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I. General Formulation for the Multiphonon
Relaxation of a Vibrationally Excited Adatom

by

A. C. Beri and Thomas F. George

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Department of Chemistry
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Theory of Laser-Stimulated Surface

Processes. I. General Formulation for

the Multiphonon Relaxation of a

Vibrationally Excited Adatom

A. C. Beri and Thomas F. George

Department of Chemistry

University of Rochester

Rochester, New York   14627

USA

ABSTRACT

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1

I. Introduction

An understanding of the fundamental interactions between a solid surface and adsorbed atoms or molecules is necessary for a proper description of many important processes such as catalytic reactions, corrosion, vapor deposition and gas-surface scattering. Theoretical studies along these lines range from classical and semiclassical to purely quantum mechanical. While most have addressed the somewhat more tractable problem of weak physisorption,[1] some models for strong chemisorption have also appeared.[2] In the present work we are concerned with the vibrational states of the system, namely the vibrational structure of the adspecies, of the bond between the surface and the adspecies, and that of the bulk solid and its surface (the phonons). In the past, the dynamical interactions between the solid and the adspecies have included multiphonon effects, one-phonon effects or no phonons. There is strong indication from some of these studies that multiphonon effects are quite important, a particular example being stimulated desorption.[3] The use of high-power lasers to initiate, control or enhance gas-phase reactions is established.[4] Lasers have also been used as heat sources on surfaces in applications such as annealing[5] and deposition via thermal reactions in the gas phase.[6] Only a few applications of low-power lasers to gas-surface reactions have been reported, however, and selective, nonthermal laser stimulated surface processes (LSSP) seem to be taking place in some of these experiments.[7,8] The present work is an attempt to set up a general formalism capable of dealing with LSSP from a microscopic point of view which is as "first principles" as practicable.

Recent calculations of gas-surface interactions within a scattering or desorption context have adopted classical and semiclassical[9] or quantum[3,10,11,12]

approaches with varying degrees of phenomenology. The semiclassical approaches, for example, represent a good compromise between the simplicity of classical trajectories and the details available from full quantum treatments. The latter tend to be computationally tedious, often provide less insight and require approximations such as simplified phonon band structure, one-phonon treatment with a linear chain model of the solid, and neglect of memory effects in the statistical reduction of the lattice many-body problem.

The gas-surface studies referred to in the previous paragraph have dealt with either physisorption or chemisorption, but no single formulation seems to be applicable to both. In the phenomenological theories of chemisorption, the strong chemisorptive bond cannot be treated perturbationally. A unitary transformation of the unperturbed states is necessary to account for this.[13,14] The states of the adatom are thereby changed to those of quasiparticles which move on the surface, carry a distortional wave along with them, and include most of the atom-surface interaction energy.

Another approach is to ignore the two-dimensional periodic nature of the surface and include only a few surface atoms close to the adatom. Such "cluster" calculations give rise to discrete energy levels in contrast to the band type energy level structures typical of systems with translational symmetries. The significance of the band structure in gas-surface dynamics is one of the questions which we address here.

The gas-surface interaction is a complex many-body problem. In treatments of the dynamics of surface processes, classical and quantum statistical theories have been advanced[3,9-13,15-18] to explain the general qualitative nature of the thermodynamics (desorption, migration, etc.). However, quantitative interpretation is difficult because fundamental parameters such as the energy relaxation rate and the surface migration rate are not easily available from experiment; they can be obtained theoretically, however, the accuracy being limited by the

type of potential used (Morse, LEPS, Lennard-Jones), the degree of dimensionality, and simplifying assumptions such as additivity of transition rates due to different forces. In the case of LSSP, we further need to include the (possibly synergistic) effects of the absorption of coherent electromagnetic radiation by the adsorbed species.

A few experimental studies of LSSP have been reported.[7,8] Large enhancements of the rates of reactions (relative to the rates for thermally initiated reactions) involving hydroxyl and amino groups on a silica surface have been obtained using low-power (~10 W/cm^2) CO_2 laser radiation.[7] These reactions take place on the surface, but the exact mechanism responsible for the enhancement is unclear. Efficient selective laser pumping of particular vibrational modes of the adsorbed species, followed by dissociation and desorption of OH and NH groups have been suggested. Alternatively, a mechanism involving a "hopping" electron-transfer mechanism has been proposed. While both mechanisms seem plausible, there is no conclusive evidence from theoretical or experimental studies to support either. An estimated very short lifetime (~ 10^{-11} s) of the vibrationally excited states of, say, the Si-N bond would tend to favor the electron-transfer mechanism.[7] However, lifetimes as short as these do not appear universally, and one cannot dismiss the vibrational pumping mechanism. Other instances of LSSP have been reported, some involving absorption of the radiation in the gas phase with subsequent surface reaction, and others involving absorption of radiation during an actual surface process.[8]

Recent theoretical attempts aimed at understanding the mechanisms in LSSP have adopted a mainly statistical kinetic approach.[3,7,17,18] They have pointed out the sensitivity of LSSP to the laser frequency and fluence, and have shown that the critical parameter is the rate of energy transfer from the

4

vibrationally excited adspecies to the solid. This energy relaxation rate in turn depends on the nature of the coupling between the adspecies and the solid. While lattice vibrations represent the primary means for energy transfer in nonmetals, in metals the quasicontinuum of conduction electrons can exchange energy with excited vibrational states of the adspecies.[19] Evaluation of these rates seems to be the primary bottleneck in a quantitative understanding of LSSP.

In this paper, a formalism is presented to deal with the energy relaxation of a vibrationally excited adatom pumped by an infrared laser and coupled to phonons of the solid. This represents only a small portion of the vast array of processes occuring in a laser-irradiated gas-surface system, but extension to other aspects of the problem is possible.

The core of this formalism is presented in Section II. The discussion in Section III includes limiting cases and suggests points of departure where contact can be made with other formalisms, mainly phenomenological ones. The main points of the paper are summarized in Section IV.

II. Formalism for Multiphonon Relaxation of an Adatom After IR Laser Irradiation.

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The physical processes which this formalism attempts to describe involve the absorption of infrared laser radiation by an adatom bound by the periodic (in 2D) potential at a solid surface. The vibrationally excited state thus created then decays via energy transfer to the various modes of vibration of the solid. For the sake of simplicity we do not consider relaxation to electronic degrees of freedom which would be quite important for metals. Furthermore, it is assumed that a good representation of the potential at the surface can be obtained either in coordinate space or in the Fourier space. For example, in many cases, particularly physisorption, the surface potential can be approximated by a sum of pair potentials,[10] the Fourier expansion of which converges rapidly enough to make the problem computationally tractable. The fact that only energy transfer to phonon modes of the solid is being considered means that adatom-adatom interactions, which lead to T_2^- or phase-relaxation processes, are being ignored. In other words, a low-coverage situtation is being envisaged.

