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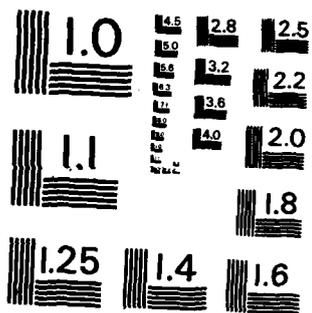
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The Role of Phonons in the Excitation
and Relaxation of Adspecies

by

A. C. Beri, Ki-Tung Lee and Thomas F. George

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QUANTUM GENERALIZED MASTER EQUATION	LOCAL HEATING OF SURFACE ATOMS

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)* The IR laser excitation of an adbond is studied by both a quantum mechanical generalized master equation approach and a classical generalized Langevin approach. The role of phonons in the energy flow between the adbond and the surface is considered. The latter approach looks further at local heating via direct excitation of surface atoms. It is seen that the Markovian approximation is in general inadequate, and that local heating is an important mechanism for desorption.

THE ROLE OF PHONONS IN THE EXCITATION AND RELAXATION OF ADSPECIES

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Abstract

The IR laser excitation of an adbond is studied by both a quantum mechanical generalized
master equation approach and a classical generalized Langevin approach. The role of phonons
in the energy flow between the adbond and the surface is considered. The latter approach
looks further at local heating via direct excitation of surface atoms. It is seen that the
Markovian approximation is in general inadequate, and that local heating is an important
mechanism for desorption.

Introduction

The coherence, monochromaticity and high energy density of lasers have recently been ex-
ploited to influence dynamical processes occurring at a solid surface. The many diverse
applications include catalysis, localized melting, chemical vapor deposition and charged
particle generation. While some of the macroscopic aspects of the phenomena occurring
during the laser-stimulated surface processes have been studied theoretically, a fundamental
microscopic understanding is lacking. In this paper we shall address the role of phonons in
the excitation and relaxation of adspecies. In Section II we present a quantum mechanical
approach utilizing the generalized master equation to obtain the probability destribution of
a laser-excited adbond. In Section III we present a classical generalized Langevin approach,
with application to flash desorption. Here, laser excitation of surface atoms in addition
to the adbond is also considered. Conclusions are presented in Section IV.

Quantum Generalized Master Equation

In a recent paper[1] we formulated a general theory of vibrational excitation of an adatom-
surface bond (adbond) by an IR laser, accompanied by relaxation via vibrational energy ex-
change between the adbond and lattice vibrations. That formalism is based on a first-
principles Hamiltonian approach utilizing first-order perturbation theory, and the effective
potential appearing in the zero-order Hamiltonian for the adbond is assumed to be a sum of
pair potentials between the adatom and the lattice atoms at their equilibrium positions.
For the sake of simplicity, we modeled a process in which a short pulse of radiation excites
the vibrational states of the adbond which subsequently decays via energy transfer to the
phonons. Here we extend that earlier work to include more general types of laser excitation
and introduce an alternative type of effective potential.

Time Evolution of the Laser-Adbond-Solid System

We are primarily interested in the time evolution of the vibrational states of the adbond,
which is excited by IR laser radiation and is coupled to the phonon modes of the solid. We
choose a laser whose frequency is close to a normal mode frequency of the adbond but not to
any of those of the solid. The total Hamiltonian of the system can be written as

$$H = T_a + \sum_\ell V_{a\ell} + \sum_\ell T_\ell + \sum_{\ell\ell'} V_{\ell\ell'} + H_r + H_{ar} . \tag{1}$$

Here T_a is the kinetic energy operator for the adparticle, $V_{a\ell}$ is the interaction between
the adparticle and the ℓ-th lattice atom, T_ℓ is the kinetic energy of the latter, $V_{\ell\ell'}$ is
the interaction energy between the ℓ-th and ℓ'-th lattice atoms, H_r is the Hamiltonian for
the free radiation field and H_{ar} is the interaction between the adbond and the laser radi-
ation. The study of the time evolution of the vibrational states of the adbond then in-
volves extracting the relevant information from the equations of motion of operators O for
the whole system

$$\frac{dO}{dt} = -i\left[\frac{H}{\hbar}, O\right] = -iLO , \tag{2}$$

In addition, we also need to specify a set of initial conditions compatible with the history
of the system prior to the time the experiment is initiated.

