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Multiple Roles of Highly Vibrationally Excited Molecules in the Reaction Zones of Detonation Waves

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Recent experimental and theoretical advances in the understanding of high-pressure, high-temperature chemical kinetics are used to extend the nonequilibrium Zeldovich−von Neumann−Doring (NEZND) theory of self-sustaining detonation in liquid and solid explosives. The attainment of vibrational equilibrium behind the leading shock front by multiphonon up-pumping and internal vibrational energy redistribution establishes a high-temperature, high-density transition state or series of transition states through which the chemical decomposition proceeds. The reaction rate constants for the initial unimolecular decomposition steps are accurately calculated using high-temperature, high-density transition-state theory. These early reactions are endothermic or weakly exothermic, but they channel most of the available energy into excited vibrational states of intermediate product species. The intermediate products transfer some of their vibrational energy back into the transition states, accelerating the overall reaction rates. As the decomposition progresses, the highly vibrationally excited diatomic and triatomic molecules formed in very exothermic chain reactions are rapidly vibrationally equilibrated by "supercollisions", which transfer large amounts of vibrational energy between these molecules. Along with vibrational−rotational and vibrational−translational energy transfer, these excited vibrational modes relax to thermal equilibrium by amplifying pressure wavelets of certain frequencies. These wavelets then propagate to the leading shock front and reinforce it. This is the physical mechanism by which the leading shock front is sustained by the chemical energy release.

1. Introduction

The nonequilibrium Zeldovich−von Neumann−Doring (NEZND) theory of a self-sustaining detonation wave[1−5] was developed as a framework in which to study the major chemical and physical processes that precede and follow exothermic chemical reaction. These nonequilibrium processes determine the time required for the onset of chemical reaction, control the energy release rates, and supply the mechanism by which the chemical energy sustains the leading shock wave front. The three-dimensional shock wave front structure, the nonequilibrium excitation and relaxation processes, and the chemical reaction rates in gaseous detonation waves are fairly well understood.[6] However, the high pressures (20−40 GPa), densities (2.5 g/cm^3), and temperatures (3000−5000 K) generated in less than a microsecond in condensed phase detonation waves traveling at velocities approaching 10 mm/μs create environments that are extremely difficult to study experimentally and theoretically. In this paper, recent experimental progress in understanding vibrational excitation of shocked molecules, high-temperature unimolecular decomposition reaction rates, and vibrational energy transfer among highly excited reaction product molecules is used to extend the NEZND model of self-sustaining condensed phase detonation waves.

Figure 1 shows the four main regions of the NEZND reaction zone for a detonation wave in a solid or liquid explosive containing carbon, hydrogen, oxygen, and nitrogen atoms ($C_wH_xO_yN_z$). The first region is the leading shock wave front, which consists of a three-dimensional arrangement of Mach stem interactions. The familiar cellular patterns of gaseous detonation wave fronts have been observed on a much smaller spatial scale in homogeneous liquid explosives.[7] The current state of knowledge of the leading shock front in solid explosives was recently reviewed by Tarver et al.[5] The shock front in detonating heterogeneous solid explosives is more complex than those in homogeneous liquids or perfect single crystals, because the presence of voids, grain boundaries, and internal crystal flaws creates an irregular shock compression process.[5] Within this complex shock front, the explosive is compressed and accelerated, and the phonon modes of the explosive molecules are excited to an extremely high phonon quasitemperature within a picosecond.[8]

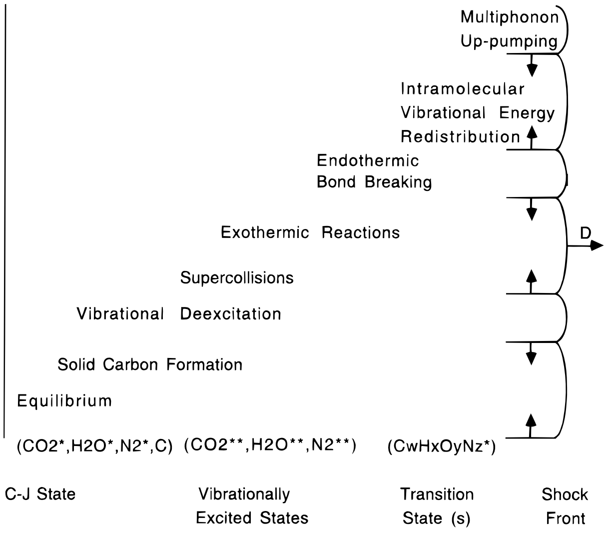

Figure 1. Nonequilibrium ZND (NEZND) model of detonation in an organic solid or liquid explosive $C_wH_xO_yN_z$.

