

- (8) H. Goff, G. N. La Mar, and C. A. Reed, *J. Am. Chem. Soc.*, **99**, 3641 (1977).
- (9) J. Mispelter, M. Momenteau, and J. M. Lhoste, *Mol. Phys.*, **33**, 1715 (1977).
- (10) D. Brault and M. Rougee, *Biochemistry*, **13**, 4591 (1974).
- (11) J. P. Jesson in "NMR of Paramagnetic Molecules", G. N. La Mar, W. D. Horrocks, Jr., and R. H. Holm, Eds., Academic Press, New York, 1973, pp 1-52.
- (12) G. N. La Mar, D. B. Viscio, K. M. Smith, W. S. Caughey, and M. L. Smith, *J. Am. Chem. Soc.*, **100**, 8085 (1978).
- (13) W. S. Caughey, J. O. Alben, W. Y. Fujimoto, and J. L. York, *J. Org. Chem.*, **31**, 2631 (1966).
- (14) The mesoporphyrin-DME complex was used because its superior solubility eliminated the need to prepare the diisopropyl ester. A crude preparation of the latter ester yielded the same hyperfine shifted resonances as the DME complex, verifying that the nature of the ester group affects solubility but not the aggregate structure in solution.
- (15) This is based on a reasonable ≥ 3.2 Å interplanar spacing in the face-to-face dimer.
- (16) The selective suppression of the intensities of the narrower methyl lines upon significantly increasing the pulse repetition rate indicates that the differential line widths arise primarily from T_1 relaxation (ref 7).
- (17) F. K. Fong and V. J. Köster, *J. Am. Chem. Soc.*, **97**, 6888 (1975).

Dynamical Model of Selective vs. Nonselective Laser-Stimulated Surface Processes. 2. Analytical Methods and Applications to Surface Rate Processes

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The nature of laser-stimulated surface processes (LSSP) is quantitatively discussed in terms of the level population dynamics of multiphoton multiphonon processes. The multilevel system is reduced to a few-level system in the Heisenberg-Markovian picture, and the populations of different normal modes of the adspecies/surface system are calculated by the Laplace transform technique. It is shown that the selective and nonselective nature of LSSP are characterized by the pumping rates, the coupling factors, and the damping rates among the optically active mode and the inactive modes. The multiphonon features of the microscopic coupling constant and the damping factors are analyzed by the energy-gap law. The laser-enhanced rate processes are related to the site probability which is governed by a laser-stimulated master equation.

I. Introduction

The interactions of laser radiation with matter in the gas phase and liquid and solid states have been extensively studied in the past several years. For homogeneous systems (e.g., gas phase), much has been done on the multiphoton processes of dissociation, ionization, and induced chemical reactions.^{1,2} For the field-free condensed phase (e.g., guest molecules in solids), energy relaxation phenomena have also been extensively studied in which the multiphonon processes were discussed.³ However, for heterogeneous systems (e.g., species chemisorbed on a solid surface) the laser-stimulated surface phenomena (migration, recombination, decomposition, desorption, and rate processes) involve both multiphoton and multiphonon processes. Here the energy excitation and relaxation dynamics are much more complicated and thus relatively little work has been reported to date.⁴⁻¹⁵ Experimental evidence has suggested that the laser-stimulated surface processes (LSSP) may be characterized by selective excitations and hence are nonthermal in nature.^{4,5} In contrast to a homogeneous gas-phase system (governed by picosecond phenomena), it has been numerically shown that the excitation and relaxation time scales of LSSP are in the range of microseconds (with the corresponding pumping rates $V \approx 10^8-10^9$ s⁻¹) in a previous paper (referred to as I).¹⁶ LSSP has been studied by model microscopic Hamiltonians in which both the harmonic^{11,12} and anharmonic¹³⁻¹⁵ models were proposed for computing the average excitations by use of Markovian statistics. Furthermore, multiphoton desorption processes have been studied by the Schrödinger equation (for coherent excitations)¹⁴ and the master equation (for incoherent excitations).^{13,15} However, single-phonon processes have been

considered in this work, and only recently multiphonon multiphoton processes were studied.^{16,17} In the present paper, we shall present a multiphoton multiphonon model describing the nature of LSSP (selective vs. nonselective excitations) both analytically and numerically by calculating the level populations of a few-level system which may be reduced from a multilevel system.

In section II, the equations of motion of a multilevel system characterized by multiphoton multiphonon processes are developed from a microscopic Hamiltonian. The level populations of one-photon and two-photon processes are calculated both analytically and numerically in sections III and IV, respectively. The level populations of multiphoton processes governed by an infinite-level system are solved exactly for the harmonic- and equal-Rabi cases in section V. In section VI, we present a simple application of the calculated level populations on laser-enhanced rate processes, where the site probability of a two-dimensional surface is computed by solving the master equation. Finally, we schematically discuss the nature of LSSP (selective, local heating, and nonselective thermal heating) and qualitatively discuss the multiphoton coupling factor and the damping factor of the adspecies/surface system by the energy-gap law in section VII. In Appendices A and B we present some techniques which reduce multilevel coupled equations to a few-level system.

II. Multiphoton Multiphonon Processes of Multilevel Systems

We consider a system consisting of species (atoms or molecules) chemisorbed on a solid surface and subject to low-power infrared radiation (with intensity of 10-100 W/cm²). The density of states of the system (adspecies/surface), in the frequency domain, may be grouped into three types of normal modes: the optical active (A) mode with high frequency (1000-3000 cm⁻¹), the inactive

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(B) mode(s) with intermediate frequency (200–500 cm⁻¹), and all the other low-frequency modes (C modes). The active (A) mode usually is the vertical stretching mode of the system (adspecies/surface) and the B mode(s) may be the inactive stretching or bending modes of the system, while the C modes are all the other low-frequency modes including some vibrational modes of the adspecies/surface and the optical and acoustic phonon modes of the solid. Due to the energy gaps among the A, B, and C modes, the single-phonon vibrational relaxations of the A and B modes are not significant, and the photon energy is selectively transferred to the A mode and then relaxes to the B and C modes via mainly multiphonon vibrational relaxation processes. By the concept of "energy-gap law", we shall consider only the couplings of A–B modes and B–C modes and neglect the direct coupling of A–C modes, which is a very weak coupling.

The total Hamiltonian describing the above system may be expressed as

$$H(t) = H_0' + H'(t) \quad (1)$$

H_0' is the field-free vibrational Hamiltonian of the adspecies/surface given by the kinetic energies KE and the potential energy V of the system (with total number of normal modes S and the normal coordinates Q_A and Q_i of the A mode and the (B + C) modes, respectively)

$$H_0' = KE + V(Q_A, Q_1, Q_2, \dots, Q_{S-1}) \quad (2)$$

$H'(t)$ is the field–A mode interaction Hamiltonian given by

$$H'(t) = \mu E \cos \omega t \cos \eta \quad (3)$$

where μ is the dipole moment of the A mode and E is the electric field of the laser radiation of frequency ω and linearly polarized at an angle η with respect to the active dipole moment.

In order to express the total Hamiltonian of eq 1 in a second-quantized form, we shall now expand the field–A mode and the intramode interaction Hamiltonian in terms of the normal coordinates as follows (the derivatives are evaluated at the related equilibrium points):

$$H'(t) = [\mu_0 + \mu_0' Q_A + \dots] E \cos \omega t \cos \eta \quad (4)$$

$$V = V_A + V_B + V_C + V_{AB} + V_{BC} + \dots \quad (5)$$

where

$$V_A = \frac{1}{2} \left(\frac{\partial^2 V}{\partial Q_A^2} \right)_0 Q_A^2 + V_A^{\text{anh}} \quad (5a)$$

$$V_B = \frac{1}{2} \left(\frac{\partial^2 V}{\partial Q_B^2} \right)_0 Q_B^2 + V_B^{\text{anh}} \quad (5b)$$

$$V_C = \frac{1}{2} \left(\frac{\partial^2 V}{\partial Q_C^2} \right)_0 Q_C^2 + V_C^{\text{anh}} \quad (5c)$$

$$V_{AB} = \frac{1}{2} \sum_{j_1} \left(\frac{\partial^2 V}{\partial Q_A \partial Q_{j_1}} \right)_0 Q_A Q_{j_1} + \dots + \frac{1}{(m+1)!} \sum_{j_1, j_2, \dots, j_m} \left(\frac{\partial^{m+1} V}{\partial Q_A \partial Q_{j_1} \dots \partial Q_{j_m}} \right)_0 Q_A \prod_{j=j_1}^m Q_{j_j} + \dots \quad (5d)$$

$$V_{BC} = \frac{1}{2} \sum_{j_1, k_1} \left(\frac{\partial^2 V}{\partial Q_{j_1} \partial Q_{k_1}} \right)_0 Q_{j_1} Q_{k_1} + \dots + \frac{1}{(n+1)!} \sum_{j_1} \sum_{k_1, k_2, \dots, k_n} \left(\frac{\partial^{n+1} V}{\partial Q_{j_1} \partial Q_{k_1} \dots \partial Q_{k_n}} \right)_0 Q_{j_1} \prod_{k=k_1}^n Q_{k_k} + \dots \quad (5e)$$

$$V_A^{\text{anh}} = \epsilon_{1A} Q_A^3 + \epsilon_{2A} Q_A^4 + \dots, \text{ etc.} \quad (5f)$$

Here only the linear multiphonon couplings of Q_A in V_{AB} and Q_j in V_{BC} are considered and the (very low) probabilities of nonlinear multiphonon processes are neglected. We assume a low coverage system in which the direct coupling and the indirect coupling (via B modes) between the A modes (for the case of a group of adspecies) are neglected. Furthermore, all the "exchange couplings" which result in a T_2 dephasing relaxation are not included, and only the T_1 energy relaxation couplings which change the energy population of the modes are considered. [A model without the above assumptions has been developed.¹⁷] By quantizing the normal coordinates, $Q_A = \alpha_A (a^\dagger + a)$, $Q_j = \alpha_j (b_j^\dagger + b_j)$, $Q_k = \alpha_k (c_k^\dagger + c_k)$, where the quantization constant α_A is related to the A mode frequency ω_A and the reduced mass m_A by $\alpha_A = (\hbar/2m_A\omega_A)^{1/2}$, etc., we obtain a microscopic total Hamiltonian of a multilevel system (N levels in the A mode, M levels in each B mode, and L levels in each C mode) as follows:

$$H = H_0 + H_{AB} + H_{BC} + H_{AF} \quad (6)$$

$$H_0 = \mathcal{S}_N \hbar \omega_i a_i^\dagger a_i + \mathcal{S}_M \mathcal{S}_j \hbar \omega_j b_j^\dagger b_j + \mathcal{S}_L \mathcal{S}_k \hbar \omega_k c_k^\dagger c_k \quad (6a)$$

$$H_{AB} = \mathcal{S}_N \mathcal{S}_M \mathcal{S}_j \hbar g_{ij} a_i b_j^\dagger + \mathcal{S}_N \mathcal{S}_M \mathcal{S}_j \hbar g_{ij} a_i \prod_{j=j_1} b_{j_1}^\dagger + \text{hc} \quad (6b)$$

$$H_{BC} = \mathcal{S}_M \mathcal{S}_L \mathcal{S}_j \mathcal{S}_k \hbar K_{jk} b_j c_k^\dagger + \mathcal{S}_M \mathcal{S}_L \mathcal{S}_j \mathcal{S}_k \hbar K_{jk} b_j \prod_{k=k_1} c_{k_1}^\dagger + \text{hc} \quad (6c)$$

$$H_{AF} = \sum_{i \neq f} \hbar V_{if}(t) a_i^\dagger a_f + \text{hc} \quad (6d)$$

