INITIATION AND IGNITION OF NANO-ALUMINUM IN TEFLON

BY

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DISSEPTION

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ABSTRACT

The combustion of nano-aluminum in Teflon was studied using time-resolved laser spectroscopy. This reactive material has a stored energy of \( \sim 21 \text{ kJ cm}^{-3} \), nearly twice the energy content of the best molecular explosives. Experiments investigated the fundamental combustion processes of initiation and ignition. Initiation occurs when the first bonds break in the material. This step usually requires energy, but allows the material to undergo the widespread release of energy, known as ignition. These experiments used pulsed laser absorption to heat Al nanoparticles to \( \sim 3000 \text{ K} \) in \( \sim 100 \text{ picoseconds} \). This activated the materials, allowing reactions to proceed. Initiation was studied by tracking changes in the vibrational band structure of Teflon using transient absorption of a femtosecond mid-IR laser pulse. Ignition was studied by analyzing the UV/visible burst of emission from flash-heated materials with an ultrafast streak camera detector. After flash-heating, hot Al attacked the surrounding Teflon, consuming CFO groups in \( \sim 50 \text{ ps} \). A confined Al plasma created by the laser registered the \( \sim 100 \text{ ps} \) release of energy from the relaxation of nascent AlF, an elementary reaction product observed in the electronic ground-state within \( \sim 200 \text{ ps} \).
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For Larry and Barbara
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Chapter 1. General Introduction

1.1. Al/Teflon

This work studies the combustion of aluminum (fuel) in Teflon (oxidizer). This novel energetic material has a stored energy of ~21 kJ cm\(^{-3}\).[1] By comparison, TNT and HMX, some of the best molecular explosives, have energy densities of ~7.6 and 11.7 kJ cm\(^{-3}\), respectively.[1] Unlocking the energy potential of this material has proven elusive until very recently. This is due to Al/Teflon being a “non-ideal” energetic material, where the fuel and oxidizer components are spatially separated. This usually results in slower reactivity and incomplete combustion[1], limited by the transport of reacting species and physical barrier created by newly formed products.

Recent advancements in nanotechnology have made this system viable.[2] Aluminum nanoparticles can better mix with the polymer than larger forms. This shortens the distance between the bulk of the fuel (particle core) and the oxidizing species, which speeds up reaction rates and improves combustion efficiency.[2] A detailed chemical mechanism of how Al nanoparticles + Teflon react in the solid material is missing. Also absent is full understanding of what controls and ultimately limits energy release at the onset of reactions.

Al/Teflon also falls into a class of multifunctional materials called “reactive materials.”[3, 4] Reactive materials require a relatively large amount of energy to initiate reactions, making them insensitive to all but extreme conditions. They can then be readily processed into a structural element, possibly replacing the steel jacket of a projectile.[3] When launched at a wall or intended target, the material will give a different response based on the dynamic load (see Fig. 1.1).
At relatively slow ballistic speeds, the projectile punches the surface, causing slight deformation and no reaction (left panel of Fig. 1.1). Slightly higher speeds may result in the projectile fracturing but not reacting (center panel). Once a critical threshold has been reached, chemical reactions initiate as shown by the gas formation (right panel). In this way, an Al/Teflon jacket could either punch through or make a small explosion (from transient gases)[5], before delivering its ordinance.

1.2. Nano-Engineered Energetic Materials

Al/Teflon composites also fall within a category of materials called “nano-engineered energetic materials.”[6] Either the fuel or the oxidizer components need at least one major size dimension on the order of ~100 nm or less. These particles have high specific surface areas, which can increase reaction rates by orders of magnitude compared to micron-sized counterparts.[1, 6]
1.2.1. Enhanced Reactivity

The most widely studied aluminum nanoparticle fuels have roughly spherical, core-shell structures.[1, 2] The core metal fuel is passivated with an oxide shell that forms during synthesis.[7] The oxide grows to form a stable layer ~3-5 nm thick, which protects the metal core from further reaction. For a micron-sized or larger particle, the oxide shell accounts for a fraction of a percent of the total weight. By comparison, this layer can represent more than 50% of a nanoparticle.[8]

In micron-size particles, diffusive transport controls the reaction rate.[2] The fuel and oxidizing species must make their way across the ever-growing oxide layer to further react. This can be shown by looking at combustion times of isolated particles, initiated by a flame and burning in an oxygen atmosphere (see Fig. 1.2). At diameters greater than 10 μm, the burn time is proportional to the particle diameter and only weakly-dependent on the ambient oxygen concentration, indicating a diffusion-controlled process. These larger particles ignite (sustained reaction) only when heated by flame temperatures in excess of ~2300 K (see Fig 1.3). This temperature corresponds to the oxide layer melting.

In these gas-phase studies, particles with diameters less than 10μm showed dramatically different behavior. These particles began to ignite at lower temperatures. The burn times were dependent on both the oxygen concentration and particle temperature and did not monotonically decrease with size. This indicated that diffusion was not the rate-determining step. Reactions were controlled instead by chemical kinetics.[2] Nanoparticle ignition approached the much lower melting temperature of the aluminum cores (~933 K).
Figure 1.2. Burn Times of Aluminum Particles. Fig. 6 from Ref. [2]. Particle burning times as a function of diameter. Copyright The Combustion Institute.

Figure 1.3. Ignition Temperatures of Aluminum Particles. Fig. 7 from Ref. [2]. Particle ignition temperatures as a function of diameter. Copyright The Combustion Institute.
Much of the condensed-phase work on aluminum nanoparticle combustion has focused on their addition to thermite reactions.[1, 2, 5, 6, 8-12] Thermites release a large amount of energy by exchanging oxygen from one metal oxide to form a more stable metal oxide. Typical formulations with micron particles require ignition temperatures in excess of ~3000K and burn at speeds on the order of meters per second.[5] By comparison, the detonation velocity of a high explosive like HMX is ~9000 m s$^{-1}$.[1]

The thermite reaction of Al and molybdenum trioxide (MoO$_3$) is compared to Al/Teflon in Figure 1.4.[5] Samples consisted of loose-packed powder mixtures loaded into channels. Samples were prepared either with 50 nm or 1-3μm Al particles and varying amounts of fuel. Powder mixtures were then left open to the air or confined. Materials were ignited at one end of the channel and a high-speed camera monitored the flame front propagation (measuring the burn speed). Mixtures near the stoichiometric values for complete combustion (or slightly fuel-rich) achieved the highest burn rates. Other fuel-oxidizer ratios include material that cannot participate in the reaction thus slowing it down.

For Al/MoO$_3$ (left panel C of Fig. 1.4), nanoparticle samples burned 100 times faster than their micron counterparts. This was due to better sample mixing with smaller particles and overall shorter distances between reactants discussed above. Confining the reacting powders had little effect on the nanoparticle rates (compare right panel C of Fig. 1.4), but did enhance the micron particle reactions. By comparison, the open-air Al/Teflon reactions (left panel A) were slow compared to Al/MoO$_3$ with only modest nanoparticle enhancement. This was attributed to the thermal degradation and degassing of Teflon at much lower temperatures. Confinement resulted in Al/Teflon burn rates that were comparable to Al/MoO$_3$ (right panel A).
Figure 1.4. Comparison of Al/Teflon and Al/MoO₃. Figs. 7 and 8 from Ref. [5]. Left: Flame propagation speeds in open configurations: (A) Al/Teflon; (B) Al/MoO₃/Teflon; (C) Al/MoO₃. The diamonds represent nano-Al while the squares represent micrometer Al. Graphs presented in (B) and (C) have a logarithmic scale. Right: Flame propagation speeds in confined configurations: (A) Al/Teflon, (B) Al/MoO₃/Teflon, (C) Al/MoO₃. The diamonds represent nano-Al while the squares represent micrometer Al. Copyright The Combustion Institute.
1.2.2. Passivation Schemes

In addition to the particle size, the passivation layer plays an important role in both nanoparticle reactivity and how composite materials behave. The previous section and all of experiments performed here use aluminum nanoparticles coated with the native oxide layer. This layer forms spontaneously when the nanoparticles are exposed to air, and generally represents a portion of the fuel that cannot further react or is “deadweight”. Experiments have shown that presence of the oxide layer may actually enhance reaction rates for nanoparticles (see below).[13, 14]

Another passivation scheme that has received considerable attention is the formation of a self-assembled monolayer (SAM) on the nanoparticle surface (see Fig. 1.5).[1, 13, 15]

Figure 1.5. SAM Passivation of Aluminum. Fig 3. from Ref. [15] Schematic diagram illustrating Al surface and passivation types. Copyright American Chemical Society.

Nanoparticles created in the solution-phase become passivated when molecules added to solution (carboxylic acids for aluminum) oxidize the particle surface atoms forming chemical bonds
Passivation is complete when the SAM fully covers the particle and the material is air-stable when dried. The monolayer can be functionalized to react with the nanoparticle fuel (with some initiation energy) or to coordinate the fuel in a desired way with the oxidizing species.[1, 2] The system on the right in Figure 1.5 represents an Al nanoparticle that has been coated with a perfluorinated SAM. The particle was grown to a size (<100 nm) to form a stoichiometric equivalence between the fuel and oxidizer.[15]

### 1.2.3. Structure-Function Relationship

The study of nano-engineered energetic materials tries to link the fundamental and practical levels.[1, 2, 16] First, systems are found that have large amounts of stored energy (the currency of interest). Nanoscale reactions are then investigated on fast times in controlled environments. The goal is to obtain detailed reaction mechanisms, and then to determine what influences and ultimately optimizes the intrinsic rate of energy release.[1] This might include parameters like the method of initiation (shock, thermal, electrostatic discharge), passivation schemes (oxide, SAM, non-oxidizing metal), material density, and so.

When a good basic understanding is found, the components are integrated like building blocks into a real material (see Fig. 1.6).[16] In this figure, nanometric forms of fuel and oxidizer are held together by a binder. Their surfaces are modified, possibly with a SAM (left in Fig. 1.5), which allow them to selectively aggregate or disperse in the binder. This adjusts the effective rates of reaction. Finally, regions with different microstructures can be layered to create a macroscopic material, with function tailored to a specific task.
Figure 1.6. **Nano-engineered Energetic Materials.** Slide 5 of Ref. [16]. Integrated approach to the development of nano-engineered energetic materials.

### 1.3. Oxide Passivation Layer

In Al nanoparticles, the oxide layer accounts for a significant portion of the total mass. Alumina is thermodynamically stable and will not react further with most energetic components (exception below). If this layer is truly deadweight, it limits the energy contribution per mass of fuel added to an energetic formulation. A better understanding of the nature of this layer, and its role with nanoparticles and in mediating aluminum combustion, is needed.
1.3.1. Dynamic Processes

The Dlott group uses laser spectroscopy to initiate and study reaction dynamics in nanoenergetic materials. The strong optical absorption of Al nanoparticles is exploited by exposing materials to high intensity picosecond laser pulses. Absorbed energy causes temperatures jumps of \( \sim 10^3 \) K in less than a nanosecond (see Sects. 2.1 and 2.4). Laser energy is selectively absorbed in the metal cores of the nanoparticles (see Sect. 2.4) causing a thermal gradient to form between the metal core and its oxide shell. Previous work in the Dlott group found this could cause the nanoparticles to explode, resulting in shockwaves sent radially outward. [14, 17, 18] When the nanoparticles were embedded in a polymer like Teflon, these shocks resulted in widespread polymer breakdown (see Sect. 3.1.2).[14]

The volume of decomposed polymer was described by its diameter \( d_{rxn} \), shown in Figure 1.7.[1] “Short” 100 ps pulses were compared to “long” 25 ns pulses. In the long pulses, heating rates slow enough for hydrodynamic expansion and better equilibration between the core and shell. 60 nm Al particles with thin (2.5 nm) and thick (6 nm) oxide layers were compared to study role of oxide stability during this process. For long pulses (triangles in Fig. 1.7), the polymer (nitrocellulose) would undergo decomposition (thermal explosion) after enough energy was absorbed into the sample volume. \( d_{rxn} \) was proportional to cube root of the absorbed energy \( E_V^{1/3} \) above the threshold value. The oxide layer thickness had no effect on this process, merely acting as deadweight. With short pulses or high heating rates (circles in Fig. 1.7), polymer breakdown occurred at a much lower threshold and \( d_{rxn} \) increased linearly with absorbed energy. A thicker oxide resulted in a more powerful shock by longer confinement of hot Al, which enhanced the polymer breakdown for a given laser energy.
1.3.2. Proposed Mechanisms of Oxidation

The precise mechanism of nanoparticle oxidation is unknown, including the role of the oxide layer. At elevated temperatures but below the melting point of Al, oxygen is thought to slowly diffuse through the oxide layer.[19, 20] When temperatures rise above the melting point, Al can diffuse outward.[2, 19] This is agreement with the formation of the hollow particles in Figures 1.8c and 1.8d.[19]
The thermal expansion mismatch between the metal cores and oxide shell also contributes to depassivation.\[2, 5\] By the melting point of Al, the core will expand 6% exerting outward pressure on the shell. \[5\] This causes the brittle shell to crack and liquid Al to seep out until diffusive transport takes over the reaction. It has been debated how the heating rate influences crack formation and resulting dynamics. Some argue that heating rates greater than $10^6 \text{ K s}^{-1}$ (much slower than the previous section) can create pressures great enough to overwhelm and
shatter the oxide layer. This even has been proposed to cause violent dispersion of liquid metal outward into the material, enhancing the reaction rate.[5] Others have shown that diffusive transport controls ignition times at these high heating rates and cracking of the oxide shell is likely to be less catastrophic.[20]

Large-scale molecular dynamics simulations have also modeled nanoparticle oxidation, shown in Figure 1.9.[21]

Figure 1.9. Molecular Dynamics Simulations of Nanoparticle Oxidation. Fig. 2. of Ref. [21]. Color snapshots of the nanoparticle at different times with initial core temperature of (a) 3000, (b) 6000, and (c) 9000 K. The core aluminum is shown as white; shell aluminum, yellow; shell oxygen, red; and environmental oxygen, blue. Copyright American Institute of Physics.
This work simulated the case of an initially hot ~50 nm nanoparticle that reacts in an oxygen gas atmosphere. The initial core temperature was hot enough to overcome passivation from a 4 nm thick oxide shell. Superheated nanoparticle cores were prepared as analogues to the laser flash-heating experiments described in Section 1.3.1 and this work. At a temperature just above the boiling point of Al (Fig 1.9a), the nanoparticle expanded and primarily oxygen diffused inward. At 6000K (Fig. 1.9b), Al vapor permeated the oxide shell, dissolving it into a less stable suboxide state. This resulted in collapse to form a less understood liquid AlO material. Al vapor could break free from the shell at this temperature. At 9000K (Fig. 1.9c), the attack of Al vapor caused rapid oxide expansion and eventual explosion, resulting in significantly more Al vapor escape.

1.3.3. Interaction with Teflon

At slow heating rates, Teflon degraded the oxide shell of Al nanoparticles.[22] This occurred near 440°C (measured using differential scanning calorimetry) and was attributed to liquid Teflon reacting with Al₂O₃ to form β-AlF₃ which converted to the thermodynamically stable α-AlF₃ near 550°C. An exotherm for β-AlF₃ formation was absent or negligible with micron particles. AlF₃ went on to catalyze Teflon decomposition near 550°C, with nearly 25% sample mass loss below the melting of Al for 50 nm Al/Teflon.

1.4. Reaction Stages

In the experiments that follow, the proposed sequence of the Al/Teflon reaction are activation or depassivation → initiation → ignition → propagation or explosion → termination.[4, 17, 18] These processes may overlap in time. This work uses laser pulses to
rapidly heat the Al nanoparticles. This overcomes passivation from the oxide layer allowing the
metal fuel to react. The activation/depassivation process is endothermic because it requires
absorbed energy from the laser. The second stage occurs when the hot aluminum attacks the
Teflon oxidizer and breaks the first chemical bonds in the polymer. This initiation process is
also endothermic because energy is needed to sufficiently breakdown the oxidizer for widespread
reaction. These reactions lead to the formation of hot nascent species, which release energy back
into the material. This release of energy is termed ignition, and is associated with heat, light, and
mechanical work.[1, 2] When enough energy is released, the reactions are self-sustaining and
propagation throughout the material will occur. If reactions lead to the formation of more
volatile species (transient suboxides like AlF or AlO), explosion will occur. Finally, after
reaction energy is spent and materials condense to form final products, reactions reach
termination.

1.5. Experimental Goals

The primary goal of this work is study the initiation and ignition of Al nanoparticle
combustion in Teflon. These condensed-phase processes occur just after depassivation but
before reactions propagate or the material explodes. In order to study this system, a second goal
has been to develop the spectroscopic techniques to observe chemistry in highly energetic
materials, on fast time scales and near their original state before violent decomposition.
1.5.1. Condensed-Phase Emission

To study condensed-phase combustion, conditions must be determined where the nanoparticles are sufficiently depassivated but below or near the threshold for shock chemistry (see Fig. 1.10 and Sects. 1.3.1 and 3.1.2). To prevent loss of material from laser heating and production of transient gases in Al/Teflon chemistry, samples will be confined.

**Figure 1.10. Unconfined Al/Teflon After Flash-heating.** Fig 2. of Ref. [23]. Time series of images obtained by flash-heating an Al/Teflon\textsuperscript{AF} thin film in an unconfined geometry, using a 100 ns duration 1064 nm laser pulse. The beam diameter is 50 μm and the pulse energy is 40 μJ. The images show the Al/Teflon\textsuperscript{AF} surface at far left. The flash-heating pulses are input from right to left. The images show the explosive ablation of material from the surface at the indicated times. The hemisphere is a blast wave in the air. Reproduced from ref. [24]. Copyright Materials Research Society.
Ignition will be monitored by observing the time-dependent emission from flash-heated materials. Most of previous work studying the emission of aluminized energetic materials focused on the post-detonation, luminous fireball (Fig. 1.11).[25] This plume moves away from the solid material (Fig. 1.11a and 1.11b) leaving a wake of reacting species and products (Fig. 1.11c).

**Figure 1.11. Fireball Spectroscopy.** Figs. 3 and 7 of Ref. [25]. Digital framing camera images following a typical detonation of PBXIH-135 explosive. Image exposure times were 5 ns and the time delays (with respect to the detonator trigger) were 16 and 34 µs for images (a) and (b), respectively. (c) Three selected streak camera tracks are presented. One spectrum was recorded at a streak delay of 11 µs (dashed line) and another at 19 µs (solid line). These spectra were extracted from the image in Fig. 2. A third spectrum (dotted line) shows the light emission recorded from the perpendicular streak camera aligned 100 mm below the surface of the explosive charge at a time delay of 38 µs. Assignments of the well-known emission lines of Al and AlO are made. Copyright American Institute of Physics.
The fireball is optically opaque, and the observed emission offers little information about reactions occurring inside it.[26, 27] Emission measurements here will study confined samples with a focus on early times before appreciable expansion occurs.

1.5.2. Time Scales of Combustion Chemistry

The burn measurements in Figure 1.4 suggest that steady-state reactions in Al/Teflon proceed near \( \sim 1 \text{ km s}^{-1} \). This is equivalent to a micron per nanosecond. The reaction zone for steady-state reactions in a material is typically near \( \sim 1 \mu\text{m} \).[1] By comparison, the average distance between nanoparticles in Teflon is much smaller when the concentration approaches stoichiometric values (see Sect. 3.1.2). These experiments have then focused on samples with thicknesses near a micron (avoiding propagation) over the first \( \sim 10 \text{ ns} \) after flash-heating.