We rewrite our Hamiltonian in the form

$$H = H_a + H_p + H_r + H_{ap} + H_{ar} \quad , \tag{3}$$

where

$$H_a = T_a + \sum_\ell \tilde{V}_{a\ell} \quad , \tag{4}$$

$$H_p = \sum_\ell (T_\ell + \sum_{\ell'(>\ell)} V_{\ell\ell'}) \quad , \tag{5}$$

$$H_{ap} = \sum_\ell (V_{a\ell} - \tilde{V}_{a\ell}) \quad , \tag{6}$$

$\tilde{V}_{a\ell}$ is the thermodynamic average of $V_{a\ell}$ over the initial equilibrium configuration of the phonon field:

$$\tilde{V}_{a\ell} = \langle\langle V_{a\ell}\rangle\rangle_p \equiv Tr_p \rho_p(0) V_{a\ell} \quad , \tag{7}$$

$\rho_p(0)$ being the initial equilibrium density operator for the phonon field. The adbond is now described by the Hamiltonian H_a. The radiation field is assumed to be that due to a single-mode laser of frequency ω_L and polarization vector $\hat{\varepsilon}$. Accordingly,

$$H_r = \hbar\omega_L a^\dagger a \quad , \tag{8}$$

and, in the dipole approximation, $e^{\pm i\vec{\kappa}\cdot\vec{r}} = 1$, with effective adatom charge e_0,

$$H_{ar} = -ie_0 \sqrt{\frac{\hbar\omega_L}{2\varepsilon_0\tau}} \ \vec{r}\cdot\hat{\varepsilon}(a - a^\dagger) \quad , \tag{9}$$

where $a^\dagger, a$ are creation-annihilation operators for photons, τ is a quantization volume and $\vec{\kappa}$ is the wave vector of the radiation field.

Using the projection operator technique,[2] we arrive at a set of coupled integrodifferential equations for the matrix elements of a projected density operator ρ for the system:

$$\rho_{ss}(t) = -2\hbar^{-2} \sum_{\bar{s}} \int_0^t dt' \ Re\left[\langle\langle\Delta_{s\bar{s}'}(t')\Delta_{\bar{s}s'}\rangle\rangle e^{i\omega_{\bar{s}s}t'}\right]\rho_{ss}(t-t')$$

$$- Re\left[\langle\langle\Delta_{s\bar{s}'}(t')\Delta_{\bar{s}s'}\rangle\rangle e^{-i\omega_{\bar{s}s}t'}\right]\rho_{\bar{s}'\bar{s}'}(t-t') \tag{10}$$

where

$$\rho_{ss}(t) = \langle s|\rho(t)|s\rangle \tag{11}$$

$$\rho(t) = Tr_p Tr_r W(t) \tag{12}$$

with Tr_p and Tr_r representing traces over the phonon and radiation spaces. $|s\rangle$ is an eigenstate of H_a with energy E_s, $\omega_{ss'}$ is given as

$$\omega_{ss'} = (E_s - E_{s'})/\hbar \quad , \tag{13}$$

and $W(t)$ is the density operator of the whole system.

Application of a Linear-Chain Model

In most cases of chemical interest, some charge transfer takes place between an atom and a surface during adsorption. We shall assume the atom to have an effective charge e_0 and the charge transferred to the solid to be distributed throughout the latter so that it is still essentially neutral. Image-charge effects will be important for the case of metals, but we shall think in terms of nonmetals here to keep the treatment simple.