In considering the interaction between the laser and the adatom, previous models have often assumed the existence of a well-defined "active" mode,[17,18,20] that is one associated with a transition between states of the adatom-solid system which are separated by an energy gap nearly equal to the laser frequency. In the Bloch picture of delocalized adatom states, the energy levels appear as bands, with band gaps which are complicated functions of the 2D wave vectors in the 2D Brillouin zone of the surface. The identification of a particular single active mode is difficult in this case. In dealing with direct transitions of the adatom from states in one band to

those in another, the "resonance" condition may occur at many different parts in the 2D $\vec{k}$-space, and it is the cumulative effect of all such transitions which will distinguish one laser frequency from another. For the moment the only restriction that may be applied to the laser is that its frequency be of the same order of magnitude as the expected gaps in the energy level band structure of the adatom under the influence of the surface potential.

The other interaction being considered is that between the vibrationally excited adatom and the phonon modes of the solid. If adsorption is not very strong, one may proceed by solving the zero-order problem of the adatom in t: potential field of the solid frozen in its equilibrium configuration, and applying the influence of the motion of the lattice particles on the adatom as a perturbation. With zero-order states of the system represented by combinations of the above zero-order states of the adatom and phonon states of the harmonic lattice in the absence of the adatom, multiphonon relaxation of the adatom is described by transitions between these many-quasiparticle states. The strength of these transitions involves matrix elements of the perturbation operator mentioned before.

A. The Total Hamiltonian.

Let $\mathcal{H}_a^0$ be the Hamiltonian of the adatom of mass m under the influence of the potential $V^0(\vec{r})$ due to the solid at equilibrium,

$$\mathcal{H}_a^0(\vec{r}) = -\frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + V^0(\vec{r}), \tag{1}$$

$$V^0(\vec{r}) = \sum_{\ell} \mathcal{V}(\vec{r} - \vec{R}_{\ell}^0), \tag{2}$$

where $\vec{r}$ is the position vector of the adatom and $\vec{R}_\ell^0$ is the equilibrium position of the ℓth lattice particle. Here $\mathcal{V}(\vec{r}-\vec{R}_\ell^0)$ is a suitably chosen pair potential between the adatom and the ℓth lattice particle. The actual potential can be written as

$$V(\vec{r}) = \sum_\ell \mathcal{V}(\vec{r}-\vec{R}_\ell), \tag{3}$$

where $\vec{R}_\ell$ is the instantaneous position of the ℓth lattice particle. The difference between $V(\vec{r})$ and $V^0(\vec{r})$ is the perturbation $\Delta\mathcal{H}$ responsible for phonon relaxation of the vibrationally excited adatom,

$$\Delta\mathcal{H} = V(\vec{r}) - V^0(\vec{r}) = \sum_\ell \left[\mathcal{V}(\vec{r}-\vec{R}_\ell) - \mathcal{V}(\vec{r}-\vec{R}_\ell^0) \right] . \tag{4}$$

To get the complete Hamiltonian for the system, the contributions $\mathcal{H}_v^0$ and $\mathcal{H}_r$ due to vibrations of a harmonic lattice and interaction with the laser field, respectively, must be included, i.e.,

$$\mathcal{H} = \mathcal{H}_a^0 + \mathcal{H}_v^0 + \mathcal{H}_r + \Delta\mathcal{H} . \tag{5}$$

We employ solutions of the two zero-order problems, namely one set for the adatom in the potential $V^0(\vec{r})$,

$$\mathcal{H}_a^0 \mid \alpha j \vec{n} > = \epsilon_{\alpha j \vec{n}}^0 \mid \alpha j \vec{n} > , \tag{6}$$

and another set for the normal modes of vibration of the lattice in the harmonic approximation ,

$$\mathcal{H}_v^0 \Upsilon_v^0 = \epsilon_v^0 \Upsilon_v^0 , \tag{7}$$

with

$$\mathcal{H}_v^0 = (1/2) \sum_{\vec{k}b} \{ \dot{q}_b^2(\vec{k}) + \omega_b^2(\vec{k}) q_b^2(\vec{k}) \} . \tag{8}$$

8

In Eqs. (6)-(8), α, j and $\vec{\eta}$ are quantum numbers representing a band index, quantization of motion along the $\underline{z}$ axis and quantization of motion in the $\underline{xy}$-plane, respectively ($\vec{\eta}$ is a 2D wave vector); the eigenvalues $\varepsilon_{\alpha j \eta}^{0}$ correspond to the stationary states of the adatom in the potential V^0; Ψ_v^0 and ε_v^0 are the many-phonon wave function and energy, respectively, for the whole crystal; and $q_b(\vec{k})$ and $\dot{q}_b(\vec{k})$ are the normal displacement coordinate and momentum, respectively, for a phonon with wave vector $\vec{k}$ in the phonon branch b and frequency $\omega_b(\vec{k})$.

The Hamiltonian for the interaction of the system with the laser field is simplified by assuming that, due to a near-resonance condition, most of the radiation is absorbed by the surface-adatom bond. The Hamiltonian $\mathcal{H}_r$ then becomes

$$\mathcal{H}_r = \frac{1}{2m} e_0 \, (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}), \tag{9}$$

where $\vec{p}$ is the momentum operator for the adatom, e_0 is some residual effective charge on the adatom and $\vec{A}$ is a vector potential for the laser field at time t,

$$\vec{A}(\vec{r},t) = A_0 \, \vec{\varepsilon} \, \exp[i(\vec{\kappa} \cdot \vec{r} - \omega t)] + c.c. \quad , \tag{10}$$

$\vec{\varepsilon}$, $\vec{\kappa}$ and ω being the unit polarization vector, wave vector and frequency, respectively . If it is further assumed that the incoming flux of photons is large enough so that absorption dominates over emission, then the complex conjugate part (c.c.) of Eq. (10) can be neglected.

B. Solutions of the Zero-Order Problem.

The zero-order problem is represented by the Hamiltonian

$$\mathcal{H}^0 = \mathcal{H}_a^0 + \mathcal{H}_v^0 \tag{11}$$

For simplicity the assumption that $\mathcal{H}_a^0$ and $\mathcal{H}_v^0$ can be solved separately [Eqs. (6) and (7)] is made. The solutions so obtained are then combined to provide a description of the overall problem defined by the Hamiltonian in Eq. (5). The two zero-order problems are discussed below.

