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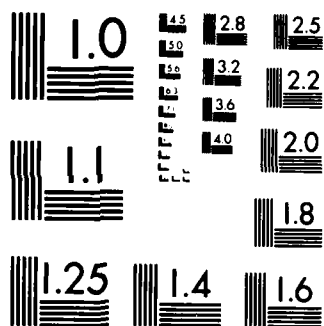
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Quantum Model of Dephasing-Enhanced Laser  
Desorption: Master Equation Approach

by

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QUANTUM MODEL OF DEPHASING-ENHANCED LASER DESORPTION:

MASTER EQUATION APPROACH

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Abstract

A new model for laser-induced desorption is proposed based on a master equation for the photon population in a closely-coupled subsystem involving the relevant degrees of freedom. The validity of approximations such as the Born and Markovian approximations is discussed in terms of the laser pulse duration and multiple time scales of the adspecies-surface system. The desorption rate is numerically calculated from the photon population and the threshold number of photons absorbed by the adspecies. The effects of anharmonicity, dephasing and laser detuning on the desorption rate are examined. The mechanism of dephasing and the possible direct and indirect desorption channels are discussed.

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## I. Introduction

Laser-stimulated surface processes (LSSP) have been investigated during the past several years, due both to their academic interest and industrial potential. Recent progress in experimental<sup>1</sup> and theoretical<sup>2,3</sup> studies and in applications<sup>4</sup> of LSSP has been reported. Laser excitation and/or desorption of adspecies have been investigated theoretically by a variety of techniques, including harmonic,<sup>5</sup> anharmonic<sup>6</sup> and Morse<sup>7,8</sup> potential models and master equation approaches,<sup>7-16</sup> where attention has been focused on the excitation of the active mode and the population of its vibrational states. The desorption rate is usually overestimated by the harmonic model,<sup>5</sup> whereas it is underestimated by the one-dimensional Morse potential model.<sup>7,8</sup>

In the present paper, we propose a new model in which all the degrees of freedom of a closely-coupled subsystem (including the active mode of the adspecies) are treated on an equal footing. The desorption rate is calculated from the photon population and the threshold number of photons absorbed by the adspecies as a whole, rather than from the average excitation of the active mode. In Section II, the generalized master equation is developed within the Born approximation, and a reduced master (rate) equation including the anharmonicity of the adspecies surface potential is investigated within the Markovian approximation. Numerical results are shown in Section III, where dephasing-enhanced desorption is suggested. In Section IV, the mechanism of dephasing and a variety of desorption channels are discussed.

## II. Master Equation

Let us first define our model system, which is particularly appropriate for admolecules with very fast intramolecular relaxation. In the frequency domain, the total adspecies-surface system is divided into two subsystems,

$S_1$  and  $S_2$ , where  $S_1$  consists of the active mode (A) and the strongly-coupled modes (B) within the adspecies, and  $S_2$  consists of the remaining lower frequency modes serving as a heat bath (see Fig. 1). From the concept of the energy-gap law, we expect intramode relaxation within  $S_1$  to be much faster than intersystem relaxation, i.e.,  $\gamma_{AB}, \gamma_{BB} \gg \gamma_{BC}, \gamma_{AC}$ , where  $\gamma_{ij}^{-1}$  is the relaxation time between the  $i$  and  $j$  modes. When the system is irradiated by a laser field,  $S_1$  will be excited through the active mode and its coupling to the B modes. The excitation rate of  $S_1$ , after a short time of  $\gamma_{AB}^{-1}$ , is proportional to the absorption cross section of the active mode. We can therefore express the interaction between the laser field and  $S_1$  as

$$H_{SF}(t) = V(t)(a^\dagger + a), \quad (1)$$

where  $V(t) = \gamma_{AB} \mu' E(t) \cos(\omega t)$  is proportional to the derivative of the active-mode dipole moment,  $\mu'$ , the coupling factor between A and B,  $\gamma_{AB}$ , and the laser field amplitude,  $E(t)$ , with a frequency  $\omega$  which is near-resonant to that of the active mode.  $a^\dagger$  and  $a$  are the ladder operators for  $S_1$  defined in photon space, i.e.,  $a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle$ , where  $|n\rangle$  is a basis function for  $S_1$  as a whole, rather than for just the active mode which reaches steady state in the time  $\gamma_{AB}^{-1}$ .

The vibrational Hamiltonian of the system is

$$H = H_{S_1} + H_{S_2} + H_S + H_{SF}(t), \quad (2)$$

where  $H_S$  couples  $S_1$  and  $S_2$  (it is generally time-independent). The density matrix for the total system obeys the Liouville equation<sup>16</sup>

$$\frac{d\rho}{dt} = -\frac{1}{\hbar} [H, \rho] \equiv -\frac{1}{\hbar} (L_{S_1} + L_{S_2} + L_S + L_{SF}) \rho. \quad (3)$$