Following shock front compression, the second region in Figure 1 is dominated by the flow of the excess phonon energy into the low-frequency vibrational modes of the molecule and the subsequent energy flow from the low-frequency modes to the high-frequency modes. Dlott and Fayer[9] plus Tokmakoff et al.[10] termed the phonon excitation process "multiphonon up-

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pumping" and labeled the lowest frequency vibrational modes "doorway modes" through which the vibrational energy flows. The excitation of the high-frequency modes occurs by intramolecular vibrational energy redistribution (IVR).[11] These processes are now being intensively studied experimentally and theoretically. Dlott et al.[12,13] recently measured the up-pumping and IVR rates in liquid nitromethane and found that complete equilibration required approximately 100 ps. They also found that some intermediate frequency vibrational levels couple better with the low-frequency modes than others, and these modes temporarily acquire more vibrational energy than that corresponding to the final equilibrium temperature. They called the subsequent equilibration of these intermediate levels "vibrational cooling". Molecular dynamics studies of these relaxation rates have shown that the equilibration time depends on the number of doorway modes and the shock pressure. For example, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)[5] and triaminotrinitrobenzene (TATB),[14] which have several low-frequency vibrational modes, equilibrate in approximately 10 ps compared to 100 ps for nitromethane, which has fewer low-frequency modes. The longest times for vibrational equilibration behind strong shock waves in condensed materials are approximately 10 ns for diatomic liquids, such as N_2 and CO, measured by Schmidt et al.[15] The establishment of vibrational equilibration behind the leading shock front is a necessary condition for chemical decomposition, because the initial bond breaking reaction proceeds through a transition state created by the vibrational excitation of one of the highest frequency modes.

The first two regions of the NEZND model for detonating solid explosives are being studied by several investigators, so this paper focuses on the third and fourth regions where chemical reaction dominates the flow process. The third region of Figure 1 begins at the internally equilibrated transition state (or states), which is followed by the chemical reconstitution process in which the large organic molecules eventually produce several stable reaction product molecules. Little is known about this region which is referred to as the "von Neumann spike" or "chemical peak" in condensed phase explosives literature, because spikes or peaks in pressure or particle velocity are observed in or inferred from hydrodynamic experiments. Recent experimental and theoretical research has yielded some information about the state which precedes the exothermic chemical reaction. Direct observation of transition states in gaseous reactions is now possible,[16] but a direct probe of the transition state in a detonating solid or liquid explosive is not. However, Sheffield[17] has observed using laser interferometry a plateau in particle velocity preceding product expansion that lasts several nanoseconds in detonating nitromethane. Spectroscopic studies of nitromethane shocked to pressures approaching those in detonation waves have measured the rates of disappearance of some nitromethane peaks and the appearance of some reaction product peaks in the submicrosecond time frame.[18,19] The unreacted Hugoniot states calculated[3] using realistic high-pressure, high-temperature equation of state assumptions[20] agree with those measured by nanosecond time resolution probes.[21−23]

Once the exothermic chain reaction process begins, highly vibrationally excited product molecules form and interact with the transition states and each other to greatly increase the rates of decomposition. Recently "supercollisions", in which large amounts of vibrational energy are transferred between highly excited molecules in gas-phase collisions, were discovered.[24] Similar supercollisions are likely to dominate the energy transfer in the dense mixture of highly vibrationally excited detonation products. This new phenomenon is applied to condensed phase detonation reaction zones in section 2.

The fourth region in Figure 1 is dominated by the expansion and vibrational deexcitation of the stable reaction products plus the diffusion-controlled formation of solid products, such as carbon particles in underoxidized explosives. Experimental techniques with nanosecond time resolution for measuring pressure,[25] particle velocity,[26] and temperature[27] have yielded average values for these parameters as the Chapman−Jouguet (C−J) state of thermal and chemical equilibrium is approached in several solid and liquid explosives. This region is discussed in detail in section 3.

In addition to vibrational−rotational and vibrational−translational energy transfer, an essential process in the attainment of thermal equilibrium in the reaction products is the amplification of pressure wavelets by the energy released during transitions from higher to lower vibrational levels during compression by these wavelets. It has long been known that the complex three-dimensional structure of self-sustaining detonation waves develops because the shock wave front is unstable to pressure wavelets of certain frequencies[28] and that a substantial fraction of the chemical energy released must somehow be communicated to the shock front.[1] In this paper, amplification of these pressure wavelets by vibrational deexcitation is identified as the physical mechanism by which the internal chemical energy of the product molecules sustains the leading shock front at an overall constant velocity. This mechanism is discussed in detail in section 4, and some of its implications are discussed in section 5.

