks in laser-launched flyer plates probed by photon Doppler velocimetry

Authors:

Keywords: shock waves, laser launch, target impact

Abstract: We investigated the launch and impact with glass targets for four different thicknesses of Al laser-launched flyer plates by monitoring the flight with photon Doppler velocimetry (PDV). The amplitudes and damping times of the reverberating shocks in the flyers, created by short laser pulse launching, were investigated as a function of pulse duration using 10 or 20 ns laser pulses. The shorter pulse duration showed a surprisingly more efficient damping process in the thicker flyers. The durations of the supported shocks in the glass targets were also measured as a function of flyer thickness. The supported shock durations were significantly shorter than the common picture of shock round-trip transit time in the flyer.

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Journal: Journal of Physics: Conference Series

Publication Identifier Type: DOI

Publication Identifier: 10.1088/1742-6596/500/18/182010

Volume: 500

Issue: 18

First Page #: 182010

Date Submitted:

Date Published:

Publication Location:

Article Title: Using laser-driven flyer plates to study the shock initiation of nanoenergetic materials

Authors:

Keywords: shock initiation, energetic materials

Abstract: A tabletop system has been developed to launch aluminium laser-driven flyer plates at speeds of up to 4 km/s. The flyers were used to initiate nanoenergetic reactive materials including aluminium/iron oxide and aluminium/molybdenum oxide thermites produced by arrested reactive milling. The flyer flight and impact was characterized by photon Doppler velocimetry and the initiation process by time-resolved emission spectroscopy. Impact initiation thresholds were determined for 50 μ m thick flyer plates producing 10 ns shocks. The intensities, delays and durations of the emission bursts, and the effects of nanostructure and microstructure on them were used to investigate fundamental mechanisms of impact initiation.

Distribution Statement: 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Journal of Physics: Conference Series

Publication Identifier Type: DOI

Publication Identifier: 10.1088/1742-6596/500/14/142011

Volume: 500

Issue: 14

First Page #: 142011

Date Submitted:

Date Published:

Publication Location:

Article Title: Laser-driven flyer plates for shock compression spectroscopy

Authors:

Keywords: shock wave, laser launch, energetic materials

Abstract: A laser-driven mini flyer plate system, with 8 GHz photon Doppler velocimeter and high-speed spectroscopic diagnostics, was developed for shock compression spectroscopy. The properties of the flyer plate platform are discussed, and its use in two applications is reported. The two applications were impact initiation of nanotechnology reactive materials and molecular optical emission sensors to monitor mesoscale effects in a shock-compressed polymer.

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Propellants, Explosives, Pyrotechnics

Publication Identifier Type: DOI

Publication Identifier: 10.1002/prop.201400027

Volume: 39

Issue: 3

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Date Submitted:

Date Published:

Publication Location:

Article Title: Ignition of Nanocomposite Thermites by Electric Spark and Shock Wave

Authors:

Keywords: Reactive materials · Energetic materials · Ignition delay · Burn time · Impact ignition · ESD ignition

Abstract: Nanocomposite 8Al · MoO₃ thermite particles were prepared using arrested reactive milling and ignited using two experimental techniques. In spark ignition, a monolayer of powder was placed on a conductive substrate and heated in air by a pulsed electrostatic discharge. In shock ignition, an individual particle was targeted by a miniature, laser-driven flyer plate accelerated to a speed in the range of 0.5–2 km s⁻¹. In both experiments, time-dependent optical emission produced by the ignited material was monitored and recorded. The heating rates achieved in the present experiments are on the order of 10⁹–10¹¹ K s⁻¹. These ignition methods result in a very fast combustion with characteristic burn times reduced by 1–3 orders of magnitude compared to the burn times measured previously for the same material ignited in the CO₂ laser beam, where it was heated at a much lower rate of about 10⁶–10⁷ K s⁻¹. Ignition delays observed in both shock and spark ignition experiments are close to each other.

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Publication Status: 1-Published

Journal: AIP Confer Proc

Publication Identifier Type:

Publication Identifier:

Volume:

Issue:

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Date Submitted: 7/24/18 12:00AM

Date Published:

Publication Location:

Article Title: Studies in shocked nitromethane through high dynamic range spectroscopy

Authors: Mithun Bhowmick, Erin J. Nissen, Sergey M. Matveev and Dana D. Dlott

Keywords: detonation nitromethane shock waves

Abstract: We have developed a tabletop apparatus to study shocked liquid explosives. We use 0–6 km s⁻¹ laser-launched flyer plates and an array of liquid microcells that are probed with high-speed Doppler velocimetry and emission spectroscopy. Here we studied nitromethane (NM) and each cell containing about 2 mg of explosive. We showed there was a reaction threshold at a flyer plate velocity of 3.1 km s⁻¹ (P = 15 GPa). The reaction began immediately after the shock entered the NM, which reacted at a temperature of 3700 K (±280 K). A series of careful tests showed the incoming shock was initially planar and steadily driven for several ns. The shock and the explosive emission were highly reproducible and experiments could be run at a rate of 50 shocks per day.

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Journal: AIP Confer Proc
Publication Identifier Type: **Publication Identifier:**
Volume: **Issue:** **First Page #:**
Date Submitted: **Date Published:**
Publication Location:

Article Title: Laser driven flyers for investigations of shock initiation of explosives

Authors: Will P. Bassett, Belinda P. Johnson and Dana D. Dlott

Keywords: shock initiation, energetic materials

Abstract: A full description and characterization of a tabletop laser-launched flyer plate system with associated high-speed diagnostics is presented. With this tabletop system, we can investigate shock initiation and detonation of energetic materials with hundreds of shots per day. The present study focuses on application of the 32-channel pyrometer developed in our group for optical temperature measurements of hot spots in shock-initiated energetic materials. Extremely high temperature (>6000 K) hot spots have been observed in fine powders of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and the shock duration dependence on chemical kinetics has been studied. Polymer bound (PBX) charges with controllable microstructure were used to identify the origins of high temperature hot spots. Hot spot temperatures were reduced to 4000 K when an elastomeric binder was used to fill void spaces between powder grains. We attribute these high temperatures to adiabatic compression of gases in micro

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Conference Name: International symposium on shock waves 31
Date Received: **Conference Date:** 10-Jul-2017 **Date Published:**
Conference Location: Nagoya, Japan
Paper Title: Shock compression spectroscopy under a microscope
Authors: Dana D. Dlott
Acknowledged Federal Support: Y

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Publication Type: Thesis or Dissertation
Institution: University of Illinois at Urbana-Champaign
Date Received: 24-Jul-2018 **Completion Date:** 7/10/18 10:06PM
Title: Shock initiation of explosives under the microscope
Authors: Will P. Bassett
Acknowledged Federal Support: Y

Publication Type: Thesis or Dissertation
Institution: University of Illinois at Urbana-Champaign
Date Received: 29-Jan-2019 **Completion Date:** 8/12/16 12:47AM
Title: Reactive solids under shock compression
Authors: William L. Shaw
Acknowledged Federal Support: Y

RPPR Final Report
as of 31-Jan-2019

Introduction. W911NF-13-1-0217 is a four-year grant that began 1 July 2013. Just about that time our group won a MURI grant from ONR and suddenly received a significant input of funding. We were not able to spend the ARO money in a timely fashion, so we arranged for the project to be extended until Apr. 30, 2019. Now we have expended all funds and we are bringing the project to a close. The goal of this project is to understand the fundamental mechanisms of shock initiation of reactive materials (RM) or energetic materials (EM) using advanced shock compression instrumentation and diagnostics developed by us. Our experiments are radically different from the usual shock compression techniques that involve using large guns or bombs. We do our experiments on a tabletop under a microscope, and we can do hundreds of shots per day. This means we can study shock with unprecedented detail and under a wide variety of conditions, and we can develop advanced diagnostics by troubleshooting them with shot after shot. Our tabletop experiments produce planar shocks that are as powerful and as well-characterized as the most advanced gas gun systems.¹ However our shocks are tiny, 0.5 mm in diameter, and the duration is short, less than 20 ns. So the method has limitations in that it cannot study large scale, long time phenomena such as the blast effects of a bomb, but it is ideal for understanding the short time-short length scale phenomena that reveal fundamental mechanisms. In particular our techniques allow us to understand shock initiation of RM and EM at the atomistic level and at the mesoscale level.

Instrument development. The technology we have developed is called the “shock compression microscope,” which is diagrammed in Fig. 1 and shown in Fig. 2. It uses laser-launched 0-4.5 km/s flyer plates, a photon Doppler velocimeter (PDV) to measure velocities, pressures and densities, an optical pyrometer to measure temperature profiles, and a high –speed camera interfaced to the microscope to produce diffraction-limited nanosecond imaging of shocked microstructures. In order to study molecular composition, we have developed a separate mid-IR reflection-absorption microscope shown in Fig. 2.

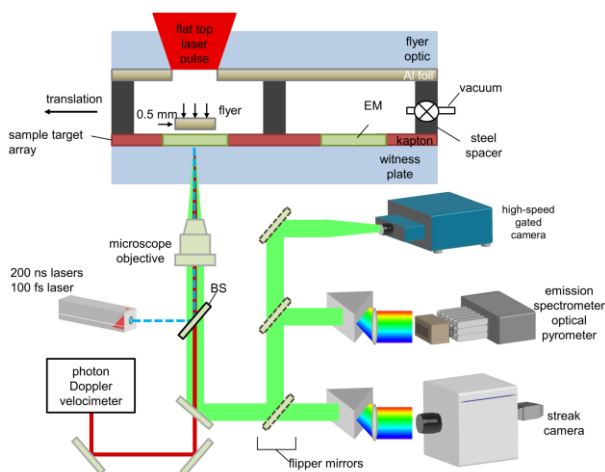


Fig. 1. Schematic of the shock microscope with 0-4.5 km/s flyer plates and a multielement shock target array. The instrument can measure the pressure, density, temperature, composition and microstructure of a shocked energetic material (EM).



Fig. 2. Shock compression microscope and associated diagnostics.

Since shock measurements invariably destroy the target, we have developed methods to produce arrays of explosive charges. We can make arrays with 50 tiny cuvettes of liquid explosives, arrays with nanoparticle explosives, either as a continuous sheet (e.g. Al/Teflon^{AF}) or as tiny wells packed with nanothermite powders (e.g. Al/MoO₃). We can produce arrays with about 200 well-characterized tiny cylindrical charges of plastic-bonded explosives (PBX) 1 mm in diameter with thicknesses ranging from 25 to 250 μm . Figure 3 shows an array with 186 PBX charges as well as electron microscope and x-ray images of RDX or TATB 1 mm diameter cylinders.

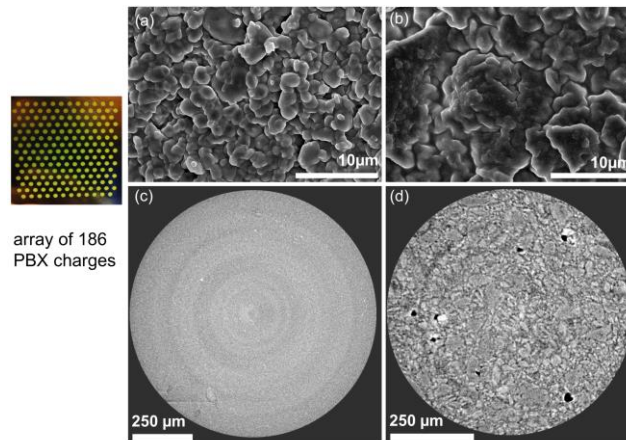


Fig. 3. (left) Shock target array. (right) Scanning electron microscope (SEM) and x-ray computed tomography (CT) images of PBX charges made with RDX (left) or TATB (right) with PDMS binder.

Optical pyrometer. We developed an optical pyrometer with 32 independent spectral channels, that obtains streams of 10,000 emission spectra, one every 800 ps. We fit each spectrum to a graybody function to determine temperature, and with so many spectral channels, we can assess the presence of non-graybody emission, typically emission from hot atoms or molecules, and separate the graybody part from the nongraybody part, for greatly increased temperature accuracy, as illustrated in Fig. 4.

Data from two illustrative shots are shown in Fig. 4, where an Al/CuO nanothermite is impacted at 0.5 km/s or a 1 km/s impact with a small amount of HMX on a glass slide.² First note the log time axis used to display the multiscale nature of the data. There are two distinct phases of reaction, one occurring in the nanosecond range which corresponds to reactions during or immediately after the shock, and one in the microsecond range which corresponds to deflagration of the material that did not react during the shock.

One of the biggest problems with optical pyrometry of explosives is that the graybody emission used to determine

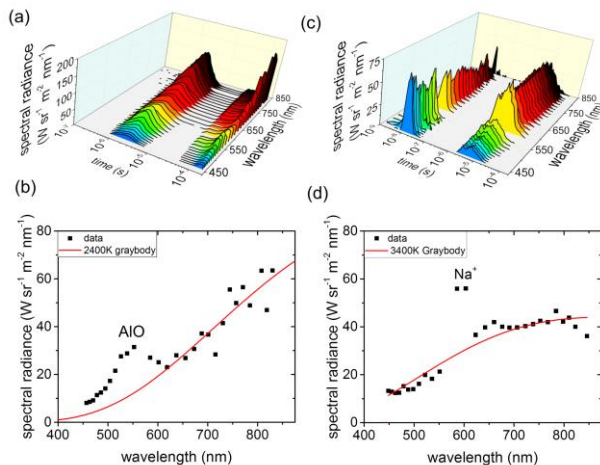


Fig. 4. Graybody temperature measurements in the presence of molecular band or atomic line emissions for (a-b) Al/CuO nanothermite at 0.5 km/s or (c,d) a few micrograms of HMX on a glass window at 2 km/s. The best fits to a graybody (smooth curves) give the temperature and emissivity. The nanothermite makes AlO vapor and the HMX vaporizes some of the glass to produce the bright yellow sodium ions.

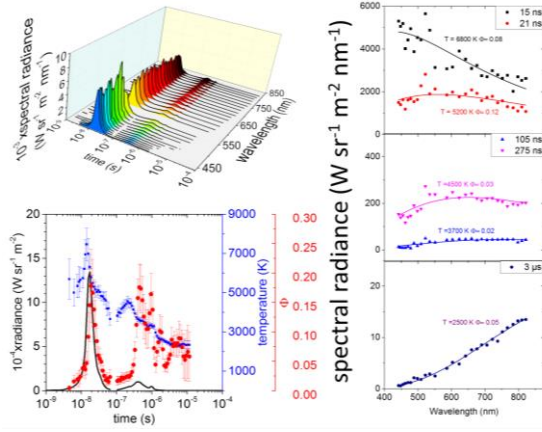


Fig. 5. Graybody from 30 μg of HMX at 2.0 km/s. A few spectral radiances at different times and the graybody fits are shown at right. The emissivity (red) shows two stages of chemical reactivity, hot spots following the nanosecond shock and deflagration of the unreacted material in the microsecond time range.

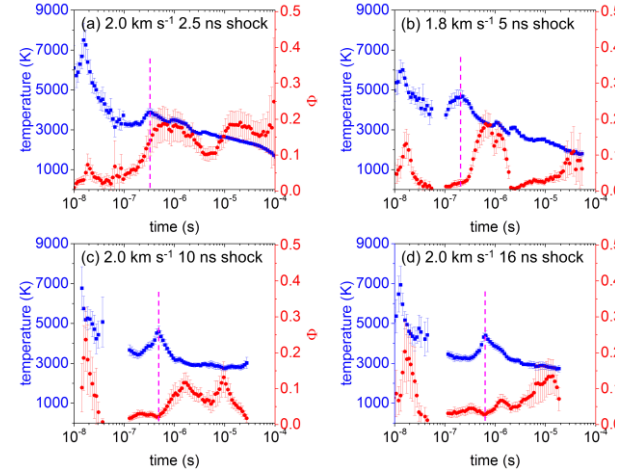


Fig. 6. A series of shots on HMX at 2.0 km/s with different duration shocks. The emissivity shows a nanosecond and a microsecond process, representing two stages of chemical reactivity. With longer duration shocks, an increasing amount of the chemical reactivity happens in the nanosecond regime.

temperature is sometimes contaminated by molecular or atomic line emissions. If the pyrometer does not have good spectral resolution, these interfering lines totally ruin the ability to measure temperature. Our solution to this problem comes from the large number of discrete wavelength channels, as shown in Fig. 4. It then becomes easy to identify the molecular emission (in this case the unresolved vibronic bands of AlO) or the atomic emission (in this case Na^+ emission from the glass), and extract the underlying graybody spectrum.

Figure 5 shows how we analyze and plot data from the pyrometer. The sample is fine HMX powder and the impact velocity is 2 km/s. The pyrometer output from one shot, in the form of spectral radiance, is plotted with $\log(\text{time})$. At any time (a few are shown), the spectral radiance can be analyzed to obtain the temperature T and the emissivity ϕ . Generally speaking, the temperature comes from the wavelength-dependence and the emissivity from the intensity. The spectral radiance can be integrated over wavelength to give the radiance. The radiance is the intensity of light emitted. The temperature is the temperature. The emissivity shows how the optical properties of the sample change. Large changes in emissivity indicate large-scale chemical reactivity. The HMX reacts in two stages.³ The first stage starts near the end of the shock and it lasts for a few tens of nanoseconds. The second stage, which is a deflagration at ambient pressure, starts at a few hundred nanoseconds and lasts for 10 μs or more.

Figure 6 shows results from another very interesting and unique HMX experiment. The impact velocity was held at 2.0 km/s while the shock duration was varied from 2.5 to 16 ns using Al foil flyers of different thicknesses (12.5 to 75 μm thick). This allows you to roughly map out chemical kinetics in the shock reaction zone. As in Fig. 6, we see a two stage reaction in the

emissivity. As the shock duration increases, the faster part becomes bigger at the expense of the slower part. With longer-duration shocks, there is more time for the reaction during the shock and less unreacted material left over to feed the later deflagration. When the shock is short in duration, it interrupts the HMX shock reaction. If the shock were a bit longer than 16 ns, we should be able to get all the HMX to react during the shock stage, and that time would be the time constant for the HMX reaction.

Origin of hot spots in PBX. The data in Figs. 7-9 use our homemade PBX, which consists of 80% PETN with 20% PDMS binder. This recipe was intended to produce a PBX quite similar to the commercially available PBX denoted XTX-8003^{4,5} (hereafter just XTX). We made the XTX in two microstructural forms. We dilute the PDMS with hexanes and mix in the (insoluble) PETN crystals and let it dry. The result is the highly microporous structure shown in Fig. 7. We then took the microporous XTX and compressed it with a hydraulic press to squeeze out the pores. This compression step is also used in the synthesis of the commercial XTX. After compression, the scanning electron microscope image in Fig. 7 shows that there are no visible pores larger than 1 μm , the instrumental resolution. This procedure makes a nanoporous or homogenized XTX. Shock initiation of these two microstructures produces dramatically different results, as shown in Fig. 7. With the microporous XTX, the shock produces a massive concentration (a large emissivity change) of hot spots that reach more than 7000K. Then there is a slower, messy process where the unreacted material deflagrates on the microsecond time scale. With the homogenized XTX, the hot spot concentration is small and the initial temperature is 4000K. The deflagration is orderly and it occurs in a time band centered at 2 μs . We have shown that the massive concentration of hot spots produced in the microporous XTX results from adiabatic compression of gas in the pores.⁶ Gas compression produces much higher temperatures than solid compression due to the much larger volume change with gas.⁷ Figure 8 shows temperature histories with 2.8 km/s impacts when the gas in the pores was air, Ar, N₂, O₂, C₂H₂ and C₄H₁₀. The polyatomic gases make much lower initial temperatures than the monatomic and diatomic gases due to their higher heat capacities. This shows that the high temperature hot spots are created by gas compression. It is very interesting that we see the same behavior when the sample is in vacuum as when it is filled with

polyatomic gases. We have shown that when the sample is in vacuum, the shock causes the PETN to outgas and fill up the pores with polyatomic molecule gases.⁶ This means that experiments where people put the sample in vacuum do not really eliminate gas in the pores. The pores are promptly filled with gas produced by the explosive.

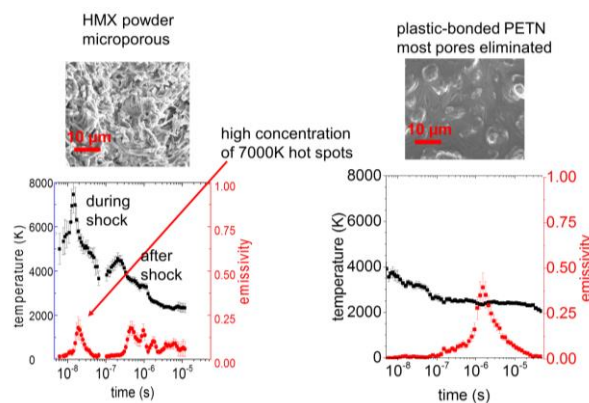


Fig. 7. Experiments at 2.7 km/s on PETN-based plastic explosive XTX-8003 made either microporous or nanoporous. The microporous material has many hot spots up to 7000K. Homogenizing the material eliminates the hot spots and concentrates the reactivity into a narrow time range around 2 μs .

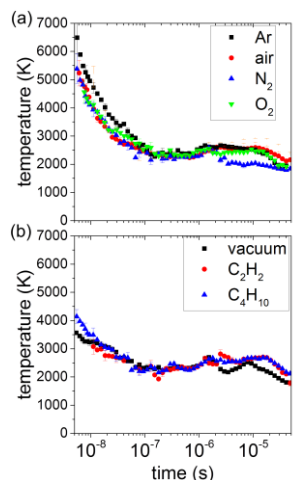


Fig. 8. Temperature histories for XTX-8003 at 2.7 km/s with the pores filled with different gases. The peak temperatures are much lower with the polyatomic gases.

