

FINAL PROGRESS REPORT

“SHOCK INITIATION OF SOLID STATE EXPLOSIONS”

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Principle Investigator: Professor V. Ara Apkarian
Department of Chemistry
University of California, Irvine
Irvine, CA 92697-2025
(949) 824-6851

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13. ABSTRACT (Maximum 200 Words) <p>In this collaborative effort on shock initiation in solids, advances were made in fundamental concepts and methods of investigation. A new theory was developed for shock-induced vibrational excitation, based on translation to vibration energy conversion. The key novelty of this work is the treatment of multiple correlated impulsive forces acting coherently on the internal degrees of the molecule as the shock wave passes. This theory is in excellent agreement with explicit simulations. The experimental effort has focused on the development of tools for initiation and monitoring of shock-induced microscopic dynamics. In the published work, two specific studies are notable. In the molecular solid of chlorine, we have demonstrated the mechanism of positive feedback in exciton-phonon transfer, leading to the formation of catastrophic hot spots in the solid. In superfluid He, under strong-field excitation, we have demonstrated the clear mechanism of cascade driven electronic-phonon energy transfer leading to bubble formation and breakdown. More generally, we have advanced four-wave mixing spectroscopies as both initiator and interrogator of shocks in condensed media. The results of these studies, in the gas solid and liquid phases, are now being published.</p>				
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Final Report Shock Initiation of Solid State Explosions

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V. Ara Apkarian and C. C. Martens
Department of Chemistry
University of California
Irvine, CA 92697-2025

I. Theory (C. C. Martens): Coherent ultrafast vibrational excitation of molecules in shock fronts.

The major theoretical accomplishment resulting from AFOSR support was the development of a new theory of shock-induced vibrational excitation of molecules in solids.¹ In contrast with previous work that treats multiphonon up-pumping of molecules from lattice vibrations that are heated by the passing shock wave,^{2,3} our model focuses on the ultrafast dynamics occurring within the shock front itself, and is built on the theories of translational to vibrational energy transfer first introduced in the 1960's.⁴⁻⁸ The key novel aspect of this work is treatment of multiple correlated impulsive forces acting *coherently* on the internal degrees of the molecule as the shock wave passes. We have illustrated this approach for the case of a one-dimensional monatomic solid, and found that the model developed provides a qualitative description of the behavior observed in molecular dynamics simulations, and in some cases, gives quantitative predictions of the vibrational energy uptake as a function of collider (and thus shock) velocity. Although our published work on this problem has considered a one-dimensional model, we have observed similar qualitative behavior in simulations of two-dimensional solids, and an appropriate generalization of present theory should be applicable there as well.

The problem of energy uptake of molecules in shocked solids has been the subject of a number of previous studies. The formal theories developed to describe this phenomenon have focused on the mechanism of multiphonon up pumping of the intramolecular degrees of freedom by a (locally) hot lattice.^{2,3} The thermal excitation of the lattice results from energy decay of the passing shock front into collective phonon degrees of freedom. The physics of this process, and the theories developed to model it, treat the lattice vibrations as *incoherent*, with no well-defined relationship between the phases of the various phonon modes. In contrast, the mechanism we have proposed involves multiple impulsive collisions affecting the atoms of the molecule being excited. This results from the nature of the traveling shock wave: highly localized in space, and with a well-defined velocity. In phonon language, this leads to a *coherent* mechanism for excitation: the phase relation between different lattice vibrations is well defined. Our model is based on a simple, but manifestly nonlinear, description of the molecule-shock wave interaction.