\mathcal{S} 's denote the summations

$$\mathcal{S}_N = \sum_{i=1}^N \quad \mathcal{S}_M = \sum_{j_1, j_2, \dots, j_m}^M \quad \mathcal{S}_L = \sum_{k_1, k_2, \dots, k_n}^L \quad (6e)$$

$$\mathcal{S}_j = \sum_{j=j_1}^{j_m} \quad \mathcal{S}_k = \sum_{k=k_1}^{k_{n-m-1}}$$

and $\omega_i = \omega_A - \epsilon_A^* a_i^\dagger a_i$, $\omega_j = \omega_B - \epsilon_B^* b_j^\dagger b_j$, $\omega_k = \omega_C - \epsilon_C^* c_k^\dagger c_k$, where ω_A , ω_B , and ω_C are the fundamental frequencies (with anharmonicities ϵ_A^* , ϵ_B^* , and ϵ_C^*) of the A, B and C modes, respectively; V_{if} is the pumping rate for a transition from state i to the state f of the pumped A mode; g, K , and g, K are the coupling factors of A–B modes and B–C modes for single-phonon and multiphonon processes, respectively. In deriving the quantized Hamiltonian of eq 6 from the classical Hamiltonian of eq 1, we assume the rotating wave approximation (i.e., neglecting off-resonance contributions to the couplings) and use the contact transformation technique to obtain the excitation-dependent anharmonic corrections, $\epsilon_A^* a_i^\dagger a_i$, etc., of the multilevel anharmonic quantum oscillators.^{14,15}

The ensemble-averaged equations of motion of the Bose operators in the Heisenberg–Markovian picture (HMP) are^{18,19}

$$i \frac{da_i}{dt} = \omega_i a_i + \sum_{f \neq i} V_{if} a_f + \sum_{\nu} g_{i\nu} B_{\nu} \quad (7)$$

$$i \frac{dB_{\nu}}{dt} = \omega_{\nu} B_{\nu} + \sum_{i=1}^N g_{i\nu} n_i a_i + \langle [B_{\nu}, H_{BC}] \rangle \quad (8)$$

$$i \frac{dC_{\nu}}{dt} = \omega_{\nu} C_{\nu} + \langle [C_{\nu}, H_{BC}] \rangle \quad (9)$$

where $\omega_{\nu} = \sum_j \omega_j$, $\omega_{\nu} = \sum_k \omega_k$, $n_i = \prod_j (\bar{n}_j + 1) - \prod_j \bar{n}_j$, \bar{n}_j obeys the Bose–Einstein distribution for a surface temperature T_s , $\bar{n}_j = [e^{\hbar\omega_B/kT} - 1]^{-1}$, and the multiphonon

operators are given by $B_\nu = \prod_j b_{j\nu}$, $C_\nu = \prod_{k\nu} c_{k\nu}$. The coupled eq 7 and 8, describing a multilevel system subject to laser radiation, are not analytically solvable due to the many-body effects of the interaction Hamiltonian H_{BC} . For tractable results, we shall use the Markovian (or, equivalently, the Weisskopf) approximation and treat the C modes as condensed states where the summation over all the C modes may be replaced by an integral over the associated density of states. This procedure enables us to reduce the multilevel system to a few-level system, and the coupled eq 7 and 8, in the rotating frame (i.e., $\bar{a}_i = a_i e^{i\omega_i t}$, etc.) become [see Appendix A for the derivation]

$$i \frac{d\bar{a}_i}{dt} = \sum_{f \neq i} V_{if} \bar{a}_f \exp(-i\Delta_f t) + \sum_\nu g_{i\nu} \bar{B}_\nu \exp(-i\Delta'_f t) \quad (9a)$$

$$i \frac{d\bar{B}_\nu}{dt} = \sum_{i=1}^N g_{i\nu}^* n_\nu \bar{a}_i \exp(i\Delta'_f t) - \frac{\gamma_\nu}{2} \bar{B}_\nu \quad (9b)$$

where

$$\Delta_f = (\omega_f - \omega_i) - \omega \quad (9c)$$

$$\Delta'_f = m\bar{\omega}_B - (\omega_f - \omega_i) \quad (9d)$$

$$\gamma_\nu = 2\pi |K(\bar{\omega}_B/p)|^2 \rho(\bar{\omega}_B/p) n_C \quad (9e)$$

$\bar{\omega}_B$ is the mean fundamental frequency of the B modes and p is the order of the multiphonon coupling between B and C modes (i.e., $p \approx \bar{\omega}_B/\bar{\omega}_C$). Notice that the multilevel system is reduced to a few-level system in which the decaying upper levels of the B modes are due to the many-body effects of the condensed phonon modes (C modes). For multiphoton processes, we shall treat the A mode as an N -level system, and the equations in eq 9 are in fact $(2N+1)$ coupled equations which still cannot be solved analytically or numerically when N is a large number. We shall consider N -photon processes only for the case of a harmonic oscillator (equal level spacings) in the following sections.

III. Single-Photon Multiphonon Processes

In this section we shall consider a single-photon excitation in which the A mode may be described by a two-level system coupled to the B modes which in turn decay to the bath (C) modes. Two tractable cases are considered: (A) The upper level of the A mode is coupled to the m th level of the B mode (single mode with frequency ω_B) via m -phonon processes (i.e., $\omega_A \approx m\omega_B$), referred to as the effective three-level decaying system; and (B) the upper level of the A mode is coupled to the m th manifold level of the B mode, referred to as the effective two-level decaying system.

A. *Effective Three-Level Decaying System.* The equations of motion eq 9 are reduced to the (complex) coupled equations with the pumping rate $V_{10} = V_{01} = V$, the multiphonon coupling factor g and the damping rate of the m th level of the B mode γ as follows:

$$\frac{d\bar{a}_0}{dt} = -iV\bar{a}_1 \exp(-i\Delta_1 t) \quad (10)$$

$$\frac{d\bar{a}_1}{dt} = -iV\bar{a}_0 \exp(i\Delta_1 t) - ig\bar{B}_1 \exp(-i\Delta'_1 t) \quad (11)$$

$$\frac{d\bar{B}_1}{dt} = -ig^* n_\nu \bar{a}_1 \exp(i\Delta'_1 t) - \frac{\gamma}{2} \bar{B}_1 \quad (12)$$

with the detunings $\Delta_1 = \omega_A - \omega$, and $\Delta'_1 = m(\omega_B - 2\epsilon_B^* m) - \omega_A$ for the fundamental frequencies ω_A and ω_B of the A and B modes, respectively. The order of the multiphonon relaxation is given by the integer of the ratio $\omega_A/(\omega_B - 2\epsilon_B^* m)$. The Laplace transform of the amplitude operators

$a_0(s) = \int_0^\infty \bar{a}_0(t) \exp(-st) dt$, etc. gives the coupled equations (with the initial values $a_0(t=0) = 1$, and $a_1(t=0) = B_1(t=0) = 0$)

$$(s - i\Delta_1)a_0(s) + iVa_1(s) = 1 \quad (13a)$$

$$iVa_0(s) + sa_1(s) + igB_1(s) = 0 \quad (13b)$$

$$ig^* n_\nu a_1(s) + (s + \gamma/2 + i\Delta'_1)B_1(s) = 0 \quad (13c)$$

For the case of $\Delta_1, \Delta'_1 \neq 0$, the solutions of eq 13 involve solving for the roots of a six-order polynomial in s . We are interested in the case of exact resonance, $\Delta_1 = \Delta'_1 = 0$. The inverse Laplace transform of the solutions of eq 13 for this case gives the level populations defined by $P_0(t) = |\bar{a}_0(t)|^2$, $P_A(t) = |\bar{a}_1(t)|^2$, and $P_B = |\bar{B}_1(t)|^2$ in the following closed forms:

$$P_0(t) = |1 - V \sum_{i=1}^3 A_i [\exp(\lambda_i t) - 1] / \lambda_i|^2 \quad (14)$$

$$P_A(t) = |\sum_{i=1}^3 A_i \exp(\lambda_i t)|^2 \quad (15)$$

$$P_B(t) = |g|^2 n_\nu \left| \sum_{i=1}^3 [\exp(\lambda_i t) - \exp(\gamma/2)] / A_i (\lambda_i + \gamma/2) \right|^2 \quad (16)$$

where λ_i are the three roots of the cubic equation

$$s^3 + (\gamma/2)s^2 + (|g|^2 n_\nu + V^2)s + \gamma V^2/2 = 0 \quad (17)$$

and the coefficients are given by

$$A_i = V(\gamma/2 + \lambda_i) / \lambda_{ij} \lambda_{ik} \quad (18a)$$

$$\lambda_{ij} = \lambda_i - \lambda_j \quad \lambda_{ik} = \lambda_i - \lambda_k \quad (18b)$$

