Picosecond dynamics of shock compressed and flash-heated nanometer thick films of δ-HMX

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Abstract. Progress towards probing molecular dynamics of octahydro-1,3,5,7-tetranitro-1,3,4,7-tetrazocine (HMX) subjected to shock compression of a few GPa and/or temperature excursions exceeding thermal decomposition values (T > 500 K) is described. Due to shock velocities of a few nm/ps, nanometer-thick layers are needed for picosecond time resolution. Therefore, 5-10 nm thick films of δ-HMX were deposited on metallic substrates with a template of a 4-nitrobenzoic acid monolayer. A polymer layer a few microns thick was spin-coated on top of δ-HMX for shock confinement. The monolayer and HMX layer were probed simultaneously utilizing an ultrafast nonlinear coherent vibrational spectroscopy, termed vibrational sum-frequency generation (SFG). Shock pressures were estimated via comparisons with the monolayer nitro transition frequency blueshift in hydrostatic pressure measurements. Temperature determinations were made based on the reflectance of the metallic substrate.

1. Introduction
Recent progress is described towards probing the dynamics of octahydro-1,3,5,7-tetranitro-1,3,4,5-tetrazocine (HMX) when shock compressed and/or flash-heated to pressures of a few GPa or temperatures greater than 500 K. The primary goal is to understand shock initiation and thermal degradation of molecular explosives. Specifically, for shock compression what are the first molecular bond-breaking events? This question has primarily been probed theoretically [1], where it was shown that NO₂ and/or HONO were the first fragments released during shock compression of the related explosive RDX. Our work focuses on studying the shock compression of molecular explosives experimentally on the same length and time scales as atomistic simulations.

To gain insights into the first bond-breaking events, molecules must be probed with picosecond temporal resolution. However, shock velocities through a sample are on the order of a few km/s or a few nm/ps [2,3]. Consequently, samples must be nanometers thick in order to resolve picosecond dynamics during shock loading. A sensitive probe technique must be used to monitor such thin layers. In this work, a nonlinear vibrational spectroscopy with ~1 ps time resolution, termed broadband multiplex vibrational sum-frequency generation with nonresonant suppression (SFG) [4], was used to probe vibrational transitions, specifically nitro transitions, of the thin layers in real time. SFG signal intensities are sensitive to molecular number density and molecular orientation. The samples consisted of porous polycrystalline δ-HMX. The δ-form of HMX is effective because it is noncentrosymmetric, which results in large SFG signal intensities [5], and it is shock sensitive [6]. As shown here, more sensitive materials are useful in order to observe chemistries in real time.
To develop the shock compression and flash-heating techniques, a model system was studied, consisting of a self-assembled molecular monolayer (SAM) of 4-nitrobenzoic acid. SFG was used to probe the nitro stretching transitions of the SAM. In previous monolayer shock experiments [7], we used SAMs made from benzenethiol or nitrobenzenethiol, which form on Au surfaces. Those thiol-on-Au layers are still used in our temperature jump experiments, but not in the more-recent shock experiments. Au is a poor impedance match to the SAM layers, which greatly limited the shock pressure transmitted to the monolayer. In the present studies, we replaced the Au layer with Al, which provided a much better impedance match, and used a SAM that bonded to Al via a carboxylate group. Transient pressures induced via shock loading were estimated with respect to Raman measurements under hydrostatic pressure in a SiC anvil cell, and temperatures in flash-heating experiments were measured via transient reflectance of the Au layers. The use of SFG to probe nanometer films of δ-HMX will also be examined.

2. Experimental

2.1. Sample preparation

Borosilicate glass slides, 5x5 cm² in area and 1.6 mm thick, were cleaned in a 3:1 solution of sulfuric acid to 30% hydrogen peroxide. Slides were then washed in distilled water followed by electronic grade isopropyl alcohol. A Telemark electron beam evaporator, at pressures < 0.4 mPa, was employed to deposit metal films on one side of the cleaned substrates. Well-ordered self-assembled monolayers (SAMs) were then grown on the metal surfaces by solution deposition for no less than 24 hrs [8].

2.1.1. Flash-heating substrate. Substrate design is explained elsewhere [9]. A 0.8 nm adhesive Cr layer followed by a 50 nm film of Au was deposited on the cleaned borosilicate glass. The freshly prepared metal surface was then soaked in a 1 mM ethanol solution of 4-nitrobenzenethiol (Aldrich) to form a SAM of the respective thiolate. The Cr adhesion layer kept Au from debonding during substrate soaking [10,11].