Within the Born approximation,  $L_{S_1} + L_{S_2} + L_S \approx L_{S_1} + L_{S_2}$ , and for Markovian processes where the characteristic time of the heat bath ( $S_2$ ) is much shorter than other time scales of the system, the  $S_2$  variables may be eliminated. We can then work with a reduced density matrix,  $\bar{\rho} \equiv \text{Tr}_B(\rho)$ , which obeys the equation

$$\frac{d\bar{\rho}}{dt} = -\frac{i}{\hbar}(L_{S_1} + L_0 - iL_1 + L_{SF})\bar{\rho}, \quad (4)$$

where the effects of the interaction between  $S_1$  and  $S_2$ ,  $L_S$ , are now reduced to a constant frequency shift,  $L_0$ , and a damping factor,  $L_1$ . We now introduce the Markovian approximation for the relaxation associated with  $L_S$  (assumed to be time independent), but retain memory effects due to the off-diagonal matrix elements associated with the laser excitation. For a Hamiltonian such as given by Eq.(1), we obtain a generalized master equation for the diagonal matrix element,  $P_n \equiv [\text{Tr}_B \rho]_{nn}$ , as<sup>9</sup> (detailed discussions of the generalized master equation are available in the literature<sup>16-18</sup>)

$$\begin{aligned} \frac{dP_n}{dt} = & \gamma_1 [(n+1)P_n - nP_n] \\ & + \int_0^t dt' \{ W_{n,n-1}(t-t') [P_{n-1}(t') - P_n(t')] + W_{n,n+1}(t-t') [P_{n+1}(t') - P_n(t')] \}, \end{aligned} \quad (5)$$

with the time-dependent photon absorption/emission rates given by

$$W_{n,n+1}(\tau) = 2(n+1) \Omega(t) \Omega(t') e^{-i\Gamma\tau} \cos(\Delta_{n+1}\tau) \quad (6)$$

$$W_{n,n-1}(\tau) = 2n \Omega(t) \Omega(t') e^{-i\Gamma\tau} \cos(\Delta_n\tau), \quad (7)$$

Here,  $\Omega(t) = V(t)/\cos(\omega t)$ ;  $\tau = t-t'$ ;  $\Delta_m = \omega_{mn} - \omega = \Delta - 2\epsilon m$ , where  $\omega_{mn}$  is the transition frequency between levels  $m$  and  $n$ ,  $\Delta = \omega_{10} - \omega$  is the laser detuning with respect to the fundamental frequency  $\omega_{10}$ , and  $\epsilon$  is the anharmonicity;



and  $\Gamma = \gamma_1/2 + \gamma_2$  is the total damping associated with the off-diagonal matrix elements, where  $\gamma_1$  and  $\gamma_2$  denote the energy and (pure) dephasing factors, respectively. We have used the rotating-wave approximation and the dipole transition for the  $n$  dependence of  $W_{m,n}$  (such that  $m = n \pm 1$ ) for absorption ( $m < n$ ) and emission ( $m > n$ ). Note that  $P_n$  is the probability of the adspecies as a whole ( $S_1$  subsystem) absorbing  $n$  photons, in which the active-mode state is given by its steady-state excitation, i.e.,  $n_A(\text{s.s.}) = \gamma_{AB} \sigma I / \hbar \omega$ , where  $\sigma$  is the steady-state absorption cross section.

For a very short laser pulse with duration  $t_p \leq \Gamma^{-1}$ , the transient solution of Eq.(5) contains the memory effects of the population function, and the Markovian approximation may not be applied to this time-dependent excitation. We shall, instead, focus on the case of a long pulse excitation, e.g., a  $\text{CO}_2$  laser pulse with  $t_p \approx 10$  ns which is much longer than the dephasing time  $\Gamma^{-1}$ , such that the population function  $P_n(t)$  and  $\Omega(t)$  are slowly varying and may be factored out of the integrals in Eq.(5). Employing this adiabatic, Markovian approximation, the transition rates  $W_{m,n}$  have no memory effects, although they are still time dependent due to the laser temporal profile  $E(t)$ , and a simpler master equation is then obtained:<sup>9,16</sup>

$$\frac{dP_n}{dt} = \gamma_1 [(n+1)P_{n+1} - nP_n] + 2\Gamma\Omega^2(t) \left\{ \frac{n(P_{n-1} - P_n)}{[\Delta - 2\epsilon(n-1)]^2 + \Gamma^2} + \frac{(n+1)(P_{n+1} - P_n)}{(\Delta - 2\epsilon n)^2 + \Gamma^2} \right\}. \quad (8)$$

Several features of this equation are: (i) the absorption cross section for the adspecies ( $S_1$  subsystem) is saturated at a higher photon population due to the anharmonicity; (ii) the first two terms describe the actual energy flow from  $S_1$  to the surface ( $S_2$ ); (iii) the pure dephasing factor ( $\gamma_2$ ) changes only the intramolecular phase without changing the energy populations; (iv) the multi-phonon relaxation factor ( $\gamma_1$ ) is generally strongly temperature dependent and

is a strongly decreasing function of the energy gap between  $S_1$  and  $S_2$ ;  
 (v) the remaining terms containing the factor  $r$  indicate that the effect of the applied field is always intimately related to the phase dissipation or broadening mechanisms.