The roots of the cubic eq 17 (governed by the relative magnitudes of the pumping rate V , the coupling factor g , and the damping factor γ) may be three real roots or one real root and two complex conjugate roots. The excited level populations in eq 15 and 16 may be expressed in more explicit forms. For the complex roots $\lambda_1 = -R_1 + iI$, $\lambda_2 = -R_2 - iI$ (with $R_1 = R_2, I_1 = I_2$), and $\lambda_3 = -R_3$, the long time behaviors of the populations may be well represented by the root which has significant smaller real part than the others. For $R_3 < R_1 = R_2$, we obtain the analytical forms for the excited level populations [for a time t in which $\exp(-R_1 t) \ll \exp(-R_3 t)$]

$$P_A(t) = |V(R_3 - \gamma/2)/Z_1|^2 \exp(-2R_3 t) \quad (19)$$

$$P_B(t) = n_\nu |gV/Z_1|^2 [\exp(-R_3 t) - \exp(-\gamma t/2)]^2 \quad (20)$$

For $R_1 = R_2 < R_3$, we obtain

$$P_A(t) = \left(\frac{V}{2I_1 Z_1} \right)^2 \left\{ 2Z_1 \left[\left(R_1 - \frac{\gamma}{2} \right)^2 + I_1^2 \right] - 2(Z_2^2 - R^2) \cos(2I_1 t) - 4RZ_2 \sin(2I_1 t) \right\} \exp(-2R_1 t) \quad (21)$$

$$P_B(t) = |g|^2 n_\nu \left(\frac{V}{2I_1 Z_1} \right)^2 [2R_{31} \exp(-\gamma t/2) - Z \exp(-R_1 t)]^2 \quad (22)$$

where

$$Z_1 = R_{31}^2 + I_1^2$$

$$Z_2 = R_{31}^2 (\gamma/2 - R_1) + I_1$$

$$R_{31} = R_3 - R_1$$

$$R = (R_3 - \gamma/2)I_1$$

$$Z = R_{31} \cos I_1 t + 2I_1 \sin I_1 t \quad (23)$$

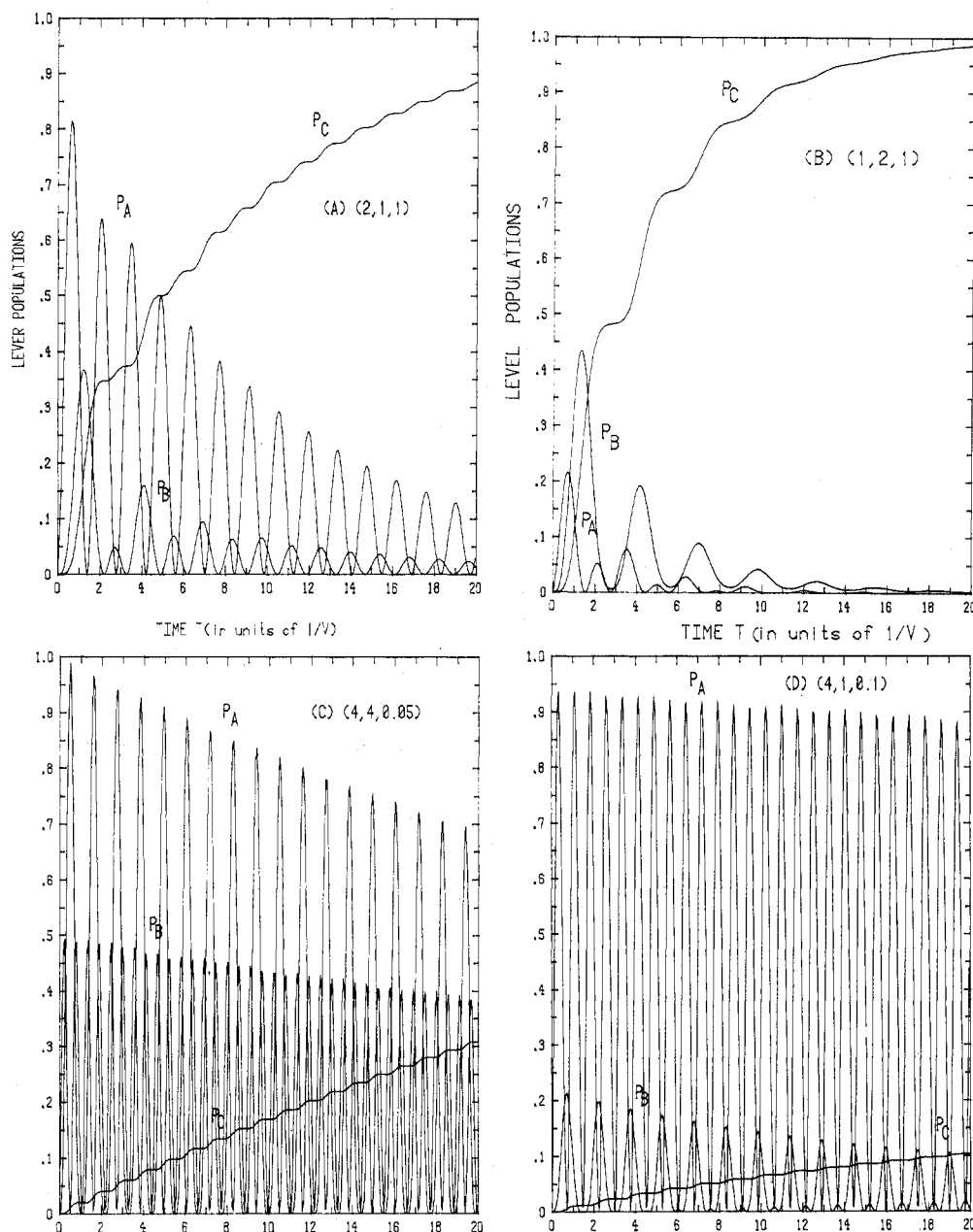


Figure 1. The level populations P_A (for the active A mode), P_B (for the B mode), and P_C (for the C modes) of single-photon multiphonon processes for different sets of the pumping rate (V), the coupling factor ($|g|$), and the decaying rate (γ): ($V, |g|, \gamma$) = (A) (2, 1, 1), (B) (1, 2, 1), (C) (4, 4, 0.05), and (D) (4, 1, 0.1).

Notice that the level populations P_0 , P_A , and P_B represent the probabilities of finding the system (field-ad-species/surface) at the states of $|1,0,0\rangle$, $|0,1,0\rangle$, and $|0,0,m\rangle$, respectively, where $|n_p, n_A, n_B\rangle$ denotes the state vector of the system in which n_p , n_A , and n_B are the vibrational quantum numbers of the laser quanta, A mode and B mode, respectively (for single-photon m -phonon processes). Therefore P_A and P_B describe the population dynamics of the laser photon energy deposited in the A and B modes, respectively. We introduce another level population $P_C = 1 - (P_0 + P_A + P_B)$ for describing the energy loss of the (A + B) modes, referred to as the nonselective thermal heating effects of the laser field on the solid surface [i.e., the photon energy transferred to the low-frequency phonon bath modes (C modes)].

The numerical solutions of the coupled eq 10–12, for low surface temperature $n_\nu \approx 1$, which give the level populations are shown in Figure 1A–D for different sets of the pumping rate (V), the coupling factor of A–B modes (g), and the damping rate of the B mode (γ). We see that

oscillation amplitudes of P_A are higher than those of P_B when the pumping rate (V) exceeds the relaxation rate (g), and vice versa [Figure 1, parts A and B]. Figure 1C shows highly selective excitations of the A and B modes without appreciably heating the C modes, where we observe that the optimal condition for high excitation of the B mode is $|g| = V$ (the analytical discussion will be shown later). Figure 1D shows that only the A mode is selectively excited and both the B and C modes are not significantly “heated”, where a high pumping rate (V), weak coupling factor (g), and small damping (γ) are chosen. From a comparison of Figure 1A–D, it is apparent that in the first two cases (with large damping rate γ) the nonselective thermal effects are the dominant component, while in the last two cases (with small damping) the energy populations are highly selective and nonthermal in nature.

Another way to view LSSP (selective and nonselective excitations) is through the integrated populations [defined by the time integrals over the instant populations of eq 15 and 16]. We should point out that these are not

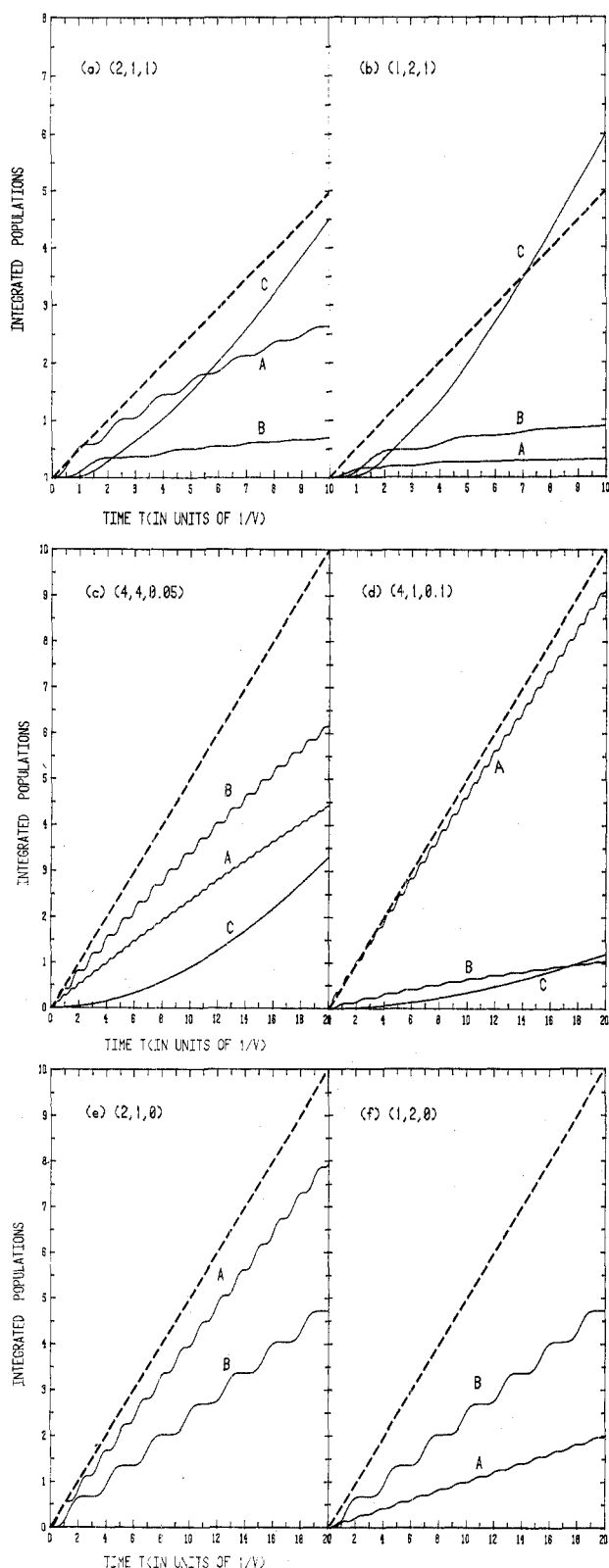


Figure 2. The integrated populations of the A, B, and C modes (denoted by A, B, and C, respectively) for single-photon processes with $(V, |g|, \gamma) =$ (a) (2, 1, 1), (b) (1, 2, 1), (c) (4, 4, 0.05), (d) (4, 1, 0.1), (e) (2, 1, 0), and (f) (1, 2, 0). The dashed lines show the case of a closed system with $|g| = \gamma = 0$.

physical observables, although one might imagine that their slopes give information about the average populations (e.g., $\bar{P}_A = 0.5$ for a closed two-level system, and for an open system \bar{P}_A decreases to zero due to coupling to the B mode). The numerical results are illustrated in Figure 2a-f. The nonselective thermal excitations of the C modes are shown in parts a and b of Figure 2 while the highly

selective excitations of A and B modes are shown in parts c and d of Figure 2. The closed system of (A + B) modes (with the damping factor $\gamma = 0$) is illustrated by parts e and f of Figure 2. The dashed lines in Figure 2a-f show the integrated populations of an isolated two-level system for the A mode (with $|g| = \gamma = 0$) in which the average population $\bar{P}_A = 1/2$ is shown by the slopes of the dashed lines. We note that for the cases of $\gamma \neq 0$ [Figure 2a-d] the long time behavior of the integrated populations is dominated by the thermal excitations of the C modes since both the populations of A and B modes are decaying. Therefore the selectivity of the excitations shall be defined within the lifetimes of the populations.

