

On the correlation between energy transfer rates and drop hammer sensitivities of some explosives

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Energy transfer rates between molecular vibration (vibron) and lattice vibration (phonon) of crystalline explosives were estimated on the basis of a simple master equation analysis. Ab-initio molecular orbital calculations were performed to construct vibrational energy level diagrams of explosives at the B3LYP/6-31G(d) level of theory. By using these calculated vibrational frequencies, vibrational excitation rates were calculated with the assumption of a preferential energy transfer for resonant processes between vibrons and phonons. Resulting vibrational excitation rates of some explosives such as NQ, NTO, TNB, TNT, RDX, HMX, Tetryl, and PETN were compared with the drop hammer sensitivities. Beside of very crude assumption used in the model, correlation was found between excitation rates and impact sensitivities.

1. Introduction

Understanding of impact sensitivities of explosives is essential for the safe handling of these materials. Such knowledge is also required for the design of new high performance explosives. Several studies have been performed in the past in order to clarify factors that govern the impact sensitivities. As a result of these studies, many correlations were found between impact sensitivities and molecular properties. These findings include correlations with values of OB_{100} which is a measure of oxidant balance¹⁾, the electrostatic potential at the midpoint of the longest C-NO₂ bond in polynitroaromatic molecules²⁾, molecular electronegativities³⁾, and energy levels of electronically excited states and structures of molecules⁴⁾. In addition, there has been numerous computational analysis of the role of molecular structure and crystal state⁵⁾. In spite of these efforts, there are still many problems in the understanding of impact sensitivity. Empirical correlations between sensitivity and molecular

property give some insight of chemical processes in the impact initiation of explosion, but it only gives information of the static nature of the processes. Since impact initiation is essentially dynamical process, impact sensitivity can largely be affected by a dynamical behavior of the molecule. For example, Kohno et al. recently performed ab-initio and MD (Molecular Dynamics) calculations for the initiation of nitramines⁶⁾. They suggested importance of the intra-molecular energy transfer among N-NO₂ moieties in the initial decomposition of nitramines.

One of the most popular and oldest methods used to determine impact sensitivities of explosives is the drop hammer test. Typical results of drop hammer test show that ignition of a 50 mg explosive sample occurs when the change in kinetic energy of the drop hammer is on the order of a few joules and that initiation occurs from several to tens of microseconds after the impactor comes in contact with the sample⁷⁾. As pointed out by McNesby and Coffey⁸⁾, the change in sample temperature for the typical test of 50 mg RDX with impact energy of 2J is only 30 K. This temperature rise is clearly insufficient to initiate reaction in practically all explosives. Therefore, the kinetic energy of the impactor must be localized over a small fraction of the entire

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sample, and the initiation process should be highly non-thermal and non-equilibrium process. One of the possible factors contributing to low energy impact initiation is the rate that determines the onset of chemical reactions. When a mechanical impact is imposed to molecular crystalline explosives, the excess mechanical energy is eventually dissipated into a bath consisting of low frequency mode of lattice vibrations (phonons). The excess phonon energy is then transferred to vibrational energy of explosive molecules in a crystal. As a result of this vibrational excitation, the weakest bond of the molecule is broken and radicals will be produced. These radicals initiate chain reactions, which cause the onset of detonation. This general picture of the shock/impact initiation was proposed by Dlott et al. and described in Ref.9 in detail.

Actual initiation of explosion in the drop hammer test can be caused by the formation of hot spot^{11,12)}, which is formed by adiabatic compression of small void in the sample powder. In this case, impact sensitivity is largely dependent on the physical property of the sample not only on the chemical properties. However, it has been shown that shock sensitivity is strongly correlated to impact sensitivity¹²⁾. Given the strong correlation between shock and impact sensitivity, we expect that impact sensitivity is also related to the energy transfer rates that govern the shock sensitivity. Indeed, the impact sensitivities estimated by the drop hammer tests is found to correlate with energy transfer rates between phonons and vibrons. Fried and Ruggiero¹³⁾ have calculated the total energy transfer rate from phonons into a given vibron band in terms of the density of phonon states and the anharmonic vibron-phonon coupling factors. They estimated the phonon up-conversion rates as a function of temperature and vibrational frequency, and demonstrated that the energy transfer rate at 425 cm^{-1} is linearly dependent on the impact sensitivity. They pointed out that the vibrational frequency around 425 cm^{-1} corresponds to nitro group vibration in the explosives examined in their work. This suggests that nitro group motions could possibly play an important role in determining impact sensitivity.

