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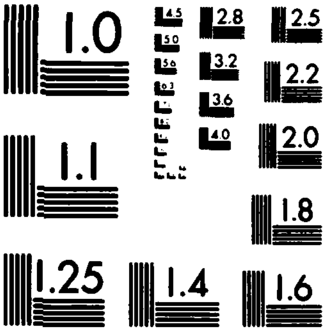

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Phase-Dissipative Mechanisms for Laser-Induced Surface Desorption/Dissociation Processes

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Vibrational excitation and relaxation for a molecule adsorbed on a surface is investigated in connection with desorption/dissociation processes. The population equations for a laser-driven anharmonic oscillator involving both energy- and phase-relaxation mechanisms are derived with the Zwanzig projector technique and eigenfunction-expansion method due to Weidlich. Phase relaxation is seen to assist in the excitation of the resonant active mode.

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PHASE-DISSIPATIVE MECHANISMS FOR LASER-INDUCED SURFACE DESORPTION/DISSOCIATION PROCESSES

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Abstract

Vibrational excitation and relaxation for a molecule adsorbed on a surface is investigated in connection with desorption/dissociation processes. The population equations for a laser-driven anharmonic oscillator involving both energy- and phase-relaxation mechanisms are derived with the Zwanzig projector technique and eigenfunction-expansion method due to Weidlich. Phase relaxation is seen to assist in the excitation of the resonant active mode.

I. Introduction

Infrared laser radiation impinging onto a molecule adsorbed on a solid surface can resonantly excite the admolecular internal vibrational/rotational modes, or deposit photon energy in the adbond with which the molecule is bound to the surface.[1-5] It has been shown experimentally[6,7] that SF_6 and CH_3F molecules adsorbed on NaCl surfaces at low temperatures can be desorbed by the resonant excitation of the adsorbate internal vibration, namely, the ν_3 mode. The treatment of the problem of many degrees of freedom for the molecule-surface system is very complicated and generally an insoluble problem. Interactions between the resonant active vibrational mode and the other inactive modes, and between the admolecule and surface excitations - surface phonons, surface plasmons, reflected photons (i.e., photons emitted by the admolecule and reflected by the surface), etc. - create a large number of dissipative channels by which absorption, dissociation, desorption or chemical reaction on the surface are strongly influenced. (Desorption is the breaking of the adbond between the admolecule and the surface, and dissociation is the breaking of a bond within the admolecule.) In this Letter, we are especially interested in the influence of surface-dephasing relaxation on the excitation of the resonant mode, which plays an important role in the process of desorption/dissociation.

II. Theory

Under normal circumstances, due to the vast number of degrees of freedom of the admolecule-surface system, the intrasystem relaxation can be very fast, and in fact, comparable to or faster than the rate of photon absorption. In this case, energy randomization or statistical thermodynamical behavior may at least partly occur in desorption/dissociation processes on surfaces.[8] The IR-laser-driven resonant active mode absorbs photons and transfers its energy to other vibrational modes or the surface, and then "interference" superposition of these many vibrations can instantaneously accumulate energy in the weakest bond to lead to molecule dissociation or desorption from the surface, if this energy is beyond the appropriate theshold.[9,10] As an example, the threshold temperature for thermal dissociation of SF_6 in the gas phase is measured to be 1600 K.[8] At this temperature, the average occupation number of the resonant mode (ν_3) of SF_6 is $\bar{n}=0.76$, which means that, while the energy deposited in the molecule has gone into the ν_3 mode to exceed the critical value for dissociation, the other modes remain in low excited states.

We shall confine ourselves here to the excitation and relaxation of the active anharmonic vibrational mode which is driven by a resonant coherent field and controlled by both energy (T_1) and phase (T_2) relaxation. For this purpose, we treat the many other non-active modes and surface excitations (i.e., phonons, plasmons, reflected photons, etc.) as a large thermal reservoir, by which dissipation mechanisms are provided. A reduced density operator W for the resonant mode obeys the master equation

$$\frac{dW}{dt} = \left[\frac{dW}{dt}\right]_{\text{coherent}} + \left[\frac{dW}{dt}\right]_{\text{incoherent}}$$

$$= \left[-iL_c + \Lambda_1 + \Lambda_2\right]W. \tag{1}$$

The reversible term is $-iL_cW \equiv -(i/\hbar)[H,W]$, where $H = H_M + H_F$ is the sum of anharmonic oscillator and external field interactions,[11]

$$H_M = \hbar(\omega-\omega_L)a^+a - \hbar\varepsilon a^+a(a^+a+1) \tag{2}$$

$$H_F = \mu E(t)(a^{+}+a). \tag{3}$$

Here a^{+} and a are oscillator ladder operators, μ is the molecular dipole moment, $E(t)$ is the applied electric field, ω_L is the laser frequency, and ε is a positive anharmonicity. The dissipative terms are given by[12,13]