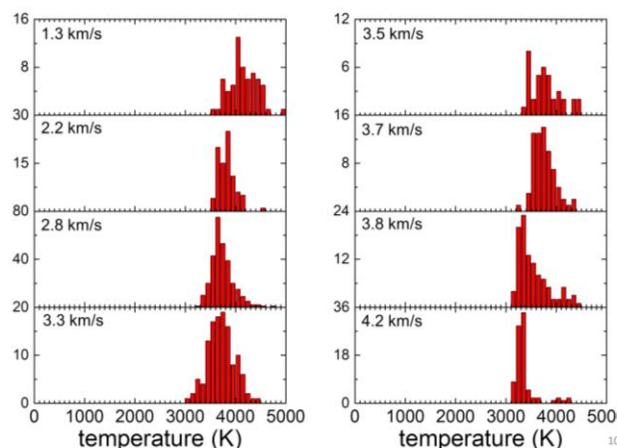


Fig. 9. Temperature histograms (initial peak temperature) for XTX-8003 at different impact velocities. The 2.8 km/s flyer launches a detonation-strength shock in this material.

With our high shock repetition rate, we can study statistical variation in the initiation of EM and RM. Some preliminary results are shown in Fig. 9 using our XTX samples with many hundreds of shots. We have plotted the initial temperatures of the shocked homogenized XTX. We have shown the temperature variations are not due to error in the temperature measurements, but rather to differences in the microstructures of the individual charges.

Shock initiation of reactive materials. We have collaborated with Prof. Edward Dreizin of NJIT, who produces and characterizes nanothermites, to study shock initiation and to compare shock to spark ignition, and we have studied nano-Al in Teflon produced in our own laboratory.

Most of the quantitative measurements reported to date and characterizing reactions leading to ignition of reactive nano-materials have relied on thermal analysis. Measurements associated with faster processes have also been reported, including time-resolved mass-spectrometry following ignition of nano-thermites, micro- and nano-calorimetry, and measurements of optical emission and pressure generated by the material coated on an electrically heated filament. In all those measurements, the heating rates were sufficiently low and the ignition delays were sufficiently long to ensure the temperature uniformity within the ignited nanocomposite structure. A model describing exothermic reactions for the thermally initiated, fully dense nano-thermite particles has been proposed quantifying individual reaction steps and predicting a thermal runaway to occur in vicinity of the experimental ignition temperature. However, additional processes, including the release of oxygen prior to ignition and a burst of ions produced by the rapidly heated nano-thermites, possibly associated with the oxygen release, have been reported but have not been well understood. Such processes can affect ignition and ensuing combustion of reactive nano-materials; the effect may depend on the rate of heating and respective ignition delay.

Different ignition stimuli are expected to be important for different potential applications of the newly developed reactive nano-materials. In particular, rapid initiation processes, such as

electric spark or shock wave may produce a situation when the igniting nano-material is not uniformly heated; in addition, shocks may cause both bulk and local deformations, and fractures. Some parts of the sample may be substantially hotter than others, fresh direct contacts between fuel and oxidizer may be generated at the mechanically affected locations generating hot spots and leading to localized ignition. Such localized ignition may not necessarily be well described by the earlier kinetic models, dealing with a homogeneously heated material. Furthermore, for the samples that are heated relatively slowly, the nanostructure may be lost when they burn and their temperature exceeds the melting points of the major components; conversely, the nanostructure may be preserved in very rapid reactions, occurring faster than the characteristic times required to change the material structure and morphology. Thus, the heating rate and the method of initiation of the nano-composite reactive material may affect both its ignition kinetics and combustion dynamics.

Ignition of fully-dense, nanocomposite thermite particles prepared by Arrested Reactive Milling (ARM) was studied experimentally using two methods leading to a very fast initiation. In one experiment, the particles placed on a conductive substrate are ignited using an electric spark (or an electro-static discharge, ESD). In the other experiment, the particles are struck by a supersonic flyer plate and are ignited as a result of the induced shock. In both cases, the observed ignition delays are of the order of 100 ns, which is insufficient for the temperature equilibration in the ignited particles.

The nanocomposite powder, metal-rich thermite $8\text{Al}\cdot\text{MoO}_3$ produced by ARM, has been used in several recent studies focused on its ignition and combustion. It was prepared using an aluminum powder, -325 mesh, 99.5% purity by Atlantic Equipment Engineers and molybdenum oxide powder, -325 mesh, 99.95% purity by Alfa Aesar. The starting powders were blended together and milled in hexane under argon environment for 30 min using a Retsch PM 400MA planetary mill.

An SEM image of the prepared powder particles is shown in Fig. 10. The metal and oxidizer appear to be well mixed with no visible formation of aluminum oxide or reduced metallic phase. The material consists of irregularly shaped, roughly equiaxial composite particles ranging from about 0.5 to 50 μm . The particle size distribution obtained using a Beckman-Coulter LS230 Enhanced Particle Analyzer is shown in Fig. 11, indicating 21.8 μm as the specific volumetric mean particle size.

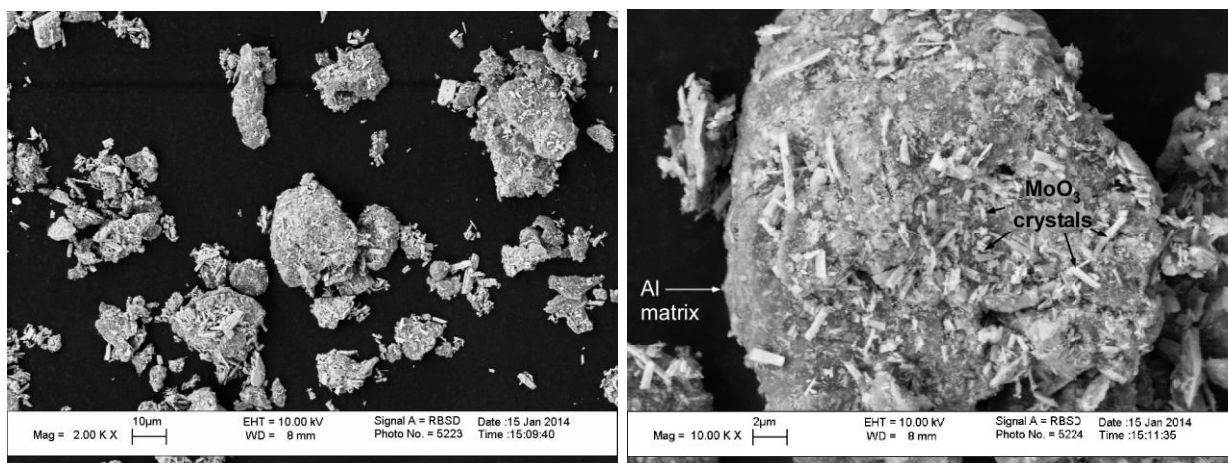


Figure 10. SEM images showing the particle shapes and surface morphology for the prepared $8\text{Al}\cdot\text{MoO}_3$ nanocomposite powder.

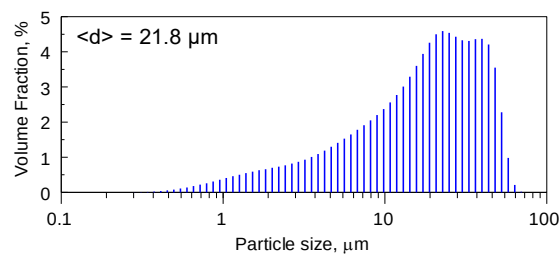


Figure 11. Particle size distribution for the prepared $8\text{Al}\cdot\text{MoO}_3$ nanocomposite powder.

A monolayer of $8\text{Al}\cdot\text{MoO}_3$ powder was used in all present experiments. A small amount of powder was placed on a double-sided carbon tape attached to an 18-mm diameter custom-made polished brass support. Excess powder was blown away, and the powder remaining on the tape formed a monolayer, as was confirmed by inspection of the prepared samples using an SEM. The sample holder was grounded. A needle-electrode was fixed approximately 0.2 mm above the powder surface, following a standard methodology (MIL-STD-1751A). A spark was triggered using FTS. All experiments were performed in room air.

The discharges with different energies were produced using a 2000-pF capacitor charged to a voltage varied from 3 to 8 kV. Typically, five experiments were performed for each voltage.

An inductance coil model 110 A with a 1 V/10 A ratio by Pearson Electronics was used to measure the spark current. Current traces were recorded by a LeCroy WaveSurfer 64Xs Series oscilloscope. The powder resistance, R_p , was determined based on the current traces recorded for the same ESD settings for the sample holders with and without powder. For each experiment, the current trace, showing a decaying oscillatory pattern, was matched with that calculated for an R - C circuit connected in series (where the capacitance, $C=2000$ pF). The traces were matched to each other by adjusting the circuit impedance, R , so that the equivalent resistance for each experiment was obtained. The circuit impedance was assumed to remain constant during the discharge. The current traces were matched with a 95% confidence interval. The difference between resistances for the powder-loaded and empty sample holders was

assumed to represent R_p . Joule heating energy was obtained by numerical integration of $I^2(t)R_p\Delta t$, where I is the recorded ESD current, t is time, and Δt is the time step of the data acquisition.

In all present experiments, ignition was accompanied by multiple streaks of ejected and individually burning particles. The emission produced by the igniting powder was measured using a Hamamatsu, H3164-10 photomultiplier tube (PMT) with 0.8 ns rise time equipped with a 486-nm interference filter. The PMT output was recorded using a LeCroy WaveSurfer 64Xs Series oscilloscope.

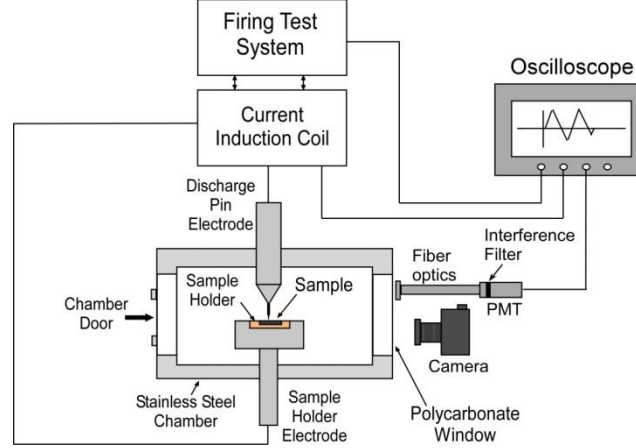


Figure 12. Schematic of the experimental set-up for ESD ignition.

Aluminum laser-driven flyer plates were used to shock individual 10-20 μm 8Al·MoO₃ thermite particles, and the resulting optical emission was time resolved. The Al disks fly in vacuum across a 350 μm gap before colliding with the target. As they fly, the edges of the plates become distorted, but upon impact the flyers have an estimated 160 μm diameter planar region in the center, much larger than the target particles. This type of impact process produces a planar shock in the thermite particles. The shock duration is dependent on the material being impacted, but with the flyers used here, the duration was ~ 10 ns.

The targets consisted of 8Al·MoO₃ thermite particles adhered to a glass window by a thin layer of cement. The targets were prepared by spin coating a 0.75 μm thick layer of UV curable acrylic cement (Dymax 401) onto a 1/4 inch thick BK7 glass window. The 8Al·MoO₃ thermite powder, suspended in hexane, was deposited onto a glass slide and the hexane was allowed to evaporate. The thermite was then tapped off the slide onto the cement layer. A UV lamp was used to cure the glue and fix the particles while the sample was attached to a spin coater. The quantity of thermite was chosen so that the thermite layer was mainly in the form of isolated individual particles. A microscope image of a typical target is shown in Figure 10b.

This apparatus allows us to target an individual, size-selected thermite particle, launch a flyer plate at a selected velocity, monitor the velocity history of the flyer, and detect the time-resolved emission from the shocked thermite. The velocity histories of the flyer plates are measured using PDV operating at 1550 nm laser wavelength. The PDV is detected by electronics, including a digital oscilloscope, with a combined bandwidth of 7.4 GHz, which is

capable of monitoring speeds up to 5.4 km/s. The PDV data were analyzed using a short-time Fourier transform analysis. There was an estimated 1 ns uncertainty in measuring the timing of flyer impact.

A 10x microscope objective and a dichroic beamsplitter was used to observe the thermite particles, direct the PDV beam onto the flyer, collect the returned PDV signals and collect the thermite emission. The PDV beams were collimated and 60 μm in diameter, so enough of the PDV beam passed by the thermite particles (Figure 10a) to monitor the flyer plates.

In our apparatus, we could insert a mirror that allowed us to observe the target with a homebuilt video microscope. We translated the target until a particle of suitable size was centered in the image, and we stopped down an iris so that we observed only the 50 μm diameter region immediately adjacent to the selected single thermite particle. An image of a roughly 20 μm thermite particle within the iris aperture is shown in Fig 10c. We then removed the mirror and directed light from the thermite particle into a photomultiplier tube (Hamamatsu, H10720-20) with a 0.8 ns rise time. The PMT signals were digitized using the same oscilloscope that detected the PDV signals. The photomultiplier tube (PMT) and PDV time delays were determined. This synchronization procedure involved simultaneous measurements of 10 ns laser pulses by both devices, and we have estimated the synchronization error between flyer impact and emission risetime to be 5 ns.

We should note that when we cite the size of the irregularly-shaped thermite particles, we refer to the diameter of the minimum circle that could be circumscribed around the particle image. Thus particles with the same cited diameter may have significantly different masses and volumes.

When the laser-driven flyer-plate impacts a particle, the pressure, density, and temperature of the particle jump as the shock front passes through the sample. We do not have an accurate equation-of-state for these thermite particles, or a truly accurate way to describe a shock in such a nanostructured medium. However, we can illustrate the shock properties by describing what would happen if the particles were pure Al and nonreactive, and the flyer speeds were either 1 km/s or 2 km/s. Using the well-known Hugoniot-crossing method and the principal Hugoniot of Al, we find that with a 1 km/s flyer, the shock transit time across a 20 μm thick particle would be 3.5 ns, the pressure would be 8.2 GPa and the compression would be 8.5%. We can also estimate the peak temperature during the shock. With a 1 km/s flyer, a particle initially at 300K would be briefly heated to 366K. The corresponding values for a 2 km/s flyer would be 3.1 ns transit time, 17.8 GPa pressure, 15% compression and 493K. These conditions are crude estimates for the temperatures of shocked thermite particles on short times scales that precede the onset of exothermic reactivity. Given that it takes only 3.1 ns for the particle to be shocked, the heating rate is close to $6.3 \cdot 10^{10}$ K/s.

In the actual shocked thermite particles there may be multiple shock reverberations at the interfaces between grain boundaries. There may be defects or voids which the shock may collapse. There may be frictional heating at moving edge dislocations. There will be reflections from the thermite-glue-glass interface. All these factors can create nanometric regions with

transient temperatures that exceed the bulk temperature rises, i.e. the complicated nanostructure and microstructure of the thermite particles can promote the creation of hot spots.

Figure 10d shows an image of a target after the 20 μm particle shown in Figure 13c was impacted by the 700 μm diameter flyer plate at 1 km/s. Besides the Al crater left over from the flyer plate, one can see a smaller faint image in the central region, that is about the same size as the original thermite particle. We believe this region denotes debris from the shock-reacted thermite particle.

Ignition experiments carried out for $8\text{Al}\cdot\text{MoO}_3$ powder monolayers always produced multiple burning particles resulting in an emission signal similar to that shown in Fig. 14. An initial fast rise is followed by a slower increasing emission intensity. The slow rise segment becomes more apparent and extends to longer times at greater spark energies. The time axis is broken between 30 and 90 μs , while the signal continues to decrease. The overall duration of the recorded emission signal, corresponding to the time of combustion varied from ca. 120 to 200 μs and did not apparently depend on the spark energy. These times are determined from the emission traces, such as shown in Fig. 14 while the signals exceeded three times the amplitude of fluctuations observed at the zero emission level (prior to the spark). Images in Fig. 6 show a photograph of burning particle streaks observed in a typical experiment and partially burned particles captured on a Cu foil placed approximately 2 mm from the powder.

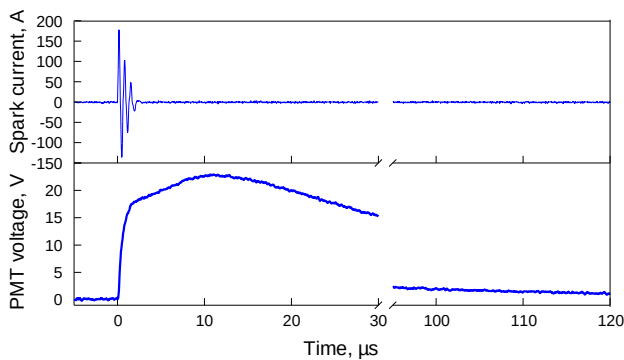


Figure 13. An ESD spark current trace and a PMT voltage corresponding to the emission of the burning sample recorded in an ignition test with a monolayer of nanocomposite $8\text{Al}\cdot\text{MoO}_3$ powder. The spark voltage is 8 kV.

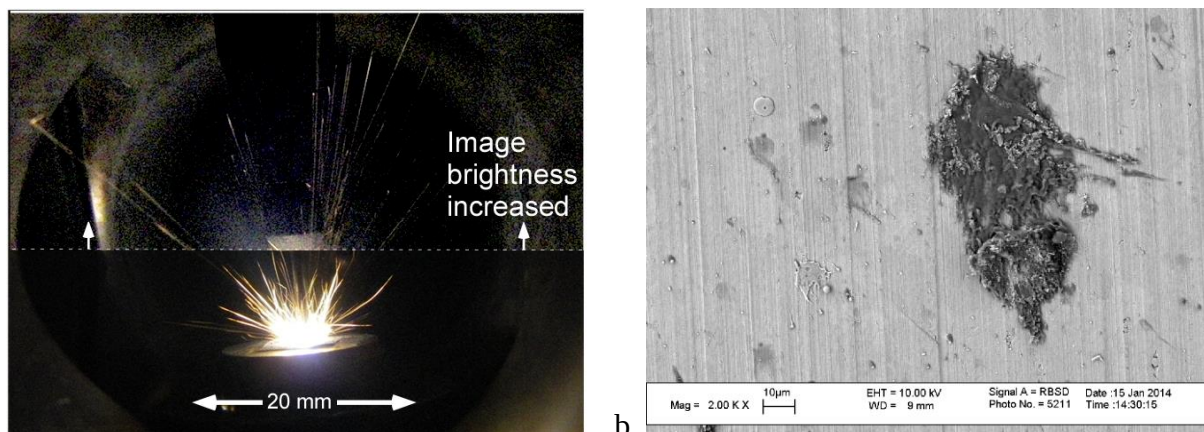


Fig. 14. a. A photograph of the burning particle streaks recorded in an ESD ignition test with the spark voltage of 8 kV. b. An SEM image taken with backscattered electrons showing partially burned particles captured on a Cu foil placed 2 mm away from the spark-ignited powder.

In the photograph, the brightness and contrast for the top part are additionally enhanced to clarify the images of few particle streaks extending beyond the brightest area of the image. The maximum streak length is close to 50 mm. Considering the overall emission time of about 150-200 μ s, this suggests that the fastest burning particles move at a speed of about 300 m/s, approaching the speed of sound in air.

The partially burned particles captured on the Cu foil appear molten and form splattered imprints on the surface. The sizes of the captured particles change in a wide range, which appears to be similar to the original size distribution of the nanocomposite thermite (cf. Fig. 11). A large particle with portions containing what appears to be a composite structure similar to the original nanocomposite material is seen on the right. Multiple smaller particles are seen on the left, for which almost no internal structure could be resolved.

A close inspection of the recorded spark current and emission traces showed that the onset of the emission signal is delayed compared to the spark current. These delays are clearly observed in Fig. 15, showing the initial parts of the emission traces overlapped with the respective ESD current signals. These short delays were ignored in an earlier paper [37] where the focus was on much longer ignition delays observed when the powder was placed in a thick layer and ignited after an aerosolized cloud of the ejected particles was formed.

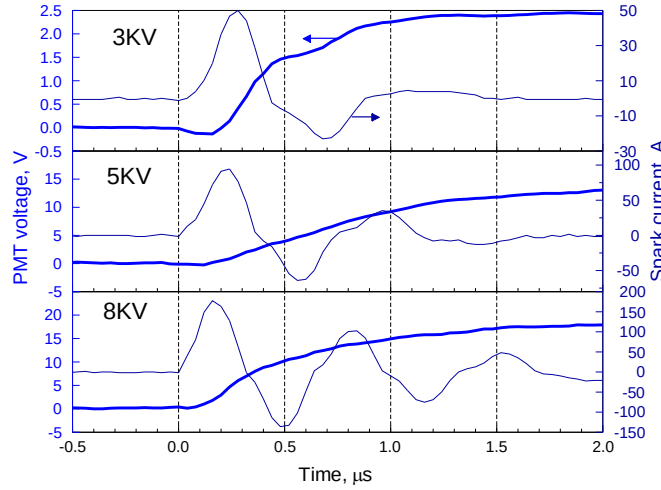


Figure 15. Optical emission and spark current traces showing onset differences for $8\text{Al}\cdot\text{MoO}_3$ powder monolayer ignited at different ESD energies.

The emission signals were further processed to obtain ignition delays defined as the difference between onset times for the spark current and PMT voltage, 90% of the fast rise time for the PMT signal, and integrated emission intensities determined using the PMT voltage traces. For consistency the onset instants for the current signals were defined when their values were at 10% of the maximum. The 10% and 90% values of the fast rise represents 10% and 90% of the time difference between the onset of the emission signal and the inflection point between its fast and slow rise segments, respectively. The results of the processing are shown in Fig. 8 as a function of the spark's Joule energy. The Joule energy was consistently increased at greater spark voltages.

