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Quantum Dynamical Model of Laser/Surface-Induced Predissociation: Multiphoton-Multiphonon Processes and Photon/Phonon-Dressed States

by

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Quantum Dynamical Model of Laser/Surface-Induced Predissociation: Multiphoton-Multiphonon Processes and Photon/Phonon-Dressed States*

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By the dynamical energy populations of a photon/phonon-dressed quantum system, laser-stimulated surface predissociation (LSSPD) of an adsorbed diatomic molecule, characterized by the laser pumping rates, the phonon-induced damping factor (level width), the field detuning, and the phase detuning (Landau-Zener form), is studied. The optimal detunings for the enhancement of LSSPD are shown by the numerical results of a set of coupled generalized quantum equations (GQE). The important features of LSSPD and the possible predissociation of a multilevel multistate system via multiphoton-multiphonon processes are discussed.

A

1. Introduction

The interaction of laser radiation with matter (atoms and molecules) of homogeneous systems,[1] e.g., multiphoton dissociation and ionization, have been intensely and systematically studied since the tunable and high-power lasers arrived at the beginning of the 1970's. The study of the influence of lasers on the dynamics of heterogeneous gas/surface systems, however, is still in its infancy.[2-14] The complexity of laser-stimulated surface processes (LSSP) is not only due to the heterogeneity of the system (where the many-body effects of the surface atoms are essential) but also due to the laser-stimulated (or enhanced) dynamical phenomena of the adspecies, e.g., surface migration, desorption, decomposition, predissociation, recombination and other surface rate processes.

The influence of IR radiation (with vibrational excitations) in LSSP has been theoretically studied in our laboratory. Some of the important features and the related methodology in our previous model systems are:[14]

(1) The average excitation (photon energy absorbed) of the active mode, the absorption cross section (or the line shape) and the pumping rate of the radiation are characterized by the field intensity and detuning, the T_1 and T_2 relaxation factors, the phonon coupling factor and nonlinear effects due to the anharmonicity. The results have been obtained either by a quantum approach (in the Heisenberg-Markovian picture)[6-8] or by a stochastic classical approach via the generalized Langevin theory.[11-13]

(2) The mechanism of laser-controlled surface phenomena (selective desorption and migration) may be investigated by combining the *Langmuir kinetic* equation with the laser rate equation (in the energy space) or generalized master equation (in the energy plus lattice site space).[5]

(3) By using Heisenberg equations of motion (in the rotating-wave approximation), we are able to find the dynamical level populations of different normal modes and investigate the nature of LSSP, mode-selective, local heating (molecular-selective) or simply thermal (nonselective) heating of the system.[9,10]

In this paper, we shall study another aspect of LSSP, namely laser-stimulated surface predissociation (LSSPD), by investigating the synergistic effects of surface and two lasers, providing both vibrational and electronic transitions of the adspecies, which may dissociate only with negligible probability (at low temperature) in the presence of the surface or a single laser. Since the phonon-induced damping factor and the surface potentials of the adspecies are not experimentally available to date, instead of focusing on a specific real system we shall study the general dynamical feature of LSSPD by using parameterized quantities. The main purpose of the present paper, therefore, is to predict and suggest some possible enhancement mechanism of LSSPD for real systems based on the resulting feature of a model system.

2. LSSPD of Photon/Phonon-Dressed Multilevel System

We consider a heterogeneous model system consisting of an optically active mode and a group of inactive modes (phonon modes plus the inactive modes of the adspecies) and subject to two lasers of different frequencies. While the active mode is vibrationally excited by the first laser (IR), the adspecies is also electronically excited by the second laser (UV or visible), where the curve crossings among the electronic states in turn cause the vibrational predissociation of the adspecies (diatomic molecule) on the solid surface. When the species is adsorbed (particularly in the case of chemisorption) on a solid surface, its vibrational levels may be shifted and broadened not only by its intramolecular anharmonic coupling but also by the phonon coupling (usually, multiphonon processes) and the dynamical coupling, e.g., surface migration-induced or collision-induced.[6]

The time-dependent Schrödinger equation of the photon/phonon-dressed state may be written as

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[H_0^{eff} + H'(t) \right] \Psi . \qquad (1)$$

H_0^{eff} is the effective field-free Hamiltonian of the phonon-dressed state characterized by a complex form

$$H_0^{eff} = H_0 - \hbar \left(\delta\omega_{mn} + i\,\Gamma_{mn}/2 \right) , \qquad (2)$$

where H_0 is the unperturbed molecular Hamiltonian, and $\delta\omega_{mn}$ and γ_{mn} are, respectively, the frequency-shift and the level-broadening (damping factor) of the phonon-dressed state $|m,n\rangle$ [m and n represent the m-th electronic and the n-th vibrational states, respectively]. Considering only the dominant factor of the frequency-shift and the level-broadening, i.e., via multiphonon coupling, these two phonon parameters may be expressed by[8,10,15]

$$\gamma_{mn} \simeq 2\pi |K(\omega_{mn}/p)|^2 \rho(\omega_{mn}/p)\, \bar{n} \,, \tag{3a}$$

$$\delta\omega_{mn} \simeq P \sum_j |K(\omega_j)|^2 \bar{n} / (\omega_{mn} - \omega_j) \,, \tag{3b}$$

$$\bar{n} \simeq (kT/\hbar\omega_D) [\exp(\hbar\omega_{mn}/kT) - 1] \,, \tag{3c}$$

where K is the coupling factor; ρ and ω_j are the density of states and frequencies of the phonon modes, respectively; p is the smallest order of the multiphonon coupling given by the conservation of energy $p \approx \omega_{mn}/\omega_D$; ω_D and ω_{mn} are the Debye frequency and the frequency of the active mode (for a transition between states $|m,n+1\rangle$ and $|m,n\rangle$), respectively; and T is the surface temperature.

