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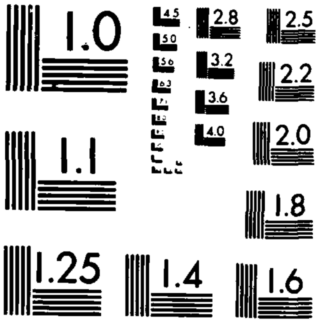
MODE OF A DIATOMIC..(U) STATE UNIV OF NEW YORK AT
BUFFALO DEPT OF CHEMISTRY A PEREMANS ET AL. NOV 86
UNCLASSIFIED UBUFFALO/DC/86/TR-17 N00014-86-K-0043 F/G 7/4 NL



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Contract N00014-86-K-0043

R & T Code 413f001---01

TECHNICAL REPORT No. 17

Infrared-Laser Excitation of the Internal Vibrational Mode of a Diatomic Molecule Adsorbed on a Metal Surface

by

André Peremans, Jacques Darville, Jean-Marie Gilles and Thomas F. George

Prepared for Publication

in

Physical Review B

Departments of Chemistry and Physics
State University of New York at Buffalo
Buffalo, New York 14260

November 1986

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S) UBUFFALO/DC/86/TR-17

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Depts. Chemistry & Physics
State University of New York

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION

6c. ADDRESS *(City, State and ZIP Code)*
Fronczak Hall, Amherst Campus
Buffalo, New York 14260

7b. ADDRESS *(City, State and ZIP Code)*
Chemistry Program
800 N. Quincy Street
Arlington, Virginia 22217

8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract N00014-86-K-0043

8c. ADDRESS *(City, State and ZIP Code)*
Chemistry Program
800 N. Quincy Street
Arlington, Virginia 22217

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.

11. TITLE Infrared-Laser Excitation of the Internal Vibrational Mode of a Diatomic Molecule Adsorbed on a Metal Surface

12. PERSONAL AUTHOR(S) André Peremans, Jacques Darville, Jean-Marie Gilles and Thomas F. George

13a. TYPE OF REPORT

13b. TIME COVERED FROM ________ TO ________

14. DATE OF REPORT *(Yr., Mo., Day)* November 1986

15. PAGE COUNT 34

16. SUPPLEMENTARY NOTATION Prepared publication in Physical Review B

17. COSATI CODES

FIELD	GROUP	SUB. GR.

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
DIATOMIC ADSPECIES
METAL SURFACE
INFRARED LASER EXCITATION
ELECTRON-HOLE EXCITATIONS
CO/Cu SYSTEM
LASER-ENHANCED SURFACE REACTIONS

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

The infrared-laser excitation of the internal vibrational mode of a diatomic molecule adsorbed on a metal surface is analyzed theoretically. This vibrational energy is damped into the metal by electron-hole excitations. Simple expressions for the populations of the vibrational levels, the mean number of vibrational quanta and the rate of energy transfer between the infrared laser and the metal surface at the steady state are derived. An equation of evolution can readily be solved numerically to determine the time necessary to reach this steady state. The criteria of applicability of the Markov approximation (which leads to the golden rule) is clearly established, where it is seen that this approximation may not be used to compute the evolution of the populations of the vibrational levels. The random-phase approximation is shown to give the correct kinetic equation for the populations of the vibrational levels. The excitation of carbon monoxide adsorbed on a copper surface is analyzed quantitatively.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☒ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson

22b. TELEPHONE NUMBER *(Include Area Code)* (202) 696-4410

22c. OFFICE SYMBOL

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE.

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

Physical Review B, in press

INFRARED-LASER EXCITATION OF THE INTERNAL VIBRATIONAL MODE OF A DIATOMIC MOLECULE ADSORBED ON A METAL SURFACE

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Abstract

The infrared-laser excitation of the internal vibrational mode of a diatomic molecule adsorbed on a metal surface is analyzed theoretically. This vibrational energy is damped into the metal by electron-hole excitations. Simple expressions for the populations of the vibrational levels, the mean number of vibrational quanta and the rate of energy transfer between the infrared laser and the metal surface at the steady state are derived. An equation of evolution can readily be solved numerically to determine the time necessary to reach this steady state. The criteria of applicability of the Markov approximation (which leads to the golden rule) is clearly established, where it is seen that this approximation may not be used to compute the evolution of the populations of the vibrational levels. The random-phase approximation is shown to give the correct kinetic equation for the populations of the vibrational levels. The excitation of carbon monoxide adsorbed on a copper surface is analyzed quantitatively.

