Quantum Model of Selective Multiphoton Processes: The Role of External (Field) and Internal (Anharmonic Coupling) Detunings*

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Quantum equations of motion describing the energy transfer dynamics via intramolecular anharmonic coupling are presented and solved numerically. Dynamical features of the average excitations of a homogeneous system (SF_6) and a heterogeneous system (H/W) are quantitatively discussed in terms of the intramolecular vibrational relaxation (IVR) rates. Possible mechanisms of surface-enhanced desorption via low-power laser radiation are proposed.

Key words: Multiphoton excitation – Anharmonic coupling – Optimal detuning – Intramolecular vibrational relaxation.

1. Introduction

The selective nature of laser-induced processes, which crucially depend on the intramolecular vibrational relaxation (IVR) rate and on the pumping rate of the laser radiation, have been widely studied for homogeneous (gas-phase) systems [1–3] and more recently for heterogeneous systems [4–7].

For homogeneous systems, several types of selectivity have been discussed in terms of the relative magnitudes of the pumping rate, the IVR rate, the intermolecular vibration-vibration and vibration-translation rates: (1) mode selective (for fast pumping), (2) molecule-selective (for fast IVR rate), (3) nonselective vibrational excitation (for strong intermolecular vibration-vibration coupling) and (4) thermal excitation of the system [1].

For heterogeneous systems, e.g., molecules (atoms) adsorbed on a solid surface, the nature of the laser selective effects are characterized not only by the intra- and intermolecular relaxation processes of the adsorbed species and the pumping rate of the laser field, but also by the surface-induced damping factor (via multiphonon processes) and the laser-induced surface dynamical phenomena, e.g., migration, desorption and predissociation [8–11]. The laser-stimulated surface processes then may be: (1) mode selective, (2) adspecies selective, (3) migration (lattice-site) selective, (4) local heating and (5) nonselective thermal heating [8].

In a homogeneous system, the mode- and/or molecule-selective excitations are possible by a high-power short pulse when the IVR rate is small [1, 12]. For a heterogeneous system, the laser-stimulated selective surface bond breaking (desorption) is also possible when the phonon-induced damping rate is small for high-order multiphonon processes [5, 13]. The IVR rate therefore plays the essential role in the nature of the laser-selective excitations, both for homogeneous and heterogeneous systems. In this paper, the dynamical features of the intramolecular modes governed by the intramolecular anharmonic couplings are studied for two systems: (A) SF_6 (gas phase) and (B) H/W (hydrogen atom adsorbed on a tungsten surface).

2. Quantum Equations of Motion for a Nonlinear Open System

The total Hamiltonian describing an anharmonic quantum oscillator subject to laser (IR) radiation of an open system may be written as

$$H(t, Q_1, Q_2, \ldots Q_N) = H_0^{\text{eff}} + \lambda H_{anh} + H'(t) \tag{1}$$

where H_0^{eff} is the effective unperturbed Hamiltonian of the system (with N normal modes), λH_{anh} is the intramolecular anharmonic coupling and $H'(t)$ is the laser field interaction Hamiltonian. In a second-quantization representation, the individual terms of the total Hamiltonian may be expressed by

$$H_0^{\text{eff}} = \sum_j \hbar \omega_j a_j^+ a_j - i \sum_j \hbar \Gamma_j / 2, \tag{2.a}$$

$$H_{anh} = \sum_{i \neq j \neq k} \sum_{l,m,n} [F_{lmn}^{ijk} (a_i^+ a_i)^l (a_j^+ a_j)^m (a_k^+ a_k)^n + G_{lmn}^{ijk} (a_i^+)^l (a_j^+)^m (a_k)^n] + \cdots, \tag{2.b}$$

$$H'(t) = \sum_j V_j(t)(a_j^+ + a_j). \tag{2.c}$$

In Eq. (2.a), the imaginary part of the complex effective Hamiltonian Γ_j takes account of the level broadening of the open system due to factors such as collisional (pressure) broadening for a homogeneous system or surface-phonon-induced damping for a heterogeneous system. In Eq. (2.b), two typical terms of the anharmonic coupling are shown: the first term representing T_2 phase relaxation processes, where no vibrational energy among the intramolecular modes is

exchanged, and the second term representing the T_1 energy relaxation processes where the photon energy is deposited in the active mode(s) and populated in all the other inactive mode via anharmonic coupling. In Eq. (2.c), $V_j(t) \propto V_{j0} \cdot \cos \omega t$ is proportional to the derivative of the dipole moment and the effective local electric field of the j-th mode with laser frequency ω. We note that the anharmonic coupling factors F_{lmn}^{ijk} and G_{lmn}^{ijk} are related to the p-th derivatives of the anharmonic potential energy (with respect to the normal coordinates) with $p = l + m + n$ being the order of the multiquantum coupling.