Previous work using coherent anti-stokes raman spectroscopy (CARS) found that flash-heated Al consumed nitro (-NO\(_2\)) species in nitrocellulose (NC) in nearly \( \sim 200-300 \text{ ps} \) after flash-heating (see Fig 1.12).[18] The lifetime for this process was independent of Al concentration and the flash-heating laser fluence. This suggested that this loss was due to Al + NC reactions in the immediate environment around the particles. A slower loss of material (nanosecond lifetime) was also observed and was attributed to shock chemistry from nanoparticle explosions.
Figure 1.12. CARS Results For Al + Nitrocellulose Chemistry. Fig. 11 of Ref. [18]. Nitro survival fraction $S(t)$ versus time at various laser fluences, for a sample containing 1.0% ALEX. The $S(t)$ decay occurs in two parts whose relative amplitudes depend on fluence. The time constants for the two processes, which do not depend strongly on fluence, are ~300 ps and ~2 ns. The faster process is identified with hot spot initiation (ALEX reacting with NC shell) and the slower with initiation propagation (shock reactions between ALEX particles). ALEX is a nanoparticle aggregate fuel. Copyright American Chemical Society.

1.6. References


Chapter 2. Experimental Methods

2.1. Introduction

Two complementary probes were developed to study the reaction dynamics of Al nanoparticles in Teflon. The first follows the chemical decomposition of Teflon and the second observes the radiative release of energy. In each case, the samples consist of a composite thin film of material sandwiched between two substrates. The nanoparticles in the films are flash-heated through optical absorption of a near-IR laser pulse. The heating rates here are about $10^{12}-10^{13}$ K/s. This absorbed energy overcomes the reaction barrier imposed by the oxide layer, allowing the metal fuels to attack the surrounding oxidizer. Reaction dynamics are then followed over the first 20 ns after flash-heating.

The experimental techniques were developed sequentially. This meant that the sample parameters chosen for the chemical probe were modified in the development of the emission probe. Specifically, the emission samples became thinner (~300 nm versus 1-2 μm) and contained 50 nm nanoparticles, which were more widely available than the 30 nm nanoparticles used previously. The near-IR flash-heating wavelength also changed between the two experiments. Laser energies were comparable by accounting for the absorption cross-section at each wavelength.

2.2. Sample Preparation

The following sections give an overview of how the samples were prepared. They also include what materials were used and relevant sample properties. Much of this information has been published previously. [1-3]
2.2.1. Aluminum Nanoparticles

The aluminum nanoparticles used here were commercially available. They were roughly spherical, with a representative distribution shown in Figure 2.1.

![Figure 2.1. Distribution of Nanoparticles. Scanning electron micrograph of 50 nm nanoparticles. Courtesy of Dr. Ying Fang.](image)

The nanoparticles were passivated with a native oxide layer, forming a core/shell structure. The manufacturers, Technanogy (Santa Ana, CA) and Novacentrix (formerly Nanotechnologies; Austin, TX), provided information about the mean particle sizes and oxide layer thicknesses (see Table 2.1).

<table>
<thead>
<tr>
<th>Company</th>
<th>Part. Dia. (nm)</th>
<th>Oxide Layer (nm)</th>
<th>Active Al Content (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technanogy</td>
<td>30.2</td>
<td>2</td>
<td>62.9</td>
</tr>
<tr>
<td>Novacentrix</td>
<td>50</td>
<td>2</td>
<td>76.0</td>
</tr>
</tbody>
</table>

*Table 2.1. Aluminum Nanoparticle Properties. Properties as specified by the manufacturers.*
2.2.2. Suspensions

The final samples were composites of Al nanoparticles embedded in a Teflon polymer matrix. The nanoparticles were first suspended in a solvent that could also dissolve Teflon. This was prepared by making a 4% w/w nanopowder in ethanol slurry, which was sonicated 30-60 minutes with the fluorinated surfactant, 1H,1H,2H,2H-perfluorodecyl-triethoxysilane (Alfa Aesar). Sonication broke up nanoparticle agglomerates and the siloxane surfactant chemisorbed onto the alumina layer (similar to the left panel in Fig. 1.5). The mass ratio of nanoparticles-to-surfactant in the slurry was 3:1. After sonication, it was stirred overnight. The ethanol was then evaporated in an oven at about 100°C to leave dry, caked solids. The final mass of material revealed negligible loss of surfactant.

The clumps/flakes of surfactant-coated aluminum were added to the fluorinated solvent, FC-77 (Synquest Labs, Inc.), to create a nanoparticle suspension. This suspension was mixed in a paint shaker with zirconia beads (Zircoa, Inc.) for 15-30 minutes. At this step, there is about 4-20 mg of suspended aluminum per gram of suspension. The suspension should be used within 5-10 minutes or the solids begin to settle. A few minutes of sonication/shaking prior to the next step regenerated the suspension.

2.2.3. Teflon\textsuperscript{AF}

The “Teflon” used in all of these experiments was actually Teflon\textsuperscript{AF} 1600 (Dupont), a copolymer of tetrafluoroethylene (TFE) and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (dioxole) (see Fig. 2.2).
Figure. 2.2. Teflon\textsuperscript{AF}. Base units of the Teflon\textsuperscript{AF} polymer.

This polymer was chosen because it forms an optically clear, amorphous solid. It was also soluble in fluorinated solvents, making it easily processed. Teflon\textsuperscript{AF} was purchased from Dupont as a 6\% w/w polymer suspension in a fluorinated solvent (product # 601S2-100-6).

This polymer was not a pure fluorocarbon. The TFE:dioxole ratio in Teflon\textsuperscript{AF} 1600 is 34:66, resulting in about 1 oxygen for every 7 fluorine atoms. If Al were to completely react with the Teflon\textsuperscript{AF} to form Al\textsubscript{2}O\textsubscript{3} and AlF\textsubscript{3}, the composite mixture would have a mass ratio of Teflon\textsuperscript{AF} to Al of 2.3:1, or equivalently be 30\% w/w Al.

2.2.4. Spin-coating and Substrates

The nanoparticle suspension was added to the polymer suspension to create a composite suspension. This solution was then spin-coated to create a composite thin film. A flat optical substrate was held with a vacuum onto a spinner (adapter plate fixed to the shaft of a variable-speed motor). The solution was poured evenly across the substrate and the spinner started to a pre-selected speed. Inertia would force the solution outward causing it to spread and thin. The solvent evaporated, leaving the nanoparticles trapped in an uniformly thick layer of polymer.

Film thickness was mostly controlled by solvent viscosity and spin speed. Viscosity was varied by changing the amount of suspended solids in the solvent. For experiments studying the
chemical decomposition of Teflon, a film thickness of ~1-2 μm was chosen to give absorbances >1 for the Teflon vibrational bands. These samples were made using a spin speed of 600 rpm. For experiments studying time-dependent emission, better optical transmission required thinner samples (~300 nm). These were prepared at 400 rpm using less concentrated suspensions. The low concentration suspensions had ~10-20 mg of solids per gram of suspension. A practical limitation on this concentration was that a minimal viscosity was needed to overcome the poor wettability of fluorocarbons on the substrates.

Calcium fluoride substrates were used for mid-IR experiments. These were typically 1.5” in diameter with a thickness of 2 mm, and had good transmission down to a wavelength of 10 μm. Emission experiments used two substrates, borosilicate glass and quartz. Both had 4” diameters and a thickness of ¼”. Quartz was necessary for UV measurements, having good transmission to about 220 nm.

2.3. Laser Systems

The following sections describe the laser systems used to generate ~100 picosecond pulses for flash-heating. The lasers predate this work, and only the relevant details to this project are discussed.
2.3.1. Ti:Sapphire

A diagram of the 800-nm Ti:sapphire is shown in Fig. 2.3.

![Diagram of Ti:Sapphire Laser and Fast IR Setup](image)

**Figure 2.3. Schematic of Ti:sapphire Laser and Fast IR Setup.** Fig. 3 of Ref. [3] Schematic of Ti:sapphire laser system. The samples are flash-heated by stretched 120 ps duration 800 nm near-IR pulses and probed by femtosecond IR pulses generated by an optical parametric amplifier (OPA). The dual-beam IR system uses a 32 x 2 element HgCdTe (MCT) detector array. Courtesy of Mikhail Zamkov.

A femtosecond oscillator (Kapteyn-Murnane) generates a seed pulse that is stretched to ~120 ps and sent into a chirped pulse amplifier (Quantronix Titan).[4] The amplifier consists of a regenerative amplifier and a two-pass power amplifier operating at 1 kHz. The amplified pulse passes through a beam splitter where 30% of the power serves as the 800-nm flash-heating pump pulse. The remaining 70% is compressed to ~150 fs and passed into an optical parametric amplifier (see Sect. 2.4.2.). An optical chopper wheel lowers the repetition rate of the output.
pulses to 100 pps. This lower rate is needed to be compatible with the motorized sample positioner used in these experiments.

### 2.3.2. Nd:YLF

A 1.053-μm Nd:YLF was used to generate ~120 ps flash-heating pulses (see Fig. 2.4).

![Figure 2.4. Schematic of Nd:YLF Laser](image)

**Figure 2.4. Schematic of Nd:YLF Laser.** CD=cavity-dumper; QS=Q-switcher; ML=mode-locker; SPS=single-pulse selector; HR=high reflector; OC=output coupler; photodiode.

This type of laser has been described in detail previously.[5] A cw Nd:YLF laser is Q-switched with an intracavity acousto-optic modulator (AOM) to create a ~200 ns pulse. The laser repetition rate is controlled by an external function generator to modulate the RF power applied to this Q-switching AOM. A second AOM actively mode-locks the laser, creating a 120 ps pulse within the 200 ns pulse train. The light bleeding from the high reflecting end of the cavity is directed into a photodiode used to trigger two Pockels cells. The first Pockels cell cavity-dumps the laser to generate a lone 120-ps pulse. The second, external Pockels cell removes any
pre- or post pulses to improve the contrast ratio to ~1000:1. This laser can be operated at rates up to 300 Hz, but 15 Hz was chosen for these experiments.

2.4. Laser Flash-heating

Laser flash-heating of Al nanoparticles is a nearly adiabatic, isochoric process in which the metal cores of the nanoparticles are heated to their boiling point (~3000 K) in ~100 picoseconds.[6-8] Absorption occurs via conduction electrons at the surfaces of the metallic cores. Nanoparticles, with their high surface area-to-volume ratios, are much stronger absorbers than their bulk counterparts. An interband transition for aluminum occurs in the near-IR and also contributes to its absorbance.[9]

100-ps flash-heating was slow enough that the electrons equilibrate with the lattice and that heat is thermally conducted throughout the nanoparticle.[6-8] Laser pulses created hot spots of Al (near vaporization) that burst through the oxide layer and react with the surrounding Teflon.

As the nanoparticles are flash-heated, they can volatilize in a process called “laser ablation”.[10] Behavior falls into one of two regimes depending on the duration of the laser pulse. For nanosecond ablation, the material undergoes hydrodynamic expansion. This lowers the density and creates a “laser plume,” which contains ions, unbound electrons, and neutrals, as well as atoms and clusters.[11, 12] In femtosecond ablation, the heating is isochoric with negligible expansion. The metal is partially ionized to create a high-density plasma that is more strongly absorbing than the cold metal.[13] The 100-ps pulses used here lie between these two regimes, implying that finite hydrodynamic expansion occurs during flash-heating. A laser-created plasma was also the dominant emitting species in the material.
2.5. Transient Mid-IR Absorption

The following sections describe the experimental approach to monitoring chemical changes in the material. This method uses transient absorption of a tunable, mid-IR laser pulse to study the vibrational band structure of Teflon and has been described previously.[3]

2.5.1. Pumping Conditions and Sample Confinement

The 800-nm flash-heating pulse was focused to a 250-μm region (1/e² beam diameter) at the sample plane. The beam had a Gaussian spatial distribution and a pulse energy of 0.2 mJ. This gave a peak fluence, at the center of the focused beam, of 0.8 J/cm². [6, 7]

The Al/Teflon composite film was sandwiched with a second calcium fluoride window, as shown in Fig. 2.5.

![Figure 2.5. Pump-Probe Scheme of Confined Al/Teflon. Fig 1. of Ref. [3]. Schematic diagram of IR transient absorbance flash-heating measurements on Al nanoparticle-doped Teflon films. The samples used in this work were 18 wgt% Al (30 nm, 2 nm oxide passivation) in Teflon AF polymer. Courtesy of Mikhail Zamkov.](image-url)

Figure 2.5. Pump-Probe Scheme of Confined Al/Teflon. Fig 1. of Ref. [3]. Schematic diagram of IR transient absorbance flash-heating measurements on Al nanoparticle-doped Teflon films. The samples used in this work were 18 wgt% Al (30 nm, 2 nm oxide passivation) in Teflon AF polymer. Courtesy of Mikhail Zamkov.
This was done to maintain condensed-phase conditions and retain reacting species (see Fig 1.10) in the collection window. This sandwich configuration was held in place using a standard threaded lens mount and retaining ring. Samples were rastered across the flash-heating beam with a motorized translation stage to expose a fresh region of material to every laser shot.

2.5.2. Mid-IR Probe Pulses

70% of the amplified 800-nm laser pulse was not used for flash-heating (see Sect. 2.3.1). Instead it was compressed to 150 fs and used to pump an optical parametric amplifier (Light Conversion TOPAS 800/fs DFG 1,2). This produced ~200 fs pulses of mid-IR light, with a bandwidth of ~150 cm⁻¹ and a tunable center wavelength of 2.5 – 18 μm (or 4000-600 cm⁻¹). The OPA output ranged from ~30 uJ at shorter wavelengths to ~1 uJ for the longest. These pulses were focused at the sample plane, with 150 μm representing the largest region probed.

2.5.3. Transient Absorption Scheme

The schematic of the mid-IR absorption experiments is shown in Figure 2.3. The flash-heating pump pulse was first sent down an optical delay line before being focused at the sample plane. This beam took two passes along the delay line to give a maximum path length difference of ~6 m (or variable delay of ~20 ns). The mid-IR output pulse from the OPA was split into a probe and reference beam. The probe pulse was focused at the sample plane using a gold-coated, off-axis parabolic mirror. Transmitted light was collimated with a second off-axis mirror and sent into the detector along with the reference beam.

Care was taken to spatially and temporally overlap the pump and probe pulses (see Fig. 2.5). A portion of the Al/Teflon film was removed to place a 100-μm pinhole between the
calcium fluoride windows at the sample plane. The mid-IR probe was first aligned through the pinhole by optimizing the transmitted light reaching the detector. The flash-heating pulse (partially visible) was then brought along a noncollinear path and spatially overlapped through this pinhole. A long-range 10x optical microscope was used to see this beam. This alignment procedure was then repeated with a hole blasted in the Al/Teflon (from a series of heating pulses) in place of the pinhole. When the relative pump-probe delay was changed, the spatial overlap was rechecked. Temporal overlap of the pulses was determined by placing LiNiO₃ powder at the sample plane and observing optical mixing in the nonlinear material.

2.5.4. Spectrograph and Detector

The mid-IR probe and reference pulses were analyzed with a f/8 imaging spectrograph (Chromex) and liquid nitrogen cooled HgCdTe (MCT; Infrared Associates) array detector. The spectrograph has a 3-grating turret with the following gratings: 20 l/mm blazed at 10.6 μm, 50 l/mm blazed at 9 μm, and 75 l/mm blazed at 3 μm. Probe and reference pulses were imaged onto the entrance slit of the spectrograph at different heights. This permitted two dispersed beams to fall on separate 32-channel rows of the 32 x 2 MCT element array. The IR-6416 Multi-Channel Laser Pulse Spectroscopy System (Infrared Development Corp) handled signal acquisition and integration. Typically 30 pulses were averaged per pump-probe delay.

2.6. Ultrafast Emission Spectroscopy

The following sections describe the experimental approach to observing the release of chemical energy in the material. This is done by collecting an ultraviolet/visible burst of
emission, which is then analyzed with a spectrograph and streak camera. This method has been described previously.[1, 2]

2.6.1. Pumping Conditions and Sample Confinement

The emission experiments explored a wider range of pumping conditions. Flash-heating pulses (1.053 μm, 120 ps) with energies, $E_p$, of ~20-300 μJ were focused to a spot diameter, $2r_0$, of ~180 μm. The pulse energy was controlled with a variable attenuator (waveplate/polarizer pair). The focused beam created a Gaussian spatial distribution of intensities, or fluences $J(r)$, at the sample (see Eq. 2.1).

$$J(r) = \frac{2E_p}{\pi r_0^2} \exp\left(-\frac{2r^2}{r_0^2}\right) = J_c \exp\left(-\frac{2r^2}{r_0^2}\right)$$  \hspace{1cm} (2.1)

$J_c$ corresponds to the peak fluence at the beam center. The collection optics selectively apertured emission from the beam center, making $J_c$ more useful for describing the flash-heating pulse. Peak fluences of 0.15-2.0 J cm$^{-2}$ were used in these experiments.

In order to retain reacting species and study condensed-phase phenomena, the samples were sandwiched with a second substrate (borosilicate glass). In an upgrade from previous experiments, the sandwiched samples were then loaded into the vacuum chuck shown in Fig 2.6b. A vacuum pulled from the side evacuated the region between the windows. Atmospheric pressure would then push from the outside, squeezing the windows together. This cell was then rastered across the pump beam using a motorized translation stage to expose fresh regions of material.
2.6.2. Collection Setup V.1

The first emission experiments used the experimental setup shown in Fig. 2.6a.[1]

![Diagram of experimental setup]

**Figure 2.6. Original Ultrafast Emission Setup.** Fig. 1 of Ref. [1]. Schematic of (a) laser apparatus and (b) sample cell. Key: QS/ML/CD = Q-switched, mode locked and cavity-dumped; SPS = single-pulse selector; PD = photodiode.

Samples were flash-heated on one side with emission collected on the opposite side. This required that the samples be optically thin, to ensure uniform pumping and to limit the attenuation of light transmitted through the sample. This setup was limited to the concentrations of aluminum in Teflon < 10% w/w or enough aluminum to consume 33% of the Teflon.

A broadband burst of emission was observed from the near-IR to the UV. Aluminum-coated off-axis parabolic mirrors (Newport Corp.) were chosen to maximize optical transmission...
while eliminating chromatic aberration. These mirrors were f/4 with a 6” effective focal length. This gave a long working distance and imaged 1:1 onto the slit of the f/4 spectrograph and detector. The spectral work range of this setup was ~240-700 nm.

2.6.3. Collection Setup V.2

Initial emission experiments were limited by the fact that nanoparticles are strong absorbers in the near-IR and strong scatterers in the UV. Even if care was given to ensure that samples were optically thin at the pump wavelength, a significant amount of UV emission was lost as it propagated through the material (see Fig 2.7.)[2]

![Graph showing optical properties of Al/Teflon samples.](image)

**Figure 2.7. Optical Properties of Al/Teflon Samples.** Fig. 2 of Ref. [2]. Percentage absorption at the 1.053 μm wavelength of the flash-heating laser (left axis) and percentage transmission at 280 nm near the AlF absorption (right axis), as a function of Al nanoparticle concentration.
To overcome this limitation and study samples with higher concentrations of Al (up to stoichiometric equivalence), the emission probe was upgraded (see Fig. 2.8).

**Figure 2.8. Upgraded Ultrafast Emission Setup.** Fig. 1 of Ref. [2]. Schematic of (a) laser apparatus and (b) sample cell. Key: QS/ML/CD = Q-switched, mode-locked, cavity-dumped; SPS = single-pulse selector; PD = photodiode; SHG = second-harmonic generation; THG = third-harmonic generation; vac = vacuum pump.