2. Transition State and Chemical Reconstitution Region

Once the high-frequency vibrational modes are thermally equilibrated, the large explosive molecule can begin its decomposition process through one or more[29] transition states. Since the initial endothermic bond breaking reactions are the rate-limiting steps, a great deal of effort has been applied to calculating their reaction rate constants as functions of temperature and pressure for shock and detonation conditions. A large body of experimental evidence for gas-phase unimolecular decomposition reactions under shock conditions have demonstrated that the rates do not follow a simple Arrhenius dependence at high temperatures, but instead "fall-off" to a less rapid rate of increase.[30] Nanosecond time-resolved measurements of the reaction zone profiles of solid explosives "supracompressed" or "overdriven" by external pistons to pressures and temperatures much higher than those attained in self-sustaining detonations showed that their reaction rates increase very slowly with shock temperature.[31] Eyring[32] attributed this "falloff" in unimolecular rates at the extreme temperatures and densities attained in shock and detonation waves to the close proximity of vibrational states, which causes the high-frequency mode that becomes the decomposition pathway in the transition state to rapidly equilibrate with the surrounding vibrational modes by IVR. These interacting modes then form a "pool" of vibrational energy in which the energy required for decomposition is shared. Any large quantity of vibrational energy that a mode receives from an excitation process, such as the relaxation of an electronically excited state to a ground state with the resulting high vibrational level excitation,[33] are equilibrated by IVR before decomposition can occur. Conversely, sufficient vibrational energy from the entire pool of oscillators is statistically present in the decomposition mode long enough to cause reaction. The main effect of this rapid IVR at high densities is to decrease the rate constant dependence at high temperatures. The reaction rate constant K for this transition state is given by

$$K = (kT/h)\, \mathrm{e}^{-E/\kappa} \sum_{i=0}^{s-1} (E/RT)^i \mathrm{e}^{-E/RT}/i! \qquad (1)$$

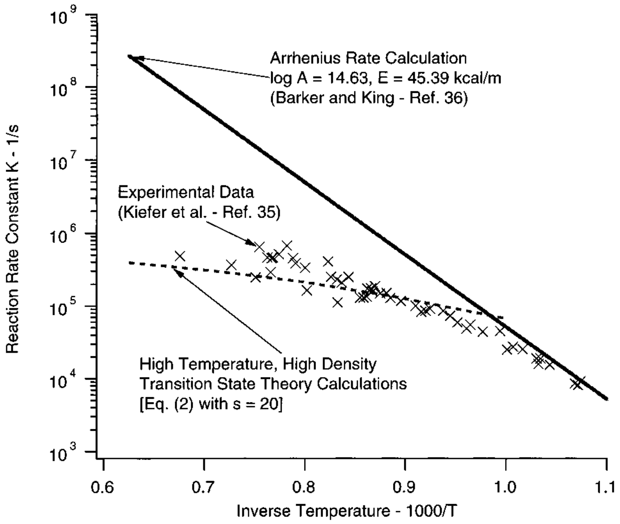


Figure 2. Reaction rate constant versus inverse temperature for the unimolecular decomposition of norbornene.

where E is the activation energy; T is the equilibrated temperature; k, h, and R are Boltzmann's, Planck's, and the gas constant, respectively; and κ is the average vibrational energy and s is the number of the vibrational modes interacting with the dissociation mode. When the total energy in these vibrational modes equals the activation energy, $\kappa = E/s$, and eq 1 becomes

$$K = (kT/h)\mathrm{e}^{-s} \sum_{i=0}^{s-1} (E/RT)^i \mathrm{e}^{-E/RT}/i! \qquad (2)$$

Tarver[3] demonstrated that accurate reaction rate constants could be calculated for detonating solid and liquid explosives using eq 2 with realistic equations of state and reasonable values of s.

Currently the only experiments in which unimolecular reaction rate "falloff" can be measured directly are shock tube studies of rather simple molecules at low concentrations in inert gases. Several reactions have demonstrated unimolecular rate "falloff" under shock conditions,[34] but the first one to be studied completely is the decomposition of norbornene to 1,3-cyclopentadiene and ethylene in a krypton bath by Kiefer et al.[35] The unimolecular reaction is