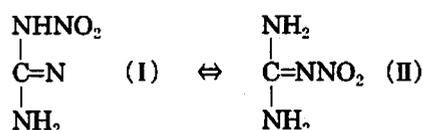
McNesby and Coffey⁸⁾ also demonstrated such a correlation between impact sensitivity and phonon-

vibron energy transfer rates. Their theory used Raman spectra of energetic materials to construct vibrational energy diagram, which were then used to calculate the rate of energy transfer from phonon to near-resonant vibron. Overall rates of vibrational excitation were calculated by solving a master equation, in which Fermi's Golden Rules determined the energy transfer rates among vibrational levels. Good correlation was found between calculated overall vibrational excitation rates and impact sensitivities.

Investigation of the relationship between energy transfer rates and impact sensitivities is important for the understanding of initiation mechanism for explosives. In the present work, we modify the model of McNesby and Coffey in order to test the correlation between energy transfer and impact sensitivity for more wide range of explosives. To this end, vibrational frequencies of all normal modes were obtained by using ab-initio molecular orbital calculations for NQ (nitroguanidine), NTO (5-nitro-1, 2, 4-triazol-3-one), TNB (trinitrobenzene), TNT (2, 4, 6-trinitrotoluene), RDX (hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine), HMX (octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocine), PETN (pentaerythritol tetranitrate), and Tetryl (2, 4, 6-trinitrophenylmethyl-nitramine). These vibrational frequencies are used as inputs for the master equations describing the energy transfer processes between phonon and vibron. Results are compared with drop hammer impact sensitivities of these explosives.

2. Vibrational Frequencies and Vibrational Density of States

Structures and normal mode vibrational frequencies of explosives molecules were obtained by using Gaussian98 program¹⁴⁾. Structure optimization was performed at the B3LYP/6-31G(d) level of theory, and resulting structures used in the present work are given in Fig.1. Some of the explosives studied in this work have several isomers. For example, two melting points ($232\text{ }^{\circ}\text{C}$ and $257\text{ }^{\circ}\text{C}$) are reported for NQ, and two isomers exist¹⁵⁾:



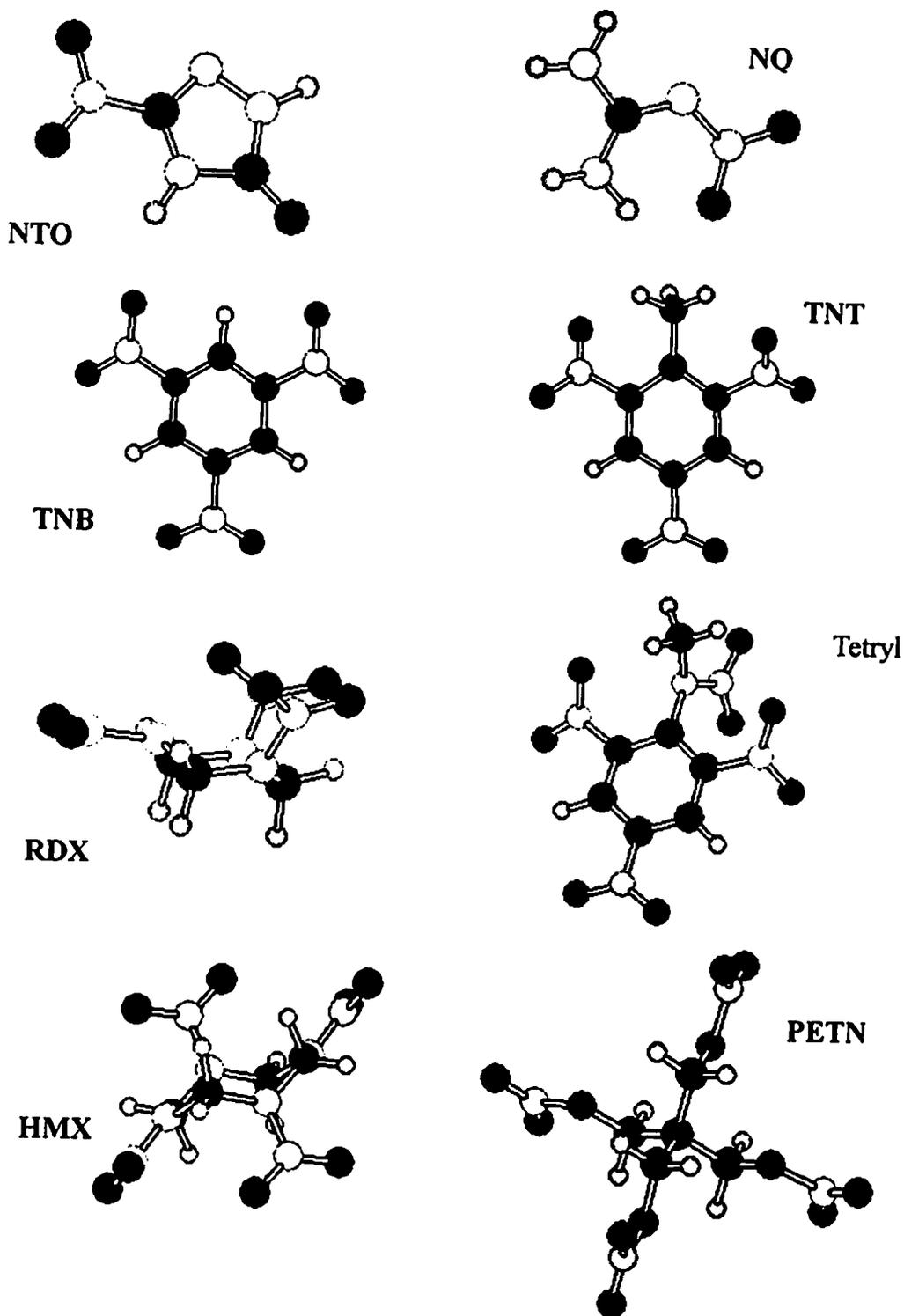


Fig. 1 Optimized molecular structures of explosives obtained at the B3LPY/6-31G(d) level of theory.

Usual NQ may contain both forms, but more stable isomer (II) is considered in the present work. RDX also has several conformers. The conformers of RDX differ mainly in the position of the nitro groups relative to ring atoms. The ring atoms are arranged in the chair conformation. The conformers are

labeled according to axial (A) or pseudo-equatorial positioning (E) of the nitro groups about the ring¹⁶⁾. Four conformers, AAA, AAE, AEE, and EEE are possible. Neutron diffraction measurements of solid α -RDX (the form that is stable at room temperature) provided the crystal structure and

atomic arrangements of the molecules in the crystal that was consistent with AAE form. On the other hand, the AAA and EEE conformers are suggested as possible structures for RDX in vapor and β -solid phases both have C_{3v} symmetry. These structures are thought to be very unstable. The AAE conformer is considered in the present study and is shown in Fig.1. HMX has four isomers known as the α , β , γ , and δ form. The β form is stable at room temperature and is used in the general application. The structure and vibrational frequencies of the β form is calculated in the present work, and the β form structure is shown in Fig.1.

Following the geometry optimization in the DFT calculations, normal mode analysis is performed to obtain the vibrational frequencies. The frequencies obtained at the B3LYP/6-31G(d) level of theory are scaled by a factor of 0.9613.

The vibrational frequencies are calculated for isolated molecules. On the other hand, molecules in the explosives are in the molecular solid crystals. Vibrational frequencies in the crystal should be different from those for isolated molecules. However, intermolecular interaction in the molecular crystal is generally very weak, and it is expected that the differences in vibrational frequencies are small. In order to confirm this, we took high resolution Raman spectra of these explosives at low temperatures and compared with the calculated vibrational frequencies for isolated molecules¹⁷⁾. Although there are some small discrepancies (with in 50 cm^{-1} difference), overall agreement between observed and calculated values is quite satisfactory. Therefore the values of vibrational frequencies for isolated molecules are used for the further analysis without any correction for the intramolecular interaction in the solid phase.