Emission was now collected from the surface directly pumped by the laser. This permitted detection of light down to about ~200 nm, where the optics and detector ultimately limited sensitivity.
2.6.4. MS257 Spectrograph

Emission was collected and imaged onto the 100-μm entrance slit of an Oriel MS-257 imaging spectrograph. The spectrograph was equipped with a 4-grating turret, although two gratings were primarily used for these experiments: 50 l/mm blazed at 600 nm and 110 l/mm blazed at 253.8 nm. A UV-absorbing filter was added to suppress second-order diffraction when acquiring visible emission. The spectrograph had horizontal magnification of 1.1 and a vertical magnification of 1.6.

2.6.5. Triggering and Synchronization

After passing through the single pulse selector, a small portion of the flash-heating laser pulse was sent into a photodiode with a <1 ns rise time (see Sect. 2.3.2 and Fig. 2.6). The output of this photodiode triggered the electronics of the streak camera detector. The flash-heating pulse was then delayed almost 100 ns to account for inherent electronic delay of the detector—a delay that changed with the sweep time. The laser pulse passed through optical White cell to arrive slightly after the streak camera time window. A switchable electronic delay line was added to adjust this time window and catch the delayed laser pulse. Arrival of the laser pulse (zero-of-time) was determined by adding a frequency-doubling or frequency-tripling crystal to the focused beam path. The resulting 527 nm or 351 nm light was then scattered from the sample plane onto the collection optics.

When the emission apparatus was upgraded, a portion of the laser light was used to generate a visible or UV pre-pulse at -300 ps (see Figs. 2.8 and A.2). This pre-pulse corrected for a 50-ps drift in the zero-of-time over the course of a daylong experiment. The laser pulse, with bandwidths <1 cm⁻¹, was also used to determine the spectral resolution of the instrument.
2.6.6. Picosecond Streak Camera

A streak camera (Hamamatsu C4334-01) was placed at the exit slit of the spectrograph. The basic operation of the streak camera is shown in Figure 2.9.

![Figure 2.9. Principle Operation of a Streak Camera. Adapted from Hamamatsu literature.]

Spectrally-resolved light enters the streak camera and hits the photocathode, thereby ejecting photoelectrons. Our streak camera is sensitive to a spectral range of 200-850 nm. The photocathode is held at a high voltage (30 kV) with respect to an anode, which causes the photoelectrons to undergo rapid acceleration. The anode has a 5 mm by 70 μm slit, by which the photoelectrons are ejected into the drift region of the detector. They then experience a time-dependent voltage ramp, which vertically deflects the electrons to different spatial locations on a microchannel plate (MCP). The MCP serves as an image intensifier (see Fig. A.4) before the final readout with a phosphor screen and a CCD.

The horizontal slit of the detector, along with the vertical slit and magnification of the spectrograph (see Sect. 2.6.4), imply that the streak camera looks at a 100 μm x 44 μm region at the center of the 180 μm diameter flash-heated region. The C4334 streak camera has a temporal resolution of ~15 ps on a 1-ns sweep, or about 67 resolving units per frame (1 resolving unit = 7.2 pixels). This means that 5-ns and 20-ns sweeps have a resolutions of 75 ps and 300 ps,
respectively. This resolution is limited by the detector slit and repulsion of photoelectrons in the drift region.[14]

2.7. References


Chapter 3. Chemical Initiation of Al/Teflon

3.1. Introduction

The *initiation* process of aluminum nanoparticles and Teflon was studied using time-resolved infrared spectroscopy.[1] *Initiation* occurs when the first chemical bonds break in the material. This process was followed by monitoring changes in the Teflon vibrational bands in those first instances after nanoparticle depassivation.

3.1.1. Stoichiometric Shell

In Al/Teflon, the nanostructure of the Al plays an important role. A cartoon illustrating this notion is shown in Figure 3.1. The aluminum is not dispersed as atoms intermixed throughout the polymer (Figs. 3.1a and 3.1b). Rather, it exists as a solid lump of fuel within the polymer (Fig 3.1c). In the hypothetical case of dispersed atoms, the mixture could either be fuel-lean (Fig. 3.1a) or fuel-rich (Fig. 3.1b). A fuel-lean mixture would only consume a fraction of the oxidizer through combustion. A fuel-rich mixture would consume all of the oxidizer. In the case of a nanoparticle (Fig. 3.1a), there is enough metal fuel to consume all of the polymer oxidizer in its direct vicinity, termed the “stoichiometric shell”. The Al nanoparticle + Teflon shell might be viewed as a nanometric hot spot. For the 30 nm Al particles used here, this shell has an outer diameter of about 45 nm. When more nanoparticles are added to the polymer, their reaction shells encroach upon each other and eventually overlap. These experiments study fuel-lean mixtures where there are regions of no overlap (and no corresponding reaction).

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1 This chapter is largely derived from the work published in Ref. [1]. These experiments were conducted by Dr. Mikhail Zamkov. My contributions were sample preparation and a literature review of the chemical composition of Teflon<sup>AF</sup>. This aided the analysis by treating the polymer as a binary system, its behavior could be explained with 2-component dynamics.
3.1.2. Shock Chemistry and Interparticle Spacing

In addition to combustion chemistry, there are shock-induced reactions that can play a role in the breakdown of material. Previous work in the Dlott group studied shock-induced reactions using much lower concentrations (<3% w/w) of nanoparticles (see Sect. 1.3.1).[2-4] A model representing the overlap of reaction spheres (due to shock processes) is shown in Figure 3.2.
Figure 3.2. Overlap of Reaction Shells from Shock Chemistry. Fig. 2 of Ref. [2]. (a) An Al nanoparticle with its passivating Al$_2$O$_3$ layer has diameter $d_{Al}$. The diameter of the surrounding shell containing just enough polymer to oxidize the Al is $d_{sh}$. After flash heating of the Al, an expanding spherical shock front causes chemical decomposition of the surrounding oxidizer, creating a reaction volume with diameter $d_{rxn}$. (b) When $d_{rxn} < d_{avg}$, where $d_{avg}$ is the mean distance between Al nanoparticles, the sample remains intact. (c) When $d_{rxn} > d_{avg}$, the reaction volumes coalesce and the irradiated volume undergoes laser ablation. Copyright American Institute of Physics.

Upon flash-heating, the nanoparticles undergo laser ablation and explode, generating shockwaves that dissipate radially outward depositing energy into the polymer. The decomposed regions of polymer extend well past the volume expected from Al combustion (top in Fig. 3.2).

Laser ablation and shock-induced reactions were viewed as competition for the fluorination of aluminum and substantial energy release. To make combustion chemistry more competitive, samples were made with higher concentrations of aluminum (18% w/w) and were flash-heated near or below the laser ablation threshold of the material. Materials were confined
with a second substrate to prevent loss of material (refer to Sect. 2.5.1 and Fig. 1.10). At this concentration, the average distance between particles approached the value of the stoichiometric shell discussed above. The mean interparticle spacing $d_{\text{avg}}$ can be estimated, according to Ref. [2] by the following equation,

$$d_{\text{avg}} = \left( \frac{1 + V_{\text{Al}}}{\rho_{\text{ox}} w / m_{\text{Al}}} \right)^{1/3} \approx \left( \frac{m_{\text{Al}}}{\rho_{\text{ox}} w} \right)^{1/3},$$

(1)

where $V_{\text{Al}}$ corresponds to the volume fraction of Al, $\rho_{\text{ox}}$ the density of the oxidizer, $w$ the weight fraction of Al, and $m_{\text{Al}}$ the mass of a nanoparticle. A plot of mean interparticle distance as a function of Al loading is shown in Figure 3.3.

**Figure 3.3. Average Interparticle Distance.** Interparticle distance for 30 nm nanoparticles as function of aluminum fuel loading for concentrations up to stoichiometric equivalence with Teflon (30% w/w).
18% w/w Al/Teflon corresponded to an interparticle spacing of about ~55 nm, compared to the stoichiometric shell of 45 nm.

3.2. Experimental Considerations

18% w/w Al/Teflon was flash-heated with a fluence \( J = 0.8 \text{ J cm}^{-2} \). The absorption cross-section at 800 nm for these nanoparticles is \( \sigma = 1.4 \times 10^{-12} \text{ cm}^2 \), about 55% of the 1053 nm value [5]. The volumetric energy absorbed by the nanoparticle cores is given by the equation,

\[
E_V = \frac{\rho J \sigma}{m_{\text{Al}}},
\]

where \( \rho = 2.7 \text{ g/cm}^3 \), and the mass of the Al cores \( m_{\text{Al}} = 2.5 \times 10^{-17} \text{ g} \). [2] If adiabatic heating is assumed, \( E_V = 120 \text{ kJ cm}^{-3} \). As a point of reference, the vaporization of solid Al with slow heating from room temperature requires \( E_V = 31 \text{ kJ cm}^{-3} \).[6] This weight percent corresponds to enough Al to theoretically consume half of the Teflon.

Upon flash-heating, there is a visible burst of emission from the samples and an audible popping sound. This was previously associated with a weakly ionized Al plasma.[2] At delays coincident with the flash-heating pulse and shortly thereafter, a broad, featureless increase in optical depth in the mid-IR was observed. This was attributed to plasma formation (see Sect. 4.1.1). At higher fluences, this effect was stronger and more Teflon was lost. Because the plasma effect had no clear association with Al + Teflon chemistry (see Chs. 4 and 5 for a detailed examination of the plasma), a flash-heating fluence (0.8 J cm\(^{-2}\)) was chosen to maximize Teflon consumption while minimizing effect of the plasma in the mid-IR.
3.3. IR Spectroscopy of Teflon$^{AF}$

Teflon was chosen to serve as a fluorine-based oxidizer. The Teflon$^{AF}$ polymer used here was not a pure fluorocarbon like polytetrafluoroethylene (PTFE). Rather, it was a co-polymer of tetrafluoroethylene and a fluorinated dioxole unit (see Section 2.2.3).

3.3.1. Teflon$^{AF}$ and PFTE

The vibrational spectrum of Teflon$^{AF}$ is shown in Figure 3.4.

![FTIR spectrum of Teflon$^{AF}$](image)

**Figure 3.4. FTIR of Al/Teflon$^{AF}$.** Fig. 4 of Ref. [1]. (a) IR spectra of Teflon$^{AF}$ thin film with and without an 18 % w/w load of Al nanoparticles. (b) IR spectrum of poly-(tetrafluoroethylene) (PTFE, obtained from stretched Teflon tape). (c) FTIR spectra of Al-doped Teflon$^{AF}$ films sandwiched between two IR windows, prior to flash-heating and after flash-heating. Courtesy of Mikhail Zamkov.
Fig. 3.4a shows that the nanoparticles and surfactant have a negligible effect on the IR absorbance. Pure PTFE, shown in Fig. 3.4b, has two main bands associated with the CF$_2$ symmetric and asymmetric stretches at 1155 and 1220 cm$^{-1}$, respectively. [7] The additional bands in Teflon$^{\text{AF}}$ (Fig. 3.4a) are attributed to the dioxole groups.

The grade of Teflon$^{\text{AF}}$ used here contains 66 mol% dioxole/34 mol% TFE. FTIR spectra of the pure homopolymers, along with co-polymers with different ratios of the base units are shown in Figure 3.5.[7]

![Figure 3.5. FTIR of Teflon$^{\text{AF}}$ and PTFE](image)

Fig. 2 of Ref. [7]. IR spectra for films derived from source powders of the designated mole fractions. Copyright Elsevier B.V.
In 66% dioxole copolymer, the vibrational bands at 727, 988, 1105, and 1309 cm$^{-1}$ are assigned to the dioxole groups. The bands at 1148, 1210, and 1250 cm$^{-1}$ are assigned to mixed bands of both dioxole and TFE.

### 3.3.2. Vibrational Bands of Interest

The goal in these experiments was to identify what regions of the polymer that were consumed through chemical reactions and at what rates. Three vibrational bands were studied in particular: 988, 1148, and 1250 cm$^{-1}$. The first band at 988 cm$^{-1}$ was assigned to the CF$_3$ groups of dioxole. The bands at 1148 cm$^{-1}$ and 1250 cm$^{-1}$ have contributions from both the CF$_2$ groups of TFE (1155 and 1220 cm$^{-1}$) and CFO groups of dioxole (1150 cm$^{-1}$ and 1245 cm$^{-1}$) (refer to dashed lines in Fig. 3.4). These vibrational bands fall in the amalgamation limit, where the difference between the band center frequencies is on the order of the bandwidths.[8-12] In a simple approximation, it is possible to treat the total band intensity as the summation of the vibrational amplitude from each moiety and a center frequency that shifts linearly between the two pure cases. The absolute amplitude corresponding to each moiety is unknown. The band around 1250 cm$^{-1}$ should contain a larger contribution from the CFO stretches of dioxole though.

### 3.4. Fast IR with Flash-Heating

Upon flash-heating, a roughly 200 μm diameter by 1-2 μm thick volume of Al/Teflon is initiated containing about ~50 ng of material. FTIR measurement of the exposed sample region (Fig. 3.4c) showed a noticeable decrease in vibrational band intensity across the mid-IR.
3.4.1. Transient Absorption Spectra

The femtosecond, mid-IR (hereafter IR) laser pulses have limited bandwidths. This required making two separate measurements to acquire full time-dependent Teflon spectra. The IR pulses were tuned to either the 1100-1300 cm\(^{-1}\) region (CF\(_2\) and CFO) or to ~1000 cm\(^{-1}\) (CF\(_3\)). Figure 3.6b shows time-dependent spectra and how they compare to a FTIR measurement (Fig. 3.6a). Time-resolved spectra were obtained from delays of -0.1 ns (before flash-heating) to 18 ns (after). Spectra at these delays, as well as the time just after flash-heating, are indicated Fig. 3.6b. The broadband offset due the creation of a plasma at short times has been removed.

![Image of spectra](image)

**Figure 3.6. Transient IR Spectra.** Fig. 5 of Ref. [1]. (a) FTIR spectrum of Al/Teflon\(^{AF}\) sample. The outlined regions are shown in detail below. (b) Time-resolved IR spectra at the indicated delay times. Near t = 0 the entire spectrum shows an broad underlying absorbance feature attributed to the Al plasma. As time progresses and Teflon\(^{AF}\) is consumed, the IR transitions lose absorbance. Courtesy of Mikhail Zamkov.
In addition to transient absorption spectra at these wavelengths, a range from about 3.3-9 μm (3000-1100 cm\(^{-1}\)) was surveyed for products. No peak appeared above the background. The most likely vibration to appear from Al fluorination would be the AlF stretch of AlF\(_3\) near 640 cm\(^{-1}\) (solid) or 940 cm\(^{-1}\) (gas).[13, 14] This was beyond the working range of CaF\(_2\) substrates. Also detection near 16 μm (640 cm\(^{-1}\)) would require upgrading the optical parametric amplifier to achieve substantial output.

### 3.4.2. Survival Fractions

The vibrational band heights (proportional to area if the peak shape is unchanged) were measured as a function of time delay (see Fig. 3.7).

![Figure 3.7. Method to Calculate Survival Fraction](image)

**Figure. 3.7. Method to Calculate Survival Fraction.** Band areas of transient Teflon IR spectra, measured as a change in peak height (dashed vertical lines) from a common baseline (dashed horizontal lines).
Time-dependent amplitudes were then normalized by their pre-flash-heating value to determine the survival probability of those regions of Teflon (see Figure 3.8). Phenomenologically, this data can be described by a biexponential decay and an offset. In other words, there is a portion of the Teflon that reacts (which causes the decay) and a portion that remains unreacted (long-time plateau). The portion of Teflon that reacts has fast and slow processes. This is given by the following equation, which is convolved (*) with 120 ps FWHM heating pulse $P(t)$,

$$I_i(t) = P(t) \ast \left[ A_i \exp(-k_1 t) + (1 - A_i - B_i) \exp(-k_2 t) + B_i \right],$$

(3)

where $A_i$ and $B_i$ represent the fractions contributing the fast decay and long-time plateau, respectively, and $k_1$ and $k_2$ are the respective fast and slow decay rates. Smooth curves obtained from the best fit of this equation are also shown in Figure 3.8.

![Figure 3.8. Survival Fractions. Adapted from Fig. 6 of Ref. [1]. Time-dependent survival probability obtained from three Teflon$^{AF}$ IR transitions. The smooth curves are a fit to Eq. (3) which assumes a faster and a slower exponential decay to a long-time plateau. The flash-heating pulse is 120 ps fwhm. The curves are color-coded to the corresponding regions of Teflon$^{AF}$. Original courtesy of Mikhail Zamkov.](image-url)
The best fit data is contained in Table 3.1.

<table>
<thead>
<tr>
<th>wavenumber (cm(^{-1}))</th>
<th>(A) (amplitude of faster process)</th>
<th>(B) (amplitude of longer-time plateau)</th>
<th>((k_1)^{-1}), ps</th>
<th>((k_2)^{-1}), ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>988</td>
<td>0</td>
<td>0.5</td>
<td>50 (±20)</td>
<td>0.7 (±0.05)</td>
</tr>
<tr>
<td>1148</td>
<td>0.1</td>
<td>0.6</td>
<td>50 (±20)</td>
<td>0.7 (±0.05)</td>
</tr>
<tr>
<td>1250</td>
<td>0.35</td>
<td>0.5</td>
<td>50 (±20)</td>
<td>0.7 (±0.05)</td>
</tr>
</tbody>
</table>

**Table 3.1. Best Fit Data to Survival Fraction Transients.** Parameters used to fit the the IR absorption transients in Figure 3.8 to equation 3.[1] Courtesy of Mikhail Zamkov.

The faster decay, with a 50 ps lifetime, only occurred for transitions that has some contribution from the CFO regions of the polymer. The amplitude of this decay increased with the band contribution of CFO, suggesting that the fast decaying process should be associated with this group. All groups (CF\(_3\), CF\(_2\), and CFO) experienced the slower 0.7 ns loss of intensity.

### 3.4.3. Time-dependent Frequency Oscillation

The vibrational band near 1150 cm\(^{-1}\) experienced a frequency shift, which oscillated in time. The center frequency as a function of time delay is shown in Figure 3.9.
Figure 3.9. **Frequency Oscillation with Teflon Consumption.** Fig. 7 of Ref. [1]. Frequency oscillation in the 1148 cm$^{-1}$ vibration. Starting at the 1148 cm$^{-1}$ value characteristic of Teflon$^{AF}$, the frequency shifts toward the TFE value with a 50 ps time constant and then back toward the Teflon$^{AF}$ value with a 0.7 ns time constant. The smooth curve is calculated using a model where Al nanoparticles react faster with CFO than with CF$_2$. Courtesy of Mikhail Zamkov.

After flash-heating, the center frequency quickly blueshifts from 1148 cm$^{-1}$ to 1155 cm$^{-1}$ before a slow redshift back to the pre-flash heating value. This amalgamated band contains contributions from both the CF$_2$ and CFO groups of the polymer. The dashed lines represent the center frequency of PTFE (top at 1155 cm$^{-1}$) and the 66% dioxole copolymer (bottom at 1148 cm$^{-1}$), which were obtained from Figure 3.5. We believe this time-varying shift can be explained by the time-dependent composition of the Teflon shell around the nanoparticles. It is possible that part of the shift can be attributed to the transient high temperatures and pressures. However, no frequency oscillation was detected in the other vibrations, which would be subject to the same conditions. Instead, the center frequency shifts away from the copolymer value as the CFO groups are consumed by the Al, before slower reactions consume the CF$_2$ groups as well. This is consistent with both the survival fraction data (Fig. 3.8), where the fast drop in intensity
correlates with the CFO regions of the polymer, and the FTIR measurements (Fig. 3.4c), where
the exposed sample regions have a similar Teflon\textsuperscript{AF} spectrum with half the amplitude.

