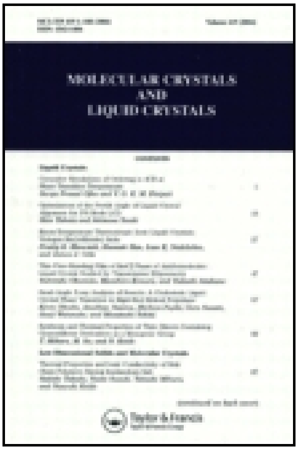

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Ultrafast Spectroscopy of Laser-driven Shock Waves in Molecular Materials

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Ultrafast Spectroscopy of Laser-driven Shock Waves in Molecular Materials *

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The "nanoshock technique" for generating shock waves in molecular materials at high repetition rates is described. Ultrafast spectroscopy is used to study shock waves in crystalline anthracene, a high explosive NTO, and a molecular nanomachine, the heme protein myoglobin.

Keywords: shock waves, molecular crystals, ultrafast spectroscopy

INTRODUCTION

The unconventional photoactive material used in our research is a transparent thin layer which explodes when irradiated by intense short near-IR laser pulses[1]. This thin layer is coated upon the sample material of interest. When the short laser pulse (the "shock pulse") is absorbed by the thin layer, the recoil from the explosion launches a shock wave through the sample. The shock wave effects are monitored by ultrafast laser spectroscopy. This technique, although quite new, is not terribly difficult in practice provided one has a picosecond or femtosecond pulse laser of sufficient energy (≥ 0.1 mJ). The technique can be used with a wide variety of molecular materials as shown in this brief article. After the thin layer is exploded and the sample is shocked, the material becomes irreversibly damaged, so experiments must be designed to account for the single-shot damage problem. In practice, the thin exploding layer and thin sample layer are coated on a relatively large area substrate (100 cm^2). The laser pulse which launches the shock wave is focused to an area of about 10^{-4} cm^2. The substrate is scanned through the focused laser beam by a motorized positioner, so it is possible to produce about one million individual shock events on a single sample, at a high repetition rate of up to 100 shocks/s. Since the mass of sample material being shocked is typically a few ng for a sample a few microns thick, and the duration of the shock wave is a few ns, this method is termed[2] the "nanoshock technique".

The shock waves we produce are very tiny, but they are very powerful. A typical shock pressure[2] is 40,000 atm (40 kilobar or 4 GPa). In ordinary molecular materials, this pressure reduces intramolecular distances by 10-20%, and raises the temperature by several hundred degrees[3] for a brief time interval of a few nanoseconds[2-4].

What is interesting about the nanoshock technique? At the present time shock wave experiments are mainly performed at large facilities such as government laboratories, where the shock is generated by a large gun or an explosive charge at a rate of perhaps one per week. In contrast, ultrafast

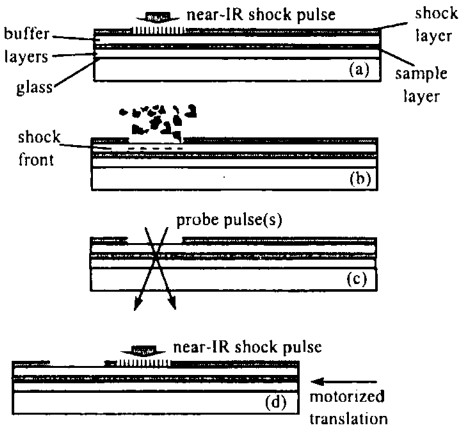

FIGURE 1 Schematic description of a nanoshock experiment on a thin layer of molecular material. After the shock layer explodes, spectra are taken as the shock front passes through the sample layer. From ref. 4.

spectroscopic studies of laser photochemistry are performed at a repetition rate of typically 1000/s, in thousands of laboratories throughout the world, using benchtop laser facilities. Nanoshock studies can be viewed as an alternative to photochemistry, as a technique for studying the dynamical response of molecular materials. Instead of putting molecules into an electronically excited state, molecules are rapidly put into a state of high pressure and temperature. There are several areas of keen scientific interest:

(1) *Optical studies of materials under extreme conditions.* Materials under extreme conditions can be studied by pressurizing and heating them. With nanoshocks, the pressurizing and heating process takes place in about 25 picoseconds. It thus becomes possible to study materials which decompose too quickly to study in the conventional high pressure and high temperature apparatus. It also becomes possible to study the dynamical response of materials to high pressure, e.g. the dynamics of phase transitions.