1. Zero-Order Problem for the Adatom, $\mathcal{H}_a^0$.

As in most problems involving periodicity, it is convenient to transform to the Fourier space. At the surface of a perfect solid, the potential is periodic along the surface plane (the xy-plane) but not in the z direction. The appropriate Fourier expansion of $V^0(\vec{r})$ is based on the condition

$$V^0(\vec{r} + \vec{X}_\ell^0) = V^0(\vec{r}), \tag{12}$$

where $\vec{X}_\ell^0$ is a lattice vector along the surface plane

$$\vec{X}_\ell^0 \equiv (x_{1\ell}^0, x_{2\ell}^0) = n_1 \vec{a}_1 + n_2 \vec{a}_2, \tag{13}$$

n_1, n_2 being integers and $\vec{a}_1$, $\vec{a}_2$ primitive surface lattice vectors. As a result of Eq. (12) we can write $V^0(\vec{r})$ as a Fourier series

$$V^0(\vec{r}) \equiv V^0(\vec{X}, z) = \sum_{\vec{G}} V_{\vec{G}}^0(z) e^{i\vec{G}\cdot\vec{X}}, \tag{14}$$

where the Fourier transform $V_{\vec{G}}^0(z)$ is given by

$$V_{\vec{G}}^0(z) = \frac{1}{A_u} \times \int_{\substack{2D \\ \text{unit cell}}} d\vec{X} \, V^0(\vec{X}, z) \, e^{-i\vec{G}\cdot\vec{X}}, \tag{15}$$

A_u being the area of a 2D unit cell, $A_u = |\vec{a}_1 \times \vec{a}_2|$. The expansion in Eq. (14) is over all 2D reciprocal lattice vectors (RLV) $\vec{G}$ for the exposed surface plane,

10

$$\vec{G} = m_1 \vec{b}_1 + m_2 \vec{b}_2 \quad , \tag{16}$$

$$\vec{b}_1 = \frac{2\pi \, (\vec{a}_2 \times \hat{z})}{\vec{a}_1 \cdot (\vec{a}_2 \times \hat{z})} \quad , \qquad \vec{b}_2 = \frac{2\pi \, (\hat{z} \times \vec{a}_1)}{\vec{a}_1 \cdot (\vec{a}_2 \times \hat{z})} \quad , \tag{17}$$

where $\hat{z}$ is a unit vector normal to the surface (xy- or $a_1 a_2$-) plane. Thus for any plane parallel to the surface plane, the 2D RLV are completely specified by two integers m_1 and m_2 to be used as subscripts, for example $V_{\vec{G}}(z) \equiv V_{m_1 m_2}(z)$.

The surface potential is, in general, a smoothly varying function, and the Fourier expansion can be expected to converge quite rapidly. This is borne out by recent calculations,[10,21] using summed pair potentials (Morse, Yukawa etc.), where $V^0_{m_1, m_2}(z)$ was found to be appreciable only for $m_1, m_2 < 2$, and by the qualitative success of models using pure sinusoidal functions for $V^0(\vec{r})$.[22] The maximum value of (m_1, m_2) can therefore serve as one measure of the degree of approximation in actual computations.

The stationary states for a single particle with a periodic Hamiltonian $\mathcal{H}^0_a$ are characterized by a quasicontinuum of quantum numbers, namely 2D wave vectors

$$\vec{\eta} = \frac{\nu_1}{N_1} \vec{b}_1 + \frac{\nu_2}{N_2} \vec{b}_2 ; \tag{18}$$

ν_1 and ν_2 are integers, and N_1 and N_2 signify the (large-) number of unit cells along the $\vec{a}_1$ and $\vec{a}_2$ directions, respectively, beyond which the crystal surface is repeated. The single-particle states ϕ^0 must then satisfy the Born-von Karman boundary condition on a surface

$$\phi^0(\vec{r} + N_1\vec{a}_1) = \phi^0(\vec{r} + N_2\vec{a}_2) = \phi^0(\vec{r}), \tag{19}$$

leading to the Bloch functions

$$\phi^0_{a\vec{J}\vec{\eta}}(\vec{r}) = \sum_{\vec{G}} \phi^0_{a\vec{J}\vec{\eta}+\vec{G}}(z) e^{i\vec{G}\cdot\vec{X}} e^{i\vec{\eta}\cdot\vec{X}}. \tag{20}$$

In Eq.(20), summing over $\vec{G}$ allows us to restrict $\vec{\eta} = \vec{\eta}_1 + \vec{\eta}_2$ to the 2D first Brillouin zone (FBZ), namely the area defined by

$$-\frac{b_1}{2} < \eta_1 < \frac{b_1}{2} \; ; \; -\frac{b_2}{2} < \eta_2 < \frac{b_2}{2} \; . \tag{21}$$

Using Eqs. (1), (14) and (20) in Eq. (6), we get

$$\sum_{\vec{G}} \left[-\frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + \sum_{\vec{G}'} V_{\vec{G}'}^0 (z) e^{i\vec{G}'\cdot\vec{X}} - \varepsilon_{\alpha j \vec{\eta}}^0 \right] \phi_{\alpha j \vec{\eta}+\vec{G}}^0 (z)$$

$$\times \exp(i\vec{G}\cdot\vec{X}) \exp(i\vec{\eta}\cdot\vec{X}) = 0. \tag{22}$$

Using symmetry associated with translation of the reciprocal lattice by RLVs we obtain

$$\sum_{\vec{G}} \left\{ \left[-\frac{\hbar^2}{2m} \nabla_z^2 + \frac{\hbar^2}{2m} (\vec{\eta}+\vec{G})^2 - \varepsilon_{\alpha j \vec{\eta}}^0 \right] \phi_{\alpha j \vec{\eta}+\vec{G}}^0 (z) \right.$$

$$\left. + \sum_{\vec{G}'} V_{\vec{G}-\vec{G}'}^0 (z) \phi_{\alpha j \vec{\eta}+\vec{G}'}^0 (z) \right\} \exp\{i(\vec{\eta}+\vec{G})\cdot\vec{X}\} = 0 \; , \tag{23}$$

which leads to a set of coupled differential equations for the $\phi_{\alpha j \vec{\eta}+\vec{G}}^0 (z)$, namely,

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + \frac{\hbar^2}{2m} (\vec{\eta}+\vec{G})^2 - \varepsilon_{\alpha j \vec{\eta}}^0 \right] \phi_{\alpha j \vec{\eta}+\vec{G}}^0 (z)$$

$$+ \sum_{\vec{G}'} V_{\vec{G}-\vec{G}'}^0 (z) \phi_{\alpha j \vec{\eta}+\vec{G}'}^0 (z) = 0. \tag{24}$$

The solution of the set of equations (24) represents the first major computational task in a treatment of the stationary states of an adsorbed atom.