The interaction Hamiltonian which couples the active mode with the lasers is given by

$$H'(t) = V_1 \cos\omega_1 t + V_2 \cos\omega_2 t \,, \tag{4}$$

where $V_1 \propto u_0' E_1$ (due to the first laser) is proportional to the derivative of the dipole moment, u_0', (with respect to the active-mode normal coordinate) and $V_2 = uE_2$ (due to the second laser) is proportional to the dipole moment of the excited species, u. E_1 and E_2 are the envelopes of the electric field (assumed to be slowly varying or constant in time) of the first laser for vibrational excitation (with frequency ω_1) and of the second laser for electronic excitation (with frequency ω_2), respectively.

Using this photon phonon-dressed state governed by a complex effective Hamiltonian, we may then introduce the generalized quantum equations of motion (GQE) in the Heisenberg-Markovian picture and the rotating-wave approximation (RWA):

$$\frac{dC_{mn}}{dt} = -\frac{i}{\hbar}\sum_{\substack{m'\neq m\\ n'\neq n}}\left[V_{mn}^{m'n'} - i\hbar\left(\frac{\partial}{\partial t}\right)_{mn}^{m'n'}\right]\cdot \exp\left\{-\frac{i}{\hbar}\int_0^t\left[W_{m'n'}(R) - W_{mn}(R) - \hbar\omega_1\delta_{m'm} - \hbar\omega_2\delta_{n'n}\right]dt'\right\}C_{m'n'} - \frac{1}{2}\Gamma_{mn}C_{mn}, \tag{5}$$

$$V_{mn}^{m'n'} = \langle \phi_{m'n'}^{0}(r,R)\,|\,V_1\delta_{m'm} + V_2\delta_{n'n}\,|\,\phi_{mn}^{0}(r,R)\rangle, \tag{6a}$$

$$\left(\frac{\partial}{\partial t}\right)_{mn}^{m'n'} = \langle \phi_{m'n'}^{0}(r,R)\,|\,\frac{\partial}{\partial t}\,|\,\phi_{mn}^{0}(r,R)\rangle, \tag{6b}$$

where $W_{mn}[R(t)]$ is the real part of the diagonal element of the field-free phonon-dressed effective Hamiltonian H_0^{eff} is the basis-state representation of the unperturbed vibronic state $\phi_{mn}^0(r,R)$; r and R represent the coordinates of the electrons and of the nucleus, respectively; $\delta_{m'm}$ and $\delta_{n'm}$ are Kronecker delta functions assigned for the first and second lasers which cause vibrational (m'=m) and electronic (n'=n) transitions, respectively.

We note that GQE [eq.(5)] reduces to the usual Heisenberg equations of motion (in RWA)[16] in the atomic viewpoint, i.e., where one atom is viewed as perturbed by another atom and $W_{mn}(R)$ is a complex time-independent quantity, $W_{mn}(R) = E_{mn} - i\hbar\gamma_{mn}/2$, and by using the transformation $\bar{C}_{mn}(t) = C_{mn}(t)\exp[\gamma_{mn}t/2]$,

$$\frac{d\bar{C}_{mn}}{dt} = -\frac{i}{\hbar}\sum_{m',n'} V_{mn}^{m'n'} \exp\left\{-\frac{i}{\hbar}\left(E_{m'n'} - E_{mn} - \hbar\omega_1\delta_{m'm} - \hbar\omega_2\delta_{n'n}\right)\right\}. \quad (7)$$

Furthermore, GQE may be reduced to the semiclassical equations of motion (in the molecular viewpoint) for phonon-free case,[17] i.e., $\gamma_{mn}=0$. It is also worth noting that the equations of motion in the molecular viewpoint may be developed by simply including the secular terms on the right-hand side of eq.(7) and using the transformation

$$\bar{\bar{C}}_{mn}(t) = \bar{C}_{mn}(t)\exp\left\{\frac{i}{\hbar}\int_0^t V_{mn}^{mn}(t')\,dt'\right\}. \quad (8)$$

3. LSSPD of a Two-Level Two-State System

GQE shown in eq.(5), describing a multilevel (vibrational) multistate (crossing electronic curves) photon/phonon-dressed system, is in general characterized by multiphoton-multiphonon processes. These coupled first-order differential equations in principle may be decoupled into a single high-order differential equation,[18] or solved by the Laplace transform technique.[10] However, the analytic solutions are not usually available due to the vibrational couple terms but also due to the time-dependent classical trajectory factor $W_{mn}[R(t)]$. To investigate the synergistic effects of the lasers and the surface phonons by some tractable means, we shall consider the physical situation that the adspecies may be predissociated by absorbing two photons (one IR and one UV, or visible photon). We shall also assume that there is only one electronic curve crossing (or one of the crossings contributes the dominate predissociation channels).

