

Vibrational Excitation of Molecules in a Lattice due to Shock Induced Molecular Deformation

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A simple formalism is developed to calculate the rate of internal vibrational excitation of a molecule in a lattice due to abrupt deformation of the bonds of the molecule as a result of the application of a shock pulse to the lattice. The excitation rate is calculated as a function of rise time of the pulse and peak pressure for the case of 1,3,5-trinitro, 1,3,5-triazocyclohexane. It is shown that large vibrational excitation rates can be achieved if the rise time of the shock pulse is in the order of the period of vibration of the bond. The possible role of this process in shock induced chemical reactions in solids is considered.

Key words: Vibrational excitation – Shock – Molecular deformation – Lattice.

1. Introduction

Shock pulses are known to cause chemical reactions in solids. A most dramatic evidence of this is shock induced detonation of organic solids resulting from high rate exothermic reactions. Recent studies using shock pulses below pressures needed to cause detonation have allowed identification of the internal bonds of the molecules of the lattice which break when the lattice is shocked [1, 2]. For example in triamino trinitro benzene, $C_6(NH_2)_3(NO_2)_3$, it has been demonstrated that a shock pulse severs the C–N bond between the NO_2 group and the carbon ring. Although it is likely that this bond breaking is a result of high temperatures induced by the shock pulse, it has been suggested that mechanical disturbance of the molecules of the lattice could cause bond breaking [3]. For example it has been shown that mechanical fracture of pentaerythritoltrinitrate (PETN) breaks different bonds than slow thermal decomposition [4]. The first step in a unimolecular bond breaking process is the internal excitation of either the vibrational or electronic states of the molecule. In this work the possibility will

be considered whether an abrupt deformation of a bond of a molecule in a lattice due to the passage of a shock pulse can cause a sufficiently high rate of internal vibrational excitation which could lead to bond breaking. A simple formalism is developed in terms of experimentally accessible parameters allowing calculation of the rate of internal vibrational excitation as a function of peak shock pressure and shock rise time. There have been some preliminary attempts to estimate vibrational excitation rates of molecules in a lattice due to shock heating which require transfer of excited lattice phonons to internal vibrational states of the molecule [5]. However, there has been no attempt to investigate the possibility of internal molecular vibrational excitation due to abrupt mechanical deformation of the molecules in the lattice as the result of a passage of a shock pulse.

2. Theory

Studies of the effect of hydrostatic pressure on solids using IR or Raman spectroscopy show that frequencies of internal modes of molecules of the lattice increase with increasing pressure indicating that the molecules are being compressed [6, 7]. This means when a shock pulse passes over a solid containing molecules, the molecules will undergo a time dependent compression in a time comparable to the rise time of the shock pulse. The question to be considered here is can this abrupt compression of the molecule cause an internal vibrational excitation of the molecule at a sufficiently high enough rate to lead to bond rupture. To answer the question it is necessary to develop a formalism to calculate the rate of vibrational excitation of the internal modes of the molecule, W_{10} , due to the compression of the bond lengths as a function of peak pressure and rise time of the shock pulse. The probability for an excitation from ground vibrational state to the first excited state is $a_{10}a_{10}^*$ where a_{10} is given by,

$$a_{10} = \frac{1}{i\hbar} \int_0^t H_{10} \exp i\omega_{10}t \, dt \quad (1)$$

where $H_{10} = \langle 1|H|0\rangle$ and $|1\rangle$ and $|0\rangle$ are the excited and ground state wavefunctions of the unperturbed harmonic oscillator. The H is the perturbation of the oscillator due to the abrupt distortion of the molecule which in the first approximation can be shown to be $K\Delta(t)X$, where K is the force constant, Δ the time dependent deformation of the bond and X the normal coordinate of vibration. Eq. (1) becomes,

$$a_{10} = \frac{k}{i\hbar} \langle \psi_1|X|\psi_0\rangle \int_{-\infty}^{\infty} \Delta(t) \exp i\omega_{10}t \, dt. \quad (2)$$

In order to calculate a_{10} it is necessary to assume a specific time dependence for the deformation. It will be assumed, for the sake of mathematical simplicity, that the deformation has a Gaussian time dependence.