(2) *Studies of fast thermochemical processes.* In photochemistry studies, it is straightforward to turn a chemical reaction on and then turn it off in a very short time, using a short pulse of light. Using a short duration nanoshock pulse, a thermochemical reaction can be turned on by jumping the temperature as much as several hundred degrees. In contrast to ordinary temperature jump methods, with nanoshocks the high temperature can be *turned off* in a very short time. That is because with ordinary temperature jump, the high temperature decays with a slow thermal diffusion time constant, whereas with a nanoshock the high temperature decays by very fast adiabatic expansion.

(3) *Studies of highly vibrationally excited molecules.* When a nanoshock front passes through a molecular material, a great deal of mechanical energy is added to each molecule. If the risetime of the shock is much slower than the characteristic time for vibrational energy redistribution processes, then the shock front simply heats the molecule. But when the risetime is faster than this time, highly nonequilibrium vibrationally excited states are produced. In molecular materials, vibrational energy redistribution takes place in tens or even hundreds of picoseconds. We have produced nanoshock pulses with a

risetime of <25 ps, which is fast enough to produce a highly nonequilibrium vibrational population.

(4) *Studies of large amplitude molecular mechanics*. Virtually all techniques which probe the mechanical responses of molecules, e.g. vibrational spectroscopy, acoustic attenuation, and Brillouin scattering and stimulated Brillouin scattering, produce only tiny displacements (perhaps 10^{-4-5} Å) from the equilibrium geometry. Important basic molecular processes such as chemical reactions, enzyme and nucleic acid function, etc., involve much larger displacements (typically angstroms). Therefore it is very interesting to probe molecular dynamics with large amplitude displacements. Our nanoshock pulses produce compression factors[3] of 10-20%. For example in a protein or membrane measuring 50Å across, the driven dynamic molecular displacement may be 5-10Å.

In our laboratory, the nanoshock technique has been under development for the last two years. At the present time we have developed a very useful design for shock generation and detection, although we cannot say we have yet perfected this design. We have obtained very high quality vibrational spectra of shocked materials using picosecond coherent Raman scattering (ps CARS). We are now adding the capability of measuring transient absorption spectra. Our first experiments, intended to characterize the nanoshock method, were performed on a model molecular material anthracene. In recent months we have extended this work to the study of an energetic material, NTO (5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one), and the study of a molecular nanomachine, the heme protein myoglobin. In the remainder of this paper we will briefly discuss these initial studies.

SHOCK WAVE BASICS

Figure 2 depicts some of the basic properties of shock waves[5]. Imagine a weight falling at velocity *v* onto a sample. (In our experiments, it is not a falling weight but the rapid expansion of the exploding layer which launches the shock wave, but the basic concepts are identical). If the velocity *v* is small, an acoustic wavefront is launched. The acoustic front moves through the sample at the speed of sound, and the densities ahead of and behind the front are identical to the ambient density ρ_0. If the velocity v is large (a significant fraction of the acoustic velocity), then a shock front is launched. The compression of matter behind the front leads to a higher density ρ_1 behind the front than ahead of the front. For example, if the velocity v is 10% of the acoustic velocity, $\rho_0/\rho_1 \sim 0.9$. The shock front velocity is approximately the velocity of the shock compressed matter plus the acoustic velocity, in this example about 1.1 times the acoustic velocity.

Figure 2(d) is a P-V diagram for isothermal, isentropic and shock compression processes, computed using tabulated data for anthracene. For a given volume change ΔV, the work done $\int$Pdv for the isothermal compression is the lowest. In an isentropic (reversible adiabatic) compression, the temperature rises in the sample during compression, so more work is required for the same volume change ΔV. A shock is an *irreversible* adiabatic compression. The irreversible shock adiabat is termed the "Hugoniot", and the work for a given ΔV for shock compression is the greatest of all[5].

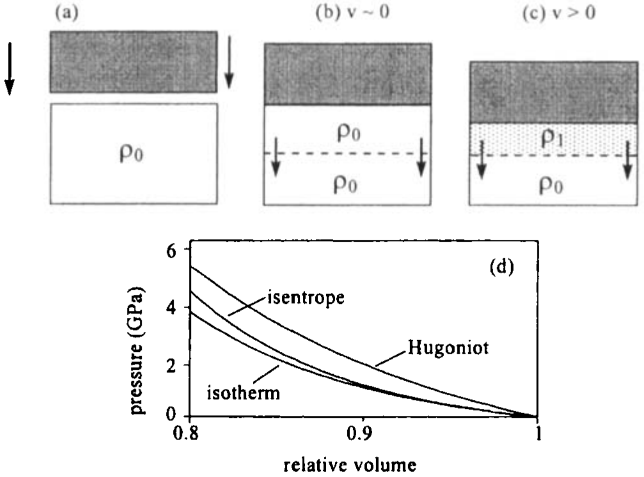

FIGURE 2 (top) A shock wave is produced when a sample is struck by a moving mass at velocity $v > 0$, so material behind the front is compressed to a higher density ρ_1 than the density ρ_0 ahead of the front. (bottom) Isotherm, isentrope (reversible adiabat) and Hugoniot (shock adiabat) for anthracene.