$$\begin{aligned}\Lambda_1 W = {} & \gamma_{\downarrow}([a,Wa^{+}] + [aW,a^{+}]) \\ & + \gamma_{\uparrow}([a^{+},Wa] + [a^{+}W,a]),\end{aligned} \tag{4}$$

$$\Lambda_2 W = \eta([a^{+}a,Wa^{+}a] + [a^{+}aW, a^{+}a]). \tag{5}$$

$\Lambda_2 W$ is responsible for a pure dephasing in the decay of the off-diagonal matrix elements,[14] and $\gamma_{\uparrow}$, $\gamma_{\downarrow}$ and η contain implicit information about the reservoir, including the surface. With the dissipative terms [Eqs. (4) and (5) only], the relaxation behavior of the expectation values of the amplitude and number operator is governed by the equations $\frac{d}{dt}\langle a\rangle = -(\gamma_{\downarrow}-\gamma_{\uparrow}+\eta)\langle a\rangle$ and $\frac{d}{dt}\langle a^{+}a\rangle = 2(\gamma_{\downarrow}-\gamma_{\uparrow})\langle a^{\dagger}a\rangle + 2\gamma_{\uparrow}$. Λ_2 thus affects only the off-diagonal elements of the density operator by providing a pure phase-destroying term with a rate of η. In the Born approximation, the diagonal parts of the density matrix obey the equation

$$\frac{d}{dt} W_n = \langle n|\Lambda_1 W_r|n\rangle - \int_0^t d\tau \, \langle n|PL_i e^{-iL_M(t-\tau)} e^{\Lambda_2(t-\tau)} L_i \, W_r(\tau)|n\rangle , \tag{6}$$

where L_i is a Liouville operator due to the oscillator-field interaction, P is a projection operator used to obtain the diagonal part of the density operator,[15] and $W_r \equiv PW$ is the relevant part of the density matrix.

The difficult problem here is the explicit evaluation of the matrix elements that appear inside the integral in Eq. (6). We use the Weidlich eigenfuntion-expansion method[12,13] to evaluate these elements. The "eigenstate" of the super-operators Λ_2 and Λ_2^{+} are $||A_{pq})$ and $||B_{pq})$, respectively, and under the Markoff assumption, the "eigenvalues" of Λ_2 have the form $\lambda_{pq} \approx -\eta q^2$, where $p = 0, 1, 2, \cdots$ and $q = 0, \pm1, \pm2, \cdots$. The equations of motion for the diagonal parts of the density matrix are then given as

$$\dot{W}_n = \langle n|\Lambda_1 W_r|n\rangle - \int_0^t d\tau \sum_{pq} e^{-\eta q^2(t-\tau)}$$

$$\times \, \mathrm{Tr}(B^{+}_{pq} L_i W_r(\tau)) \langle n|L_i e^{-iL_M(t-\tau)} A_{pq}|n\rangle. \tag{7}$$

By a lengthy but straightforward algebraic calculation, we obtain a simpler set of coupled differential equations to describe the excitation and relaxation behavior for the resonant vibrational mode:

$$\dot{W}_n = 2\kappa\,[(n+1)\,W_{n+1} - nW_n] - 2\eta\left[\frac{\Omega_R(t)}{\eta}\right]^2 \left\{\frac{n(W_n-W_{n-1})}{1 + [2\frac{\varepsilon}{\eta}(n-1) - \frac{\Delta}{\eta}]^2}\right.$$

$$\left. + \frac{(n+1)(W_n-W_{n+1})}{1 + (2\,\frac{\varepsilon}{\eta}\,n - \frac{\Delta}{\eta})^2}\right\}. \tag{8}$$

The decay parameters κ ($\equiv \gamma_{\downarrow} - \gamma_{\uparrow}$) and η are determined by the internal mode-mode coupling and the admolecule-surface interaction, and for a fixed temperature and admolecule-surface distance they can be considered as constants (here a cold surface of 0 K has been assumed), $\Omega_R(t)$ is the Rabi frequency, and Δ is the detuning between the admolecular fundamental and laser frequencies.

The first two terms with the factor of 2κ on the right-hand side of Eq. (8) describe the energy relaxation processes which always lead to population loss in the resonant mode. In the next terms with the factors of η describing the influence of the phase relaxation, we notice that there are competitive factors: upon an increase of the value of η, the phase relaxation tends to diminish the detuning and anharmonicity "bottleneck" effects, and the effective Rabi frequency $\Omega_R/\eta^{\frac{1}{2}}$ tends to decrease.