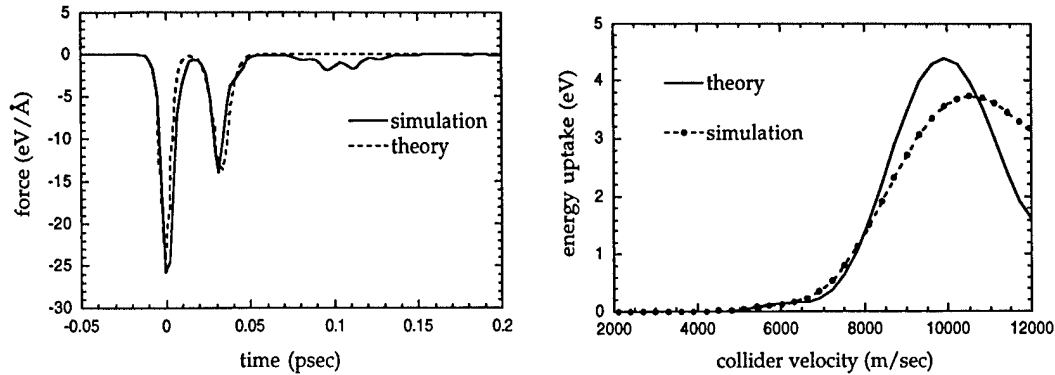


Figure 1: Comparison of simulation and theory of shock-induced excitation of molecules in solids. Left: impulsive forces on intramolecular bond, simulation vs. analytic theory. Right: energy uptake vs. collider velocity, simulation vs. analytic theory. Note nonmonotonic energy excitation resulting from correlation between impulsive collisions.

In related, unpublished work, we have developed a simple but novel theory of ultrafast energy uptake of *many-body systems* (in contrast with the single internal degree of freedom considered above) under the influence of impulsive forces, such as those occurring in a traveling shock wave front. Results obtained on this problem have applications in a number of contexts, both of direct relevance to the initiation of detonation and to a broader range of condensed phase dynamical processes. In the case of detonation, the “many-dimensional system” can represent the internal degrees of freedom of a polyatomic molecule (such as nitromethane) undergoing the influence of a passing shock wave, or, alternatively, can describe the intermolecular (phonon) degrees of freedom of a solid being impulsively driven by the fragments of a highly exothermic reaction.

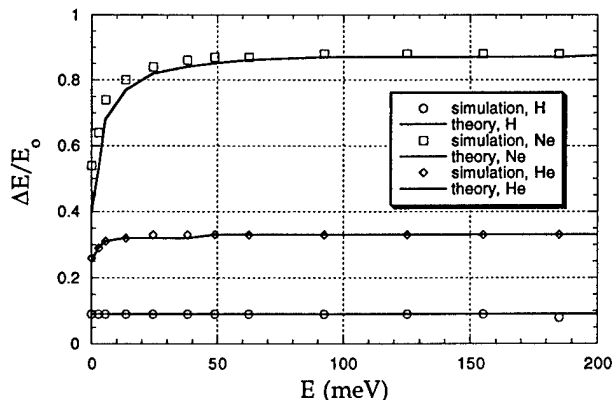
Our model is an extension of the collisional energy transfer-based approach we described previously to the problem of many driven degrees of freedom. In its simplest version, this theory treats the doorway modes of the many-body system in the normal mode approximation. For simplicity, assume for now that the impulsive (e.g., shock-induced) force acts on a single atom of the system; this can be easily generalized. For an external force $F(t)$, the energy uptake of a normal mode of frequency ω_j is found to be

$$\Delta\epsilon(\omega_j) = AL^2(\omega_j) |\hat{F}(\omega_j)|^2 \quad (1)$$

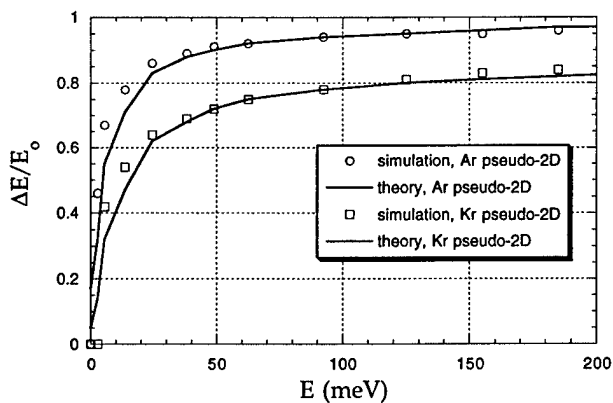
where $L(\omega_j)$ is the coefficient describing the projection of the j^{th} normal mode on the perturbed atom, $\hat{F}(\omega_j)$ is the Fourier transform of the perturbing force, evaluated at the oscillator frequency ω_j , and A is a constant. For a many-atom system, we can approximate the discrete normal mode spectrum as a continuum, characterized by a density of states $g(\omega)$. The total uptake of the perturbed system is then given by an integral over the frequency spectrum:

$$\Delta E = \int_0^{\infty} \Delta\epsilon(\omega) g(\omega) d\omega. \quad (2)$$