$$C_7H_{10} \rightarrow C_5H_6 + C_2H_4 \qquad (3)$$

Detailed modeling of these experiments by Barker and King[36] using Rice−Ramsperger−Kassel−Marcus (RRKM) reaction rate models showed that the dissociation incubation (induction) times were at least a factor of 3 greater than the measured IVR times; the unimolecular falloff at temperatures above 1000 K could be calculated only with the measured lower temperature activation energies by assuming incubation (induction) times of 5−15 μs; and the average $\langle \Delta E_{\mathrm{down}} \rangle$, the average energy lost by the norbornene per collision with a Kr bath molecule, used in the calculations was reasonable. Figure 2 shows that the reaction rate constants at temperatures exceeding 1000 K calculated directly using eq 2 with $s = 20$ and $E = 45.39$ kcal/m agree extremely well with those measured by Kiefer et al.,[35] which are considerably slower than the Arrhenius rate expression in Figure 2 that fits several sets of experimental data below 1000 K.[36] Twenty is a reasonable number of neighboring vibrations for this reaction, because only the modes involving 6 or 7 of the 17 atoms in the norbornene molecule are close enough to influence the transition state. Equation 2 is an accurate representation of the norbornene reaction kinetics above 1000 K without using assumptions concerning the incubation (induction) time or the preexponential factor. In detonation waves of condensed phase explosives, the densities of the shocked, unreacted explosives are much greater, the temperatures are similar, and obviously there are no inert-gas collisions to decrease the internal energy of the transition state. Thus the effects of the nearest-neighbor intramolecular vibrational modes and perhaps even intermolecular modes in a strongly hydrogen-bonded lattice, such as that of TATB, on the transition state are very strong. However, the vibrational modes on the opposite end of a large explosive molecule have little or no effect on this transition state. Thus it is not surprising that $s = 20$ in eq 2, rather than $s = 78$ for the entire HMX molecule for example, yields reasonable unimolecular decomposition rates at the states attained in detonation waves.[3]

When the decomposition from the explosive molecule's initial transition state begins, smaller fragments are formed. Although the initial reactions are endothermic or slightly exothermic, the available internal energies are channeled mainly into vibrational energy, unless there is a large energy barrier at a relatively large distance into the exit channel for the fragments requiring substantial translational energy to surmount.[37] Even in this case, the fragment does not retain this translational energy for long, because the high-density ensures prompt collisions which transfer energy to the rotational and vibrational modes. Since the number of vibrational levels decrease with the size of reaction product fragments, the new vibrational levels on the average contain more vibrational energy. For example, HMX and the related molecule 1,3,5-trinitro-*s*-triazine (RDX) are known to decompose thermally through several possible mechanisms,[38] involving the breakdown of ring structure into mono-, di-, and trimolecular fragments of methylene nitramine, $CH_2{=}N{-}NO_2$. One such decomposition path is

$$C_4H_8N_8O_8 \xrightarrow{1} C_3H_6N_6O_6 + CH_2{=}N{-}NO_2 \qquad (4)$$

$$CH_2{=}N{-}NO_2 \xrightarrow{2} CH_2{=}O^* + N_2O^* \text{ (or } HCN^* + HNO_2^*) \qquad (5)$$

$$CH_2{=}O^* + N_2O^* \xrightarrow{3} H_2O^{**} + N_2^{**} + CO^{**} \qquad (6)$$

$$2\,CO^{**} \overset{4}{\leftrightarrow} CO_2^{**} + C \qquad (7)$$

where * denotes low levels of vibrational excitation and ** denotes high levels of vibrational excitation. At the high pressures and temperatures reached in detonation reaction zones, the carbon equilibrium lies to the right in eq 7, so mainly CO_2 and solid carbon are present. Other possible decomposition pathways begin with the breaking of the N−N bond and the formation of NO_2 radicals, but the following general statements about internal vibrational excitation of the intermediate radicals and products hold for any decomposition scheme. If another stable transition state for the monomer unit $CH_2{=}N{-}NO_2$ in eq 5 exists for any length of time, its decomposition kinetics will be based on its vibrational levels and their degrees of excitation. As HMX decomposes and smaller products are formed, the exothermic chemical energy released resides in fewer vibrational modes. The overall numbers of internal modes for HMX and its products under detonation conditions are

$$C_4H_8N_8O_8 \rightarrow 4CH_2{=}N{-}NO_2 \rightarrow 4CH_2{=}O + 4N_2O \rightarrow 4N_2 + 4H_2O + 2CO_2 + 2C \qquad (8)$$

$$3 \rightarrow 12 \rightarrow 24 \rightarrow 36 \text{ translational modes}$$

$$3 \rightarrow 12 \rightarrow 24 \rightarrow 24 \text{ rotational modes}$$

$$78 \rightarrow 60 \rightarrow 36 \rightarrow 24 \text{ vibrational modes}$$

Classical dynamics simulations of the unimolecular decomposition of RDX by Chambers and Thompson[39] and $CH_2{=}N{-}NO_2$ by Rice et al.[40] have yielded relative reaction rates and product energy distributions for some of the possible reaction schemes. These calculations predicted significant levels of vibrational excitation in intermediate products such as CH_2O^*, HONO*, and H_2CN^*.