For a two-level two-state system, GQE [eq.(5)] reduces to a set of coupled equations of the amplitude vectors $C_{11}(t)$, $C_{12}(t)$ and $C_{2c}(t)$ representing the states of bound-ground, bound-excited and the continuum (predissociated) states, respectively:

$$\dot{C}_{11}(t) = -i V \exp(-i\Delta t)\, C_{12} \;, \tag{9a}$$

$$\dot{C}_{12}(t) = -i V \exp(i\Delta t)\, C_{11} - i G \exp(-i\alpha t^2/2)\, C_{2c} - (\gamma/2)\, C_{12} \;, \tag{9b}$$

$$\dot{C}_{2c}(t) = -i G \exp(i\alpha t^2/2)\, C_{12} \;. \tag{9c}$$

The pumping rates V and G are given by [from eq.(6.a)], $V=V_{11}^{12} \propto E_1$ and $G = V_{12}^{2c} \propto E_2$; γ is the level width of the phonon-dressed upper level referred to as the damping factor of the pumped system; $\Delta = \omega_A - \omega_1$ is the field detuning with ω_A is the fundamental frequency of the phonon-dressed state; and $\alpha = (S_2 - S_1) v_0/\hbar$ is the phase detuning obtained by the usual Landau-Zener model, i.e., $W_{2c}(R) - W_{12}(R) - \hbar\omega_2 \approx \alpha t$.[17] There are some important features of the above coupled equations:

(i) The two-photon predissociation processes are two-step excitations governed by the pumping rates V (due to the first laser) and G (due to the second laser), (ii) due to the damping factor γ (energy sink), both the populations of the bound state $|C_{11}(t)|^2$ and $|C_{12}(t)|^2$ are decaying, while the probability of predissociation $P_D(t) = |C_{2c}(t)|^2$ will rise to a saturated value, and (iii) the oscillatory behavior due to the phase detuning $[\exp(i\alpha t^2)]$ is significantly different from that of the field detuning [exp(-iΔt)], and we shall see later that the corresponding optimal detunings show different character.

The analytical solutions of the coupled equations are available in some specific situations where one may use perturbation methods. However, we are more interested in the exact solutions which are available by using numerical method, for e.g., Runge Kutta. The numerical results of the level population $P_A = |C_{12}(t)|^2$ (for photon energy deposited in the active mode), the predissociation probability $P_D = |C_{2c}(t)|^2$ and the energy population of the phonon (bath) modes $P_B = 1 - |C_{11}(t)|^2 - P_A - P_D$ are shown in Figs. 1-4. There are five parameters characterizing the dynamical feature of LSSPD: $(V,G,\gamma,\Delta,\alpha)$. For systematic analysis of the numerical results, we investigate the following physical features:

(i) Fig. 1 shows the effect of the phase detuning α (for γ=0) on the steady-state predissociation probability ($P_D^{s.s.}$). It is seen that instead of α=0, the optimal phase detunings for $P_D^{s.s.}$ having peak values are $\alpha^* \simeq \pm 1.0$ and $\alpha^* \simeq \pm 3.5$; and for $|\alpha| > 3.5$, the values of $P_D^{s.s.}$ show exponential decaying. This is a significantly different feature from that of the field detuning, where there are no dips in the absorption profile and the optimal detunings are Δ^*=0 for a two-level system while $\Delta^*>0$ (red-shift) for a multilevel system with anharmonic nonlinear effects.[6,7]

(ii) The effect of the phonon-induced damping factor (γ) is shown in Fig. 2(A)-(D), for $(V,G,\Delta,\gamma,\alpha) = (4,1,\Delta^*,\gamma,\alpha^*)$ with the optimal detunings Δ^*=0 and α^*=3.5 and the damping factor increasing from γ=0 (surface free) to $\gamma = 1$ (strong phonon coupling).

(iii) The effect of the phase detuning on the dynamical populations and the time-dependent predissociation is shown in Fig.3(A)-(B), for the cases of exact phase resonance ($\alpha=0$) and far-off resonance ($\alpha=9$). We note that $P_D^{s.s.} \simeq 0.06$ for $\alpha=0$, and $P_D^{s.s.} \simeq 0.15$ for $\alpha=9$.

(iv) Finally, we show the high Rabi oscillation cases (governed by the first laser pumping rate V) for $\gamma=0$ and $\gamma=0.1$ with the other optimal phase detuning $\alpha^*=1$. The other important physical quantity is the mean predissociation rate which may be approximately defined as $\bar{R} \simeq P_D^{s.s.}/t^*$, with t^* being the rising time of the predissociation probability $P_D(t)$. We can estimate, from Fig.2(C) and 2(D), that the mean predissociation rates (per unit time of 1/G) decrease from $\bar{R} \simeq 0.21$ to $\bar{R} \simeq 0.14$ when the damping factor increases from $\gamma=0.1$ to $\gamma=1$.

