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A PROGRAM OF FUNDAMENTAL RESEARCH ON EXPLOSIVES AT LOS ALAMOS

The Fundamental Research on Explosives (FRE) program was initiated as a five-year program beginning in FY 1982. It was established as a Laboratory-wide coordinated theoretical and experimental effort to gain a fundamental understanding of detonation behavior using state-of-the-art techniques not previously applied to explosives. During the five years a variety of significant scientific achievements was made in both theory and experiment by developing new methods and techniques to study equation-of-state (EOS), shock initiation, and detonation phenomena.

The FRE program comprised scientific experimental and theoretical investigations into the chemical and mechanical processes leading to and subsequently sustaining detonation of the simple liquid prototypical explosive, nitric oxide (NO). The goals of the FRE program were to understand the energetics and chemistry of initiation and detonation in liquid NO at the molecular level; and to understand the details of the maintenance of steady detonation of liquid NO and to compare experimental results with existing theory. The knowledge gained and the techniques developed have led not only to advances in explosives science but in the theoretical and experimental sciences in general.

Significant developments resulted from both experimental and theoretical efforts in the study of equations of state of the NO detonation products. Intermolecular potentials were calculated for N_2-N_2 using ab initio and electron gas methods. These N_2-N_2 potentials were used to calculate the shock Hugoniot for N_2 .

Our newly developed methods of treating nonspherical potentials of molecular fluids with effective spherical potentials coupled with existing mixing rules, such as Van der Waals single fluid mixing, was used to model the EOS of the detonation products of NO. Intermolecular potentials used as input were calculated using ab initio and semi-empirical computations.

These results correlated well with experimental shock Hugoniot measurements. Shock Hugoniot were measured for N_2 as well as for liquid $N_2 + O_2$ mixtures and for shocked liquid NO. These measurements allow an assessment of the extent to which equilibrium compositions are attained in liquid NO. Advances in the field of effective spherical potentials for molecular fluids have been made as a result of the development of a perturbation theory for the sphericalization of molecules. Results of the EOS work are illustrated in Fig. 1.

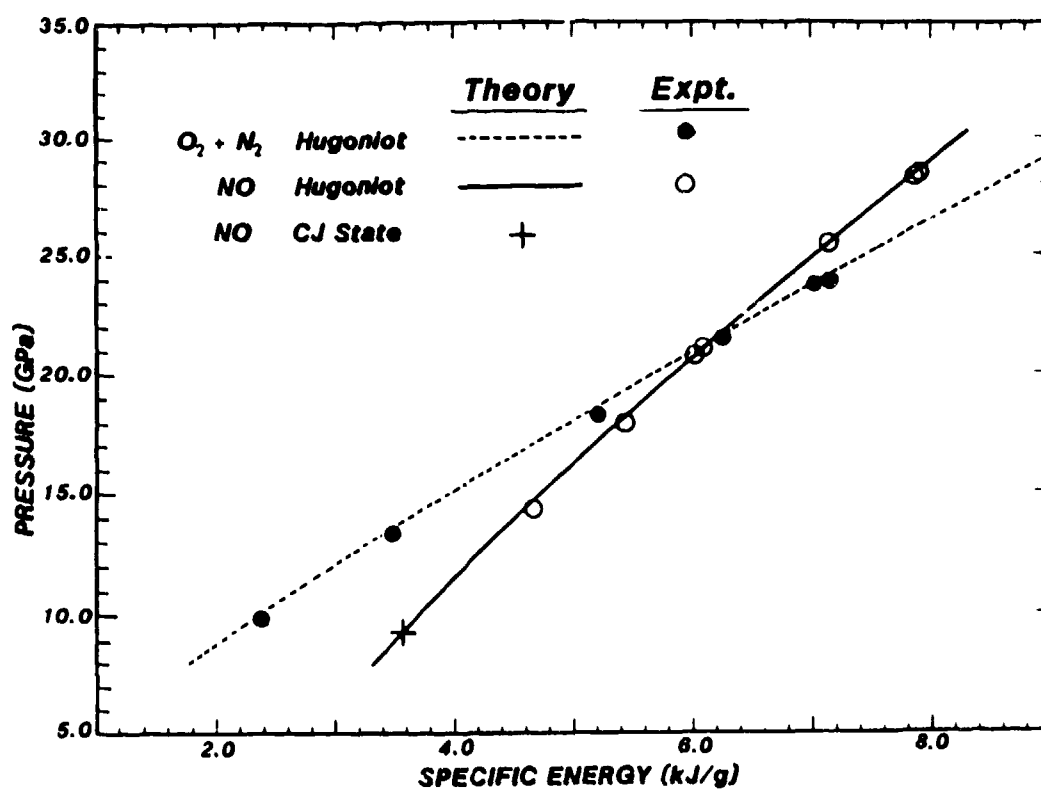


Figure 1. Equation of state for NO products.

