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Coherent Ultrafast Vibrational Excitation of Molecules in Localized Shock Wave Fronts

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We present a theory of coherent shock-induced vibrational excitation of molecules in solids. We treat an idealized impulsive shock wave traveling through a one-dimensional monatomic lattice doped with a diatomic impurity and focus on the ultrafast dynamics occurring within the localized shock front itself. We present a simple classical mechanical model based on the theory of collision-induced translational to vibrational energy transfer, modified to treat the multiple correlated impulsive forces acting on the internal degrees of the molecule as the shock wave passes, and compare the predictions of the theory with classical molecular dynamics simulations. It is found that our approach provides a qualitative description of the behavior observed in molecular dynamics simulations and, in some cases, gives quantitative predictions of the vibrational energy uptake as a function of shock velocity. The potential relevance of the model to shock-induced chemical processes in solids is discussed.

I. Introduction

Shock waves in solids create extreme nonequilibrium conditions which can lead to a range of novel physical and chemical processes. A particularly interesting and important example is the detonation of an energetic material, which can be initiated by energy transfer from a propagating mechanical shock wave into intramolecular degrees of freedom. This excitation leads to activation of the reaction coordinate for molecular decomposition and, ultimately, to the exothermic chemistry underlying the detonation process. A great deal of interest has recently been directed at understanding the elementary dynamical steps underlying the initiation of detonation in shocked energetic materials.[1,2] Aside from its fundamental interest as a many-body ultrafast dynamical process, there is considerable practical importance associated with this problem, particularly as it relates to the design of energetic materials that are resistant to accidental shock-induced detonation. Recent advances in time-resolved experimental methods,[3−15] combined with developments in computer simulation and analytic theories,[16−33] are providing an increasingly detailed molecular view of the early events of shock-induced chemistry in solids.

One mechanism that contributes to shock-induced solid state chemistry involves the thermal activation of intramolecular degrees of freedom by hot lattice vibrations in the wake of the traveling shock front. A multiphonon up-pumping model has been proposed to describe this process and has been the subject of both experimental[9,10,13,34,35] and theoretical[8,16,24,26,31] studies. The model predicts a time scale for up-pumping on the order of 100 ps. For shock velocities in the range 10^3-10^4 m s^{-1}, this corresponds to a spatial region behind the shock wave of order 10^3-10^4 Å in thickness. Defects, impurities, and other imperfections of the solid enhance the decay of the localized shock wave energy into thermal lattice motion and cause the formation of “hot spots” in the solid, where initiation by multiphonon up-pumping can occur more readily.[7,9,18,24,28,36−41]

Although the thermal activation mechanism undoubtedly plays an important role in shock-induced solid state chemical processes, alternative mechanisms can be imagined, where *direct* energy transfer from the shock front itself into molecular vibrations occurs. Experiments, continuum theories, and atomistic molecular dynamics simulations suggest that the traveling shock front can be highly localized on atomic distance scales.[20,21,30,42−50] This highly localized and coherent pulse of mechanical energy can, in turn, subject the intramolecular modes of molecules in shocked solids to highly impulsive forces on ultrafast time scales, qualitatively similar to those experienced by molecules in high kinetic energy collisions.[51]

In this paper, we investigate the ultrafast vibrational excitation of molecules in shocked solids from a theoretical perspective. We focus on the dynamics of coupled intramolecular and intermolecular motion that occurs within the advancing shock front itself. We treat a highly idealized model, consisting of an atomically sharp shock front traveling down a one-dimensional monatomic lattice containing a single diatomic impurity, and employ classical mechanics to model the dynamics. We develop a simple analytic theory which captures the key aspects of the ultrafast dynamics of vibrational excitation and compare its predictions with the results of classical molecular dynamics simulations. The goal of this work is to study the qualitative dynamical mechanisms underlying ultrafast vibrational excitation of molecules in solids by the passage of localized shock fronts. We pursue this goal in the computationally tractible and intuitively appealing setting of classical mechanics of a one-dimensional system, at the expense of realism and its associated complexities. In particular, we ignore the quantum mechanical nature of molecular vibrations, multidimensional effects, and the possibly ill-defined spatial structure of the shock wave front. Nonetheless, we believe that the general principles identified in this work apply at least qualitatively to the more complex processes in real systems and may contribute to understanding the potentially important but relatively unexplored role of coherent ultrafast excitation in shock-induced chemistry.