As the reactions in the decomposition process start forming relatively stable intermediates (CH_2O^*, N_2O^*, HCN*, HNO_2^*, etc.) in slightly exothermic steps and then final products (H_2O^{**}, N_2^{**}, CO_2^{**}, and CO**) in very exothermic steps, the internal vibrational excitation increases enormously, because most of the chemical energy is initially released into the vibrational modes.[41] The transfer of vibrational energy in IVR processes in dilute gaseous diatomic product molecules at relatively low levels of excitation occurs in steps of one quantum of energy with the probability of relaxation per collision increasing with the square of vibrational energy level.[42] This rate of deexcitation could not account for the rapid expansion of the products observed in detonation reaction zone measurements. However, "supercollisions" have recently been observed in which large amounts of vibrational energy are transferred between highly vibrationally excited polyatomics in one collision.[43] Experiments have shown that supercollisions, while relatively rare in inert-gas baths, still transfer significant amounts of vibrational energy accelerating the IVR process.[44] Several quanta of vibrational energy are transferred between excited large molecules, such as toluene[45] and pyrazine,[46] and CO_2, and among triatomics (NO_2, CO_2, and N_2O).[47]

Therefore, within the chemical reconstitution region of a condensed phase detonation wave, supercollisions should dominate, and the transfer of vibrational energy between highly excited small product molecules and the remaining large explosive fragments should be extremely efficient. The chain reaction processes start immediately following the initial reaction, because a greater percentage of collisions involving highly vibrational excited species are reactive.[1−5] Within nanoseconds, a mixture of highly vibrationally excited H_2O^{**}, N_2^{**}, CO**, and CO_2^{**}, along with atoms and/or ring fragments of carbon, is created. The most highly excited molecules react immediately in chain branching reactions[1] or vibrationally equilibrate with their nearest neighbors by IVR. Some examples of supercollisions occurring during HMX decomposition are

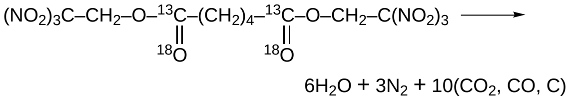
$$CO_2^{**} + C_4H_8O_8N_8 \rightarrow CO_2^{*} + C_4H_8O_8N_8^{*} \quad (9)$$

$$H_2O^{**} + C_3H_6N_6O_6 \rightarrow H_2O^{*} + C_2H_4O_4N_4 + CH_2{=}N{-}NO_2 \quad (10)$$

$$N_2^{**} + CH_2{=}N{-}NO_2 \rightarrow N_2^{*} + CH_2{=}O^{*} + N_2O^{*} \quad (11)$$

$$CO_2 + H_2O^{**} \rightarrow CO_2^{*} + H_2O^{*}, \text{etc.} \quad (12)$$

During supercollisions between two or more highly excited polyatomic molecules, atom-exchange reactions are energetically possible. This process offers an explanation of the results of detonation calorimetry experiments on isotopically labeled solid explosives. McGuire and Ornellas[48] found that isotopically labeled carbon (^{13}C) and oxygen (^{18}O), originally present in the C═O groups of bis(trinitroethyl) adipate (BTNEA), which are the strongest bonds in that molecule, were equally distributed among the reaction products containing carbon and oxygen. The BTNEA reaction is



$$(NO_2)_3C{-}CH_2{-}O{-}{}^{13}\underset{\underset{^{18}O}{\|}}{C}{-}(CH_2)_4{-}{}^{13}\underset{\underset{^{18}O}{\|}}{C}{-}O{-}CH_2{-}C(NO_2)_3 \longrightarrow 6H_2O + 3N_2 + 10(CO_2, CO, C) \quad (13)$$

Since the ^{13}C and ^{18}O were not preferentially found in CO and CO_2, the isotopic labeled atoms were exchanged for other C and O atoms during highly excited reactive collision processes, such as

$$^{13}C{=}^{18}O^{**} + C{=}O^{**} \rightarrow {}^{18}O{=}C{=}O^{**} + {}^{13}C \quad (14)$$

$$^{13}C + CO_2^{**} \rightarrow {}^{13}CO^{*} + CO^{*} \quad (15)$$

$$^{13}CO^{*} + CO_2^{**} \rightarrow {}^{13}CO_2^{**} + CO^{*} \quad (16)$$

$$H_2O^{**} + {}^{18}O{=}C{=}O^{**} \rightarrow H_2{}^{18}O^{**} + CO_2^{**}, \text{etc.} \quad (17)$$

Isotopically labeled ^{13}C experiments on detonating mixtures of trinitrotoluene (TNT) and RDX by Anisichkin et al.,[49] in which the methyl groups of TNT had an increased level of ^{13}C, yielded nearly complete scattering of the carbon. There was only some localization of ^{13}C in the small amount of ethylene formed, because the decomposition of TNT starts at the methyl groups. Thus the presence of such supercollisions correlates with the rapid IVR observed among the highly vibrational excited reaction products and the atom randomization found in isotopically labeled calorimetry experiments.