The ignition delay decreases from ca. 240 to 160 ns with the increase in the spark's energy. Similarly, a reduction in the 90% fast rise time was observed with the increasing energy. Integrated emission intensities showed an opposite trend and were observed to increase at greater spark energies.

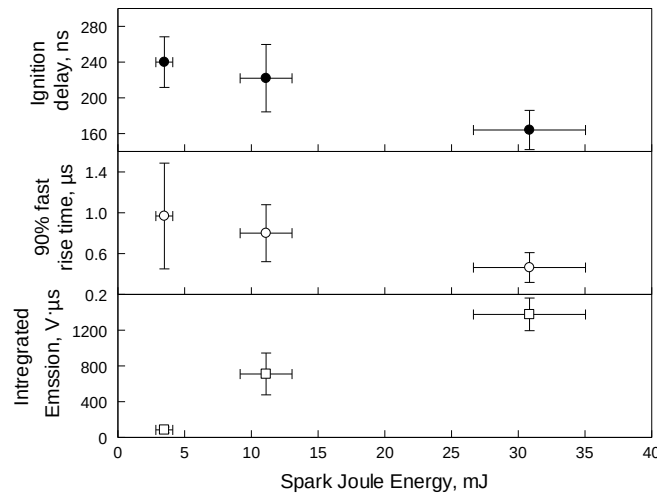


Figure 16. Ignition delay, 90% fast rise time and integrated emission as a function of Joule energy for $8\text{Al}\cdot\text{MoO}_3$ powder monolayer ignited by spark.

A time-resolved emission transient for the impact velocity of 1.34 km/s is plotted in Figure 17. Time zero is the moment of flyer impact measured by PDV with a 5 ns uncertainty. In addition, the flyer plate speed as measured by PDV is shown. Below flyer speeds of ~ 0.5 km/s, there were no obvious signs of thermite emission, but above 0.5 km/s the thermite particles produced intense emission bursts, so 0.5 km/s is taken as an impact velocity ignition threshold. This velocity threshold almost certainly depends on the shock duration as controlled by flyer thickness, and might be lower for thicker flyers.

Above this velocity threshold, the emission transients consist of two bursts, with the first burst lasting ~ 30 ns, followed by a delay of a few hundred ns and a second burst lasting a few μ s. As the flyer plate impact velocity was increased, the intensity of both bursts increased. The first, short high amplitude burst and flyer speed are shown with an expanded time scale in the inset in Fig. 9. The PDV data show the flyer at $t < 0$ moving at constant speed through the vacuum. Abruptly at $t = 0$ the flyer speed declines due to the impact. After this initial decline there is a ~ 10 ns period of constant velocity when the shock is steady. Following this 10 ns shock, the flyer undergoes a more gradual deceleration over ~ 30 ns. Figure 9 shows that the rapid rise of the first emission burst is coincident with the flyer impact. The initial emission burst ends at about the time the flyer comes to rest, or perhaps slightly later.

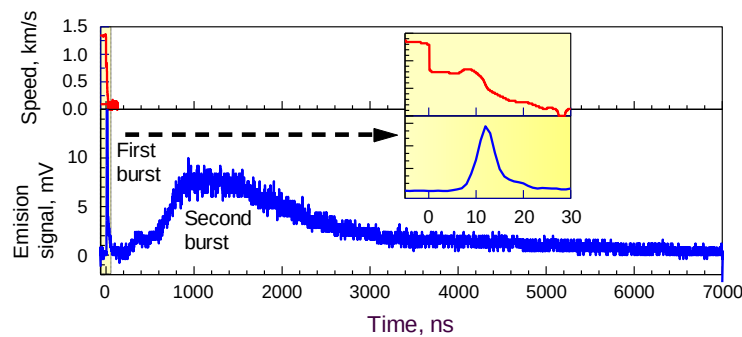


Figure 17. Characteristic shock induced emission trace and flyer speed as a function of time for a 10-20 μ m 8Al $\cdot$ MoO₃ particle. The impact velocity is 1.34 km/s.

Figure 18 shows the emission intensities for three different impact velocities. As the flyer speeds increase, the onset of the second burst moves to shorter time and the rise of the second burst becomes faster. We did a number of experiments where flyers impacted only glass, or only glass and acrylic cement. Although there was a detectable amount of emission from these other materials, the emission intensities from impacted thermite particles vastly exceeded that of glass or acrylic cement. The signal from the cement and glass was undetectable during the time the first short burst was observed for the thermite particle. The signal rose and showed a detectable baseline during the time the second burst was observed. The amplitude of the baseline was about 15 times smaller than the signal produced by an ignited thermite particle.

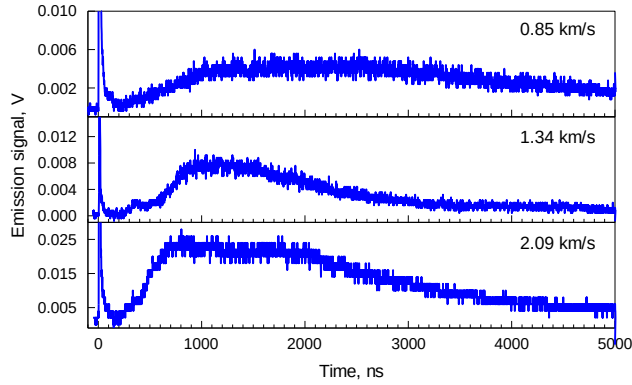


Figure 18. Emission traces for 8Al·MoO₃ particles ignited by impacts at different speeds.

In Figure 19 we show the flyer-speed dependence of three properties of the second emission bursts, the time delays between impact and the second bursts (Figure 11a), the risetimes (10-90%) of the second bursts (Figure 11b), and the integrated areas of the second bursts (Figure 11c). The time delay is the time when the second emission burst reaches 10 % of its maximum. The risetime is the 10%-90% rise of the second emission burst.

The ignition delay stay in a narrow range of ca. 150-200 ns for all except the lowest impact energy, for which the delay is much longer. The risetime is consistently decreasing and the integrated signal increasing with the impact energy.

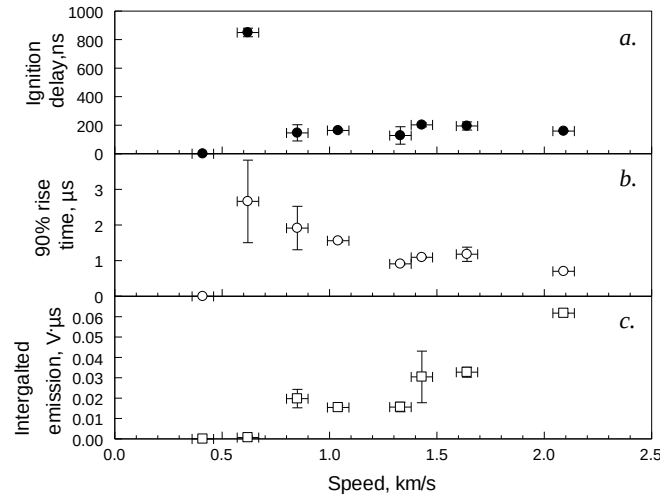


Figure 19. Properties of the second emission burst as a function of flyer impact speed. (a) Delay is the time between impact at $t = 0$ and the 10% point of the second burst rise. (b) Rise time is the time for 10%-90% rise of the emission burst. (c) Integral is proportional to the time-integrated emission burst intensity.

Both initiation techniques considered here result in very fast heating of the nanocomposite thermite particles. A simple estimate discussed above for the shock initiation indicates the heating rate on the order of 10^{10} - 10^{11} K/s. Although the temperature achieved as a result of shock compression is relatively low, as mentioned above, localized hot spots with substantially greater temperature are likely to be formed; for those even greater heating rates are

expected. For the spark ignition experiment, the heating rate can be roughly estimated assuming that the emission signal becomes noticeable at 486 nm when at least portions of the material are heated to ca. 1000 K. Because this occurs after the delays varied around 150 – 250 ns (cf. Fig. 8), the heating rates are estimated to be $0.5\text{--}1\cdot 10^{10}$ K/s. For spark ignition, the heating occurs locally because most of the heat release occurs at the points of maximum resistance, i.e., at the contact between the conductive substrate and the particle. For the composite material, it is also possible that the Joule energy is partially released at heterogeneities and material boundaries within the particle. The time required for the temperature to equilibrate within a 10- μm aluminum particle is estimated to be approximately 1 μs , which is much longer than any of the ignition delays reported here. An even longer thermal equilibration time is anticipated for the composite particle. Thus, if local hot spots are formed in the impact or spark initiated particles, it is likely that the ignition is also localized and combustion begins around those hot spots.

A very rapid initiation with the characteristic ignition (and thus local heating) times shorter than the time required for the temperature equilibration within the particle appears to be the principle difference between the present experiments and laser ignition measurements reported for the same material recently [27]. When the particle was heated while passing through a CO_2 laser beam, its heating time was close to 50-70 μs and the heating rates were on the order $10^6\text{--}10^7$ K/s. Thus, the particle temperature was uniform before its ignition and, likely, during its combustion. Remarkably, the burn times reported in Ref. [27] are of the order of several ms, much longer than the present data: few μs for the shock ignition and 120 – 200 μs for the spark ignition. Note that in spark ignition experiments multiple particles are ignited and the measured emission time characterizes combustion of the largest particles ignited after the longest delays. In other words, the actual particle combustion times in the spark ignition experiments were likely noticeably shorter than the entire duration of the measured emission signal.

The difference in burn times observed here and in laser ignition experiments is likely associated with the mode of combustion. When laser ignited particles are heated above the melting point of aluminum, it is likely that the nanostructure present in the starting material disappears and the particle burns as a molten drop of aluminum attached to a solid or molten particle of MoO_3 . However, in present experiments the characteristic ignition times are so short that the nano-structure of the starting material may be preserved. In this case, the reaction will be driven by heterogeneous diffusion of components occurring over a very large surface area existing in the nanocomposite material. The rapid rise in temperature causes this reaction to accelerate dramatically before a finite product layer between Al and MoO_3 is grown, which could lead to the very short reaction times observed. Note also that in the shock ignition experiment, the flyer plate remains in contact with the particle, which could quench the reaction before its completion. Additional work is necessary to fully understand the present combustion mechanisms.

In shock ignition, the observed ignition delay corresponds roughly to the timing of transverse decompression waves from the flyer plate [36]. These generate shear forces which might initiate a reaction in 8Al· MoO_3 nanocomposite material. It is intriguing that the ignition delays observed in both shock and spark ignition experiments (cf. Figs. 17 and 18) are close to each other. Thus, these delays may represent an intrinsic time necessary for the heterogeneous reaction to accelerate in this material. This time must be a function of the chemical composition

and structure. Experiments with different materials would be useful in clarifying the processes governing the observed ignition delays in both experiments.

Similarly, it is interesting to compare the rise times for the optical signals observed in both experiments. Because the spark cathode and anode spots are reported to be in the range of several μm , it is likely that the spark directly heats one particle initially; after that particle ignites, the heating propagates to the rest of the sample. The rapid emission ramp is likely to be indicative of the ignition of the particle directly heated by the spark; the slower rising part of the emission signal characterizes the reaction propagation to the rest of the sample (cf. Fig. 13). The rise times presented in Figs. 17 and 18 are close to each other, however, they are somewhat shorter for the spark ignition tests. If these times represent ignition of an individual particle, the shorter times for the spark ignition tests can be readily interpreted recalling that the electrostatic discharge remains active during this time, while the shock loading of the particle has been completed. In addition, as noted above, the shock ignited particles remain in contact with the flyer plate, resulting in additional heat losses, although such losses are relatively small for the short times considered.

An ignition delay reported in Fig. 16 can be used to estimate the initial particle temperature for the spark ignition tests. This estimate must assume the homogeneous particle heating; thus the temperatures achieved in the hot spots are expected to be higher. The temperature was estimated considering an adiabatic Joule heating of a particle with diameter equal to the mean volumetric particle size of $21.8\ \mu\text{m}$ during the 150-240 ns ignition delay. The real-time recorded spark current signal was used, and the powder impedance was assumed to remain constant. The results of this estimate are shown in Fig. 20. Estimated temperatures compare well with the range of 800-900 K, for which ignition of the same $8\text{Al}\cdot\text{MoO}_3$ powder is observed when it is coated on an electrically heated wire. Based on this estimate, it is reasonable to expect that such heterogeneous reactions as considered in the multi-step ignition model for a similar nanocomposite thermite are also active in the present experiments. However, because of the lack of pre-ignition reactions, Al and MoO_3 remain in nearly intimate contact, and the rate of these reactions can be substantially increased.

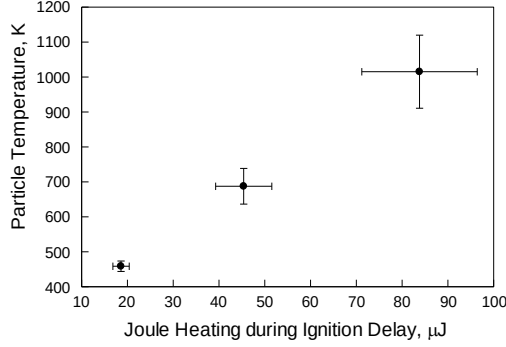


Figure 20. Estimated temperature to which the volumetric mean particle size is heated by the spark current during the delay time for 8Al·MoO₃ powder monolayer.

Micron-sized, nanocomposite 8Al·MoO₃ thermite particles were ignited using both shock compression and spark ignition techniques with very high heating rates on the order of 10^9 - 10^{11} K/s. These ignition methods result in a very fast combustion with characteristic burn times reduced by 1 – 3 orders of magnitude compared to the burn times measured previously for the same material ignited in the CO₂ laser beam [27], where it was heated at a much lower rate of about 10^6 - 10^7 K/s. It is proposed that the greater burn rates achieved after a very rapid ignition are associated with the preserved nano-structure and respectively very high heterogeneous reaction rate achieved at the high combustion temperatures. Ignition delays observed in both shock and spark ignition experiments are close to each other and vary in the range of 120 – 200 ns. The times of characteristic rapid increase in the optical emission of the ignited particles are also close to each other for the two experiments; however, these times are somewhat shorter (less than one μs) for the spark ignition tests compared to few μs observed for the shock initiated particles. The spark-ignited nanocomposite thermite particles are observed to be ejected from the substrate at the speeds approaching the speed of sound in surrounding air.

We have studied impact initiation of nano-Al/Teflon reactive material (RM) by planar impacts with thin Cu flyer plates^{1,8,9} in the 0-1.7 km·s⁻¹ range, using a high dynamic range spectrally-resolved emission apparatus.² This study is a follow-up to a 2013 paper¹⁰ where we studied a related system, Al/Teflon in the form of Al nanoparticles mixed with Teflon microparticles, using a streak camera. Here we used a denser and much more homogeneous material consisting of 40 nm oxide-passivated Al particles embedded in a Teflon thin film (3 μm thick) on sapphire windows, using the soluble Teflon^{AF} material.¹¹⁻¹⁶ Hereafter we will denote the mixture of nano-Al and Teflon^{AF} simply as Al/Teflon. The flyer plate produced a spatially-uniform shock throughout the region observed by emission spectroscopy, the 0.1 mm region at the center of the 0.5 mm flyer plate.^{2,9} The new emission apparatus has orders of magnitude greater dynamic range than the streak camera, and the combination of high dynamic range emission detection and a high level of sample homogeneity allowed us to make shock-initiation emission measurements with a much greater level of detail and reproducibility than has been possible before. An important feature of this study is the use of the emission apparatus as a highly-accurate optical pyrometer^{2,3,17} to provide temperature histories of the shock initiation process and the subsequent combustion process with nanosecond time resolution.

Nano-Al Teflon is a multifunctional RM.¹⁸ As a projectile, it has the penetrating power of a Teflon bullet, but upon impact it can theoretically produce about three times the energy of

TNT. There have been a number of prior studies of Al/Teflon combustion,¹⁹⁻²⁴ but few studies of high-speed impact initiation,^{10,23,25-28} for which the detailed mechanisms have not yet been elucidated. In Al/Teflon, the oxide-passivated Al nanoparticles serve as fuel and the fluorinated polymer as oxidizer. The kinetics resulting from having separate fuel and oxidizer components are slower than typical molecular explosives. When Al/Teflon reactions are initiated by shock, we expect to observe two phases, a faster part that occurs during the first few tens of nanoseconds during and immediately after the initiating shock, and a later part after the shock unloads. The later part, which occurs at ambient pressure should be regarded as ordinary (ambient pressure) combustion of whatever material remained after shock.

The Al/Teflon reaction has been described as high-velocity combustion^{24,29} or low-velocity detonation.²⁶ Shock initiation of Al/Teflon by explosive detonators or high-velocity impacts was studied by Dolgoborodov and co-workers about a decade ago.^{26,30} They described the explosive process as occurring in a relatively slow ($\sim 1 \text{ km}\cdot\text{s}^{-1}$) detonation-like regime. In 2012, Densmore and co-workers used thermal imaging to study sabots of Al/Teflon pressed powders that were shot at $1.7 \text{ km}\cdot\text{s}^{-1}$ onto a steel anvil. Two cameras were used to obtain images of the emission from the ignited material at either 700 nm or 900 nm and the two-color intensity ratio was used to determine temperature. The pressed powder sample disintegrated upon impact, and the temperatures were spatially inhomogeneous. There was a temperature spike to 3700K in the first millisecond, and the spatial-average temperature over the next 10 ms or so was $\sim 2700\text{K}$. The steady ignition temperature was estimated as 3300K.³¹

Mock and Drotar²⁵ studied shock initiation of micron-sized (9 μm and 120 μm) Al in Teflon using a fast framing camera to observe the impact of the Al/Teflon sabot with a steel plate. They determined an initiation threshold of 2.6 GPa based on the appearance of “first light”, i.e. a rising light signal above their detection threshold. The smaller Al particles produced more light. The time to initiation was 74 μs near threshold, decreasing to 14 μs at 6.4 GPa.

There are two key events in shock initiation of Al/Teflon. First, the shock heats the more compressible Teflon oxidizer to a greater extent than the Al fuel,¹⁰ and in the first few nanoseconds there is not enough time for thermal conduction to equalize the temperatures, so the initial shocked state should be viewed as hot shocked Teflon reacting with oxide-passivated Al nanoparticles. As the Teflon breaks down into Teflon fragments,^{29,32} the fragments must penetrate the protective oxide passivation layer, typically about 3 nm thick,³³ to reach the Al fuel. The initiation process has been variously described as diffusion of Teflon fragments through the oxide,²⁰ chemical breakdown of the oxide layer by Teflon fragments,¹⁹ and cracking of the oxide shell weakened by Al thermal expansion,³⁴ by the tensile forces generated by shock unloading.¹⁰

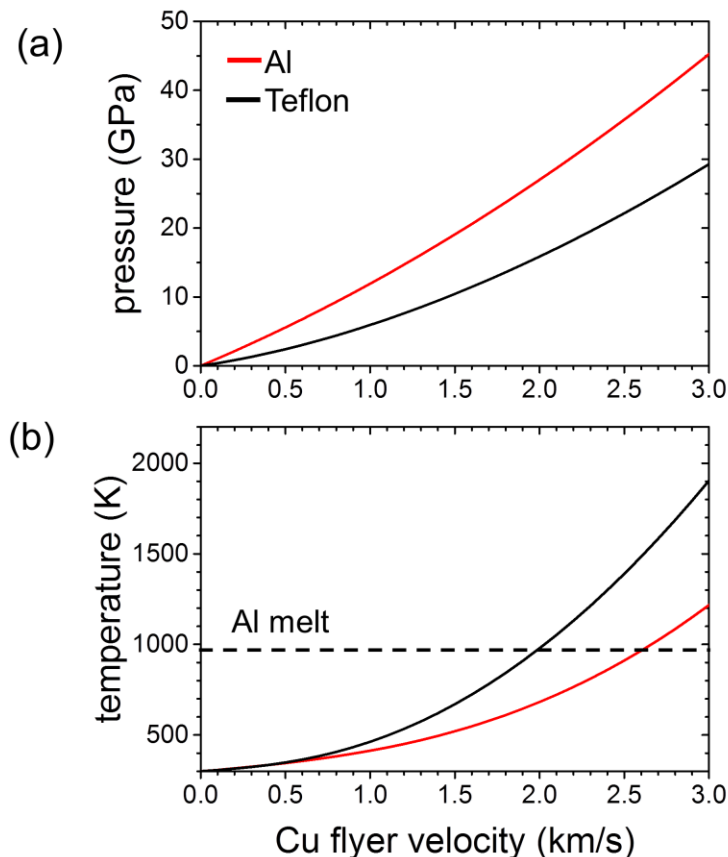


FIG. 21. (a) Computed shock pressures Al or Teflon impacted by a Cu flyer. (b) Computed temperatures for unreactive Al and Teflon. This figure is the same as Fig. 1 of ref. ¹⁰, which was computed for Al flyers, modified to account for Cu flyers used here.

For an estimate of the effects of shock on Al and Teflon, our group previously calculated the initial temperatures of both, assuming unreactive behavior.¹⁰ Figure 21 is the same data adjusted for the use of Cu flyer plates here rather than Al plates used previously using the well-known Hugoniot crossing method.⁷ Transient Raman studies of shocked Teflon indicated the polymer begins to break down at about 2.3 GPa,³⁵ which according to Fig. 21 would occur with a Cu plate at 0.48 km·s⁻¹. An impact that would bring Al to the melting temperature would, according to Fig. 1, require a 2.7 km·s⁻¹ impact, which is far faster than anything used here.