In order to study the energy transfer among the intramolecular modes, we shall first set up the equations of motion of the energy-related relevant quantities. The solution of the time-dependent Schrödinger equation

$$i\hbar[\partial\Psi/\partial t] = H\Psi, \tag{3}$$

with the total Hamiltonian H given by Eq. (1) may be written as [14]

$$\Psi(t) = \exp\left\{-\frac{i}{\hbar}H_0^{\text{eff}}t + A(t) + \sum_j (B_j(t)a_j^+ - B_j^*(t)a_j)\right\}\Psi(0), \tag{4}$$

where $A(t)$ and $B(t)$ are time-dependent coefficients.

Substituting Eq. (4) into Eq. (3) with the expression of the total Hamiltonian [Eqs. (1) and (2)], we find the equations of motion of the amplitude functions $B_j(j = 1, 2, \ldots N)$ to be

$$i\hbar\frac{dB_j}{dt} = \lambda \sum_{i\neq j\neq k} \sum_{lmn} m\{F_{lmn}^{ijk}(B_i^*B_i)^l(B_j^*)^{m-1}(B_kB_k)^n$$

$$+ G_{lmn}^{ijk}(B_i^*)^l(B_j^*)^{m-1}(B_k)^n \exp(i\Delta_I t)\}$$

$$+ (V_{j0}/2)\exp(i\Delta_E^j t) - (i\Gamma_j/2)B_j, \tag{5}$$

where the external detuning (Δ_E^j) and the internal detuning (Δ_I) are defined by $\Delta_E^j = 2\pi(\nu_{j+1} - \nu_j) - \omega$ and $\Delta_I = 2\pi(l\nu_i + m\nu_j - n\nu_k)$. In deriving Eq. (5), we have used the usual rotating-wave approximation and operator algebra such as [14]

$$[\exp(B^*a)]F(a^+)[\exp(-B^*a)] = F(a^+ + B_j^*), \tag{6}$$

where $F(a^+)$ is any operator function and B_j are c-numbers.

The important features of the quantum equations of motion [Eq. (5)] are: (1) the j-th normal mode of the system is strongly coupled to the laser field when $V_{j0} \neq 0$ and the external detuning is not far-off the resonance condition $\Delta_E^j = 0$ (due to the anharmonicity, we shall find later that the optimal detuning is red-shifted, i.e., $\Delta_E^j > 0$); (2) the intramolecular coupling is governed by the coupling strengths λF_{lmn}^{ijk}, λG_{lmn}^{ijk} and the internal detuning Δ_I: for the intramolecular coupling to be significant, we shall expect a near resonance $\Delta_I \approx 0$, which was also shown by a classical treatment [7, 15]; (3) by Eq. (5) and its complex conjugate, we find that the equation of motion for $B_j^*B_j$ contains no T_2 dephasing term, i.e., no vibrational energy is exchanged among the intramolecular modes due to the T_2 dephasing processes; (4) the amplitude

function is related to the average excitation in the Poisson distribution [16]

$$P_{n_j}(t) = \exp(-\bar{n}_j)\bar{n}_j^{n_j}/n_j!,\tag{7}$$

where P_{n_j} is the energy population of a harmonic oscillator (for $\lambda = 0$) and n_j and $\bar{n}_j$ are the vibrational quantum number and the average excitation of the j-th mode, respectively; and

$$\bar{n}_j(t) = |B_j(t)|^2 = \sum_{n_j} n_j P_{n_j}(t).\tag{8}$$

Therefore the average excitation $\bar{n}_j = |B_j|^2$ is a relevant quantity in describing the energy distribution among the intramolecular modes.

3. Dynamical Excitation and Optimal Detuning

3.1. SF_6 Gas-Phase System

To show the role of the external and internal detunings in IVR, we now first consider the gas-phase SF_6 system in the collisionless low-pressure regime (i.e. $\Gamma_j = 0$) and focus on the case of the fourth-order anharmonic coupling $\varepsilon Q_3 Q_2^2 Q_6$, where ε is the anharmonicity and Q_3, Q_2 and Q_6 are the normal coordinates of the ν_3 (active), ν_2 and ν_6 modes. The corresponding internal detuning then is $\Delta_I = 2\pi(\nu_3 - 2\nu_2 - \nu_6)$ and the external detuning is $\Delta_E = 2\pi\nu_3 - \omega$, where ω is the frequency of the tunable CO_2 TEA laser which is near resonant to the ν_3 mode. The quantum coupled equations of motion [Eq. (7)] for this case become