In addition to the problem of energy uptake of polyatomic molecules in shocked solids, this formalism can be applied to a number of other physical contexts, such as the inelastic scattering of atoms from surfaces. In the surface scattering case, the quantity $g(\omega)$ is interpreted as the phonon density of states. In fig. 1, we show the results of a calculation of the inelastic scattering of several atoms (H, He, Ne) from a one-dimensional model of an anharmonic solid consisting of Argon.



In fig. 2, we show similar results for a pseudo-two dimensional model of heavy atom (Ar and Kr) scattering from an Argon surface (we find that a purely one-dimensional model does not provide a good representation of surface scattering when the collider mass is larger than that of the lattice atoms).



In the figures, the relative energy pickup $\Delta E / E_0$ predicted by the theory is plotted as a function of the initial collider energy E_0 and compared with the results of direct molecular dynamics simulations. The agreement between the harmonic theory and the fully anharmonic many-body calculations is quite good. The results show that, at the high-energy limit, the energy transfer is simply that expected from a binary hard sphere collision:

$$\Delta E / E_0 = 4m_s m_c / (m_s + m_c)^2, \quad (3)$$

where m_s and m_c are the masses of the surface and collider atoms, respectively. As the energy decreases, the relative energy drops off from this impulsive limit. This can be understood by considering the interplay of the spectral density of the force

and the phonon density of states: At high energies, the collider-surface collision occurs very quickly in time. In the frequency domain, this leads to a broad power spectrum, which completely encompasses the region the frequency domain where $g(\omega)$ is significant. Mathematically, this leads to the impulsive result of Eq. 3. As the energy is decreased, the duration of the collision increases in time, leading to a complementary narrowing of the power spectrum. As this trend continues, the high frequency part of $g(\omega)$ begins to extend to higher frequencies than the spectrum of the force $\hat{F}(\omega)$. Under these conditions, only the lower frequency modes of the system can be excited. This corresponds to an adiabatic separation of the high frequency lattice modes from the driving force, which can thus not be excited by the impulsive force. This “freezing out” of the high frequency modes is responsible for the drop off of $\Delta E/E_0$ at low collisional energies.

The above simple theory can also be applied to the problem of energy accommodation of the lattice “cage” surrounding an energetic event in the solid phase, such as photodissociation of a molecule embedded in an inert matrix. In the context of energetic materials detonation, the accommodation of energy generated rapidly by exothermic bond formation during the early steps of initiation by the surrounding lattice modes will greatly influence the ability of this event to drive further *chemistry* or simply lead to indiscriminate lattice heating.

II. Experiments (V. A. Apkarian)

A) Explosion due to positive feedback between electronic and vibronic degrees of freedom:

Fain and Lin [9] have proposed the mechanism of a positive feedback between electronic and vibronic excitations leading to a catastrophic rate of energy deposition in phonon modes, and subsequent explosion. This important consideration of the dynamics of highly excited systems has little direct verification. Our experimental studies in thin films of molecular chlorine, may constitute one of the most direct verification of this process. Briefly, when a molecular solid of Cl_2 is dissociatively pumped in the UV spectral range, rapid recombination leads to population of the molecular A/A' states, while dumping ~ 2 eV in the lattice. This excess energy is not sufficient for causing any feedback. When two-photon excited up to the ionic manifold of the solid, rapid relaxation leads again to the formation of the A/A' states, but now ~ 6 eV is dumped into the lattice per excited molecule. This very high local excitation diffuses away from the excitation center through vibron-vibron energy transfer, however the pile-up of local vibronic population also triggers electronic relaxation of the molecule, a process in which an additional ~ 1.5 eV of vibronic excitation is created. The effect could be directly observed as fluence dependent non-exponential decay of the electronic population, and demonstrated to be strictly due to this feedback mechanism through kinetic simulations. A manuscript detailing these results has appeared in press [10].