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I. Introduction

The excitation of a molecular vibration can significantly contribute to overcoming the activation barrier of a chemical reaction. This fact has led to many attempts to modify the course of surface processes by resonant excitation of vibrational modes by means of infrared laser radiation [1]. Due to their importance in catalysis, laser-stimulated reactions at metal surfaces have been investigated [2-6]. For example, it has been shown that focused infrared laser radiation can induce resonant ionization of adspecies [2] or gaseous species above a surface [3], where the fragments from the latter process can then undergo surface reactions which are not possible with the original molecules. Even when the laser is not focused, the resonant excitation of a gaseous species can decrease the likelihood of physisorption [4] or increase the tendency for dissociative chemisorption [5]. When laser radiation impinges on a gas-solid interface, it can excite the substrate, adsorbate and/or species in the gas phase. Chuang [7] has demonstrated that resonant excitation of the adsorbate can stimulate etching of a silicon surface by SF_6. While this mechanism of adsorbate resonant excitation has been proposed for experiments involving metal surfaces [6], it is perhaps not as obvious here since the vibrational energy of a metal adsorbate quickly damps into the metal, as observed by infrared reflection absorption spectroscopy [8,9]. This leads to two questions: (1) Can an infrared laser beam maintain a high surface concentration of vibrationally-excited molecules, and (2) what is the rate of energy transfer from the laser to the metal through the adsorbed molecules? Such energy transfer leads to resonant heating of the substrate, which can then "thermally" enhance a surface reaction or the desorption of the adsorbate before reaction occurs. These questions have motivated us to carry out a theoretical study of the simple case of the resonant interaction of infrared laser radiation with a diatomic molecule adsorbed on a metal surface.

The spectral infrared absorption width of a diatomic molecule in the gas phase is of the order of 10^{-2} cm^{-1}. When the molecule is adsorbed on a metal, this width may reach many cm^{-1} [8]. This broadening was successfully explained by Persson in terms of electron transfer between the adsorbate and the substrate [10], and this mechanism has been confirmed by means of cluster calculations [11]. The lifetime of an excited vibrational state was estimated to be of the order of 10^{-12} s. This is much shorter than the lifetime due to other mechanisms such as phonon-phonon energy transfer ($\sim 10^{-9}$ s) [12-17] or dipole-hole-electron interactions ($\sim 10^{-10}$ s) [18]. We shall thus assume electron transfer to be the only mechanism responsible for energy tranfer between the substrate and the adsorbate.

Theoretical studies already presented in the literature related to the interaction of an infrared laser beam with adsorbed molecules are focused on the phonon-phonon energy transfer between the substrate and the adsorbate. The computational techniques used are the "golden rule" [13,14] and the transformation to dressed states [15-17]. The Zwanzig projector technique [19] within the Born, the random-phase and the Markov approximations has been used to compute molecular desorption rates [12]. We shall use the Zwanzig projector technique within the Born approximation only, and shall obtain simple expressions describing the kinetic and the steady state of our system. Furthermore, our results will provide criteria for the applicability of all the approximations listed above.

In Section II we present our model and write down the Hamiltonian. In Section III we derive the kinetic equation for the density operator characterizing the vibrational state of the adsorbed molecule. In Section

IV we analyze the memory kernels, where the validity of the Markov approximation is questioned. In Section V we derive the properties of the steady state and the equation of evolution of the populations of the vibrational levels, where we look at the effect of anharmonicity by restricting our equations to a two-level system. In Section VI we present some numerical results, and we end with the conclusions in Secion VII.