2.1.2. Shock compression substrate. Shock target arrays contained a 1 nm adhesive Cr layer followed by 300 nm of Al on the borosilicate glass. Soaking in a 5 mM ethanol solution of 4-nitrobenzoic acid (Aldrich) formed a monolayer of the respective benzoate. An optional ~5-10 nm layer of HMX was spray-coated from a 10 mL solution of 15 µM HMX in acetone. The rapid evaporation of solvent during spray-coating yielded δ-HMX [5]. A 4.5 µm layer of poly(methyl) methacrylate (PMMA) or poly(vinyl) alcohol (PVA) was then deposited over the thin molecular film via spin-coating for shock confinement [7]. PMMA was used as the overcoat for only the monolayer. Aqueous solutions of PVA were needed to spin-coat over δ-HMX since HMX is insoluble in water.
Figure 2. (a) HMX. (b) 4-nitrobenzoate (NBA). (c) Laser-driven shock compression setup with SFG probe. Sample contains a poly(methyl)methacrylate (PMMA) overcoat layer for shock confinement as well as an optional 5-10 nm layer of $\delta$-HMX. (d) Intensity profile of the drive pulse, shaped into top-hat with a diffusive optic.

Figure 3. Shock loading of an NBA SAM, where the symmetric nitro stretch, $\nu_s(\text{NO}_2)$, was probed by SFG. Shock tilted the monolayer molecules away from the surface normal. Tilting was elastic and recovered completely after shock unloading with lower drive pulse fluences. Higher fluences yielded incomplete SFG signal recovery.

2.2. Laser apparatus

A detailed description of the Ti:sapphire chirped-pulse amplified laser apparatus (figure 1) can be found elsewhere [9,12]. Briefly, 4.5 mJ, ~100 ps (full-duration at half maximum) stretched pulses at a 1 kHz repetition rate were generated and split into pump and probe pulses, which were directed into separate compressors. For flash-heating experiments, 200 fs pump pulses were frequency-doubled with a $\beta$-barium borate crystal to create up 70 $\mu$J at 400 nm, where a bandpass filter eliminated any residual 800 nm light. Flash-heating pulses produced temperature jumps (T-jumps) with $\Delta T > 200$ K. T-jumps were monitored with respect to room temperature and were ascertained based on thermoreflectance measurements [9] from the Au metal layer. At the sample, the diameter (1/e$^2$ points) of the Gaussian flash-heating pulse was 700 $\mu$m.

Shock loading experiments used an 800 nm, 10 ps drive pulse. As seen in figure 2d, the drive pulse was spatially shaped into a top-hat with speckle, with a diameter at the sample of 330 $\mu$m, using a diffusive optic (Holo/Or TH-033-X-Y-A) [7]. The focused drive pulse created a planar shock front in the monolayer (figure 2c). Both flash-heating and drive pulses were focused onto the substrate at normal incidence and had diameters significantly larger than the regions probed by SFG. After each shock, the sample was moved to expose a fresh spot to the laser beams.

Probe pulses were split into two parts. One part was sent into an optical parameteric amplifier (OPA) to generate broadband infrared pulses (BBIR). The remainder was filtered by an étalon to produce narrowband visible pulses (NBVIS). The NBVIS and BBIR pulses were overlapped on the sample to generate an SFG signal.

3. Results and Discussion

3.1. Shock compression

SFG transients are shown in figure 3 for the shock loading of a 4-nitrobenzoate (NBA) monolayer, on Al, with a PMMA overcoat. The symmetric nitro vibrational stretch, $\nu_s(\text{NO}_2)$, of NBA near 1335 cm$^{-1}$ was probed. Intensity transients demonstrated a loss-plateau-recovery structure. The delay between time zero, when drive pulses arrived at the substrate, and the signal loss was caused by the shock propagation. Risetimes for the signal loss were 13 ps and 15 ps for the lower and higher fluence drive pulses. Both were slightly less than the drive pulse duration (1/e$^2$ points) of 17 ps. Duration of the
plateau increased from 10 ps to 18 ps with increased fluence. At 0.3 J/cm², the SFG intensity recovery was found to be almost fully elastic. However, an enduring deformation was observed at 0.5 J/cm².