B) Degenerate four-wave mixing for generation and detection of shock waves:

One of the mundane issues in experimental studies of shock initiated dynamics in the solid state is that of repeatability, the fact that most approaches are destructive, and therefore quite difficult to repeat. Our search for non-destructive means of creating and detecting density waves led us to studies in glasses, and in an

important family of materials, sole-gels doped with metal and metal oxide clusters. The former studies were carried out in commercial neutral density filters, consisting of metal oxide doped glasses, in which we were able to generate and observe shock waves. In the latter, a giant photo-acoustic response (also large electronic third order nonlinear susceptibility), diffracting as much 50% of the incident radiation was observed, yet no evidence of shock waves could be detected. The experimental set-up used in these measurements consisted of the standard arrangement for degenerate four wave mixing, except we have been able to carry out the same measurements with fs to ms time resolution, which has been an important means of identifying the various third-order nonlinearities. In these measurements, the two pump beams generate an optical grating, and the diffraction from the probe beam is monitored as a function of delay between pump and probe. The diffraction can be due to pure electronic, electronic population, density, or thermal gratings. The various mechanisms are most conveniently sorted out with a large dynamical range in the time dependence. A typical signal observed in the ND filter is shown in figure 3. In 3a, three cycles of the density wave are shown and marked. The separation of 3.4 ns between the maxima, with the known grating spacing, yields the acoustic velocity of the glass as 5×10^5 cm/s. The time origin is also clearly marked by the spike due to the electronic grating. The notable aspect in this signal, in 3a, is the fact that the first maximum develops almost instantaneously. The arrows with the primed numbers mark the expected location of the maxima: in order for the density gradient to be established a $\pi/2$ phase must lag [11]. A higher time resolution scan is shown in Fig. 3b. It is clear that this process does happen, that the density gradient takes time to establish, however, the first half cycle is advanced in time. On average, the propagation velocity of the density wave now proceeds at twice the normal speed of sound: $t_2/t_1=1.9$. Moreover, the substructure on the main wave shows that there is significant dispersion in these propagation times. In these solids, shock waves are generated long before the damage threshold. A search for this effect in other systems has failed. For example, in color filter glass or the sole-gels discussed below, we observe the normal acoustic grating. A literature search turned up only one other example where this behavior was observed, namely in large proteins, and the mechanism there is not understood.