3.5. Loss of Material

After flash-heating, nearly 50% of the Teflon was consumed (refer to the amplitudes of
the long-time plateau in Table 3.1). The materials were loaded with enough Al to theoretically
react (via combustion chemistry) with half of the Teflon. A straightforward view would be that
all of the Al + Teflon that could react, did—that the nanoparticles reacted radially outward
consuming on average ~8 nm of Teflon, leaving 10 nm swaths of the polymer untouched. In this
view, the transient survival fraction of 1250 cm\textsuperscript{-1} (Fig. 3.8) could be interpreted as a 70% drop in
intensity from a 50 ps Al + CFO reaction followed up with the slower 700 ps consumption of the
CF\textsubscript{2} groups. This would qualitatively describe the 1148 cm\textsuperscript{-1} behavior with the relative
amplitudes of each vibrational group changed.

Interpreting these transient losses become more difficult when one considers that shock
processes from laser ablation (see Sect. 3.1.2) may contribute to the loss of Teflon. The Al
nanoparticles in these experiments were heated with more than twice the energy needed to
vaporize the aluminum cores (see Sect. 4.2.3.). The laser fluence relatively was relatively low
compared to the previous shock studies\cite{2}, and the samples were confined better here.
However, a 1-2 \textmu m sample with 18% w/w Al absorbs over 70% of the laser energy. This creates
a thermal gradient as nanoparticles on the first sample surface experience the full laser energy,
which attenuates as the heating pulse propagates. In the experiments that followed, sharp
threshold were found for Al/Teflon ablation (see Sect. 4.2.3).\cite{15} A more appropriate thickness
for uniform heating at higher Al concentrations was determined to be ~300 nm (see Fig 2.7 and Append. B)

A competing explanation of the transient losses in Teflon would then involve reactions only happening in the first 50 % (incident surface) of the material. Almost all of the original polymer in this region would decompose. At least 70% of the CFO groups in Teflon would be consumed in a 50 ps reaction with Al. CF₂ and CF₃ would then be lost through 700 ps reactions with Al or ablation to create volatile species or losses due to imperfect confinement.

3.6. Model of Frequency Oscillation

A kinetic model was developed to describe the three cases of Figure 3.1 and to model the frequency oscillation of the 1150 cm⁻¹ band. It used the following scheme for the chemical kinetics:

\[
\begin{align*}
\frac{d[A(t)]}{dt} &= k_1[A(t)][B(t)] + k_2[A(t)][C(t)] \\
\frac{d[B(t) - B_0]}{dt} &= k_1[A(t)][B(t)] \\
\frac{d[C(t) - C_0]}{dt} &= k_2[A(t)][C(t)]
\end{align*}
\]

(4)

\(B\) and \(C\) represent the components of a binary oxidizer with the \(Al\) fuel. \(B_0\) and \(C_0\) represent the fraction of the oxidizer that does not react. \(k_1\) and \(k_2\) are the rates that fit the IR transients in Figure 3.8 and Table 3.1. The time-dependent frequency \(\nu\) of the amalgamated band would then be determined by

\[
\nu = \nu_B + \chi_C (\nu_C - \nu_B) \\
\chi_C = \frac{C(t) + C_0}{B(t) + B_0 + C(t) + C_0}
\]

(5)
The three cases of Figure 3.1 were modeled as an oxidizer with $B(t=0) = C(t=0) = 0.5$. The results of this model are shown in Figure 3.10.

**Figure 3.10.** Fig. 9 of Ref. [1]. Top panel: results from the kinetic model Eq. (4), where Al fuel can react with a two-component oxidizer consisting of a faster-reacting B and a slower-reacting C component. Lower panel: time-dependent frequency shift of an amalgamated vibration whose frequency is described by Eq. (5). Figures (a)-(c) correspond to the physical situations depicted in Figs. 3.1(a)-(c). Courtesy of Mikhail Zamkov.

For the cases of no fuel nanostructure, the fast decaying component B is consumed with negligible consumption of C. As B is consumed, the peak frequency of the amalgamated band shifts to the value of C. When enough fuel is added to consume half of the oxidizer, the final material is essentially C.
In the case of nanostructure, the fuel can only react with its immediate surroundings, so there is a portion of the oxidizer is left unreacted. Note that this could also be applied to the case on nonuniform sample pumping with material on the back surface left intact. All of B in the immediate surroundings of the heated fuel is rapidly consumed. The remaining C in this region is consumed by the fuel or lost to shock-induced ablation[2]. The frequency first shifts toward C in time after the initial loss of B before returning to the initial value. The solid curve in Figure 3.9 was generated from this model with $(\nu_B + \nu_C)/2 = 1148 \text{ cm}^{-1}$ and $\nu_C = 1162 \text{ cm}^{-1}$.

3.7. References


Chapter 4. Partial Ignition of Al/Teflon

4.1. Introduction

The ignition of aluminum nanoparticles in Teflon was studied using time-resolved emission spectroscopy.[1] Ignition occurs when the exothermic processes of combustion begin to release energy in the material. This is typically accompanied by a burst of light from a radiative portion of this energy. When Al nanoparticles were laser flash-heated with the ~100 ps laser pulse used here, a confined plasma was created in the material. This plasma was the principle source of emission in this work. What follows are experiments designed to characterize this emission and to develop an understanding of how physical changes in the material influence emission behavior. From this information, we have tried to disentangle what the ignition process of Al/Teflon from the plasma dynamics.

4.1.1. Plasma Formation

In the intense optical fields of a laser pulse, there is a finite probability for multiple photons to be simultaneously absorbed by a material.[2, 3] If fields are high enough, it is possible for a portion of that material to become ionized, creating free electrons (quasi-free for liquids and solids) in a process called multi-photon ionization. The work function of bulk aluminum is about 4.1 eV, so this process would require approximately four near-IR photons (~1.2 eV). Alternatively, with the strong linear absorption by the nanoparticles here, partial ionization could occur thermally.

---

1 This chapter is largely derived from the work published in Ref. [1]. A preliminary version of the experiment, apparatus, along with the laser, vacuum cell, translation stage, spectrograph, and the streak camera detector, was assembled by Dr. Selezion Hambir. After overhauling the collection optics and gratings, I was responsible for sample optimization and performing all experiments.
The initial free electron density need only be small. With the long picosecond/short nanosecond pulses used here, free electrons created early in the pulse will absorb laser energy through the inverse Bremsstrahlung process (rapid electron acceleration in an electric field) and collide with the surrounding atoms.[2, 4] Secondary free electrons are then created through electron impact ionization. These will further absorb laser energy to create more free electrons, resulting in an avalanche process. When the free electron density exceeds a critical value[2], a portion of the starting material will effectively be in an ionized (plasma) state that strongly absorbs and radiates energy.

4.1.2. Energetics of Aluminum Fluorination

The simplified chemical equation of the Al + Teflon reaction is

$$\text{Al} + (3/2)\text{CF}_2 \rightarrow \text{AlF}_3 + (3/2)\text{C}.$$ (1)

Without a detailed understanding of the reaction mechanisms, it is possible to think of this reaction thermodynamically as the formation of three successive Al—F bonds and the breaking of three C—F bonds. The heats of formation of each aluminum fluorination reactant and product (in the gas phase) were calculated using ab initio computational techniques.[5] The first, second, and third Al—F bond energies $B.E.$ were estimated using the heats of formation $H$ and the equation,

$$B.E.(F_{x-1}Al - F) = H(AlF_x) - H(AlF_{x-1}) - H(F); \quad x = 1,2,3.$$ (2)

The reaction enthalpies $\Delta H_{rxn}$ of these fluorination steps in the Teflon reaction were estimated using the equation

$$\Delta H_{rxn} = B.E.(F_{x-1}Al - F) - B.E.(C - F).$$ (3)
The bond energies and fluorination step enthalpies, using a value of -485 kJ mol\(^{-1}\) for the C—F bond energy\(^6\), are shown in Table 4.1.

<table>
<thead>
<tr>
<th>Product</th>
<th>B.E. (kJ mol(^{-1}))</th>
<th>(\Delta H_{rxn}) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al—F</td>
<td>-684.0</td>
<td>-199.0</td>
</tr>
<tr>
<td>FA1—F</td>
<td>-447.7</td>
<td>+37.3</td>
</tr>
<tr>
<td>F(_2)Al—F</td>
<td>-657.9</td>
<td>-172.9</td>
</tr>
</tbody>
</table>

Table 4.1. Estimated Energetics for Successive Fluorination of Aluminum.

In addition, the heat of condensation for AlF\(_3\) to form the final solid product is about -240 kJ mol\(^{-1}\).\(^7\) The overall reaction in eq. 1 was calculated separately using solid reactants and products to be about -895 kJ mol\(^{-1}\).

The absolute numbers in Table 4.1 are probably not meaningful, but they do give insight into some of the reactions involved in Al combustion. The first fluorination step is highly exothermic, possibly accounting for 25-33\% of the total energy. The second step, with the formation of a radical species, is not as favorable (and possibly endothermic). The final fluorination step and subsequent condensation of the product account for most of the energy released.

### 4.1.3. Control Samples and Experimental Conditions

To understand how the Al + Teflon chemistry influenced the Al plasma emission, control samples were developed. The first control was Al nanopowder spun evenly across a substrate and then sandwiched in the vacuum chuck (see Sect. 2.6.1). This determined the intrinsic nanoparticle emission using our laser pulses and sample confinement techniques. The second control was a composite thin film of Al nanoparticles in polybutadiene (PB), a poorly oxidizing
hydrocarbon. This nominally inert matrix helped determine the effect of loading flash-heated nanoparticles into a polymer environment with thermal losses and better inertial confinement. Reaction energy from this system was minimal.

The nanoparticles were the strong absorbing and primary emitting species, so care was taken to ensure that the three systems had the same mass of aluminum. It was determined previously (see Append. B) that the thickness of the polymer needed to be large with respect to the nanoparticle diameter to serve as a reaction matrix. Therefore, the volumes of Teflon and polybutadiene (or number density of nanoparticles) were matched (see Table 4.2). Owing to the different densities of Teflon ($\rho = 2.1 \text{ g cm}^{-3}$) and polybutadiene ($\rho = 0.9 \text{ g cm}^{-3}$), the weight percents of Al in each sample were very different.

<table>
<thead>
<tr>
<th>nominal Al weight %</th>
<th>actual Al weight % Teflon</th>
<th>actual Al weight % PB</th>
<th>number density $10^{-14}$N (cm$^{-3}$) Teflon</th>
<th>number density $10^{-14}$N (cm$^{-3}$) PB</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>2.7</td>
<td>6.1</td>
<td>4.2</td>
<td>4.3</td>
</tr>
<tr>
<td>10</td>
<td>10.0</td>
<td>20.7</td>
<td>17.0</td>
<td>17.1</td>
</tr>
</tbody>
</table>

Table 4.2. Al Sample Concentrations. Table 1 of Ref. [1]. Al nanoparticle densities in Teflon and polybutadiene samples.

Sample series were labeled with respect to Al/Teflon, and the results of 2.5% and 10% w/w Al were treated as the low and high concentrations for these emission experiments. The series contain enough Al to consume 10% and 33% of the Teflon, respectively.

Al/PB samples were made in the procedure outlined in Section 2.2, with hexanes (Sigma-Aldrich) as the solvent, octyltrimethoxysilane (Aldrich) as the surfactant, and polybutadiene ($cis$- and $trans$-, Aldrich) as the polymer. The spin-coating speed remained at 400 rpm. The absorption cross-section at 1053 nm for 50-nm Al in PB was determined to $\sim 10.4 \times 10^{-12}$ cm$^2$,
about 20% larger than the Al/Teflon value of 8.8 \( \times 10^{-12} \) cm\(^2\). Al nanopowder samples were fabricated by spinning a 2% w/w suspension of 50 nm Al in acetone in multiple layers at 1500 rpm until samples with comparable absorbance at 1053 nm were made. Both control samples required soaking the substrates in a KOH/ethanol/water bath for ~4 hours to remove residual vacuum grease.

4.2. Optical Microscopy of Exposed Samples

The samples were analyzed post mortem under an optical microscope. This aided interpretation of the emission spectroscopy by correlating possible physical changes occurring in the material at the flash-heating fluences used. Regions exposed to a single flash-heating pulse are shown in Figure 4.1. By measuring a series of increasing laser fluences, three distinct optical changes were observed in Al/Teflon: a bleach, darkening, and ablation (see discussion below).

The rationale for exposing materials to a series of laser fluences was to determine the energy required to depassivate the Al nanoparticles (allowing the material to react) and to understand how laser pumping influenced the emission. At low fluences, the absorbed laser energy is small with respect to the stored chemical energy. As the fluence increased, absorbed energy will overwhelm chemical energy and dominate the response.

4.2.1. Radial Distribution of Fluences

The focused laser beam exposes the samples to a Gaussian spatial distribution of fluences. Optical changes in Figure 4.1 occur at relatively sharp thresholds. These thresholds can be estimated by finding the smallest center of beam fluence \( J_c \) to induce change. Thresholds determined this way are prone to errors in measuring the beam radius \( r_0 \) at the sample plane.
Figure 4.1. Microscope Images of Exposed Samples. Fig. 2 of Ref. [1]. Microscope images of samples from the 10% series exposed to single 180 µm diameter flash-heating pulses at the indicated fluences. Images (a), (d) and (g) were obtained in transmission mode and the others in reflection mode. The interference fringes result from the thin polymer film on a glass substrate. In Al/Teflon, (a) bleaching, (b) darkening and (c) ablation processes are observed at successively greater fluences. The exposed spots are ~150 µm in diameter. See the scale bar in (a).

A better method measures the exposed area $S$ at a series of increasing fluences. The “local threshold” model states that a process (leading to the observed change) only occurs when the local fluence exceeds the threshold $J_{th}$.[8-10] This model is described by the equation,

$$S = \begin{cases} 0 & J_c < J_{th} \\ \frac{S_0}{2} \ln \left( \frac{J_c}{J_{th}} \right) = \frac{S_0}{2} \ln \left( \frac{2E_p}{J_{th}S_0} \right) & J_c \geq J_{th} \end{cases},$$

(4)

where $S_0 = \pi r_0^2$ (the focused beam area) and $E_p$ is the laser pulse energy. The exposed region $S$ then grows logarithmically with fluence or pulse energy after crossing the threshold value. The
area $S$ vs. $\ln(E_p)$ is a linear relationship with a slope equal to half the focused beam area and an x-axis intercept equal to $J_{th}$.

### 4.2.2. Bleaching Process

The first change observed in the materials was a decrease in sample opacity, or “bleach,” given by the lighter regions in the first row of Figure 4.1. The threshold for the bleaching process was determined from the data in Figure 4.2a. Nanoparticles were the strong absorbing species in the samples. A bleaching process indicated that the nanoparticles were heated to a temperature where irreversible damage occurred. Included in Figure 4.2a are vertical bars corresponding to the estimated values for the adiabatic isochoric melting and vaporization of the Al metal cores. We ignore heat dissipation to the surrounding polymer as we believe it to be slow compared to the 100 ps laser pulses.[11, 12] These thermodynamic phase transitions were estimated from bulk Al values[7] and should serve only as rough guidelines for the nanoparticles.

The bleaching process for all three materials occurred when Al in a hot molten but not quite vaporized state. Al powder required less laser energy than Al/Teflon, which required less than Al/PB. Thresholds are independent of Al concentration. Possible explanations for the bleach can include redistribution of molten fuel by phase explosion or liquid nanoparticles agglomerating into larger droplets with lower surface area-to-volume ratios (and correspondingly lower absorption). At $J_{th} = 0.15-0.20$ J cm$^{-2}$, the bleaching process requires approximately two-thirds of the laser fluence needed to generate and observe emission (see Sect. 6.6 for plasma emission threshold).
4.2.3. Ablation Process

At higher laser fluences, the polymer samples undergo an ablation process where material was blasted away from the exposed region, shown in the bottom row of Figure 4.1. Sample confinement was imperfect, largely due to the surface roughness of the substrate windows (see Fig. 6.1). Bare Al powder could freely expand to fill the volume left between the windows. While polymer ablation did not apply to the powder samples, there was metal vapor deposition...
observed by the white ring (high reflectivity) in Figure 4.1i. The $J_{th}$ values for ablation were determined from data in Figure 4.2b for Al powder, Al/Teflon, and Al/PB to be 0.45, 0.60, and 0.90 J cm$^{-2}$, respectively. Al/Teflon ablation required twice the fluence (or energy) needed to vaporize Al. Al/PB required over three times this amount. The ablation process demonstrated a small concentration dependence. Nanoparticles in the 2.5% samples were only twice as far apart as the 10% w/w samples (Sect. 3.1.2)—a small difference in the context of shock-induced chemistry.[12]

### 4.2.4. Darkening of Al/Teflon

Between the bleach and ablation thresholds, Al/Teflon exhibited a “darkening” process not observed in Al/PB (compare Figs. 4.1b and 4.1e). Unlike the other processes, the darkening threshold depended on the nanoparticle concentration (see Fig. 4.3.) This threshold moved from just under ablation for 1% w/w Al/Teflon (not shown) to just above the bleach at 10% w/w Al/Teflon.

Darkening behavior in Al/Teflon was previously observed by Parker et al. (see Fig. 4.4.).[13] Those experiments used larger aluminum particles (500 nm), initiated reactions by Teflon decomposition through absorption of a microsecond laser pulse, and held samples held under high pressures in a cubic zirconia cell. In samples that contained Al (circles in Fig. 4.4), there was an initial increase in visible transmission that corresponded to either an laser-aluminum particle interaction or Al consumption of Teflon. Nearly 50 μs after laser initiation, there was a sudden darkening of the Al/Teflon, which was attributed to the condensation of graphitic carbon residue from reactions.
Figure 4.3. **Darkening Threshold.** Fig. 4 of Ref. [1]. (a) Laser fluence threshold data for darkening process in 2.5% and 10% Al/Teflon. (a) Darkened area $S$ versus laser pulse energy $E_p$. (b) Darkened area $S$ versus laser energy absorbed per unit volume $E_v$. The open (2.5% samples) and solid (10% samples) vertical bars indicate the computed available chemical energy densities $E_{chem}$, assuming complete reaction between Al nanoparticles and Teflon.

Figure 4.4. **Transient Absorption.** Fig. 1 of Ref [13]. Comparison of the $\Delta A$ spectra for Teflon AF and Teflon/10% Al over 90 $\mu$s. All samples are at a pressure of 1.56 GPa and laser fluence of 21 J/cm$^2$. The absorbance was monitored at 600 nm. Copyright American Institute of Physics.
The threshold for darkening was compared to the chemical energy $E_{\text{chem}}$ of Al/Teflon in Figure 4.3b. Laser fluence was converted into the absorbed energy per unit volume $E_v$ by the equation,

$$E_v = J_c \alpha$$

(5)

where $\alpha$ is the absorption coefficient.[12, 14, 15] The darkening threshold required $E_v$ that were a fraction of $E_{\text{chem}}$. While the threshold fluence may change with concentration, the onset of darkening, measured in $E_v$, are relatively closer (as well as the 1% and 5% w/w Al/Teflon data not shown). This suggests that the darkening process is more dependent on the temperature of the composite material than just the nanoparticles. As a point of reference, PTFE decomposes at $E_v \sim 0.4 \text{ kJ cm}^{-3}$. [16] Preliminary measurements of the time-dependent darkening process in Al/Teflon are given in Appendix B.