The vibrational levels of the adatom-surface bond are dictated by the effective potential seen by the adatom. This potential is quite complex, being a result of electrostatic and exchange forces due to the nuclei and electrons of the solid, and is not known for any real system. A simple representation of the effective potential, however, can be obtained by assuming independent pairwise interactions between the adatom and each lattice atom and summing over all lattice atoms. The advantage of such a procedure is that the influence of lattice atoms more than a few lattice constants away from the adatom is negligible (ten lattice atoms should be sufficient for most solids). If the sum of pair potentials can further

be fitted to a single analytic potential, the vibrational levels of the adatom-surface bond reduce to those of a diatomic molecule.

We define a one-dimensional coordinate system with origin at the mean position of the outermost lattice atom. Let z be the position of the adatom and z_ℓ the position of the ℓ-th lattice atom measured in units of $[\beta^{(0)}]^{-1}$ to be defined later,

$$z_\ell = z_\ell^{(0)} + u_\ell = -(\ell-1)a + u_\ell \,, \qquad \ell=1,2\ldots \qquad (14)$$

where u_ℓ is the displacement of the ℓ-th lattice atom from its equilibrium position $z^{(0)} = -(\ell-1)a$, all in units of $[\beta^{(0)}]^{-1}$, assuming a monatomic lattice with uniform spacing α. The interaction potential at the position of the adatom is then a sum of pairwise Morse potentials between it and all the atoms of the chain,

$$V(z,\{z_\ell\}) = \sum_\ell v(z-z_\ell) \equiv \sum_\ell V_{a\ell} \,, \qquad (15)$$

$$v(z-z_\ell) = D_e^{(0)}\left[e^{-2\{z-z_0^{(0)}+(\ell-1)a-u_\ell\}} -2e^{-\{z-z_0^{(0)}+(\ell-1)a-u_\ell\}}\right], \qquad (16)$$

where $z_0^{(0)}$ is the position of the minimum of $v(z)$, $\beta^{(0)}$ is now identified as the Morse exponent parameter and $D_e^{(0)}$ is the well depth of the Morse potential. The zero-order adbond Hamiltonian becomes

$$H_a = -\frac{(\beta^{(0)}\hbar)^2}{2m}\frac{\partial^2}{\partial z^2} + D_e\left[e^{-2(z-z_0)} -2e^{-(z-z_0)}\right]\,, \qquad (17)$$

where D_e and z_0 are effective parameters which involve the pair-potential parameters $D_e^{(0)}$ and $z_0^{(0)}$ and the lattice parameters a and $<<u^2>>$, where the last quantity is the mean square displacement of a lattice atom.

Within this model, the generalized master equation, Eq. (10), becomes

$$\dot{\rho}_{SS}(t) = 2\hbar^{-2}\sum_{S'}\sum_{\mu,\mu'=1}^{2}\sum_{\ell\ell'}\int_0^t dt' \left(Re\left[A_{\ell\ell'}^{\mu\mu'}(S{\leftarrow}S')\left[\sum_n\{Y_{\ell\ell'}^{\mu\mu'}(t')\}^n/n!\right]e^{-i\omega_{SS'}t'}\right]\rho_{S'S'}(t-t')\right.$$

$$\left. - Re\left[A_{\ell\ell'}^{\mu\mu'}(S'{\leftarrow}S)\left[\sum_n\{Y_{\ell\ell'}^{\mu\mu'}(t')\}^n/n!\right]e^{i\omega_{SS'}t'}\right]\rho_{SS}(t-t') + \rho_{r,SS}(t)\right)\,, \qquad (18)$$

where the A's are time-independent coefficients:

$$A_{\ell\ell'}^{\mu\mu'}(S{\leftarrow}S') = (-1)^{\mu+\mu'}\frac{4[D_e^{(0)}]^2}{\mu\mu'}\left[e^{-\mu(z-z_0^{(0)})}\right]_{S'S}\left[e^{-\mu'(z-z_0^{(0)})}\right]_{SS'}$$

$$\times \exp\left[-\mu(\ell-1)a-\mu'(\ell'-1)a + \frac{\mu^2+\mu'^2}{2}<<u^2>>\right] \qquad (19)$$

