

Title:

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PARTICLE VELOCITY MEASUREMENTS OF THE REACTION ZONE IN NITROMETHANE

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The detonation reaction-zone length in neat, deuterated, and chemically sensitized nitromethane (NM) has been measured by using several different laser-based velocity interferometry systems. The experiments involved measuring the particle velocity history at a NM/PMMA (polymethylmethacrylate) window interface during the time a detonation in the NM interacted with the interface. Initially, Fabry-Perot interferometry was used, but, because of low time resolution (>5 ns), several different configurations of VISAR interferometry were subsequently used. Early work was done with VISARs with a time resolution of about 3 ns. By making changes to the recording system, we were able to improve this to ~ 1 ns. Profiles measured at the NM/PMMA interface agree with the ZND theory, in that a spike (~ 2.45 mm/ μ s) is measured that is consistent with an extrapolated reactant NM Hugoniot matched to the PMMA window. The spike is rather sharp, followed by a rapid drop in particle velocity over a time of 5 to 10 ns; this is evidence of early fast reactions. Over about 50 ns, a much slower particle velocity decrease occurs to the assumed CJ condition – indicating a total reaction zone length of ~ 300 μ m. When the NM is chemically changed, such as replacing the hydrogen atoms with deuterium or chemically sensitizing with a base, some changes are observed in the early part of the reaction zone.

INTRODUCTION

Over the years the reaction zone length of a one-dimensional (1-D) nitromethane (NM) detonation has been estimated to be between a few μ m and a few hundred μ m. These estimates depended both on the experimental method and also on the method used to interpret the data. Prior to this report, the best estimate was made by Engelke and Bdzil¹. They used front curva-

ture measurements on NM detonating in long glass cylinders to develop an estimate that the reaction zone was ca. 36 μ m (~ 6 ns) long.

It has been suggested that it is impossible to measure a 1-D reaction zone in NM. This viewpoint is based on observations of detonation in NM diluted with acetone.² In these experiments, a cellular structure was observed, apparently caused by waves reflecting laterally off of

the walls of the confining tube. These observations indicate three-dimensional (3-D) flow. The assumption has been that this phenomenon also occurs in detonating neat NM, but on a smaller space/time scale. However, there have not been conclusive measurements on pure NM that confirm this. Further, conditions under which 1-D flow undergoes a change to 3-D flow (i.e., cross wave structures) have not been determined.

A number of techniques have been used to directly or indirectly study the 1-D reaction zone in detonating explosives. These have included plate push experiments, detonation front curvature experiments, emitted light measurements and laser velocity interferometry. Because of the high time resolution needed, laser velocity interferometry has yielded the best reaction zone measurements. Using various interferometer setups (ORVIS³, Fabry-Perot⁴⁻⁵, VISAR⁶), studies of a number of explosive materials have been made. Time resolution ranged from 10 ns to < 1 ns, depending on the type of interferometer and the recording technique.

Our objective in this study is to probe the NM reaction zone using laser-based velocimetry and obtain its shape (length, time). Particle velocity profiles at a detonating NM/PMMA window have been measured with time resolutions ranging from about 10 ns to ~1 ns using velocity interferometry. Measurements have been made for pure NM, commercial grade NM, chemically sensitized NM, and deuterated NM.

EXPERIMENTAL DETAILS

Design of the Experiment

It is very difficult to make in-situ measurements of the reaction zone in explosives using embedded gauges. Most gauging methods have time resolutions that are on the order of tens of nanoseconds. Additionally, in the case of NM, it is difficult to mount gauges because it is a liquid. The next best method is to make the measurement at an interface between the detonating HE and an inert material. If the inert material is transparent, laser-based interferometry methods can be employed.

Ideally, one would like the inert window to

not affect the flow in the HE. In practice, this is impossible for the following reasons. First, the HE is reacting and the window is not. Second, the reactant Hugoniot and the product isentrope have different mechanical impedances. Therefore, it is not possible to simultaneously match the impedance of both the reactants and products with one window. Third, the choice of window materials is limited. The best that can be done is to select a window that has a mechanical impedance as close as possible to both the reactant HE and product isentrope.