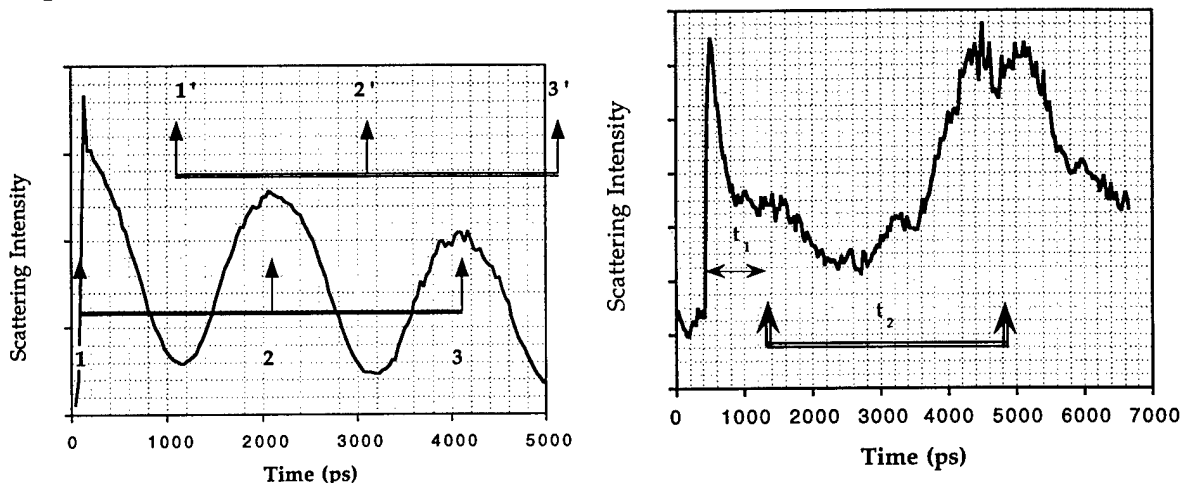


Figure 3: Scattering from density grating. a) The observed scattering maxima are identified by the numerals, the expected maxima for normal acoustic waves is marked with the primed numerals. b) A magnification shows that indeed the formation of the first density maximum does take time, however, this time lag is nearly half what is expected for acoustic waves, and clearly an indication of supersonic propagation. The substructure is reproducible, ascribed to dispersion in the generated shock waves.

Sol-gels doped with chromium-oxide clusters were studied as a variant of the above. The metal oxide centers act as strong optical absorbers with very fast energy relaxation into the lattice phonons. The release of this energy into the lattice, the subsequent establishment of density and thermal waves was investigated with some care. A large third order susceptibility was observed with 70 ps pulses, but not with fs pulses, indicating that these solids may be useful as photo refractive materials. More important to our interests, we observed very large diffraction efficiency from the density waves, a giant photo-acoustic response comparable only to what has been achieved in liquid [12]. All efforts at observing wave propagation at supersonic speeds failed, reaching damage threshold prior to such an observation. The large acoustic response implies a large density fluctuation, consistent with the fact that these are very low-density solids. Given the potential of device applications for photo refractive and photo acoustic materials, we will pursue these systems with some systematics with targeted synthesis based on mechanistic understanding. The group of Prof. K. Shea in our department synthesizes the samples, and a manuscript summarizing these results has been reported [13].

C) Time-Frequency resolved CARS (TFCARS):

The theoretical discussion given in the first section provides a perspective for the possible novel schemes of probing the anatomy of a shock wave in model systems. The proposed approaches are made to extract the detail in dissection to dynamics that propagates on a long-range with molecular scale resolution. This is aimed to complement what we have learned about lattice dynamics through the eyes of the chromophore [14], namely, the nonlinear processes that feedback along the coordinate that provides the initial impulse. An important lesson learned from our studies in iodine is that, although the ultrafast pump-probe experiments provide a wealth of information, a very accurate knowledge of the many-body electronic potentials is necessary for the uncovering of such information. Moreover, the pump-probe measurements that rely on LIF as the signal will be limited to systems in which radiation remains a major channel for electronic relaxation - a highly limiting requirement. With these considerations in mind, we developed the fs TRCARS technology in our laboratory, as a coherent four wave spectroscopic tool that allows us to study both ground and excited states of virtually all systems, with high sensitivity and discrimination. The universality of the tool is due to the fact that it relies on the third order nonlinear susceptibility elements of the hyperpolarizability tensor, which will always have non-zero members. Its species discrimination capability is based on the fact that by tuning the difference wavelength between pump and Stokes beams to a chosen vibration, we single out a molecular species to monitor in a complex system. Finally, since it is a nonlinear spectroscopy, the available peak powers in fs pulses allow us to work under optimal conditions, just below the white light generation threshold. The experimental design uses two independently tunable fs OPAs, and three beams in the BOX-CARS geometry. As an example for the analysis of dynamics in condensed phase, we show data from liquid CS₂ at room temperature in Fig. 4.