2. Zero-Order Problem for the Lattice Vibrations, $\mathcal{H}_v^0$.

The transformation of the actual Hamiltonian of a vibrating lattice to the form of Eq. (8) is based on a Born-Oppenheimer (adiabatic) approximation, and the inclusion of only harmonic terms in the expansion of the interatomic potential Φ_Ξ; here Ξ denotes a particular electronic state of the crystal. The normal-mode transformation reduces the vibrating lattice to a set of $3\beta N$ noninteracting one-dimensional harmonic oscillators, where β is the number of atoms in a unit cell and N is the number of unit cells in the crystal.

In principle, we can write Eq. (7) as a Schrödinger equation,

$$\frac{1}{2} \sum_{\vec{k}b} \left\{ -\hbar^2 \frac{\partial^2}{\partial q_b^2(\vec{k})} + \omega_b^2(\vec{k}) q_b^2(\vec{k}) \right\} \Psi_v^0 = \varepsilon_v^0 \Psi_v^0 \quad . \quad (27)$$

and write Ψ_v^0 as a product of single-oscillator wave functions

$$\Psi_v^0 = \prod_{\vec{k}b} \phi_{v_b(\vec{k})}^0 [q_b(\vec{k})] \quad , \quad (28)$$

since $\mathcal{H}_v^0$ is a sum of independent single-oscillator Hamiltonians, with $v_b(\vec{k})$ the number of quanta of the $(\vec{k}b)$ vibration in the system. Eq. (27) can now be written as a series of single-oscillator equations

$$\left\{ -\frac{\hbar^2}{2} \frac{\partial^2}{\partial q_b^2(\vec{k})} + \frac{1}{2} \omega_b^2(\vec{k}) q_b^2(\vec{k}) \right\} \phi_{v_b(\vec{k})}^0 \left[q_b(\vec{k}) \right]$$

$$= \varepsilon_{v_b(\vec{k})}^0 \phi_{v_b(\vec{k})}^0 \left[q_b(\vec{k}) \right] \quad . \quad (29)$$

whose solutions are $\left[v \equiv v_b(\vec{k}), q \equiv q_b(\vec{k}), \omega \equiv \omega_b(\vec{k}) \right]$

13

$$\phi_v^0(q) = \sqrt{2^v \left(\frac{\omega}{\pi\hbar}\right)^{(1/2)} v!} \; e^{-(1/2)\omega q^2/\hbar} \; H_v\left(\sqrt{\frac{\omega q^2}{\hbar}}\right), \qquad (30)$$

where H_v is the vth Hermite polynomial. Also,

$$\epsilon_v^0 \equiv \epsilon_{\{v\}}^0 = \sum_{\vec{k}b} \epsilon_{v_b(\vec{k})}^0 = \sum_{\vec{k}b} \left[v_b(\vec{k}) + (1/2)\right] \hbar\omega_b(\vec{k}) , \qquad (31)$$

where the subscript $\{v\}$ represents a specific set $\{v_b(\vec{k})\}$ of $3\beta N$ vibrational quantum numbers which describes the state of the system.

The dispersion relation embodied in the functional form of $\omega_b(\vec{k})$ is the primary information necessary for a complete description of the phonon spectrum. Extensive experimental and theoretical work has been done in this area, and highly accurate phonon band structures and dispersion relations are known from neutron scattering, infrared absorption, Raman scattering, Brillouin scattering and X-ray scattering. [23]

3. Solutions of $\mathcal{H}^0 = \mathcal{H}_a^0 + \mathcal{H}_v^0$.

In the harmonic approximation, the equilibrium positions of the atoms in a crystal, $\vec{R}_\ell^0$, do not represent dynamical variables. The total zero-order Hamiltonian, Eq. (11), can then be written as

$$\mathcal{H}^0 = \left[-\frac{\hbar^2}{2m}\nabla_{\vec{r}}^2 + V^0(\vec{r})\right] + \sum_{b\vec{k}}\left[-\frac{\hbar^2}{2}\frac{\partial^2}{\partial q_b^2(\vec{k})} + \frac{1}{2}\omega_b^2(\vec{k})q_b^2(\vec{k})\right]. \qquad (32)$$

14

The solutions of a Hamiltonian which is the sum of independent single-particle Hamiltonians, in this case for one adatom and $3\beta N$ phonons, are products of solutions of the individual single-particle Schrödinger equations,

$$\Psi^0_{\alpha j \vec{n} \{v_b(\vec{k})\}} \left[\vec{r}, \left\{ q_b(\vec{k}) \right\} \right] = \phi^0_{\alpha j \vec{n}}(\vec{r}) \prod_{b\vec{k}} \phi^0_{v_b(\vec{k})} \left[q_b(\vec{k}) \right]. \qquad (33)$$

These will be denoted $| \alpha j \vec{n}; \{v_b(\vec{k})\} >$, and the $(\vec{r}, q)$ representation will be implied. Also, the abbreviated forms v, q and ω will be used instead of $v_b(\vec{k})$, $q_b(\vec{k})$ and $\omega_b(\vec{k})$, respectively, wherever appropriate.

C. Absorption of Laser Radiation and Phonon Relaxation.

Eq. (5) is the total Hamiltonian for the system. One possible way of viewing it is to ascribe to ΔH and H_r the status of perturbations imposed on a system otherwise described by the zero-order Hamiltonian $\mathcal{H}^n = \mathcal{H}^0_a + \mathcal{H}^0_v$. Such a description is not appropriate for all cases of physical interest, and it is necessary to clearly define the limitations of such an approach as well as alternate routes for cases falling outside these limits.

The recent phenomenological studies of LSSP [17,18] have provided some insight into the above questions. It is seen that relative time scales for the vibration of the adatom/surface bond and the phonons, the associated energy gap and the effective coupling between the two must be considered in deciding what kind of perturbative approach, if any, is applicable. Thus, for high temperatures (large $\Delta\mathcal{H}$), high optical pumping rates (large $\mathcal{H}_r$), very strong bonding between the adatom and the surface, or a very small energy difference between the adatom/surface vibrational frequencies and the Debye frequency of the solid, straightforward application of a perturbation approach may be inadequate. In such cases it may become meaningless to separate the

degrees of freedom of the solid from those of the adatom/surface bond, and a basis-set transformation may be necessary to describe the new degrees of freedom which would in general differ considerably from the original ones. Such transformations have been discussed previously [13,14] in the context of phenomenological treatments within a second-quantized formulation of phonon-mediated energy transfer in condensed systems. We shall not pursue this aspect of the problem but restrict ourselves to cases where $\Delta\mathcal{H}$ and $\mathcal{H}_r$ can, in fact, be considered as perturbations of $\mathcal{H}_a^0 + \mathcal{H}_v^0$.