At pressures of approximately 21 GPa, the same state is reached by shocking either liquid NO or liquid $N_2 + O_2$ mixture. This condition allowed us to verify that an equilibrium condition exists.

Our EOS work addressed two major deficiencies that exist in present theoretical techniques for evaluating the EOS of dense, hot mixtures of molecular fluids; namely, the deficiencies in treatment of anisotropy of molecules and in mixing of fluids. We have developed a new, approximate variational method for sphericalization and mixing, and a new virial technique for mixing different species.

Quantum-mechanical calculations to determine the structures of NO, its dimers and trimers, and plausible reaction products were done. All geometry optimizations were carried out using a minimal-basis set. Further single-point calculations were done at optimum geometries with a larger basis set and using fourth-order perturbation theory to include correlation effects. These calculations give relative energies for the various species. They also predict heats of formation reasonably close to many experimental values.

Theoretical methods that can be used to calculate the redistribution of internal energy and the subsequent decomposition of a molecule were developed. We found that a very large number of asymmetric transition states exists for N_2O_2 , the dimeric form of NO found in the liquid. This could play a significant role in the mechanism for initiation of a condensed-phase explosive and suggests that no orientation need be preferred for a reaction to occur. Also, an important by-product resulting from this work is that a new numerical technique was developed to accurately and rapidly integrate a large number of differential equations related to the condensed-phase reaction dynamics.

We obtained the first coherent anti-Stokes Raman spectroscopy (CARS) data in materials shock-compressed using a two-stage-light gas gun. The gas gun was used to accelerate a polycarbonate projectile to a desired velocity. The projectile struck a stainless-steel target plate to produce a shock wave that ran forward into a 3-mm-thick liquid sample of either benzene or nitromethane. Liquid NO experiments were also carried out. CARS signals, produced in the shocked samples, were detected and recorded (see Figure 2).

The initial analysis of the spectral shape of the ring-stretching mode of benzene at 10.6 GPa required two spectral lines to fit the measured profile. This differs dramatically from the results for benzene at 7.4 GPa. Spectra from the CN-stretching mode of nitromethane were obtained at several pressures between ambient and 7.6 GPa, where temperatures are approximately 950 K. The results tend to confirm the existence of both benzene and nitromethane intact behind the shock front on a microsecond time scale. The additional lines we observed are believed to be caused by some form of energy transfer or chemical reaction. A schematic of the apparatus is shown in Fig. 2.