Within the idealizations of our treatment, the ultrafast excitation of a molecule in a shocked solid occurs via impulsive collisions between the molecule and constituent lattice atoms as the localized shock front encounters and passes through the impurity. However, unlike the case of collisional translation−vibration (T−V) energy transfer, the spatial localization of the traveling shock front will lead to different parts of the molecule experiencing these forces at different times, so that the internal modes of the molecule will be perturbed by *trains* of localized pulses, in a manner reminiscent of molecules interacting with

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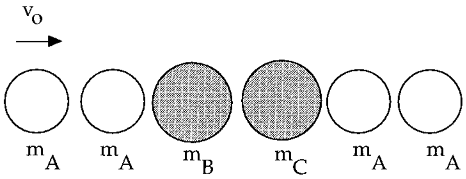

Figure 1. Schematic view of a small region of the one-dimensional solid. The host lattice atoms with mass m_A are shown as open circles, while the diatomic impurity with atomic masses m_B and m_C are shown as larger, shades circles.

shaped optical pulse sequences in spectroscopic control experiments.[52−56] A localized shock front traveling at 3 × 10^3 m s^{-1} will cross a molecule of width 3 Å in under 100 fs. These time scales are short enough for the timings of these impulsive forces to interact with molecular vibrational motion in a coherent manner: the correlation between the intrinsic phases of the intramolecular oscillators and the timing of the multiple collisions plays a key role in the overall energy transfer.

The simple model of coherent ultrafast energy uptake by molecules in localized shock fronts developed in this paper takes this correlation explicitly into account. Our approach is based on the classical mechanical theories of collisional excitation of molecular vibrations developed in the 1960s and 1970s.[51,57−61] This previous work treated single encounters between (usually diatomic) molecules and atomic collision partners. Here, we extend the gas phase theory to treat the effect of highly correlated multiple collisions experienced by molecules in shocked solids. Our model is developed for the simplest case of a diatomic impurity embedded in a one-dimensional atomic solid, and its predictions are compared with molecular dynamics simulations. It should be noted, however, that similar phenomenology is also observed in higher dimensional simulations, and thus the model presented here is more general than our one-dimensional development. The process of shock-induced vibrational excitation is complementary to a related coherent energy transfer mechanism that we have studied recently: coherent pulse trains of nanoscale shock waves created by photodissociation of molecular impurities in atomic solids.[62]

The rest of this paper is organized as follows: In section II, the one-dimensional model studied is described. In section III, the classical theory of collisional excitation of molecular vibrations is briefly reviewed, and its extension to shock-induced excitation is presented. In section IV, the predictions of the model are compared with molecular dynamics simulations performed on the one-dimensional model problem. Finally, a discussion is given in section V.

II. System

The system considered is composed of a one-dimensional monatomic solid, made up of host atoms with mass m_A and containing a single diatomic impurity molecule with atomic masses m_B and m_C. Figure 1 shows a schematic view of a small portion of the infinite one-dimensional solid. An idealized shock wave, a single atom in width, passes through the solid from left to right with a shock velocity ν_s. The overall propagation of the shock wave occurs by sequential collisions between the lattice atoms. Except for small thermal motion, the lattice atoms move only when they are within the traveling shock front itself. They then translate with a *particle* velocity ν_0, which is less than the shock velocity. For a linear chain of hard-sphere atoms with diameter d and lattice spacing l, the particle velocities in the undoped lattice are piecewise constant functions of time (i.e., either ν_0 or zero) as a chain of elastic atom−atom collisions transmits the shock wave. In this case, the relationship between the shock and particle velocity is given by

$$\nu_s = \frac{l}{l-d}\nu_0$$

When the shock wave reaches the impurity, the left atom B of the diatomic will experience a collision with the adjacent host atom traveling toward it with velocity ν_0 (see Figure 1); we define this time as $t = 0$. If we assume for now that the diatomic is *rigid*, then simple kinematics allow us to estimate the final translational kinetic energy and velocity of the impurity after this first collision. The molecule translates to the right following the first collision for a time $t = \tau$ until it encounters the host atom to its immediate right, leading to a *second* atom−molecule collision. During the time interval $0 < t < \tau$, the impurity itself is responsible for the shock wave propagation. Within the hard-sphere idealization, this second collision can also be analyzed easily using elementary kinematics. Depending on the particular mass values chosen, the diatomic will continue to move (to the left or to the right) following this second collision, and thus more collisions may occur as well. For simplicity, however, we will neglect these higher order collisions in our development below.

During the collisions between the host atom neighbors and the diatomic molecule, its bond does not remain rigid but can undergo excitation due to the forces acting on it. Classical, semiclassical, and quantum mechanical theories of collision-induced vibrational excitation in the gas phase were developed many years ago by a number of workers.[51,57−61] In these theories, individual atom−diatom encounters were treated. In the solid, however, the diatomic molecule will experience two (or more) *correlated* impulsive interactions with multiple lattice atoms as the shock wave passes through the impurity. Together, these impulses determine the overall ultrafast vibrational excitation of the system. As we will see below, the timing of these interactions, and its dependence on collision energies and particle masses, can lead to unusual nonmonotonic dependence of the final vibrational energy on shock velocity that is in marked contrast with the conventional single-collision theory of energy exchange.