### 4.3. Integrated Emission Spectra

Emission spectra are shown in Figure 4.5. These have been time-integrated to encompass the total emission output over a spectral range of 275-700 nm. The first column corresponds to 2.5% w/w series, and the second to the 10 % w/w series. Laser fluence and resulting emission increase down the columns. Fluences range from the threshold for emission in the first row to well above ablation in the last row.

Emission spectra are composed of two basic features. The first is a broadband (BB) continuum that extends throughout the visible to the near-UV. The second are narrow bands (NB) near 310 and 400 nm. These were assigned to the electronically-excited Al vapor.
**Figure 4.5. Emission Spectra.** Fig. 5 of Ref. [1]. Time-integrated emission spectra of the 2.5% (a-d) and 10% (e-f) sample series. From top to bottom, the laser fluences were 0.3, 0.6, 1.2 and 2.0 J cm\(^{-2}\). Note the different scale bars in each panel. The emission consists of a broadband (BB) component having a peak near 320 nm and a narrowband (NB) component having two bands near 310 nm and 400 nm, which coincide with the most intense emission lines of Al atoms. The *inset* shows the instrument spectral resolution of 3.2 nm.

Closer inspection showed that the spectral shape of the BB component changes little with either sample type, concentration, or laser fluence. The distribution was peaked in the UV around 320 nm, though this was later determined to be the result of limitations in the collection scheme (refer to Fig. 6.14 for improved UV data). BB intensity increased with concentration and increased superlinearly with the laser fluence.

The NB features were absent at 0.30 J cm\(^{-2}\), but present at fluences ≥ 0.6 J cm\(^{-2}\) for most samples. With bandwidths of ∼10-30 nm, these features were significantly broadened (see
below) with respect to the instrument resolution of the ~3-4 nm. The degree of broadening increased with both concentration and laser fluence. NB intensity was more sensitive to heating fluence than concentration, and the relative intensity of 310 to 400 nm output changed significantly with fluence. The ratio shifted to the higher energy band with increasing fluence, suggesting higher atomic temperatures.

Al powder samples generated more NB emission than either polymer system. The BB intensity of the powder was comparable to Al/PB at lower fluences and greater at higher ones. Al/PB produced the least emission of all three materials. NB emission corresponding to Al vapor was largely quenched in the polymer environment. At fluences above ablation in Al/PB, weak NB emission was observed. Al/Teflon generated the most BB emission of all systems. The difference in BB output between Al/Teflon and Al/PB was the greatest at lower fluences where the available chemical energy was competitive with the laser. NB emission from Al/Teflon was also more intense than from Al/PB

### 4.4. Emission Bursts

The time-dependence of the BB emission is shown in Figure 4.6. Emission transients at one or few representative wavelengths can describe the important trends for this species. At low fluences, an emission burst rose with the flash-heating pulse (Fig. 4.6a) and decayed within 100s of picoseconds. All wavelengths gave similar time-dependences (indicating a spectral profile that remained constant). When the laser fluence was increased, the emission burst lasted longer (Fig. 4.6b), decaying on the order of a few nanoseconds.

Al powder samples (Fig.s 4.6g and 4.6h) showed a weak contribution from the fast-decaying (picosecond) emission at low fluences. This was quickly overwhelmed by the a slow-
Figure 4.6. Transients of Emission Bursts. Fig. 13 of Ref. [1]. Time-resolved BB emission intensities on 5 ns time scale. The inset indicates the apparatus time response. (a) 2.5% Al/Teflon at $J_c = 0.6$ J cm$^{-2}$, (b) 10% Al/Teflon at $J_c = 2.0$ J cm$^{-2}$. Panels (a) and (b) show the BB emission has the same time dependence at all wavelengths away from the NB emission. Note the different scale bars in panels (c)-(h). (c) Emission at 500 nm from 2.5% Al/Teflon. (d) Emission at 500 nm from 10% Al/Teflon. (e) Emission at 500 nm from Al/PB 2.5% sample series. (f) Emission at 500 nm from Al/PB 10% sample series. (g) Emission at 350 nm from bare Al 2.5% sample series; (h) Emission at 500 nm from bare Al 10% sample series.

decaying (nanosecond) emission. The slow-decaying emission burst had a slower rise, appearing as a second peak in time, < 1 ns after flash-heating.

When Al nanoparticles were trapped in a polymer matrix like polybutadiene (Fig. 4.6e and Fig. 4.6f), the faster burst dominated the emission. The slow burst was quenched or lost through relaxation with the polymer (compare 0.90 J cm$^{-2}$ curves in bold in Fig. 4.6e and 4.6g).
Only at fluences where the polymer undergoes the ablation (Figs. 4.1c and 4.1f) was there an observed slow burst in the emission. Increasing the amount of Al slightly lowered the ablation threshold, but resulted in significantly more emission in the slow burst.

The fast-decaying burst was then associated with condensed-phase Al plasma (polymer left intact). The second, delayed and slower-decaying burst was associated with ablation (structural breakdown of the environment). Al could fill any space left in the polymer or gaps between the confinement windows (see Fig. 6.1). Plasma emission in the ablation plume most likely decayed from the slow (nanosecond) expansion away from the flash-heated region.[2, 4]

If Al was flash-heated in a reactive polymer like Teflon, the emission was about 2-3 times more intense (Figs. 4.6c and 4.6d). This was always true for the fast emission burst and true at low fluences for slow emission bursts. At even higher fluences not shown (~4-6 J cm$^{-2}$), the chemical energy becomes small with respect to the absorbed laser energy and differences between the polymer environments less significant.

4.5. Time-dependent Spectra

Time-dependent emission spectra are shown in Figures 4.7-4.10. Figures 4.7 and 4.8 show the spectral evolution of Al powder and Al/PB, respectively. Figures 4.9 and 4.10 show Al/Teflon for the two concentrations.

For Al powder, a BB emission burst peaked in the near-UV generally decayed on the order of a few nanoseconds. Its intensity increased superlinearly with laser fluence, while its spectral profile changed little. The BB spectrum also changed little in time.
Figure 4.7. **Time-resolved Spectra of Al Nanopowder.** Fig. 6 of Ref. [1]. (2.5% sample series) flash-heated at the indicated laser fluences. Note the different vertical scales on each panel. The BB component dominates at shorter delay times and higher laser fluences. The NB component is most proportionately significant at longer delays and lower laser fluences.

Figure 4.8. **Time-resolved Spectra of Al/PB.** Fig. 7 of Ref. [1]. (2.5% sample series) flash-heated at the indicated laser fluences. Note the different vertical scales on each panel. The BB component dominates at earlier delay times and above the effective ablation threshold $J_{th} = 1.2$ J cm$^{-2}$. Above $J_{th}$ the NB spectrum can appear as absorption dips against the BB emission background.
Figure 4.9. Time-resolved spectra of Al/Teflon I. Fig. 8 of Ref. [1]. (2.5% sample series) flash-heated at the indicated laser fluences. Note the different vertical scales in each panel, and that the overall emission intensity is greater than Al (Fig. 6) or Al/PB (Fig. 7). The BB component dominates at earlier delay times and above the effective ablation fluence $J_{th} = 0.9 \text{ J cm}^{-2}$.

Figure 4.10. Time-resolved spectra of Al/Teflon II. Fig. 9 of Ref. [1]. (10% sample series) flash-heated at the indicated laser fluences. Note the different vertical scales in each panel. The BB component dominates at earlier delay times and above the effective ablation fluence $J_{th} = 0.9 \text{ J cm}^{-2}$. The NB component evidences prominent absorption dips above threshold.
NB emission attributed to hot Al vapor was observed within 250 ps after flash-heating. NB features broadened with increasing laser fluence (and corresponding BB intensity). These bands narrowed in time. The lifetime the NB emission was on the order of several nanoseconds.

Emission in Al/PB (Fig. 4.8) displayed the sharp drop in intensity associated with intertially confined plasma emission. This fast BB burst had a spectral profile (delay of 0.00 ns) that changed slightly with laser fluence. Above the ablation threshold, the emission decayed more slowly and was slightly redshifted with respect to the condensed-phase burst. NB emission was observed after the condensed-phase emission decayed. This emission was less intense in Al/PB than Al powder sample with similar radiative lifetimes. NB emission in Al/PB also broadened with increasing laser fluence. At early times of the confined ablation plume, there were NB absorption dips (see Figs. 4.8d and 4.8e) as well.

For Al/Teflon (Figs. 4.9 and 4.10), condensed-phase burst was more intense with a constant spectral profile. The confined ablation emission was slightly redshifted from the short time emission. Like Al/PB, NB features emerged as the condensed-phase emission decayed. NB emission was more in Al/Teflon than in Al/PB, exhibiting the same broadening effects. The degree of broadening was more pronounced at the higher concentration (Fig. 4.10). NB absorption dips, associated with cold Al vapor, were more significant at the higher concentration as well.

4.6. Condense-phase Emission Lifetimes

The time-dependence of the fast-decaying emission burst was examined more closely in Figure 4.11. Emission transients at 500 nm were obtained using the highest resolution (~15 ps)
Figure 4.11. Emission Transients at Short Times. Fig. 14 of Ref. [1]. Time-resolved BB emission at 500 nm on 1 ns scale, of 2.5% sample series (left) and 10% sample series (right). Note the different scale bars in each panel. The laser fluence $J_c$ in each row, from top to bottom, was 0.3, 0.6, 0.9, 1.2 and 2.0 J cm$^{-2}$. The smooth curve laser in (a) indicates the apparatus time response for 1.053 μm flash-heating with a 120 ps pulse.

sweep of the streak camera. The laser response is shown in Figure 4.11a. This emission burst, attributed to a condensed-phase aluminum plasma created during the laser pulse, accounted for most of the differences between Al/Teflon and Al/PB. At every concentration and fluence (including unpublished concentrations of 1, 5 and 18% w/w) about 2-3 times more emission was generated in Teflon. This emission lifetime in Al/Teflon was also longer. The lifetime for Al/Teflon or Al/PB changes little with either concentration or laser fluence (see Fig. 4.12). The emission lifetime was determine by convolving the laser response response function (given by
Figure 4.12. Lifetimes of Condensed-phase Emission. Fig. 15 of Ref. [1]. Time-resolved BB emission from Fig. 14 on expanded time scale, fit using the convolution of an exponential decay with a Gaussian that represents the apparatus time response. The ~100 ps decay constant in Al/Teflon is not strongly dependent on laser fluence or Al concentration. The decay time constant in Al/PB is ~40 ps.

The Gaussian pulse in Fig. 4.11a) with a single exponential decay. In Al/Teflon, the lifetime was ~100 ps, more than twice as long as the 40 ps observed in Al/PB.

On these time-scales with negligible volume expansion, the plasma lifetime is generally associated with the electron-ion recombination rate. [2] For a flash-heated Al plasma in polybutadiene, the lifetime of this process was 40 ps. The further release of energy, from possible fuel + oxidizer chemistry, could provide additional pumping for the plasma state and
addition emission. If the release of energy was sufficiently slow, this would control the emission lifetime. This was the most direct evidence of the lifetime for the ignition process in Al/Teflon.

In support of this interpretation, earlier experiments found that chemical initiation occurred in the CFO regions of the Teflon with a lifetime of about 50 ps (Sect. 3.4.2). Teflon demonstrated a condensed-phase darkening process not observed in PB. Lastly, the production of AlF from Al + Teflon chemistry is highly exothermic (see discussion above and Ch. 5).

4.7. Narrowband Features

NB features associated with Al vapor were prominent in the emission spectra. NB emission was most closely associated with materials undergoing confined ablation. The following sections give more detail on NB broadening and time-dependence.

4.7.1. Broadening and Absorption

Figure 4.13 expands the spectral region around the 400 nm emission band. This band was clearly broadened with respect to the instrument resolution (3-4 nm). At some delays, the bandwidths approached nearly 30 nm, with ~10-20 nm typical. The lineshapes were Lorentzian, indicating that collisional broadening was dominant. In plasmas, Stark broadening (collisions with charged species) heavily determines the degree of line broadening.[4, 17] In these experiments, the flash-heated Al was confined, so it reasonable to believe that collisions with neutral species should also contribute to the total lineshape. NB emission initially broad would narrow in time, especially as the BB continuum decayed. At delays longer than 10 ns, NB widths would approach the instrument resolution with its Gaussian lineshape.
At the early stages of confined ablation, NB absorption corresponding to cold (electronic ground-state) Al vapor was present. The absorbance (or amount) of this species increased with both the laser fluence and concentration. For all but the highest fluence (2.0 J cm\(^{-2}\)), this species was not observed beyond the first nanosecond after flash-heating.

**Figure 4.13. Narrowband Spectral Features.** Fig. 10 of Ref. [1]. Narrowband (NB) emission peak and absorption dip from 10% Al/Teflon with \(J_c = 0.9\) J cm\(^{-2}\) (c.f. Fig. 4.10c) on an expanded wavelength scale. The apparatus spectral resolution is indicated by the spectrum of the 351 nm third-harmonic of the flash-heating laser pulses (dashed curve) shifted to 370 nm to fit in this panel.
4.7.2. Difference Spectra and Transients

To more clearly show NB dynamics, the nearly constant BB component of the emission was subtracted from the time-dependent spectra in Figures 4.9 and 4.10. The wavelength 365 nm served as a BB reference point with negligible NB contribution. The resulting difference spectra for 2.5% and 10% w/w Al/Teflon are shown in Figures 4.14 and 4.15, respectively.

![Difference Spectra of 2.5% w/w Al/Teflon](image)

**Figure 4.14. I. Difference Spectra of 2.5% w/w Al/Teflon.** Fig. 11 of Ref. [1]. Time-resolved spectra of the NB component of Al/Teflon. (2.5% sample series) flash-heated at the indicated laser fluences, obtained by subtracting the BB component away from data in Fig. 4.9. Note the different vertical scales in each panel.
**Figure 4.15. Difference Spectra of 10% w/w Al/Teflon.** Fig. 12 of Ref. [1]. Time-resolved spectra of the NB component of Al/Teflon. (10% sample series) flash-heated at the indicated laser fluences, obtained by subtracting the BB component away from data in Fig. 4.10. Note the different vertical scales in each panel. Band intensities also increased with fluence, indicating that hotter Al atoms were produced.

The broadening effect with laser fluence is clearly visible. The ratio of the 310/400 nm band intensities also increased with fluence, indicating that hotter Al atoms were produced. Emission broadening and Al absorption was more prominent at higher concentrations (compare 4.14 and 4.15).

From the difference spectra, NB transients are more distinctly shown in Figure 4.16. These dynamics were compared to the BB emission from the original dataset. No NB emission was observed at the lowest fluence (Fig 4.16a). Above this, NB emission was present and
attributed to hot Al vapor ejected from solid core material. It emerged only as the condensed-phase emission decayed, indicating that this species was created as part of that process. At higher fluences and at delays < 1 ns, an absorbing species of Al was created. A portion of the hot Al may be collisionally de-excited by the cold polymer or substrate walls.
4.8. References


Chapter 5. Observation of AlF

5.1. Introduction

The time-resolved emission probe was upgraded to enhance collection efficiency deeper in the UV (see Section 2.6.3). This allowed detection of the Al + Teflon reaction product aluminum fluoride (AlF) near 228 nm.[1]

While the collection optics, gratings, and streak camera detector were all rated for UV wavelengths, optical properties of the aluminum nanoparticle in Teflon samples limited UV transmission (see Fig. 2.7). A minimal polymer thickness of ~300 nm was needed for the 50 nm Al nanoparticles to be fully contained within the Teflon matrix (see Append. B). This served as a practical limitation on how thin the samples could be made.

At the pump wavelength in the near-IR, less than 25% of the laser energy was absorbed, which held true for Al concentrations up to stoichiometric equivalence (enough Al to theoretically consume all of the Teflon). This low absorbance would ensure that the samples were uniformly heated. A caveat here is that the nonlinear emission intensity will be sensitive to even a small flash-heating gradient.

For concentrations above 30% equivalence (the 10% w/w Al/Teflon samples from Ch. 4), there was a visible difference between the light emitted on the flash-heated surface and from the opposing side. This effect was more severe in the UV (shown at 280 nm in Fig. 2.7) where less than 25% of the light was transmitted for unreacted samples with concentrations above 30% eq.

In real Al/Teflon systems, mixtures need to be at equivalence or even fuel-rich to fully ignite[2]. All previous measurements were made on samples that were full-lean, constraining the

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1 This chapter is largely derived from the work published in Ref. [1]. With Prof. Dlott’s advice, I upgraded the pumping scheme and introduced a reference pulse for a more accurate zero-of-time measurement. I was responsible for sample optimization and performing all experiments.
material performance to partial ignition. To go beyond these concentrations and improve signal collection at those wavelengths where products could be observed, emission was collected from the first surface exposed to the flash-heating pulse. Emission could come from regions receiving the full laser fluence (which improved reproducibility) and would not be obscured by the optical properties of the material.

5.2. Emission Overview

The emission from Al/Teflon is summarized in the Figure 5.1. Upon laser flash-heating, an Al plasma was created in the material. It was accompanied by an emission burst that rose with laser and had a lifetime of 10s of picoseconds. This condensed-phase species was characterized by a broad, featureless continuum peaked in the UV. If the release of chemical energy was possible, this emission was more intense and persisted longer (see Section 4.6).

Above a threshold laser fluence, the Al/Teflon would undergo violent decomposition in a process called laser ablation. This resulted in a second emission burst, which rose within the first nanosecond after flash-heating and had a lifetime of a few nanoseconds. This confined ablation plume emission was characterized by a broad continuum (albeit slightly redshifted from the condensed-phase emission). Narrowband features attributed to Al vapor escaping the solid core material. These appeared as both emitting and absorbing species at 310 nm (3p$^1 \rightarrow 3d^1$) and 400 nm (3p$^1 \rightarrow 4s^1$).[3] The elementary reaction product aluminum fluoride AlF ($X^1\Sigma^+ \rightarrow A^1\Pi$) was observed as an absorbing feature near 228 nm.[4]
Figure 5.1. Overview of Emission Regimes. Fig. 3 of Ref. [1]. A single streak image can be analyzed to show (a) a time-series of spectra or (b) time-dependent intensities at selected wavelengths. The data shown here were the average of 1000 laser shots, using 20% eq. Al/Teflon at a flash-heating fluence of 1.2 J cm$^{-2}$. The shaded regions in part (b) indicate emission from the condensed-phase core and emission during confined ablation.

5.3. Broadband Output

In previous measurements, the spectral profile of the BB emission changed little in time. Therefore, a representative wavelength $c$ could describe the time evolution (Fig. 5.1) or integrated output (Fig. 5.2) of this species. In Figure 5.2, a 10 nm spectral region around 280 nm was integrated over the first 4 ns after flash-heating. This time window encompassed most of the plasma emission (see Fig 5.1b).
Figure 5.2. Emission Output as a Function of Aluminum Concentration. Fig 4 of Ref. [1]. Broadband (BB) emission intensity at 280 nm, integrated over the first 4 ns, from flash-heated Al/Teflon. This wavelength is away from the NB emissions and absorptions and its intensity is representative of the dominant BB component. For reference, the ablation threshold for Al/Teflon is \( \sim 0.6 \text{ J cm}^{-2} \).

The total emission output in Figure 5.2 increased superlinearly with the laser fluence. For concentrations up to 30% eq, there was a nearly linear increase in intensity with the Al concentration. Above this concentration, the total output remained constant. This was consistent with a typical observation of incomplete Al combustion in explosives and propellents. This was also consistent with the plasma being sensitive to the energy release that happened during its lifetime. If a reaction step was unfavorable, like the formation of the radical AlF\(_2\) (see Section 4.1.2), the formation and substantial energy release of AlF\(_3\) might occur later.
5.4. Effects on NB Features

Figure 5.3a gives a snapshot of the effects of concentration on the NB emission features.