In some of our experiments, a shock front with a *steep risetime* (~25 ps) is launched[2,6], causing single-stage compression along the Hugoniot. As described in textbooks[5], the decompression process must be reversible (otherwise entropy would decrease across the decompression front, violating the 2nd law of thermodynamics), so decompression occurs along an isentrope originating at the final shock state. During shock compression, the sample is irreversibly compressed and heated from ambient temperature T_0 to high temperature T_s. During unloading, the sample is reversibly cooled. After a cycle of compression and decompression, the sample ends up at temperature $T_0 + \Delta T_{irr}$, which lies between T_0 and T_s. The steep risetime shock is used to study highly irreversible processes such as initiation of energetic materials.

In other experiments[4], a shock front with a *slower risetime* (400-800 ps) is produced. The slower shock compression process is close to a reversible adiabatic expansion along the isentrope. The high temperature T_{rev} is a bit lower than T_s above. During shock unloading, the sample expands and cools reversibly, and it ends up almost back to the initial temperature T_0. This ultrafast reversible compression and expansion process is useful for studying systems where it is desired to return to the original temperature and pressure very quickly, for example in turning on and off a thermochemical reaction.

SHOCK WAVE STUDIES OF ANTHRACENE

Anthracene is regarded as a model system for molecular crystal studies. Our experiments used ps CARS spectroscopy to study the most intense Raman-active vibrational transition[4], denoted ν_4, at a nominal Raman shift of 1404 cm^{-1}. We studied[4] the response of this transition to high pressure and high temperature, using a diamond anvil cell and an optical oven. It was found the transition blueshifted with increasing pressure and broadened with increasing temperature. Thus by looking at the frequency shift and width, it is possible to estimate the temperature and pressure from the vibrational spectrum[3]. Figure 3 shows a vibrational spectrum of anthracene at ambient temperature, and under shock loading where $P_s \sim 4.2$ GPa and $T_s \sim 350°C$.

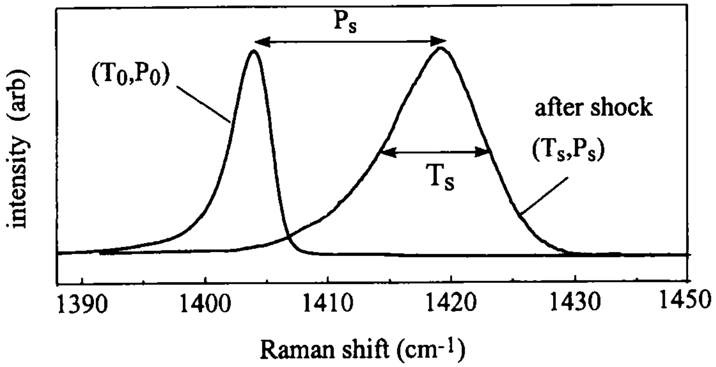

FIGURE 3 Vibrational spectra of anthracene at ambient (T_0,P_0) and under shock loading. The peak blueshift gives the pressure P_s and the width gives the shock temperature T_s. In these spectra, $P_s \sim 4.2$ GPa and $T_s \sim 350$°C.

The shock front risetime is varied by changing the thickness and dye absorber concentration of the shock layer[4]. In Fig. 4 we show spectra of a 500 nm thick layer of anthracene compressed by a slower shock front with risetime 400 ps. With this shock front, the pressure increases uniformly

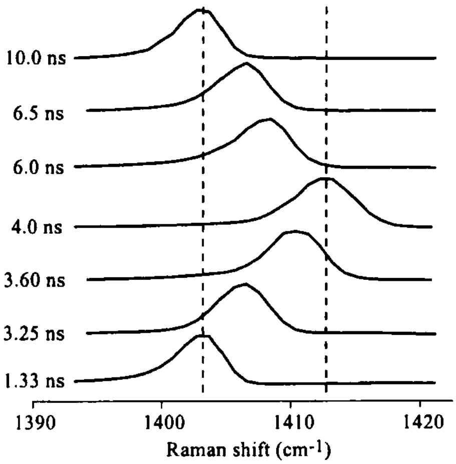

FIGURE 4 Raman (CARS) spectra of anthracene under dynamic shock compression to about 2.6 GPa. The shock arrives at the anthracene at t ~ 3 ns. The shock front risetime is about 400 ps, and the falltime is several ns. During this slower shock compression process, the anthracene is subjected to a cycle of nearly reversible compression and reversible expansion. From ref. 4.