The initial degrees of vibrational excitation in H_2O^{**}, N_2^{**}, CO**, and CO_2^{**} are difficult to calculate, because the high densities and pressures attained behind the shock front cause a significant fraction of the internal energy to be present in the form of potential or cold compression energy.[50] The complex mixture equation of state of the reaction products must account for the release of this cold compression energy upon expansion.[3,5] However, in powerful solid explosives such as HMX, there is sufficient chemical energy from the heat of reaction plus internal energy of the unreacted explosive at the transition state to populate the product molecules' vibrations to the $v = 4$ and $v = 5$ levels.[1,3] The high density of vibrational states and the anharmonicity of the levels within the various product molecules result in a wide range of energies that can be transferred by IVR in supercollisions. At the C−J equilibrium temperature of approximately 4000 K for HMX, most of the nitrogen, carbon dioxide and water molecules are in the $v = 1$ and $v = 2$ levels. Therefore all of the transitions from the $v = 4$ and $v = 5$ levels down to the $v = 1$ and $v = 2$ levels are involved in the internal energy equilibration process.

3. Vibrational Deexcitation and the Approach to Equilibrium

Once the main exothermic chain reactions are over and the product gases are formed in highly vibrationally excited states, vibrational deexcitation processes control the flow. The local pressure and density of the mixture decrease, and the translational and rotational energies increase through vibrational−translational and vibrational−rotational energy-transfer mechanisms. In the one-dimensional ZND model, the processes cause the products to expand down the Rayleigh line from the von Neumann spike state to the C−J state. Within the complex three-dimensional cellular structure, the products expand behind the individual shock wave that caused the local reaction. As the products expand, their cold compression (potential) energy is also released.

These processes can be quite fast. The time resolution of the current Fabry−Perot laser interferometers used to record particle velocity histories in detonating solid explosives is approximately five nanoseconds.[51] In Fabry–Perot studies of the nearly oxygen balanced solid explosive, pentaerythritol tetranitrate PETN ($C_5H_8N_4O_{12}$), a chemical reaction zone that is distinct from the rarefaction process beyond the C–J state has not yet been resolved.[52] The experimental particle velocity histories in PETN can be modeled by assuming an instantaneous reaction to the C–J state and a Jones–Wilkins–Lee (JWL) reaction product equation of state based on a C–J pressure of 31.5 GPa.[52] The electrical conductivity probe developed by Hayes[53] has a subnanosecond time response and detects the presence of solid carbon behind the leading shock front. Hayes observed the presence of very small quantities of carbon in high-density PETN products approximately 1 ns after shock front arrival. Thus chemical reaction and a major portion of the vibrational deexcitation of the detonation reaction product gases can occur within a few nanoseconds of the passage of the leading shock front in an oxygen-balanced explosive.

However, most condensed phase explosive molecules are carbon-rich and oxygen-poor, and thus significant amounts of solid carbon are formed early in the reaction sequence. Hayes measured the electrical conductance of the reaction products of nitromethane, composition B (a mixture of RDX and TNT) and liquid TNT, and found that the conductance began at low levels within 5 ns of detonation shock front arrival, increased to a maximum value inversely proportional to the explosive's oxygen balance over tens of nanoseconds, and then tailed off. This late time decrease was attributed to the diffusion-controlled growth of solid graphite and/or diamond particles, which are poor conductors. Hayes' interpretation has been confirmed by Fabry–Perot and ORVIS measurements of the reaction zone profiles of several explosives. Underoxidized solid and liquid explosives exhibit a rapid decay in particle velocity or pressure from the von Neumann spike state followed by a much slower rate of decay that lasts considerably longer. The fast rate of energy release is controlled by the vibrational deexcitation process, while the slower rate is controlled by solid carbon coagulation.[5] HMX exhibits a rapid energy release for approximately 40 ns, followed by a slower process requiring 100–200 ns.[30,54] TNT's main energy release occurs in about 80 ns, followed by a slower process lasting about 200–300 ns.[30,55] The same processes in TATB take approximately 100 and 300–400 ns, respectively.[30,54] Two values for the reaction time in detonating nitromethane have long been reported, with the rapid reaction lasting a few nanoseconds and a slower rate lasting tens of nanoseconds.[56] The slow energy release during solid carbon formation and the presence of a rarefaction wave immediately following the reaction zone make it extremely difficult to locate the C–J state in self-sustaining condensed phase detonation waves.[5] Therefore vibrational deexcitation of H_2O^{**}, N_2^{**}, CO_2^{**}, and CO^{**} can occur in less than 10 ns, but it is usually slowed to tens of nanoseconds by the presence of atoms or small fragments of solid carbon. This is reasonable, because the collisions between vibrationally excited molecules and carbon atoms are not effective in terms of vibrational–translational energy transfer. Carbon acts as a diluent that hinders the internal energy transfer among the vibrationally excited small gaseous molecules, so the greater the amount of solid carbon formed, the slower the relaxation process.