We begin by writing the transition rate for an adatom from a laser-pumped state $|e\rangle$ of energy ϵ_e to a state $|g\rangle$ of energy ϵ_g using Fermi's Golden rule

$$\mathcal{R}(g \leftarrow e) = \frac{2\pi}{\hbar} \left(\sum_i e^{-\beta\epsilon_i} \right)^{-1} \sum_i \sum_f (e^{-\beta\epsilon_i} W_e - e^{-\beta\epsilon_f} W_g) \qquad (34)$$

$$\times |\langle ie| \Delta\mathcal{H} |fg\rangle|^2 \, \delta \left[\epsilon_e - \epsilon_g - (\epsilon_f - \epsilon_i) \right] \,,$$

where $|i\rangle$ and $|f\rangle$ are initial and final phonon states of the lattice, respectively, with energies ϵ_i and ϵ_f, and W_e and W_g are probabilities of findings the adatom in the states $|e\rangle$ and $|g\rangle$, after a fast short pulse of laser radiation. Because of the δ-function, we must have

$$\epsilon_f - \epsilon_i = \epsilon_e - \epsilon_g = \Delta_{eg} = \hbar\omega_{eg} \,. \qquad (35)$$

which allows us to write $\mathcal{R}$ as

$$\mathcal{R}(g \leftarrow e) = \frac{2\pi}{\hbar} \left(\sum_i e^{-\beta\epsilon_i} \right)^{-1} \sum_i \sum_f e^{-\beta\epsilon_i} (W_e - W_g e^{-\beta\Delta_{eg}})$$

$$\times |\langle ie| \Delta\mathcal{H} |fg\rangle|^2 \quad \delta [\Delta_{eg} - (\epsilon_f - \epsilon_i)] \,, \qquad (36)$$

or

$$\mathcal{R}(g \leftarrow e) = \frac{2\pi}{\hbar} \left(\sum_i e^{-\beta\epsilon_i} \right)^{-1} \sum_i \sum_f e^{-\beta\epsilon_i} W_{eg} |\langle ie| \Delta\mathcal{H} |fg\rangle|^2 \, \delta \left[\Delta_{eg} - (\epsilon_f - \epsilon_i) \right] \qquad (37)$$

To simplify $\mathcal{R}(g{\rightarrow}e)$ further it is convenient to expand $\Delta\mathcal{H}$ in terms of Fourier components of the pair potential $\vec{v}(r)$. With

$$V_{\vec{q}} = \frac{1}{V_u}\int V(\vec{r})\, e^{-i\vec{q}\cdot\vec{r}}\, d\vec{r} \, , \qquad (38)$$

where V_u is the volume of a unit cell, we can write

$$V^0(\vec{r}) = \sum_{\ell}\sum_{\vec{q}} V_{\vec{q}}\, e^{i\vec{q}\cdot(\vec{r}-\vec{R}_\ell^0)} \qquad (39)$$

and

$$\vec{V}(r) = \sum_{\ell}\sum_{\vec{q}} V_{\vec{q}}\, e^{i\vec{q}\cdot(\vec{r}-\vec{R}_\ell)} \, , \qquad (40)$$

so that

$$\Delta\mathcal{H} = \sum_{\vec{q}}\left[V_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}} \sum_{\ell}\left(e^{-i\vec{q}\cdot\vec{R}_\ell} - e^{-i\vec{q}\cdot\vec{R}_\ell^0}\right)\right] \, . \qquad (41)$$

The rate then becomes

$$\mathcal{R}(g{\rightarrow}e) = \frac{2\pi}{\hbar}\left(\sum_i e^{-\beta \varepsilon_i}\right)^{-1} \sum_i \sum_f e^{-\beta \varepsilon_i} w_{eg} \sum_{\vec{q}}\sum_{\vec{q}'}$$

$$\times \left\{ \langle e|V_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}}\,|g\rangle\langle g|V_{\vec{q}'}\, e^{-i\vec{q}'\cdot\vec{r}}\,|e\rangle \cdot \sum_{\ell}\sum_{\ell'}\langle i|e^{-i\vec{q}\cdot\vec{R}_\ell} - e^{-i\vec{q}\cdot\vec{R}_\ell^0}|f\rangle \right.$$

$$\left. \times \langle f|e^{i\vec{q}'\cdot\vec{R}_{\ell'}} - e^{i\vec{q}'\cdot\vec{R}_{\ell'}^0}|i\rangle \right\}\delta\left(\Delta_{eg} - [\varepsilon_f - \varepsilon_i]\right) \, . \qquad (42)$$

17

We now use the δ-function representation

$$\delta(\Delta_{eg} - [\epsilon_f - \epsilon_i]) \equiv \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt\ e^{i\epsilon_i t/\hbar}\ e^{-i\epsilon_f t/\hbar}\ e^{i\Delta_{eg}t/\hbar} \qquad (43)$$

to transform the operator in the first phonon matrix element:

$$\langle i|\hat{\Theta}|f\rangle \longrightarrow \langle i|e^{i\epsilon_i t/\hbar}\ \hat{\Theta}\ e^{-i\epsilon_f t/\hbar}|f\rangle = \langle i|\hat{\Theta}(t)|f\rangle . \qquad (44)$$

Also, since

$$\sum_f |f\rangle\langle f| = 1, \qquad (45)$$

we get

$$R(g \rightarrow e) = \frac{1}{\hbar^2} \sum_{\vec{q}} \sum_{\vec{q}'} \mathcal{U}_{\vec{q}}\ \mathcal{U}_{\vec{q}'}^{*}\ f_{\vec{q},eg}\ f_{\vec{q}',eg}^{*}\ W_{eg}$$

$$\times \sum_{\ell} \sum_{\ell'} e^{-i(\vec{q}\cdot\vec{R}_\ell^0 - \vec{q}'\cdot\vec{R}_{\ell'}^0)} \times \int_{-\infty}^{\infty} dt\ e^{i\Delta_{eg}t/\hbar} \left\{ \left(\sum_i e^{-\beta\epsilon_i} \right)^{-1} \right.$$

$$\times \left. \sum_i e^{-\beta\epsilon_i} \langle i|\left(e^{-i\vec{q}\cdot\vec{u}_\ell(t)} - 1\right)\left(e^{i\vec{q}'\cdot\vec{u}_{\ell'}(0)} - 1\right)|i\rangle \right\} . \qquad (46)$$

where we have used the following:

$$\vec{R}_\ell \equiv \vec{R}_\ell^0 + \vec{u}_\ell \qquad (47)$$

and

$$f_{\vec{q},eg} \equiv \langle e|e^{i\vec{q}\cdot\vec{r}}|g\rangle . \qquad (48)$$