For further analytical discussion, let us now consider the case of very weak damping in which $\gamma \ll |g|, V$, whereby we may treat the (A + B) modes system to be almost isolated from the C modes. Again, by using the Laplace transform technique, eq 15 and 16, for $\gamma = 0$, give us the excited level populations

$$P_A(t) = (V/G)^2 \sin^2(Gt) \quad (24)$$

$$P_B(t) = 4n_v(|g|V/G^2)^2(\cos Gt - 1)^2 \quad (25)$$

$$G = (n_v|g|^2 + V^2)^{1/2}$$

For this case, we may introduce the time-averaged populations which are also analytically available as follows:

$$\bar{P}_A = \frac{1}{T} \int_0^T P_A(t) dt = \left(\frac{V}{2G}\right)^2 \left[2 - \frac{\sin(GT)}{GT} \right] \quad (26)$$

$$\bar{P}_B = n_v \left(\frac{|g|V}{G^2}\right)^2 \left[6 + \frac{\sin(2GT)}{GT} - \frac{8 \sin(GT)}{GT} \right] \quad (27)$$

Note that eq 24 and 26 reduce to the well-known results $P_A = \sin^2(Vt)$ and $\bar{P}_A = 1/2$, for an isolated two-level system, i.e., where the A mode is isolated and $P_B = 0$ for $|g| = 0$.¹⁹ It may be easily shown from eq 25 that the optimal condition for \bar{P}_B is $|g| = V$, which is in agreement with the numerical results in Figure 1C.

B. Effective Two-Level Decaying System. In section III.A we have considered the case where the upper level of the A mode is coupled to a nondegenerate m th level of the B mode. Here we consider the m th level of the B mode as a condensed manifold of levels and all of these levels as strongly coupled to the A mode. Replacing the summation over the manifold of levels of the B mode by the integral over the related density of states of the m th level, the multilevel coupled system [eq 9] is reduced to an effective two-level decaying system [see Appendix B for derivation] where the amplitude operators of the A mode are described by

$$d\bar{a}_0/dt = -iV\bar{a}_1 \exp(-i\Delta_1 t) \quad (28)$$

$$d\bar{a}_1/dt = -iV\bar{a}_0 \exp(i\Delta_1 t) - (\Gamma/2 - i\delta\omega)\bar{a}_1 \quad (29)$$

where Γ and $\delta\omega$ are the damping factor and the frequency shift given in eq B.6 and B.7. The exact solutions (without using the perturbation method) of the coupled equations give the level populations of the excited state of the A mode:

(A) underdamping case (large pumping rate V)

$$P_A(t) = \frac{4V^2}{DD^*} e^{-\Gamma t/2} \sin(Dt/2) \sin(D^*t/2)$$

$$D = [4(V^2 - \delta\omega) - (\Gamma/2)^2 + (\Delta_1 + \delta\omega)^2 + i\Gamma(\delta\omega - \Delta_1)]^{1/2} \quad (30)$$

(B) overdamping case (large damping rate Γ)

$$P_A(t) = \frac{4V^2}{\bar{D}\bar{D}^*} e^{-\Gamma t/2} \sinh(\bar{D}t/2) \sinh(\bar{D}^*t/2)$$

$$\bar{D} = [(\Gamma/2)^2 - 4(V^2 - \delta\omega) - (\Delta_1 + \delta\omega)^2 - i\Gamma(\delta\omega - \Delta_1)]^{1/2} \quad (31)$$

In the above cases the average populations, defined by $\bar{P}_A = (\Gamma/2) \int_0^\infty P_A(t) dt$, are characterized by Lorentzians (with fwhm = Γ) for detuning $\Delta_1 \neq 0$ and again reduce to $\bar{P}_A = 1/2$ for $\Delta_1 = \Gamma = \delta\omega = 0$.^{20,21}

IV. Two-Photon Multiphonon Processes

We now extend the single-photon excitation (section III) to the two-photon excitation followed by a multiphonon relaxation in which the A mode is described by a three-level system and coupled to the m level and the $2m$ level of a decaying B mode via m -phonon processes. The equations of motion for the amplitudes of the operators [eq 9] in this case are

$$d\bar{a}_0/dt = -iV_1\bar{a}_1e^{-i\Delta_1t} \quad (32a)$$

$$d\bar{a}_1/dt = -iV_1\bar{a}_0e^{i\Delta_1t} - iV_2\bar{a}_2e^{-i\Delta_2t} - ig_1\bar{B}_1e^{-i\Delta_1t} \quad (32b)$$

$$d\bar{a}_2/dt = -iV_2\bar{a}_1e^{i\Delta_2t} - ig_2\bar{B}_2e^{-i\Delta_2t} \quad (32c)$$

$$d\bar{B}_1/dt = -ig_1^*n_1\bar{a}_1e^{i\Delta_1t} - (\gamma_1/2)\bar{B}_1 \quad (32d)$$

$$d\bar{B}_2/dt = -ig_2^*n_2\bar{a}_2e^{i\Delta_2t} - (\gamma_2/2)\bar{B}_2 \quad (32e)$$

where V_1 and V_2 are the pumping rates for the transitions from the ground level to the first excited level and from the first excited to the second excited level of the A mode, respectively; g_1 and g_2 are the coupling factors of the first excited level of the A mode (coupled to the m level of the B mode) and of the second excited level of the A mode (coupled to the $2m$ level of the B mode), respectively; γ_1 and γ_2 are the decay rates of the m th level and the $2m$ level of the B mode; Δ and Δ' are the detunings of the related levels (which are near resonant) of the A and B modes. The coupled equations of the above effective five-level system may be solved in part by the Laplace transform method or by diagonalizing a 10×10 real matrix. The level populations may be expressed in the forms of

$$P_A(t) = \sum_{i=1}^5 A_i \exp(\lambda_i t) \quad (33a)$$

$$P_B(t) = \sum_{i=1}^5 B_i \exp(\lambda_i t) \quad (33b)$$

where A_i and B_i are some appropriate coefficients and λ_i are the five roots of a fifth-order polynomial. The numerical results are shown in Figure 3A–C for $V_1 = V_2 = V$, $g_1 = g_2 = g$, $\gamma_1 = \gamma_2 = \gamma$, at exact resonance and low surface temperature. Notice that the level populations $P_1 = |a_0|^2$, $P_A = |a_1|^2 + |a_2|^2$, $P_B = |B_1|^2 + |B_2|^2$ are the probabilities of finding the total state vector at $|2,0,0\rangle$, $|1,1,0\rangle + |0,2,0\rangle$, and $|0,0,m\rangle + |0,0,2m\rangle$, respectively. Therefore P_A and P_B describe the population dynamics of the photon (two photons) energy deposited in the A and B modes, respectively, while $P_C = 1 - (P_1 + P_A + P_B)$ describes the population loss of the (A + B) modes and is referred to as thermal heating effects (i.e., the photon energy randomly populated in the bath phonon C modes). Figure 3A shows a highly selective excitation of the A mode with an overdamping of the B mode. A nonselective thermal heating of the C modes is shown in Figure 3B while the highly selective excitations of the A and B modes are shown in Figure 3C.

The selective and nonselective nature of LSSP are illustrated more explicitly by the integrated populations of

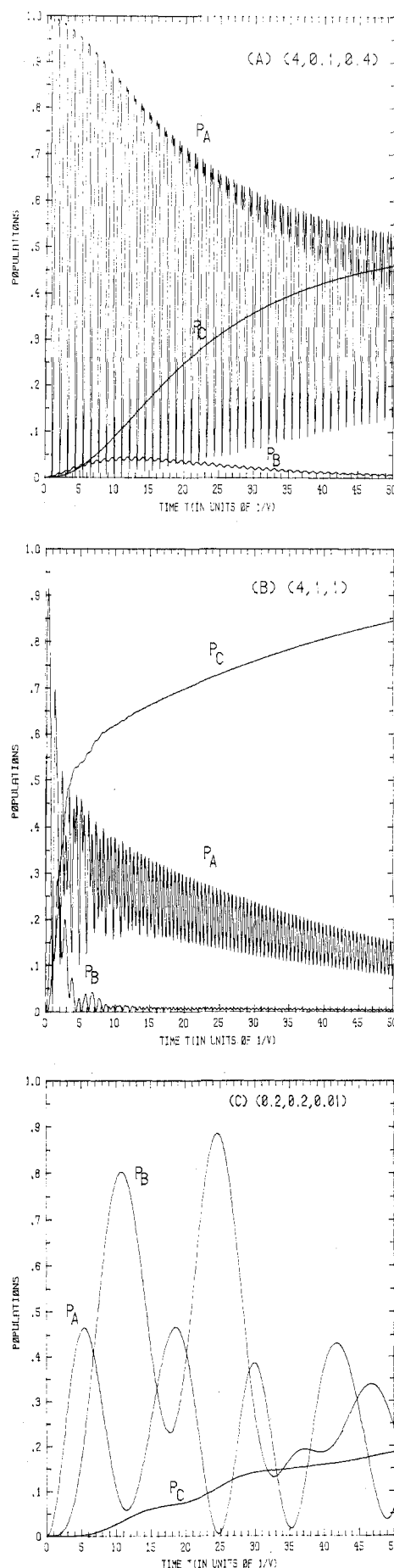


Figure 3. The level populations of A, B, and C modes of two-photon multiphonon processes for $(V, |g|, \gamma) =$ (A) (4, 0.1, 0.4), (B) (4, 1, 1), and (C) (0.2, 0.2, 0.01).

the A, B, and C modes (denoted by the curves A, B and C, respectively) in Figure 4a-d for the cases of $V_2 = 2^{1/2}V_1$ (referred to as the harmonic-Rabi transition) and $V_2 = V_1$ (the equal-Rabi transition) with different sets of the coupling factors ($g_1 = g_2 = g$) and damping rates ($\gamma_1 = \gamma_2 = \gamma$). Figure 4a clearly shows the selective excitations of the A mode ($A > C > B$) while Figure 4b shows the nonselective heating of the C modes ($C > A > B$). The selective excitations of (A + B) modes are shown in part c and d of Figure 4 for low pumping ($V_1 = 0.6$) and high pumping ($V_1 = 4$), respectively.