and the Y's are phonon displacement correlation functions,

$$Y_{\ell\ell'}^{\mu\mu'}(t) = \mu\mu'<<u_\ell(t)u_{\ell'}>> \,. \qquad (20)$$

The term $\rho_{r,SS}(t)$ is the contribution to $\dot{\rho}_{SS}(t)$ due to the radiation field. Replacing ρ_{SS} by P_S, we can write Eq. (18) as

$$\dot{P}_S(t) = \int_0^t dt'\left[\sum_{S'\neq S}\left\{K_{SS'}(t')P_{S'}(t-t')-K_{S'S}(t')P_S(t-t')\right\}\right]\,, \qquad (21)$$

where K consists of contributions due to the phonons and the radiation field,

$$K_{SS'}(t') = K_{SS'}^{(p)}(t') + K_{SS'}^{(r)}(t')\,. \qquad (22)$$

For a system such as oxygen on germanium, the amplitude of $K_{SS'}^{(p)}$ is seen in Fig. 1 to be many orders of magnitude larger than that of $K_{SS'}^{(r)}$ due to a 1 W/cm^2 laser. However, the
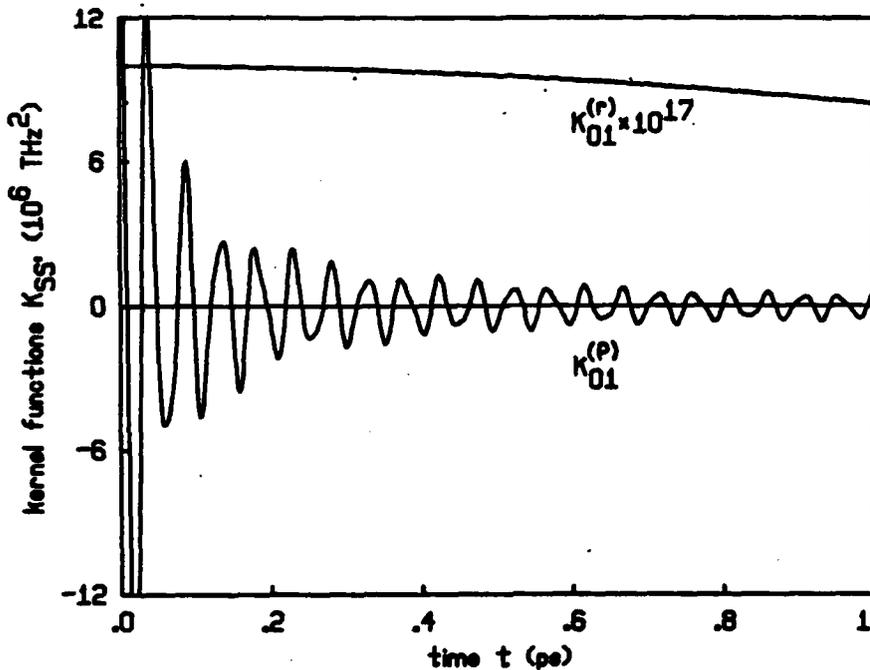
Fig. 1. Kernel functions $K_{01}^{(P)}$ and $K_{01}^{(r)}$ for O/Ge. One-, two- and three-phonon processes are included. The laser-adbond mismatch is 3 cm^{-1}.

"frequency" of $K_{SS'}^{(P)}$ is dictated by the Debye frequency of the solid, whereas that of $K_{SS'}^{(r)}$ depends on the degree of resonance between the laser and the levels of the adbond and can be made arbitrarily small within the rotating-wave approximation. For probability functions P_S that change slowly during the vibrational period of typical phonons, the contribution due to $K_{SS'}^{(r)}$ will be subject to cancellations, whereas that due to $K_{SS'}^{(r)}$ will not. Whether this dynamical effect can bridge the gap due to the difference in magnitude of the amplitudes of $K_{SS'}^{(P)}$ and $K_{SS'}^{(r)}$ depends on the sharpness of the laser-adbond resonance, the details of $K_{SS'}^{(P)}$ and the total irradiation time.