Once the passivation shell has been breached, a variety of complicated chemical processes may ensue, and with quite a bit of oversimplification, the reaction can be expressed as,^{12,29,32,36}



A more detailed picture of Al/Teflon chemistries has resulted from both experiment and theory. Zamkov, Connor and Dlott¹² showed that after reaction initiation by flash heating (rather than shock), the different functional groups of Teflon^{AF}, CF₂, CFO and CF₃, reacted with Al at different rates. Losada and Chaudhuri,^{29,32} used quantum chemistry to explain the elementary steps in the reaction of small (nonpassivated) Al clusters with various Teflon fragments.

In our 2013 study,¹⁰ shock compression of the porous microcomposite Al/Teflon produced a lot of heat and light on the nanosecond time scale. During ~ 10 ns duration shocks, Al/Teflon on glass underwent an explosive reaction characterized by an emission burst that began just as shock unloading was complete. The burst peaked at 30 ns and lasted ~ 500 ns. The reaction threshold, judged by the method of “first light”, was about $1 \text{ km}\cdot\text{s}^{-1}$ with Al flyers, corresponding to $0.67 \text{ km}\cdot\text{s}^{-1}$ with Cu flyers. A weaker emission was observed from Teflon particles without nano-Al, that denotes the onset of shock-induced Teflon decomposition, began at $0.7 \text{ km}\cdot\text{s}^{-1}$ with Al flyers, corresponding to $0.47 \text{ km}\cdot\text{s}^{-1}$ with Cu flyer plates.

An experimental schematic is shown in Fig. 22a. The flyer plate launch apparatus,^{8,9} the photon Doppler velocimeter (PDV) used to measure flyer velocities,⁹ and the emission spectrometer² were described in detail previously. The 0.5 mm diameter flyers were launched by a pulsed Nd:YAG laser from $25 \mu\text{m}$ thick Cu foils. The flyers traveled across a $375 \mu\text{m}$ vacuum gap before impacting the Al/Teflon spread as a thin layer on a 50.8 mm diameter sapphire substrate 6.35 mm thick. We covered the substrate with a $375 \mu\text{m}$ thick stainless steel spacer/mask to create 59 independent regions for shock measurements.

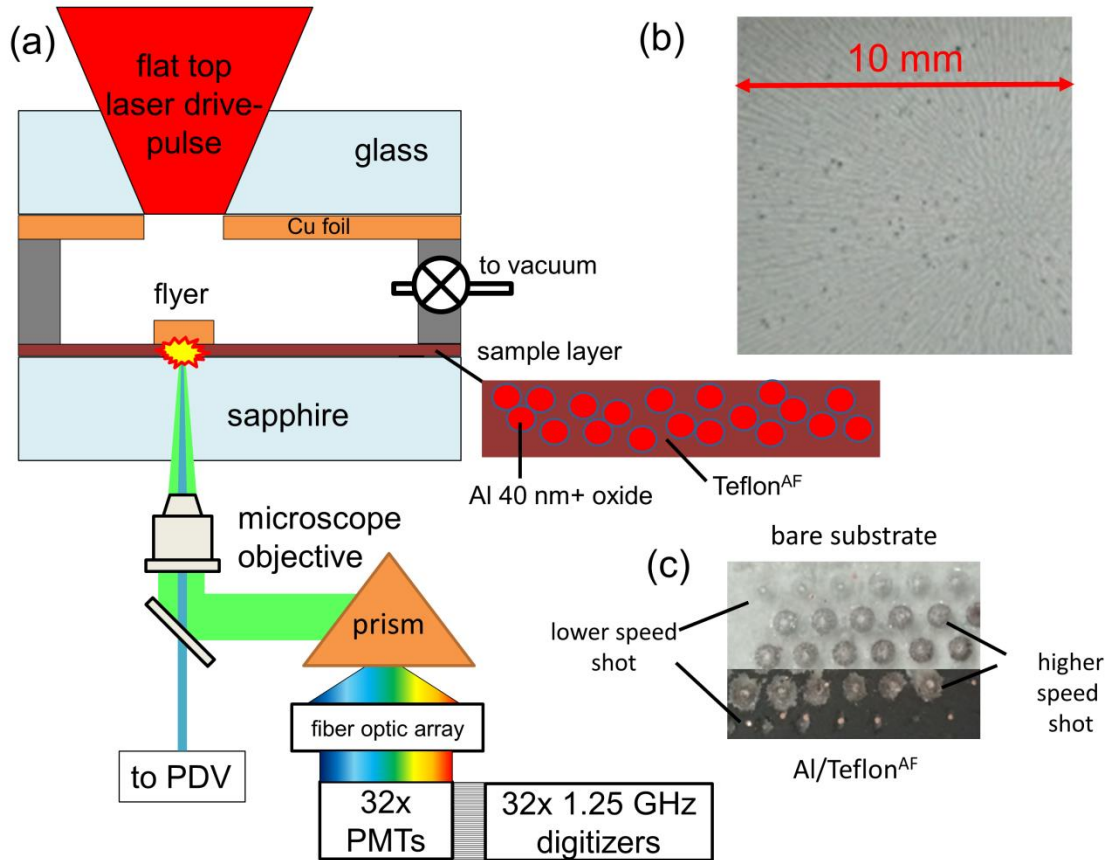


FIG. 22. (a) Schematic of the apparatus using laser-launched $25 \mu\text{m}$ thick Cu flyers to shock a $3 \mu\text{m}$ thick film of Al/Teflon. (b) Optical micrograph of Al/Teflon film on sapphire. (c) A sample after the experiment. The bare region was used to precisely calibrate flyer velocity

versus launch laser energy. The darker region with Al/Teflon shows reacted regions for lower-speed ($0.7 \text{ km}\cdot\text{s}^{-1}$) and higher-speed ($1.5 \text{ km}\cdot\text{s}^{-1}$) shots. The reaction produced with the higher-speed shots extends several mm beyond the 0.5 mm diameter flyer.

Figure 23 shows PDV data for a typical flyer plate impact with sapphire, across a $375 \text{ }\mu\text{m}$ vacuum gap. Figure 3a shows the complete velocity history. The 20 ns laser drive pulse causes a small reverberation in the flyer that damps out long before impact at about 439 ns. Figure 23b is a close up of the impact, where time zero was shifted to indicate the instant of impact. The free-flight velocity $U_f = 1.01 \text{ km}\cdot\text{s}^{-1}$. After impact, the velocity of the flyer-sapphire interface dropped to $U_p = 0.91 \text{ km}\cdot\text{s}^{-1}$, and U_p remained constant for 7 ns. The flyer speed then decelerated to zero velocity (the slight offset from zero velocity in Fig. 3b results from our computational low-pass filter) at 15 ns. Since the samples were so thin ($3 \text{ }\mu\text{m}$), the shock rang up in the sample within 1-2 ns, so the velocity history with the sample would be hardly different than what is displayed here.

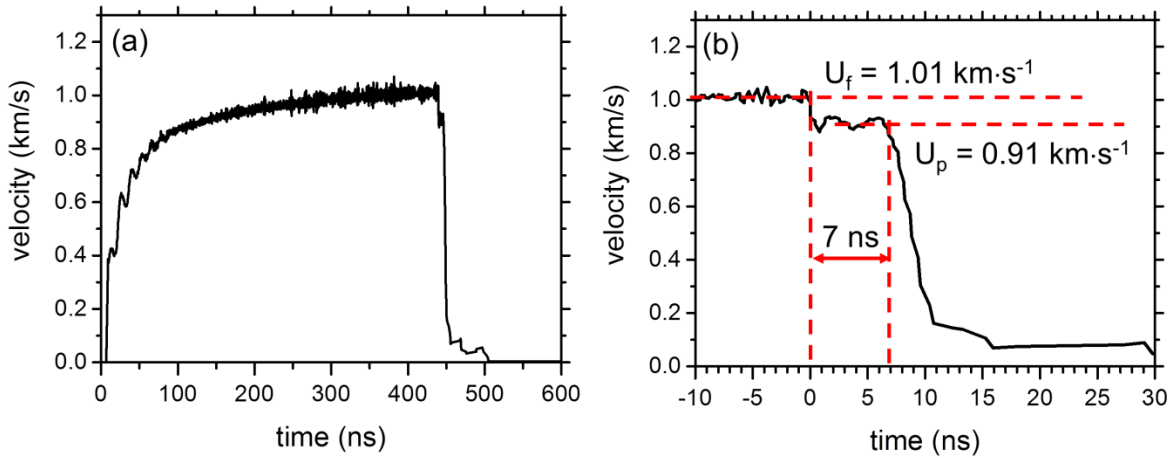


FIG. 23. (a) PDV velocity history for $25 \text{ }\mu\text{m}$ Cu flyer launched at $1 \text{ km}\cdot\text{s}^{-1}$ onto a sapphire window. Time zero was 90% of the way up the rising edge of the launch laser pulse. (b) Impact region on an expanded time scale. Now time zero denotes the instant of impact. The incoming flyer at $U_f = 1.01 \text{ km}\cdot\text{s}^{-1}$ drops to $U_p = 0.91 \text{ km}\cdot\text{s}^{-1}$ after impact with sapphire. The steady shock drive lasts 7 ns. The flyer velocity dropped to zero at 15 ns.

The emission apparatus² consisted of microscope optics and spatial filter adjusted so only a $100 \text{ }\mu\text{m}$ diameter region at the center of the 0.5 mm flyer was observed, a spectrograph with a prism as the dispersing optic, a linear array of 32 fiber optics that transported the dispersed light from 450-825 nm to 32 fast photomultiplier tubes, and 32 10-bit digitizers with 1.5 GHz bandwidth, $1.25 \text{ GS}\cdot\text{s}^{-1}$ acquisition rate, and 2 GB of onboard memory. The overall system time response was $<2 \text{ ns}$.² The absolute spectral radiance of the emission was determined by comparison to a calibrated 2700K source (StellarNet Inc.) at the sample position.²

To display data over a wide time range (nanoseconds to milliseconds), we used $\log(\text{time})$ plotting and averaging methods.² The digitizer output at 0.8 ns intervals, was averaged into 25 points per time decade. This greatly improved the signal-to-noise ratio in the later decades. We dealt with the time zero problem in $\log(\text{time})$ plots as follows. Time zero could be variously set

as the instant of impact, the instant the shock reached the Al/Teflon/window interface, or the end of the 7 ns duration steady shock drive. Our Doppler velocimeter could detect the instant the shock broke out of the Al/Teflon sample. Since it took roughly 1 ns for the shock to propagate through the 3 μm thick sample, we arbitrarily set the minimum time in our displayed data as 10^{-9} s. This procedure caused a couple of nanoseconds of uncertainty in the first displayed time decade but hardly affected the later decades.

Sample preparation was based on a procedure described previously.¹⁶ Samples were 3 μm thick films spin-coated on sapphire (A-plane sapphire, >99.995% purity, 2" diameter x 1/4" thick), from Rubicon Tech., Inc. (Bensenville, IL). The 40 nm oxide-passivated spherical Al particles, produced by electrical explosion, were obtained from US Research Nanomaterials, Inc., and a fresh batch was used to obtain the displayed data. The nanoparticles were >99.9 % pure on a metal basis, and the manufacturer provided no information about the oxide layer thickness. Teflon^{AF} was obtained as a 6% w/w Teflon^{AF} solution in fluorocarbon solvent from Chemours (Wilmington, DE). To assist the dispersion of Al in Teflon, the Al was suspended in ethanol and treated with a fluorinated surfactant, 1H,1H,2H,2H-perfluorodecyl-triethoxysilane, that binds to the oxide layer. After stirring overnight, the ethanol was evaporated to leave dry surfactant-treated Al nanoparticles, which were added to FC-770 fluorocarbon solvent from Syn Quest Laboratories, Inc. (Alachua, FL) to make a 2% nanoparticle suspension. The nanoparticle suspension was then added to a quantity of the Teflon^{AF} solution to produce the desired Al loading ratio. The nanoparticle suspension in the Teflon^{AF} solution was shaken and sonicated extensively. To increase adhesion to the sapphire windows, prior to spin coating the windows were soaked in a 2% solution of fluorosilane in 95% ethanol to create a fluorocarbon surface.

The ideal stoichiometric composition of Al/Teflon is 2.57:1 Teflon:Al.²⁵ Whereas Teflon consists solely of polymerized tetrafluoroethylene, Teflon^{AF} is a copolymer of tetrafluoroethylene and 2,2-bis (trifluoromethyl)-4,5-difluoro-1,3-dioxole, and the stoichiometric composition for Al/Teflon^{AF} was previously computed to be 2.3:1 Teflon:Al.¹⁰ In addition to this composition, we made samples with one-half and one-fourth the Al load. Henceforth we will refer to these concentrations as 1.0 Al/Teflon = the stoichiometric mixture, 0.5 Al/Teflon = 1/2 the Al load, and 0.25 Al/Teflon = 1/4 the Al load.

Figure 22b shows a photo of a small region of an Al/Teflon sample. The coating had good adhesion and continuity. Despite our best efforts to disperse the Al and make a smooth coating, in Fig. 22b we see occasional tiny clumps of Al nanoparticles and radial striations in the coating. When we saw a region with such clumps under the optical microscope, we purposefully avoided measurements in that region. As shown in Fig. 22c, we stripped part of the Al/Teflon off the substrate to create a transparent region used for calibration shots so PDV could determine the precise laser fluence needed to achieve the desired flyer velocities.

Spectral radiances ($\text{W Sr}^{-1} \text{m}^{-2} \text{nm}^{-1}$) from shocked Al/Teflon are interpreted as arising from graybody emission. Graybody emission methods, where the emissivity $\varepsilon(\lambda, T)$ is assumed independent of wavelength λ and temperature T , have been found to give good results for reactive nanomaterials.³⁷⁻³⁹ Plank's Law gives the spectral radiance L of a thermal body,

$$L(T, \lambda) d\lambda = \varepsilon \times \frac{2hc^2 d\lambda}{\lambda^5 [\exp(hc / kT\lambda) - 1]},$$

where $L(T, \lambda)$ is the spectral radiance and ε is the graybody emissivity. This equation can be forced into a linear form by neglecting -1 in the denominator, which is correct in the limit of short wavelength and low temperature.⁴⁰ In our experiments, where $\lambda < 1 \mu\text{m}$, this approximation creates an error of $<1\%$ at 3000K. In this case,

$$Z = \ln\left(\frac{2hc^2}{\lambda^5} \times L(T, \lambda)^{-1}\right) = \frac{hc}{k\lambda T} - \ln(\varepsilon),$$

and at a given temperature T , when Z is plotted versus λ^{-1} , a graybody emitter yields a linear plot with slope hc/kT and intercept $-\ln(\varepsilon)$.

Figure 22c shows part of a sample after impacts with a few flyer plates. The lower-speed shots were $0.7 \text{ km}\cdot\text{s}^{-1}$ and the higher-speed shots were $1.5 \text{ km}\cdot\text{s}^{-1}$. The lower-speed Al/Teflon shots showed little effect outside the flyer diameter, but the higher-speed Al/Teflon shots showed evidence of energetic chemical reactions extending radially out several millimeters.

Figure 24 shows our determination of the impact initiation threshold (for Cu flyers $25 \mu\text{m}$ thick) based on detection of shock-induced emission.²⁵ Emission is expressed in terms of “total radiance”, which was obtained by integrating the spectral radiance over all wavelengths from 450-825 nm, and all times from 1 ns to 20 μs . The choice of this upper time limit is explained below. The units of total radiance are joules of light emitted per steradian per meter squared of Al/Teflon.

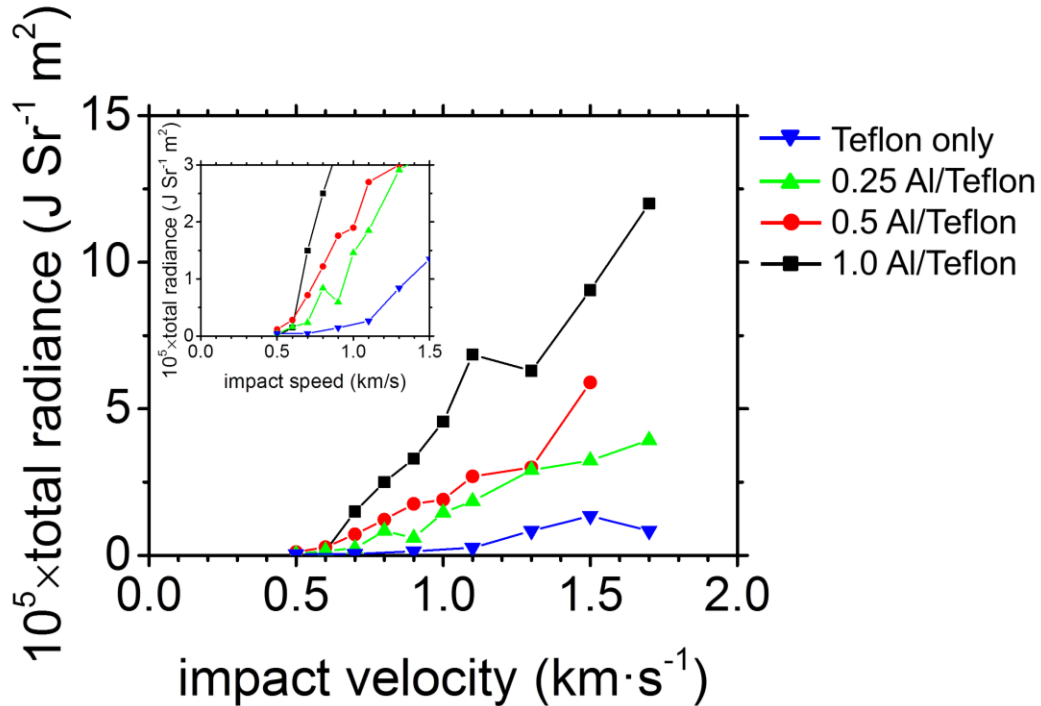


FIG. 24. Impact thresholds for Teflon and Al/Teflon with different Al loads, determined by the shock-induced emission intensity. Total radiance is the time- and wavelength-integrated spectral

radiance. The *inset* shows that emission is above our detection threshold near $0.5 \text{ km}\cdot\text{s}^{-1}$ for both Teflon and Al/Teflon, but at higher velocities, the total radiance for Al/Teflon becomes much greater than Teflon. The threshold for shock initiation of Al/Teflon is $0.6 (\pm 0.1) \text{ km}\cdot\text{s}^{-1}$.

When the emission rose above our detection threshold, at $0.5 \text{ km}\cdot\text{s}^{-1}$, the Teflon and Al/Teflon samples emitted with similar intensities (Fig. 24 inset), so since the emission apparently arises from Teflon and not from Al reactions with Teflon, it does not make sense to make the threshold $0.5 \text{ km}\cdot\text{s}^{-1}$. But at $0.6 \text{ km}\cdot\text{s}^{-1}$ and above, the Al/Teflon mixtures emitted with significantly greater intensity than Teflon. Therefore we find the impact initiation threshold to be $0.6 (\pm 0.1) \text{ km}\cdot\text{s}^{-1}$.

Figure 25 shows some examples of spectral radiance transients, from which the results in Fig. 24 were derived, with $1.5 \text{ km}\cdot\text{s}^{-1}$ impacts. According to Fig. 21a, the initial shock pressure in Teflon with $1.5 \text{ km}\cdot\text{s}^{-1}$ Cu flyers would be about 8 GPa. Figures 25a-c refer to impacts with bare sapphire, Teflon^{AF} on sapphire, or 0.5 Al/Teflon on sapphire. Figure 25d is a log plot of the radiance transients (watts per steradian per meter squared of Al/Teflon), obtained by integrating the spectral radiance from 450 to 825 nm. As shown in Fig. 25d, sapphire windows have the useful property that impact-induced autoemission occurs only within a narrow time window $\sim 150\text{-}220 \text{ ns}$, so it is easy to temporally distinguish window emission from Al/Teflon emission. In fact, when the flyer plate hit Teflon on sapphire (Fig. 25b,d) rather than bare sapphire, the Teflon cushion suppressed the sapphire shock emission, so we need not worry about sapphire emission.

The Teflon on sapphire emission (Fig. 25d) appeared immediately after shock arrival. When nano-Al was added to Teflon at the 0.5 level (Fig. 25d), the emission consisted of two bursts. The first burst, in the 20-100 ns time range, was about ten times more intense than Teflon alone, and it peaked about 25 ns after the shock arrived. The second burst, around $1 \mu\text{s}$, did not appear with Teflon only; it appeared only with Al/Teflon. Although the μs burst in Al/Teflon was lower in intensity than the nanosecond burst, due to its longer duration it represented a significant fraction of the emitted light, as discussed below. The nanosecond burst represents the initiation of exothermic chemistries triggered by impact. The microsecond burst represents exothermic combustion chemistries at ambient pressure, after the shock has unloaded.