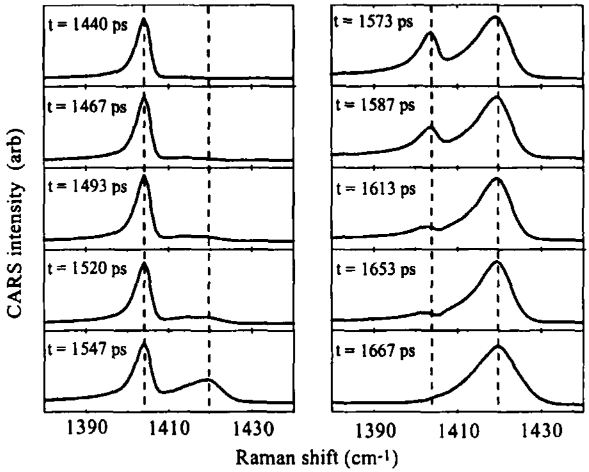

FIGURE 5 Spectra of a 700 nm thick layer of anthracene with a shock with a very fast risetime (<25 ps) passing through. When the front is in the anthracene, it divides the layer into ***two regions***, one at ambient pressure and the other at high pressure (here 4.3 GPa). The anthracene spectra consist of ***two peaks*** with time dependent intensities. The front arrives at the layer at ~1.5 ns and exits at ~1.7 ns. From ref. 2.

in the anthracene, so a single peak is observed, which first blueshifts (pressure rising) and then redshifts (pressure releasing). In Fig. 5 we show spectra of a layer of anthracene ~700 nm thick, with a very sharp shock front whose risetime is <25 ps. When the shock front is in the anthracene layer, two peaks are observed. One corresponds to ambient anthracene and the other to shocked anthracene. As the front moves through the anthracene, the intensity of the ambient peak declines and the intensity of the shocked peak increases. Using these time dependent intensities and knowing the anthracene layer thickness, the shock velocity (here 4.3 km/s) can be determined[2].

SHOCK WAVE STUDIES OF ENERGETIC MATERIALS

Ultrafast shock compression studies of high explosives are intended to investigate the initial fast chemical reactions in shock wave initiation, and the mechanical properties of rapidly compressed materials. For our initial studies[7] we chose NTO, which is a highly insensitive (safe) explosive[8].

CARS spectra were obtained on shocked NTO in the region (~1350 cm^{-1}) of the totally symmetric NO_2 stretching transitions. As shown in Fig. 7, there are two Raman transitions seen in this region. When the shock front arrives, one transition blueshifts and the other hardly shifts at all. At the time of maximum shock loading (t ~ 2000 ps), a smaller third peak is observed, which vanishes when the shock unloads (t > 3000 ps). After the shock has unloaded (t > 3000 ps), the intensity of the lower frequency peak declines over the next few ns. We have shown the area under this peak remains constant with time and the peak intensity decline is actually due to a time-dependent increase in the width of the transition[7].

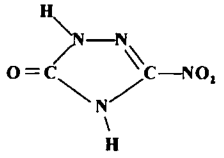

FIGURE 6 NTO.

More work is needed to understand the origins of these interesting phenomena: (1) the temporary appearance of a third peak; (2) a nanosecond time scale broadening of the lower energy peak after shock unloading. However it seems clear these observations can be related to fast time-dependent distortion of crystal structure. In these NTO crystals, there are eight mole-

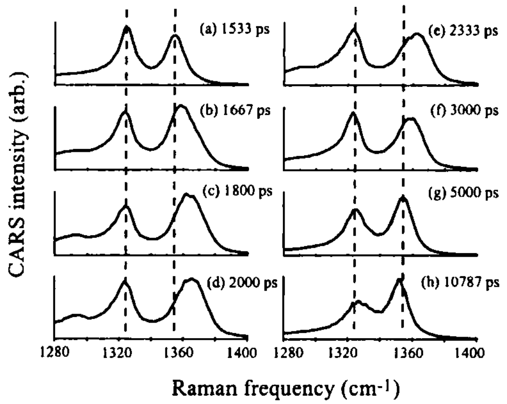

FIGURE 7 CARS spectra of 1 μm thick NTO. (a) The shock front has not reached the NTO, (b) - (e) the shock front is inside the NTO layer and (f) - (h) the shock pressure is decaying away. The vertical dotted lines indicate the ambient pressure frequencies of the two Raman transitions. From ref. 7.