$$\Delta(t) = \Delta_0 \exp -(t/\tau)^2 \quad (3)$$

where Δ_0 is the maximum deformation. Choice of this function allows an analytical function to be obtained for the integral in Eq. (2). The transition rate, W_{10} , between the ground and first vibrational excited state is obtained to be

$$W_{10} = \frac{m}{2\hbar} \omega^3 \Delta_0^2 \pi \tau \exp -(\omega\tau)^2/2. \quad (4)$$

Eq. (4) indicates that the possibility for excitation of an internal molecular vibration due to a time dependent compression of the bond will depend on the magnitude of the maximum deformation, the length of time it takes to achieve the maximum deformation, which in turn are determined by the maximum pressure of the shock pulse and the rise time of the pulse. If the rise time of the deformation of the bond is considerably longer than the period of vibration of the bond the probability for vibrational excitation will be small.

3. Results

In order to assess the possibility of a mechanically induced vibrational excitation the model will be applied to the case of 1,3,5-trinitro, 1,3,5-triazocyclohexane, (RDX) molecule because high pressure Raman data for the internal mode frequencies is available, and because the material is known to undergo high rate reactions when subjected to shock pulses. Shock pulses have been shown to sever the bond between the ring nitrogen and the NO_2 group [1]. The studies of the effect of hydrostatic pressure on the Raman active internal vibrational frequencies of RDX show that the frequency of the N—N bond increases linearly with pressure with a slope of $0.2 \text{ cm}^{-1}/\text{Kbar}$ and the C—N ring stretch has a slope of $0.38 \text{ cm}^{-1}/\text{Kbar}$ [8].

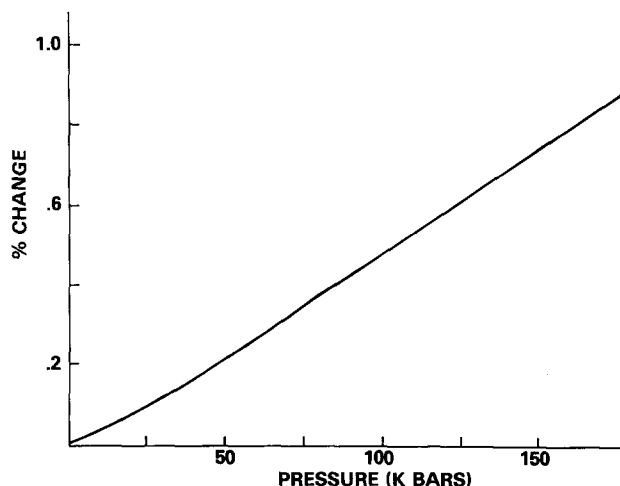


Fig. 1. Estimated percent decrease in internal N—N bond length of RDX molecule as a function of hydrostatic pressure applied to the lattice

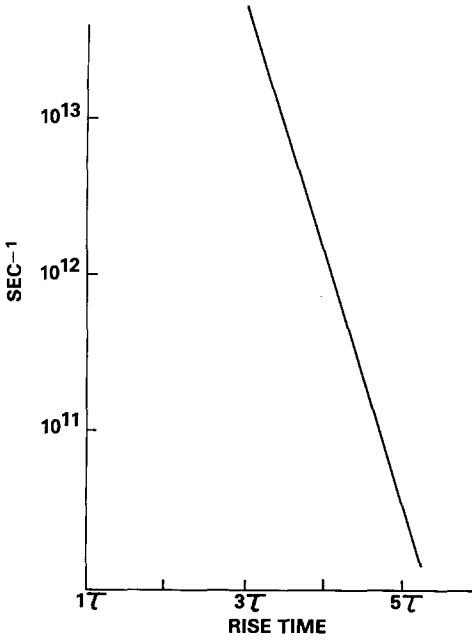


Fig. 2. Plot of the log of the internal vibrational excitation rate of the N—N vibration as a function of the rise time of a Gaussian deformation for a constant pressure of 170 Kbars. τ is the period of vibration of the bond