From the numerical results in Figures 1 and 3 or the analytical results eq 19 and 20, we may estimate the lifetimes of the excited level populations [defined by $P(t) = P(t=0)/e$, where $P(t)$ is the oscillation amplitude of the level population] to be in the range of microseconds (with corresponding pumping rate $V \approx 10^8$ – 10^9 s⁻¹ or laser intensity $I \approx 10$ – 100 W/cm²), which are much slower than those of picosecond phenomena for gas-phase systems (with high-power pumping rate $V \approx 10^{11}$ – 10^{13} s⁻¹). This is one of the important features of LSSP, where a low-power continuous wave laser is used to study the excitation and relaxation dynamics of heterogeneous systems.^{4,5}

V. Multiphoton Processes in a Decaying *N*-Level System

For multiphoton excitations, the active (A) mode may be described by a *N*-level system linked by couplings with the B mode. The level population may, in principle, be expressed by the roots of an *N*th order polynomial which are of little practical use. For analytical results of the level populations in terms of some well-known special functions, we shall consider two simple cases:²¹ (A) harmonic-Rabi in which the pumping rates of the *N* transition (V_n) are related to that of the lowest transition (*V*) by $V_n = n^{1/2}V$ and (B) equal-Rabi in which the pumping rates are all equal $V_n = V$, where in both cases the pumped A mode is approximately described by extending the finite *N* levels to infinite levels and is resonantly excited.

A. Harmonic-Rabi Case. The equations for the amplitude operators \bar{a}_n [eq 28 and 29] in this case are

$$d\bar{a}_n/dt = -iV(n^{1/2}\bar{a}_{n-1} + (n+1)^{1/2}\bar{a}_{n+1}) - (\Gamma/2)\bar{a}_n \quad (34)$$

where we assume that all the damping factors are equal (i.e., $\Gamma_n = \Gamma$) and extend the truncated *N* levels to infinite levels (i.e., $n = 0$ to ∞). For low surface temperature, we may assume that the population initially resides in the ground level $n = 0$, whereby the probability amplitude is

$$\bar{a}_n(t) = [(-iVt)^n / (n!)]^{1/2} \exp[-(V^2t^2 + \Gamma t)/2] \quad (35)$$

which gives the population of the *n*th level of the A mode as

$$P_n(t) = |\bar{a}_n(t)|^2 = [W^n / n!] \exp(-W) \exp(-\Gamma t) \quad (36)$$

$$W(t) = (Vt)^2 \quad (37)$$

We note that eq 36 is the well-known Poisson distribution (with a decay factor) for the level population of a quantum harmonic oscillator with finite *n* levels.¹⁸ However, for the finite-level case the average excitation \bar{W} (defined by $\bar{W} = \langle n \rangle = \sum_n n P_n$ with $\Gamma = 0$) is different from that of the infinite-level case and is given by¹⁵

$$\bar{W}(t) = \frac{V^2}{\Delta^2 + (\Gamma/2)^2} [1 + e^{-\Gamma t} - 2e^{-\Gamma t/2} \cos(\Delta t)] \quad (38)$$

which reduces to eq 37 when $\Delta = 0$ and $t \ll 2/\Gamma$. Therefore we note that the truncated *n* levels may be well represented by infinite levels for the short time behavior

of the population. For example, when $\Gamma = 0.1V^{-1}$ the average excitation of the finite-level system is very close to that of the infinite level system up to 15 pumping cycles, and after that time the average excitation of the finite level is bent to a steady-state value $\bar{W}_{ss} = (2V/\Gamma)^2$ which is linearly dependent on laser intensity. Notice that the average excitations [eq 37 and 38], instead of the simple power dependence of the laser fluence (ϕ = intensity \times time) $\bar{W} \propto \phi$, are characterized by the power law $\bar{W} \propto \phi^{\alpha\beta}$, where the power indices α and β depend on the time scales of the relaxation dynamics.

B. Equal-Rabi Case. The equation of motion in this case is

$$d\bar{a}_n/dt = -iV(\bar{a}_{n+1} + \bar{a}_{n-1}) - (\Gamma/2)\bar{a}_n \quad (39)$$

By changing variables $A_n = (-i)^n \bar{a}_n$, $x = 2Vt$, eq 39 becomes

$$dA_n/dx = \frac{1}{2}(A_{n-1} - A_{n+1}) - (\Gamma/2)A_n \quad (40)$$

which is just the equation satisfying the recursion relation of the Bessel function $J_n(x)$ with decay rate $\Gamma/2$. Thus the solution of eq 40 leads the population of an infinite-level system with equal transition rates:

$$P_n(t) = J_n^2(2Vt) \exp(-\Gamma t) \quad (41)$$

Notice that the ground-state population of the pumped (A) mode, $P_0(t) = J_0^2 \exp(-\Gamma t)$, starts at $P_0 = 1$ and oscillates under the exponentially decaying envelope, while all the other excited state populations initially equal zero and are successively excited by the laser radiation. The corresponding average excitation for this case is found to be $\langle n \rangle = 4Vt/\pi$, for $t \gg V^{-1}$.

The selective excitation of the A mode of multiphoton-multiphonon processes may be described by the population dynamics of $P_A(t) = \sum_{n=1} P_n(t)$ which characterizes the photon energy residing in the pumped (A) mode, while the quantity $1 - P_A(t) - P_0(t)$ describes the energy population of all the other modes (B + C).

VI. Application to Rate Processes

We shall now use the level populations obtained in the previous sections to discuss LSSP by computing the site probabilities (the probabilities of finding the adspecies residing at a specific lattice site at time *t*) which govern the diffusion-controlled rate processes. We consider a model system consisting of adspecies chemisorbed (with low coverage) on a two-dimensional well-defined surface with lattice site coordinates (*m, n*), where the time-dependent site probability may be described by the generalized master equation (GME) as follows:²³⁻²⁵

$$dP(m, n, j, t)/dt = \int_0^t dt' \sum_{m', n', j'} [W_{mm', nn'}^{jj'}(t-t')P(m', n', j', t') - W_{m'm, n'n}^{j'j}(t-t')P(m, n, j, t')] \quad (42)$$

$P(m, n, j, t)$ is the site probability of finding the adspecies at the lattice site (*m, n*) and the *j*th level at time *t*, $W_{mm', nn'}^{jj'}(t)$ is the rate of a transition from state (*m', n', j'*) to (*m, n, j*) and $W_{m'm, n'n}^{j'j}$ is the associated reverse transition rate. We note that for a general form of the transition rate the GME is not analytically solvable. Instead of working on a complex system, we shall consider a simple, tractable model and focus on the laser-stimulated site probability which is not only characterized by the lattice site coordinates (*m, n*) but also by the level population of the excited modes which is governed by the laser intensity (or pumping rate), the coupling factor, and the damping rate. For this purpose, we shall assume the following: (1) the adspecies is initially excited (via multiphoton processes) to the *j*th level which has a higher site transition rate than that of

the lower levels and a long enough lifetime for migration across a few lattice sites before it decays to the lower levels (i.e., the case of the strong coupling and weak damping rate); (2) the memory effects of the transition rates will be removed by assuming the Markovian approximation; (3) the time-dependent level population will be replaced by a mean constant value; and (4) only the nearest neighboring transitions will be considered. By using the above simplifications, we can write the transition rate in the form of

$$W_{mm',nn'}^{jj'}(t) = W_x^{jj'}(t)(\delta_{m,m'+1} + \delta_{m,m'-1})\delta_{n,n'}\delta(t) + W_y^{jj'}(t)(\delta_{n,n'+1} + \delta_{n,n'-1})\delta_{m,m'}\delta(t) \quad (43)$$

The GME is then reduced to the two-dimensional master equation

$$dP(m,n,t)/dt = \bar{W}_x[P(m+1,n,t) + P(m-1,n,t) - 2P(m,n,t)] + \bar{W}_y[P(m,n+1,t) + P(m,n-1,t) - 2P(m,n,t)] \quad (44)$$

where the mean level populations have been absorbed in the mean transition rates \bar{W}_x and \bar{W}_y for the x direction transition $(m \pm 1, n, j, t) \rightarrow (m, n, j, t)$ and the y direction transition $(m, n \pm 1, j, t) \rightarrow (m, n, j, t)$, respectively. By considering the recursion formula of the modified Bessel function, the site probability with initial value $P(m, n, t=0) = 1$ is found to be

$$P(m, n, t) = e^{-2\bar{W}_x t} I_m(2\bar{W}_x t) e^{-2\bar{W}_y t} I_n(2\bar{W}_y t) \quad (45)$$

where I_m and I_n are the m - and n th order modified Bessel functions, respectively. We note that the simple expression of eq 45 is available only when the transition rates (which are level population dependent and hence time dependent) are replaced by the average constant rates. In general, for time-dependent transition rates with long-range interactions, the site probability may be solved by the Laplace transform techniques and numerical methods are required.

Let us now express the laser-stimulated transition rates in terms of the average level populations. For single-photon multiphonon processes with a very small damping rate, the average level population of the B mode (referred to as a bending mode in this case) given by eq 27 enables us to write the mean transition rates (averaging out the oscillation terms) in more explicit forms as

$$\bar{W}_x = 6\nu_x(|g_x|V/G_x^2)^2 \exp[-(E_x - E_j)/kT_s] \quad (46a)$$

$$\bar{W}_y = 6\nu_y(|g_y|V/G_y^2)^2 \exp[-(E_y - E_k)/kT_s] \quad (46b)$$

$\nu_x(\nu_y)$ and $E_x(E_y)$ are the jumping frequency and the migration barrier energy in the $x(y)$ direction of the surface, respectively, with the associated coupling factors $|g_x|$ ($|g_y|$) of the bending (B) modes. E_j and E_k are the potential energies across the surface in the x and y directions where the B modes are excited via $j(k)$ -phonon processes, that is, $\omega_A \approx j\omega_x + k\omega_y$, where ω_A , ω_x , and ω_y are the fundamental frequencies of the active (A) mode and x and y bending frequencies of the B modes, respectively. We note that the site probability $P(m, n, t)$, initially at the lattice site (m, n) , is a decaying function of the mean transition rates \bar{W}_x and \bar{W}_y which are in general not equal (since $|g_x| \neq |g_y|$ and $E_x \neq E_y$, for $\omega_x \neq \omega_y$). We therefore may selectively enhance the transition rates of the adspecies in a specific direction (or vibrational normal modes) on the solid surface which in turn increases the mobility of the adspecies in that specific direction and controls the diffusion-limited rate processes by laser radiation.