III. Theory

In this section, we briefly review the classical theory of collision-induced vibrational excitation[57−61] and describe our extension to the case of shocked solids. The simplest gas phase version of this model treats a collinear A + BC atom−diatom collision. The diatomic vibration is approximated by a harmonic oscillator with frequency ω, and the intermolecular interaction is modeled by a purely repulsive exponential potential, given by

$$V(d) = V_0 e^{-(d-d_0)/L} \tag{1}$$

where d is the distance between atoms A and B, d_0 and $V_0 = V(d_0)$ are constants, and L is the exponential scale parameter of the potential. We can express this interaction in terms of the distance between the collider and the diatomic center of mass (R) and the B−C bond length (r):

$$d = R - \frac{m_C}{m_B + m_C} r \equiv R - \alpha r \tag{2}$$

This defines the mass ratio

$$\alpha = \frac{m_C}{m_B + m_C} \tag{3}$$

In terms of $\delta r = r - r_e$, the deviation of the oscillator from its equilibrium bond length, r_e, the interaction potential can be written as

$$V(R,\delta r) = V_0 \exp\left[-\frac{\alpha r_e}{L}\right] \exp\left[-\frac{R - d_0}{L}\right] \exp\left[\alpha \frac{\delta r}{L}\right] \tag{4}$$

In this simple theory, we assume that the vibrational motion is of small amplitude and described by a harmonic potential. In the limit $\delta r \ll L$, the factor $\exp(\alpha\delta r/L) \cong 1$, and the equations of motion for $R(t)$ can be solved analytically. In this limit, the diatomic molecule is treated as a rigid composite particle with mass $m_D = m_B + m_C$. The forces acting on the diatomic bond as the result of this atom–rigid diatomic collision then determine, approximately, the energy uptake by the B–C vibration. (Note that this theory does not conserve total energy.)

The atom A initially approaches the stationary B–C diatomic molecule from the left with a particle velocity ν_0. We define the reduced mass $\tilde{\mu}$ of the host–rigid diatomic molecule as

$$\tilde{\mu} = \frac{m_A m_D}{m_A + m_D} = \frac{m_A(m_B + m_C)}{m_A + m_B + m_C} \tag{5}$$

The kinetic energy of the collider in the lab frame is given by

$$K_0 = {}^1/_2 m_A \nu_0^{\,2} \tag{6}$$

The *relative* kinetic energy of the collider–diatomic system is

$$E_0 = {}^1/_2 \tilde{\mu} \nu_0^{\,2} \tag{7}$$

We now select the parameters d_0 and V_0 such that $V_0 \exp(-\alpha r_e/L) = E_0$. Then, $R = d_0$ corresponds to the turning point of the $R(t)$ motion. Defining $X(t) = R(t) - d_0$, and choosing the zero of time such that $X(0) = 0$, Newton's equation of motion for $X(t)$ can be solved exactly to yield:[51,57−61]

$$\exp\left(-\frac{X(t)}{L}\right) = \mathrm{sech}^2\left(\frac{\nu_0 t}{2L}\right) \tag{8}$$

We now return our attention to the vibrational motion of the B–C molecule. The approximate equations of motion for $r(t)$ are obtained by keeping (here) a *linearized* approximation to the factor:

$$\exp\left(\frac{\alpha\delta r}{L}\right) \cong 1 + \frac{\alpha\delta r}{L} \tag{9}$$

In addition, the explicit (but approximate) time dependence of $X(t) = R(t) - d_0$ is incorporated into the interaction potential, yielding

$$V(r,t) = E_0\, \mathrm{sech}^2\left(\frac{\nu_0 t}{2L}\right)\left[1 + \alpha \frac{\delta r}{L}\right] \tag{10}$$

The resulting Newton's equation of motion for $\delta r(t)$ is then given by

$$\mu\, \delta\ddot{r} + \mu\omega^2\, \delta r = F(t) \tag{11}$$

where the diatomic reduced mass is defined as

$$\mu = \frac{m_B m_C}{m_B + m_C} \tag{12}$$

and ω is the harmonic frequency of the diatomic vibration. The time-dependent force acting on the diatomic bond is given by the negative derivative of the time-dependent potential:

$$F(t) = -\frac{\alpha E_0}{L}\, \mathrm{sech}^2\left(\frac{\nu_0 t}{2L}\right) \tag{13}$$

The resulting forced harmonic oscillator problem can be solved exactly.[51,57−61] For zero initial excitation, the final energy of the vibrating diatomic is given by the square of the Fourier transform of the force, evaluated at the oscillator frequency ω:

$$E_{\mathrm{vib}} = \frac{1}{2\mu}\left|\int_{-\infty}^{\infty} F(t) e^{i\omega t}\, dt\right|^2 \tag{14}$$

For the force given in eq 13, this integral can be evaluated analytically, giving the result

$$E_{\mathrm{vib}} = \left(\frac{\alpha E_0}{L}\right)^2 \left(\frac{1}{2\mu}\right) \left(\frac{4\pi\omega L^2}{\nu_0^{\,2}}\right)^2 \mathrm{csch}^2\left(\frac{\pi\omega L}{\nu_0}\right) \tag{15}$$