4. Discussion and Conclusion

As an extension of the model system described in the previous section, we shall now suggest a possible enhancement of surface predissociation of a multilevel (vibrational) and multistate (electronic curve-crossing) system via the combination of two lasers as follows:

(1) LSSPD may be enhanced by absorbing two laser photons where the optimal detuning condition ($\Delta=\Delta^*$ and $\alpha=\alpha^*$) is available when both lasers (with frequencies ω_1 and ω_2) are tunable.

(2) Effective predissociation channels induced by surface magnetic field can be opened in the absorption of one or few IR photons, i.e., preparing the adspecies in a vibrational level above the highest surface-split electronic states[19] and providing the external photon

energy source to balance the energy loss due to the phonon coupling of the adspecies. We note that in this case the net enhancement of LSSPD is governed by the competition between the surface-split (which opens more possible predissociation channels) and the surface-induced energy damping. Therefore, the gaining of a significant steady-state predissociation $P_D^{s.s.}$ or the rate of predissociation $\bar{R}$ is governed by the competition between the (IR) multiphoton and the (surface) multiphonon processes,[8] and moreover by the coupling strength of the Landau-Zener local transition probability characterized by the pumping rate of the second laser (G) and the phase detuning (α).[17]

(3) For a multilevel-multistate system (see Fig.5), the enhancement of LSSPD may also be generated by multiphoton processes where the average excitation of the multilevel active mode (with energy population governed approximately by a Poisson distribution)[6,20] matches one of the peak values of the Franck-Condon factors which show structure patterns as a function of the vibrational level.[21]

In conclusion, we have shown, by the numerical solutions of a set of coupled GQE, how the synergistic effect of two lasers and the surface phonons on the dynamical feature of LSSPD are characterized by the pumping rates (V,G), the multiphonon coupling factor (γ), the field detuning (Δ) and the phase detuning (α). For significant enhancement of LSSPD, we expect a small ratio of γ:V and matching detunings to the optimal condition, i.e., $\Delta=\Delta^*$ and $\alpha=\alpha^*$.

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†Camille and Henry Dreyfus Teacher-Scholar.

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Figure Captions

Fig. 1. The steady-state predissociation probability ($P_D^{s.s.}$) as a function of the phase detuning (α) for $(V,G,\gamma,\Delta) = (4,1,0,0)$. V,G,γ and Δ are the pumping rates, phonon-induced damping factor and the field detuning, respectively.

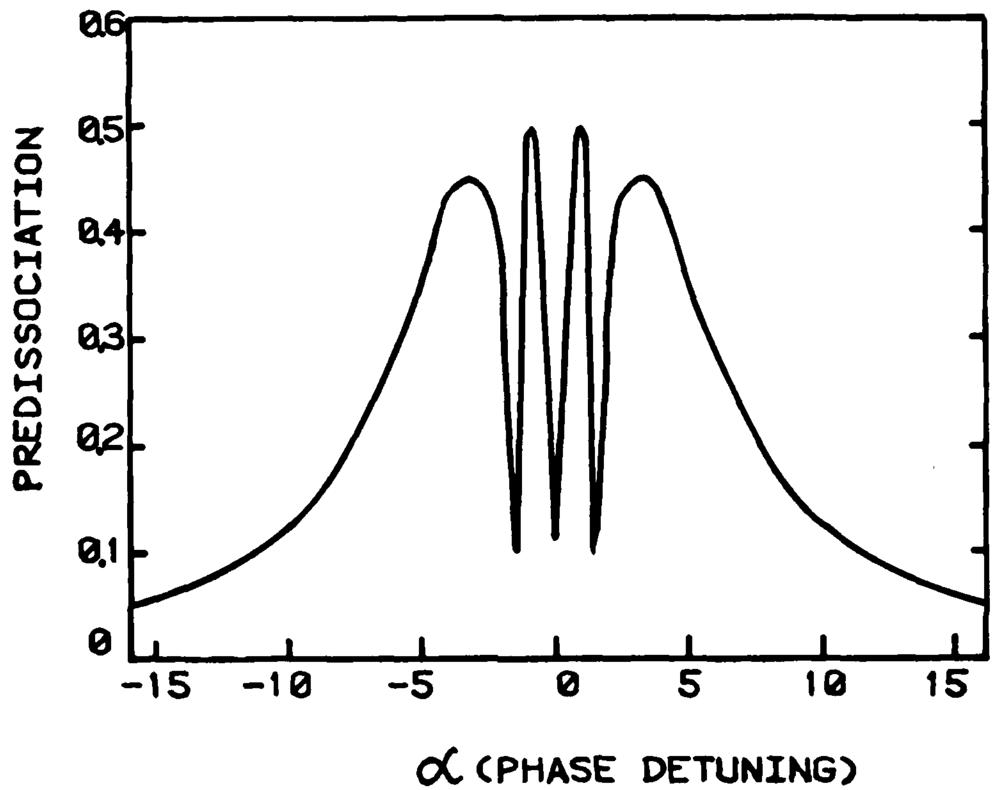
Fig. 2. The time evolutions of the energy populations of the active mode (P_A) and the phonon(bath) modes (P_B), and the predissociation probability (P_D) for $(V,G,\gamma,\Delta,\alpha)$ = (A) (4,1,0,0,0) [phonon-free at exact resonance], (B) (4,1,0,0,3.5) [phonon-free at optimal detuning], (C) (4,1,0.1,0,3.5) [weak phonon-coupling], and (D) (4,1,1,0,3.5) [strong phonon-coupling].