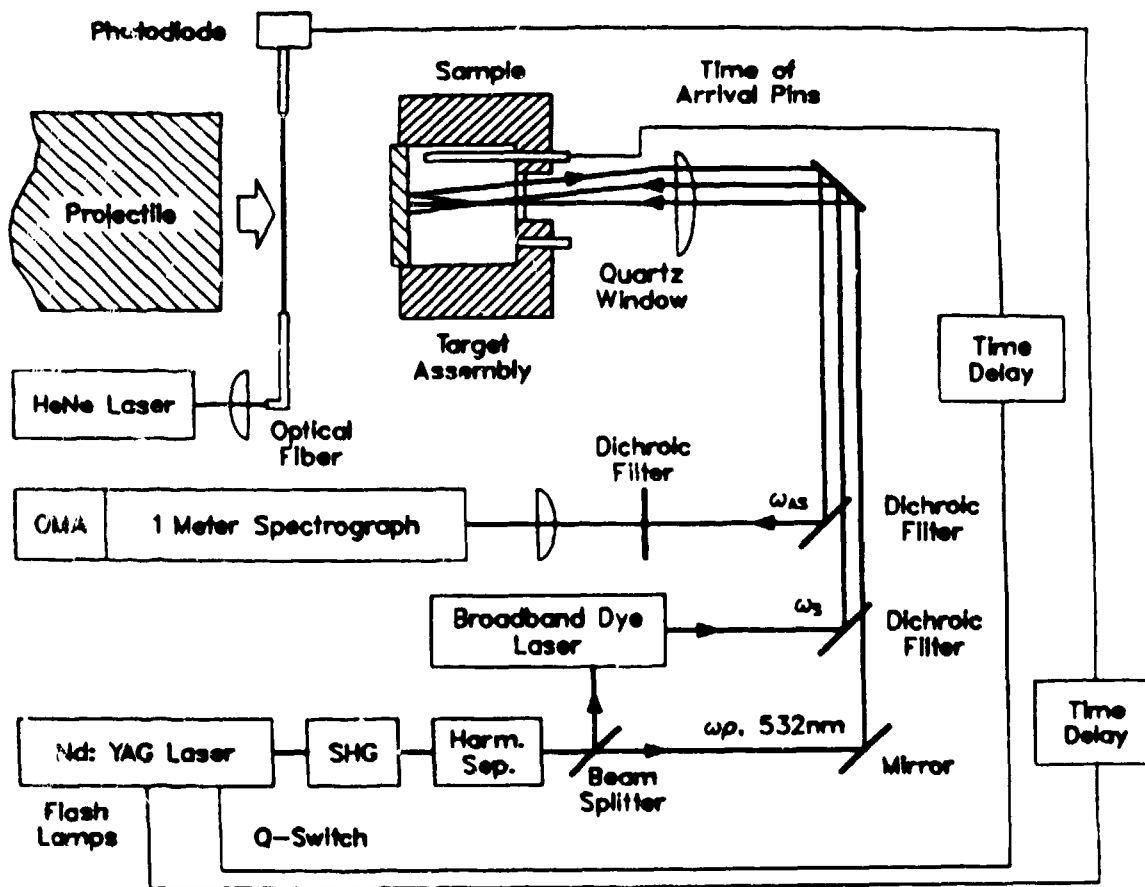


Fig. 2. Schematic of the reflected broadband coherent anti-Stokes Raman scattering experiments.

Much data from analyses of products from pressure-induced chemical reactions of liquid NO have been obtained. These experiments are primarily performed in diamond-anvil cells because they allow us to view the complex chemical reactions of liquid NO, which occur in response to pressures of the same magnitude as those that initiate detonation, but on a longer time scale.

Diamond-anvil-cell research results indicate that N_2O_2 undergoes pressure-induced chemistry that is extremely phase dependent. From a single crystal N_2O_2 we observe N_2 and O_2 as well as N_2O_4 and N_2O . This indicates that the pathway that occurs when liquid N_2O_2 is pressurized is topochemically hindered in solid N_2O_2 . Moreover, the pressure-induced intermediate observed, probably a dimer or trimer of N_2O_2 , is chemically distinct from it and is formed irreversibly. The products N_2O_4 , N_2O_3 , and N_2O appear when this intermediate is subsequently warmed to 300 K, but no N_2 or O_2 result from the reaction. Figure 3 illustrates the diamond-anvil-cell design used in these experiments.

Laboratory-scale studies of NO using a molecular-beam apparatus were done. Nitric oxide was deposited onto a station of a carousel at 25-30 K from a gas flow directed by an adjustable nozzle. The deposited NO was shocked using a slapper/booster arrangement, and the shocked products were analyzed mass spectrometrically. Our resulting data suggest that a fraction of the solid NO detonates upon being shocked using a 22-mg PETN booster pellet. About 20% of the products can be attributed to the reaction $2NO \rightarrow N_2 + O_2$, whereas the reaction $3NO \rightarrow N_2O + NO_2$ accounts for the balance.

Hydrodynamic experiments were performed to determine qualitatively mechanical and inferred chemical phenomenology of initiation and of transmission of detonation in liquid NO. We used image-intensified photography of emitted light, viewed time-resolved along a line with a streak camera. This technique appears to be most advantageous for investigating detonation initiation and wave structure in liquid NO. Composite results of two instances of delayed detonation in shocked liquid NO are illustrated in Fig. 4. Measurements were made by wave arrivals at sample boundaries in one shot and direct, image-intensified streak photography of visible wavelength light in another.