$$i\hbar\dot{B}_1 = \lambda' C_1^4 B_1^* B_1^2 + \lambda' C_1 C_2^2 C_3 B_2^2 B_3^* \exp(i\Delta_I't) + (V_{10}/2)^2 C_1 \exp(i\Delta_E't),\tag{9.a}$$

$$i\hbar\dot{B}_2 = \lambda' C_2^4 B_2^* B_2^2 + 2\lambda' C_1 C_2^2 C_3 B_1 B_2^* B_3 \exp(-i\Delta_I't),\tag{9.b}$$

$$i\hbar\dot{B}_3 = \lambda' C_3^4 B_3^* B_2^2 + \lambda' C_1 C_2^2 C_3 B_1^* B_2^2 \exp(i\Delta_E't),\tag{9.c}$$

where $B_j(j = 1, 2, 3)$ are the related amplitude functions of the normal modes ν_3, ν_2 and ν_6, respectively; $\lambda' = 12\lambda$, $\Delta_I' = 2\pi(\nu_3' + \nu_6' - 2\nu_2')$ and $\Delta_E' = 2\pi\nu_3' - \omega$, with $\nu_j'(j = 2, 3, 6)$ are the anharmonic-corrected frequencies, i.e., $\nu_j' = \nu_j - \lambda' C_j/\hbar$; C_j are the quantization constants $C_j = (\hbar/2m_j\omega_j)^{1/2}$. The above system, for the case of exact resonance $\Delta_E' = 0$, was discussed and the related IVR was estimated by Gan et al. [12]. Here we shall show the dynamical features of IVR and find the optimal external and internal detunings by solving the coupled equations of motion numerically. We investigate the time evolution of the average excitations, $\bar{n}_1 = |B_1|^2$, $\bar{n}_2 = |B_2|^2$ and $\bar{n}_3 = |B_3|^2$, governed by Eqs. (9) with the initial Boltzmann populations at room temperature ($T = 300$ K), $B_1(0) = 0.10$, $B_2(0) = 0.214$ and $B_3(0) = 0.417$, and the initial phases $\tan^{-1}[I_j(0)/R_j(0)] = 0$, where I_j and R_j are the imaginary and real parts of $B_j(j = 1, 2, 3)$.

Fig. 1 shows the peak value of the average excitation ($\bar{n}_1^*$) of the active (ν_3) mode as a function of the external detuning with laser intensity $I = 10^8$ W/cm^2. It is seen that the optimal external detuning $\Delta_E^* \simeq 17$ cm^{-1} and the value of $\bar{n}_1^*$ decreases rapidly for Δ_E' larger than Δ_E^*. This "red-shift" behavior of the optimal
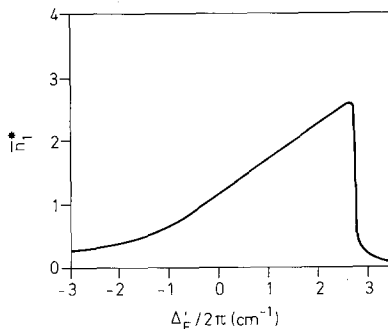
Fig. 1. The peak value of the average excitation of the active mode $(\bar{n}_1^*)$ vs. the external detuning (Δ_E'). [SF$_6$ system]