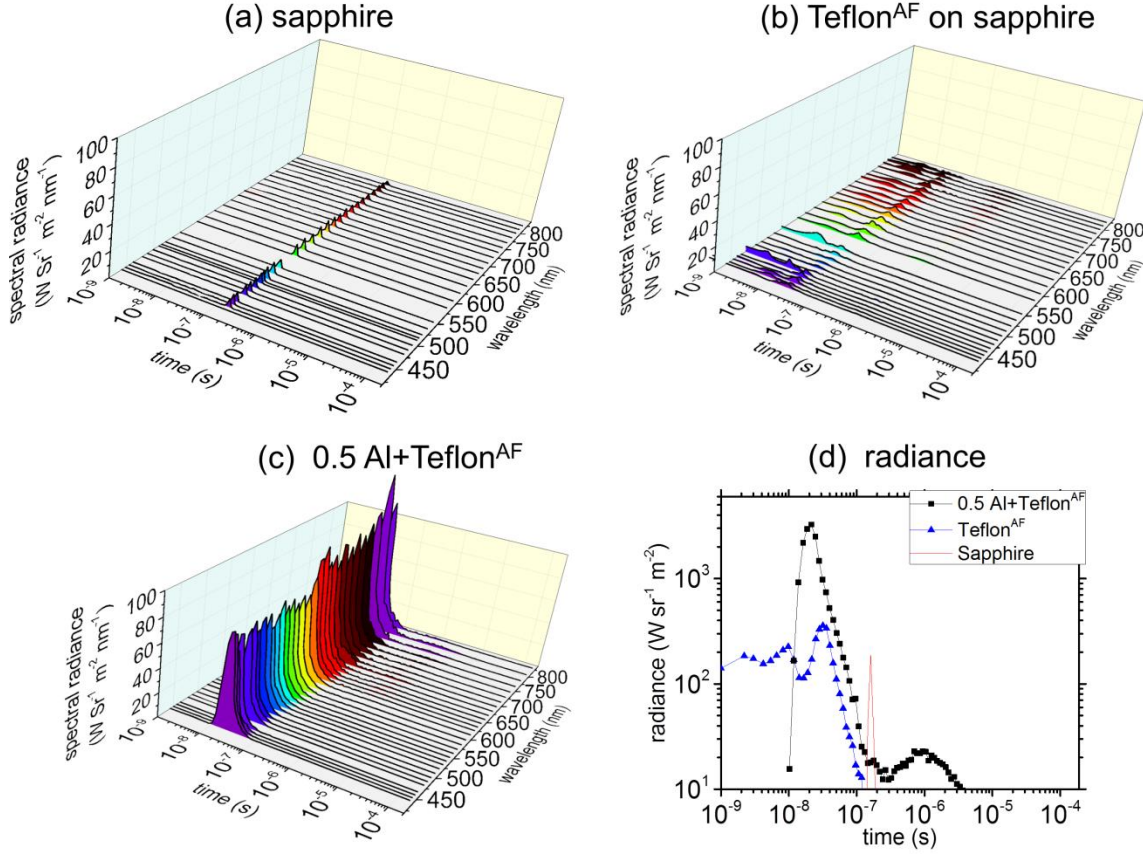


FIG. 25. Spectral radiance transients produced by impacts with 25 μm thick Cu flyers at 1.5 $\text{km}\cdot\text{s}^{-1}$ for (a) sapphire substrate, (b) 3 μm Teflon^{AF} on sapphire and (c) 3 μm Al/Teflon^{AF} on sapphire with 0.5 of the stoichiometric nano-Al load. (d) Radiance transients (wavelength-integrated spectral radiances). Sapphire emission was restricted to a narrow time window near 150 ns, and sapphire emission was not observed when flyer plates impacted the thin films on sapphire. Teflon emission began promptly, but Al/Teflon emission was delayed by 25 ns.

Figure 26 is an example of our graybody analysis for the case shown in Fig. 25c, where 0.5 Al/Teflon was impacted at 1.5 $\text{km}\cdot\text{s}^{-1}$. The radiance transient in Fig. 26a, with its two emission bursts, is the same as Fig. 25d. In Fig. 26a we also plotted the time-integral of the radiance, normalized to unity. Since there is very weak light emitted even at 100 μs (the dying embers of Al/Teflon combustion), this integral kept increasing with time, so there is a truncation issue in computing the integral. We chose to truncate our integrations at 20 μs , which was just beyond the end of the intense emission from combustion. Whatever uncertainty was introduced by our truncation choice, Fig. 26a clearly shows that the total emitted light from the weaker microsecond burst was roughly comparable to the light from the more-intense nanosecond burst.

In Fig. 26a, at four representative times indicated by arrows, we show examples of graybody analysis to determine temperature, as illustrated in Figs. 26b,c, where the y-axis is the quantity z defined above. The spectral radiances plotted in this manner gives a linear plot when the emission is graybody, and the slope gives the graybody temperature.⁴⁰ The error bars are 95% confidence limits (i.e. $\pm 2\sigma$) for the temperature determinations.³ Then, in Fig. 26a we plotted the temperatures and error bars at all times when the radiance was large enough to

support a temperature determination. In Fig. 26a we superimposed temperatures from three independent shots, to demonstrate reproducibility.

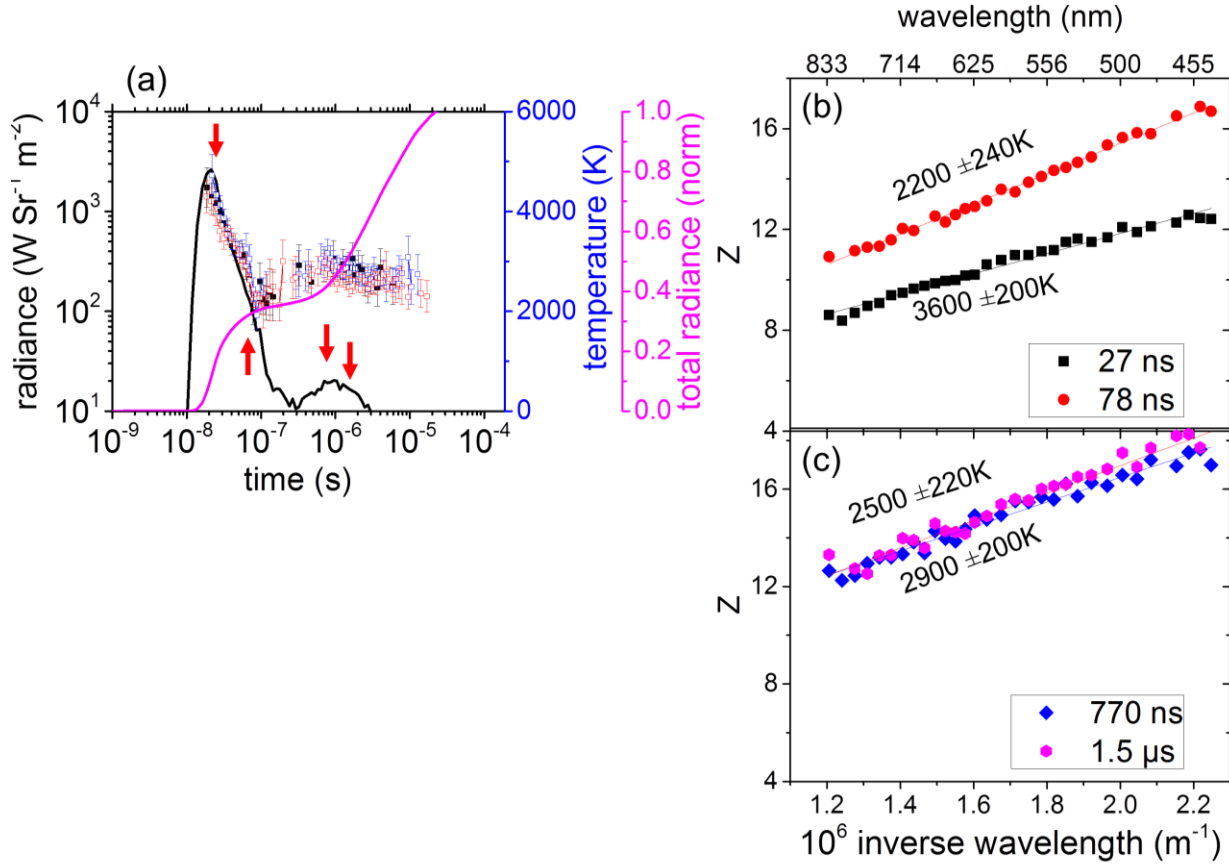


FIG. 26. Graybody analysis to derive temperature histories for a $1.5 \text{ km}\cdot\text{s}^{-1}$ impact with 0.5 Al/Teflon (as in Fig. 4c). (a) The two-burst radiance transient from Fig. 4d. The normalized integral (truncated at $20 \mu\text{s}$) shows that the total radiance from each burst was about equal. (b) and (c) Plots of the spectral radiance at the four times indicated by arrows in (a). The quantity z was defined in Eq. (3). When this plot is linear, the emission spectrum fits a graybody distribution and the slope gives the temperature. Temperatures derived in this manner are plotted at all times in (a) for three individual shots, to demonstrate the high degree of reproducibility.

Figure 27 shows radiances for Teflon and Al/Teflon at flyer speeds from 0.5 – $1.7 \text{ km}\cdot\text{s}^{-1}$, on log plots that display the full dynamic range. The intensities of both bursts in Al/Teflon increased with flyer impact velocity and Al load.

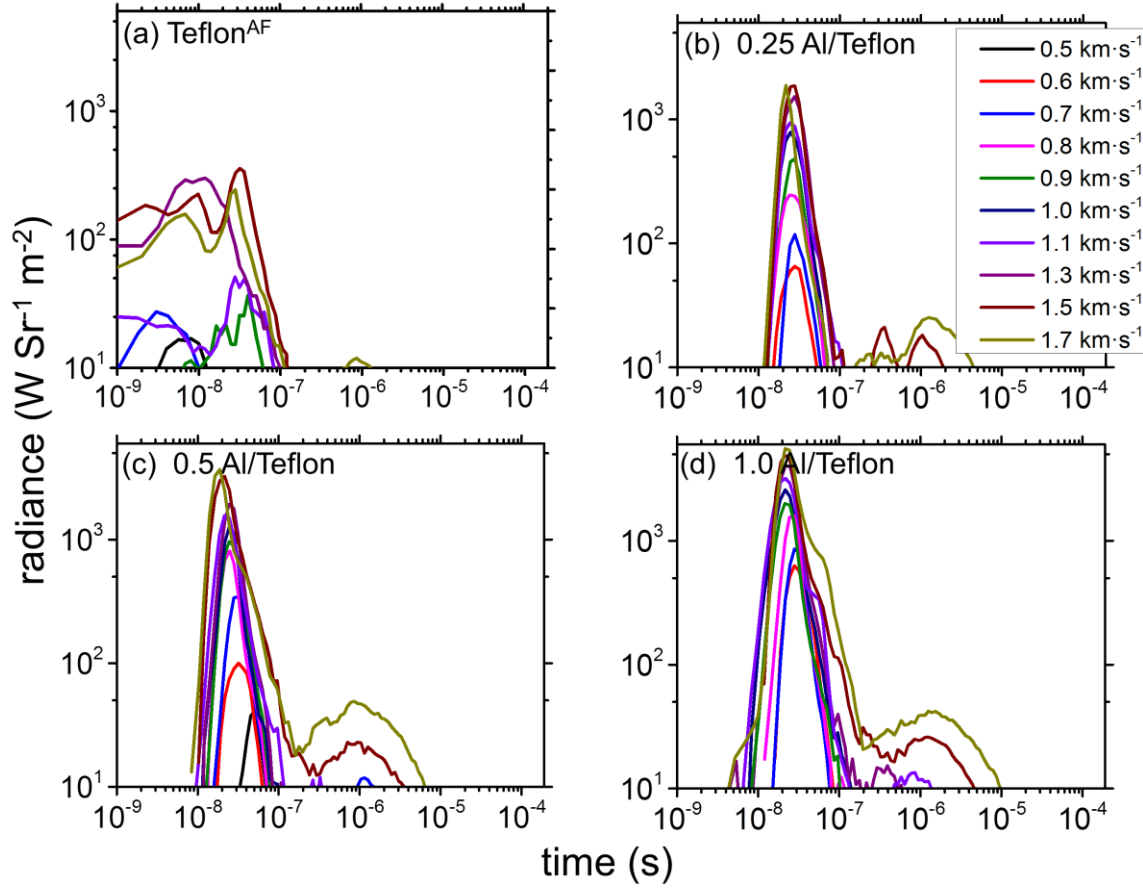


FIG. 27. Radiance transients at indicated flyer velocities. Emission from shocked Teflon preceded emission from the Al/Teflon samples. Al/Teflon always has a two-burst structure. Just above the impact threshold ($0.6 \text{ km}\cdot\text{s}^{-1}$), the first burst appeared with a time delay of 40 ns, and far above threshold the time delay was 25 ns. The later burst, occurring after the shock unloads, represents ambient pressure combustion.

Figure 28 shows the first emission bursts on an expanded (linear) plot for the 0.25 and 1.0 Al/Teflon samples. Figure 28 shows that, although the intensity with 0.25 Al/Teflon was about three times lower than with 1.0 Al/Teflon, the above-threshold temporal behavior of these emission bursts depended little on concentration and impact velocity. Just above threshold, at $0.6 \text{ km}\cdot\text{s}^{-1}$, the time delay to the burst maximum was 40 ns, but further above threshold the time delay decreased to 25 ns. The duration of the first emission peak was about 75 ns.

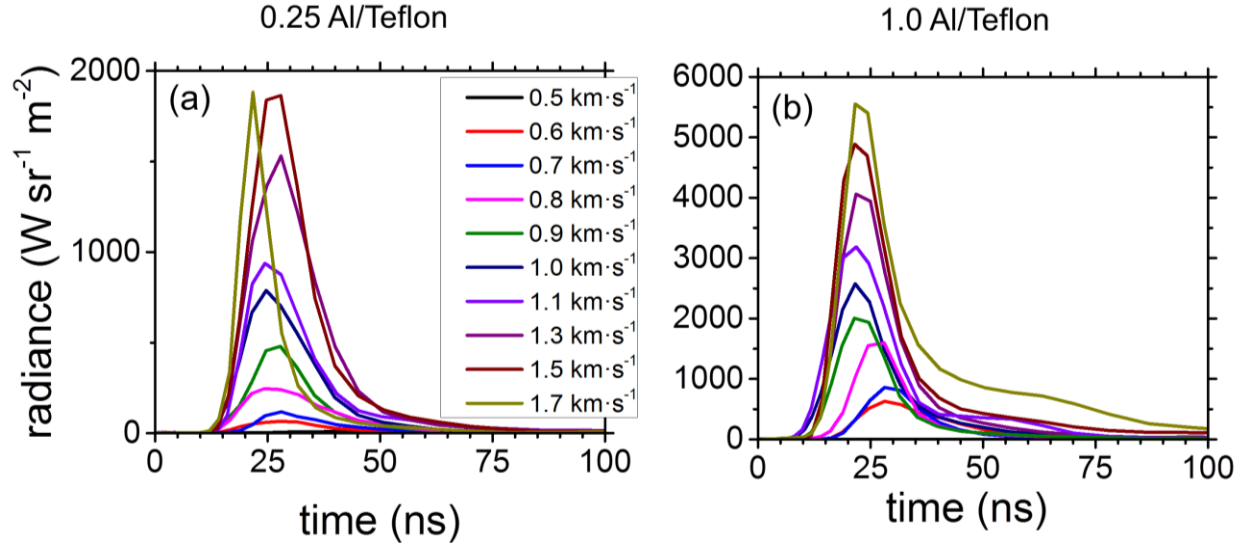


FIG. 28. The first burst of the two-burst radiance transients on an expanded (linear) scale. Time zero denotes shock breakout from the Al/Teflon sample. The emission began about 15 ns after shock arrival and it peaked at about 25 ns, except at the lowest impact velocities where the peak occurred at 30-35 ns.

Figure 29 shows representative temperature histories for Al/Teflon with impacts at 0.7 $\text{km} \cdot \text{s}^{-1}$, 1.0 $\text{km} \cdot \text{s}^{-1}$ and 1.5 $\text{km} \cdot \text{s}^{-1}$ and Al loadings of 0.25, 0.5 and 1.0. As in Fig. 26a, we superimposed temperature histories for three independent shots in each panel to demonstrate reproducibility. We could determine graybody temperatures only when the emission was sufficiently intense. For the nanosecond burst, temperature determinations were possible only near the peak, given the short duration of the burst. In the interval between the two bursts we could not determine temperatures at the lower impact velocities, but at 1.5 $\text{km} \cdot \text{s}^{-1}$ we obtained unbroken temperature records from 30 ns to 50 μs .

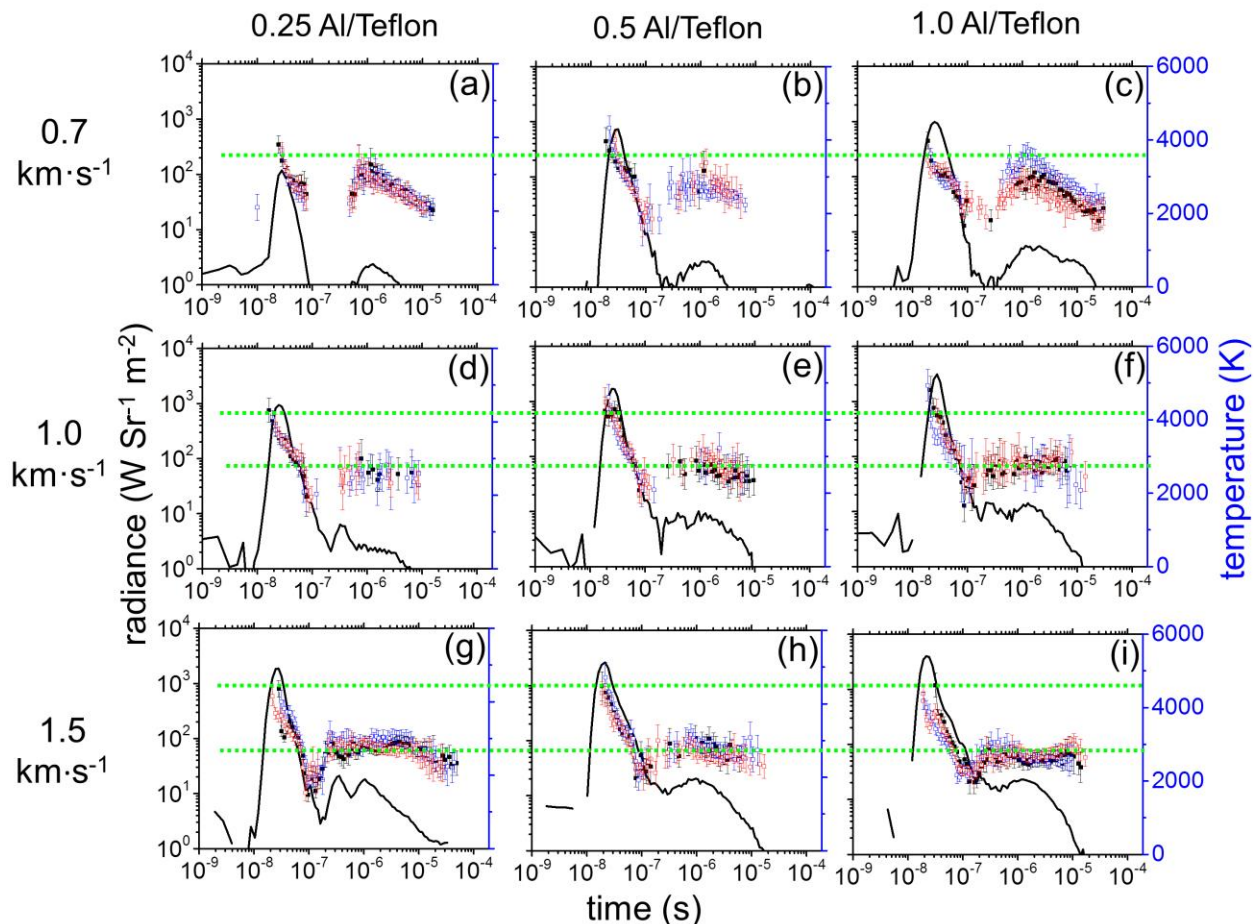


FIG. 29. Temperature histories for Al/Teflon at three flyer velocities (threshold was $0.6 \text{ km}\cdot\text{s}^{-1}$). The radiance curves and the dashed lines are visual guides. In each panel we display temperature histories for three individual shots, to demonstrate reproducibility.

The temperatures for the microsecond burst, attributed to Al/Teflon combustion, were in the range reported by Densmore et al.³¹, who deduced a steady combustion temperature of 3300K by averaging temporal and spatially inhomogeneous temperature distributions. Our temperatures depended little on Al load, but increased slightly with impact velocity. With $0.7 \text{ km}\cdot\text{s}^{-1}$ impacts (Figs. 28a-c), the combustion temperatures were not steady. They peaked at $\sim 3300\text{K}$ at $1 \mu\text{s}$ and then dropped off subsequently. With 1.0 and $1.5 \text{ km}\cdot\text{s}^{-1}$ impacts, the combustion temperatures were steady for about $10 \mu\text{s}$ at the value of $2800\text{K} (\pm 100\text{K})$.

Temperatures near the peak of the nanosecond emission burst again did not depend much on Al load, but did increase with impact velocity. At $0.7 \text{ km}\cdot\text{s}^{-1}$, peak temperatures were about 3700K . At $1.0 \text{ km}\cdot\text{s}^{-1}$, peak temperatures increased to about 4200K , and at $1.5 \text{ km}\cdot\text{s}^{-1}$, peak temperatures further increased to about 4600K .

We performed extensive tests to insure that our emission transients could be attributed to Al + Teflon exothermic chemistries. We showed the emission did not originate from the substrates. The emission from Teflon alone was much smaller than from Al/Teflon and had a different time dependence. Since there was a small possibility that a reaction might occur

between an Al flyer and Teflon, we used unreactive Cu flyer plates. We achieved a high level of reproducibility using the most homogeneous nonporous samples we could prepare. We obtained hundreds of shots, and we are confident that the data presented here does not contain any outliers or artifacts, but are truly representative of the shock-induced reactivity. Our temperature measurements were referenced against a calibrated thermal emitter. Since we spectrally resolved the emission into 32 channels over the 450-825 nm wavelength range, we are confident we are observing emission that was an excellent fit to the graybody distribution without the possibility of interference from atomic or molecular emission.² Our temperature histories were highly reproducible from shot to shot (Fig. 29).