Equation (8) may be referred to as the usual rate equation in which no memory effects are preserved either in the relaxation or the excitation process. For weaker dephasing systems subject to a short pulse excitation, the "most general" form of the generalized master equation is given by Eq.(5) in which the relaxation terms are replaced by<sup>18</sup>

$$\frac{2}{\hbar^2} \text{Re} \sum_m \int_0^t dt' \langle H'_S(t) H'_S(t') \rangle [P_m(t') - P_n(t')] e^{-(i\omega_{mn} + \Gamma_{mn})(t-t')}, \quad (9)$$

where  $\Gamma_{mn} = (\gamma_m + \gamma_n)/2 + \gamma_2$  is the total surface-induced damping. Furthermore, for a short-pulsed laser with high intensity, the Born approximation may not be valid. Improvements can be made by performing a trace over the photon(laser)-dressed states of the heat bath ( $S_2$ ). For the case of strong coupling between  $S_1$  and  $S_2$ ,  $H'_S$  may not be used as a perturbation, and again the Born approximation is questionable. To go beyond this, we may carry out a unitary transformation on  $S_1$  with subsequent laser interaction with the phonon(surface)-dressed states.<sup>2</sup> These improvements allow for both multiphonon (relaxation) and multiphoton (excitation) processes. The absorption cross section for the  $S_1$  subsystem, for example, will be related to the laser intensity by a power law  $\sigma \propto I^n$  for n-photon processes. We also note that a nonlinear power law,  $\sigma \propto I^m$  with  $m < 1$ , is also possible by anharmonic saturation.<sup>3</sup>

### III. Desorption Rate

For a first-order desorption process, the rate constant is related to the inverse of the mean first-passage time,  $\bar{t}$ , and is given by<sup>19</sup>

$$K_D = \frac{1}{\bar{t}} = \left( \sum_{n=0}^{n^*} \int_0^{\infty} dt P_n(t) \right)^{-1}, \quad (10)$$

where  $n^*$  is the desorption threshold number of photons absorbed by the adspecies. Numerical results are shown in Figs. 2 and 3. From Fig. 2 we see that the desorption rate is a strongly-decreasing function of the anharmonicity. Dephasing-enhanced desorption is seen in Fig. 3, where an optimal value at  $\gamma_2 = 1.8$  is found for a maximal desorption rate. This is realized by the fact that the dephasing tends to compensate for anharmonicity "bottleneck" effects. An enhancement factor of about 3 is possible if we tune the dephasing to the optimal value of  $\gamma_2 = 1.8$ , in comparison with  $\gamma_2 = 4$ . We note that the dephasing-enhanced effects caused by the nonlinear behavior are absent in a harmonic model, where  $K_D$  is always a decreasing function of  $\gamma_2$ .

In Fig. 4 we show the time evolution of the desorption probability, defined by

$$P_D(t) = \sum_{n=n^*}^{\infty} P_n(t). \quad (11)$$

Again, we see the nonlinear behavior of the dephasing effects. For a fixed time, say  $t = 100$  units,  $P_D$  increases when  $\gamma_2$  increases from 1 to 5, but it decreases at higher values of  $\gamma_2$ .

#### IV. Discussion

##### A. Mechanism of Dephasing

As indicated in the previous section, the dephasing factor changes only the phase of the excited subsystem  $S_1$  without changing its energy populations. In the language of gas-phase scattering theory, this can be referred to as an "elastic" scattering process. In the presence of a laser field, dephasing can be viewed as energy transfer from the excited subsystem to a

"virtual" state of the field and back to the original excited state. Within the adspecies/surface system itself, the dephasing is due to one or more of the following:<sup>6,20,21</sup> (i) dephasing of the active dipole of the adspecies (or dephasing of the laser field itself); (ii) fluctuation of the conformation of the adspecies due to the thermal energy provided by either the initial surface temperature or laser-heating effects; (iii) librational and rotational relaxation within the vibrational manifold of the excited  $S_1$  subsystem; (iv) intramolecular mode-mode coupling within  $S_1$  and intermolecular coupling between  $S_1$  and  $S_2$ ; (v) lateral motion or migration-induced elastic collisions between adspecies and with the substrate surface; (vi) surface phonon-dispersion-induced level broadening of the vibrational manifold.

We note that the dephasing factor  $\gamma_2$ , introduced in Section II, is formally derived from the Liouville equation within the Markovian approximation, where the laser field amplitude is assumed to be generated by a coherent source. However, the field itself may often be only partially coherent and hence will cause additional dephasing of the excited subsystem. To demonstrate this mathematically, we start with the reduced density matrix equation of motion for  $P_{mn} \equiv [\text{Tr}_B \rho]_{mn}$ ,  $m \neq n$ ,

$$\frac{dP_{mn}}{dt} = -i[\omega_{mn} + \bar{\omega}(t)]P_{mn}, \quad (12)$$

where we have introduced a stochastic frequency shift of the system,  $\bar{\omega}(t)$ , caused by the partially coherent behavior of the laser field. By assuming a "white noise,"  $\langle \bar{\omega}(t) \rangle = 0$ , and a Markovian correlation,  $\langle \bar{\omega}(t)\bar{\omega}(t') \rangle = \bar{\gamma}_2 \delta(t-t')$ , we obtain an ensemble-averaged (over the stochastic variable) equation

$$\left\langle \frac{dP_{mn}}{dt} \right\rangle = -[i\omega_{mn} + (\Gamma_{mn} + \bar{\gamma}_2)]\langle P_{mn} \rangle, \quad (13)$$