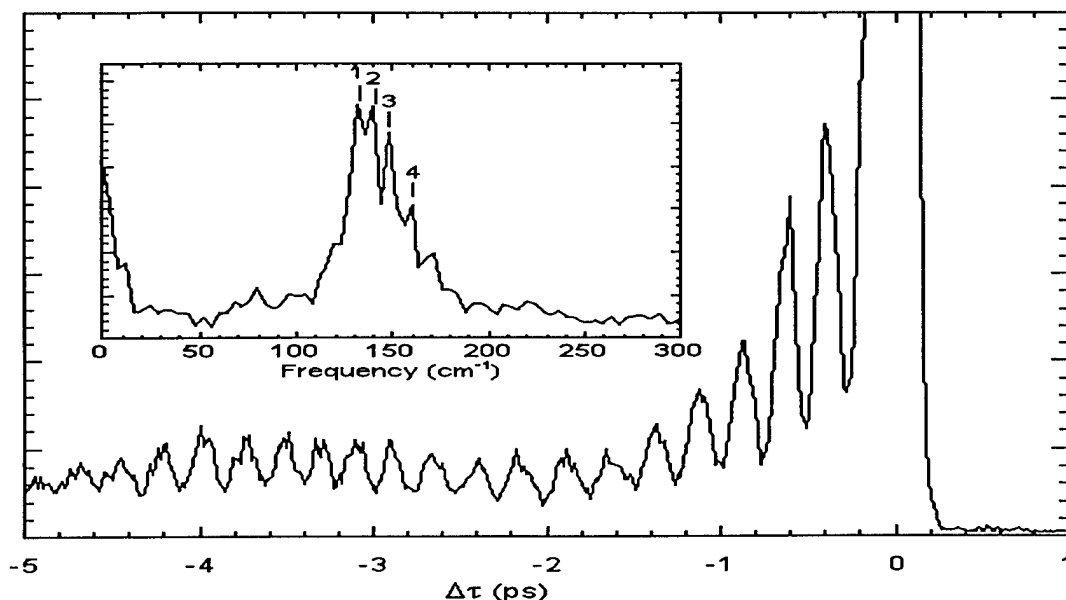
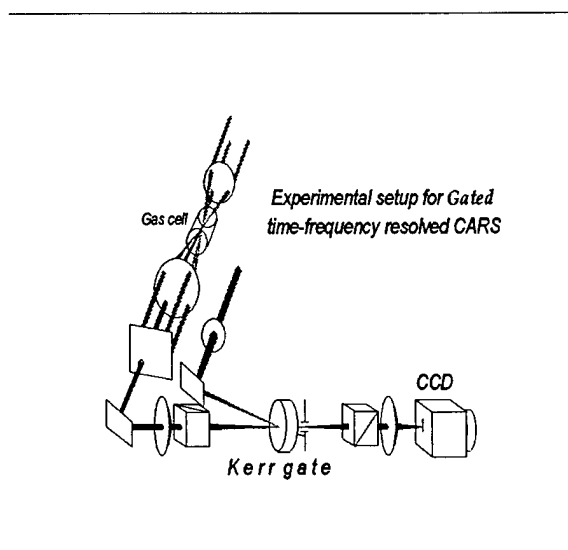
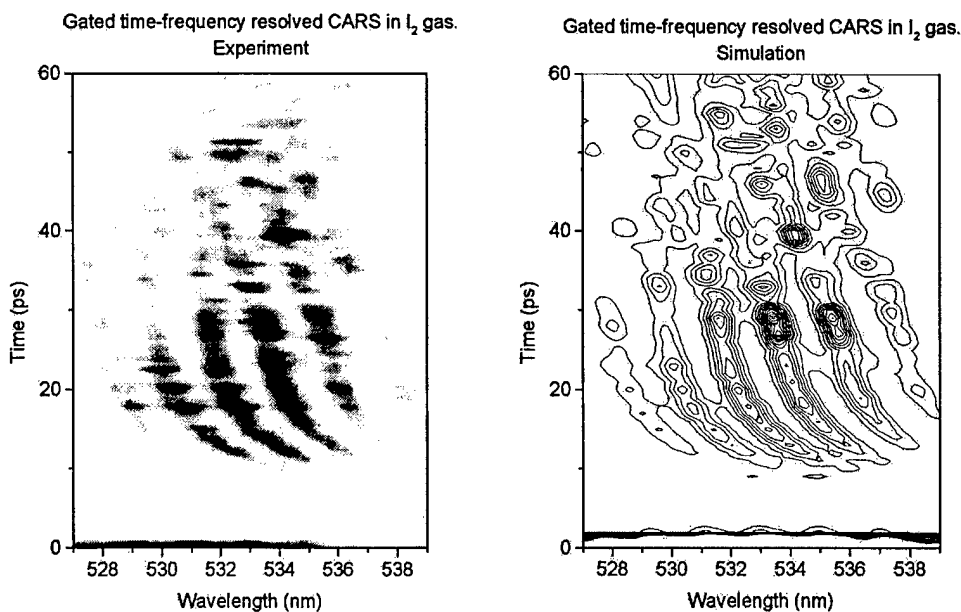