Our combustion temperatures compare reasonably well with the Densmore result of 3300K,³¹ despite major differences in experimental methods. The Densmore results refer to a sabot of pressed Al/Teflon powder that was fired into a steel plate, producing a spatially-inhomogeneous temperature distribution that was not time resolved. Our measurements with 2 ns time resolution refer to a small (100 μm diameter x 3 μm thick) homogeneous layer on a sapphire window subjected to a spatially-uniform impact with a Cu flyer.

At a velocity of 0.7 km s^{-1} , slightly above threshold where the initiating shock was weak, the combustion temperature was never steady. It briefly reached a peak temperature of 3000K and then cooled quickly. At higher velocities of 1.0 and 1.5 km s^{-1} , the combustion process remained at a steady temperature of 2800K ($\pm 100\text{K}$). This is our best value for the steady combustion temperature but we must note that, as with the Densmore result, this temperature refers to combustion of material that was at least partially reacted during the initiating shock. The factor that limits the duration of the steady temperature in our experiments is the small quantity of material undergoing combustion.

Our initiation threshold of 0.6 (± 0.1) $\text{km}\cdot\text{s}^{-1}$ is similar to what was obtained by Mock and Drotar,²⁵ who assigned a threshold at 2.6 GPa. According to Fig. 1a, 2.6 GPa corresponds to impact with a Cu flyer at 0.53 $\text{km}\cdot\text{s}^{-1}$. However our measurements of initiation delay of 25 ns are a thousand times faster than their observed initiation delays of tens of microseconds, obtained using a camera with 100 ns exposure time and 2 μs interframe time. Presumably, our much faster delays represent an intrinsic time delay for the Al/Teflon reaction, unhindered by the much slower time resolution and possibly bulk effects associated by observing side views of large diameter charges.

Having established the highly-controlled nature of our shock process and our thermal histories, and general agreement with previously measured temperatures and thresholds, we now look in more detail at the shock initiation process. Peak temperatures observed shortly after the shock (Fig. 29) were higher than combustion temperatures, and temperatures up to 4600K were observed at 1.5 $\text{km}\cdot\text{s}^{-1}$. These temperatures increased only a bit with increasing Al loading, but did increase with impact velocity, so we interpret these higher than ambient combustion temperatures as combustion enhanced by shock heating and also possibly by an enhancement of chemical reaction rates under shock loading.

The best view of exothermic chemistries during and immediately after the shock was presented in Fig. 28. Figure 28 shows a time delay for initiation of 25 ns which changed very

little with shock strength above threshold or Al concentration. The relative insensitivity of the initiation delay to Al concentration or impact velocity above threshold is suggestive of an autocatalytic runaway individual nanoparticle process, since the initiation delay does not depend much on heat generated by nearby nanoparticles and the time to exotherm does not depend much on the intensity of the initiating shock.

As discussed earlier, mechanisms for Al/Teflon initiation might be classed above as either mechanical, where tensile forces from the unloading shock crack the oxide shell, or chemical, where shock-induced chemical breakdown of Teflon produces reactive species that break down or diffuse through the oxide shell. In our previous study,¹⁰ we observed that emission from shocked Teflon preceded emission from Al/Teflon reactions, so that Teflon chemical breakdown indeed preceded the Al/Teflon reactions, and that observation is confirmed here rather dramatically in Figs. 27-28. Figure 27a shows a prompt emission for Teflon starting immediately after impact at 1 ns, whereas Figs. 27b-d and 28a,b show the much more intense Al/Teflon emission onsets at 15 ns, which was exactly the time the flyer plate velocity dropped to zero (Fig. 23b), and the emission peaked at 25 ns. We also suggested that depassivation of the oxide-covered Al nanoparticles was primarily mechanical, based on our observation that the onset of Al/Teflon emission coincided with the end of the shock compression and unloading process.¹⁰ So if the chemical mechanism dominated, it would have to, perhaps coincidentally, coincide with the end of the initiating shock.

It is difficult to experimentally distinguish between the mechanical and chemical initiation processes, and in fact both may be important. In our present study, the nano-Al particles are embedded in a dense polymer film, compared to the previous study on a porous pile of nano-Al particles and micro-Teflon particles. The dense polymer film prevents interparticle collisions that might contribute to oxide shell cracking, so our new results appear to favor a chemical mechanism.

It may be possible to devise experiments that better distinguish between mechanical and chemical initiation depassivation mechanisms. Such experiments might include varying the shock duration,^{3,17} the particle concentration, particle size and oxide layer thickness,⁴¹ the Teflon molecular weight, and treating the oxide-passivated particles with reagents that affect the permeability of the oxide shell.¹⁹ Discriminating among these effects, which might be subtle, might now be now possible due to our ability to generate large quantities of highly-reproducible high dynamic range data for shock initiation.

This study provides the most detailed look ever of shock initiation of a reactive material, Al/Teflon. We found that the velocity threshold for impact initiation of 40 nm Al in Teflon^{AF}, with Cu flyers producing 7 ns steady shock drive, was $0.6 (\pm 0.1) \text{ km}\cdot\text{s}^{-1}$. Using the Hugoniot crossing method we can adjust the threshold for impacts with other materials such as Al or steel. The threshold for Al/Teflon initiation was above the appearance of first light from Teflon, indicating that shock breakdown of Teflon is the first step in the initiation process. Al/Teflon reactions, which produced far more light than Teflon alone, began at the end of shock unloading, at 15 ns, with the emission maximum at 25 ns.

At the peak of the nanosecond emission burst, the temperature was in the 3800-4600K range, depending on Al load and impact velocity. These temperatures are so much greater than what we compute for shocked unreacted materials (Fig. 21b) that they must be caused by heat generated by exothermic Al/Teflon chemistries. At constant flyer velocity, the temperature increased about 200K when the Al concentration was increased fourfold, but temperatures increased about 800K when the impact velocity was raised from 0.7 to 1.5 km·s⁻¹. The minimal dependence on Al loading indicates these peak temperatures arise primarily from reactions of individual Al nanoparticles with little influence from the nearby heat sources. These individual-particle Al/Teflon reactions initiated by shock can last up to ~75 ns. After the shock unloads, the temperature drops to about 2000K, and then the Al/Teflon material not consumed during the shock reignites after several hundred nanoseconds and can burn steadily at 3000K.

It is difficult to distinguish between the mechanical and chemical initiation mechanisms. Results previously obtained on a loose pile of particles appeared to support the mechanical mechanism, but results obtained here in a dense nonporous polymer film were quite similar.

Detonation on a tabletop. We recently showed that the shock compression microscope can produce tiny, well-characterized detonations. These tiny detonations were probed by high-speed high-spatial resolution optical and optomechanical diagnostics including photon Doppler velocimetry (PDV), optical pyrometry and high-speed videography. Although there have been many prior studies of the shock-to-detonation transition in NM in bomb-sized charges,^{42,43} those studies used longer-duration, lower-pressure initiating shocks which took typically microseconds to develop a detonation. When the initiation process takes that long, it becomes difficult to study the far faster molecular processes in the detonation. To do that, decades of experience show that the process of interest, in this case detonation, needs to be reproducibly triggered by a short-duration pulse. Here we show we can produce realistic detonations with 4 ns input shocks and reduce the time-to-detonation to about 12 ns.

Nitromethane is a flammable liquid under ambient conditions. But when shocked, it becomes a high explosive, and NM has served as a model system to understand the shock-to-detonation transition in homogeneous condensed-phase explosives for over 50 years.^{42,43} Detonations in NM propagate at 6.3 km/s (6.3 μm/ns) and produce a temperature^{38,44} of about 3500K and a peak pressure of about⁴⁵ 20 GPa while generating a powerful mechanical energy flux of about 12 TW/m². Despite the extensive body of prior experiments^{38,39,42,44,46-52} and many theoretical models or simulations of NM,⁵³⁻⁶¹ we still do not understand the fast and complex fluid mechanical and chemical processes occurring in the reaction zone behind the detonation shock front for lack of tools to measure them.

A detonation is a shock wave sustained by heat and pressure-generating chemical reactions.⁶² A steady detonation, to an observer moving at the detonation velocity, is one where the structure of the reaction zone appears unchanging in time.⁵¹ But inside this nominally unchanging reaction zone, the molecules themselves are highly active. They are reacting and producing heat and doing work. A widely-used model for the reaction zone is the nonequilibrium Zel'dovich von Neumann Doering (ZND) model.⁶³⁻⁶⁶ In the ZND model, a detonation shock front is a high-pressure spike called the von Neumann spike (VNS).⁶² As the highly-compressed fluid in the VNS spike immediately behind the shock front expands, the fluid

density and sound velocity decline. At a critical location in the expansion behind the shock front, denoted the Chapman-Jouguet plane (CJ plane), the sound velocity drops to a level too low for molecular processes behind the plane to affect the structure of the shock front.⁶² This region between the VNS and CJ-plane is the reaction zone.^{62,65} The length of the reaction zone in detonating NM has been measured, estimated and computed in various ways to be on the order of 100 μm , and the associated reaction zone duration τ_{rxn} is on the order of tens of nanoseconds.^{48,50,51,60,61}

In the more usual methods to study NM shock-to-detonation experiments, where lower-pressure initiating shock durations and times-to-detonation are typically microseconds and no faster than 100 ns,⁶⁰ as shown in 1961 by Campbell, Davis and Travis,⁴³ the initiating shock wave enters NM and compresses and heats the liquid. As the shock continues to propagate downstream, exothermic chemical reactions begin at or near the entry point, which is the place where the NM has been the hottest for the longest time. The hot NM ignites and undergoes a volume explosion that launches a second shock, this time in the precompressed medium, called a superdetonation. The superdetonation catches up to the original shock, producing an overdriven detonation which then decays into a steady detonation. All this takes time: the time for the shocked NM to simmer and explode, the superdetonation overtake time and the detonation formation time. If these times could be reduced to their minimum values, as we have done here, then the time-to-detonation would become controlled by the fundamental molecular processes that generate heat and do work, and those processes could be probed in real time.

We are producing the superdetonation and the overdriven detonation from a more intense shorter-duration shock, and the sequence of events is somewhat different. When we adjusted the input shock pressure to the right value, it created a shocked layer in the explosive that was thinner than the reaction zone and about as hot and dense as the VNS. The NM in this thin layer ignited very quickly, producing a volume explosion, and a superdetonation that quickly relaxed into a chemically-driven shock that maintained a constant profile as it propagated downstream. As we will show below, this chemically-driven shock had all the known properties of bomb-sized NM detonations, so despite its small size and limited run distance we will call it a detonation.

We did not study the initiating shock-duration dependence³ in the present work, so it might be possible to create NM detonations shocks even shorter than the 4 ns used here. We did vary the input shock pressure to find the minimum time-to-detonation. Weaker inputs produced shocks that decayed away and stronger inputs produced overdriven states that would need longer time to develop into a detonation. Thus, in our experiments we are quite close to having the minimum time-to-detonation, which gives us the most favorable conditions to study dynamical processes within the reaction zone.

In studies of our tiny detonations, we determined the VNS spike pressure and the CJ pressure. We determined the length and duration of the reaction zone. We determined the temperature of the VNS and the thickness of the shock front that produced the intense thermal emission. We observed the chemical production of heat and work via the temperature and pressure build up. We directly observed the creation of the steady reaction zone in real time.

The shock compression microscope⁶⁷ used in these studies is diagrammed in Fig. 30a. The target in the microscope was an array of about 50 microcuvettes filled with NM. The flyer plate launcher,^{1,8,9} the photon Doppler velocimeter (PDV)⁹ and the optical pyrometer² have been discussed in detail in previous publications. The 0.5 mm diameter flyer plates were Al 1100 foils 25 μm thick that could be launched at velocities from 0-4.3 km/s by spatially-homogeneous 20 ns duration pulses from a Q-switched Nd:YAG laser producing pulse energies up to 2J.^{8,9} There is often concern that laser-launched flyer plates, as a result of intense laser irradiation, are heated, melted, vaporized, or even partially converted to plasma.⁶⁸ That is not a problem here. We used a shock-assisted launch mechanism that minimized launch laser heating of the flyer plate.^{8,9} Although there is some laser heating of the flyer plates, the flyer plate itself did not contact NM directly. Instead the flyer drove a shock into NM through a thin layer of Al 1100 (the “lid” that caps the cuvette) that was never exposed to the launch laser pulses. As depicted in Fig. 1b, the flyer plate and the shock produced by it are nominally cylinders 0.5 mm in diameter. It is important to note that the PDV and optical pyrometry probes were arranged to view only the central region of the shocked cylinder about 0.1 mm in diameter. This central region experiences a planar shock until transverse release waves arrive from the cylinder edges. These release waves, whose velocity is on the order of the shock velocity, must travel about 250 μm from the edge to the probed region. The shocks used in these experiments can propagate at

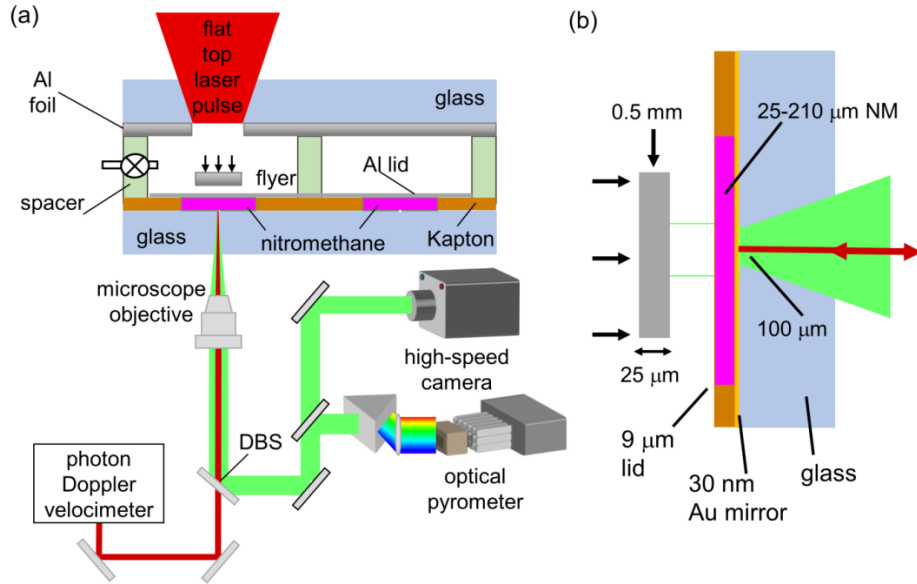


FIG. 30. Experimental schematic. (a) A laser launches flyer plates that create planar shocks in disposable microcuvette arrays containing nitromethane (NM). Shock and material velocities are measured by photon Doppler velocimetry (PDV), and high temperatures and their spatial distributions are determined by optical pyrometry and high-speed video photography. (b) Close-up of a single microcuvette. Shocks were transmitted to NM through a thin impedance-matched lid. Cuvettes with no Au mirror were used to measure the input shock and thermal emission burst. Cuvettes with ultrathin Au mirrors were used to measure the shock exiting NM into glass.

least 250 μm downstream before losing planarity in the probed region. All the measurements shown here were performed in this geometry, where the run distances were less than 250 μm , and therefore we probed only planar shock compression and the planar detonation.

We fabricated a series of cuvette arrays with different NM charge thicknesses ranging from 32 to 210 μm . Even the thickest microcuvettes contained no more than 150 μg of NM, so when the NM was detonated, the kinetic energy release small enough as to be intrinsically safe. The structure of an individual cuvette is shown in Fig. 30b. Some of the cuvettes in each array were optically transparent while others had nonperturbative 30 nm thick electron-beam deposited Au mirrors on precision borosilicate glass windows. The cuvettes without mirror were used to observe the shocked NM with a high-speed camera, to measure the incoming shock profiles and to observe the thermal emission bursts. The NM cuvettes were sealed using 9 μm thick Al 1100 foil lids. This foil thickness was about the thinnest we could handle without tearing, and the foil was flexible enough to serve as a gasket that sealed the liquid inside the cuvette. When the 25 μm thick Al 1100 flyer plate impacted the 9 μm thick impedance-matched lid, the lid was thin enough to transmit a significant portion of the input flyer energy into the NM.

When flyer plates impacted the lid, we measured the velocity at the lid-NM interface using PDV. This velocity measurement gave the input NM particle velocity (or since NM is a fluid, the flow velocity) denoted U_p . Knowing U_p and the NM Hugoniot, we can compute input shock pressures, fluxes and fluences.^{7,69,70} The flux and fluence will be needed below to determine the shock energy input to and output from the NM. The output shock from NM was measured in cuvettes with the Au mirror. Even though the Au mirror is not a good impedance match for NM or glass, we consider the Au mirror nonperturbative. The mirror, because it is so thin (30 nm), has a shock ring-up time on the order of a few tens of picoseconds, so the shock propagation through the mirror hardly affects our 1 ns time scale measurements.

When shocks exit the NM and pass through the Au mirror into glass, they produce an attenuated replica of the NM shock which can be detected by PDV measurements of the Au mirror velocity profile. Given the measured velocity profile in the glass window, the shock pressure in NM can be determined from the known NM and glass Hugoniots via the method of Hugoniot crossing.⁷

The cuvette array was fabricated on 2" squares of borosilicate glass 1/4" thick from Chemglass, Inc. Part of each glass square was coated with the 30 nm Au mirror. Adhesive KaptonTM tapes 30, 40, 64, 90, 170 or 210 μm thick (the thicknesses were measured using a stylus profilometer) were applied and a laser milling machine was used to cut an array of about 50 wells in the Kapton, each well 2 mm in diameter. The wells were filled with NM >99% (Sigma Aldrich) and sealed with the 9 μm thick Al foil lid (Alufoil, Hauppauge, NY). We examine each microcuvette in the microscope before firing the flyer plate to verify there were no bubbles in the liquid or wrinkles in the lid material. Imperfect cuvettes could also be easily identified by poor PDV profiles of the input shock.

Single snapshots of the visible light emission from the shocked NM were obtained using an Andor iStar sCMOS camera with a 2560×2160 array of 6.5 μm pixels. The camera viewed the sample through a 10X microscope objective. The spatial resolution was determined to be 2.2

μm using a 1951 USAF calibration target with a 2 mm field of view. The camera image intensifier was gated with a 5 ns pulse, which defines the acquisition or shutter time. Images were recorded as an unformatted matrix and processed using MATLAB software to create TIF images.

Our 8 GHz PDV measures material velocities U_p at the lid/NM interface or the NM/glass interface (Fig. 30b). Velocities measured by PDV were corrected for the optical properties of the NM and glass at the 1550 nm PDV wavelength using the method described by Jensen et al.,⁷¹ using published borosilicate glass⁷² and NM⁷³ refractive index data. The correction factors were 1.001 for NM and 1.0627 for glass.

As discussed below, the NM Hugoniot under 3 km/s (c.f. Fig. 32b) was observed to be a linear function,

$$U_s = 1.64U_p + 1.65 \text{ km/s.}$$

For our borosilicate glass, we used the tabulated Hugoniot for Pyrex,⁷⁰ a material quite similar to what was used here. The glass U_s versus U_p Hugoniot is nearly horizontal to $U_p = 2$ km/s, and then it rises steeply above 2 km/s. We approximated the glass Hugoniot as

$$\begin{aligned} U_s &= -0.18U_p + 5.03 \text{ km/s} & (U_p \leq 2 \text{ km/s}) \\ U_s &= 1.27U_p + 2.40 \text{ km/s} & (2 \text{ km/s} < U_p < 3 \text{ km/s}). \end{aligned}$$

The glass Hugoniot shows that borosilicate glass is not a simple shock medium. When the shocked NM impacts the glass at velocity U_p , the glass appears relatively soft below 2.0 km/s, but it stiffens up above 2.0 km/s. There is some uncertainty in knowing the precise conditions and speed where the glass stiffening occurs. Almost all of our measurements, including measurements of the detonation waveform, involve velocities $U_p < 2$ km/s, so the precise location of the stiffening will not matter in that case. However during the run-up to detonation, U_p was briefly as high as 2.7 km/s, so in that regime there was an additional uncertainty in the pressure determination.

The direct observable in our shock waveform PDV measurements is U_p . For our energy input and output measurements we need to determine the mechanical energy fluence in the NM. To make comparisons to other works that used different output window materials, we need to determine the pressure in the glass. We can do both of these things using the equations for linear Hugoniots of the form $U_s = mU_p + b$.⁷⁴ The NM Hugoniot is linear at all needed velocities, and for the glass, we simply have to split up the equations below into the 0-2 km/s and 2-3 km/s ranges where, according to Eq. (2) the glass Hugoniot is linear. In terms of particle velocity U_p , the shock flux is given by,⁷⁴

$$\text{flux}(t) = \frac{1}{2} \rho_0 [b + mU_p(t)] U_p^2(t),$$

where ρ_0 is the ambient density. The fluence is the time-integral of the flux,⁷⁴

$$fluence(t) = \int_{-\infty}^{+\infty} flux(t) dt .$$

In a NM detonation the flux is about 12 TW/m^2 . The fluence depends on the shock duration, and it is about 12 kJ/m^2 for a detonation shock of about 10 ns.

The pressure profile $P(t)$ is given by,^{7,69,74}

$$P(t) = \rho_0 U_s U_p(t),$$

where we assumed a steadily-running shock and neglected the time dependence of the shock velocity U_s .