![Figure 5.3](image)

**Figure 5.3. Narrowband Features and Time-dependent Broadening.** Fig. 5 of Ref. [1]. (a) Near-UV emission spectra at a delay of 1 ns, near the emission intensity maximum of the confined ablation process (c.f. Fig. 3b) at a flash-heating fluence of 1.6 J cm\(^{-2}\). The absorption and emission bands near 310 nm are attributed to Al atoms and the absorption band near 228 nm is attributed to AlF. (b) Linewidth of the 310 nm atomic Al emission line with 10% eq. Al.

These spectra were obtained at a time delay of one nanosecond after flash-heating with a laser fluence of 1.6 J cm\(^{-2}\). The effect of laser fluence on the atomic emission at 310 nm and 400 nm was described in more detail in Section 4.7.
The emission band at 310 nm broadened significantly with concentration. Above 40% eq, it was indistinguishable from the continuum, except at long time delays where the continuum had died out. At times early in the confined ablation plume, there was narrowband absorption at 309 nm attributed to cold Al atoms. This absorption was backlit by emission from the plasma continuum and hot atomic Al escaping the solid core material. The absorption was narrow with respect to the emission and greater concentration (see below). The emitting species could redshift by as much as ~4 nm corresponding to the largest bandwidths. This was most likely due to the Stark effect, which also contributed to the broadening.[5, 6]

AlF absorption near 228 nm was also backlit by the continuum emission. At concentration above 30% eq, the feature broadened significantly. It was unclear if this was broadened AlF or the production of a new absorbing species. Above 40% eq., no continuum emission from was detectable below ~240 nm for duration of the experiment. For 10% and 20% eq, there was an emitting species near 235 nm that was unassigned.

To quantify the NB features, they have been fit to Lorentzians (and Voigt profiles where appropriate; instrument resolution given by a ~4.5 FWHM Gaussian). The continuum was fit to a line segment. Due to the significant broadening with concentration, the absorption of AlF and emission of atomic Al could only be fit for concentrations below 30% eq.

In Figure 5.3b, the temporal evolution of the 310 nm emission bandwidth is shown for 10% eq. Al/Teflon (corresponding roughly to the 2.5% w/w series of Ch. 4). A fluence of 0.8 J cm\(^{-2}\) was just above the ablation threshold, and a small continuum was observed. At this fluence, hot Al vapor (initially broad) escaped the solid material filling the volume left by the imperfect confinement windows before slow expansion (narrowing in time) to the edges and then out of the probe region. The initial bandwidth increased with laser fluence. There was a substantial spike
in the bandwidth within first nanosecond after flash-heating. Higher laser fluence would result in sharper rise (approaching $< 0.5$ ns) and larger peak broadening. Higher energies above ablation would enhance the catastrophic breakdown of the material and result in more colliding species in the confined volume. The bandwidth of the emitting species may report the time dependence of high pressure and temperature conditions inside the confined ablation plume.

5.5. Absorbing Species Dynamics

While the atomic emission was experiencing the rapid broadening in Figure 5.3b, the absorbing species corresponding to ground-state Al atoms became more abundant, as shown in Figure 5.4. A portion of the hot Al atoms escaping the solid core material apparently became collisionally cooled upon interaction with polymer fragments or the quartz substrate walls. This species experienced a delayed $\sim 200$ ps rise and a sub-nanosecond lifetime for low Al concentrations. Figure 5.5 show that both the absorbance and lifetime of this species increases with Al concentrations up to equivalence.

Ground-state AlF was also observed nearly $\sim 200$ ps after flash-heating. This species experienced a two-part rise. A fast part coincided with both formation of ground-state Al and the rapid broadening of the atomic emission. The slow part of the rise matched well with decay of ground-state Al, suggesting that a portion of the AlF was formed during ablation-phase reactions. A longer ground-state Al lifetime at higher concentration samples (Fig. 5.5) may indicate stiffer competition for Teflon reactants in this environment. This could be related to the plateau of total emission output in Figure 5.2.
The AlF lifetime was \( \sim 1-2 \) ns. This was attributed to either expansion out of the collection window or the production of polyfluorinated species. The AlF lifetime was shorter than the plasma continuum backlighting it. This meant that the loss of AlF was early in the ablation plume, before the density fell below a critical value to observe a continuum.[7] This was also in qualitative agreement with the darkening process in Al/Teflon, where increased opacity remained over these time scales (Append. B) with substantial loss of material occurring later (\( > 10 \) ns).
Figure 5.5. Al Absorption at Higher Concentrations. (a) Peak absorbance of Al at 309 nm as a function of Al concentration in Teflon. Error bars were obtained from averaging the results of different laser fluences. (b) Time-dependence of Al absorbance for concentration above 40% eq. Al/Teflon for concentrations above 40% eq.

5.6. References


Chapter 6. B/Teflon

6.1. Introduction

Boron nanoparticle combustion in Teflon was studied using time-resolved emission spectroscopy.[1] This served as an analogous energetic material to nano-aluminum in Teflon. The two metal fuels are isoelectronic and have high heats of combustion. Chemical equations for the simplified systems are

\[
\text{Al}(s) + (3/2) \text{CF}_2(s) \rightarrow \text{AlF}_3(s) + (3/2) \text{C}(s) \quad (1)
\]

and

\[
\text{B}(s) + (3/2) \text{CF}_2(s) \rightarrow \text{BF}_3(g) + (3/2) \text{C}(s), \quad (2)
\]

with volumetric heats of combustion of about 20 kJ cm\(^{-3}\) and 13 kJ cm\(^{-3}\), respectively. By comparison, B/Teflon chemistry has nearly twice the heat of detonation of TNT.[2, 3]

The smaller atomic weight and lower density of boron makes it attractive as a fuel additive in rocket propellants, where light weight is paramount.[4, 5] In practical application though, the full energy potential of boron has yet to be realized.[4, 6-8] This is due to formation of HBO\(_2\) in formulations were hydrogen is present. This stable intermediate prevents further reaction to form B\(_2\)O\(_3\) and full energy release. The addition of fluorine to the combustion environment has been shown to get around this limitation.[4, 6] At the high temperatures of combustion, BFO becomes the dominant species, even in hydrogenated atmospheres. BFO can further react to form B\(_2\)O\(_3\).

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1 This chapter is largely derived from the work published in Ref. [1]. I was responsible for sample optimization and performing all experiments.
6.1.1. Energetics of Boron Fluorination

In a simplistic view that does not take into account any detailed mechanisms, the combustion of B + Teflon to form BF₃ can be treated of as three successive fluorination steps where a C—F bond is broken to form a B—F bond. This is comparable to the analysis for Al + Teflon in Section 4.1.2. The bond dissociation energies $D_0$ for the fluorination sequence[9] as well the estimated energy $\Delta H_{rxn}$ for that reaction step[10] with Teflon are shown in Table 6.1.

<table>
<thead>
<tr>
<th>Product</th>
<th>$D_0$ (kJ mol⁻¹)</th>
<th>$\Delta H_{rxn}$ (kJ mol⁻¹)</th>
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<tr>
<td>B—F</td>
<td>-707.1</td>
<td>-222.1</td>
</tr>
<tr>
<td>FB—F</td>
<td>-460.2</td>
<td>+24.8</td>
</tr>
<tr>
<td>F₂B—F</td>
<td>-753.1</td>
<td>-268.1</td>
</tr>
</tbody>
</table>

Table 6.1. Estimated energetics for successive fluorination of boron.

The formation of BF is highly exothermic, followed by the much less favorable formation of the radical BF₂. Final formation of BF₃ is also highly exothermic. This sequence is similar to the Al progression in Table 4.1, with stronger B—F bonds formed in each step.

Equations 1 and 2 take into account solid reactants and respective final products, give overall heat of combustion in Teflon to be about -895 kJ mol⁻¹ for Al and -521 kJ mol⁻¹ for B.[11] A key difference these materials is the condensation of AlF₃ to a solid for Al. B + Teflon produces BF₃, which is a gas under ambient conditions.
6.1.2. Thermodynamics of Al and B Systems

In addition to the reaction energetics, Al and B systems, which include the metal fuels, their oxide layers, and final combustion products, have thermophysical differences that may affect their reaction dynamics. The phase transitions of these components at atmospheric pressures are given in Table 6.2.

<table>
<thead>
<tr>
<th></th>
<th>mp (K)</th>
<th>bp (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>933</td>
<td>2792</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>2327</td>
<td>3270</td>
</tr>
<tr>
<td>AlF\textsubscript{3}</td>
<td>1276\textsuperscript{sp}</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2348</td>
<td>4273</td>
</tr>
<tr>
<td>B\textsubscript{2}O\textsubscript{3}</td>
<td>723</td>
<td>2133</td>
</tr>
<tr>
<td>BF\textsubscript{3}</td>
<td>146</td>
<td>173</td>
</tr>
</tbody>
</table>

mp = melting point, bp = boiling point, sp=sublimation point

Table 6.2. Phase transition temperatures of metal fuels, oxides and reaction products. Table 1 of Ref.[1]

These temperatures correspond to the bulk materials[11], which may differ from their nanoscale forms but are useful for discussion. According to Table 6.2, B melts and vaporizes at much higher temperatures than Al. B\textsubscript{2}O\textsubscript{3} will vaporize before Al\textsubscript{2}O\textsubscript{3} melts. Boron fluorination also creates permanent gases, creating the potential for more explosive work. For Al particles, the cores melt first, followed by the melting of the oxide layer, and finally the vaporization of the cores. For B particles, the oxide will melt and boil off before the metal core melts and eventually vaporizes.
6.1.3. Experimental Conditions

B/polybutadiene (PB) was studied as an unreactive control system. This was analogous to earlier work on Al (Ch. 4). B was studied here for two basic reasons. First, it was a different fuel that reacts with Teflon. And secondly, a B plasma created during the laser flash-heating dominated the emission signal and analysis could strengthen our understanding of how the plasma (Al or B) responds to both the picosecond laser pulses and available chemistry.

To compare B and Al materials, a number of criteria were matched. First, the amount of polymer in a film was unchanged, giving an approximate thickness of ~300 nm. The nanoparticles were also similar sizes, as shown in Table 6.3.

<table>
<thead>
<tr>
<th></th>
<th>Aluminum</th>
<th>Boron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Diameter (nm)</td>
<td>50</td>
<td>62</td>
</tr>
<tr>
<td>Oxide Layer Thickness (nm)</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Absorption cross-section at 1053 nm (cm²)</td>
<td>8.8 (x10⁻¹²)</td>
<td>8.1 (x10⁻¹²)</td>
</tr>
</tbody>
</table>

Table 6.3. Nanoparticle Properties. Table 2 of Ref. [1].

Due to differences in atomic weight, systems were compared based on consumption estimates of the Teflon oxidizer and not on the mass loading of the fuel. A fractional equivalence (eq) of 1.0 meant that just enough fuel was added to theoretically consume all of the Teflon. A 1.0 eq metal + Teflon$_{AF}$ mixture would have an oxidizer-to-fuel mass ratio of 2.3:1 for Al and 5.75:1 for B. Since plasma created in the nanoparticles was the dominant source of emission, B/Teflon and B/PB matched the mass of B and volume of polymer (see Sect. 4.1.3).
The core-shell nanoparticles have somewhat different absorption cross-sections and cross-sectional areas (see Table 6.3). We have chosen to compare pumping conditions by the absorbed energy density per mole of metal atoms and not the laser fluence used in previous chapters. The absorbed energy density per nanoparticle is given by,

\[ E_{\text{np}} = J_c \sigma, \]  

where \( J_c \) is the laser fluence at the beam center and \( \sigma \) is the absorption cross-section. Note that absorption cross-section for PB systems is about 20% larger than with Teflon. Using the average nanoparticle size and specified oxide layer thickness, we calculated the volume of the metal cores that absorb all of the laser energy. If we assume these cores have the density of bulk metals, we can estimate the average metal mass per nanoparticle, which allows us to determine the absorbed energy density per mole. Al nanoparticles absorbed over 4 times the laser energy of B nanoparticles on a per mole basis. For the laser fluences used here (~0.2-2.0 J cm\(^{-2}\)), the absorbed energy densities ranged from about 100-3500 kJ mol\(^{-1}\).

6.2. Emission Overview and Optical Microscopy

In the experiments on Al/Teflon, two distinct sets of emission behavior were observed depending on whether the materials were flash-heating above or below the ablation threshold. A cartoon representing this phenomenon is shown in Figure 6.1. Below ablation (Fig 6.1b), the polymer remained largely intact and the emission burst from an inertially confined Al plasma rose with the laser pulse and decayed within ~40-100 ps. The flash-heated nanoparticles could react with their immediate surroundings, which resulted in more emission that persisted longer. The additional intensity and extended duration of the emission burst was attributed to the \textit{ignition} process (energy-releasing chemistry).
Figure 6.1. Schematic of Flash-heating Process and Sample Confinement. Fig. 1 of Ref. [1].

(a) The flash-heating laser pulses are incident on the side where emission is collected. The pulses are absorbed by Al or B fuel nanoparticles but not by the unreactive polybutadiene (PB) or strongly oxidizing Teflon polymer matrix. (b) At lower fluences, reactions between the flash-heated nanoparticles and the polymer occur at roughly condensed-phase densities. (c) At higher fluences a confined ablation process occurs where the ablation plume expands into a larger volume due to imperfect confinement.

Above ablation (Fig. 6.1c), the polymer structure breaks down and hot Al fills any voids or gaps left by the confinement windows before a final expansion away from the exposed region. A second burst of emission is observed during this process, which had a slower, delayed rise over ~0.5-1.0 ns before decaying within a couple of nanoseconds. It was during this second emission regime that Al vapor and the product AlF (see Ch. 5) was observed. The predominant emission from Al powder samples followed this ablation-phase behavior (see Sect. 4.4).
This picture from Figure 6.1 emerged from a *post mortem* microscope analysis of exposed sample regions, where material changes were correlated to the emission behavior (see Sect. 4.2). Figure 6.2 gives an overview of the physical changes observed in Al/Teflon (with corresponding emission) and how B/Teflon compared.

**Figure 6.2. Comparison of Microscope Images to Emission.** Fig. 2 of Ref. [1]. Microscope images of Al/Teflon and B/Teflon samples exposed to single flash-heating pulses with a Gaussian radial profile that produce the indicated energy densities (~200-2000 kJ mol\(^{-1}\)) in the nanoparticles. Alongside each image is a representative transient showing the emission time dependence at 500 nm. The time profile of the flash-heating laser pulse is shown in (d). The top row shows a bleaching process attributed to nanoparticle depassivation. The middle row shows a sample darkening attributed to chemical reactions. The bottom row shows samples where ablation has occurred. Below ablation, emission consists of a single burst lasting 100-400 ps. B/Teflon has an additional nanosecond tail associated with liquid B emission. Above ablation a dual-burst emission is observed. The second burst peak in ~0.5-1.0 ns and persists for a few ns.
Al/Teflon (Figs 6.2a-6.2c) would undergo bleach, darkening, and ablation processes, described in Section 4.2 and below. B/Teflon (Figs. 6.2g-6.2i) demonstrated all three processes with key differences discussed below. In general, the thresholds for B required lower absorbed energy densities than Al. The picosecond emission bursts from B samples lasted nearly 3 times longer than Al (compare Fig 6.2d and 6.2j). And the B emission lifetime depended on the absorbed laser energy (compare Fig. 6.2j and Fig. 6.2k), which was not apparent for Al (see Fig. 4.12).

6.2.1. Bleaching Process

The bleaching process was associated with the reduction of nanoparticle absorption. This may be due to the redistribution of molten fuel by a phase explosion or having the metal condense to form larger droplets with comparatively lower absorbing surface areas. The data used to determine bleaching thresholds for Al and B (according to the method described in Sect. 4.2.1) are shown in Figure 6.3. For Al/Teflon, this threshold occurred near \(~200\) kJ mol\(^{-1}\), compared to 300 kJ mol\(^{-1}\) for Al/PB. B/Teflon would bleach near 100 kJ mol\(^{-1}\), with a correspondingly higher value for B/PB. The threshold to observe plasma emission was slightly higher (see Sect. 6.6). The bleaching threshold displayed no concentration dependence, indicating that it was a nanoparticle (and its immediate surroundings) specific process.

Included in Figure 6.3 are potential phase transitions (horizontal bars) in the metal nanoparticles during flash-heating. These assume that bulk temperatures (Table 6.1) and thermodynamic constants \[11\] can be applied to the nanoparticles and should only serve as rough guidelines of the temperatures involved and state of the materials. The oxide layers were assumed to reach thermal equilibrium with the metal cores, which may not be true at these high heating rates.[13]
The bleach effect in Al/Teflon and Al/PB (Fig 6.3a) was associated with flash-heating pulses that deliver enough energy to melt the Al₂O₃ shells and to melt and partially vaporize the aluminum cores (T ~ 2800 K). The bleach effect in B/Teflon and B/PB (Fig 6.3b) was associated with absorbed energy densities to vaporize the B₂O₃ shells and to melt the boron cores, near 2400K. The bleach was the first irreversible physical change observed in the materials, and may be viewed as indicative of the energy (or temperature) needed to effectively depassivate the nanoparticles due to laser flash-heating.

Figure 6.3. Bleach Threshold of Al and B. Fig. 3 of Ref. [1]. Data used to determine thresholds for the bleach process observed in Fig. 6.2a,g. The area S of the bleached spot is plotted versus the log of the absorbed energy density. The threshold energy density (lower axis) or threshold fluence (upper axis) is where the best linear fit intersects the x-axis. The shaded regions denote the state of the metallic cores and oxide shells at given energy densities, based on thermal data in Ref. [11], assuming the properties of the bulk materials. S = solid; L = liquid, V = vapor.
6.2.2. Ablation Process

At the highest laser energy densities, the materials undergo confined laser ablation, which resulted in loss of the material from exposed regions. This loss in Al/Teflon was attributed to the gaseous ablation products that escaped through gaps left by the “rough” confinement windows (see Fig. 6.1c). The data used to determine ablation thresholds for B/Teflon and Al/Teflon are shown in Figure 6.4.

Figure 6.4. Ablation Threshold of Al and B. Fig. 4 of Ref. [1]. Data used to determine thresholds for the ablation process observed in Figs. 6.2c,j at two nanoparticle fuel concentrations (eq). The area S of the ablation spot is plotted versus the log of the absorbed energy density. The threshold energy density is where the best linear fit intersects the x-axis. The shaded regions denote the state of the metallic cores at given energy densities, based on thermal data in Ref. [11], assuming the properties of the bulk materials. S = solid; L = liquid, V = vapor.

The ablation threshold of Al/Teflon was \(~1000\) kJ mol\(^{-1}\) with a slight enhancement observed at higher concentrations. For B/Teflon, the ablation threshold was \(~300-400\) kJ mol\(^{-1}\), less than half the value of Al/Teflon.

For Al/Teflon, ablation occurred at twice the threshold for emission and nearly three times this value in Al/PB. Emission always displayed the dual-burst behavior in Figure 6.2f.
Phase transitions in Figure 6.4 indicate the ablation threshold for Al/Teflon required nearly twice the energy density needed to vaporize the Al.