Fig. 3. The dynamical feature of P_A, P_B and P_D for $(V,G,\gamma,\Delta,\alpha)$ = (A) (4,1,0.5,0,0) [exact resonance with phonon-coupled], (B)(4,1,0.5,0,9) [far-off phase detuning].

Fig. 4. The dynamical feature of P_A, P_B and P_D for the cases of high Rabi frequency (pumping rate V) with $(V,G,\gamma,\Delta,\alpha)$ = (A) (10,1,0.1,0,1), for phonon-coupled and (B) (10,1,0,0,1), for phonon-free system.

Fig. 5 (A) Schematic energy diagrams of a multilevel-multistate system subject to two lasers with frequencies ω and ω', respectively.
(B) The vibrational energy population of the photon/phonon-dressed state P_n vs. n (vibrational quantum number).
(C) The structure pattern of the Franck-Condon factors for a multistate (curve-crossing) system.

Fig. 1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α (PHASE DETUNING)

Fig. 2

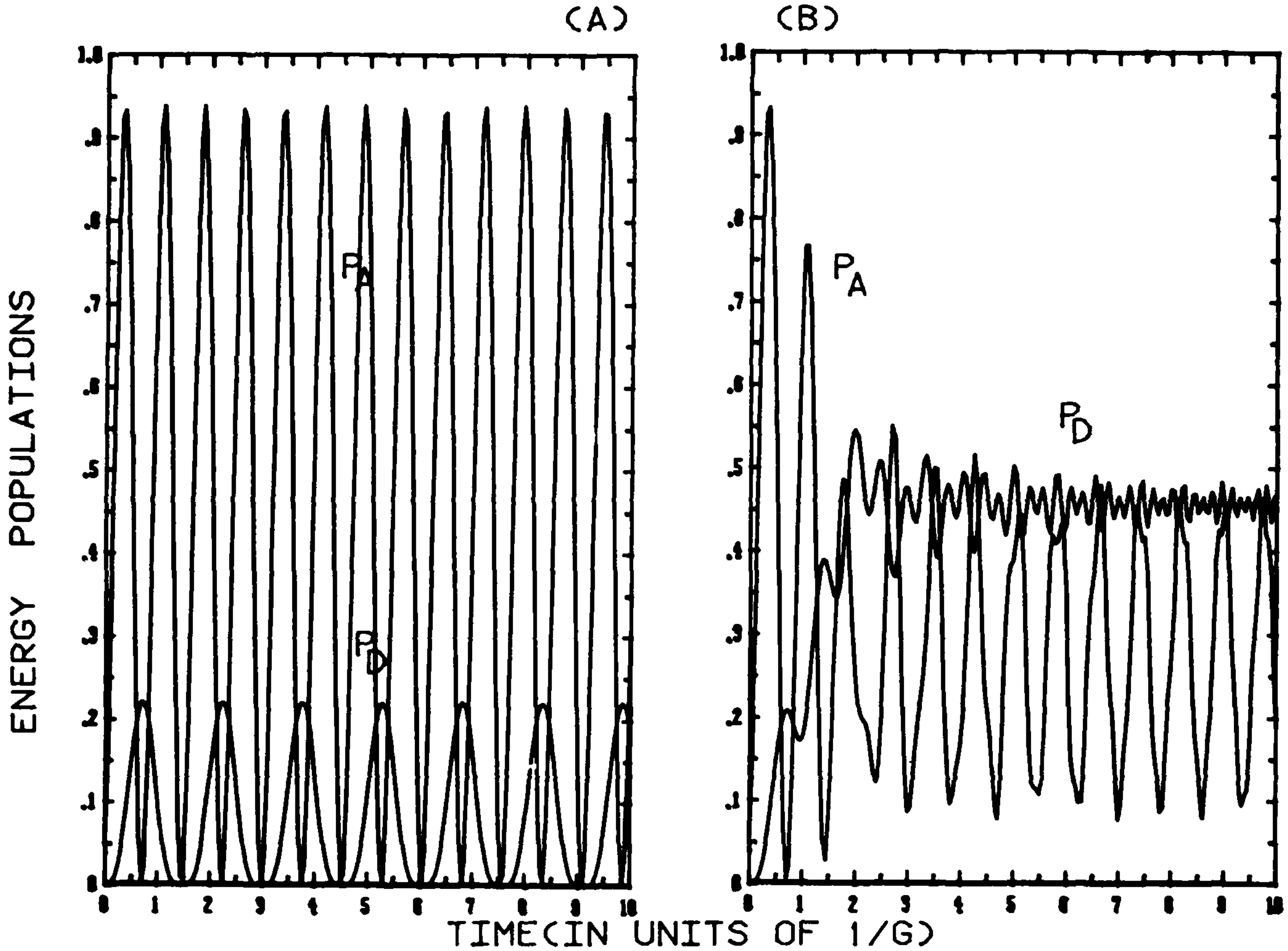


Fig. 2

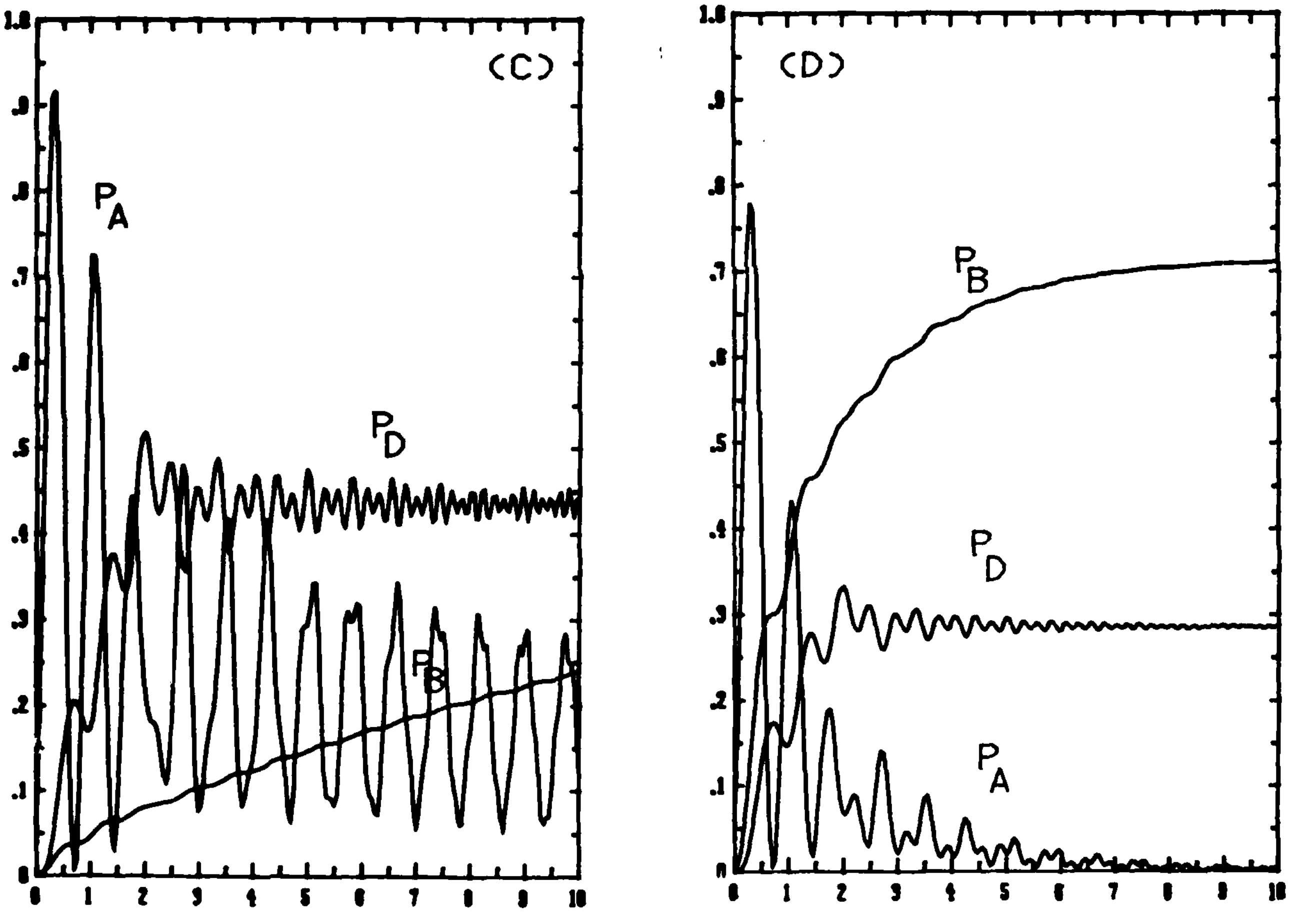


Fig.3

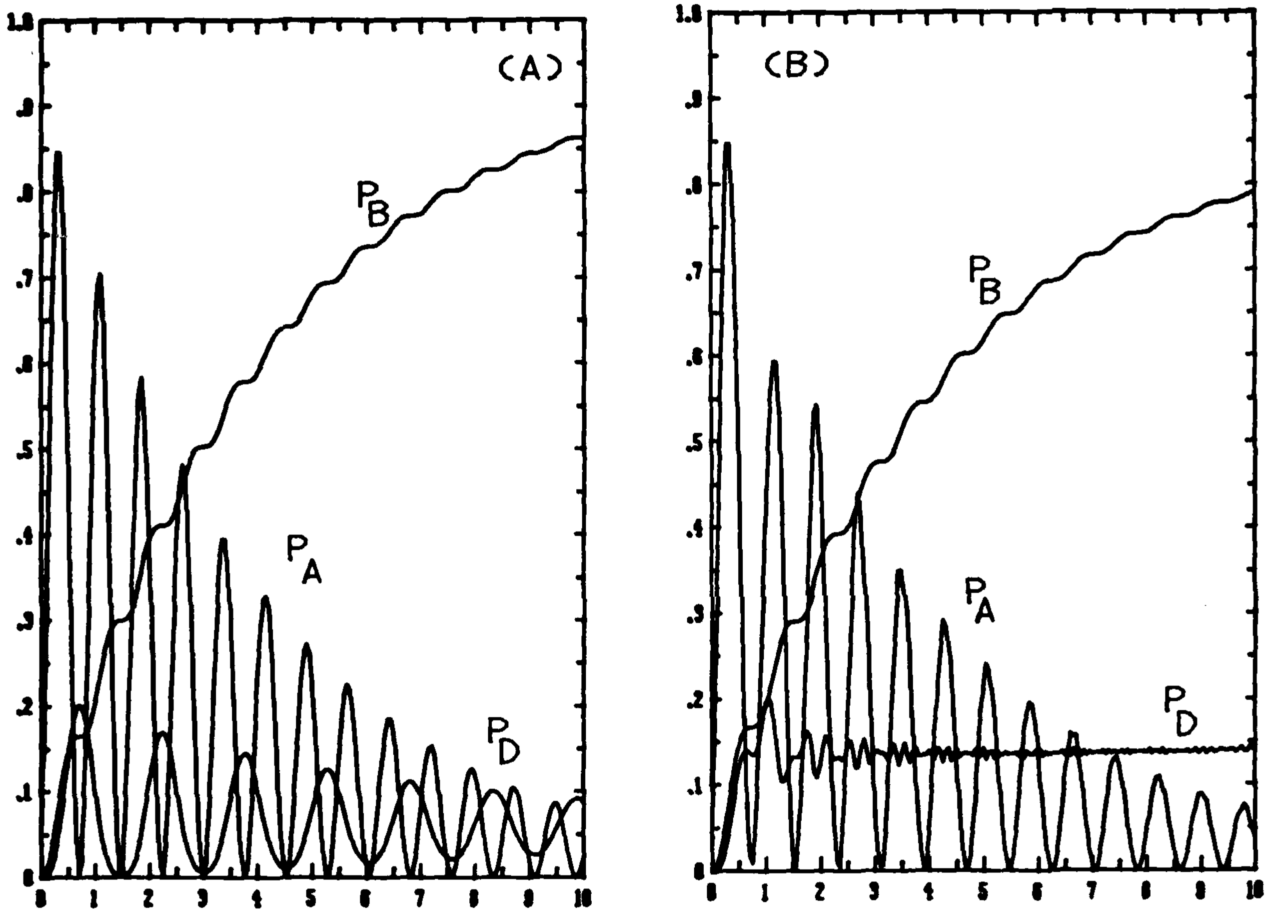
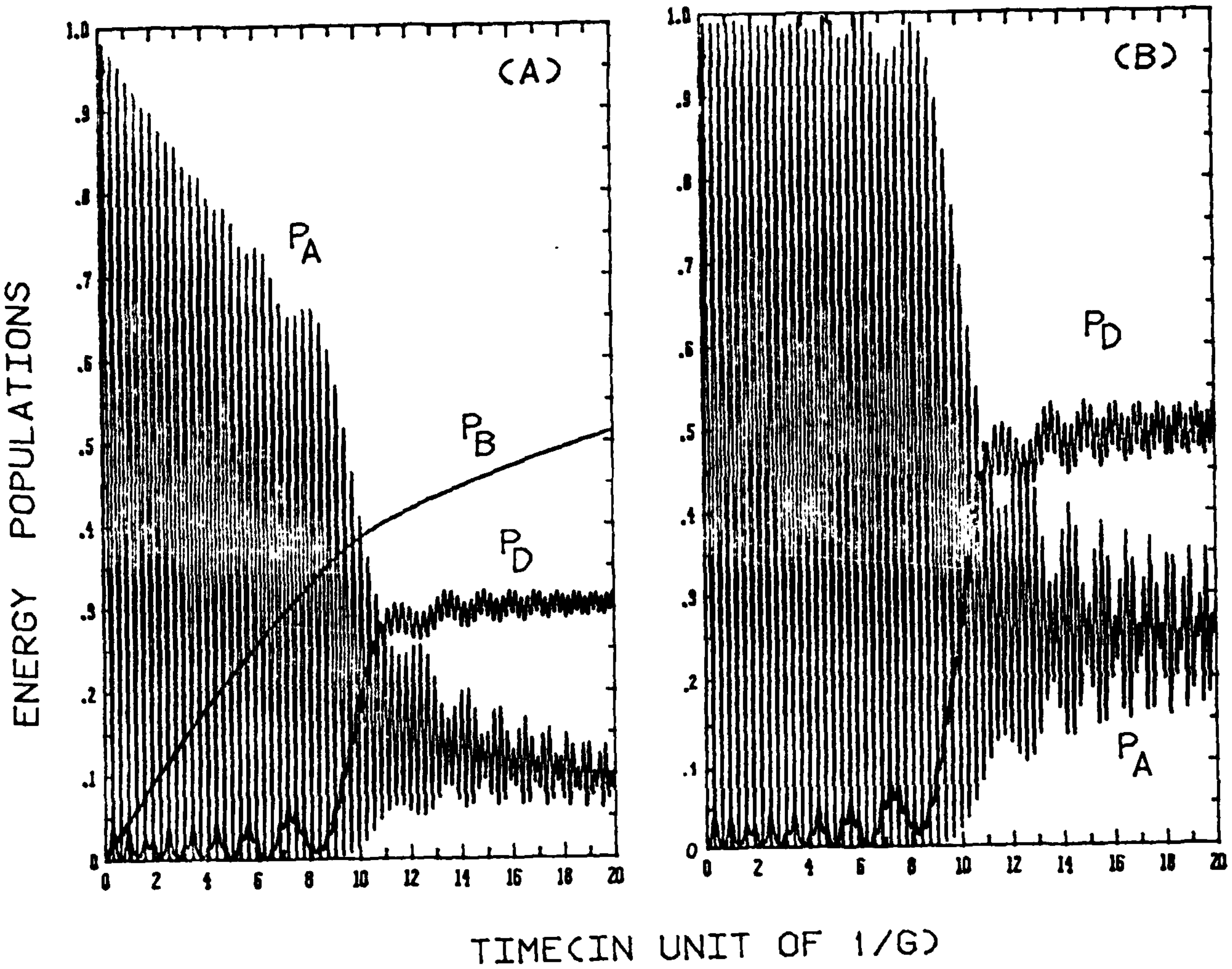