We illustrate measurement reproducibility in Fig. 31. We previously showed that the flyer plate velocities and impact times were quite reproducible. With the $25 \mu\text{m}$ Al flyers used here, the velocities and impact time variations (1 standard deviation) were 0.56% and 0.81 ns, respectively.¹ The least reproducible part of our experiments was the lid velocity profile, and some examples are shown in Fig. 31a, where the flyer plate velocity was 3.4 km/s. Ideally, the lid velocity profile should have a steep onset and remain at a constant velocity for the 4 ns shock duration. The lid velocity onset was indeed quite sudden, with a rise time $< 1 \text{ ns}$, and the lid velocity profile did remain constant for 4 ns (Fig. 31a). However the

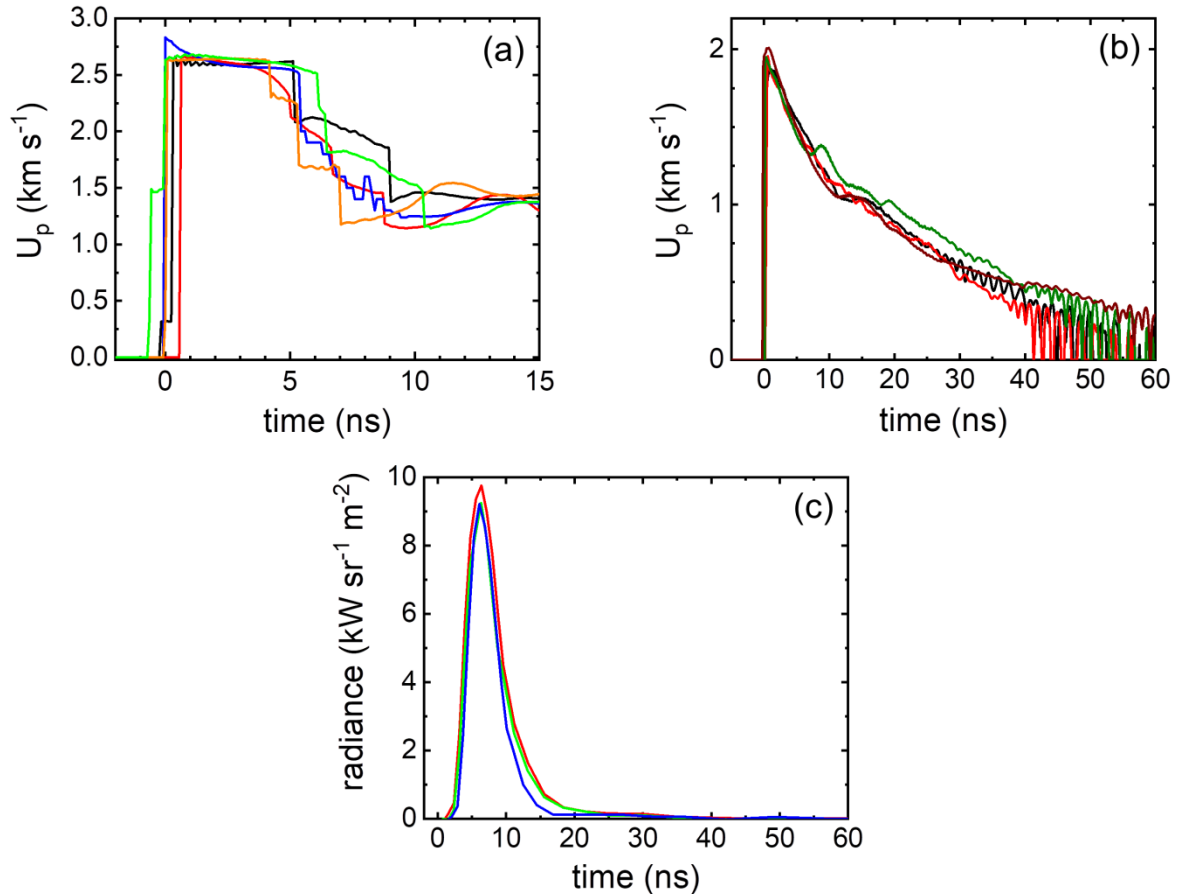


FIG. 31. Reproducibility measurements. (a) PDV measurements of the Al/NM interface with a 3.4 km/s impact show a steeply-rising 4 ns duration rectangular shock with a less-reproducible but much-weaker trailing shock. (b) PDV measurements of detonation waveforms in a 170 μm thick cuvette with a 4 km/s impact. (c) The radiance from NM thermal emission bursts after a 4 km/s impact with NM in a 40 μm thick cuvette.

subsequent lid motion was less reproducible. That is not a problem for these measurements, since the slower motion of the lid launched weak trailing shocks that minimally affected propagation of the much stronger, much faster shock downstream. Figure 31b shows output shocks in the detonation case, where the flyer velocity was 4 km/s and the run distance was 170 μm , and these had excellent reproducibility. Figure 31c shows the thermal emission burst intensities with a 4 km/s impact and a 40 μm thick run distance, and these were also quite reproducible.

In our shock waveform measurements, we obtained data on a minimum of three shots and more usually five or more, and the entire body of experimental data for this study encompassed hundreds of shots. The multiple shot comparison allowed us to discard any outlying shots due to imperfect cuvettes or laser misfires, so we are confident that the shock profiles displayed below reliably represent the behavior of shocked NM.

An example of an input and output shock waveform is shown in Fig. 32a, where we produced an NM detonation using a 4.0 km/s flyer impact with a 90 μm thick NM cuvette. The shock input to NM had a rectangular 4 ns profile; the output shock had a triangular profile with a full-width half maximum of about 12 ns, and the thermal emission was a burst of roughly the same duration as the output shock. The input shock is a shock into NM and the output shock is a shock into glass. To put the input and output shock measurements on comparable footing, we do not want to compare U_p measurements, since the same U_p in the different media give quite different pressures and energies. We converted the $U_p(t)$ data into shock flux (TW/m^2). The red dashed line in Fig. 32a illustrates how we cut off the weak input shock tail before doing the integration to compute the input fluence.

Measurements such as Fig. 32a, repeated at different flyer speeds, were used to determine the NM Hugoniot in the form of U_s versus U_p . The shock velocity U_s was the measured thickness of the NM layer divided by the time interval between the incoming and outgoing shock fronts. Our NM Hugoniot is shown in Fig. 3b. This Hugoniot is not an equation of state, since it was obtained in a reacting material with short-duration shocks, but it serves as the effective NM Hugoniot for these measurements. Our Hugoniot agrees quite well with results from the 1980 Los Alamos Laboratory database⁷⁰ and more recent results from Brown et al.⁵²

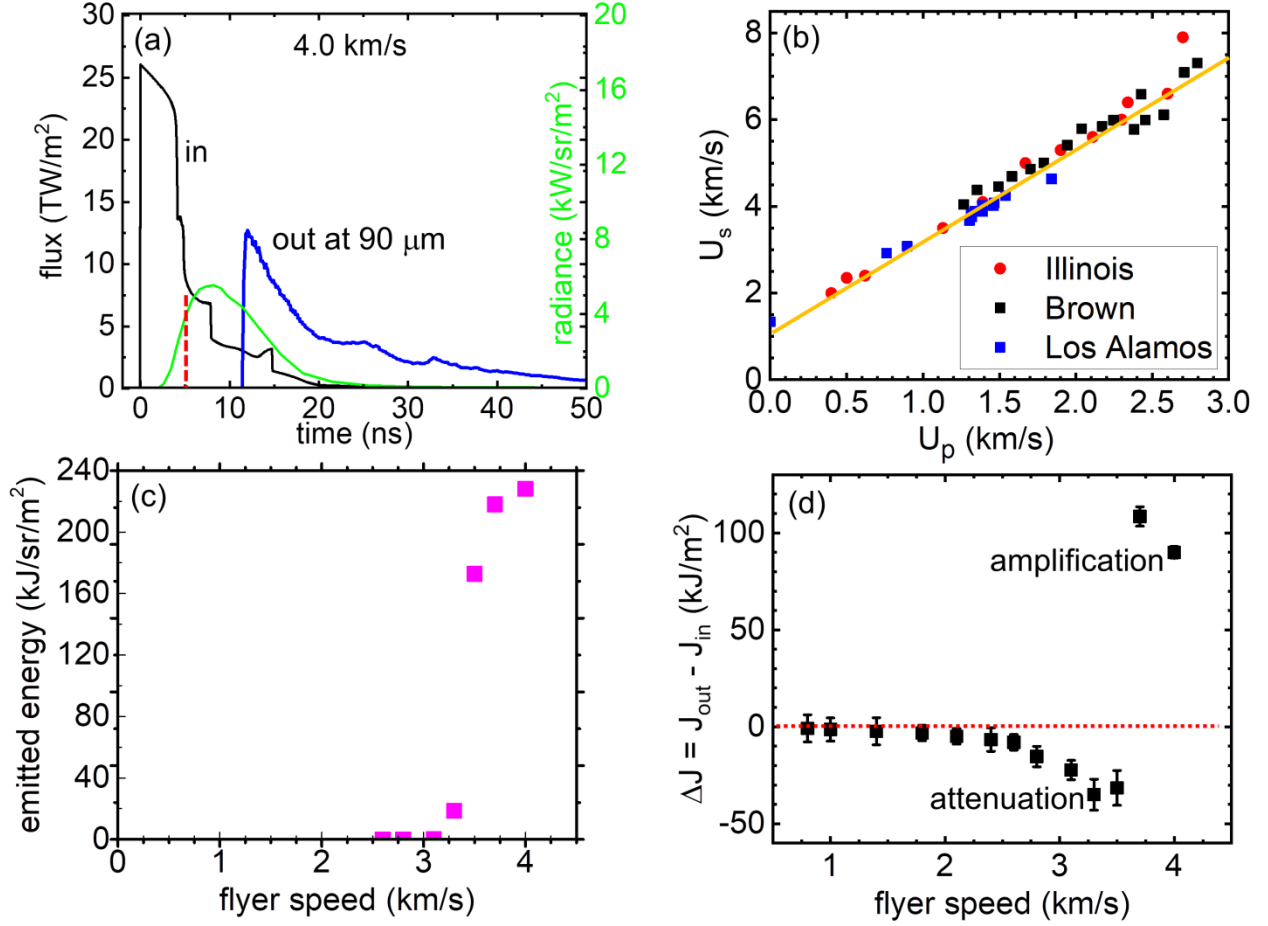


FIG. 32. Work done, heat released and shock Hugoniot of NM. (a) Typical input and outgoing shock flux waveforms with thermal emission burst, in this case for a NM layer thickness of 90 μm and a 4.0 km/s flyer plate impact. (b) Our NM Hugoniot compared to results from Brown et al.⁵² and the Los Alamos database compiled by Marsh.⁷⁰ (c) Thermal emission produced by 40 μm thick shocked NM plotted as the time integral of the radiance. (d) Shock attenuation and amplification in NM plotted as the difference between the outgoing and incoming shock fluence J . The error bars are the variance of five shots.

In Figs. 32c and 32d we show results from 40 μm thick NM charges that determined the thermal energy emitted by the exploding NM and the attenuation and amplification of the input shocks. The thermal emission energy, expressed as kJ/sr/m² in Fig. 32c, was the time integral of radiance measurements such as the data shown in Fig. 32c. As discussed previously, we calibrated our radiance and spectral radiance using a fiberoptically-coupled NIST-traceable lamp with a known radiance, spectral radiance and emissivity.² Thermal emission first became visible with 2.5 km/s impacts and dramatically increased at 3.5 km/s. The difference in energy between the input and outgoing shocks was expressed in Fig. 32d as the output fluence minus the input fluence. At lower flyer plate velocities, the input shock was transmitted through NM with minimal attenuation. We began seeing significant shock attenuation (i.e. absorption of shock energy by NM) at the same impact velocity, about 2.5 km/s, where the thermal emission first appeared (Fig. 32c). At 3.5 km/s and above, where the thermal emission was most intense, the input shock was amplified (Fig. 32d).

Figure 33 shows the progression through NM of planar shocks over 30 to 170 μm run distances with a range of flyer impact velocities. Note that our U_p values were measured with NM shocks propagating into hard glass windows, so they were about 30% smaller than values reported by other groups where the NM shock was transmitted into softer PMMA windows.⁴⁸ With a 2.4 km/s impact (Fig. 33a), the shock at 30 μm had almost the same amplitude as the input shock, and therefore little shock energy was absorbed by the NM. The 2.4 km/s input shock to NM decayed monotonically as it ran. With a 3.1 km/s impact (Fig. 33b), the shock amplitude 30 μm downstream was noticeably smaller than the input shock, indicating strong NM shock attenuation accompanied by shock energy absorption by NM. After the strong absorption, the input 3.1 km/s shock also decayed monotonically as it ran. With 3.3 km/s and 3.7 km/s impacts

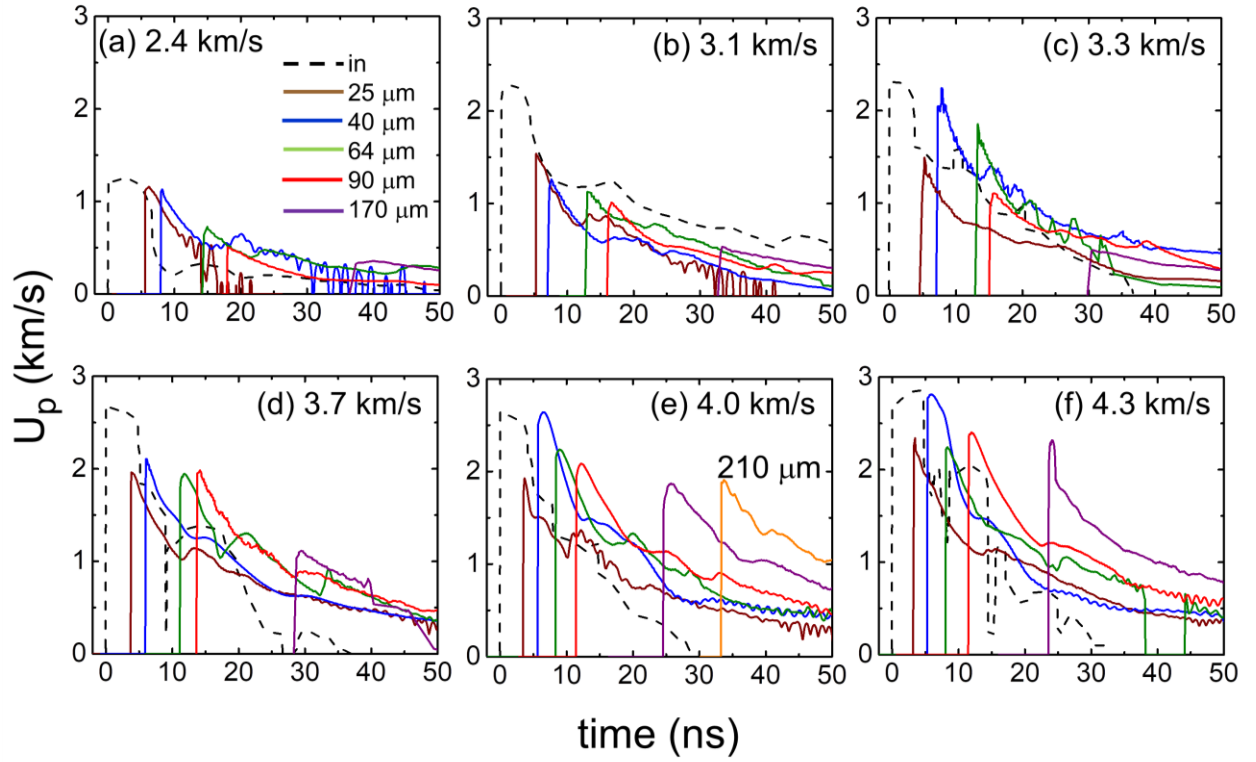


FIG. 33. Shock waveforms as a function of distance and time in NM. (a) At 2.4 km/s the shock was hardly absorbed and it decayed as it propagated. (b) At 3.1 km/s there was substantial absorption followed by shock decay. (c) At 3.3 km/s, shock absorption was followed by a volume explosion in NM starting at about 8 ns. (d) At 3.7 km/s, after the volume explosion the shock decayed monotonically. (e) At 4.0 km/s, the shock after 12 ns propagated with a steady waveform, indicative of a detonation. (f) At 4.3 km/s, the shock changed shape as it propagated.

(Figs. 33c-d) something new happened. The input shock was attenuated during the first 30 μm , but as it continued to run to 40 μm it became strongly amplified by a NM volume explosion. This volume explosion is likely similar to what was seen in its initial stages by Brown and co-workers in experiments using 300 ps shocks.⁵² Subsequent to the volume explosion, the shock decayed monotonically. With 4.0 km/s impact (Fig. 33e) the amplified shock did not decay.

After about 12 ns it ran steadily with minimal change in amplitude or profile. We ran an additional experiment, shown in Fig. 4e, using a 210 μm layer of NM, to confirm that this profile remained steady over this longer run distance. At 4.3 km/s (Fig. 33f) we also saw a shock that ran 170 μm without decaying. However this shock changed shape as it ran. We believe this shock created by a 4.3 km/s impact was an overdriven state that ought to eventually relax into the detonation waveform, but the 4.3 km/s impact would clearly take longer to reach detonation than the 4.0 km/s impact. Thus the 4.0 km/s impact was the one that produced, in the minimum time, the steadily-running planar shock we attribute to a detonation.

Pyrometry measurements with the 4.0 km/s flyer impact-to-detonation are shown in Fig. 34 using a 40 μm thick NM layer. The lowest temperatures our pyrometer can detect are about 2000K.^{2,75} As shown in Fig. 34a, the 2000K level was reached within 1.4 ns after the shock entered the NM, and this 2000K shocked fluid had a low emissivity. Figure 34b shows the rather noisy spectral radiance at 2.2 ns with our best graybody^{2,47} fit giving a temperature of 2200K. Over the next five nanoseconds the temperature climbed to about 3430K and the (425-800 nm) emissivity rose to 0.4 as the detonation formed. The high temperature and emissivity remained constant for about 5 ns. Figure 34b shows the optical emission spectrum averaged during this 5 ns constant-temperature interval and the best graybody fit with $T = 3430 \pm 240\text{K}$ and emissivity $\phi = 0.40 \pm 0.18$. From the emissivity build-up at shorter times we can estimate the thickness of the emissive layer that produced the 3430K thermal emission.⁴⁷ The emissivity grew to its maximum value after the shock propagated for about 4 ns. Since the detonation runs at 6.2 km/s,⁴⁵ the thickness of this emitting layer was $<25 \mu\text{m}$. Thus with the high-speed pyrometry measurements we were able to measure, in real time, the rate of heat production and the optical changes in the shocked NM (via the emissivity) that signaled the onset of exothermic chemistries.

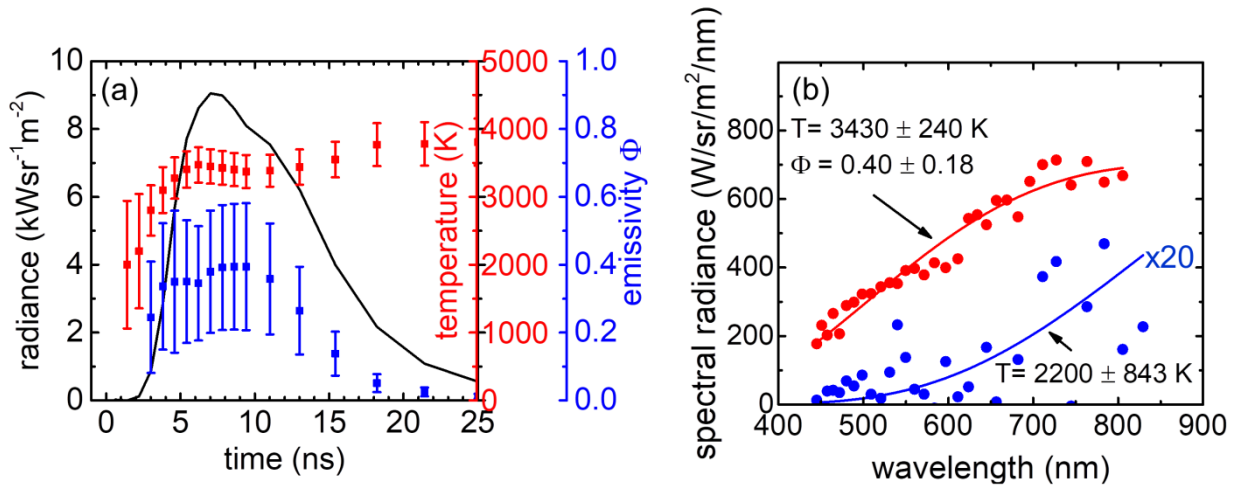


FIG. 34. Temperature measurements of NM detonation by optical pyrometry. (a) The NM thermal emission in the run-up to detonation first became detectable at 1.4 ns when temperature reached 2000K. Over the next 5 ns the temperature rose and steadied, and the emissivity rose to $\phi = 0.4$. (b) Thermal emission spectrum (blue) during the first 2.2 ns when the temperature was 2200K, and (red) the average during a 5 ns interval when the temperature was steady at 3430K. The solid curves are best fits to the graybody model. The error bars in (a) are the variance between the data and best graybody fit.