An important consequence of the nature of $K_{SS'}^{(P)}$ is that the dynamics is seen to be non-Markovian since there is no indication that $K_{SS'}^{(P)}$ is localized in time. In general, one expects very complicated nonlocal effects due to the combined laser phonon fields, and great caution must be used when applying a Markovian approximation to such processes. Numerical investigation of the detailed time evolution of a number of laser-adbond-solid systems is in progress and should provide some more definitive answers.

Classical Generalized Langevin Equation

In this section, we shall formulate the problem of flash desorption via a Langevin approach. We model the problem as an incoherent process. Thus, the motions of the phonons serve as a heat bath for the adspecies.

We start with the equation of motion for the i-th atom in a three-dimensional solid

$$m_i \ddot{r}_i = -\sum_j k_{ij} r_j + r_i \sum_{i \neq j} a_{ij} r_j + \sum_j b_{ij} r_j^2 + r_i \sum_{i \neq j} e_{ij} r_j^2 + r_i^2 \sum_{i \neq j} d_{ij} r_j + \sum_j e_{ij} r_j^3 + \cdots \quad (23)$$

where m_i and r_i are the mass and position of the i-th solid atom, and k_{ij}, a_{ij}, b_{ij}, etc. are the elastic and higher-order nonlinear force constants. For simplicity, let us consider the atoms to have unit masses and also assume the nonlocal, nonlinear effects to be unimportant. Hence, Eq. (23) reduces to

$$\ddot{r}_i = -\sum_j k_{ij} r_j + r_i \sum_j a_{ij} r_j + r_i \sum_j e_{ij} r_j^2 + r_j^2 \sum_{i \neq j} d_{ij} r_j + \cdots \quad (24)$$

We rewrite Eq. (24) in matrix notation as

$$\ddot{r} = -kr + r'ar + r'br + r'cr + \cdots \tag{25}$$

with r' and v' diagonal matrices, $r'_{ii} = r_i$ and $v'_{ii} = v_i = r_i^2$.

We now define projection operators P and Q such that

$$y(t) = P\,r(t), \quad z(t) = (1-P)r(t) = Q\,r(t), \quad PQ = 0, \quad PP = P \tag{26}$$

$\{y(t)\}$ are coordiantes of those solid atoms interacting with the adspecies, and $\{z(t)\}$ are coordinates of the remaining solid atoms. Applying these projection operators to Eq. (25), we obtain

$$\ddot{y}(t) = [-k_{PP} + y'(t)\,a_{PP} + y'(t)b_{PP}\,y'(t) + \cdots]y(t) +$$
$$[-k_{PQ} + y'(t)\,a_{PQ} + y'(t)\,b_{PQ}\,z'(t) + \cdots]z(t) \tag{27}$$

and

$$\ddot{z}(t) = [-k_{QQ} + z'(t)\,a_{QQ} + z'(t)b_{QQ}\,z'(t) + \cdots]z(t) +$$
$$[-k_{QP} + z'(t)\,a_{QP} + z'(t)b_{QP}\,y'(t) + \cdots]y(t) \tag{28}$$

$z'(t)$ and $y'(t)$ are diagonal matrices with $z'_{ii}(t) = z_i(t)$ and $y'_{ii}(t) = y_i(t)$, and $k_{PP} = PkP$, $k_{PQ} = PkQ$, etc.

In general, Eq. (28) cannot be solved analytically, so that we seek an approximate solution. First, we obtain the homogeneous solution by applying the equivalent linearization procedure.[3] Thus, we have

$$z_0(t) = \cos[\psi(a)]\,q \quad \text{and} \quad \psi(a) = \Omega(a)t + \phi, \tag{29}$$

where q is the amplitude vector of the bath oscillators, and Ω the frequency matrix and ϕ the phase matrix. Hence, we can write down a first-order formal solution for $z(t)$ as

$$z(t) = z_1(t) + z_2(t) \;, \tag{30}$$

where

$$z_1(t) = \cos[\psi(a)]\,q + \int_0^t dt'\;\Omega^{-1}\sin[\Omega(t-t')]k_{QP}\,y(t') \tag{31}$$