The initial state of the carbon formed in the reaction zone depends on the structure of the explosive molecule. In HMX and RDX, the carbon atoms are separated by nitrogen atoms and thus the carbon coagulation process starts at individual atoms. Greiner and Blais[57] have observed the sequential arrival of various carbon species C, C_2, C_3, C_4, C_5, etc., in mass spectrometric studies of detonation products escaping from a free surface. In carbon-rich aromatic explosives, such as TNT and TATB, most of the carbon becomes solid-state diamond or graphite, so the majority of the benzene rings do not have to decompose to carbon atoms. It would be extremely unfavorable energetically for the entire explosive molecule to decompose to atoms before the exothermic reactions begin. The reconstitution reactions begin forming intermediate products as soon as the first endothermic bond-breaking reactions occur, so the reaction sequence progresses rapidly from molecules to intermediate fragments to stable products. Recent experimental and theoretical results have shown that benzene and anthracene can dimerize under shock compression.[58] Thus the solid carbon coagulation process in aromatic explosives proceeds mainly through the attachment of benzene rings and fragments of rings rather than individual carbon atoms. The growing masses of solid carbon agglomerate together at the active sites as they diffuse through the turbulent reaction product gases. The solid carbon phase diagram at these high temperatures and pressures is very complex.[59] Graphite, diamond, amorphous, and even liquid carbon[60] can be formed in the reaction zone. The study of the formation of solid carbon particles in detonation waves is a very active field of research, especially in the former Soviet Union, where the nanometer-size diamonds recovered from the detonation of solid explosives are used commercially.[61]

When the carbon coagulation is complete, the pressures, particle velocities, densities, and temperatures are very close to those predicted by the chemical and thermal equilibration assumptions of C–J theory. Wood and Salzburg[62] proved that the equilibrium sound velocity in the reaction products controls the rate of propagation of any detonation wave. In condensed phase detonations, chemical and thermal equilibrium are attained, but more time is required for internal energy relaxation and carbon coagulation, and thus reaction zone lengths are longer than previous estimates.[63]

4. Wavelet Amplification by Vibrational Deexcitation

Although carbon formation determines the overall reaction zone length, it does not contribute chemical energy to the support of the leading shock front. This energy comes from the deexcitation of the initially highly vibrationally excited diatomic and triatomic product molecules, which occurs earlier in the equilibration process.

Cowperthwaite and Adams[64] showed using a polytropic equation of state that the chemical energy released in the reaction zone must supply approximately three-eighths of the total energy required to sustain the leading shock front. For gaseous detonations, using experimental product energy distribution results, the amount of vibrational energy initially present in the products was shown to be greater than the vibrational energy at the C–J state plus the chemical energy required for wave support.[1] In condensed explosives, the problem is more complicated, because the difference between the cold compression (potential) energy of the unreacted explosive and the products at the C–J state accounts for some of the total energy released.[3] However, a similar fraction of the chemical energy released is required to sustain the shock front. Since the products are initially excited to $v = 4$ or higher, and the C–J equilibrium vibrational energy levels at 3000–5000 K are significantly lower, generally $v = 1$ or $v = 2$, there is sufficient "excess" vibrational energy initially present in the products to provide the necessary chemical energy for shock front support.[3]

The physical mechanism by which this excess vibrational energy communicates with the leading shock front and maintains the cellular structure is intimately coupled to the inherent instability of the detonation wave. Erpenbeck[65] and others demonstrated that the leading shock wave front is unstable to perturbations introduced into the reaction zone, because this

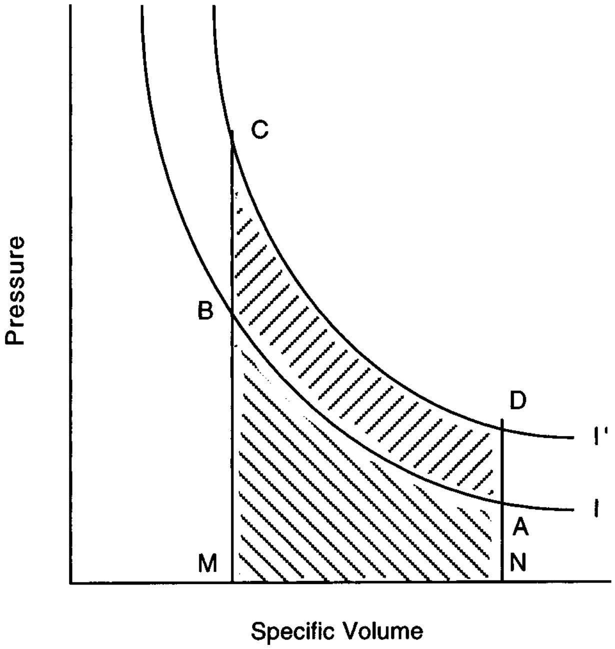


Figure 3. Pressure-specific volume diagram compression cycle of a vibrationally excited molecule by a pressure wavelet.