To understand the spatial structures produced during the run-up and detonation, we used the high-speed camera that could acquire high-spatial resolution ($2.2\ \mu\text{m}$) images with a 5 ns acquisition time. The camera was focused where the shock first entered NM, at the inner lid surface. The images in Figs. 35 and 36 do not use external illumination. They are showing the thermal emission from the hot NM averaged over the 5 ns acquisition window. In Fig. 35 we

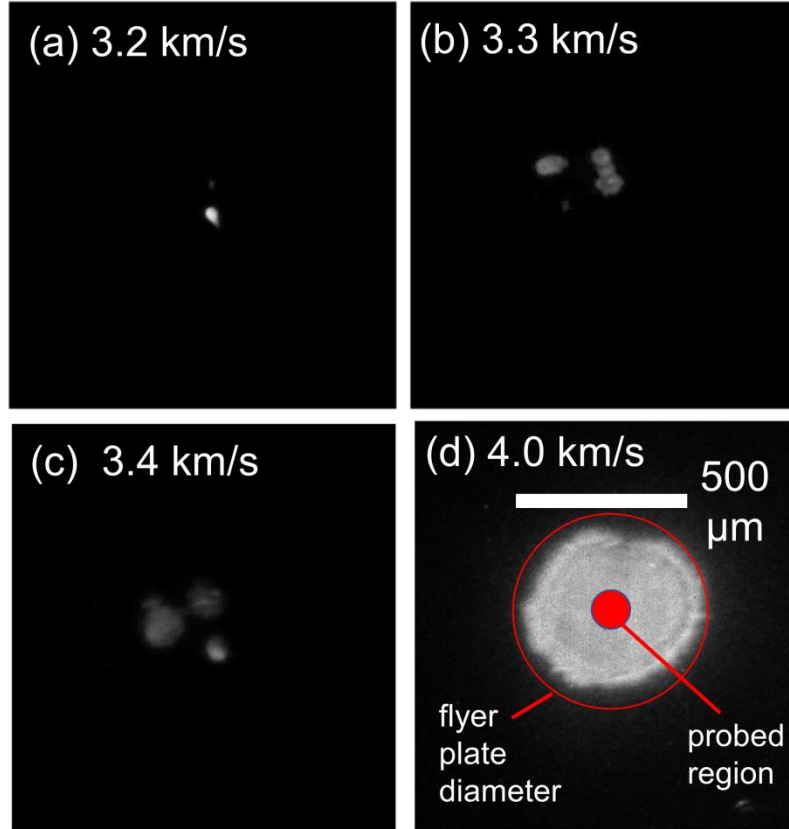


FIG. 35. High-speed thermal images (in visible light) obtained during the first 5 ns of shock compression in NM produced by impacts at the indicated velocities. (a), (b), (c) Lower-speed impacts initially produced hot spots. (d) The 4 km/s impact produces a detonation that appears as a disk slightly smaller than the flyer plate diameter. The slightly darker region near the perimeter indicates the radial release wave front. The probed region is in a planar shock far away from the radial release wave front.

show the flyer speed dependence. With the 3.2, 3.3 and 3.4 km/s velocity impacts (Figs. 35a-c), where the shock decays away, the hot regions of the shocked NM near the entry face appear as hot spots tens of μm in diameter. We do not know the origin of the hot spots, which might result from variations of the Al texture at the lid/NM interface, density fluctuations, chemical reaction instabilities or dust. But with the 4.0 km/s input shock, in Fig. 35d, the hot NM was a continuous disk slightly smaller in diameter than the 0.5 mm flyer plate. In Fig. 35d there is some turbulent structure⁷⁶ in the NM and a thin annular region visible near the perimeter. This annular region denotes the radial release wave front. As mentioned above, it takes longer that the duration of

the experiment for this release wave to reach the central region of the shock probed by PDV and optical pyrometer.

Figure 36 shows a time sequence of images with a 5 ns acquisition window, where a 4 km/s impact produced a detonation in a 170 μm thick charge. The camera was focused onto the inner surface of the lid, but as the shock ran downstream, the images became slightly defocused. Between 3 ns and 11 ns, the area of the hot shocked disk in NM increased noticeably. This area increase corresponds to the sudden jump in shock pressure observed 40 μm downstream in Fig. 33e, and it confirms our description of that process as a volume explosion. Figures 36 c-f show the shocked disk of hot NM maintained its integrity up to 21 ns, which is just short of the time the detonation reached the output window.

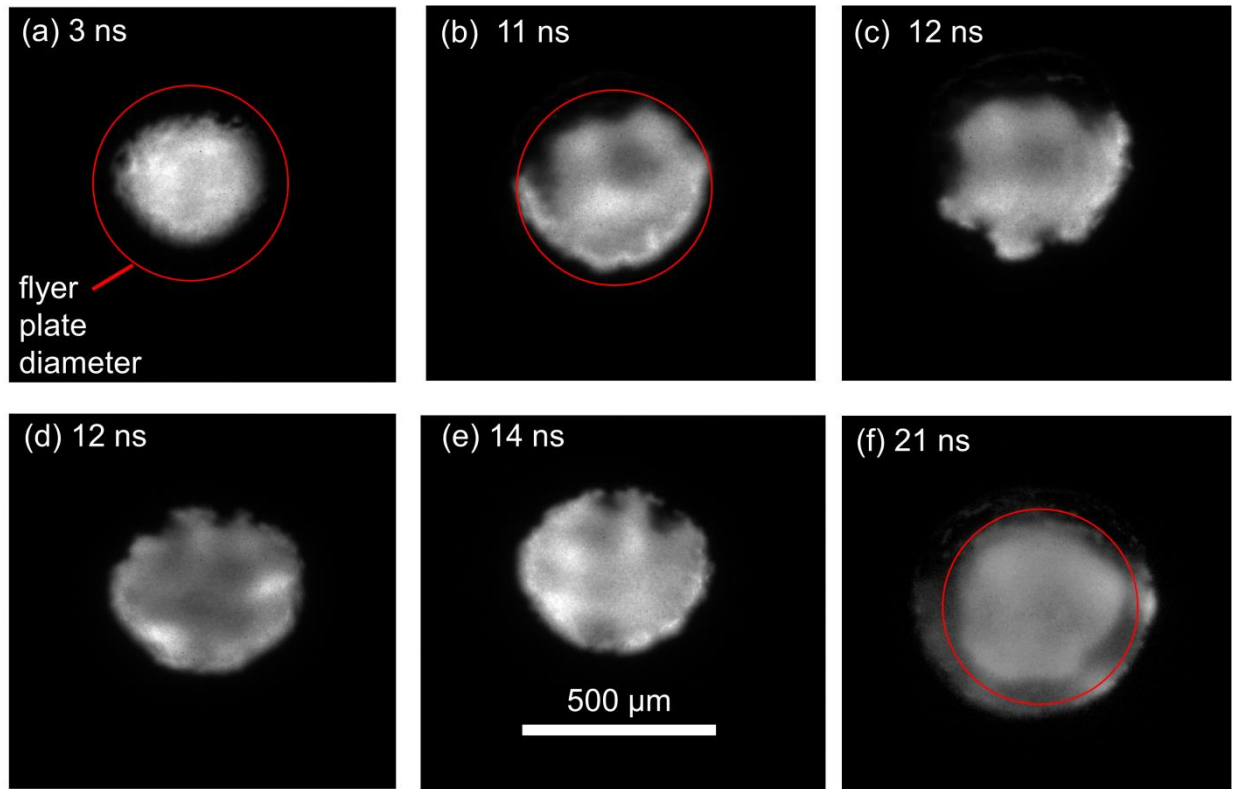


FIG. 36. High-speed thermal images (in visible light) with 5 ns acquisition time at different times during the run-up and detonation produced in a 170 μm thick cuvette by a 4 km/s impact. The camera is focused on the Al/NM interface where the shock enters the NM, so the image becomes progressively out of focus as it propagates. The volume explosion that starts near 6 ns can be seen by comparing (b) to (a).

The run-up to NM detonation with the apparent minimal time-to-detonation is shown in more detail in Fig. 37a. To compare our results to other studies, we converted the PDV velocity measurements to NM pressure. The 4 km/s impact that produced a steady detonation in the shortest time created an input pressure in NM of about 18 GPa. The volume explosion that occurred around 10 ns produced a peak pressure of about 35 GPa. This volume

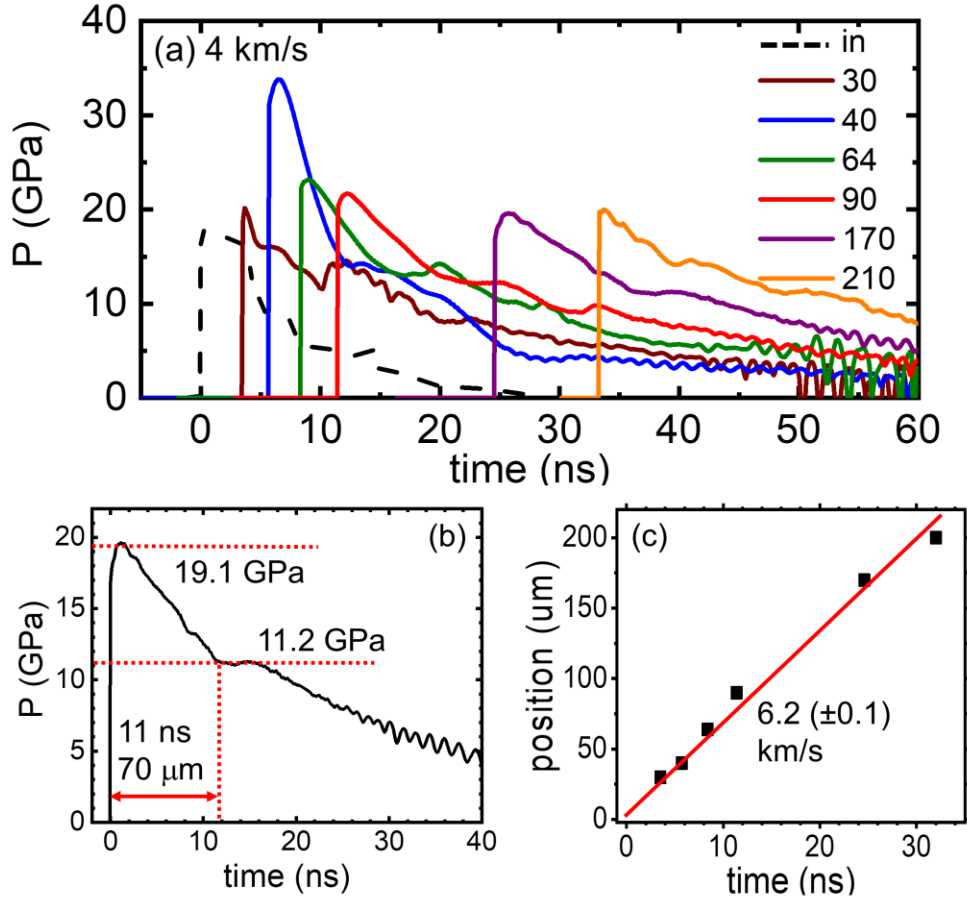


FIG 37. Properties of the detonation in a volume containing about 40 μg of NM impacted by a 4.0 km/s flyer plate. (a) Formation of a steady detonation wave from an input 21 GPa shock lasting 4 ns. (b) Detonation velocity. (c) Detonation waveform 170 μm downstream indicating VNS and CJ pressures and reaction zone length and duration.

explosion, which most likely corresponds to the superdetonation reported by others,⁴³ then decayed into the steady detonation. We cannot precisely determine the time-to-detonation because we only measured the shock at a few specific locations. The detonation waveforms at 90, 170 and 210 μm in Fig. 8a had almost the same profiles and amplitudes. But the shock at 90 μm was slightly bigger than the shocks at 170 μm and beyond, so we can say the detonation had developed a stable profile soon after 90 μm but before 170 μm . As shown in Fig. 37a, these distances correspond to times between 12 and 24 ns, so the run time-to-detonation was between 12 and 24 ns. Let's just say about 15 ns for the time-to-detonation.

Using the shock propagation data in Fig. 37a, we plotted the shock front and position versus time in Fig. 37b. The shock velocity obtained by this procedure was $6.2 (\pm 0.1)$ km/s.

Figure 37c examines the detonation profile 170 μm downstream. The VNS pressure was 19.1 GPa. There is known to be a significant uncertainty in measurements of the CJ pressure due to the difficulty of pinpointing the CJ plane from the detonation waveform alone.⁶⁰ In Fig. 37c, at 11 ns the detonation shock has decayed to a plateau that lasted for about 5 ns before a second

decay. The downstream waveforms had similar plateaus and the plateaus were a reproducible feature (e.g. Fig. 31b). We attribute the plateau to the onset of CJ behavior. In a bomb-sized detonation, the plateau would continue for a long time, but in our tiny cuvettes the plateau decays by exhausting the fuel in the thin cuvette. Menikoff has discussed the possibility of a slow tail in the NM chemical kinetics,⁶⁰ and we cannot rule out that possibility as contributing to the post-plateau decay as well. The CJ pressure in our attribution was 11.2 GPa, the width of the reaction zone was 70 μm , and the associated reaction zone duration was $\tau_{rxn} = 11$ ns.

The run-to-detonation is frequently presented using a method called the Pop-plot. Menikoff and Shaw⁶⁰ constructed an NM Pop-plot from various sources, in the log-log form of time-to-detonation versus input shock pressures up to 13 GPa, and we plotted the data from their paper along with ours in Fig. 38. Extrapolating the Pop-plot data in Fig. 38 to our 18 GPa input shock predicts that the time-to-detonation would be 1 ns, but in fact it was more than an order of magnitude greater than this prediction, about 15 ns. Figure 38 thus indicates that our shock-to-detonation results with intense 4 ns input shocks fall into a different physical limit than the other

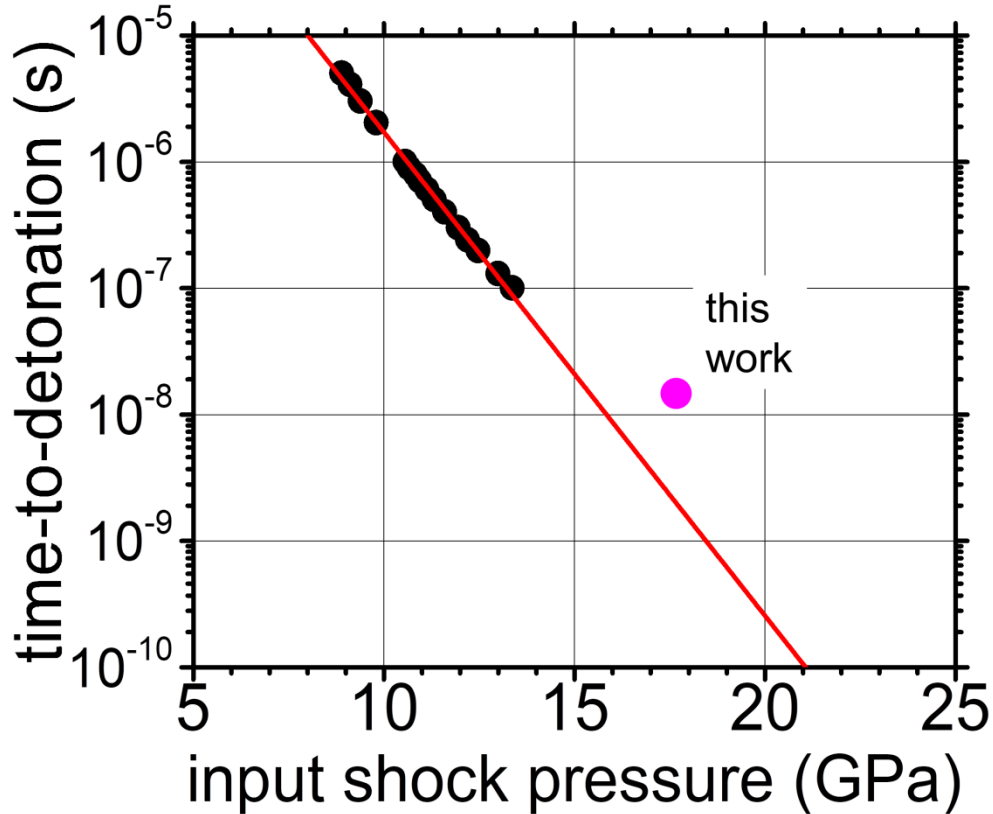


FIG 38. Pop-plot for pure NM, based on compilations in Menikoff and Shaw⁶⁰ and Dattelbaum et al.⁷⁷, with the time-to-detonation from this work. The size of the symbol is the same as the error introduced by measuring the detonation propagation at only a small number of fixed locations. Our time-to-detonation was more than an order of magnitude than would be expected from earlier works using longer-duration input shocks.

measurements with 100 ns and longer-duration input shocks. There must be a physical process occurring in the NM that prevents the time-to-detonation from becoming faster than about 10 ns. That process is the molecular and chemical dynamic response to the initiating shock. Thus our 4 ns input shock is faster than the fundamental molecular response and chemical kinetics occurring in the reaction zone.

Our Hugoniot determination in Fig. 31b and the shock waveform measurements presented in Fig. 37 provide confirmation that the shock waveform we observed had the same properties as the bomb-size detonations studied in many previous works. Our Hugoniot agrees with more than one previous study.^{52,70} The NM detonation velocity from an explosives handbook was 6.29 km/s compared with our 6.2 km/s.⁴⁵ Measurements of the CJ pressure--and recall it is hard to pin down this pressure precisely--were discussed in Menikoff and Shaw,⁶⁰ where the CJ pressure was calculated to be 10.34 GPa. Other calculations with CHEETAH software codes gave 11.4-13.2 GPa.⁴⁴ Dattelbaum and co-workers gave the CJ pressure as 12.5 GPa.⁷⁷ We obtained 11.2 GPa. The VNS pressure has been computed and measured in various ways. Menikoff and Shaw calculated it to be 21.1 GPa⁶⁰ and Partom calculated it to be 19.1 GPa,⁶¹ compared to our 19.1 GPa. The reaction zone width was deduced to be 36 μm by Engelke and co-workers⁵⁰ and calculated to be 11 μm by Menikoff and Shaw,⁶⁰ compared to our 11 μm . Pyrometry by Yoo and co-workers gave a detonation temperature of 3600K,^{38,39,46} which was the same as obtained by Bouyer and co-workers.^{44,47} We obtained 3430 (± 240)K. Bouyer and co-workers^{44,47} deduced that the emission originated from a thin layer, but did not provide a numerical value that can be compared to our $<25 \mu\text{m}$ thickness. Because the intensity of thermal emission scales as T^4 , measurements on samples with temperature distributions are strongly biased toward the hottest part of the sample, so the 3400K (or 3600K) temperatures refer to the VNS region rather than the CJ region, where models⁶¹ have given predicted CJ temperatures closer to 2200K.

We found the threshold impact velocity, $\sim 2.5 \text{ km/s}$ (Fig. 31d) where NM begins to attenuate input shocks and starts to absorb significant quantities of shock energy. As discussed previously,⁷⁸⁻⁸⁰ the absorption mechanism in NM involves shock-induced multiphonon up-pumping of NM molecular vibrations, so we have found the shock pressure where multiphonon up-pumping becomes efficient. In run-to-detonation experiments, the shock-induced temperature jump in NM has two distinct causes, the (nonreactive) adiabatic compression and the heat evolved by chemical reaction. In order to separate these two effects, it would be necessary to adiabatically compress NM faster than chemical reactions could produce additional heat. We probably did not compress the NM that fast, but we did see that a VNS-strength input shock with properties similar to the leading edge of an NM detonation heated NM within 2.2 ns to about 2200K, which was far below the detonation temperature of 3430 K. This suggests that most of the heating during the first 2 ns was due to adiabatic compression without the additional contribution of heat from exothermic chemical reactions.

The optical properties of the shock front have been studied theoretically by Reed and co-workers.^{55,57,81,82} They have concluded that a fraction of the bonding electrons become delocalized in the VNS region, producing a semimetallic layer⁵⁵ with absorption, emissivity and reflection⁸² greater than unshocked NM, which is nominally transparent in the visible. Ultrafast shock experiments by Brown and co-workers showed the appearance of an absorbing layer

within 300 ps.⁵² Our observation of 0.4 emissivity in a layer <25 μm thick is supportive of the presence of a free-electron plasma at the shock front, but does not conclusively prove or disprove the existence of semimetallic or metallic states in the detonation front.

We can trigger detonation in NM with a 4 ns input shock at an input pressure quite close to the VNS pressure of 19 GPa with a run-to-detonation time of about 15 ns. The Pop-plot discussion associated with Fig. 38 indicates that it is unlikely that a detonation in NM can be produced in less than 10 ns because the run-to-detonation time is limited not by the input shock conditions which can be controlled, but by the intrinsic rates of fundamental molecular processes in the reaction zone. Since our input shock was 4 ns and the reaction zone was 11 ns, we could measure the characteristic times and rates for molecular heat production and work generation in the reaction zone. It took 6 ns for the temperature to reach the detonation temperature of 3430K. The high pressure that does the work was produced at about 8 ns.

Being able to study physical and chemical processes initiated with short-pulses, rather than in steady-state, has revolutionized our understanding of molecular dynamics by allowing us to directly observe transient behavior in real time. Being able to use short-pulse triggering with high explosives to produce reproducible detonations in a convenient and intrinsically safe tabletop format should make it possible to investigate the molecular dynamics underlying the detonation in a wide variety of energetic liquids and solids.

Concluding remarks. In this project, we developed a unique instrument, the “shock compression microscope”. It allows us to subject tiny explosive charges to high-velocity impacts to study shock initiation and shock initiation to detonation. We also developed the capability to produce arrays of tiny solid and liquid explosives, so high throughput experiments become possible. We did a lot of work characterizing the flyer plates and showing they produce high quality reproducible shocks. We studied shock initiation of reactive materials, including Al/MoO₃ composites and Al/Teflon. We studied PBX initiation and found the origin of high-temperature hot spots. Finally, we demonstrated the ability to produce true detonations on a tabletop, which means we can now study tame detonations at our leisure. The PI expressed his appreciation to the Army Research Office and the Army Research Laboratory for supporting this project.

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