Figure 1 displays the relevant Hugoniot and isentropes for NM and our window material of choice, PMMA (polymethylmethacrylate), in the pressure(stress)–particle velocity ($P-u_p$) plane. Note that the PMMA window Hugoniot (dashed line) lies midway between the NM reactant Hugoniot (solid lines) and products isentrope (dotted line). This is very close to an ideal situation. The PMMA window should have a mini-

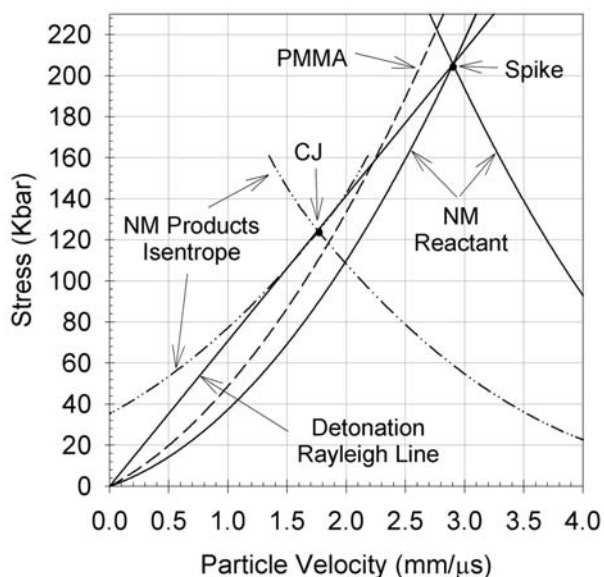


FIGURE 1. NM REACTANT AND PMMA HUGONIOTS AND NM PRODUCTS ISENTROPES USED FOR UNDERSTANDING THE REACTION ZONE MEASUREMENTS IN NM.

mal effect on the flow. Details used to calculate each of the curves follow.

NM reactants Hugoniot: NM reactant Hugoniot data has been taken from 3 sources⁷⁻⁹ with data selected having $u_p \geq 1.25$ mm/ μ s. The data were then fitted to a straight line,

$$U_s = C + Su_p. \quad (1)$$

In Eq. 1, U_s is the shock velocity and C and S are constants which, in the case of NM reactants, have the values of 1.76 mm/ μ s and 1.56, respectively. The shock pressure is then calculated as,

$$P = \rho_0 U_s u_p, \quad (2)$$

where ρ_0 is the initial density (1.128 g/cm³).¹⁰ Note that all the data used to construct the NM Hugoniot were at particle velocities of less than 2 mm/ μ s. The Hugoniot has been extrapolated to 3 mm/ μ s to obtain a prediction of the ZND spike point.

PMMA Window Hugoniot: The Hugoniot of the PMMA window can also be calculated using equations 1 and 2. The following parameters were used; $\rho_0 = 1.186$ g/cm³, $C = 2.59$ mm/ μ s, and $S = 1.52$.¹¹ Because of a chemical reaction or phase transition in PMMA, these parameters are only useful up to a particle velocity of 2.9 mm/ μ s but this is within the range of the present experiments.

NM Products Isentrope: We have assumed that the CJ isentrope of NM products could be approximated by the JWL form;

$$P_s = Ae^{-R_1 V} + Be^{-R_2 V} + CV^{-(\omega+1)}, \quad (3)$$

where P_s is the pressure on the isentrope, $V = v/v_0 = \rho_0/\rho$ is the relative volume, and A , B , C , R_1 , R_2 , and ω are constants. For NM, Dobratz¹⁰ has listed the following values: $A = 2092$ kbar, $B = 56.89$ kbar, $C = 7.70$ kbar, $R_1 = 4.40$, $R_2 = 1.20$, and $\omega = 0.30$.

The isentrope given in Eq. 3, is transformed from the $P-v$ plane to the $P-u_p$ plane using

$$u_p = u_{CJ} + \int_{v_{CJ}}^v \sqrt{\frac{dP_s}{dv'}} dv'. \quad (4)$$

In Eq. (4), v_{CJ} is the CJ volume, and u_{CJ} is the CJ particle velocity. Both can be computed using the jump conditions if P_{CJ} (detonation pressure) and D_{CJ} (detonation velocity) are known. Dobratz¹⁰ gives these values as $P_{CJ} = 125$ kbar, and $D_{CJ} = 6.28$ mm/ μ s.

The CJ isentrope is shown in Fig. 1 as a dotted line. Note that u_{CJ} , the CJ particle velocity is ~ 1.75 mm/ μ s. This goes to ~ 1.8 mm/ μ s when impedance matched onto the PMMA window.