According to the theory proposed by Dlott et al.⁹⁾, impact and shock sensitivity is determined by the rate of excitation to the low frequency vibrational modes (so called "doorway" modes). The rate of vibrational excitation is faster for the vibrational manifold having larger density of state. Therefore, it is expected that the sensitivity has strong correlation to the density of state at low vibrational frequencies. Vibrational densities of states were calculated by a direct counting method. Results are

shown in Fig.2 for eight explosives studied in this work. The Density of states may be larger for the molecules containing more atoms. However, it is also largely dependent on the structure of the vibrational spectrum. A molecule having lower frequency has higher density of state and the rate of energy transfer from phonons (lattice vibrations) may be faster. It is noted that sensitive explosives such as HXM, PETN, and Tetryl have very large density of states, whereas the densities of states are quite low for less sensitive explosives such as TNB, NTO, and NQ, as shown in Fig.2.

3. Energy Transfer Model

Most of secondary explosives are molecular solids consisting of large organic molecules. Because secondary explosives are stable molecules with large energy barriers to chemical reaction, a sizable amount of energy must be transferred from phonons to internal vibrations (vibrons) of molecules in the crystal before the onset of chemical reactions. Vibrons relevant to bond fission generally have frequencies greater than 1000 cm^{-1} , whereas phonon energies are usually less than 200 cm^{-1} . Therefore, it is clear that phonon energy must be converted to higher vibrations by multi-phonon up pumping processes.

Dlott and Fayer⁹⁾ have studied multi-phonon up conversion processes associated with shock induced chemical reaction. They derived a simple expression for the phonon-vibron energy transfer rate. In their model, the dominant mechanism for up-pumping is anharmonic coupling of excited phonon modes with low frequency molecular vibrations. The low frequency vibrational mode, which energy is resonant with the energy of multi-phonon state, is termed as "doorway mode". The mechanical energy imposed by shock is quickly deposited in the external modes and redistributed among all the phonons. This temporal "phonon rich" region is attained within about 1 ps. Vibrons are not excited yet at this stage. The energy in phonon modes is then transferred to the vibrons by multi-phonon up-pumping processes, and the two baths (phonon bath and "doorway vibration" bath) equilibrate with in about 100 ps. This temporal zone is termed as "up-pumping zone". As the vibrational modes in the doorway states are excited,