where  $\bar{\gamma}_2$  is the laser-induced dephasing.<sup>21</sup>

## B. Mechanism of Desorption

The desorption mechanism, which may involve several channels, depending on the nature of the adspecies (e.g., physisorbed or chemisorbed, adatom or admolecule, and the potential of the adbond), and the associated energy levels of the system are shown in Fig. 5. The desorption may result from direct laser excitation or indirect energy transfer processes. The details of the desorption channels from Type I to Type VI have been discussed previously<sup>3,4</sup>. As a concluding remark, we note that a complete description of laser-induced desorption should at least include the competing processes, e.g., migration-induced desorption and re-adsorption after the mean first-passage time. Furthermore, for systems with more than one active mode, desorption may occur via a two-stage process: the initial stage of absorbing  $n^*$  photons followed by thermal phonon-assisted and/or V-V energy transfer among the excited active modes. This type of process is under investigation in our laboratories.

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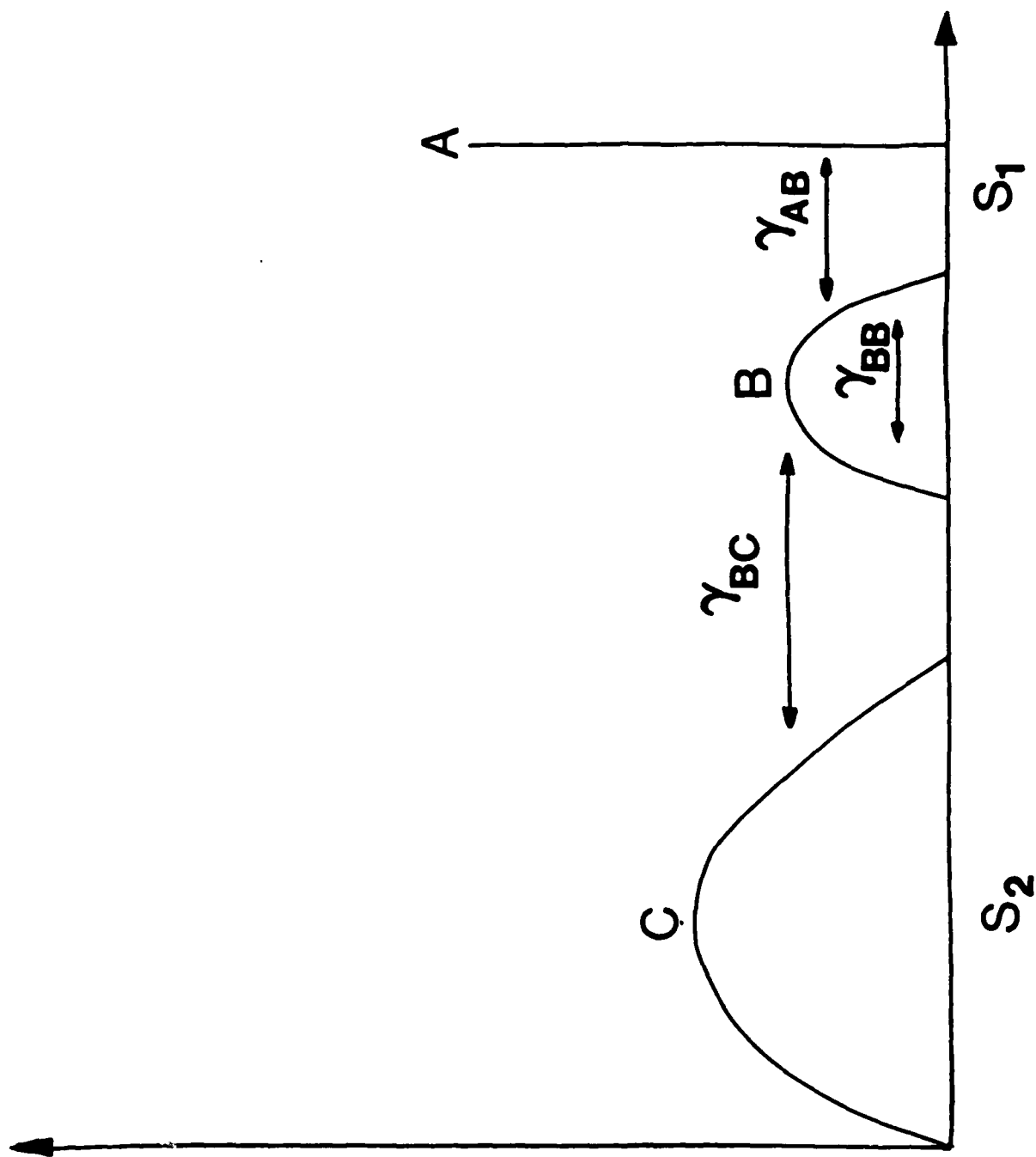
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### Figure Captions