So far in this section, we have only considered the long lifetime case of the B (bending) mode. In general, the laser radiation may selectively excite the A mode (vertical vi-

brational mode) by a high pumping rate (i.e., $V \gg g, \gamma$) which in turn may enhance the desorption probability of the adspecies or excite all the C modes by nonselective thermal heating. To illustrate the thermal effects, we shall now consider the strong coupling and fast damping case $|g| \approx \gamma \approx V$, where the photon energy is rapidly populated to the C modes and produces an effective vibrational temperature of these modes. We note that this effective temperature may be defined locally among only part of the C modes which are strongly coupled to the B mode but weakly coupled to the other part of the C modes. This local heating of the C modes may be realized by further dividing the C modes into two groups, C_1 and C_2 , in which the C_1 group (with mean frequency $\bar{\omega}_{C_1}$) is strongly coupled to the B mode while being weakly coupled to the C_2 group. This situation is possible for a system where there is a big gap between the frequencies of the C_2 group and that of the C_1 group. Now let us formally define the effective temperature T_{eff} by conservation of energy as follows:

$$S\bar{n}_C \hbar \bar{\omega}_{C_1} = \langle n \rangle \hbar \omega \quad (47)$$

S is the number of vibrational modes in the C_1 group which are strongly coupled to the B mode (i.e., where the B mode has a large damping rate γ_1) and almost isolated from the C_2 group (i.e., where the C_1 group has a very small damping rate $\gamma_2 \ll \gamma_1$); \bar{n}_C is the average occupation number of the C_1 group given by the Bose-Einstein distribution $\bar{n}_C = [\exp(\hbar \bar{\omega}_{C_1}/kT_{\text{eff}}) - 1]^{-1}$; and $\langle n \rangle \hbar \omega$ is the average photon energy absorbed per adspecies (via active mode). It may be easily seen that for high excitation, $kT_{\text{eff}} \gg \hbar \bar{\omega}_{C_1}$, eq 47 reduces to the simple expression $kT_{\text{eff}} = \langle n \rangle \hbar \omega / S$ where the effective temperature is defined as the photon energy absorbed per vibrational degree of freedom in the C_1 group. The site transition rate may then be enhanced by the local effective temperature and is given by the expression

$$W_C = \bar{\nu}_C \exp[-E_A/k(T_{\text{eff}} + T_s)] \quad (48)$$

where $\bar{\nu}_C$ is the mean jumping frequency of the C_1 modes, and E_A and T_s are the migration energy barrier and initial temperature of the surface, respectively. We note that the laser heating rate of the C_1 modes is much faster than that of the relaxation time scales between the C_1 and C_2 modes, so the C_1 group is in fact in a nonequilibrium state defined by a local effective temperature T_{eff} , which may be much higher than the initial surface temperature T_s or the new equilibrium state temperature T_s' [defined by $kT_s' = \langle n \rangle \hbar \omega / S'$, where S' is the total number of vibrational modes in the collective ($C_1 + C_2$) group]. For example, an effective temperature (in K) $T_{\text{eff}} = 2000/(0.7S)$ may be locally produced in the C_1 group in a very short time scale ($\approx 10^{-8}$ s, for $\gamma \approx g \approx V = 10^8 \text{ s}^{-1}$) by absorbing two CO_2 laser quanta (with frequency $\approx 1000 \text{ cm}^{-1}$).

VII. Discussion and Conclusion

From the numerical results [Figures 1–3], we observe that the lifetimes (or decay rates) of the excited level populations P_A , P_B , and P_C are characterized by the pumping rate (V), the coupling factor ($|g|$), and the damping rate (γ). For high pumping rate ($V > g \gg \gamma$), the A mode may be selectively excited (with a lifetime $\approx 10^{-6}$ s for $V \approx 10^8 \text{ s}^{-1}$), while for large coupling and damping ($g \approx \gamma \approx V$) the excitations of A and B modes are very low (with very short lifetimes of the populations $\approx 10^{-8}$ s) and most of the photon energy links rapidly into the phonon bath (C) modes, i.e., nonselective thermal heating is the dominant component. From the analytic result [eq 25], we are able to justify the numerical result [Figure 1C] in which $g = V$ (instead of $g > V$) is the optimum condition for the selective excitations of both the A and B modes.

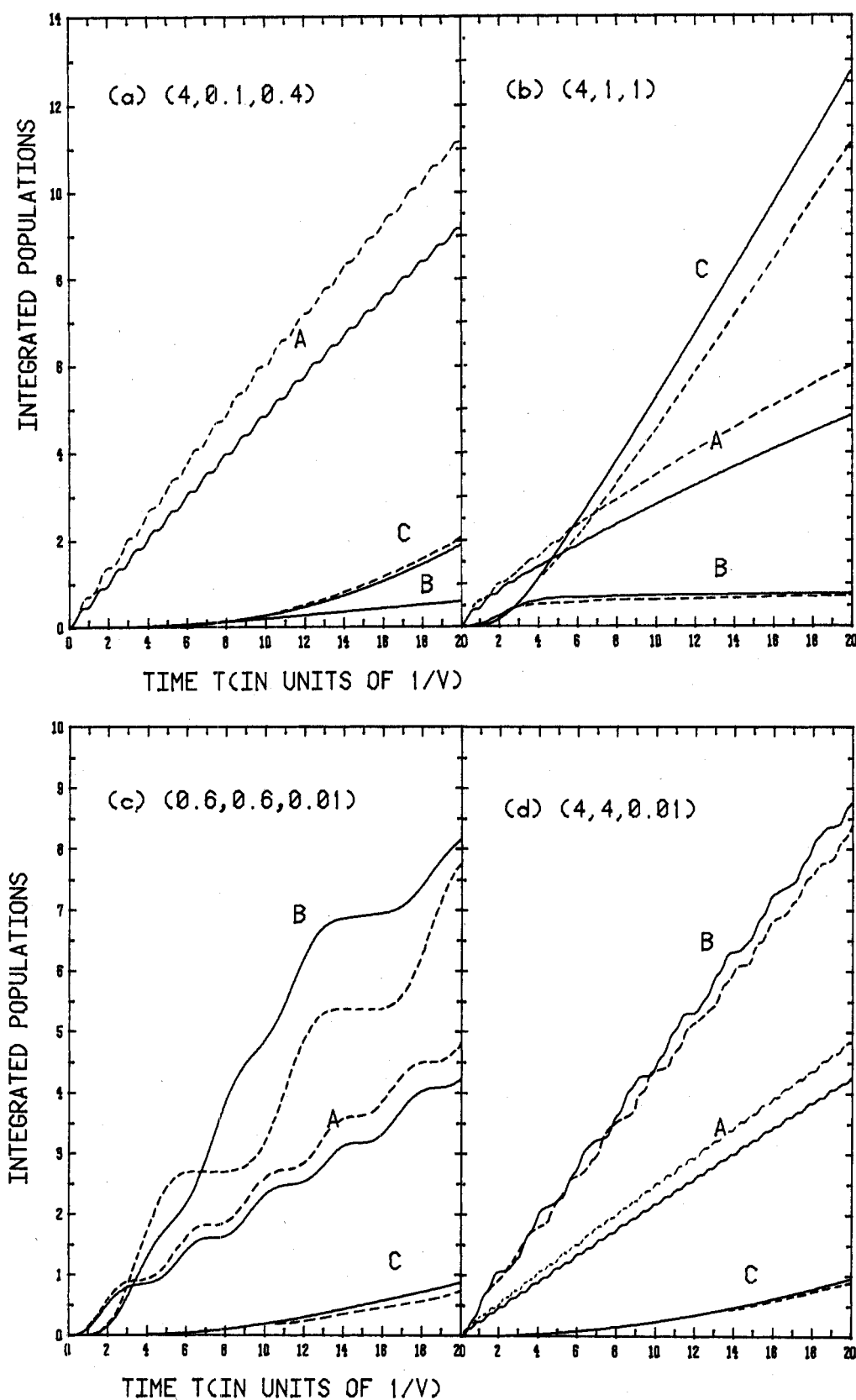


Figure 4. The integrated populations of the A, B, and C modes (denoted by the curves A, B, and C, respectively) for two-photon processes with $(V_1, |g|, \gamma) =$ (a) $(4, 0.1, 0.4)$, (b) $(4, 1, 1)$, (c) $(0.6, 0.6, 0.01)$, and (d) $(4, 4, 0.01)$, where the solid lines for the harmonic-Rabi ($V_2 = 2^{1/2} V_1$) and dashed lines for the equal-Rabi ($V_1 = V_2$).

This may be realized by the fact that the photon energy is transferred back and forth between the field (considered as a two-level state), the A mode and the B mode while being linked to the C modes from the B mode, so that a large coupling factor ($g > V$) also leads to a large energy loss via a fixed damping rate γ . From the Laplace

transform technique used in section III, we see that the dynamics of the level populations are governed by multiple decaying rates in the early stage and may be reduced to a single decay rate (given by the smallest root of the associated polynomial) for the long time behavior. However, we note that the lifetimes (τ) of the populations (these are

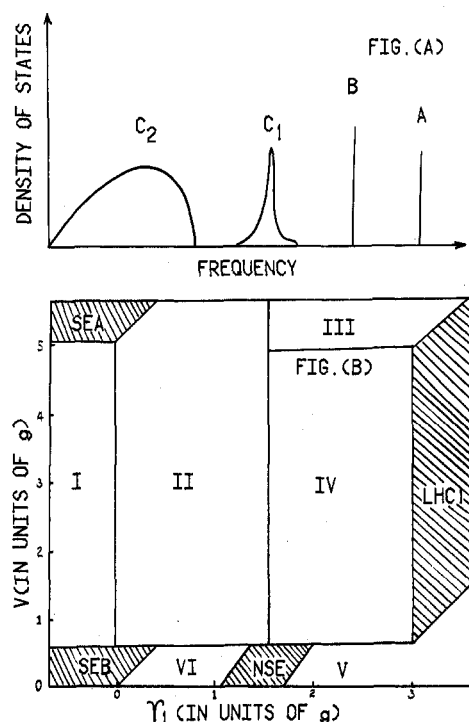


Figure 5. (A) Schematic density of states of an adspecies/surface system. (B) Schematic diagrams of the selective and nonselective excitations in terms of the ratios of the pumping rate (V), the coupling factor (g), and the damping rates (γ_1 and γ_2) of the A, B, C_1 , and C_2 modes. The nature of the LSSP is described by selective excitation of the A mode (SEA), selective excitation of the B mode (SEB), local heating of the C_1 modes (LHC1), and nonselective heating of the C_2 modes (NSE).

defined in section IV and govern the selective and non-selective nature of LSSP) are characterized by the pumping rate, the coupling factor, and the damping rate in a complicated form (instead of the lifetime of P_A simply equaling $|g|^{-1}$ and that of P_B equaling γ^{-1}). Since the roots of a fifth (or higher) order polynomial (which govern the decaying rates of the populations) are generally not analytically available, the lifetimes of the populations can only be estimated numerically. However, the nature of LSSP (selective, nonselective, and local heating) may be qualitatively described by the relative ratios of the pumping rate, the coupling factor, and the damping rate ($V:g:\gamma$). In Figure 5, we schematically show the nature of the LSSP [Figure 5B] with the associated density of states [Figure 5A] where the C modes are divided into two groups (as discussed in section VI) to demonstrate the local heating effects characterized by an effective temperature [eq 47]. In Figure 5B, both the pumping rate (V) and the damping rates (γ_1 and γ_2) are in units of the coupling factor (g), for fixed $\gamma_2 = 2g$. It is easy to see that selective excitations of (A + B) modes are possible when $\gamma_1 \ll g$ [shown by SEA and SEB] while nonselective thermal heating (NSE) will be the dominant processes when $\gamma_2 > \gamma_1 > g$. Local heating of the C_1 mode (LHC1) is possible when $\gamma_1 \gg \gamma_2$ and $V < \gamma_1$. The mixed excitation states are shown by the regions I, II, III, etc.; e.g., region I for the mixed excitations of (A + B) modes, region II for the state of (SEA + NSE), region IV for the state of (SEA + NSE + LHC1), and region VI for (SEB + NSE), etc.