Detonation Rayleigh Line: In the $(P-u_p)$ plane, the equation for the detonation Rayleigh line is,

$$P = \rho_0 D u_p, \quad (5)$$

where ρ_0 is the initial density (1.128 g/cm³), and D is the detonation velocity (6.28 mm/ μ s).

The ZND Spike Point: The spike point is determined by the intersection of the detonation Rayleigh line and the NM reactant Hugoniot. It lies in the neighborhood of 2.9 mm/ μ s and 200 kbars (See Fig. 1). The particle velocity at which the spike occurs (u_{spike}) can be calculated using

$$u_{spike} = (D - C)/S. \quad (6)$$

As is seen in Fig. 1, the spike point matches down in particle velocity to about 2.6 mm/ μ s on the PMMA Hugoniot.

Expected Observations: With Fig. 1 and the above analysis and assumptions in mind, the following conditions were expected in the interface particle velocity records: (1) the ZND spike should be observed at a particle velocity of ~ 2.6 mm/ μ s; (2) the CJ state should be observed at a particle velocity of ~ 1.8 mm/ μ s; (3) using the estimate of 36 μ m for the reaction zone made by Engelke and Bdzil¹ and the 6.28 mm/ μ s detonation velocity, the reaction zone time was expected to be about 6 ns; (4) because the PMMA window lies between the NM reactant Hugoniot and the NM CJ products isentrope, the introduction of the window was expected to have minimal impact on the observed wave profiles.

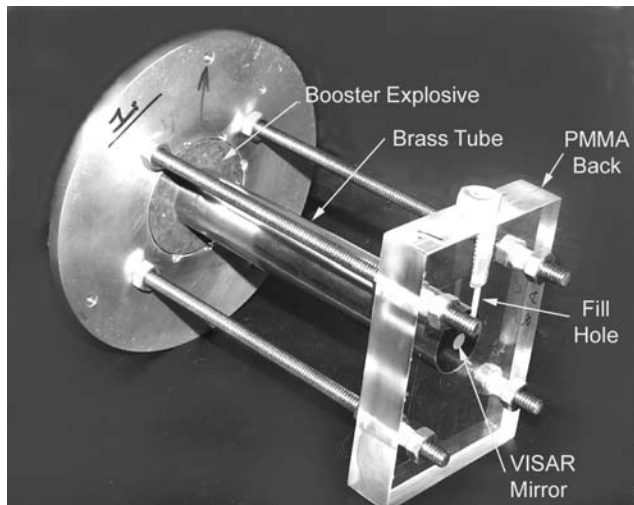


FIGURE 2. OVERALL CONFIGURATION FOR THE NM REACTION ZONE MEASUREMENT EXPERIMENTS. IN THE UPPER LEFT IS THE ALUMINUM TARGET PLATE WHICH IS IMPACTED BY THE GAS-GUN DRIVEN PROJECTILE. THE RESULTING SHOCK THEN INITIATES THE BOOSTER EXPLOSIVE WHICH INITIATES THE NM. THE NM IS CONTAINED IN EITHER A BRASS OR PYREX TUBE. TO THE LOWER RIGHT IS THE PMMA BACK/WINDOW WITH A THIN ALUMINUM LAYER VAPOR PLATED ON THE SIDE NEAR THE NM.

Therefore, the wave profiles reported here are as close to “in-situ” as possible.

Overall Experimental Configuration

The configuration for measuring the detonation wave profile experiments is shown in the photograph of Fig. 2. On the upper left is an aluminum plate with an explosive booster mounted in the center. The booster (PBX 9404 or PBX 9501 – 2 inch diameter by 1/4 inch thick) is initiated using either an explosive plane-wave generator or a gas-gun driven projectile. The detonation in the booster propagates into the NM, overdriving a planar detonation in the NM. The NM is contained in a brass or glass tube about 5 inches long by 1 inch diameter. The glass and brass tubes had wall thicknesses of 0.060 and 0.030 inch, respectively. The NM detonation runs about 5 tube diameters before it interacts with NM/PMMA interface.

In the lower right hand portion of the picture is the VISAR window that is made of 3/4 inch thick PMMA (Rohm and Haas type II UVA Plexiglas). The VISAR mirror is visible as a round spot in the center of the window. A hole, capped with a nylon screw, can also be seen in the PMMA window. This is used to introduce the NM into the tube and to provide a small ullage volume to account for temperature driven volume changes in the NM.