B/Teflon could undergo ablation without the second burst of emission (see Fig. 6.2k). This was associated with energy densities that, while sufficient to vaporize the B$_2$O$_3$ shells, were only enough to partially vaporize the liquid cores. A second emission burst, associated with the “confined ablation plume,” only appeared when the absorbed energy density was enough to fully vaporize B (see Fig 6.2l). It should be noted that microscope images were taken at practically “infinite” time (days) later. Therefore, it was possible that loss of material from B/Teflon occurred due to liquid boron chemistry beyond the lifetime of the luminous plasma.

6.2.3. Darkening Differences

Between the bleach and ablation thresholds, Al/Teflon experienced a darkening process (Fig. 6.2b) not observed in Al/PB (Fig. 4.1).[12] This process was more strongly dependent on fuel concentration (see Sect. 4.2.4). Due to its absence in Al/PB, it was associated with the onset of collective fuel + oxidizer reactions. This process was accompanied by the condensed-phase emission burst with a longer lifetime in Teflon systems. The longer lifetime was was attributed to the energy release of Al + Teflon reactions (see Sect. 4.6).

In B/Teflon, the darkening process was not as prominent. It was also associated with the loss of material at the center of the spot (Fig. 6.2h) under conditions where no second emission burst was observed (Fig. 6.2k). This loss of material was more concentration dependent than ablation process in Al/Teflon and may be due to the formation of gaseous products in the B + Teflon chemistry. A close examination of the emission transient in Figure 6.2k, did not reveal a single exponential decay, as in Figure 6.2j, but the presence of lower-amplitude, nanosecond tail.
6.3. Integrated Emission

Upon laser-flash heating, a metal plasma was created and accounted for most of observed emission. If the plasma remained inertially confined (condensed-phase), the emission decayed within 100s of picoseconds or less. Integrated visible output encompassing the condensed-phase emission is shown in Figure 6.5 for Al and B. Al data was collected with an earlier geometry (Sect. 2.6.2), where emission propagated through the material. The visible emission should still be comparable because the nanoparticles scattered less at these wavelengths and these concentrations are relatively low. In each case, the emission output increased superlinearly with the absorbed energy density. B needed less energy density than Al to generate emission, and the B emission increased at a greater rate. Part of the saturation observed in Al data was increased amounts of plasma that entered the confined ablation plume. Under those conditions, the integration limits here represent a diminishing part of the total emission output. At these concentrations of Al, about three times more emission was generated in Al/Teflon than in Al/PB. By comparison, B/Teflon generated about twice as much light as B/PB.

Time-integrated emission spectra from Al and B samples are shown in Figure 6.6 at flash-heating fluences just above the threshold for emission (Figs 6.6a and 6.6b) and just above the ablation threshold (Figs. 6.6b and 6.6d). In each case, the broadband (BB) continuum from a plasma was the dominant emission feature. Above ablation, narrowband features corresponding to atoms and molecules were observed—at 310 and 400 nm for Al vapor and 250 nm for B vapor. The BB spectral profile (peaked at 320 nm) changed little with either absorbed energy density or polymer environment. In striking contrast to Al, the spectral peak the B emission would shift by as much as 150 nm with absorbed energy density. Comparatively more UV emission was generated in B/Teflon samples than in B/PB.
The effect of changing B fuel concentration is shown in Figure 6.7, again at absorbed energy densities just above the threshold for emission and just above the ablation threshold. For concentrations up to 0.33 eq., a slightly blueshifted emission was observed in B/Teflon compared to B/PB. B vapor emission at 250 nm broadened and developed absorption features as outlined in Section 4.7 and Chapter 5.[12, 14] At 1.00 eq. B/Teflon (Figs. 6.7d and 6.7h), significantly different results were observed. At both energy densities, the emission was redshifted compared to 0.33 eq. samples, with much more visible light generated in Teflon compared to PB.
Figure 6.6 Emission Spectra of Al and B. Fig. 5 of Ref. [1]. Time-integrated emission spectra for aluminum and boron nanoparticles in Teflon or polybutadiene oxidizers with a fuel load of 0.33 eq. Note the different relative intensity scales for each panel. The top row corresponds to laser fluences slightly above the threshold for an emission burst, where primarily broadband (BB) emission is observed. The bottom row corresponds to laser fluences above the ablation threshold where both BB and narrowband (NB) features are observed. The values in each panel (kJ mol\(^{-1}\)) denote the absorbed energy density in the nanoparticles. The inset shows the instrumental spectral resolution is 3.2 nm.
Figure 6.7. Emission Spectra of B/Teflon. Fig. 6 of Ref. [1]. Time-integrated emission spectra for B/Teflon (black) and B/PB (red) at absorbed energy densities slightly above the threshold for an emission burst (203 kJ mol\(^{-1}\)) and above ablation threshold (811 kJ mol\(^{-1}\)), as a function of nanoparticle concentrations (eq). Note the different relative intensity scales in each panel. The inset shows the instrumental spectral resolution is 3.2 nm.

6.4. Emission Bursts

Both Al and B emission was characterized by either one or two broadband bursts, depending on whether the materials was flash-heating above or below the ablation threshold. The dynamics of these emission burst are characterized in the following sections.
6.4.1. Transients of Al and B

The time evolution of the BB species can be explained by looking at one or a few representative wavelengths. Figure 6.8 shows the time-dependence at 500 nm for B and Al in both polymer environments.

![Figure 6.8. Emission Transients of Al and B.](image)

**Figure 6.8. Emission Transients of Al and B.** Fig. 7 of Ref. [1]. Time-dependent emission transients at 500nm for Al and B nanoparticles in Teflon and PB polymers at a fuel load of 0.33 eq, at laser fluences producing the indicated energy densities. The time profile of the flash-heating pulse is included in (a). Note the different relative intensity scales in each panel. The emission bursts with Teflon oxidizer are always more intense than bursts with nominally unreactive PB. The top, middle and bottom rows show transients obtained close to the threshold for producing an emission burst, well above this threshold but below ablation threshold, and above ablation threshold, respectively.

The emission transients are compared for energies just above the threshold for emission (Figs. 6.8a and 6.8d), near or below the ablation threshold (Figs. 6.8b and 6.8e), and well above the
ablation threshold (Figs. 6.8c and 6.8f). In each case, more emission was generated in Teflon than in PB over the first nanosecond after flash-heating. For Al, the emission lifetime was ~100 ps in Teflon and ~40 ps in PB, and these lifetimes were independent of absorbed energy density (laser fluence used in Sect. 4.6).[12] The B emission lifetime was ~300 ps in both Teflon and PB just above the emission threshold, and the lifetime decreased substantially with energy density.

The wavelength-dependence of the BB emission bursts is shown in Fig. 6.9.

**Figure 6.9. Emission Transient Versus Wavelength.** Fig. 8 of Ref. [1]. Time-dependent emission transients for Al/Teflon and B/Teflon, as in Fig. 6.8, obtained at several wavelengths in the near-UV and visible. The wavelength transients are all normalized to the same peak intensity. In Al/Teflon, the spectral distribution of the picosecond emission burst does not change with time. The broadband component of the second nanosecond burst, observed above ablation threshold (c), also has a time-independent spectral distribution but it is redshifted from the first burst. In B/Teflon, the picosecond emission burst appears to redshift as time increases.
These transients have been normalized to their maximum intensity for comparison. Below the ablation threshold of Al/Teflon (Figs. 6.9a and 6.9b), negligible differences were observed in the emission lifetime at different wavelengths. This was equivalent to a spectral profile that remained constant in time. For Al/Teflon above ablation, the nanosecond (confined ablation) burst was found to be redshifted with respect to the picosecond (condensed-phase) burst. Its spectral profile also changed little in time.

For B/Teflon below ablation, emission transients showed a wavelength-dependence. Not only did the spectral profile blue-shift with absorbed energy density (Figs. 6.6 and 6.7), the emission would redshift over the first 500 ps (Figs. 6.9d and 6.9e). This redshift was more prominent in the higher concentration B/Teflon samples (see discussion below).

### 6.4.2. Fuel-Lean and Fuel-Rich B/Teflon

The emission spectra from 1.00 eq. B/Teflon (fuel-rich) sample had a very different spectral profile than the fuel-lean case, 0.33 eq. (compare Figs. 6.7c and 6.7g to 6.7d and 6.7h). The visible emission (500 nm) transients for both polymer systems are shown in Figure 6.10. These were compared for energy densities below ablation. By increasing the amount of energy supplied by the flash-heating laser, the energetic contribution of the stored chemical energy (Sect. 6.1.1) to the system becomes increasingly less significant. For 0.33 eq. B/Teflon, this caused peak output ratio (compared to B/PB) went from ~2.5 to 1.7 (compare Figs. 6.10a-6.10c). In other words, the emission output of Teflon and PB became similar when the laser energy supplied most of the total energy. The lifetimes for each system became noticeably shorter. For 1.00 eq. B/Teflon, with considerably more stored energy, the peak output ratio went from about ~8 to 3. The lifetime of this emission remained relatively unchanged.
6.5. Condensed-Phase Boron Emission

Below the ablation threshold, the spectral evolution of B emission was more complicated than previously observed with Al. BB emission could not be described by an unchanging spectral profile with a single exponential decay. Rather, the picosecond emission burst redshifted in time to leave a small, longer-lived tail (see Figs. 6.9d and 6.9e). The redshift and tail were both absent in the 0.03 eq. B/Teflon, only became prominent at a higher concentrations (0.33 and 1.0 eq.).
6.5.1. SVD Analysis

Singular valued decomposition (SVD) was used to analyze the condensed-phase boron emission data. This matrix technique can separate a spectroscopic signal into a few time-correlated spectral components and rank each by its overall contribution to the signal. Most of the resulting SVD spectra are meaningless, merely replicating noise features in the data. One then tries to describe the data using the smallest number of components that is reasonable. B/Teflon emission, described with two principal components, is shown in Figure 6.11.

![Figure 6.11. SVD Analysis of B/Teflon Emission.](image)

**Figure 6.11. SVD Analysis of B/Teflon Emission.** Fig. 10 of Ref. [1]. An example of singular-value decomposition (SVD) analysis of B/Teflon emission spectra. This data corresponds to 0.10 eq B/Teflon with absorbed energy density of 304 kJ mol\(^{-1}\). SVD shows that the time-dependent emission transients can be fit using just two spectral components. (a) Time-dependence at 500 nm consists of an initial picosecond emission burst and a longer nanosecond tail that first appears at about 0.25 ns. (b), (c) Spectra of the two components used to fit the data. The first, blueshifted component (red) dominates at shorter times and the second, redshifted component dominates at longer times.
One component describes the emission spectrum that dominates at shorter times and another describes the longer time profile. These components are not fixed but allowed to change with both absorbed laser energy and nanoparticle loading (see Figs. 6.12 and 6.13).

A drawback to SVD analysis is that it does not give unique solutions. In many instances, the spectral components have negative-going features, which are unphysical. In these cases, a linear combination of the significant components is needed to obtain meaningful results.

According to Figure 6.11a, the first spectral component rose with the flash-heating laser pulse and then decayed with a ~250 ps lifetime. At a delay approximately 250 ps after flash-heating, a second spectral component, redshifted from the first, appeared and persisted for a few nanoseconds. Figures 6.11b-c show how time-dependent spectra may be described by the summation of these components. At a delay of 0.25 ns, the spectrum is approximately a 3:1 ratio of the first component to the second; however by 0.75 ns, the spectrum is almost entirely composed of the second component.

General trends with concentration and absorbed laser energy for B/Teflon are shown by the spectra (Fig. 6.12) and transients (6.13) of the SVD components. The first SVD component was highly dependent on the absorbed laser energy but relatively insensitive to concentration. The lifetime of this component shortened considerably over the range of energy densities. The outlier was 1.00 eq. sample with a redshifted first component and a relatively constant lifetime (see below). The spectral profile of the second SVD component, representing the nanosecond tail, changed comparatively little with either concentration or energy density. The primary spectral changes occurred near the 250 nm emission band of B vapor. More of this second component was present in higher concentration samples (see below).
Figure 6.12. **SVD Spectral Results for B/Teflon.** Normalized spectral profiles for the 1st (red) and 2nd (blue) SVD components at energy densities (rows) and fuel loading (columns) indicated.

Figure 6.13. **SVD Transient Results for B/Teflon.** Normalized transients for the 1st (red) and 2nd (blue) SVD components at energy densities (rows) and fuel loading (columns) indicated.
6.5.2. Condensed-Phase Plasma

A useful case for understanding the first component of the boron emission is 0.03 eq. B/Teflon. The amount of nanoparticle scattering and widespread chemical reactivity were comparably low, resulting in a “clean” spectral profile shown in Figure 6.14a.

Figure 6.14. Condensed-phase Plasma Emission with Graybody Temperatures. Fig. 11 of Ref. [1]. The first SVD component from B/Teflon and Al/Teflon at a fuel nanoparticle load of 0.03 eq. and 0.10. eq, respectively. These materials are pumped to the indicated nanoparticle energy densities and fit to a graybody distribution at the indicated temperatures. The graybody distributions fit the spectral distributions well, and the relative intensities obey the Stefan-Boltzmann law where the integrated intensities are proportional to $T^4$.

As the absorbed energy density increased, the spectral peak blueshifted and more intense emission was observed. The resulting spectra fit quite well (dashed curves in Fig. 6.14) to a graybody model.[14, 15] A graybody is a blackbody where the emissivity is wavelength-independent but less than unity. Our measurements do not provide absolute spectral radiance, so
we fit all four spectra using two adjustable parameters: a temperature $T$ for each spectrum and an effective emissivity (accounting for both the detector sensitivity and sample emissivity) held constant for all four spectra. They graybody model was a good fit because it described both the spectral distribution and relative intensity of the emission. The intensities agreed with the Stefan-Boltzmann law which predicts the integrated emission intensity should be proportional to $T^4$. The graybody fits for B/Teflon were surprising because earlier results with Al/Teflon (constant spectral distributions in Ch. 4) failed to agree. Additional Al/Teflon data was collected using the same-side geometry of B/Teflon (described in Section 2.6.3) and also fit well to a graybody. The earlier failure of Al/Teflon emission to fit this model was attributed to the older experimental geometry where emission had to propagate through the material.

Temperatures obtained from the graybody fits suggest that a dense plasma was formed during flash-heating with temperatures up to ~20000K. For the laser pulses used here, an avalanche mechanism described in Section 4.1.1 accounted for the plasma formation.[16, 17] Thermodynamic calculations found that there was not sufficient energy absorbed from the laser to heat a significant portion of the metal to such high temperatures. This means that either the electronic temperature of the plasma is not in thermal equilibrium with the ions or that only a small portion of the metal participates in the plasma. This would leave a bulk of the metal atoms in either the liquid or vapor state. Narrowband emission features described of Section 4.7 have intensity ratios that suggest the Al vapor (neutral atoms) created in the plasma have temperatures of about 10000-30000 K. This supports the assertion of thermal equilibrium and the plasma representing only a small portion of the metal.
The first SVD component represents the condensed-phase plasma emission of B, comparable to the picosecond emission burst of Al in Chapter 4. The lifetimes for this component are given in Figure 6.15 for B/PB and B/Teflon.

![Figure 6.15. B/Teflon Condensed-phase Emission Lifetimes. Fig. 12 of Ref. [1]. Lifetimes of the first (picosecond) SVD component of the emission bursts for B/PB and B/Teflon. The lifetimes of the 1.00 eq samples of B/Teflon show the least dependence on the absorbed (laser) energy density. This behavior is attributed to significant ~200 picosecond time scale exothermic chemistries resulting from the reaction of hot liquid boron with Teflon.](image)

Unlike Al/PB, where an unchanging ~40 ps lifetime was observed (Fig. 4.12), the plasma lifetime of B/PB (Fig. 6.15a) was dependent on both the absorbed energy density and slightly the concentration. The plasma lifetime in Al/Teflon (~100 ps from Fig. 4.12) was always longer than Al/PB. For B concentrations of 0.03-0.33 eq., there was little difference in the observed lifetime between Teflon and PB. In sharp contrast to the other systems, the lifetime of 1.00 eq. B/Teflon was relatively insensitive to the effect of the laser, remaining near ~200 ps.
The emission lifetimes for Al and B plasmas in PB are attributed to the electron-ion recombination rates.[17] This lifetime changed for B systems with no apparent change for Al. This may simply be that B lifetimes are longer, and it is easier for our apparatus to temporally resolve these changes. Less understood are the environmental effects on the plasmas. In Al, molten oxide is also thought to be present, whereas the oxide layer of boron should be vaporized well below these energy densities. In addition, these energy densities used here were always enough to vaporize the bulk of Al. B undergoes a phase transition under these conditions from a more liquid-like to more vapor-like state. In Al/Teflon, the longer lifetime was attributed to release of chemical energy (see Sect. 4.6). If this process was sufficiently slow for B, the plasma lifetime would be unaffected. In the case of 1.00 eq. B/Teflon, the emission lifetime appeared to be governed by a process other than recombination losses.

6.5.3. Liquid Boron Emission

At flash-heating energies below ablation, a second emission component was observed in the B samples completely absent with Al. This BB species appeared nearly 250 ps after heating, just as the plasma emission burst decayed (Fig. 6.13). The emission was redshifted from plasma emission (Fig. 6.12) and decayed with a lifetime of nanoseconds. Transients and relative intensities of this species are shown in Figure 6.16. Emission intensity increased with both concentration and absorbed energy density. More intense emission was observed in Teflon than in PB.

This emission was most likely due to hot liquid boron. At these energy densities, boron is heated to a liquid state with temperatures in excess of 4000K (see Fig. 6.4). Aluminum, by
comparison, vaporizes near 2800K (Table 6.2), which was close to the threshold for plasma emission (see below). In this respect, we were unable to observe the emission of hot liquid Al.

**Figure 6.16. Liquid Boron Emission.** Fig. 13 of Ref. [1]. The time dependence of the second (nanosecond lifetime) SVD component from flash-heated B/Teflon and B/PB as a function of nanoparticle fuel load and absorbed energy density. This emission is attributed to hot liquid boron present after the decay of the picosecond plasma emission. The light output with Teflon is always greater than with PB and this emission increases with B concentration.

### 6.6. Nanoparticle Depassivation

Depassivation refers to the initial step that causes a core-shell nanoparticle to become reactive with the surrounding oxidizer.[18] At slow heating rates in an oxygen atmosphere, the first exotherm occurred near 600°C for Al[19] and 530°C for B[20]. These temperatures are
associated with liquid Al seeping through the oxide shell or the melting of boron oxide and oxidation of the solid B core, respectively.

In the context of the rapid heating rates used in these experiments, depassivation refers to a process where the nanoparticles can readily interact with their surroundings and influence dynamics measured on fast time scales. Depassivation was then associated with the bleaching process (Sect. 6.2.1) at energy densities of ~200-300 kJ mol\(^{-1}\) for Al and ~100-150 kJ mol\(^{-1}\) for B. Loss of absorbance implied that metallic fuel has been released from its oxide shell after flash-heating. These energy densities coincided with the melting of the oxide layer and partial vaporization of the Al metal core. For B, this threshold was associated with a vaporized oxide shell and molten core. It should be noted that theories of Al nanoparticle combustion with oxygen and fluorine, as well as flash-heated nanoparticle simulations, invoke Al vapor escape through the oxygen as an initial depassivation mechanism (see Sect. 1.3).[21-24] B depassivation appeared to be qualitatively different than Al.