and

$$z_2(t) = \int_0^t dt'\;\Omega^{-1}\sin[\Omega(t-t')][z_0'(t)\,a_{PQ} + z_0'(t)\,b_{PQ}\,y'(t) + \cdots]y(t'), \tag{32}$$

and again $z_{0,ii}' = z_{0,i}$. Substituting (30) into (27), we obtain the generalized Langevin equation

$$\ddot{y}(t) = -k_{PP}\,y(t) - k_{PQ}\,z_1(t) + [y'\,a_{PP} + y'\,b_{PP}y' + \cdots]y(t)$$
$$+ y'(t)\,a_{PQ}\,z(t) + y'\,b_{PQ}\,z(t)\,z(t) + \cdots \tag{33}$$

The first two terms on the RHS, which represent the harmonic approximation, are equivalent to the formalism and Adelman and Doll.[4] The third term describes the anharmonic coupling among the y-oscillators. The rest are higher-order response terms which in general can be neglected if the set of y oscillators is sufficiently big. Thus, Eq. (33) becomes

$$\ddot{y}(t) = [-k_{PP} + y'\,a_{PP} + y'\,b_{PP}y' + \cdots]y(t) - k_{PQ}\,z_1(t). \tag{34}$$

Now, we include the motion of the adspecies to form a complete set of equations of motion. Let $\{x(t)\}$ be the coordinates of the adspecies. We then have

$$\ddot{x}(t) = F_x\,(x(t),y(t),\bar{z}) \tag{35}$$

$$\ddot{y}(t) = [-k_{PP} + y'\,a_{PP} + y'\,b_{PP}\,y' + \cdots]y(t) + F_y(x(t),y(t),\bar{z}) + R(t) - \int_0^t dt'\;\beta(t-t')y(t') \tag{36}$$

with $F_x\,(x(t),y(t),\bar{z}) = -\nabla_x V(x(t),y(t),\bar{z})$ and $F_y(x(t),y(t),\bar{z}) = -\nabla_y V(x(t),y(t),\bar{z})$.

$\bar{z}$ is the equilibrium position of the bath oscillators. Here, $\beta(t) = k_{PQ}\Omega^{-1}\sin(\Omega t)k_{QP}$ is the response function and $R(t) = -k_{PQ}\cos(\Omega t+\phi)q$ is the fluctuating force. These quantities are related by the second fluctuation—dissipation theorem[6]

$$\langle \underline{R}(t)\, \underline{R}^\dagger(0)\rangle = \underline{k}_{PQ}\cos(\underline{\Omega}t)\langle \underline{z}(0)\, \underline{z}^\dagger(0)\rangle \underline{k}_{QP} = k_B T\,\underline{\theta}(t) \tag{37}$$

where we have used

$$\underline{z}(0) = \cos(\underline{\phi})\underline{q} \tag{38}$$

and

$$\langle \underline{z}(0)\, \underline{z}^\dagger(0)\rangle = \underline{\Omega}^{-2} k_B T \tag{39}$$

for the canonical ensemble average. The above formalism is ideal for the study of the dynamics of flash desorption by UV radiation, provided the excited electronic potential $V(x(t),y(t),\bar{z})$ is known. The initial vibrational temperature of the y-oscillators, which is in general higher than the bath temperature, can be chosen by means of the Franck-Condon approximation. Hence, one can study how these y-oscillators relax and transfer energy to the bath and as well as to the adspecies, which leads to (thermal) desorption. However, excited states associated with the adspecies—solid interaction are rarely known, which is the worst obstacle to solving the overall problem.