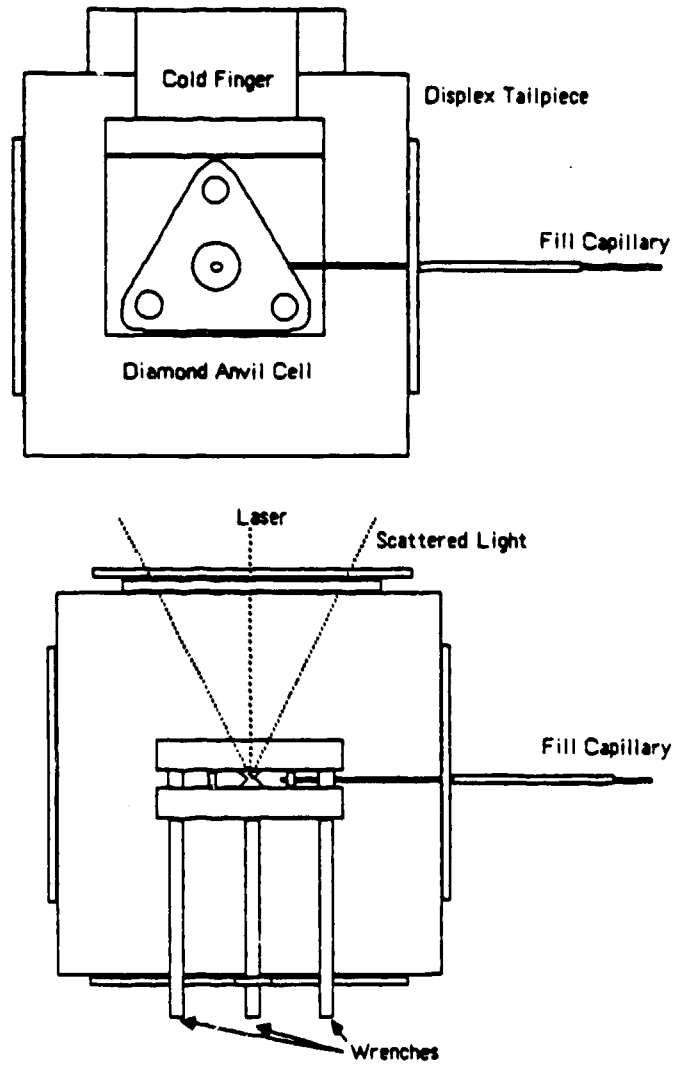


Fig. 3. Diagram of diamond-anvil-cell design for liquid
NO experiments.