entire region is subsonic with respect to the shock and thus such perturbations eventually overtake the shock. These perturbations occur naturally due to the turbulent nature of the interaction between exothermic chemical reactions and hydrodynamic flow.[66] The most complete instability analysis is that of Abouseif and Toong,[67] who demonstrated for two-dimensional detonation waves that the transverse waves of the Mach stem structure of the leading shock front develop with particular wavelengths and that a most unstable, long-wavelength transverse wave is produced which governs the cell size at the shock front. Therefore only wavelets of certain frequencies are amplified by chemical energy as they propagate through the region of highly vibrational excited products. Srinivasan and Vincenti[68] defined two necessary conditions for a bath of vibrational excited molecules to amplify acoustic waves: the degree of vibrational excitation must be sufficiently high and the vibrational relaxation time must be a decreasing function of temperature. Both of these conditions are satisfied in the highly vibrationally excited reaction products produced by the exothermic chain reactions. If a molecule undergoes a loss of one or more quanta of vibrational energy as a pressure wavelet passes over it, the amplitude of that wavelet is increased by absorbing some of this energy. Experiments[69] and theoretical instability analyses[70] have shown that weak shocks and deflagration waves can be amplified by exothermic reactions. The opposite effect, shock wave damping by a fluid which lacks vibrational energy, is a well-known phenomena.[71] These amplified pressure wavelets then propagate to the detonation front, and each shock wave in the three-dimensional front is reinforced to some extent by the arrival of pressure wavelets from the reaction zone behind it.[72]

The amplification process can be visualized by reversing the discussion of Zeldovich and Raiser on the damping of a wave in a gas which lacks vibrational energy.[73] Figure 3 shows the compression−expansion cycle in pressure−volume space for a wavelet propagating in a gas which is highly vibrational excited. The gas is rapidly compressed by the leading edge of the wavelet from point A to point B in Figure 3 along a frozen isentrope I. The work done on the gas is equal to the area ABMN. The gas temperature and pressure increase while the vibrational energy is unchanged. Then, for the time duration of the pulse, the gas density does not change. The number of collisions is increased and the highly excited molecules can more easily undergo a transition to a lower vibrational energy level. Part of this transition energy is transferred to the translational and rotational degrees of freedom, and the temperature and pressure increase from point B to point C in Figure 3. Since the volume does not change, no work is done going from B to C. After the wavelet passes, the gas expands rapidly along another frozen isentrope I′. The work done by the gas is equal to area DCMN in Figure 3. Finally there is a relatively slow transition from point D to point A at constant volume in which the pressure drops to the original value. Thus, during the expansion from C to D, the gas does more work on the surroundings than was done to it during the compression phase A to B. Therefore the gas donates to the wavelet an amount of energy ABCD in Figure 3 equal to the difference between the work on and by the relaxing gas. The wavelet is amplified or strengthened by energy from the vibrational deexcitation process. As the wavelet propagates through the excited reaction products, this amplification process is repeated many times. The amplified pressure wavelet then propagates at the local sound speed through the reaction zone and overtakes the detonation wave front. As shown by instability analyses, only wavelets of certain frequencies are effective in this process.[67]

The overall energy balance for self-sustaining detonation wave propagation requires that the energy transmitted by the pressure wavelets to the leading wave front resupply the energy lost by the individual shock waves as they compress and heat the unreacted explosive molecules. The rate at which the wavelets reinforce the detonation front in turn depends upon the overall amount of “excess” vibrational energy present and the vibrational deexcitation rates. This process of chemical amplification of pressure wavelets by vibrational deexcitation is the means by which the exothermic chemical reaction sustains the complex leading detonation wave front, which precedes the reaction zone by many nanoseconds.

5. Summary and Conclusions

The NEZND theory of detonation in condensed explosives is extended to include recent experimental and theoretical research on the vibrational excitation processes that precede, control the rates of, and follow the chemical reaction sequence. The establishment of one or more transition states following multiphonon up-pumping and rapid IVR behind the shock front is necessary to start the decomposition sequence that converts a large explosive molecule into 7−11 diatomic and triatomic product molecules. These small molecules are known to be formed in highly vibrationally excited states. They accelerate the decomposition process by transferring vibrational energy to the reacting species. These highly excited molecules vibrationally equilibrate very rapidly with each other through supercollisions that transfer several quanta of vibrational energy in one collision. The vibrational deexcitation of these equilibrated products requires many more collisions when solid carbon is present as a diluent. During this relaxation and expansion time, pressure wavelets of certain frequencies passing through the vibrationally excited products are amplified by the energy liberated during downward vibrational level transitions. These wavelets then propagate to the detonation front and interact with it to restore the energy expended by the individual shock waves as they compress and heat the unreacted explosive. The amplification of pressure wavelets by the relaxation of highly vibrationally excited products and the subsequent interaction of these wavelets with the leading shock or compression wave are also likely to be important processes in the acceleration of the leading waves during shock initiation,[74] deflagration-to-detonation transition (DDT),[75] converging detonation,[76] and other nonsteady reactive flows.[77]

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