This result was first published by Rapp[57−59] and later tested against numerical trajectory simulations by Kelly and Wolfsberg.[60] The agreement between eq 15 and simulation ranges from fairly poor to nearly quantitative. Empirical corrections to improve this agreement were proposed by Kelly and Wolfsberg.[60] An important modification of this theory was proposed by Mahan,[61] which improves the accuracy of the result and gives the proper high-energy limit. This "refined impulse approximation" recognizes that, at very high energies, the atom–diatom collision becomes the collision between the two *atoms* A and B, with C acting as a bystander. In the above theory, this modification is made by redefining the reduced mass $\tilde{\mu}$ as

$$\tilde{\mu} \rightarrow \frac{m_A m_B}{m_A + m_B} \tag{16}$$

which is appropriate for the A–B atom–atom collision.

We now extend this general model of collisional energy transfer to the problem of vibrational excitation of molecules in shocked solids. We build our theory on the approach reviewed above, but with the key modification to treat the *multiple, correlated collisions* experienced by the molecule as the shock wave passes.

As Figure 1 illustrates, the first A + BC collision is not the whole story when the molecule is embedded in a solid. Following this collision, the molecule will itself be induced to translate to the right. Assuming for now hard-sphere kinematics, the kinetic energy of the diatomic in a space-fixed frame following the first collision can be easily determined by conservation of kinetic energy and momentum. The lab frame velocity of the diatomic after the collision is

$$\nu_D = \frac{2\nu_0}{1 + m_D/m_A} \tag{17}$$

The diatomic molecule will translate for a time τ and will then experience a *second* collision, this time with the lattice atom to its right. We define the distance which the diatomic must traverse between collisions as Λ, which is effectively the difference between the equilibrium and hard-sphere molecule–lattice contact distances. The simplest estimate of the delay time of the second collision is the distance traveled divided by the velocity:

$$\tau = \Lambda/\nu_D \tag{18}$$

The theoretical predictions (see below) depend sensitively on this time delay, and a more refined estimate of τ improves the results. This can be accomplished by taking into account the finite time required for the diatomic to achieve the velocity v_D and the corresponding finite slowdown time accompanying the second collision. Using the analytic solution to the equation of motion given in eq 8, the time delay can be approximated as

$$\tau = \frac{\Lambda}{v_D} + \ln(4)\left(\frac{L_0}{v_0} + \frac{L_f}{v_D}\right) \qquad (19)$$

where L_0 and L_f are the exponential scale parameters in the interatomic potential appropriate for the first A−B collision and second C−A collision, respectively.

The second collision subjects the diatomic molecule to a second impulsive force. The form of this force is the same as given in eq 13, but with modified mass, energy, potential, and velocity parameters and a delay in time. The relative kinetic energy of the moving diatomic and stationary collision partner (which has mass m_A) is given by

$$E_D = {}^1/_2\tilde{\mu} v_D^{\,2} \qquad (20)$$

The *total* force $F(t)$ acting on the diatomic is then given approximately by

$$F(t) = F_1(t) + F_2(t-\tau) \qquad (21)$$

where

$$F_1(t) = -\frac{\alpha E_0}{L_0}\,\mathrm{sech}^2\left(\frac{v_0 t}{2L_0}\right) \qquad (22)$$

$$F_2(t) = -\frac{\beta E_D}{L_f}\,\mathrm{sech}^2\left(\frac{v_D t}{2L_f}\right) \qquad (23)$$

Both of these forces are negative and thus act to compress the diatomic bond. The mass factor β is given by

$$\beta = \frac{m_B}{m_B + m_C} \qquad (24)$$

In the frequency domain, the total force becomes

$$\hat{F}(\omega) = \hat{F}_1(\omega) + \hat{F}_2(\omega)\exp(i\omega\tau) \qquad (25)$$

where

$$\hat{F}(\omega) = \int_{-\infty}^{\infty} F(t)\,e^{i\omega t}\,dt \qquad (26)$$

is the Fourier transform of $F(t)$. From eq 14, the energy uptake in the shocked molecule is then given by

$$E_{vib} = (1/2\mu)\,([\hat{F}_1(\omega)]^2 + [\hat{F}_2(\omega)]^2 + 2\hat{F}_1(\omega)\,\hat{F}_2(\omega)\cos(\omega\tau)) \qquad (27)$$

The excitation that would result from a pair of *uncorrelated* collisions is modulated by a factor that depends on the time lag *between* the two collisions. In other words, the excitation depends on the *time correlation* of the multiple collisions affecting the molecule.

For a given diatomic frequency ω, this correlation can lead to nonmonotonic energy uptake vs shock velocity. Our model neglects the effect of vibrational excitation of the diatomic—and the resulting nonzero-amplitude oscillation—on the time or the kinematics of the second collision. We have also treatd only two collisions in the present discussion. In general, further collisions will occur; these and other effects can be incorporated into the theory at the expense of simplicity.