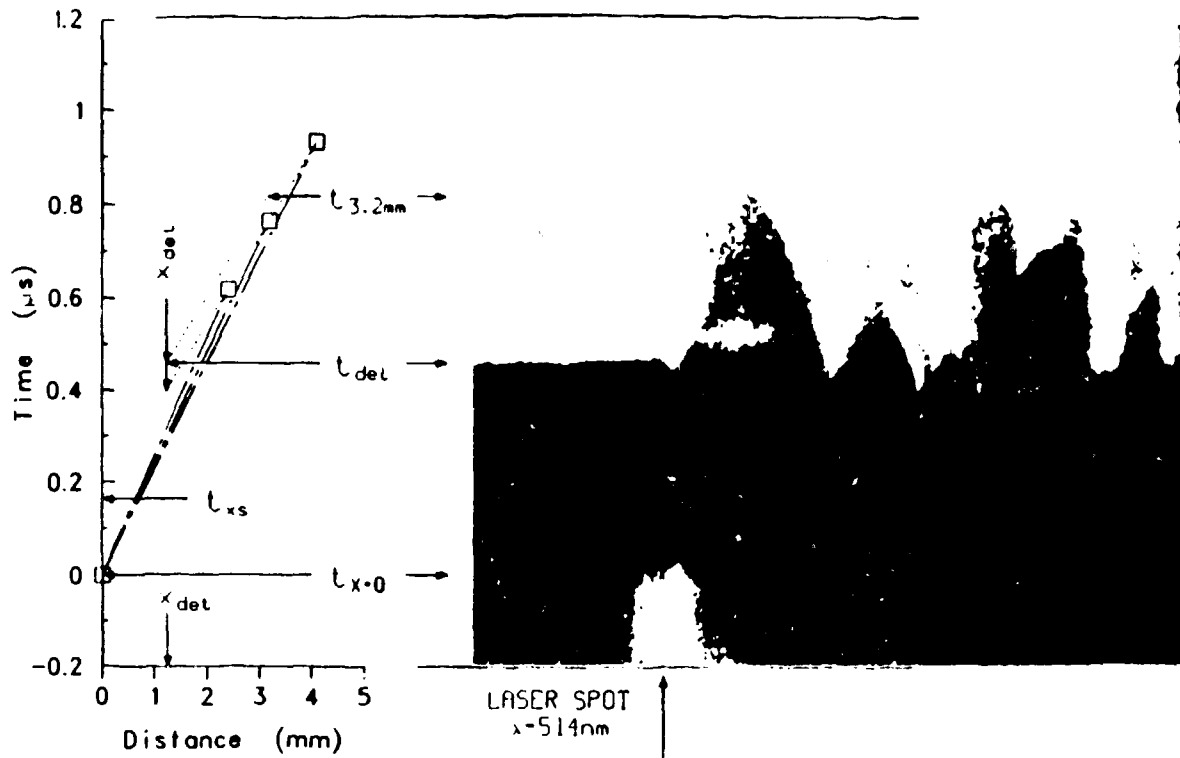


Fig. 4. Results of delayed detonation in shocked liquid NO.

A test of detonation theory is provided by comparing the measured detonation pressure with that obtained from the calculated and measured equation of state of the detonation products. The detonation pressure was inferred from the measured free-surface velocity of a 6061 Dural plate driven by the explosive at the end of its run through 355.6 mm of nitric oxide in the 25.4-mm-diameter tube.

Figure 5 is a plot in the pressure-particle-velocity plane of the Hugoniot curve for Dural and the reflected shock Hugoniot curve for the explosive. Their intersection should be at the point measured in the free-surface velocity experiments if the reflected shock Hugoniot curve is the correct one. The curve is satisfactory within the accuracy of the experimental result.

An important reason for performing these measurements was to try to answer questions raised by speculation that real detonations are weak detonations, not Chapman-Jouguet detonations. Nitric oxide is the only condensed-phase material for which it has been possible to measure the equation of state of the detonation products in separate experiments that are

not detonation experiments. The Chapman-Jouquet state and its reflected-shock Hugoniot, shown in Fig. 5, are calculated from a semiempirical equation of state of equilibrium products from liquid nitric oxide. This is based on the measured shock Hugoniots of oxygen and nitrogen individually and of nitric-oxide products in overdriven detonation states. Hence, it is independent of assumptions about the nature of the unsupported detonation of nitric oxide. The measured point plotted in Fig. 5 is not in disagreement with the assumption that the real detonation is a Chapman-Jouquet detonation. The data are not adequate to put any severe limit on the range of weak (or strong) detonation that might also be in agreement with the data.

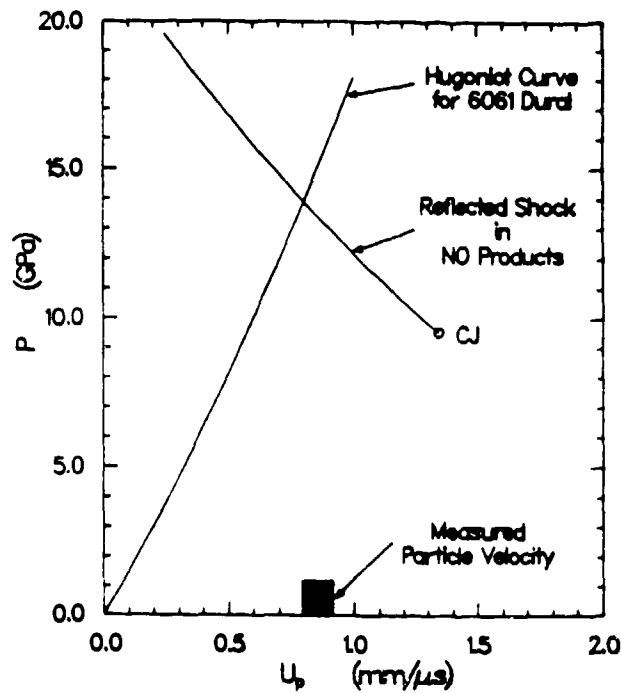


Fig. 5. Matching of NO detonation products into the Dural plate, plotted in the pressure vs particle velocity plane.

A list of publications directly resulting from the FRE program is presented as Table I.

The program officially terminated in FY 1986, with a reduced effort continuing through FY 1987. Liquid NO was chosen as a prototypical explosive because of its relative molecular simplicity. It was expected to be tractable in using modern theoretical methods and Cray computers and still handleable experimentally. Its detonation products, N₂ and O₂, were expected to remain optically transparent even under extreme shock conditions thus making modern ultrafast laser-spectroscopic techniques feasible. Even though a number of significant scientific achievements were attained, the fundamental questions on the detailed chemistry and mechanisms within the reaction zone of a detonating condensed explosive remain unanswered. It appears that even with today's advanced technology we are still not ready to take on this task.