Fig. 4



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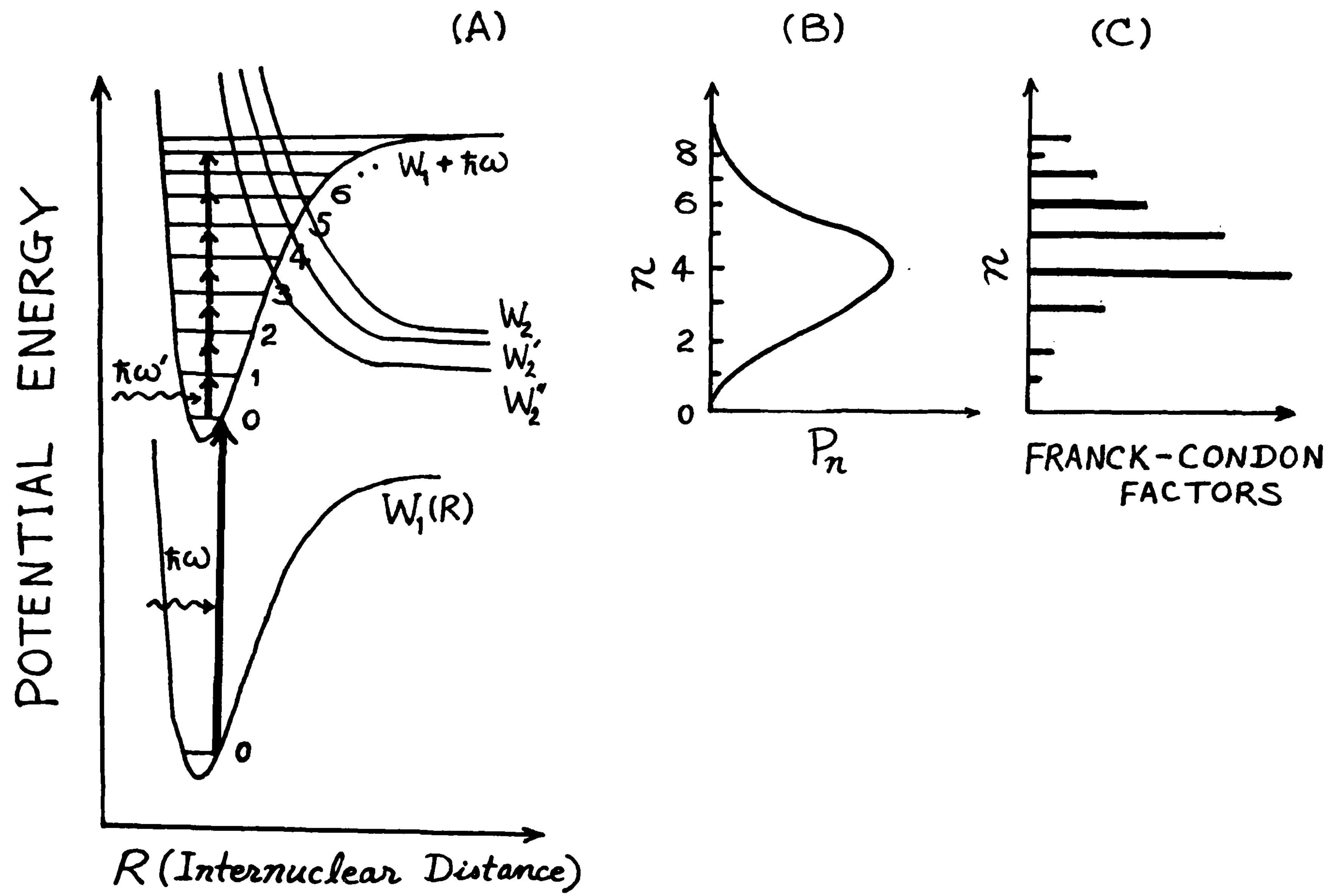
(A)
(B)
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