In taking the diagonal phonon matrix elements in Eq (46), only those terms

in the operator which correspond to the product of two exponentials will survive. The remaining terms involve operators $\hat{O}$ (other than unity) which create or annihilate at least one phonon and contribute nothing to $\langle i|\hat{O}|i\rangle$. The constant terms involved in the phonon operator lead to $\delta(\Delta_{eg}t/\hbar)$ when the Fourier transform is taken, and these also do not contribute. The overall Fourier transform can therefore be written as

$$\int_{-\infty}^{\infty} dt \; e^{i\Delta_{eg}t/\hbar} \left\langle\!\!\!\left\langle e^{-i\vec{q}\cdot\vec{u}_\ell(t)} \; e^{i\vec{q}'\cdot\vec{u}_{\ell'}(0)} \right\rangle\!\!\!\right\rangle. \tag{49}$$

The double brackets represent an ensemble average whose evaluation has been discussed extensively in the literature.[24] The operator $\vec{u}_\ell$ is linear in the creation and annihilation operators for phonons. Hence it follows that the commutator $[A,B]$ is a c-number, where A and B are the exponents in the ensemble average, that is :

$$A \equiv \vec{q}\cdot\vec{u}_\ell(t) \quad , \tag{50}$$

$$B \equiv \vec{q}'\cdot\vec{u}_{\ell'}(0) \; . \tag{51}$$

Thus

$$e^A \, e^B = e^{A+B} \, e^{(1/2)[A,B]} \tag{52}$$

and

$$\langle\!\langle \quad \rangle\!\rangle = \langle\!\langle e^{-i[\vec{q}\cdot\vec{u}_\ell(t) \; - \; \vec{q}'\cdot\vec{u}_{\ell'}(0)]} \rangle\!\rangle. \tag{53}$$

For operators $\hat{O}$ linear in harmonic-oscillator creation/annihilation operators we have[25]

$$\langle\!\langle e^{i\hat{O}} \rangle\!\rangle = e^{(-1/2)\langle\!\langle \hat{O}^2 \rangle\!\rangle_T}. \tag{54}$$

Use of the above eventually leads to the result[11,26,27]

$$\langle\langle \quad \rangle\rangle = \exp\left[-W_{\ell\ell'}(\vec{q},\vec{q}') + \vec{q}\cdot\overset{\leftrightarrow}{C}_{\ell\ell'}(t)\cdot\vec{q}'\right], \qquad (55)$$

where

$$W_{\ell\ell'}(\vec{q},\vec{q}') \equiv (1/2)\langle\langle(\vec{q}\cdot\vec{u}_\ell)^2 + (\vec{q}'\cdot\vec{u}_{\ell'})^2\rangle\rangle \qquad (56)$$

is a Debye-Waller-like factor, and

$$\overset{\leftrightarrow}{C}_{\ell\ell'}(t) \equiv \langle\langle\vec{u}_\ell(t)\vec{u}_{\ell'}(0)\rangle\rangle \qquad (57)$$

is a correlation function involving the atomic displacements at sites ℓ,ℓ' and times t and 0. The energy transfer rate thus becomes:

$$\mathcal{R}(g\rightarrow e) = \frac{1}{\hbar^2}\sum_{\vec{q}}\sum_{\vec{q}'}\mathcal{V}_{\vec{q}}\mathcal{V}_{\vec{q}'}^* f_{\vec{q},eg}\, f_{\vec{q}',eg}^{}\, W_{eg}\cdot\sum_\ell\sum_{\ell'} e^{-i(q\cdot R_\ell^0 - q'\cdot R_{\ell'}^0)}$$

$$\times \int_{-\infty}^{\infty} dt\, \exp\left[i\Delta_{eg}t/\hbar - W_{\ell\ell'}(\vec{q},\vec{q}') + \vec{q}\cdot\overset{\leftrightarrow}{C}_{\ell\ell'}(t)\cdot\vec{q}'\right]. \qquad (58)$$

The separation of the rate expression into sections depending on the adatom properties and those depending on the properties of the solid is an attractive feature of this formalism and is primarily due to the treatment of momentum transfer and energy transfer as independent variables.[28] The computational procedure now calls for the solution of the coupled differential equations for the stationary states of the adatom in the static crystal potential, calculation of transition probabilities for these states under laser irradiation, and finally the calculation of the correlation functions $\overset{\leftrightarrow}{C}_{\ell\ell'}(t)$.

One starts by utilizing the expansion of the displacement $\vec{u}_\ell$, in the harmonic case, in terms of phonon creation and annihilation operators $a^\dagger_{\vec{k}b}$ and $a_{\vec{k}b}$, respectively.[29] With M the mass of the lattice atoms in a monatomic crystal and $N = N_1 N_2 N_3$ the total number of unit cells, we can write

$$\vec{u}_\ell = \left(\frac{\hbar}{2NM}\right)^{1/2} \sum_{\vec{k}b} \frac{\vec{e}_b(\vec{k})}{[\omega_b(\vec{k})]^{1/2}} e^{i\vec{k}\cdot\vec{R}_\ell} \cdot \left[a_{\vec{k}b} + a^\dagger_{-\vec{k}b}\right], \qquad (59)$$

to obtain the correlation tensor in the form

$$\left\langle\!\!\left\langle \vec{u}_\ell(t)\, \vec{u}_{\ell'}(0) \right\rangle\!\!\right\rangle = \frac{\hbar}{2NM} \sum_{\vec{k}b} \frac{\vec{e}_b(\vec{k})\vec{e}_b^{\,*}(\vec{k})}{\omega_b(\vec{k})}$$

$$\times\, e^{i\vec{k}\cdot(\vec{R}_\ell - \vec{R}_{\ell'})} \left[(\bar{n}_{\vec{k}b} + 1)\, e^{-i\omega_b(\vec{k})t} + \bar{n}_{\vec{k}b}\, e^{i\omega_b(\vec{k})t}\right], \qquad (60)$$

where $\bar{n}_{\vec{k}b}$ is the Bose function

$$\bar{n}_{\vec{k}b} = \left(e^{\beta\hbar\omega_b(\vec{k})} - 1\right)^{-1}. \qquad (61)$$