Finally, we discuss some physical features which govern the magnitudes of the microscopic coupling factors ($|g|$, $|K|$) and the damping factors (γ , Γ) for multiphonon relaxation processes. By the concept of the energy-gap law,²⁶ the multiphonon damping factor (γ) is temperature dependent ($\gamma \propto T_s^{p-1}$, for p -phonon processes). It is characterized by

the force constants, the frequencies, and the densities of states of the coupled intramodes in a complicated form^{27,28} and decreases with increasing the order of the multiphonon coupling (p). A simple expression for the damping factor obtained by perturbation theory⁸ is $\gamma \propto (m/M)^p$, where m and M are the reduced masses of the coupled B and C modes (with the order of the multiphonon coupling $p \approx \omega_B/\omega_C$). We see that γ again decreases with increasing p since $m < M$.

Let us now consider the expressions of the damping factors $\gamma \propto |K|^2 \rho$ [eq A.10] and $\Gamma \propto |g|^2 \rho'$ [eq B.7], where K and g are the microscopic coupling constants of the B-C and B-A modes, respectively, with the associated density of states ρ and ρ' . We note that the damping factor (γ or Γ) is governed not only by the coupling constant but also by the related density of states evaluated at the normal mode frequency which is near resonantly coupled. Therefore, the lowest-order coupling (single phonon) will not produce a damping factor when there is no overlap between the densities of states of the coupled modes. Furthermore, the damping factor is characterized by some finite number of states which are strongly coupled instead of by all the states occupied in the excited level of the coupled modes. This is a significantly different feature of the multiphonon-induced damping factor compared with that of the usual Fermi golden rule. In section II, the microscopic Hamiltonians [eq 6] are derived from the Taylor's expansion of the total Hamiltonian in which the microscopic coupling constants $g(K)$ are related to the $m(p)$ th derivative of the interaction potential for an $m(p)$ -phonon process. Considering a simple repulsive potential energy $V(Q_i, Q_j) = \exp[-\alpha(Q_i - Q_j)]$, we are able to see that the coupling constant g is proportional to α^m for an m -phonon process and thus is a strongly decreasing function with increasing order of the multiphonon processes, since the characteristic repulsive length α is in general much less than unity.

In conclusion, we have shown that a multilevel system describing multiphoton multiphonon processes may be reduced to a few-level system in which the level populations were analytically obtained by the Laplace transform method for the case of single-photon excitations. Numerical results were illustrated for the single-photon and two-photon processes. An infinite-level system was presented to describe the level populations of the multiphoton excitations in closed forms. The nature of LSSP is numerically illustrated by the instant populations and the integrated populations [Figures 1-3]. Through selective excitations of specific vibrational modes, one may enhance diffusion-limited rate processes by increasing the laser-stimulated site transition rate or the mobility of the adspecies.

Acknowledgment. This research was sponsored by the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract No. F49620-78-C-0005, and the Office of Naval Research.

Appendix A. Derivation of the Coupled Equations for the Three-Level System

Equations 7-9, in the rotating frame ($\bar{a}_i = a_i \exp(i\omega_i t)$, $\bar{b}_j = b_j \exp(i\omega_j t)$, etc.) may be rewritten as

$$d\bar{a}_i/dt = -i \sum_{f \neq i} V_{if} \bar{a}_f \exp(-i\Delta_f t) - i \sum_{\nu} g_{i\nu} \bar{b}_{\nu} \exp(-i\Delta_f t) \quad (A.1)$$

$$d\bar{b}_{\nu}/dt = -i \sum_i g_{i\nu}^* n_i \bar{a}_i \exp(i\Delta_f t) - i \sum_k m K_{jk} \bar{b}_j^{m-1} \bar{c}_k \exp(i\Delta'' t) \quad (A.2)$$

$$d\bar{C}_k/dt = -iK_{jk}^* n_C \bar{b}_j \exp(-i\Delta''t) \quad (\text{A.3})$$

$\Delta_f = (\omega_f - \omega_i) - \omega$, $\Delta'_f = m\bar{\omega}_B - (\omega_f - \omega_i)$, $\Delta'' = \bar{\omega}_B - p\bar{\omega}_C$; ω_f and ω_i are the frequencies defined by the level energy of the A mode, $\omega_f - \omega_i = (E_f - E_i)/\hbar$; $\bar{\omega}_B$ and $\bar{\omega}_C$ are the mean frequencies of the B and C modes (i.e., $\omega_j = \sum_j \omega_j \approx m\bar{\omega}_B$ and $\omega_{j'} = \sum_{j'} \omega_{j'} \approx p\bar{\omega}_C$ for m -phonon and p -phonon processes, respectively). The ensemble average quantities n_ν and n_C are temperature dependent and may be explicitly expressed as

$$n_\nu = \langle [\bar{B}_\nu, \bar{B}_\nu^\dagger] \rangle = (\bar{n}_j + 1)^m - \bar{n}_j^m \quad (\text{A.4})$$

$$n_C = \langle [\bar{C}_\nu, \bar{C}_\nu^\dagger] \rangle = (\bar{n}_k + 1)^p - \bar{n}_k^p \quad (\text{A.5})$$

where $\bar{n}_j = [\exp(\hbar\bar{\omega}_B/kT_s) - 1]^{-1}$ and $\bar{n}_k = [\exp(\hbar\bar{\omega}_C/kT_s) - 1]^{-1}$, for m -phonon coupling between the A and B mode and p -phonon coupling between the B and C modes. That is, we assume that the fundamental frequencies of the A, B, and C modes (ω_A , $\bar{\omega}_B$, and $\bar{\omega}_C$, respectively) are related by $\omega_A \approx m\bar{\omega}_B$ and $\bar{\omega}_B \approx p\bar{\omega}_C$, where $\bar{\omega}_C$ is of the order of the Debye frequency of the solid. We note that $n_\nu = n_C \approx 1$ for the low temperature limit and $n_\nu \propto T_s^{m-1}$, $n_C \propto T_s^{p-1}$, for the high-temperature limit. In order to decouple eq A.2 and A.3, we assume that the solution of eq A.2 for g_{iv}^* = 0 may be written in the form $\bar{b}_j = \bar{b}_0 \exp(-\gamma t/2)$, where γ is the damping factor of the B mode to be determined. By substituting this expression of $\bar{b}_j(t)$ into eq A.3, we obtain

$$\bar{C}_k = iK_{jk}^* n_C \bar{b}_0 \left[\frac{\exp[-(i\Delta'' + \gamma/2)t] - 1}{i\Delta'' + \gamma/2} \right] \quad (\text{A.6})$$

Substituting eq A.7 into the homogeneous part of eq A.2 (for $g_{iv}^* = 0$), we then obtain the desired damping factor

$$\gamma = 2 \int_0^\infty d\bar{\omega}_C \int_0^t dt' \exp(-i\Delta''t') |K(\bar{\omega}_C)|^2 \rho(\bar{\omega}_C) n_C(\bar{\omega}_C) \quad (\text{A.7})$$

where the sum over the C modes has been replaced by an integral over the associated density of states $\rho(\bar{\omega}_C)$ and we neglect the term $\gamma \ll \Delta''$ in eq A.6.

By the following integral, for t extended to infinity

$$\lim_{t \rightarrow \infty} \int_0^t \exp(\pm i\Omega t') dt' = \pi \delta(\Omega) \pm iP(1/\Omega) \quad (\text{A.8})$$

eq A.7 becomes

$$\gamma = 2\pi |K(\bar{\omega}_B/p)|^2 \rho(\bar{\omega}_B/p) n_C(\bar{\omega}_B/p) - i\delta\omega \quad (\text{A.9})$$

where the small frequency shift $\delta\omega$ is given by the principal value of the integral eq A.7 and will be neglected. Therefore the coupled eq A.2 and A.3 are reduced to a single equation [eq 9b] in which the m th level of the B mode is damped by a factor γ which is proportional to the microscopic coupling constant K and the density of states ρ of the C mode. Notice that both K and ρ are evaluated at $\bar{\omega}_C = \bar{\omega}_B/p$ for a p -phonon relaxation where the near resonant coupling ($\bar{\omega}_B \approx p\bar{\omega}_C$) is significantly stronger than that of the off resonant. We note that the decoupled equation [eq 9.b] may be approached by several methods, e.g., the technique used in Appendix B or a more rigorous technique using the Heisenberg-Markovian picture.¹⁵ Here we just introduce a simple alternate method.