detuning is a general feature of any laser-excited anharmonic oscillator where the energy spacings are closer for higher levels. [For more detailed analysis we refer the reader to Ref. [17].] Figs. 2(a) and (b) show the exact resonance and the far-off resonance, respectively. It is seen that the peak value of the ν_2 mode $(\bar{n}_2^*)$ decreases from $\bar{n}_2^* \approx 0.4$ (for $\Delta_I' = 0$) to $\bar{n}_2^* \approx 0.1$ (for $\Delta_I' = 63$ cm^{-1}). By our numerical results, we estimate that the rising times of the average excitations t_1^* [defined by the first peak values of the average excitation $\bar{n}_1^*(t^*)$] range from
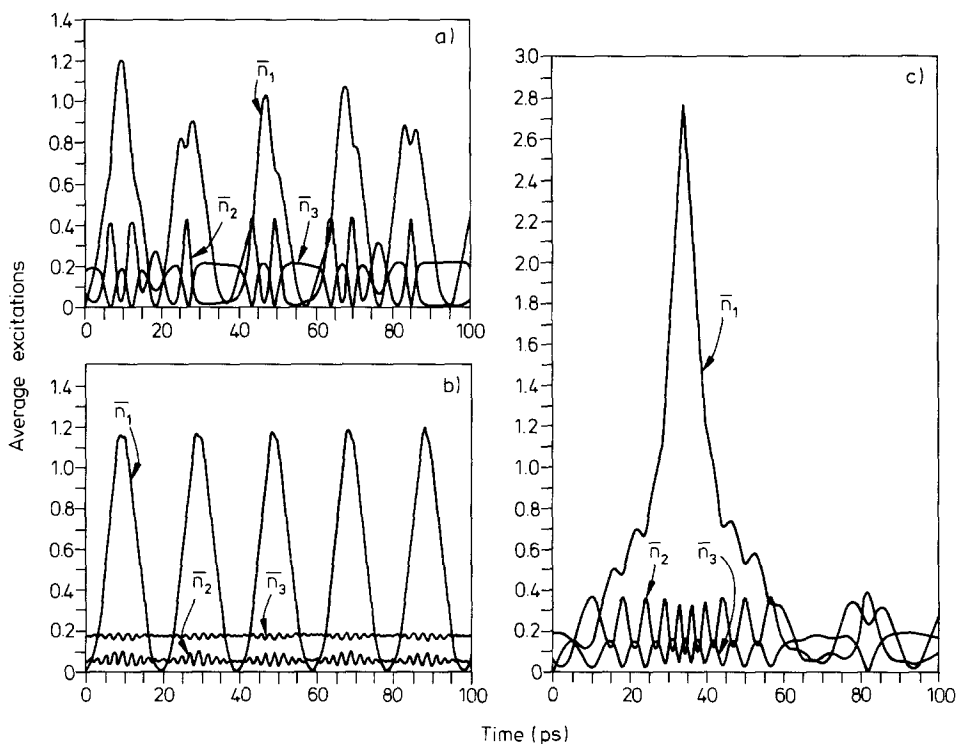

Fig. 2 a–c. The time-dependent average excitations of the active mode $(\bar{n}_1)$, the ν_2 mode $(\bar{n}_2)$ and the ν_6 mode $(\bar{n}_3)$ for the detunings $(\Delta_E'/2\pi, \Delta_I'/2\pi) = $ **(a)** (0, 0) exact resonance **(b)** (0, 20) far-off internal resonance and **(c)** (2.71, 1.00). $\Delta_E'/2\pi = 2.71$ is the optimal external detuning
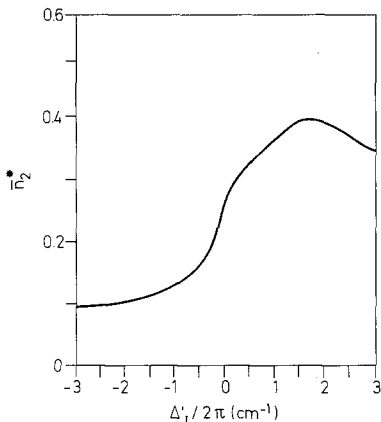
Fig. 3. The peak value of the average excitation of the ν_2 mode $(\bar{n}_2^*)$ vs. the internal detuning (Δ_I') with the optimal external detuning $\Delta_E' = \Delta_E^*$

$t_1^* = 27$ picoseconds (ps) to $t_1^* = 70$ ps depending on the internal detuning Δ_I'. However, the rising times of the ν_2 mode, i.e., the IVR times are in the order of $t_2^* \approx 10$ ps (or $3.3\ \text{cm}^{-1}$). A typical excitation diagram is shown in Fig. 2(c) for the case of $(\Delta_E'/2\pi, \Delta_I'/2\pi) = (2.71, 1.00)$.

Finally, we consider the optimal internal detuning where the intramolecular anharmonic coupling is the most significant (or the maximum excitation of the ν_2 mode $\bar{n}_2^*$). We see, from Fig. 3, that the optimal internal detuning is $\Delta_I'/2\pi \approx 1.6\ \text{cm}^{-1}$ when the external detuning is fixed at its optimal value $\Delta_E'/2\pi \approx 2.7\ \text{cm}^{-1}$.

3.2. H/W Heterogeneous System

The IR spectrum of H/W is given by (in units of cm^{-1}) [18]: $\nu_1 = 1048.6$, $\nu_2 = 645.3$ and $\nu_3 = 1290.6$. The fourth-order anharmonic coupling is given by $\varepsilon' Q_1^2 Q_2 Q_3$, i.e., $\Delta_I = 2\pi(2\nu_1 - \nu_2 - \nu_3)$, where the ν_1 mode is vibrationally excited by a CO_2 laser. Again, we investigate the average excitations of these three modes for the case of $\Gamma_j = 0$. Since the surface-phonon-induced level width (Γ_j) simply causes the decay of the energy excitations, it does not affect the rates of IVR significantly [5].