The theory developed here is based on a classical mechanical treatment of both the translational and vibrational dynamics. This was done to allow a direct comparison of the analytic theory with many-body molecular dynamics simulations (see the next section). Quantum effects in molecular vibrational dynamics can, of course, be important, especially at low temperatures and for light particles such as hydrogen atoms. An extension of the above analysis to treat fully quantum mechanical vibrations is straightforward; indeed, classical, semiclassical, and quantum mechanical versions of the energy transfer theory of gas phase collisional vibrational excitation have been developed and tested extensively,[51,57−61] and those results could be adapted to the present application. A comparison with full many-body simulations would not be straightforward in the quantum case, and so we restrict our analysis here to classical mechanics.

IV. Results

In this section, we test the predictions of our theory against molecular dynamics simulations of a model system. The model consists of a one-dimensional monatomic solid containing a single diatomic impurity molecule. The full infinite system is approximated by a chain of 20 atoms, with free boundary conditions. The impulsive shock-induced energy transfer occurs on an extremely short time scale while the shock front passes through the molecule, and the energy transfer is insensitive to the number of atoms in the system and the form of the boundary conditions.

The mass of the host atoms are chosen to be equal to that of Ar: $m_A = 39.95$ amu. We consider a homonuclear diatomic impurity molecule and examine two cases: a "light" diatomic with $m_B = m_C = m_A$ and a "heavy" diatomic with $m_B = m_C = 2m_A$. The A−A, A−B, and A−C interaction potentials are taken to be of the Lennard-Jones form:

$$V_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (28)$$

with parameters $\sigma = 3.4$ Å and $\epsilon = 83.3$ cm^{-1}; these values correspond to the values for the Ar−Ar van der Waals interaction. The diatomic bond is modeled by a harmonic potential

$$U(r) = {}^1/_2 k(r - r_e)^2 \qquad (29)$$

The force constant k is chosen to give the desired vibrational frequency ω. The equilibrium distance r_e is chosen to be $2^{1/6}\sigma$, the same as the host−host and host−diatomic equilibrium distances.

The initial conditions of the system are generated as follows. The lattice is first equilibrated at a temperature $T = 15$ K by trajectory integration and velocity rescaling. Then, the velocity of the host atom on the far left terminus of the chain is increased by a positive increment to give the initial particle velocity v_0. The result is an impulsive excitation that travels from left to right with a shock velocity $v_s > v_0$. For this system, we find that the relation $v_s \cong 1.9v_0$ is obeyed. The diatomic molecule contains no vibrational energy initially, except for a small thermal contribution. Rapid excitation of the diatomic occurs as the impulsive excitation passes through it. The simulation is continued until the diatomic energy becomes approximately constant after this excitation. We characterize the energy uptake as a function of system parameters and initial particle velocity by running single trajectories; because of the low temperature and lack of initial excitation of the diatomic, we find that averaging over trajectory ensembles yields the virtually the same results as single trajectories.

In order to apply the theory developed in the previous section, the Lennard-Jones intermolecular potential must be approximated by an exponential interaction of the form given in eq 2. We accomplish this by matching the exponential potential and its first derivative to the Lennard-Jones at the (energy-dependent) turning point d_0. For the first collision, the relative kinetic energy is E_0. The turning point on the Lennard-Jones potential is then given in terms of the energy and potential parameters by

$$d_0 = \sigma\left(\frac{2}{1+\sqrt{1+E_0/\epsilon}}\right)^{1/6} \qquad (30)$$

We then calculate the *energy-dependent* potential scale parameter by the requirement that the slope of the exponential approximate potential by equal to that of the Lennard-Jones interaction at $r = d_0$:

$$L_0(E_0) = -\left(\frac{V_{\mathrm{LJ}}(r)}{\mathrm{d}V_{\mathrm{LJ}}(r)/\mathrm{d}r}\right)_{r=d_0} \qquad (31)$$

A similar analysis, with E_0 replaced by E_{D} (see eq 20), gives the scale parameter L_{f} for the second collision.

In Figure 2, we show the force acting on the diatomic bond as a function of time for the system consisting of a "light" diatomic molecule with $\omega = 2000$ cm^{-1} and $m_{\mathrm{B}} = m_{\mathrm{C}} = m_{\mathrm{A}}$. Three particle velocities are considered: $v_0 = 6000$, 9000, and 10 500 m s^{-1} in Figure 2a–c, respectively. The results of molecular dynamics simulation are compared with the $F(t)$ predicted by the theory developed in the previous section. The qualitative form of the force, consisting of multiple impulsive collisions affecting the diatomic oscillator, is apparent in the figure. Two main impulses are visible, separated by a delay time that decreases with increasing collider velocity. The amplitudes and widths of the impulses, as well as the delay time, are well-approximated by the theory. Also visible in the figure are much smaller features at longer times, resulting from higher order collisions which are neglected in our simple model.