1. Schematic diagram for the frequency spectrum of the total system  $S_1 + S_2$ , where  $S_1 = A + B$ , with the corresponding relaxation factors indicated.
2. Anharmonicity ( $\epsilon$ ) dependence of the desorption rate  $K_D$  in arbitrary units.  
The parameters used are  $(\gamma_1, \gamma_2, \Omega_0, \Delta) = (0.1, 2.0, 0.1, 0.0)$ , with a laser pulse duration of  $t_p = 10$  ns, where  $\Omega(t) = \Omega_0 \sin^2(\pi t/t_p)$ .  $\gamma_1$ ,  $\gamma_2$ ,  $\Omega_0$  and  $\Delta$  are in the unit of  $10^{11} \text{ s}^{-1}$ , and  $n^*=3$  has been used in Eq.(10).
3. Phase-relaxation ( $\gamma_2$ ) dependence of  $K_D$ . The parameters used are  $(\gamma_1, \Omega_0, \epsilon, \Delta, t_p) = (0.5, 0.1, 1, 3, 10)$ . The envelope function of the laser pulse is the same as in Fig. 2.
4. Time dependence of the desorption probability  $P_D(t)$ , where  $n^*=3$  has been used in this calculation. A cw laser field has been assumed, and the other parameters are  $(\gamma_1, \Omega_0, \epsilon, \Delta) = (0.01, 0.1, 1.5, 3.0)$ .
5. Schematic diagrams of adspecies-surface systems and the associated energy levels, where A, B and M represent the adspecies (adatom or admolecule), C represents the substrate (or bath modes), and the laser radiation is indicated by the wiggly lines. Several types of desorption channels are illustrated: (I) direct desorption via active-mode excitation, (II) direct desorption via the quasi-continuum, (III) indirect desorption via tunneling, (IV) indirect desorption via substrate heating, (V) phonon-assisted desorption and (VI) indirect desorption via dynamics.