The entire assembly is held together using 1/4-20 brass all-thread and nuts. Seven μm thick Kapton film is epoxied to the surfaces of the PMMA window and explosive booster exposed to the NM – NM is known to dissolve these materials.

Window and Mirror Preparation

Windows and mirrors were prepared as follows. First, the PMMA windows were lapped or ground flat and then polished back to an optical finish to make sure they were flat. Second, a slightly diffuse surface where the VISAR mirror was to be was prepared using a coarse eraser. Next, about 0.4 μm of aluminum was vapor deposited on the somewhat diffuse surface. Finally, a 7- μm thick sheet of kapton film was epoxied on top of the aluminum to protect it from the NM and the hot reaction products. The epoxy bond was typically less than 1 μm thick.

VISAR Setup and System Time Resolution

Over the course of this study, several different interferometer setups were used. In the earliest experiments, Fabry-Perot interferometers were used. Fringe changes were recorded using both electronic and film-based streak cameras. The next set of experiments used a “home-made” VISAR. The latest set of experiments used Valyn VISARs purchased from Valyn International¹². These VISARs allow simultaneous recording with photomultiplier tubes (PMTs) and a streak camera.

Regardless of the interferometer or recording method, each experiment used two interferometers with different velocity per fringe (VPF) constants. This allowed the elimination of the

shock–fringe jump ambiguity. Summaries of the time response of each system follow.

For streak camera recorded Fabry-Perot interferometry, there are two components involved in estimating the time response. First, there is the “camera-time”, a combination of slit width and streak rate. Second, there is the “fill time” of the Fabry-Perot etalon. For these experiments, one system had a camera-time of 6.4 ns and a fill-time of 4.3 ns for an overall time resolution of 7.7 ns. The second system had a camera-time of 3.3 ns and a fill-time of 1.7 ns for an overall time resolution of 3.7 ns; i.e., the Fabry-Perot measurements had time responses between 4 and 8 ns.

The “home-made” VISAR used in early experiments recorded optical signals using PMTs with ~ 3 ns time resolution. Electronic signals from the PMTs were digitized on a 1 GHz scope. The overall response of this system was on the order of 3 to 4 ns.

The latest experiments using the Valyn VISAR are configured in two different ways. One used PMTs supplied by Valyn and the other used PMTs purchased from O. B. Crump. The signals were recorded with either a Tektronix TDS694 with 3 GHz bandwidth or Tektronix TDS684 with 1 GHz bandwidth.

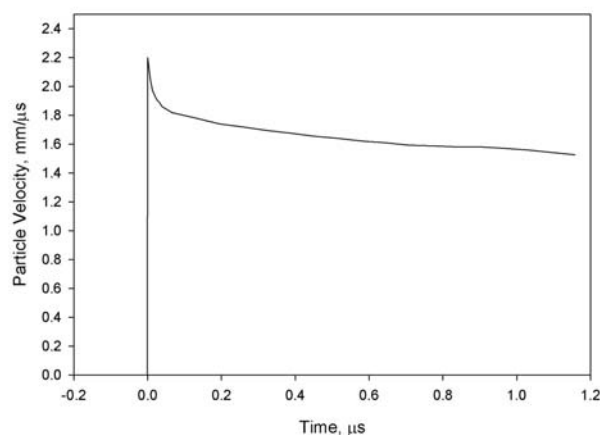


FIGURE 3. DETONATING NM/PMMA INTERFACE PARTICLE VELOCITY PROFILE OBTAINED IN COMMERCIAL GRADE NM USING FABRY-PEROT INTERFEROMETRY. WAVEFORM FROM SHOT 8-294.

Light signals from one of the VISARs was also recorded using an electronic streak camera. Time resolution for this system is estimated to be less than a ns, based on the streak rate and the size of the signal fibers. Streak information from the streak camera was recorded using a computer based CCD array.

Because there was concern that the optical fibers were causing a loss of time resolution, an open beam VISAR setup between the VISAR system and the gun target chamber was used. Light from the laser was transported through the air and then focused on the target. The light that was diffusely reflected from the target mirror was then brought back to the VISARs using lenses and mirrors. Short, ~ 1 m optical fibers were used to couple light from the VISARs to the PMTs or the streak camera.