The theoretical force $F(t)$ was calculated using eqs 21–23, with the potential parameters estimated from eqs 30 and 31. As the energy of the collisions increases, we find that inclusion of the Mahan modification of eq 16 and eq 7 leads to a more accurate prediction of the simulated forces. At the lowest collision velocity, shown in Figure 2a, the theory underestimates the amplitude of the first impulse. In this case, neglecting the Mahan modification would actually lead to better agreement. For simplicity, though, we always include this modification for the *first* collision, which is of highest energy, but use the unmodified prediction for the second collision; we find that this approximation gives fairly accurate predictions of energy transfer over a wide range of collision energies (see below). More accurate schemes are possible, at the expense of simplicity.[63]

In Figure 3, we show the spectral densities of the theoretical forces, defined as $S(\omega) = |F(\omega)|^2$, where $F(\omega)$ is given by eqs 25 and 26. Also shown is the "incoherent" result $S_{\mathrm{incoh}}(\omega) = |F_1(\omega)|^2 + |F_2(\omega)|^2$. The plots have been normalized by dividing by $S_{\mathrm{incoh}}(0)$. We treat the cases $v_0 = 6000$ and 10 500 m s^{-1} in Figure 3, a and b, respectively. The spectral density is proportional to the frequency-dependent energy uptake of the oscillator, as indicated by eq 27, while the incoherent result would be obtained if an ensemble of systems with *random* delay times between the two impulses were considered. The modulation of $S(\omega)$ around the incoherent curve results from the systematic correlation in time between the first and second collision.

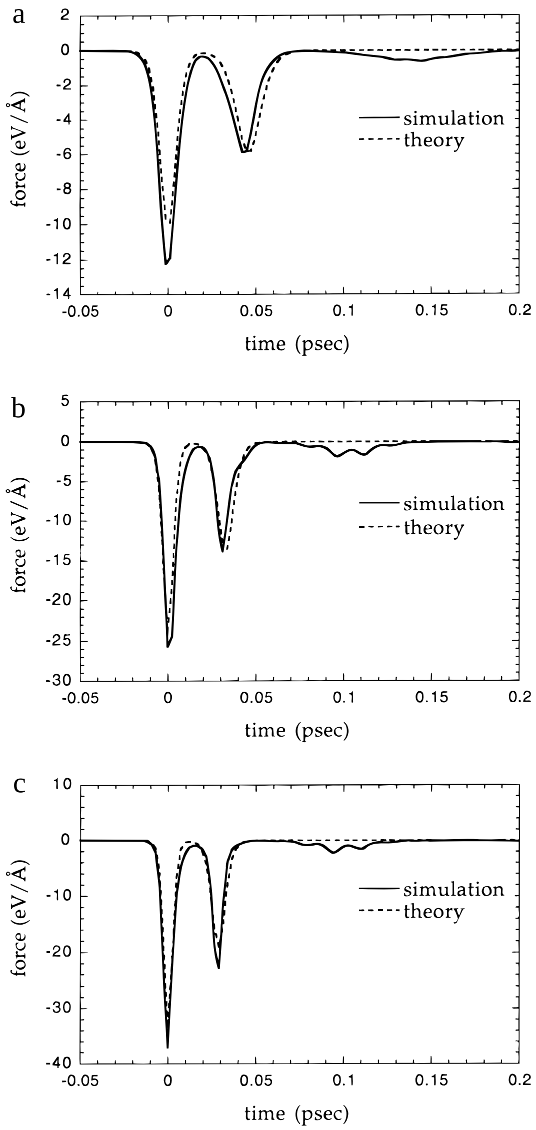

Figure 2. Forces acting on the diatomic bond vs time, for light diatomic case with $\omega = 2000$ cm^{-1}. $v_0 =$ (a) 6000, (b) 9000, and (c) 10 500 m s^{-1}. See text for discussion.

As the collider velocity is increased, the collisions become more impulsive, and the widths of the individual peaks in $F(t)$ decrease. This leads to an *increasing* width of the power spectrum with increasing collider velocity in the frequency domain. In the incoherent case, this would result in a monotonic increase in energy uptake with collider velocity for a fixed oscillator frequency ω. With the modulation of the spectral density resulting from the correlation between collisions, however, *nonmonotonic* dependence of energy uptake with collider velocity can result.