It is expedient at this point to take the continuum limit of the phonon band structure by replacing the summation over wave vectors $\vec{k}$ with an integration over $\vec{k}$ space,

$$\lim_{V\to\infty} \sum_{\vec{k}} F(\vec{k}) = \frac{NV}{8\pi^3} \int d\vec{k}\; F(\vec{k}), \qquad (62)$$

where V is the volume of the crystal, to obtain

21

$$\overset{\leftrightarrow}{C}_{\ell\ell'}(t) = \frac{\hbar V_u}{16\pi^3 M} \sum_b \int d\vec{k} \, \frac{\vec{e}_b(\vec{k})\vec{e}_b^*(\vec{k})}{\omega_b(k)} e^{i\vec{k}\cdot(\vec{R}_\ell - \vec{R}_{\ell'})} \left[e^{-i\omega_b(\vec{k})t} + 2\bar{n}_{kb}\cos\{\omega_b(\vec{k})t\} \right] . \quad (63)$$

From Eq. (58), the rate $\mathcal{R}(g\to e)$ is seen to involve the time Fourier transform of $\exp[C_{\ell\ell'}(t)]$. If a cumulants-type expansion is reasonable, the first-order term will be important, namely[29]

$$\int_{-\infty}^{\infty} dt \, e^{i\omega_{eg}t} \overset{\leftrightarrow}{C}_{\ell\ell'}(t) = \frac{\hbar V_u}{4\pi^2 M} \left\{ \bar{n}(\omega_{eg}) + 1 \right\} \text{sgn}(\omega_{eg})$$

$$\times \sum_b \int d\vec{k} \left[\vec{e}_b(\vec{k})\vec{e}_b^*(\vec{k}) e^{i\vec{k}\cdot(\vec{R}_\ell - \vec{R}_{\ell'})} \delta\{\omega_{eg}^2 - \omega_b^2(\vec{k})\} \right] . \quad (64)$$

The term involving $C_{\ell\ell'}^n(t)$ is the n-phonon term. Clearly the one-phonon term

(n=1) dominates when $|\overset{\leftrightarrow}{C}_{\ell\ell'}(t)|/a^2 \ll 1$, where a is a typical lattice parameter. Evaluation of the higher-order terms can be simplified by writing the rate as a Taylor expansion in the $\overset{\leftrightarrow}{C}_{\ell\ell'}(t)$. We first write $\mathcal{R}(g\to e)$ as

$$\mathcal{R}(g\to e) = \left(\frac{\mathcal{V}_0}{\hbar}\right)^2 \tau_D \cdot \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, e^{i\omega_{eg}t} \sum_{\ell\ell'} \mathcal{F}_{\ell\ell'} (\overset{\leftrightarrow}{C}_{\ell\ell'}(t)) , \quad (65)$$

where τ_D is the characteristic time of the highest frequency phonon. Writing

$$\vec{\mathcal{F}}_{\ell\ell'}(C_{\ell\ell'}(t)) = \sum_{\xi\xi'}\left[C_{\ell\ell'\xi\xi'}\left(\frac{\partial\mathcal{F}}{\partial C_{\ell\ell'\xi\xi'}}\right)_0 + \frac{C^2_{\ell\ell',\xi\xi'}}{2!}\left(\frac{\partial^2\mathcal{F}}{\partial C^2_{\ell\ell',\xi\xi'}}\right)_0 \right.$$

$$\left. + \cdots + \frac{C^n_{\ell\ell',\xi\xi'}}{n!}\left(\frac{\partial^n\mathcal{F}}{\partial C^n_{\ell\ell',\xi\xi'}}\right)_0 + \cdots \right] \quad , \qquad (66)$$

(ξ,ξ') being the Cartesian indices x,y,z, we get the rate in the form[29]

$$\mathcal{R}(g\rightarrow e) = \left(\frac{v_0}{\hbar}\right)^2 \sum_{n=1}^{\infty}\sum_{\ell\ell'}\sum_{\xi\xi'}\frac{1}{n!}\cdot\rho_{n,\ell\ell',\xi\xi'}(\omega_{eg})\left(\frac{\partial^n\mathcal{F}}{\partial C^n_{\ell\ell',\xi\xi'}}\right)_0 \quad , \qquad (67)$$

where

$$\rho_{n,\ell\ell',\xi\xi'}(\omega_{eg}) \equiv \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega_{eg}t}\, C^n_{\ell\ell',\xi\xi'}(t) \quad . \qquad (68)$$

Use of the relationship

$$\int_{-\infty}^{\infty}d\omega_1 F_{\omega_1}(f_1)F_{\omega-\omega_1}(f_2) = F_\omega(f_1 \cdot f_2) \quad , \qquad (69)$$

where $F_\omega(f)$ is the Fourier transform of $f(t)$ at ω,

$$F_\omega(f) = \frac{1}{2\pi}\int_{-\infty}^{\infty}dt f(t)e^{i\omega t} \quad , \qquad (70)$$

gives a recursion relation between the ρs:

23

$$\rho_{n+1,\ell\ell',\xi\xi'}(\omega_{eg}) = \int_{-\infty}^{\infty} d\omega \, \rho_{n,\ell\ell',\xi\xi'}(\omega) \, \rho_{1,\ell\ell',\xi\xi'}(\omega_{eg}-\omega)d\omega \qquad (71)$$

which is useful for computational purposes.

III. Discussion

In developing Eq. (58) for the vibrational energy transfer rate from a laser-excited adatom to phonons, the two-dimensional periodicity along the xy-plane has not been explicitly exploited. Important physical effects and simplifications of the formalism are associated with this periodicity, some of which we now examine.