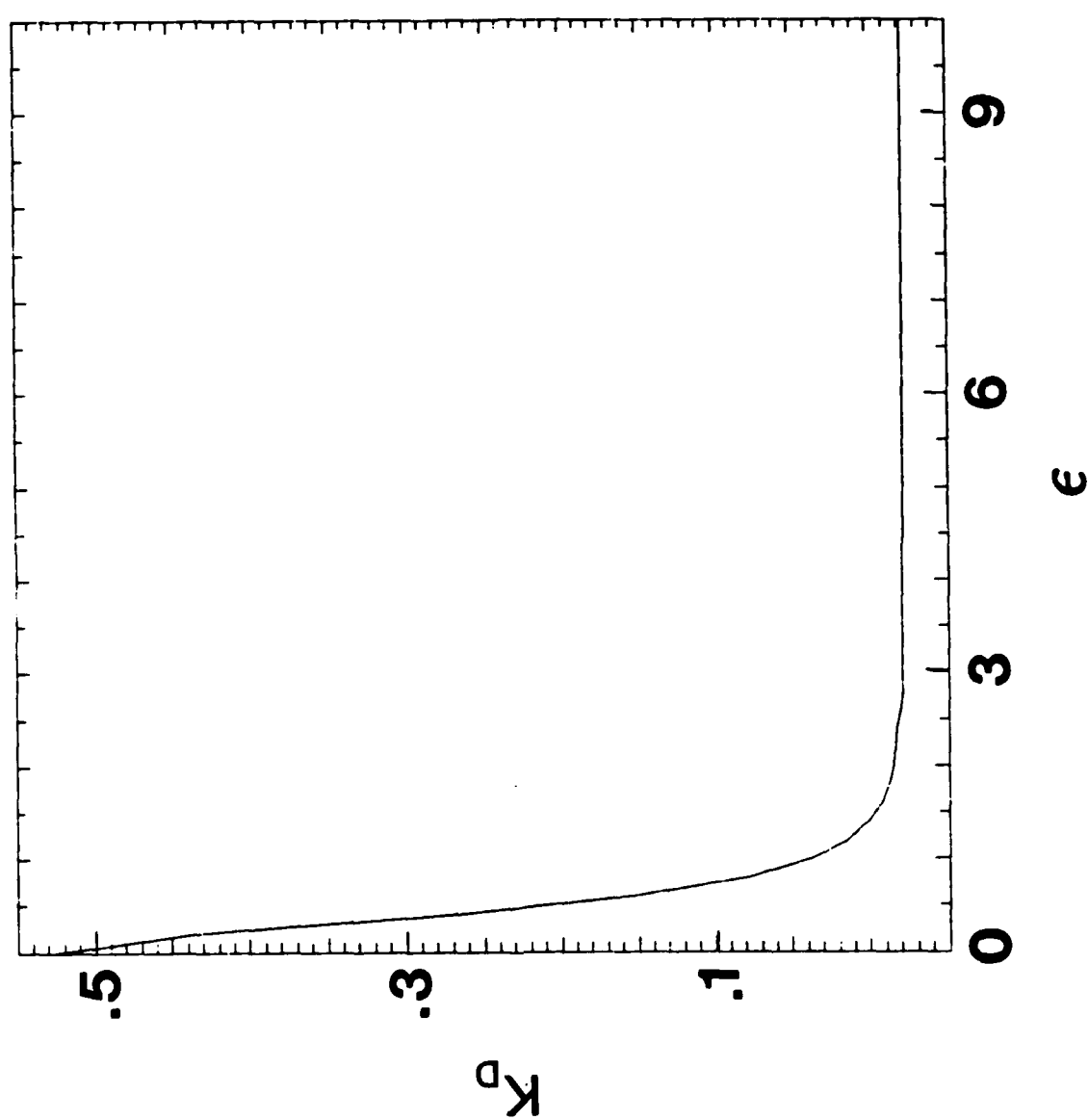
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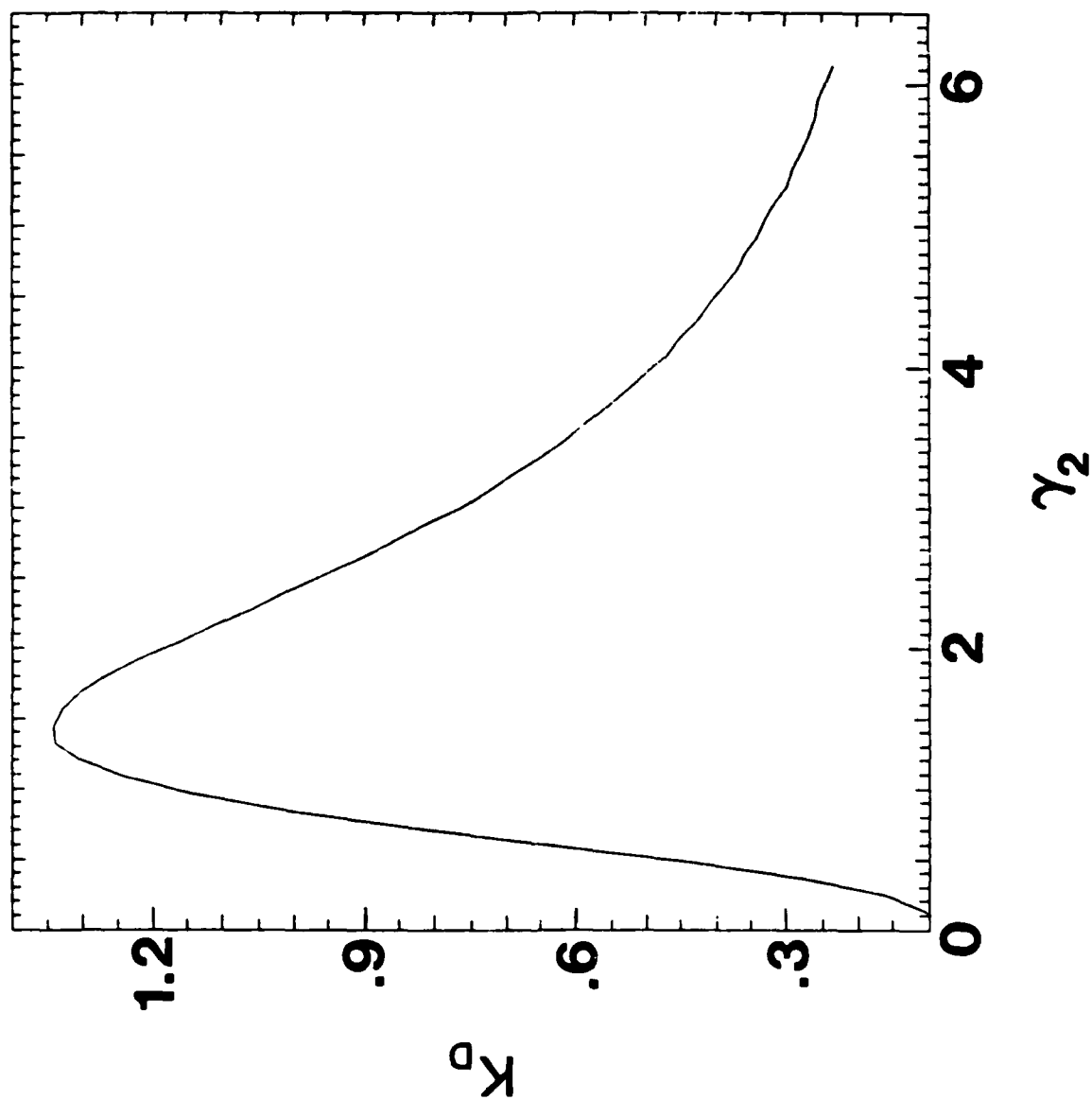
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