cules per unit cell[8]. During shock compression, the eightfold degeneracy of the NO_2 stretch can be lifted by uniaxial crystal compression, lowering the symmetry and allowing us to temporarily see new peaks. After the crystals have been rapidly compressed and unloaded, a nanosecond time scale process occurs which broadens one of the vibrational transitions. Such a broadening process is indicative of ultrafast large-amplitude material relaxation processes possibly involving generation of solid-state defect centers.

No shock-induced chemical reactions have been seen by us in NTO, probably because this material is a highly insensitive explosive. The use of more sensitive materials should permit the real-time observation of shock induced chemistry. However the NTO work is extremely interesting in how it allows us to see two different ultrafast mechanical processes, occurring on different time scales, via the time-dependence of the vibrational spectra.

SHOCK WAVE STUDIES OF PROTEIN DYNAMICS

A novel application for shock waves being pursued in our laboratory involves shocks in biological materials. Our first experiment studies the dynamics of the heme protein myoglobin (Mb). Mb is a molecular nanomachine[9] (see Fig. 8) about 4 nm in diameter, whose function is oxygen storage. Mb consists of interlocking protein helices which fold around a colored molecule called heme[9]. Oxygen binds at an active site of the heme. Like all large biomolecules, Mb is expected to have quite complicated mechanical

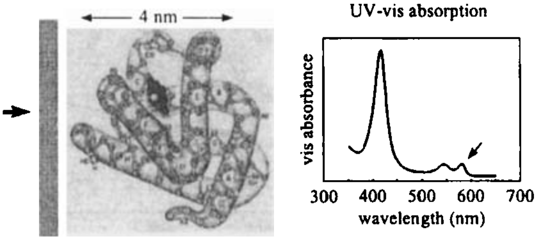

FIGURE 8 (left) Structure of myoglobin protein. (right) visible absorption spectrum of myoglobin with CO bound to the active site. The arrow indicates the wavelength region being probed in shock experiments.

properties. The folding and unfolding dynamics of proteins is one of the most exciting topics in biochemistry and biophysics today.

Shocking Mb is expected to result in a large structural distortion, since Mb undergoes denaturation[10] (unfolding) at ~80°C or 0.8 GPa. After the fast cooling process caused by shock unloading, Mb will be frozen into metastable configurational states. The quite interesting structural relaxation processes, which result as proteins return to its equilibrium configuration, can be monitored by time resolved optical absorbance spectroscopy.

In preliminary experiments[11], we have fabricated biocompatible shock target arrays, where the Mb protein (bound to CO for stability) is present in its native folded configuration. The sample layer is a thin layer of Mb-CO solution in aqueous buffer, with glycerol added to stabilize the layer. The effects of shock are detected via transient absorption spectroscopy, as shown in Fig. 9, without shock and 3 ns after shock. At delay times up to 10 ns, the Mb spectrum did not return to its initial state, indicating the presence of structural relaxation processes much slower than in anthracene or NTO. These very early experimental results illustrate the significance of the nanoshock technique for biological materials, unconventional materials, or precious materials available only in tiny quantities.

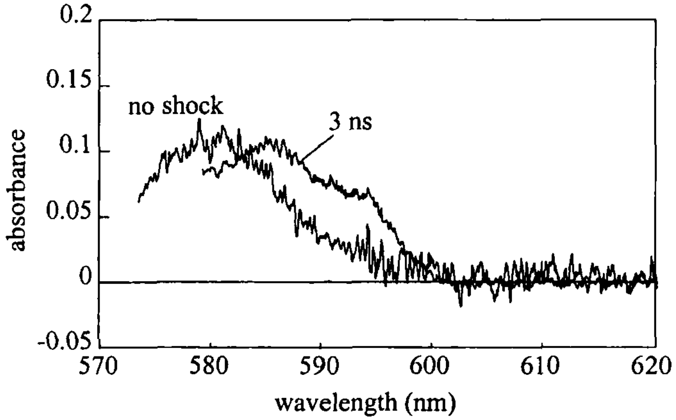

FIGURE 9 Transient absorbance spectra of myoglobin without shock, and 3 ns after shock. The spectrum does not return to the ambient unshocked state within the 10 ns time window studied. From ref. 11.

Acknowledgments

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