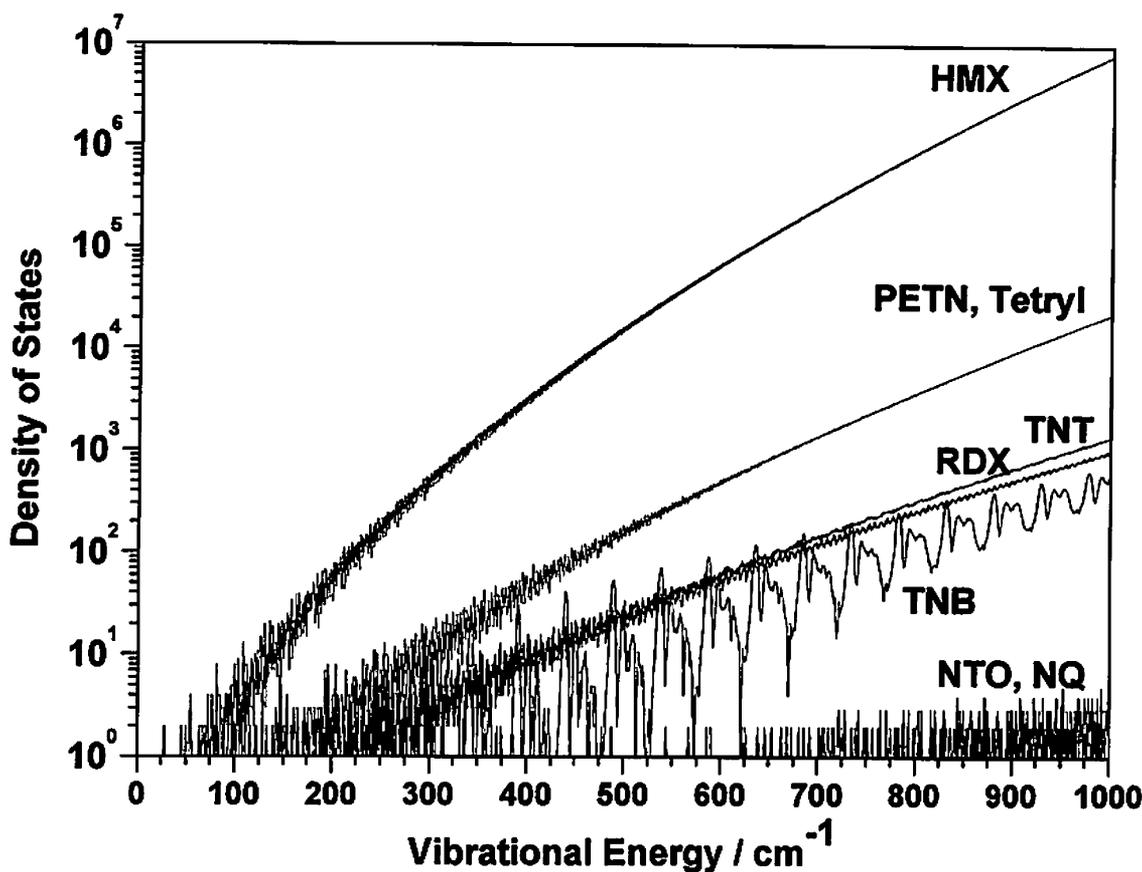


Fig. 2 Vibrational density of states for some explosives.

higher vibrational states are then excited by V-V (Vibration-to-Vibration) up-pumping processes. This V-V up-pumping process can excite some particular vibrational mode relevant to bond fission, and bond breaking will occur as a result of vibrational excitation. Time scale of this "initiation zone" is about 1 ns. The endothermic bond breaking reaction in the initiation zone will produce various radicals, which causes exothermic reactions. A detonation is initiated as a result of these rapid exothermic radical reactions and a C-J (Chapman-Jouget) state is achieved.

We adopted the energy transfer model proposed by McNesby and Coffey⁸⁾ to describe vibrational excitation followed by the phonon excitation due to mechanical impact. In the model, we postulate that the initial excitation energy by mechanical impact is instantaneously distributed among the phonon modes and those low-lying vibrational modes with fundamental energies of less than 250 cm^{-1} . Energy transfer rates between phonons and these low-lying vibrational levels are assumed to be extremely fast, and these low energy vibrational modes are

thought to be "amalgamated" mode. Boltzmann distribution is immediately realized among the phonon and these amalgamated vibrational modes. The energy boundary of 250 cm^{-1} is chosen as the maximum value of a fundamental vibration that is highly coupled to the phonon modes⁸⁾. This group of low-lying states (phonons and amalgamated vibrations) is defined as "phonon manifold". Higher energy fundamental internal vibrational levels are not affected by the initial perturbation, since time scale of this initial excitation of phonon manifold is much faster than the vibrational excitation. Impact sensitivity is determined by how fast energy is transferred from this initially excited phonon manifold to internal vibrational states with fundamental vibrational energies up to 700 cm^{-1} ("internal vibrational manifold"). Above the vibrational energy of 700 cm^{-1} , rate of internal vibrational energy redistribution (IVR) is sufficiently fast. It is assumed that Fermi's Golden Rule, which states that the resonant energy transfer is most effective, governs the rate of energy transfer between phonon manifold and internal vibrational modes. Off-resonance

energy transfer rate is a function of the product of the phonon density of states and the optical line width.