Several experiments were done to determine the time response of the latest setup. Detonation wave profile measurements, similar to those found in Ref. 6, were used. In these experiments, the detonation wave in PBX 9501 was allowed to interact with a PMMA window.

Using this method, we found the following time responses: (a) using Valyn PMTs the time response was about 2 ns; (b) using O.B. Crump PMTs, the time response was about 1 ns; (c) using the streak camera, the time response was less than a ns.

EXPERIMENTAL RESULTS AND DISCUSSION

Measurements using Fabry-Perot Interferometry

Fig. 3 shows a NM/PMMA interface particle velocity profile from an experiment using the Fabry-Perot setup. In these experiments the commercial grade NM was initiated with an explosive plane-wave lens. The data show that the spike particle velocity is ~ 2.2 km/s, lower than the Fig. 1 predicted value. This was assumed to be the case because of the 4 to 8 ns time response of the Fabry-Perot system. The time to reach the CJ particle velocity of 1.8 km/s is ~ 50 ns. This gives a reaction zone length of ~ 300 μ m, nearly an order of magnitude longer than that estimated by Engelke and Bdzil.¹

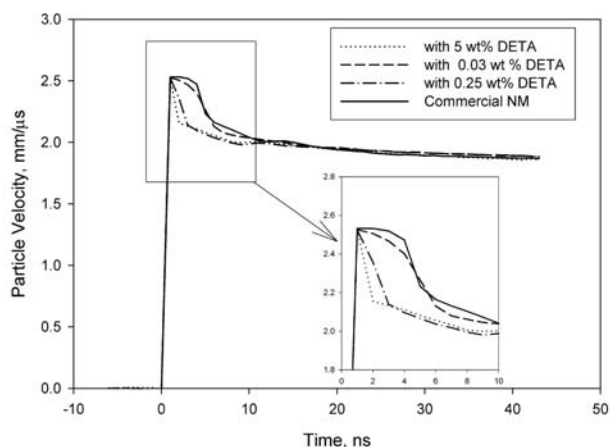


FIGURE 4. PARTICLE VELOCITY PROFILES FROM THE DETONATING NM/PMMA INTERFACE SHOWING THE REACTION ZONE. RECORDINGS WERE MADE USING THE “HOME-MADE” VISAR. THE WIDTH OF THE EARLY PART OF THE WAVEFORMS ORDER WITH THE AMOUNT OF DETA WITH THE WIDEST BEING WITH NO DETA.

Measurements using the “Home-Made” VISAR

Several gas-gun driven experiments, with the experimental configuration shown in Fig. 2, were completed using the “home-made” VISAR system to record the NM/PMMA interface particle velocity. Commercial grade NM was used in these experiments, with diethylene triamine (DETA – an organic base) used to sensitize the NM. Earlier experiments by Engelke had shown that small amounts of this material can have dramatic effects on the detonating NM failure diameter in glass.¹³ It was anticipated that changing the sensitivity would also have an effect on the 1-D reaction zone.

When the waveforms of Fig. 4 were taken, there was cautious optimism that the effect of sensitization on the NM reaction zone was being observed. However, since the differences were on the order of a few nanoseconds, there was concern that the VISAR was not accurately measuring the waveforms. This led us to wait until higher time resolution VISARs were available before publishing the data.

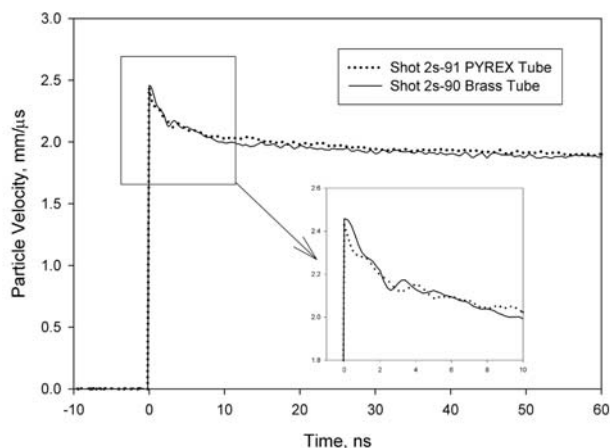


FIGURE 5. PARTICLE VELOCITY PROFILES FROM THE DETONATING NM/PMMA INTERFACE SHOWING THE REACTION ZONE. RECORDINGS WERE MADE USING THE MODIFIED VALYN VISAR WITH 1 NS TIME RESOLUTION. IN ONE EXPERIMENT THE NM WAS IN A PYREX TUBE AND IN THE OTHER A BRASS TUBE.