The response of NBA to shock loading, as depicted in figure 3, was interpreted as follows. NBA adsorbs to Al with a bridging surface coordination structure [14]. Based on SAMs of similar compositions, the NBA molecules were initially oriented at an angle of ~60° from surface normal [14,15]. When the laser-driven shock reached the monolayer, the molecules were tilted away from the surface normal, more parallel to the Al surface. The dipole moments of the probed transition lost overlap with the polarized light of the SFG pulses, reducing the SFG signals. The almost-complete signal recovery after shock indicated the shock tilting was elastic.

The increased plateau duration and incomplete SFG signal recovery at higher fluence might arise from two possible mechanisms. The first possibility was the tilt mechanism described above; where the enduring signal loss would be caused by long-lasting deformation of the monolayer molecules. The second possibility was that some of the nitro groups were dissociated by the shock front. These possibilities will be distinguished in future work by their dependence on the polarization of the SFG beams and/or by addition of a methyl group to the SAM. If the nitro group signal vanished but the methyl group signal recovered, nitro dissociation rather than the tilt mechanism would be indicated.

The pressure-induced frequency shifts of the nitro group transitions of a 4-nitrobenzenethiolate (NBT) SAM were studied in a SiC anvil cell [7,13], which is depicted in figure 4a. SiC was used rather than diamond due to the overlap between the diamond phonon and the nitro vibration. Because samples were monolayers, the underlying metal substrate was fabricated with a nanoscale texture that amplified the Raman signal by ~10⁶ via surface-enhanced Raman scattering [16]. The cell was loaded with argon hydrostatic pressure medium. A linear fit to the ν(NO₂) frequency shift data in figure 4b yielded a 2.1 cm⁻¹ blueshift per GPa. Shock compression of NBA produced a blueshift of ~3 cm⁻¹ during maximum stress on the SAM (figure 4c), indicating a shock pressure of about 1.5 GPa.

3.2. Flash-heating
To expand upon the shock compression work, the response of an NBT monolayer to large-amplitude temperature jumps was studied. The idea was to enhance the shock-induced reactivity by preheating
the molecules. The nitro moiety, specifically the $\nu_s$(NO$_2$) transition, as indicated in figure 5b was again probed by SFG. Transients were monitored for T-jumps ranging from 35 to 250 K, where time zero marked the flash-heating pulse arrival at the substrate. The SFG intensity dynamics after T-jump had an overshoot-decay-plateau structure (figure 5c), where the overshoot resulted from direct excitation of $\nu_s$(NO$_2$) by Au hot electrons generated during laser flash-heating. After the hot electron effects decayed away, a plateau was reached that indicated the SAM was in equilibrium with the flash-heated Au surface [9]. SFG intensity within the plateau regime decreased with increasing monolayer disorder, which resulted from thermal excitation of SAM rotational modes (figure 5a). The dynamic response of the SAM to flash-heating is interesting in its own right [9,11]. For the present study, though, the point is that an equilibrated, preheated layer can be shocked if the shock front is delayed ~60 ps after flash-heating, and the temperature of that layer can be well above the normal decomposition temperature.

3.3. $\delta$-HMX SFG spectrum
As a proof of principle, a ~5-10 nm layer of $\delta$-HMX was spray-coated over an NBA SAM template, and the resulting SFG vibrational spectrum was collected (figure 6). Due to laser shot rates of 100 Hz, thousands of counts of signal can easily be generated for both NBA and $\delta$-HMX within a few seconds of acquisition. The strong signals from $\delta$-HMX resulted from SFG selection rules. The SFG process is strongly allowed in noncentrosymmetric media. As shown, four different transitions of $\delta$-HMX can be probed during shock loading, and the NBA $\nu_s$(NO$_2$) transition should act as a strong marker for shock arrival at the $\delta$-HMX layer.

4. Summary
Techniques were established for probing the shock compression and flash-heating of a single molecular monolayer with picosecond temporal resolution. By monitoring the symmetric nitro stretch, vibrational sum-frequency generation spectroscopy was employed to probe the dynamics of a self-assembled monolayer of 4-nitrobenzoate and 4-nitrobenzenethiolate when respectively subjected to shock loading to a few GPa and temperature jumps up to 250 K. Calibration of pressure and temperature was accomplished via hydrostatic pressure measurements in a SiC anvil cell and thermoreflectance measurements from the metallic substrate. Preliminary experiments demonstrated the ability to probe a ~5-10 nm layer of $\delta$-HMX with excellent signal-to-noise. Presented work validates utilizing these discussed techniques to study the shock initiation and thermal degradation of $\delta$-HMX with picosecond temporal resolution.
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