In the present model, the predominant pathway of energy redistribution following a fast initial perturbation is intramolecular, and the vibrational energy transfer kinetics is unimolecular. The first-order rate constant used to describe energy transfer between vibrational levels in the solid is a function of the energy mismatch $\Delta E = E_j - E_i$, where E_i is the energy of the state initially excited, and E_j is the state to which energy is transferred. According to a simple theory for the near-resonant V-V (vibration to vibration) energy transfer process in gases¹⁸⁾, the rate constant is proportional to $\text{sech}^2(\Delta E/kT)$. For the gas phase V-V energy transfer, energy mismatch must be made up by relative translational energy or rotational energy of the colliding molecules. However, for solid-phase vibrational energy transfer, energy mismatch must be made up by phonons. Therefore, the rate constant is also proportional to the product of density of states of phonons. It may also inversely proportional to the life times of the phonon state, and hence proportional to the optical linewidth of phonons. Based on these considerations, we assumed following functional form for the first order vibrational energy transfer rate constant:

$$k_{ij} = A \text{sech}^2\left(\frac{\Delta E}{kT}\right) f_1(\Delta E) f_2(\Delta E). \quad (1)$$

Here, k_{ij} is a rate constant for the energy transfer from vibrational state i to state j , T is the temperature of phonon manifold, and A is a constant that depends on explosives. Since there is no information on the value of A (i.e., information on the solid-state vibrational energy transfer for explosives), we tentatively assume as $A = 1 \times 10^{13} \text{ s}^{-1}$, which is a typical value for the gas-phase V-V energy transfer. It is noted that choice of a value of A is not important for the comparison of relative energy transfer rates if we use the same value, since the kinetics is first order. A function f_1 is a line shape function given by a Lorentzian function:

$$f_1(\Delta E) = \frac{\gamma^2}{\Delta E^2 + \gamma^2}. \quad (2)$$

Here γ is a linewidth of phonon band. In the present calculation, a value of $\gamma = 5 \text{ cm}^{-1}$ is used for all explosives. The last term f_2 is a function for the density of states of phonons. In principle, density of states of phonons can be calculated by assuming intermolecular interactions. In addition, there are some data on the density of states obtained by neutron diffraction experiments. However, very rough estimate of the density of state is enough in the present model, because of very crude assumption used in the estimation of rate constant. We use a simple function based on the Debye model for the density of states of phonons:

$$f_2(\Delta E) = \left(\frac{\Delta E}{\omega_p}\right)^2. \quad (3)$$

Here ω_p is the cut-off (maximum) frequency of phonons and a value of $\omega_p = 100 \text{ cm}^{-1}$ is arbitrarily assumed for all of the explosives.

The time evolution of the vibrational level population is obtained by solving a set of first-order differential equations (master equation) given below:

$$\frac{dn_i}{dt} = -\sum_j k_{ij} n_i + \sum_j k_{ji} n_j \quad (4)$$

Here n_i is the population of the i -th energy levels. Equation (4) is solved with given initial conditions in order to calculate the overall energy transfer rate from phonon manifolds to internal vibrational modes. Initial populations for internal vibrational modes are calculated from the Boltzmann distribution at $T = 300 \text{ K}$, whereas populations of phonon manifolds are assumed to be the Boltzmann distribution with $T = 1000 \text{ K}$. Runge-Kutta-Gill method is used for the numerical integration of Eq.4.

Time variations of total phonon and internal vibrational energies were calculated from the solution of Eq.4 and an example of the calculation is shown in Fig.3. It is found that the Boltzmann distribution among the internal vibrational modes is not maintained during the relaxation processes. As a result, the time variation of total vibrational energy is not a single exponential curve.

4. Impact sensitivity and vibrational energy transfer

Although the total vibrational energy does not

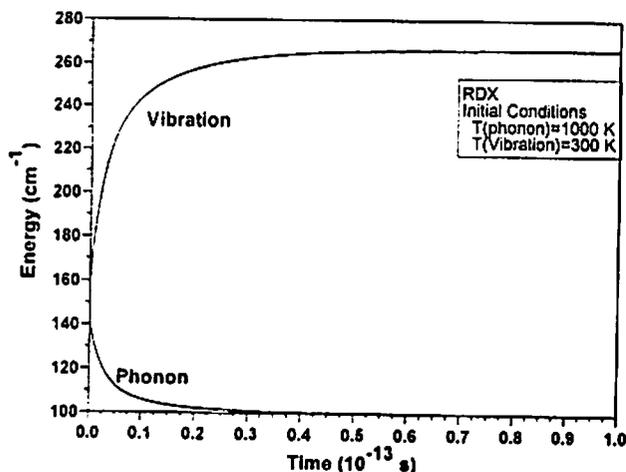


Fig. 3 Calculated time profiles of total phonon and vibrational energy. Parameters used in this calculation are: $A=10^{13} \text{ s}^{-1}$, $\gamma=5 \text{ cm}^{-1}$ and $\omega_p=100 \text{ cm}^{-1}$.