In Figure 4 a,b, we show $F(t)$ and $S(\omega)$ for the "heavy" diatomic case: $m_{\mathrm{B}} = m_{\mathrm{C}} = 2m_{\mathrm{A}}$, again with $\omega = 2000$ cm^{-1}. The collider velocity is $v_0 = 10\,500$ m s^{-1}. Figure 4a indicates that our theory does an excellent job of reproducing the simulation results for this case as well. The larger mass disparity between the host atoms and the diatomic molecule results in less collisional energy transfer during the first collision nd thus a much smaller amplitude of the second impulse. This is

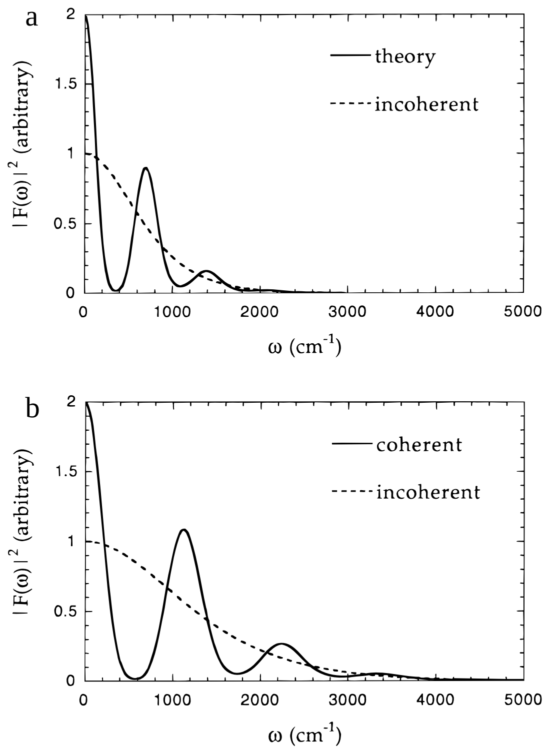

Figure 3. Normalized spectral densities of the theoretical forces, as given in eqs 25 and 26. Also shown are the incoherent results, as described in the text. v_0 = (a) 6000 and (b) 10 500 m s^{-1}.

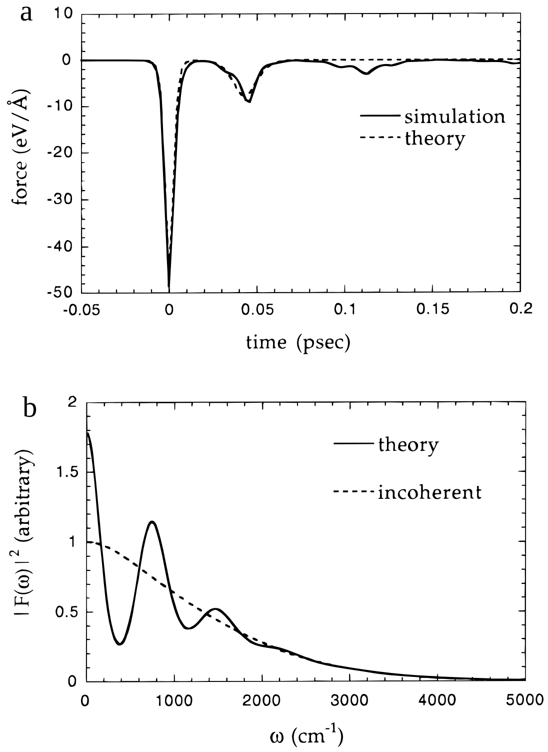

Figure 4. (a) Forces and (b) normalized spectral densities for the heavy diatomic case with $\omega = 2000$ cm^{-1}. Collider velocity is $v_0 = 10\,500$ m s^{-1}. See text for discussion.

reflected in the frequency domain by a smaller amplitude of the modulation around the incoherent result.

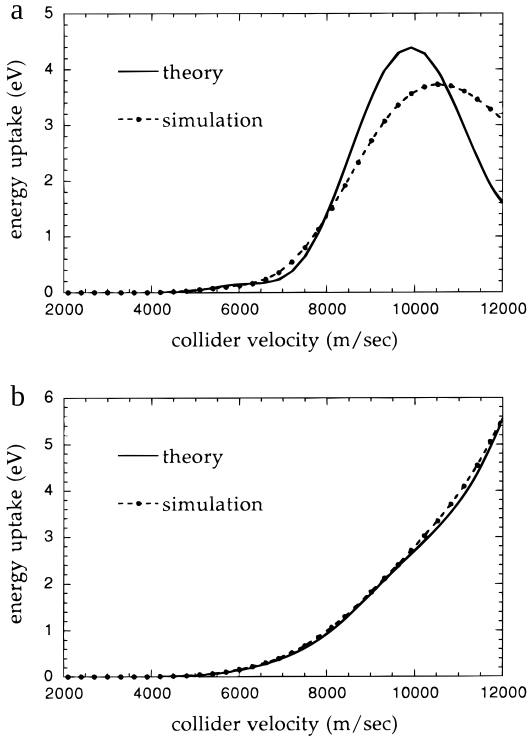

Figure 5. Vibrational excitation vs collider velocity for a $\omega = 2000$ cm^{-1} oscillator: (a) light diatomic case; (b) heavy diatomic case. See text for discussion.