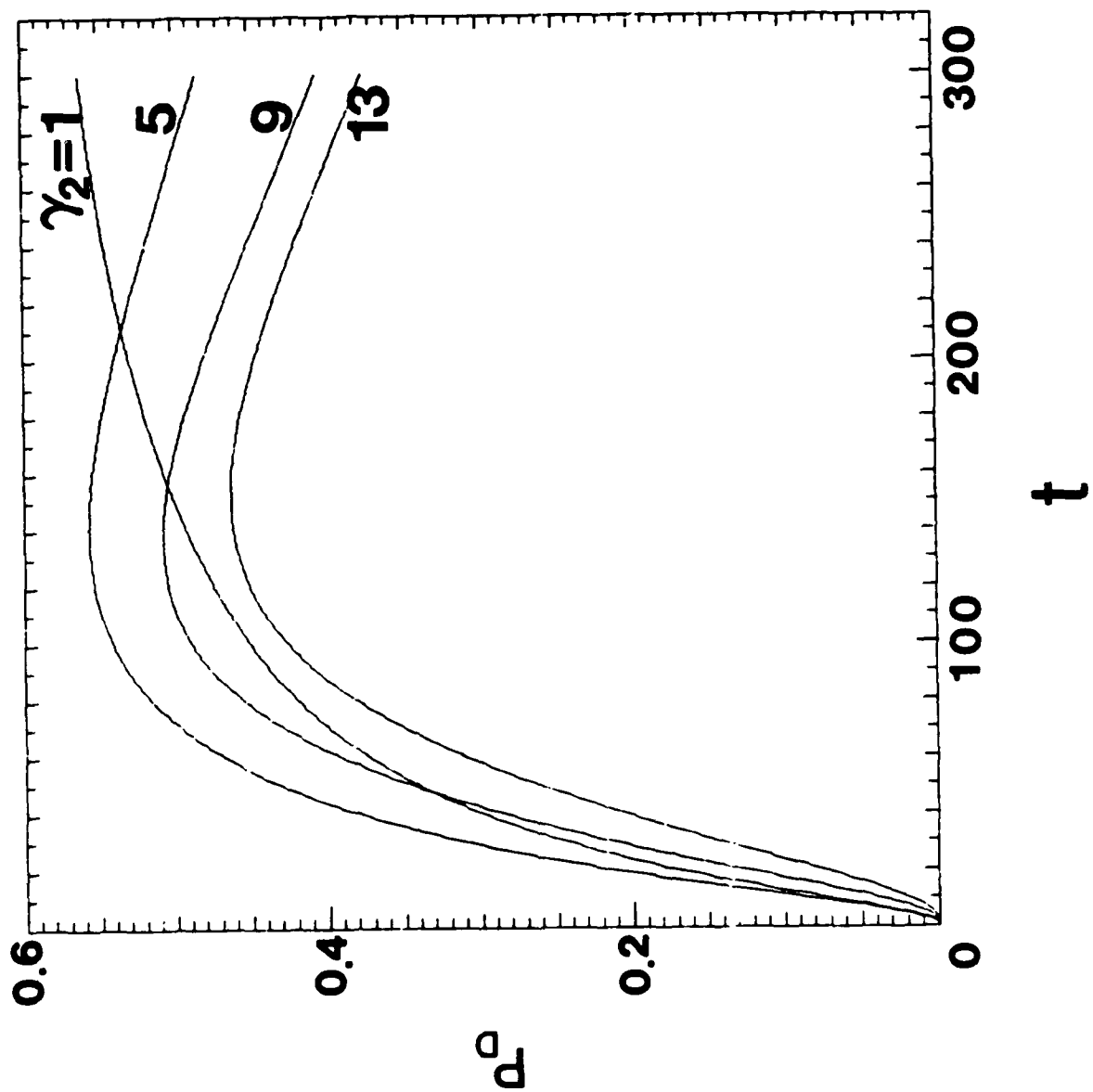
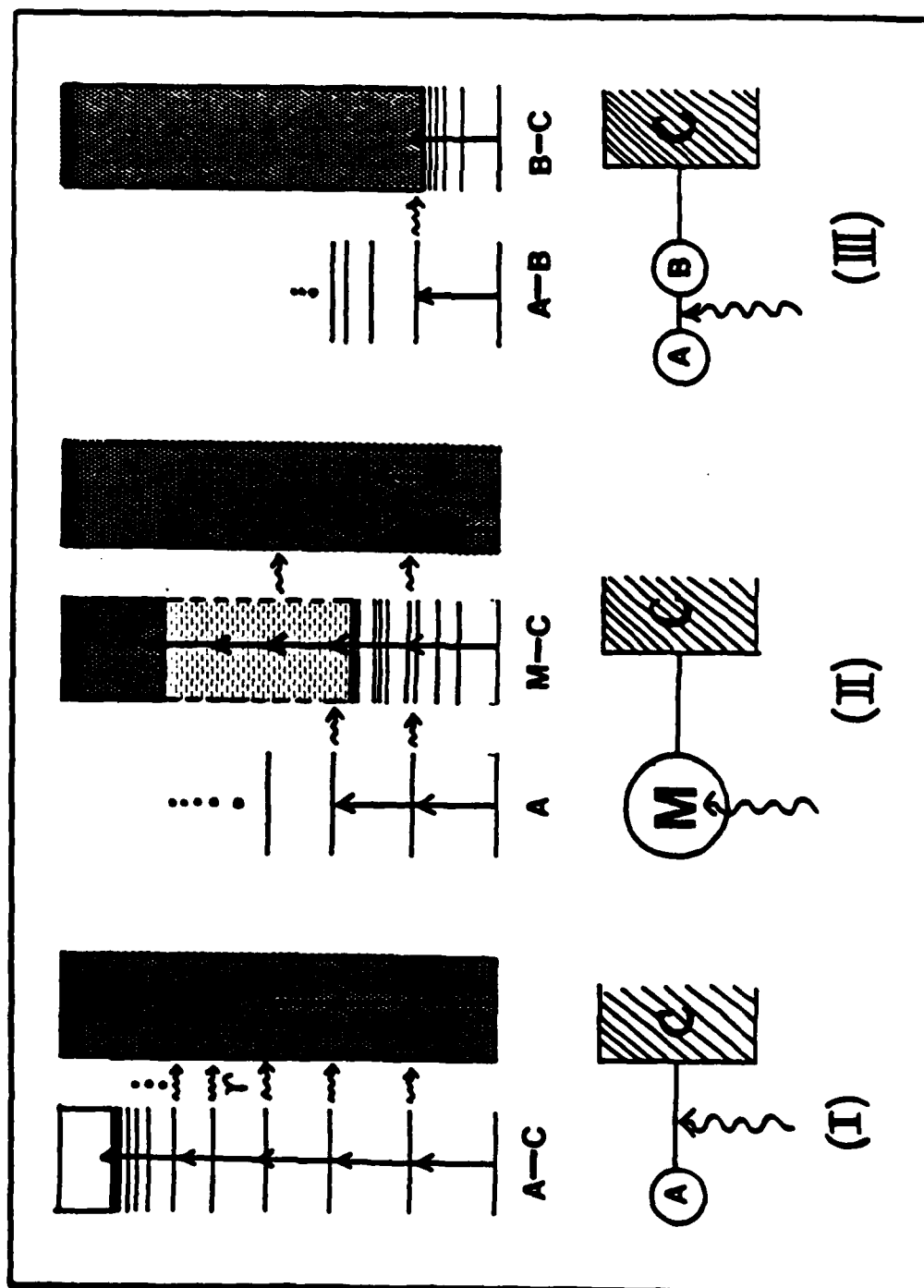
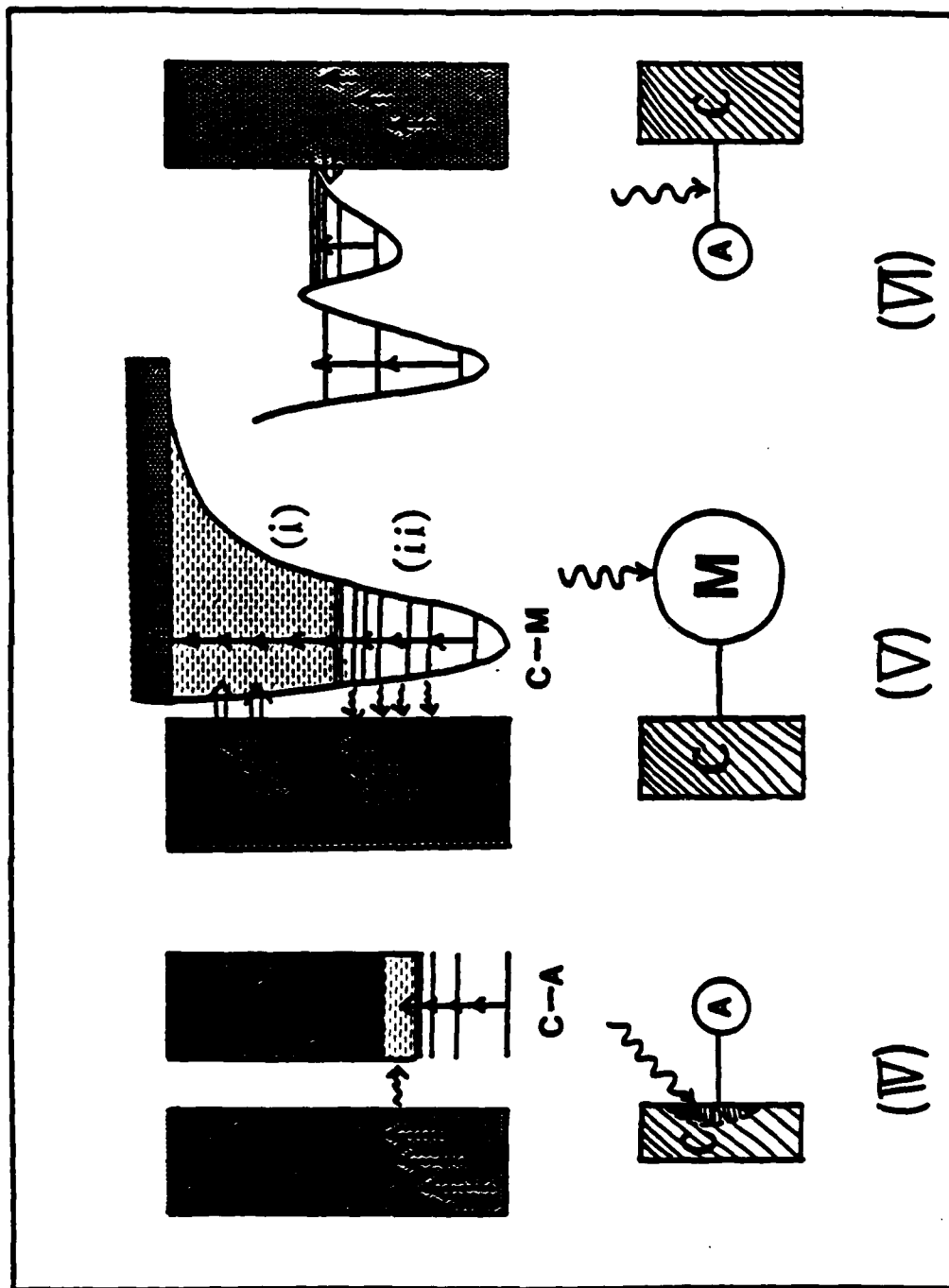


Fig. 1  
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Fig. 5 (I) - (III)



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Fig. 5 (IV)-(VI)

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