III. Calculations and Results

Figure 1 shows the influences of the phase relaxation. The time evolution for the average occupation number $\bar{n}$ of a driven damped anharmonic oscillator is displayed, with consecutive values of the phase-relaxation parameter η ($\eta = 1, 5, 9, 13$). We note that there is a range of values of η which assist the excitation of the admolecular active mode. For the optimal parameter $\eta = 5$ in our specific case, Figure 2 displays the time-dependent population distributions for several excited states, where considerable population is seen. One would generally expect the phase decay η to be much more enhanced than κ by the inactive adspecies vibrational modes and by the surface.[16] The phase-dissipation mechanism may be generated in several ways in an admolecule-surface system as follows: (a) intramolecular coupling between the active and inactive vibrational modes;[17] (b) intermolecular collisions when the admolecules can migrate on the surface;[18] (c) rotational relaxation within the vibrational level manifold of the admolecule;[11] (d) self-coupling of the admolecule due to surface-reflected photons.[19,20]

Acknowledgments

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Figure Captions

1. Time dependence of the average occupation number $\bar{n} = \langle a^{\dagger}a \rangle$ for (cw) laser-driven anharmonic oscillator in contact with a bath. The curves correspond to η = 1, 5, 9, 13, and the others parameters are (κ, Ω_R, ε, Δ) = (0.01, 0.5, 1.5, 3.0), where all rates are in the unit of the transverse relaxation[13] rate. This figure shows that when the vibrational linewidth η is smaller than the detuning Δ, the maximum vibrational excitation is small but grows as η increases. Excessively large values of η eventually reduce the average excitation level, presumably due to the spread of population within the linewidth.

2. The probability of occupation of level n, $W_n(t)$, as a function of time. η is fixed at 5, and the other parameters are given in Figure 1.