Two typical dynamical features of the average excitations $\bar{n}_1$, $\bar{n}_2$ and $\bar{n}_3$ (for ν_1 ν_2 and ν_3 modes, respectively) with laser intensity $I = 10^8\ \text{W/cm}^2$ and the anharmonicity $\varepsilon' = 5\ \text{cm}^{-1}$ are shown in Figs. 4(a) and (b). It is seen that these dynamical patterns of the excitations governed by $\varepsilon' Q_1^2 Q_2 Q_3$ are significantly different from that of the SF_6 system governed by $\varepsilon Q_3 Q_2^2 Q_6$. We note that the former system involves the operator function $a_1^{\dagger 2} a_2^{\dagger} a_3^{\dagger}$ corresponding to two-photon process followed by an anharmonic two-quanta coupling, while the latter system involves $a_3(a_2^{+})^2 a_6^{+}$ corresponding to single-photon process followed by an anharmonic three-quanta coupling. We also note that the IVR rate of the H/W system is faster than that of the SF_6 system; however, the average excitation
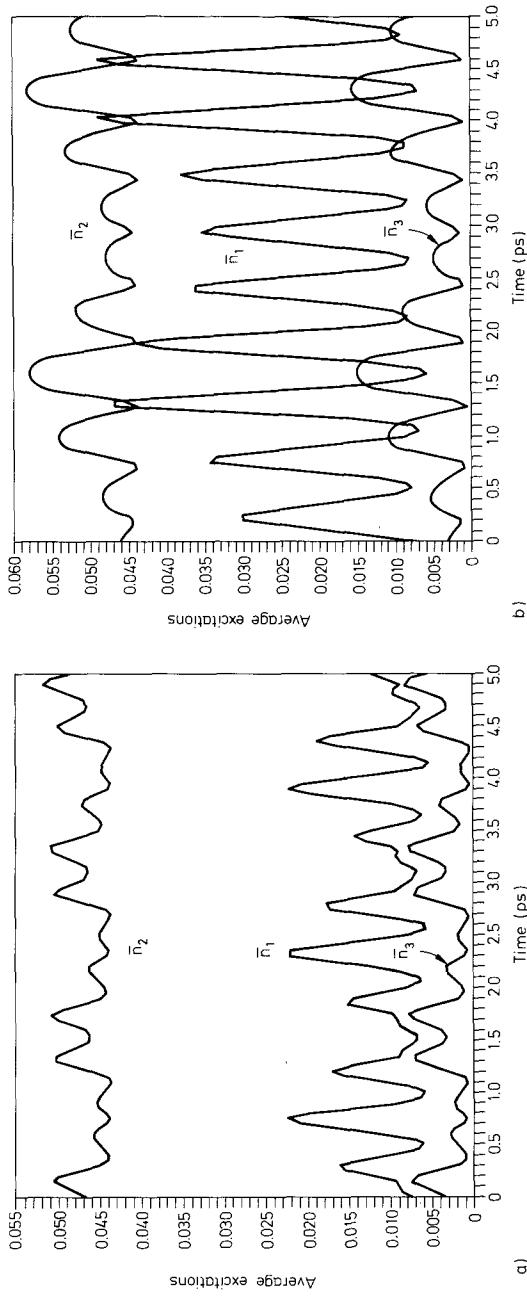
Fig. 4 a, b. The dynamical features of the average excitations of the active mode $(\bar{n}_1)$, the ν_2 mode $(\bar{n}_2)$ and the ν_3 mode $(\bar{n}_3)$ for a heterogeneous system H/W with detunings $(\Delta'_E/2\pi, \Delta'_I/2\pi) = $ (**a**) $(0, 0)$ exact resonance and (**b**) $(10, 80)$

of the active mode in H/W system is lower since the two-photon transition (governed by $\mu_0'' E Q^2$) is usually less probable than the single-photon transition, i.e., the dipole transition governed by $\mu_0' E Q$, where μ_0' and μ_0'' are, respectively, the first and second derivatives of the active dipole moment with respect to the normal coordinate Q and E is the local electric field acting on the species.

In conclusion, we note that for a heterogeneous system the local electric field acting on the adspecies may be greatly enhanced by the surface effects such as roughness [19]. Furthermore, the surface bond breaking can also be possible via van der Waals interaction or the surface-migration-induced rate processes [20, 21].

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