In these waveforms, the spike is ~ 2.5 mm/ μ s, higher than the Fabry-Perot data and more in line with Fig. 1. The CJ condition is reached at ~ 50 ns, in agreement with the Fabry-Perot measurements.

Measurements using the Valyn VISAR and Upgraded Valyn VISAR systems.

Measurements have been made using a Valyn VISAR and a Valyn VISAR with upgraded PMTs. These experimental setups were as shown in Fig. 2 and used a gas-gun driven projectile to initiate the booster explosive. Pure NM (99+% pure, used as received from Aldrich) was used in these experiments. Profiles from two experiments, one with a brass tube and the other with a glass tube, are shown in Fig. 5.

Clearly, the nearly flat region near the shock observed in Fig. 4 is not present, indicating that this feature was an artifact of the earlier measurements, i.e., the home-made VISAR. However, the spike is shown to be nearly the same, ~ 2.45 mm/ μ s. The reaction zone length appears to be somewhat longer than 50 ns of the earlier measurements.

One thing to notice about all the wave profiles shown in Figs. 3-5 is that the early part of the zone, where the shape is changing rapidly, is on the order of 5 to 10 ns long. After this, it takes a long time for the particle velocity to decrease to a level consistent with the CJ condition indicated in Fig. 1. It may be that the estimate made by Engelke and Bdzil¹ was based on this rapid change more than the overall length. It is also possible that the assumed CJ condition is wrong.

Additional NM reaction zone experiments have been conducted on deuterated NM and amine sensitized NM in brass and glass tubes. They have shown changes in the reaction zone that seem to correlate with the diameter effect curves, i.e., the early part of the reaction zone in deuterated NM is longer and amine sensitization shortens the early part of the reaction zone. However, this work is in progress and the exact nature of the correlation has not yet been determined.

Streak camera records of the VISAR information have been taken on the experiments shown in Fig. 5. However, there has been some difficulty in getting the reduction programs working to carefully analyze this data. In these experiments, the streak camera was recording at a streak rate of 10 ns/mm; faster recording will be necessary to obtain the maximum time resolution in the future. This requires extremely accurate trigger pin placement and times – we are in the process of getting this perfected.

This paper should be considered a work in progress rather than a finished study. We plan to complete this work during the next year. However, it is apparent that the reaction zone in NM has been measured with considerable accuracy and that the measurements agree with what was expected based on Fig. 1. The spike level is ~ 2.5 mm/ μ s and the reaction zone length is on the order of 50 ns or longer.

The measurements reported in this paper provide substantial evidence that the 1-D ZND picture of the reaction zone applies to the detonating NM in these experiments and that the 3-D multi-wave structure, if it is present, is of such a

small scale that it does not preclude accurate measurements.

CONCLUSIONS

The particle velocity at a detonating NM/PMMA interface has been measured with several different laser interferometry techniques. Because of the shock properties of PMMA (having a shock impedance between reactant NM and NM products), this is close to an in-situ measurement. The various measuring techniques provided measurements with time resolutions ranging from 8 ns down to 1 ns, depending on the interferometry method and the recording systems.

At the NM/PMMA interface, the spike was measured to have a particle velocity of ~ 2.45 mm/ μ s. The early part of the reaction zone changes rapidly for about 5 to 10 ns, suggesting that the estimate made by Engelke and Bdzil¹ of 6 ns applies to this region. The particle velocity then decreases slowly over about 50 ns to what is assumed to be the CJ condition. This reaction zone shape indicates the NM reaction mechanism involves some important fast reactions followed by much slower reactions. It has the same general shape as reaction zones that have been measured in solid explosives.³

The data generated in this study indicate that the 1-D ZND model of detonation applies to these NM experiments. If there are 3-D multi-wave structures present in the detonating NM, they are on a very small scale and do not effect the measured states to any significant extent. This is important new information from this study.

The chemical nature of the NM affects the reaction zone. Deuterated and amine sensitized NM experiments indicate that at least the early part of the reaction zone is changed as a result of the chemical changes. This indicates that the early reactions are those affected by small changes in chemistry. This viewpoint is consistent with production of the aci-ion in NM being one of the important early reactions in NM. More careful measurements will be required to elucidate this phenomenon completely.

ACKNOWLEDGEMENTS

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