Figure 1

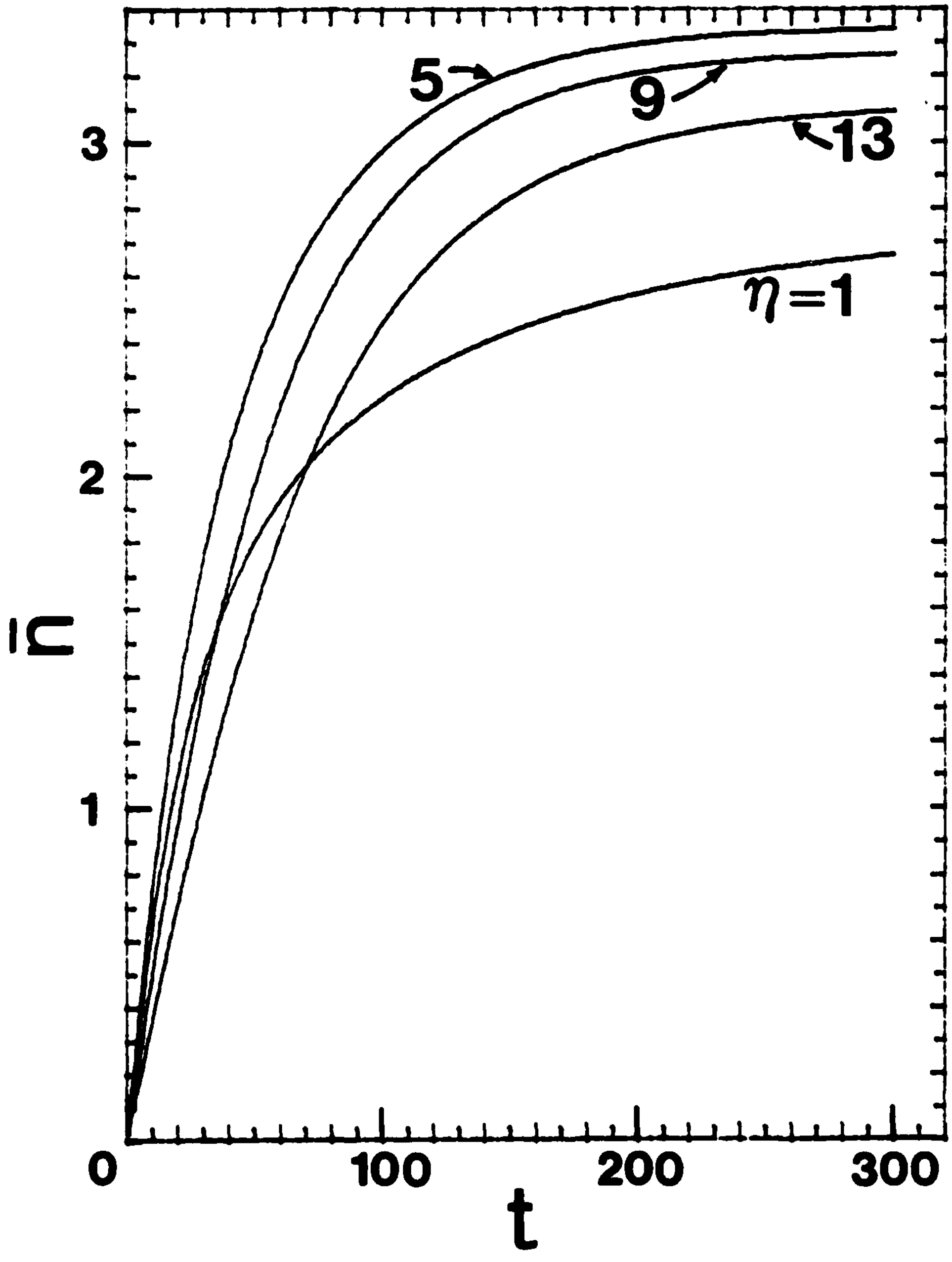
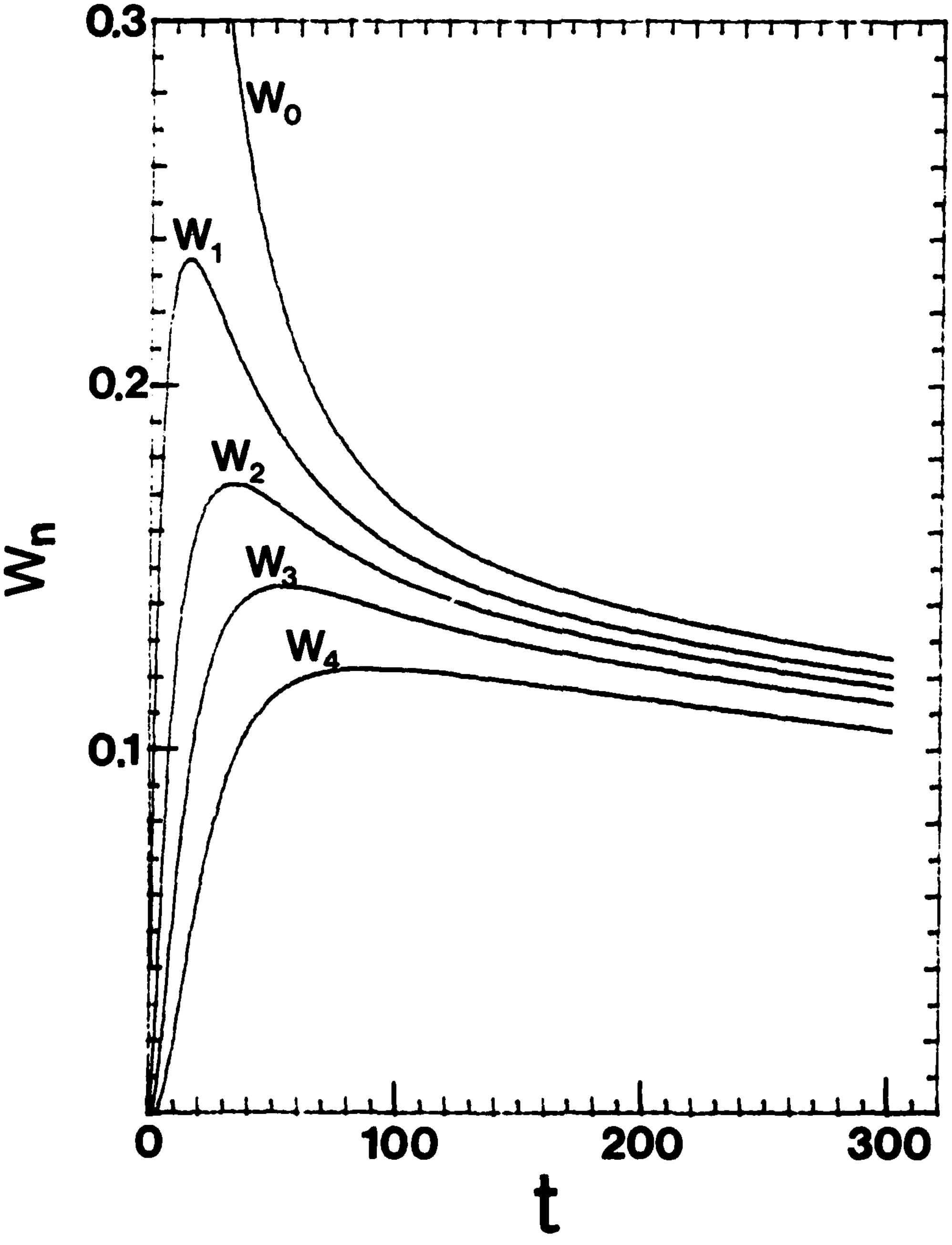


Figure 2



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