Appendix B. Derivation of the Coupled Equations of Two-Level System

In Appendix A we have reduced the few-level system to a three-level decaying system. Now we shall further reduce the coupled few-level system described by eq 9 to a two-

level decaying system. The solution of eq 9b, with initial condition $\bar{B}_\nu(0) = 0$, is

$$\bar{B}_\nu(t) = -ig_{iv}^* n_\nu \times \int_0^t dt' \bar{a}_1(t') \exp[i\Delta_1 t' + (\gamma/2)(t' - t)] \quad (\text{B.1})$$

where we consider single-photon processes in which the A mode is described by a two-level system and the upper level (with amplitude a_1) is coupled to the manifold m th level of the B modes via m -phonon vibration-vibration relaxation processes. The equation of motion for the upper level of the A mode is [from eq 9a]

$$d\bar{a}_1/dt = -iV_{01}\bar{a}_0 \exp(-i\Delta_1 t) + A_1(t) \quad (\text{B.2})$$

$$A_1(t) = -i \sum_\nu g_{iv} \bar{B}_\nu \exp(-i\Delta_1 t) \quad (\text{B.3})$$

Substituting eq B.1 into eq B.3 gives

$$A_1(t) = - \int_0^t dt' \int_0^\infty d\bar{\omega}_B |g(\bar{\omega}_B)|^2 \times \rho'(\bar{\omega}_B) n_\nu(\bar{\omega}_B) \exp \left[\left(i\Delta_1' + \frac{\gamma}{2} \right) (t' - t) \right] \bar{a}_1(t') \quad (\text{B.4})$$

where we replace the sum over the manifold states connected with the m th level of the B modes by an integral over the associated density of states $\rho'(\bar{\omega}_B)$, where $\bar{\omega}_B$ is again the mean frequency of the B modes (i.e., $\omega_\nu = \sum_j \omega_j = m\bar{\omega}_B$, for m -phonon processes).

For decoupling eq B.4 and B.2, we shall now make the Wigner-Weisskopf approximation,¹⁸ that is, the integrand of eq B.4 γ and $|g(\bar{\omega}_B)|^2 \rho'(\bar{\omega}_B) n_\nu(\bar{\omega}_B)$ are functions with value peaked at $\bar{\omega}_B = \omega_A/m$ ($\omega_A = \omega_1 - \omega_0$ is the fundamental frequency of the A mode) and may be taken out of the integral by replacing $m\bar{\omega}_B = \omega_A$. Note that, from eq A.9, the damping factor γ also depends on $\bar{\omega}_B$. By using this approximation and the integral as used in eq A.9

$$\int_0^\infty \exp(\pm i\Omega t) d\Omega = \pi \delta(t) \pm iP(1/t) \quad (\text{B.5})$$

we obtain

$$A_1(t) = -\pi |g(\omega_A/m)|^2 \rho'(\omega_A/m) n_\nu(\omega_A/m) \times \int_0^t dt' \bar{a}_1(t') \exp[\gamma(t' - t)/2] \delta(t') + i\delta\omega \bar{a}_1(t) \\ \equiv -(\Gamma/2 - i\delta\omega) \bar{a}_1(t) \quad (\text{B.6})$$

$\delta\omega$ is a small frequency shift related to the principal value of the integral eq B.4 and Γ is the damping factor (or the bandwidth) of the upper level of the A mode induced by the B mode (via m -phonon processes) and given by

$$\Gamma = 2\pi |g(\omega_A/m)|^2 \rho'(\omega_A/m) n_\nu(\omega_A/m) \quad (\text{B.7})$$

Equations B.6 and B.2 give us the equation of \bar{a}_1 [eq 29] which is now decoupled from the B modes by the complex coupling factor $(\Gamma/2 - i\delta\omega)$.

References and Notes

- (1) J. H. Eberly and P. Lambropoulos, Ed., "Multiphoton Processes", Wiley, New York, 1978.
- (2) P. A. Schulz, A. S. Sudbo, D. J. Krajnovich, H. S. Kwok, Y. R. Shen, and Y. T. Lee, *Annu. Rev. Phys. Chem.*, **30**, 379 (1979), and references therein.
- (3) J. K. Klafter and J. Jortner, *Chem. Phys.*, **47**, 25 (1980), and references therein.
- (4) M. S. Djidjoev, R. V. Khokhlov, A. V. Kiselev, V. I. Lygin, V. A. Namiot, A. I. Osipov, V. I. Panchenko, and B. I. Provotorov in "Tunable Lasers and Applications", A. Mooradian, T. Jaeger, and P. Stokseth, Ed., Springer-Verlag, Berlin, 1976, p 100 ff.
- (5) M. E. Umstead, L. D. Talley, D. E. Tevault, and M. C. Lin, *Opt. Eng.*, **19**, 94 (1980).

- (6) A. V. Khmelev, V. V. Apollonov, V. D. Borman, B. I. Nikolaev, A. A. Sazykin, V. I. Troyan, K. N. Firsov, and B. A. Frolov, *Sov. J. Quantum Electron.*, **7**, 1302 (1977).
- (7) N. V. Karlov and A. M. Prokholov, *Sov. Phys. Usp.*, **20**, 721 (1977).
- (8) M. S. Dehdzhoev, A. I. Osipov, V. Ya. Panchenko, V. T. Platonenko, R. V. Khakhlov, and K. V. Shaitan, *Sov. Phys. JETP*, **47**, 684 (1978).
- (9) V. Kalzea, *Sov. J. Quant. Electron.*, **4**, 1131 (1977).
- (10) T. F. George, I. H. Zimmerman, P. L. DeVries, J. M. Yuan, K. S. Lam, J. C. Bellum, H. W. Lee, M. S. Slutsky, and J. Lin in "Chemical and Biochemical Applications of Lasers", Vol. IV, C. B. Moore, Ed., Academic Press, New York, 1979, p 340 ff.
- (11) M. S. Slutsky and T. F. George, *Chem. Phys. Lett.*, **57**, 474 (1978).
- (12) M. S. Slutsky and T. F. George, *J. Chem. Phys.*, **70**, 1231 (1979).
- (13) J. Lin and T. F. George, *Chem. Phys. Lett.*, **66**, 5 (1979).
- (14) J. Lin and T. F. George, *J. Chem. Phys.*, **72**, 2554 (1980).
- (15) T. F. George, J. Lin, K. S. Lam, and C. Chang, *Opt. Eng.*, **19**, 100 (1980).
- (16) J. Lin and T. F. George, *Surface Sci.*, in press; this is paper 1.
- (17) J. Lin, A. C. Beri, M. Hutchinson, W. C. Murphy, and T. F. George, *Phys. Lett. A*, in press.
- (18) W. H. Louisell, "Quantum Statistical Properties of Radiation", Wiley, New York, 1973.
- (19) A. Nitzan and J. Jortner, *Mol. Phys.*, **32**, 379 (1973).
- (20) W. E. Lamb in *Lect. in Theor. Phys.*, **3**, 435 (1960).
- (21) M. P. Silverman and F. M. Pipkin, *J. Phys. B*, **5**, 1844 (1972).
- (22) V. S. Letokov and A. A. Makarov, *Opt. Commun.*, **17**, 250 (1976).
- (23) R. W. Zwanzig, *Physica*, **30**, 1109 (1964); *Lect. Theor. Phys.*, **3**, 106 (1960).
- (24) E. W. Montroll in "Fundamental Problems in Statistical Mechanics", E. G. D. Cohen, Ed., North-Holland, Amsterdam, 1962.
- (25) Y.-M. Wong, Ph.D. Thesis, University of Rochester, 1979.
- (26) A. Nitzan, S. Mukamel, and J. Jortner, *J. Chem. Phys.*, **63**, 200 (1975).
- (27) S. H. Lin, *J. Chem. Phys.*, **61**, 3810 (1974).
- (28) J. Jortner, *Mol. Phys.*, **32**, 379 (1976).

Reaction of Amines with Haloalkanes. 5. Dissolution of Copper Activated by Sulfur in *n*-Butylamine-Carbon Tetrachloride Solutions

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Earlier study has shown that oxygen causes the dissolution of copper metal in amine-haloalkane solutions. We have found that sulfur also activates copper metal for the dissolution process. A kinetic study has been made by using *n*-butylamine and CCl₄ as reactants at 30 °C. A mechanism involving an intermediate copper(I) sulfide film is proposed.

Introduction

The 1:1 charge-transfer complexes formed between amines and haloalkanes result in partial electron transfer from nitrogen to halogen atoms. It has been shown in this laboratory¹ that several different agents can cause completion of this charge transfer. When copper metal activated by oxygen is the agent, dissolution of the metal occurs.^{1c} In the absence of oxygen, neither dissolution nor the free-radical reaction resulting from the charge transfer takes place. The study reported here was undertaken to determine the nature of the activation by using sulfur in place of the oxygen. It was hoped that sulfur would act less vigorously and that its concentration could be controlled more accurately. Carbon tetrachloride and *n*-butylamine were used as haloalkane and amine, as in the earlier study. The results show that the sulfur does cause dissolution of the copper but with greatly different kinetic behavior than found for the oxygen activation. A mechanism is proposed for the effect of the sulfur.

Experimental Section²

Materials. Reagent grade *n*-butylamine (Baker) was dried over anhydrous barium oxide before distillation in the dark under nitrogen in a Todd Scientific Co. fractionating still. The purified reagent (bp 75.5 °C) was stored in a refrigerated desiccator in the dark and under nitrogen. Spectroquality CCl₄ (Matheson Coleman and Bell) was distilled (76.5 °C) in the Todd still. OFHC copper (the generous gift of Amax Copper, Inc.) was machined into cylinders of appropriate size and degreased in CCl₄. Hydrogen (Airco) was passed through an Engelhard Deoxo purifier and then an acetone-dry ice trap. Nitrogen (Airco, prepurified) was passed through an all-glass purification train. Precipitated sulfur (Baker, USP) was

recrystallized from CCl₄. Measured quantities of the dried reagent were dissolved in CCl₄ to prepare sulfur stock solutions.

Apparatus. A reactor was constructed by joining large-diameter Pyrex tubing to the bottom of a 250-mL three-neck flask. The tubing led to a Thomas Solv-Seal joint. The other end of the joint was sealed around a solid glass rod, which, projecting upward through the joint, supported the copper cylinder in the flask during reaction. One of the three necks of the reactor carried a Kontes high-vacuum Teflon stopcock, one held a vacuum stirrer (Fisher), and the third was replaced with a septum-covered sampling port.

Procedures. Great care was taken to keep the reacting systems free of oxygen, which is a much more powerful activator than sulfur. Mechanically polished copper samples were electropolished, placed in the reaction vessel, and reduced 4 h under flowing hydrogen at 500 °C. Hydrogen flow continued until the reactor was cooled to room temperature. Then the flow was stopped, hydrogen was pumped out, and nitrogen was added to a pressure slightly greater than atmospheric. CCl₄ was boiled in vacuo and put through four freeze-pump-thaw cycles before 135 mL of it was added to the reactor under nitrogen. The entire vessel was then immersed in a water-bath thermostat, and stirring was begun. After thermal equilibration, a measured volume of *n*-butylamine (four freeze-pump-thaw cycles) was injected by syringe. One minute later, sulfur stock solution (four freeze-pump-thaw cycles) was injected to initiate reaction. At various time intervals samples were withdrawn by syringe for analysis.

Reaction temperature was maintained at 30.00 ± 0.02 °C except for the few runs made at 25.0 and 40.0 °C to obtain the activation energy. Surface area was taken to