In Figure 5, the dependence of vibrational excitation on collider velocity is shown for an $\omega = 2000$ cm^{-1} oscillator. Figure 5a shows the results for the "light" diatomic case ($m_B = m_C = m_A$), while Figure 5b shows the "heavy" ($m_B = m_C = 2m_A$) diatomic results. The results of molecular dynamics simulation are compared with the predictions of eq 27. In the light diatomic case, the threshold for excitation is approximately $v_0 = 5000$ m s^{-1} and is well-reproduced by the theory. In addition, a pronounced turnover in the energy transfer vs collider velocity is observed. This feature is modeled, at least qualitatively, by the simple theory developed here. In Figure 5b, the results for the heavy diatomic are compared with the theory, and nearly quantitative agreement is obtained over the entire energy range considered. In this case, the shallower modulation of the spectral density by the "coherent" term in eq 27 is not sufficient to give nonmonotonic energy transfer, a prediction that is in agreement with the simulation data.

V. Discussion

In this paper, we have presented a simple theory of shock-induced vibrational excitation of molecules in solids. Our model focuses on the ultrafast dynamics occurring in the shock front itself and is built on the theories of translational to vibrational energy transfer first introduced in the 1960s. The key modification of this previous work is the focus on multiple correlated impulsive forces acting on the internal degrees of the molecules as the shock wave passes. We have illustrated this approach for the highly idealized case of a spatially localized shock front in a one-dimensional monatomic solid and found that the model developed provides a qualitative description of the behavior observed in molecular dynamics simulations and, in some cases, gives quantitative predictions of the vibrational energy uptake as a function of collider (and thus shock) velocity. Although we consider a one-dimensional model in this paper, we have observed similar qualitative behavior in simulations of two-dimensional solids, and an appropriate generalization of present model should be applicable there as well.

The problem of energy uptake of molecules in shocked solids has been the subject of a number of previous studies. Recent work has focused on the mechanism of multiphonon up-pumping of the intramolecular degrees of freedom by a (locally) hot lattice.[8,16,24,26,31] The thermal excitation of the lattice results from energy decay of the passing shock front into collective phonon degrees of freedom. The physics of this process, and the theories developed to model it, treat the lattice vibrations as *incoherent*, with no well-defined relationship between the phases of the various phonon modes. In contrast, the mechanism we consider in the present paper involves multiple impulsive collisions affecting the atoms of the molecule being excited. This results from the nature of the traveling shock wave: highly localized in space and with a well-defined velocity. In photon language, this leads to a *coherent* mechanism for excitation. The phase relation between different lattice vibrations plays a fundamental role in this coherent excitation. Our model is based on a simple, but manifestly nonlinear, description of the molecule−shock wave interaction in terms of collisional kinematics. A coherent generalization of the multiphonon up-pumping theories would provide an alternative approach to ultrafast molecular excitation within the traveling shock front.

The model developed here treats the shock waves as a highly idealized impulse that is sharp on the atomic scale and propagates without relaxation through a cold lattice. Continuum and atomistic theoretical treatments indeed suggest that shock fronts in multidimensional can be highly localized. In real systems, however, lattice imperfections and relaxation processes may lead to more complex shock wave structure and ill-defined shock fronts. Nevertheless, one excepts that a supersonic disturbance traveling through a solid will lead to impulsive collisional effects at the moelcular scale, suggesting least a general relevance of our basic model. To treat real systems more accurately, the theory developed here could, in principle, be generalized to represent more complex shock structure as a superposition of multiple coherent events. The specific nature of the shock front would then determine whether the relative timings were correlated or not and thus whether their effects would be added coherently or incoherently.

In our work, we have ignored the quantum mechanical nature of molecular vibrations. A generalization to include quantum effects can be achieved by simply using the spectral densities for correlated collisions as input to the time-dependent Schrodinger equation for the molecular vibrations. This has, in fact, been implemented and tested for the case of gas phase collisional energy energy transfer.[51,57−61] Here, we emphasize that the role of correlated collisions closely spaced in time would be at least qualitatively the same if the molecular vibrations were treated quantum mechanically.

The theory developed in this paper suggests a possible approach to the rational design of insensitive energetic materials. Within the scope of the simple model considered, the (limited) goal of inhibiting vibrational energy uptake can be achieved by adjusting the physical parameters of the molecular impurity (i.e., the mass and force constant) so that the diatomic vibrational frequency falls within a relative minimum of the modulated spectral density (see, for example, Figure 3). This strategy is, in a sense, complementary to the approach used in coherent control of chemical dynamics by shaped laser pulses.[52−56] In the optical control experiment, the molecular characteristics are fixed, while the perturbing forces felt by the molecule are adjusted by shaping the optical pulse wave form. Here, however, the impulsive force $F(t)$ is fixed by the shock characteristics and the geometry of the system, and the dynamical properties of the molecule are varied to give the desired response to this fixed $F(t)$. The limited goal of minimizing vibrational excitation of the diatomic molecule in a given perturbing shock environment is a highly idealized but well-defined problem. Whether or not this has any relevance to the practical problem of rational "dynamical design" of insensitive explosives remains to be seen and will be addressed in future research.

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