Figure 4: TRCARS spectrum of liquid CCl₄ showing the beat frequencies at 132.5 cm⁻¹, 140 cm⁻¹, 149.2 cm⁻¹, and 160 cm⁻¹, and 8 cm⁻¹, among the molecular (10⁰0), (02⁰0), (11¹0), (03¹0) modes.

A most complete experiment in preparing, interrogating and controlling of molecular coherences, along with spatial (bulk) polarization is obtained through the hybrid scheme of time-gated detection of the frequency resolved third-order polarization, or CARS beam, as illustrated in the experimental diagram below.



This could be nicely illustrated in gas phase molecular iodine as a test study, in which we a direct image of the molecular rovibrational coherence could be obtained. In effect, although we are making measurements with fs pulses, therefore with fs timing, the information content of the time-gated data is rotationally fully resolved. This we illustrate in the figures below, in which the experimental data are simulated with nearly an exact reproduction of the two dimensional interferogram of the third order coherence.



Clearly, the gas phase implementation gives us confidence in the full understanding of the tool. Importing this tool to the solid state has one main challenge, namely the preparation of non-scattering samples. We have succeeded at this task in thin film solid Ar, but do not yet have complete control on reproducibility. Although the funding cycle for this work has already terminated, we still plan to implement the method to follow shock propagation in the solid state. As shown in the theoretical section, there should be a well-defined shock front that corresponds to the excitation of a pair of nearest neighbor atoms, as the front propagates. Such pairs should have a strong Raman signature due not only to polarizability, but also to quadrupole exchange interactions. Despite the universality and sensitivity of this tool, it has a strong shortfall in the case of solid state applications: the samples need be of good optical quality, scattering eliminates the advantage of the coherent signal beam.

D) Strong-Field Excitation:

Electronic excitation, strong electron-phonon coupling, plasma formation, subsequent cavitation and shock, are aspects of detonation physics that are difficult to scrutinize. Guided by a variety of fundamental and practical motivations, we recently completed such studies in superfluid He [15]. We show that intense fs pulses allow controlled cascade ionization, driven by ponderomotive acceleration of quasi-free electrons. The latter correspond to valence electrons for which the Coulomb barrier is completely suppressed due to the applied radiation field. Plasma formation, runaway heating and explosion occur in clumps containing ~ 30 positive ions (60 \AA inter-ion separation) which are capable of trapping electrons produced in subsequent generations. A quantitative model that reproduces the time and space profiles of electrons was developed and implemented with great success. We have since implemented the same principles in free-standing crystals of xenon, in which by strong field pumping using 400 nm fs pulses, we have shown that excitons can be, generated with tremendous efficiency. We expect this to allow us to demonstrate the long sought after solid state Xe_2^* excimer laser at 172 nm . Based on measured number densities, we believe that we have the requisite excitonic number

density for this to occur, however, to prove the contention a direct measurement of line narrowing is planned (not yet accomplished due to the manufacturer's failure to deliver a promised solar blind photomultiplier tube).

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Personnel Supported:

Dr. Dan Rose (postdoc, theory)
Dr. Z. Li (postdoc, theory)
Dr. S. Avanesian (visiting, experiments DFWM in solids)
Dr. J. Almy (Ph. D. 1999) - Theory
Dr. R. Zadoyan, Res. Associate (experiment)
Dr. A. Benderskii (postdoc, superfluid Helium)
Dr. J. Chen Neih (postdoc, TFCARS)
Professor C. C. Martens (summer)
Professor V. A. Apkarian (summer)