The Potential. The nature of the potentials $V^0(\vec{r})$ and $V(\vec{r})$ in Eqs. (2), (3), (39) and (40) is very different along the z direction as compared to that along the xy-plane. Both must approach a constant for large z and be essentially oscillatory on the xy-plane near the surface. It may also be necessary to allow for different contributions to the potentials due to ions at or near the surface and those deep in the bulk. Formally, the latter is accomplished by affixing an extra index to the pair potential in Eqs. (2) and (3), namely,

$$V^0(\vec{r}) = \sum_{\ell} \upsilon_{z_\ell}\left(\vec{r} - \vec{R}^0_\ell\right) , \tag{72}$$

$$V(\vec{r}) = \sum_{\ell} \upsilon_{z_\ell}\left(\vec{r} - \vec{R}_\ell\right) . \tag{73}$$

Inclusion of these effects is probably most practical for purposes of a phenomenological description of LSSP. Writing Eqs. (39) and (40) in the forms

$$V^0(\vec{r}) = \sum_{q_z} \sum_{\vec{Q}} \left\{ \sum_{z^0_\ell} \left(\sum_{\vec{X}^0_\ell} e^{-i\vec{Q}\cdot\vec{X}^0_\ell} \right) e^{-iq_z z^0_\ell} \upsilon_{\vec{q}} \right\} e^{i\vec{q}\cdot\vec{r}} \tag{74}$$

and

$$V(\vec{r}) = \sum_{q_z} \sum_{\vec{Q}} \left\{ \sum_{z_\ell} \left(\sum_{\vec{X}_\ell} e^{-i\vec{Q}\cdot\vec{X}_\ell} \right) e^{-iq_z z_\ell} \upsilon_{\vec{q}} \right\} e^{i\vec{q}\cdot\vec{r}} , \tag{75}$$

the summation over $\vec{X}_\ell^0$ in Eq. (74) reduces to $\delta(\vec{Q}-\vec{G})$, with $\vec{q} \equiv (\vec{Q},q_z)$ and $\vec{G}$ a primitive 2D reciprocal lattice vector in the plane of the surface. Such a reduction does not take place in Eq. (75) because the $\vec{X}_\ell$ are not fixed vectors. Because of the smallness of the atomic displacements from equilibrium, it is reasonable to use a sharply peaked (Gaussian or Lorentzian) function $\mathcal{D}_{\vec{G}}(\vec{Q})$, with the peak at $\vec{Q} = \vec{G}$, to replace the summation over $\vec{X}_\ell$ in Eq. (75). Eqs. (74) and (75) may therefore be written as

$$V^0(\vec{r}) = \sum_{q_z} \sum_{\vec{Q}} \left[\sum_{z_\ell^0} \left\{ \delta(\vec{Q}-\vec{G})e^{-iq_z z_\ell^0} \right\} U_{\vec{q}} \right] e^{i\vec{q}\cdot\vec{r}} \tag{76}$$

and

$$V(\vec{r}) = \sum_{q_z} \sum_{\vec{Q}} \left[\sum_{z_\ell} \left\{ \mathcal{D}_{\vec{G}}(\vec{Q})e^{-iq_z z_\ell} \right\} U_{\vec{q}} \right] e^{i\vec{q}\cdot\vec{r}} \ . \tag{77}$$

The term $\mathcal{D}_{\vec{G}}(\vec{Q})$ represents the "inelasticity" of the transition process viewed as a scattering event, namely the departure from purely diffractive scattering described by $\delta(\vec{Q}-\vec{G})$ in Eq. (76). The averaging procedure implied in the use of $\mathcal{D}_{\vec{G}}(\vec{Q})$ is not always appropriate. In particular, if the characteristic time scale of the overall relaxation process is comparable to or smaller than a typical period of vibration of the atoms in the solid, no such averaging is possible. Examination of Eqs. (42) - (46) with the aim of applying the forms (76) and (77) of the potential reveals a substantial simplification by allowing a reduction of the summations over $\vec{R}_\ell$ and $\vec{R}_{\ell'}$ to those over only z_ℓ and $z_{\ell'}$. This is an important step in establishing the connection between three-dimensional and one-dimensional treatments of LSSP. The development of a formalism to exploit this two-dimensional translational symmetry is in progress.

<u>Polarization Eigenvectors.</u> The terms $N^{-1/2} \vec{e}_b(\vec{k}) e^{i\vec{k}\cdot\vec{R}_\ell}$

in Eq. (59) represent components of the eigenvectors of the dynamical matrix in the harmonic approximation.[29] The z-component of $\vec{k}$ must clearly be complex in order for the displacement function to damp out for $z \gg 0$. The displacement operator may then be written as

$$\vec{u}_\ell = \left(\frac{\hbar}{2NM}\right)^{1/2} \sum_b \sum_{\vec{K}} \left\{ \sum_{k_z} \frac{\vec{e}_b(k_z,\vec{K})e^{ik_z z_\ell}}{\omega_b(k_z,\vec{K})} \right\} e^{i\vec{K}\cdot\vec{X}_\ell} \left[a_{\vec{K}b} + a^\dagger_{-\vec{K}b} \right] . \quad (78)$$

Assuming a knowledge of the form of $\omega_b(\vec{k})$, the expression in curly brackets depends only on b, $\vec{K}$ and z_ℓ, all dependence on k_z having been absorbed in the summation. This represents another point at which a phenomenological approach could be applied effectively, since a model for $\omega_b(\vec{k})$ could be introduced along with assumptions regarding the range of values for k_z.

<u>Models for Dispersion.</u> In addition to $\vec{e}_b(\vec{k})$, a knowledge of $\omega_b(\vec{k})$ is necessary for actual evaluation of $\mathcal{R}(g\rightarrow e)$. Detailed information on the form of $\omega_b(\vec{k})$ is available from experimental and theoretical studies of a number of systems, but for the present semiquantitative study, a model such as the Einstein or Debye model may suffice. In the former, phonon dispersion is entirely suppressed by assuming the form

$$\omega_b(\vec{k}) = \omega_0 \quad , \text{ a constant,} \quad (79)$$

which neglects all correlations between displacements of different lattice atoms, and by ascribing a single vibrational frequency to all points $\vec{k}$ on all branches b. This model precludes energy transfer over a range of energies

27

but does provide the simplest picture of phonon band structure. The Debye model, on the other hand, assumes a linear dispersion

$$\omega_b(\vec{k}) = \upsilon_s\, k \tag{80}$$

independently of branch index, and thereby allows for energy transfer over a (quasi-) continuous range. The use of Eq. (80) in conjunction with assumptions of isotropy and simple cubic structure reduces the expression for $C_{\ell\ell'}(t)$ and the Fourier transforms of $[C_{\ell\ell'}(t)]^n$ to computationally convenient forms. Actual calculational procedures are currently being developed in this laboratory.

IV. Summary and Conclusions

A general theoretical technique has been developed for the treatment of multiphonon relaxation of an adatom vibrationally excited by low-power laser radiation. The dynamical processes are embodied in correlations between displacements of different atoms of the solid at different times. The correlation functions and their Fourier transforms, though complicated, provide a concise physical description of the relaxation process; the n-phonon processes involve Fourier transforms of the nth power of the correlation function. The generality of the final expressions for the relaxation rate has the advantage of providing links between phenomenological treatments of the problem and establishing the significance of various assumptions involved in the latter.

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