relax exponentially, we define a "time constant" of the total vibrational energy as measure for the rate of the vibrational excitation. A time constant for the vibrational excitation is simply defined as a $(1-1/e)$ time for the total vibrational energy. It is expected that the vibrational excitation rates are largely dependent on the values of ω_p and γ . Calculations were performed with several values of these parameters ranging from $\gamma=1 \text{ cm}^{-1}$ to 50 cm^{-1} and from $\omega_p=100 \text{ cm}^{-1}$ to $\omega_p=250 \text{ cm}^{-1}$. It is found that the value of ω_p is rather insensitive to the overall rates of vibrational excitation. On the other hand, a value of γ is very sensitive to the absolute value of the energy transfer rate, as expected. However, absolute value of the energy transfer rate is less important than the relative tendency because of the uncertainty in the assumed value of A in Eq. 1. Relative values of the vibrational energy transfer rates are insensitive to a value of γ .

Calculated time constants are compared to the impact sensitivities that are derived from drop hammer tests. We define the drop hammer sensitivity as $1/H_{50}$, where H_{50} is the 50% explosion height with a 2.5 kg drop hammer. There is a serious problem in the comparison with drop hammer sensitivity. Reported data in the literatures usually have very large scatter. In this work, data are mainly taken from refs. 19 and 20. These data are summarized in Table 1 along with the calculated values of the time constants for the vibrational excitation and plotted

Table 1 Experimental drop hammer height H_{50} and calculated time constants for vibrational excitation.

Explosives	H_{50} (cm) ^{a)}	Time constants ^{b)}
NQ	320	0.13
NTO	86	0.118
RDX	24	0.052
HMX	26	0.021
PETN	12	0.016
TNB	100	0.050
TNT	160	0.040
Tetryl	32	0.036

a) Data are taken from refs. 19 and 20.

b) In unit of 10^{-13} s . These values are derived with parameters of $A=10^{13} \text{ s}^{-1}$, $\gamma=5 \text{ cm}^{-1}$ and $\omega_p=100 \text{ cm}^{-1}$.

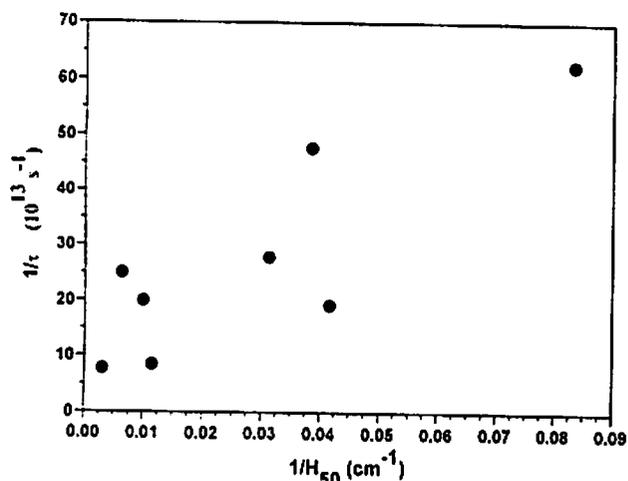


Fig. 4 Correlation between experimental drop hammer sensitivities and rates of vibrational excitation. Parameters used in the calculation are the same as in Table 1.

in Fig.4. Although there is a large scatter of the data, it seems that sensitive explosives have faster energy transfer rates.

5. Concluding Remarks

Simple model for the energy transfer between phonons and internal vibrational modes was applied to the impact initiation of several explosives and the rates of energy transfer are estimated. The assumption made in the present model is extremely crude: it assumed the same value of A , γ and ω_p for all the explosives. Of course, these assumptions are too unrealistic to predict impact sensitivity of the

real explosives. Nevertheless, some correlation is found between experimental drop hammer sensitivities and calculated vibrational excitation rates. More precise evaluation of the parameter values for A , γ and ω_p can improve the correlation, and such improvement is open for future work.

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