The presence of the oxide layer may affect the observed emission as well. Over the course of this work, most of the emission was attributed to a dense metal plasma created in high optical fields of the picosecond laser pulse.[16] For Al/Teflon, the threshold for emission was just above the bleaching threshold. The absorbed energy density versus plasma temperatures (obtained from Fig. 6.14) are plotted in Figure 6.17. The linear response of plasma temperature to the laser energy is due to the avalanche ionization process, where the inverse Bremsstrahlung cross-section at the laser wavelength determines the absorbance. [16, 17] The y-intercept corresponds to the threshold energy density that must be reached by the metals to create a plasma. According to the linear fit, the plasma thresholds are 416 kJ mol\(^{-1}\) and 72 kJ mol\(^{-1}\) for Al and B, respectively. As points of reference, vaporization of Al metal cores was estimated to
require \( \sim 416 \text{ kJ mol}^{-1} \). The vaporization of boron oxide layer to leave bare solid boron at 2133 K was estimated to be \( \sim 71 \text{ kJ mol}^{-1} \).[11, 25]

**Figure 6.17. Emission Threshold Determination.** Plasma temperature as a function of the nanoparticles absorbed energy density. Temperatures obtained from graybody fits to the data in Fig. 6.14.

These values were estimated from bulk constants using the average nanoparticles properties described in Table 6.3. The presence or lack of an oxide layer seemed to strongly affect the threshold energy to generate a plasma and the total emissivity as well (see Fig. 6.5).

### 6.7. Evidence of Boron Chemistry

The most favorable conditions for the detection of fuel + oxidizer chemistries are when the material is fuel-rich (1.0 eq.) and the energy supplied by the laser is minimal. The best example of this idea is in Figure 6.10 where the emission transients of 0.33 and 1.00 eq. B samples are compared. For these experiments, PB served as an unreactive control, offering
minimal energy release. Its output was compared to the strongly oxidizing Teflon. The largest difference between the polymer systems was observed in Figure 6.10d, where the ratio of the peak emission output was ~8. At lower concentration and increased laser energy (Fig. 6.10c), the ratio between the polymers was under 2. The lifetime of the increased emission in 1.00 B/Teflon was ~200 ps, which was spectrally redshifted (Fig. 6.7) and the least sensitive of all B systems to the laser energy (Fig. 6.15).

At lower concentrations, the lifetimes of B/Teflon and B/PB emission were similar and highly dependent on the laser. This ran completely opposite of Al/Teflon and Al/PB results, where a longer lifetime was observed in Teflon and both lifetimes were insensitive to the laser energy and the concentration (Fig. 4.12). The difference may be due to the state of the nanoparticles after flash-heating. Al is thought to be largely vaporized with better dispersion into the surrounding Teflon. B, however, is predominantly a liquid at these energy densities, which may be limited by a more collective breakdown of the Teflon to react quickly. In this light, the plasma lifetime in the 1.0 eq. B/Teflon was associated with the ~200 ps release of energy from liquid B + Teflon chemistry. Experimental observation of boron fluoride BF was attempted to help support this conclusion. Unfortunately, the lowest electronic transition of BF occurred near 206 nm[26], at the edge of our detection limits and not fully resolvable without experimental upgrades.

6.8. References


Chapter 7. Conclusions

7.1. Al/Teflon

Two spectroscopic probes were developed to study the chemical reaction dynamics of Al + Teflon in the condensed-phase environment. In these experiments, Al nanoparticles were laser flash-heated to temperatures in excess of the boiling point of Al (~2800 K). Hot Al atoms would then attack the surrounding polymer. A femtosecond mid-IR probe pulse found a sharp decrease in vibrational band absorption in the CFO regions of Teflon. This chemical initiation process had a lifetime of ~50 ps.

As the nanoparticles were rapidly heated, a dense metal plasma was also created. This species represented a small fraction of the total Al. However, it had temperatures in excess of ~10000K and corresponding graybody emission that accounted for most of the visible and UV emission from the material. Emission was recorded with a streak camera detector with a temporal resolution of ~15 ps. The plasma lifetime was longer in a reactive environment like Teflon. A lifetime of ~100 ps was attributed to the release of energy from the condensed-phase ignition process.

To this end, nascent AlF product was observed nearly ~200 ps after flash-heating. It was found in the ground electronic state as an absorption feature in a confined ablation plume. The formation of this strong chemical bond could release nearly ~7.1 eV of energy. Al + Teflon chemistry was observed in conjunction with a confined ablation process that occurred within the first nanosecond.

To help interpretation of the Al/Teflon results, B/Teflon was also studied. The thermophysical properties of Al and B and differences between their passivation layers all
affected the observed emission. Emission from hot liquid B (~4300 K) was found along with
~200 ps release of energy from B + Teflon chemistry. The formation of permanent gases
enhanced the loss of material in B reactions.

7.2. Experimental Technique

Two spectroscopic probes, mid-IR transient absorption spectroscopy and ultrafast
emission spectroscopy, successfully investigated Al/Teflon combustion chemistry on
fundamental time and length scales. This work linked the condensed-phase processes of
*initiation* and *ignition* and determined the formation time for the first reaction products.

An intrinsic sample thickness of ~300 nm balanced the optical and chemical properties of
the materials containing 50 nm Al. This thickness allowed both uniform heating of the strongly
absorbing nanoparticles and maximum light output from the flash-heated materials. In addition,
this thickness allowed the nanoparticles to be flash-heated *within* the polymer environment.

A metal plasma formed during flash-heating accounted for most of the emission. This
was an unavoidable side effect of the picosecond laser pulses and energies used here. This
plasma emission, found in both reactive and inert environments, complicated the interpretation of
the *ignition* process.

In addition to the plasma formation, the flash-heated nanoparticles would undergo laser
ablation. Shockwaves created from confined ablation could breakdown the polymer. This
complicated interpretation of the *initiation* results. Ideally, sample thickness and ablation
threshold parameters would be determined from the emission experiments before the IR
experiments. The emission detector collects all of the time information in a single shot, whereas
the IR experiments require labor-intensive acquisition of each time-dependent spectrum.
7.3. Proposed Future Work

This work found sharp thresholds for physical changes occurring in the materials. Focusing the laser beam with a simple lens creates a Gaussian spatial distribution of intensities at the sample plane. Probed regions were small to selectively study the center of exposed sample regions. These experiments could be more selective by exposing samples to a “flat-top” constant intensity beam profile below the thresholds for plasma formation and ablation.

Transient mid-IR experiments should be repeated on the 50 nm Al/Teflon samples at multiple concentrations. These samples should be near the 300 nm thickness to improve sensitivity to changes in band intensity. However, thinner samples will have lower IR absorbances, so there may be a trade-off. Sub-nanosecond times should be studied in more detail with care to minimize and carefully characterize the degree of plasma offset. The optical parametric amplifier may have the difference-frequency generation crystal upgraded to improve output near the AlF stretch near 640 cm\(^{-1}\) (solid) of 940 cm\(^{-1}\) (gas).[1, 2] Work on B/Teflon could track the formation of BF\(_3\) via the asymmetric stretch near 1505 cm\(^{-1}\).[3]

Emission experiments should study the absorbed energies between the bleaching threshold and plasma formation (emission threshold for this work). By increasing the Al concentration to fuel-rich formulations, a more complete (and traditional) ignition process may be found. Sampleses thickness may be lengthened if a critical volumetric energy or reaction zone length is required.

100-ps flash-heating pulse may also be stretched to nanoseconds to limit or control the plasma formation. Flash-heating could still activate the nanoparticles and lead to thermal emission. One problem associated with a longer pulse would be a stronger laser ablation process.
Larger nanoparticles should be studied to determine the role of diffusion on this time scale. These particles will require different sample thicknesses and laser energies. Individual particles possess stronger ablation potential but less spatial overlap between reaction spheres, which could change both their ablation threshold and transient IR results.

Finally, the role of passivation should be studied. SAM-passivated nanoparticles should be studied under comparable conditions to these nanoparticles. If dynamic transport across this layer ultimately controls reaction rates, these experiments might resolve this effect.

7.4. References


Appendix A. Corrections to a Streak Image

A.1. Background Subtraction

The Hamamatsu C4334-01 streakscope uses an 8-bit analog CCD camera to capture streak images. When no light enters the detector, there is a dark current of about 15-19 intensity units. Because dark current is a type of shot noise, the value at a given pixel fluctuates from one frame to another. Signal averaging reduces the effect of these fluctuations. There is a spatial pattern of relative dark currents that remains largely fixed (see Fig. A.1).

![Figure A.1. Dark Current Background. Integration of dark current signal from 100 frames, shown in (a). Average intensity across (b) and down (c) the CCD.](image)

Interpreting streak camera results require an accurate comparison of light collected at different places on the CCD. Therefore, it is necessary to subtract the total dark current spatial
pattern (Fig. A.1.) from a streak image. A background image is recorded with the spectrograph shutter closed.

In addition to the spatial pattern, the total dark current signal can drift by ±5% over a few hours. This is attributed to fluctuations in the temperature of the room and/or equipment. Taking multiple background images is cumbersome and inaccurate. By leaving enough negative time in an acquisition (no light hitting the top 1/4-1/5 of a streak image), the background image (acquired separately) can be scaled and correctly subtracted (see Fig. A.2).

**Figure A.2. Streak Images Before and After the Background Subtraction.** The images can be misleading because of the arbitrary assignment of the grayscale (lookup table). A trace of the intensities show that the actual signal is smaller than the integrated dark current at some pixels.
A.2. Tilt, MCP Gain, and Substrate Transmission

The streak camera operates in two basic modes: focus mode and operate mode. Focus mode involves no deflection of photoelectrons emitted into the streak tube. In operate mode, a voltage ramp is applied to deflection plates (see Fig. 2.9), and photoelectrons injected into the streak tube experience a linear (time-dependent) sweep across the CCD. Temporal resolution is obtained by having the photoelectrons originate from a fixed spatial location. This corresponds to a horizontal, 70 μm slit at the back of the photocathode. If this slit is tilted with respect to the CCD or deflection plates, there will be an apparent chirp in the signal (see Fig. A.3).

Figure A.3. Tilt Correction. Streak image before and after the tilt correction has been applied.

The degree of tilt (in pixels) can be determined from focus mode with a broadband light source.

Before CCD readout, the photoelectrons are amplified using a microchannel plate (MCP) with a user-controlled gain voltage. This lowers the detector sensitivity to observe week signals. To compare images collected with different MCP gain settings, it is important to normalize signals by their relative amplification (see Fig. A.4).
**Figure A.4. MCP Gain.** Effective amplification of a constant signal over MCP gain settings of $N = 2-14$. A 527 nm, 120 ps laser pulse was recorded on the streak camera and the peak intensity was plotted versus gain.

Experiments usually measured multiple samples created on different substrates (either quartz of borosilicate glass). All emission was transmitted through these substrates before being reaching the detector. Each substrate had slightly different impurities, which were most significant deep in the UV (<250 nm). Accurate UV transmission curves of each substrate were measured separately with UV/Vis spectrophotometer for best results..

**A.3. Flat-field and Spectral Response**

Because the full area of the CCD is used and different pixels record unique spectral/temporal information, it is important to measure the pixel-to-pixel sensitivity. In addition, the image-intensifying MCP experiences partial photodamage based on use, which may
affect the degree of amplification across the CCD. Pixel-to-pixel sensitivity is measured by exposing the streak camera to a uniform (flat) field of light that is constant in time (see Fig. A.5).

![Figure A.5. Flat-field Response.](image)

**Figure A.5. Flat-field Response.** Dark regions correspond to pixels of lower sensitivity. For scale, the dark line corresponding to the focus mode position is about 25% less sensitive than the surrounding region.

Finally, one must correct for the spectral response of the optical system. Emitted photons pass through a substrate, reflect off six aluminum mirrors, and are dispersed by a grating before reaching the photocathode (and CCD). Each optical element has a wavelength-dependent efficiency. This correction is performed by imaging a NIST-traceable radiometric calibration standard (known spectral distribution) onto the streak camera (see Fig. A.6)—a quartz-tungsten-halogen lamp for the visible/near-IR and deuterium lamp for UV.
Figure A.6. Spectral Response. The actual spectrum obtained from a deuterium lamp is compared to its expected output in (a). The ratio of these two curves is normalized in (b) to give the spectral response of the system. Note the intensity dips correspond to the dark vertical lines in Fig. A.5.

The spectral response and flat-field corrections are combined in one measurement and applied to streak image before the tilt correction (see Fig. A.7).

Figure A.7. Before and After Spectral Response/Flat-field Corrections. Streak image before and after correction with the spectral response and flat-field matrix.
The Hamamatsu C4334 streak camera does not have an internal shutter, and readout (33 ms) is much slower than the streak sweep (1 ns-1 ms). Exposing the streak camera to a constant light source, like a reference standard, results in two exposures. The first is the calibrated forward time sweep. And the second is a nonlinear return sweep as the deflection voltage resets. Light present during the return sweep (unknown time-dependence) can dominate the flat-field correction. The return sweep time for this streak camera was found empirically to be ~2-5 μs. This effect can be minimized by using a long-exposure forward sweep (>1 ms) to dominate the total signal.
Appendix B. Transient Absorption at 532 nm

B.1. Experimental Overview

Upon laser flash-heating, there are distinct optical changes observed in Al/Teflon (see Fig. 4.1.) To help interpret the emission signal and determine the time-dependence of these optical changes, a complementary probe was developed (see Fig. B.1.).

![Figure B.1. Transient Absorption Streak Experiments. Schematic of 532 nm transient absorption setup using the streak camera detector.](image)

The 532 nm light from a 30 mW cw diode laser (Intellite, Inc.) was focused to a 50 μm spot and spatially overlapped with the 180 μm flash-heated region at the sample plane. The transmitted beam was brought online with the emission collecting optics and sent into the spectrograph and streak-camera. The streak camera was triggered using the flash-heating pulse and ~1000 shots were averaged to eliminate laser power fluctuations.

The transient absorption was measured at a streak sweep of 20 ns, with a temporal resolution of ~300 ps. The laser would produce >10^7 photons/resolving unit. This intensity could easily damage the streak camera (refer to vertical lines in Fig. A.5) and neutral density
filters (and low MCP gain settings) were used to limit the output. An iris added to the collection optics improved sensitivity by spatially filtering the sample emission. This aperture was easily opened for emission experiments.

B.2. Sample Considerations

Samples were prepared using the same procedure outlined in Section 2.2. In addition to Teflon and polybutadiene, nitrocellulose (Sigma-Aldrich) was studied as an alternative oxidizing polymer. Like Al/PB, the mass of aluminum and volume of polymer ($\rho_{NC} = 1.23 \text{ g cm}^{-2}$) were matched to Al/Teflon. Al/nitrocellulose (NC) samples were prepared in magic solvent[1] using Aerosol OT® (Cytec, Inc.) as a surfactant. Nitrocellulose suspensions were more viscous than either Teflon or polybutadiene, requiring spin-coating speeds of 2000 rpm (vs. 400 rpm) to achieve comparable thicknesses. Two sample series were studied using the transient absorption probe (see Table B.1.).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al Conc (eq)</th>
<th>Sample Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al/Teflon</td>
</tr>
<tr>
<td>Series 1</td>
<td>0.50</td>
<td>90</td>
</tr>
<tr>
<td>Series 2</td>
<td>0.13</td>
<td>270</td>
</tr>
</tbody>
</table>

Table B.1. Sample Thicknesses for Transient Absorption Measurements.

These series were matched for absorbed energy per volume of the flash-heating laser pulse.

B.3. Series 1 (100-nm) Results

The first series had a nominal thickness of 100 nm, representing “thin” samples. At this thickness, higher concentrations of aluminum (enough to consume 50% of the Teflon) could be
studied without attenuation as emission propagated through the sample. Transient absorption data was obtained using the earlier emission experimental geometry (see Section 2.6.2). This data is shown in Figure B.2.

**Figure B.2. Transient Absorption at 532 nm for 100-nm Samples.** Samples made according to Table B.1. Data was collected on the 20-ns scale (temporal resolution ~300 ps), with a delay added for later times. There is an artifact at about 3 and 18 ns from damaged pixels.

The fraction change in 532 nm transmission was measured taking the ratio of the time-varying transmitted intensity to the average intensity obtained before flash-heating. The fractional change is presented here using the negative log , or more explicitly as a change in optical depth (OD). The three materials all undergo an initial increase in OD before settling to a longer time loss. The increase in OD coincides with rise of emission, and persists longer with longer-lived emission (in agreement qualitatively with the emission being an opaque plasma).
In addition to the transient absorption data, microscope images of these materials were also obtained (see Fig. B.3).

![Microscope Images for the 100-nm Samples](image)

Figure B.3. Microscope Images for the 100-nm Samples. 50 nm Al in Teflon (a),(b),(c); nitrocellulose (d),(e),(f); polybutadiene (g), (h), (i) at fluences indicated to the left of each row.

The images showed remarkably little difference for aluminum flash-heated in the three polymers. These images were also agreed with the longer time OD loss observed in the transient absorption measurements (Fig B.2). The three materials became less opaque, whether by bleach or ablation (refer to Section 4.2).
B.4. Series 2 (300-nm) Results

The second series studied “thick” samples (nominally 300 nm) at a lower concentration of aluminum. The transient absorption measurements found strong deviation from the thin samples (see Fig. B.4 and compare to Fig. B.2).

![Figure B.4. Transient Absorption at 532 nm for 300-nm Samples.](image)

At the lowest fluence, Al/Teflon had a very short jump in opacity, then a decrease over 2 ns to a longer time loss. At twice the laser fluence, Al/Teflon now darkened over 2 ns and remained dark for more than 30 ns. This increased opacity was stronger at a higher fluence, with a much slower loss that became apparent near the end of time window. This darkening affect had a lower threshold and was more intense in Al/NC. The probed material remained darkened for
over 30 ns, with a gradual (10s of nanoseconds) loss in OD. Al/PB showed no change from thin sample behavior.

The microscope images help explain the transient absorption dynamics (see Fig. B.5).

![Microscope Images for the 300-nm Samples.](image)

Al/PB behaved similarly to the 100-nm samples, resulting in only a lightening (or bleach) of the material. Al/NC would first bleach, followed by a strong darkening of the material, and finally ablation. The 10s of nanoseconds or longer decrease in opacity for Al/NC and Al/Teflon may describe the time it takes confined material to leave the collection window. Ablation-phase emission observed in Chapters 4-6 should be treated as early stage of this expansion. Al/Teflon also demonstrated a bleach, darkening, and ablation (refer to Sect. 4.2).
The aluminum nanoparticles have an average diameter of 50 nm. The results of these series suggest a physical limitation on what constitutes aluminum reacting within the polymer oxidizer. Experiments require samples that are optically thin to ensure uniform pumping and maximum signal output. The minimum length scale of 5-6 nanoparticle diameters appears to be a chemical requirement to behave like a material and not merely nanoparticles stuck to the surface of a random polymer.

**B.5. The Darkening of Al/Teflon**

Figure B.6 shown the times just after flash-heating, corresponding to the rise of darkening process in Al/Teflon.

*Figure B.6. Darkening Process in Thick Samples.* Transient absorption at 532 nm (solid lines) and emission at 350 nm (dashed lines) over the first 6 nanoseconds after laser-flashing heating.
Emission data has been included to support the assignment of short time spike in OD to the condensed-phase plasma emission (refer to Ch. 4). At times over 1-4 ns after flash-heating, the material becomes darker. This process happens even when lone-time ablation occurs, indicating that this is a transient state for that process.

Chapters 4-6 show that when the aluminum plasma experiences ablation, a second emission peak is observed at about 0.5-1.0 ns. AlF is observed in this emission regime nearly 200 ps after flash-heating, with a lifetime of 1-2 ns (refer to Ch. 5 and Fig. 5.4). The fact that Al/Teflon is still becoming darker as the AlF disappears supports the argument that the measured lifetime is the chemical consumption of AlF and not simply material leaving the collection window.

B.6. References