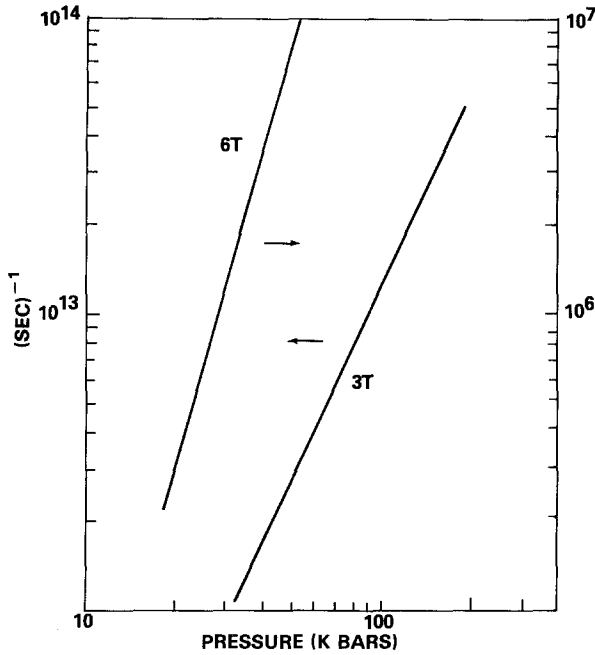


Fig. 3. Plot of $\log W_{10}$ versus \log of peak shock pressure for a pulse of rise time 6 times the period of vibration and 3 times the period of vibration

Badger [9] first pointed out that as bond between a pair of atoms becomes stronger its equilibrium length becomes shorter. A number of empirical relationships have been proposed to relate bond length to vibrational frequency. It has been suggested that the vibrational frequency may depend on the bond length, r , as C/r^6 [10]. Using this dependence and the measured pressure dependence of the N—N stretch frequency in RDX, the change in the bond length with pressure can be estimated. Fig. 1 is a plot of the estimated percent change in the N—N bond length as a function of hydrostatic pressure applied to the lattice. Using this estimate Eq. (4) may be used to calculate the rate of vibrational excitation of the N—N vibration of the RDX molecule, assuming that the magnitude of bond compression under hydrostatic pressure will represent the degree of deformation under shock compression of the lattice. The rate of internal excitation is calculated as a function of peak shock pressure and rise time of the shock pulse. Fig. 2 is a plot of the log of W_{10} as a function of rise time of shock pulse given in multiples of the period of vibration of the bond, for a constant peak shock pressure of 170 Kbars. The calculation shows a strong dependence of the excitation rate on the rise time of the pulse. When the rise time is an order of magnitude larger than the period of vibration the excitation rate is effectively zero. Fig. 3 is a plot of the calculated excitation rate as a function of peak shock pressure, for rise time of 6 and 3 times the period of vibration of the N—N bond.

4. Discussion

A model has been developed to calculate the rate of internal vibrational excitation of a molecule in a lattice due to an abrupt compression of the molecule as the result of the application of a shock pulse to the lattice. The results show that large internal vibrational excitation rates can be obtained provided the rise time of the shock pulse is in the order of magnitude of the period of vibration of the bond and that the bond undergoes sufficient deformation. For the case of unimolecular shock induced bond breaking the initial internal vibrational excitation from $N=0$ to $N=1$ must be followed by multiple excitations up to an energy level corresponding to the dissociation energy of the bond. Once W_{10} is obtained the rate for multiple excitations can be estimated, and the reaction rate can be calculated. In the case of a large molecule like RDX where there are 57 normal modes of vibration, transfer of energy between normal modes because of mode coupling will compete with multiple walks up the vibrational ladder and calculation of the rate of dissociation is more difficult if not impossible. Generally if the energy is deposited in one bond it is continuously transferred to other modes and occasionally channeled into the reactive mode, (reaction coordinate) and a bond other than the one initially excited may break.

At 170 Kbars of shock pressure a single crystal of RDX will undergo high rate exothermic reaction [11]. The internal vibrational rate calculated here due to abrupt molecular deformation at 170 Kbars for the case where the rise time of the deformation is in the order of magnitude of the period of vibration of the bond is large enough to lead to reaction.

Thus the possibility of mechanical unimolecular bond breaking of a bond will depend on whether shock rise times are in the order of magnitude of periods of vibration of internal molecular vibrations of the molecules which make up the lattice, i.e. 10^{-12} to 10^{-13} s. Shock rise times are at present not experimentally accessible but some estimates are possible. A typical shock pulse having a velocity of 1000 m/s will transit a large molecule such as RDX having an approximate width of 10 \AA in about 10^{-12} s. If shock rise times can be identified with the transit time across the molecule of the shock pulse then it would appear that a mechanical bond breaking process is possible.

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