The above formalism can also be used to study IR laser—induced desorption by simply including the oscillating force (representing the driving force via the IR laser) in both Eqs. (35) and (36). We would like to point out that previous studies[6-8] only the adbond or the internal motion of adspecies are IR active. In another words, the oscillating force is included only in Eq. (35). Here, we assume some of the surface modes (y-oscillators) are also IR active, having frequency compatible with the IR frequency. Actually, this is a reasonable assumption, since these surface atoms which surround the adspecies behave quite differently than the bulk atoms. Thus, the desorption mechanism considered here is not just a resonance process as considered previously,[7,8] but also an incoherent process which is induced by the local heating of the y-oscillators. Let T_y be the steady-state temperature of the y-oscillators and D_0 be the dissociation energy of the adbond. If $k_B T_y > D_0$, the desorption mechanism is an incoherent process. If $k_B T_y < D_0 < k_B T_y + \hbar\omega$ where ω is the frequency of the laser, the desorption mechanism is then a partially coherent process, as shown in Fig. 2. The steady-state temperature of the y-oscillators, which is in general higher than the bath temperature, is due to two complicated completing processes: multiphoton excitation and multiphonon relaxation of the surface modes. The steady-state temperature must satisfy one of the two above conditions; otherwise, an unrealistic high-power laser is required to desorb the adspecies.[7,8] One must search for an optimum laser frequency for the system of interest in order to achieve the desired steady-state
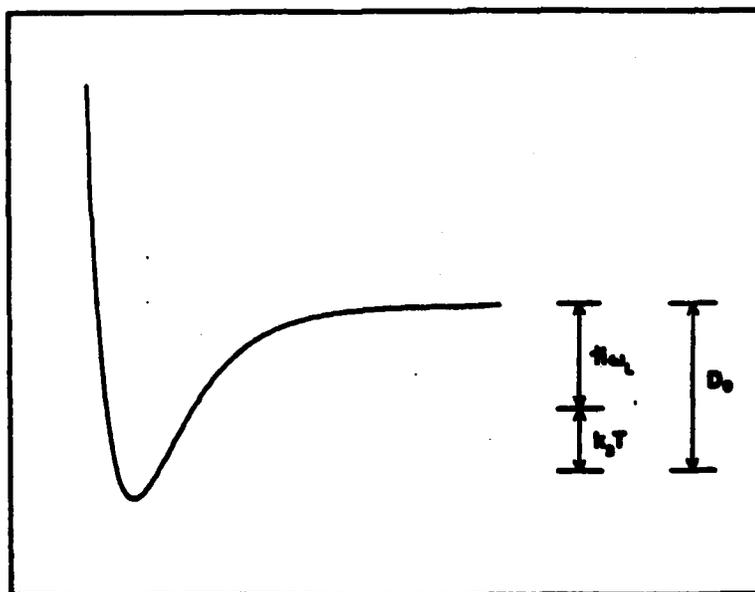

Fig. 2. D_0 is the dissociation energy of the adbond, ω_L is the laser frequency, and $E_{thermal}$ is the thermal energy due to the local heating of the y-oscillators, where $E_{thermal} \leq k_B T_y$.

temperature with a laser of reasonable power density. The steady-state temperature is given by:

$$\frac{dT_y(t_0)}{dt_0} = 0 \qquad (40)$$

with

$$T_y(t_0) = \frac{1}{\mathcal{T}k_B} \int_{t_0}^{t_0+\mathcal{T}} dt \; \langle \dot{y}(t)\dot{y}(t)\rangle \; . \qquad (41)$$

Here, $\mathcal{T}$ is the period of the IR laser.

The usual shortcomings arise in this classical approach. For example, spontaneous emission and tunneling effects are not treated. Fortunately, the deterministic mechanisms of the above desorption process are the incoherent heating and single-photon absorption. Therefore, the neglect of quantum effects will only lead to a small error in the calculation.

Conclusions

Both quantum mechanical and classical treatments of the dynamical role of phonons in the excitation and relaxation of adpsecies have been presented. Using a linear-chain model, the former treatment in Section II points out the inadequacy of the Markovian approximation. Furthermore, the laser pumping can be comparable to multiphonon relaxation for conditions such as a shallow potential well for the adbond and/or very close resonance between the laser and adbond frequencies. The latter classical treatment in Section III is better suited to a three-dimensional analysis. For example, here the response function, which is the classical analog of the kernel function $K_{gg'}$ used in Section II, is more easily obtained.[9] It is seen that local heating of the surface atom by an IR laser is an important mechanism for desorption.

Acknowledgments

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