II. Model

The internal vibrational mode of the adsorbed diatomic molecule is assumed to be harmonic, with the molecule adsorbed perpendicular to the surface. The infrared laser beam is collimated and polarized in such a way that the electric field is parallel to the axis of symmetry of the molecule. This simplification is valid because an infrared beam can only create an electric field perpendicular to the surface in its vicinity [20]. The laser is tuned in resonance with the internal molecular vibration. The adsorbate-substrate electronic system is taken to be in the ground state, so that the vibration of the adsorbed molecule creates electron-hole pairs. This causes a strong damping of the vibrational energy into the metal. This approximation is valid if $\hbar\omega >> kT$, where T is the temperature of the metal, k is the Boltzmann constant, and ω is the frequency of vibration of the molecule.

The Hamiltonian can be written in the second-quantization form as

$$H = \sum_S \varepsilon_S E_S^\dagger E_S + \sum_S [V_{aS} E_S^\dagger a + \text{h.c.}] + \varepsilon_a a^\dagger a + V_a(\xi) a^\dagger a + \sum_b \varepsilon_b b^\dagger b$$

$$+ \sum_b V_b(\xi) b^\dagger b + H^{rv} + H^r + KE \quad . \qquad (1)$$

Here $E_S^\dagger$ is the creation operator of one electron in the state $|S\rangle$ of the unperturbed metal; $a^\dagger$ and $b^\dagger$ are creation operators of electrons in the orbitals $|a\rangle$ and $|b\rangle$, respectively, of the free diatomic molecule; ξ is the coordinate associated with the stretching of the molecule; and KE is the kinetic energy associated with ξ. $|a\rangle$ is assumed to be the only molecular orbital interacting with the electronic orbitals $|S\rangle$ of the metal, and this interaction gives the factor V_{aS}. $\varepsilon_a + V_a(\xi)$, $\varepsilon_b + V_b(\xi)$ and ε_S are the Hartree-Fock energies of the electrons in the orbitals $|a\rangle$, $|b\rangle$ and $|S\rangle$, respectively. H^r is the Hamiltonian of the radiation, given by

$$H^r = \sum_k \hbar\omega_k \left(p_k^\dagger p_k + \frac{1}{2}\right) \quad . \tag{2}$$

Here k is the norm of the wave vector, $\vec{k}$, of the photons, where $\vec{k}$ is parallel to the direction of propagation of the beam, $\vec{k} = k\hat{k}_0$, and $p_k^\dagger$ is the creation operator of one photon of wave vector $k\hat{k}_0$. The light is contained within a cubic quantization volume U. H^{rv} is the interaction Hamiltonian between the molecule and the infrared beam. Since we are only concerned with the coupling between the molecular stretching and the electronic system, we have neglected the dependence of this Hamiltonian on the positions of the metal nuclei and molecule with respect to the surface. We have also assumed a weak dependence of V_{aS} on versus ξ. This is a generalization of the Hamiltonian written by Persson [10].

We can decompose H as

$$H = H^e + H^v + H^r + H^{ev} + H^{rv} \quad , \tag{3}$$

where H^e is the electronic Hamiltonian,

$$H^e = \sum_S \varepsilon_S E_S^\dagger E_S + \sum_S [V_{aS} E_S^\dagger a + \text{h.c.}] + \varepsilon_a\, a^\dagger a + \sum_b \varepsilon_b\, b^\dagger b \quad , \tag{4}$$

and can be formally diagonalized to give

$$H^{e} = \sum_{\beta} \varepsilon_{\beta}\, C^{\dagger}_{\beta} C_{\beta} + \sum_{\beta} \varepsilon_{b}\, b^{\dagger} b \qquad (5)$$

where

$$a = \sum_{\beta} \langle a|\beta\rangle\, C_{\beta} \quad . \qquad (6)$$

The vibrational Hamiltonian is given by

$$H^{v} = \langle g|V_{a}(\xi)a^{\dagger}a + \sum_{b} V_{b}(\xi)b^{\dagger}b\; |g\rangle + KE \quad , \qquad (7)$$

where $|g\rangle$ is the ground state of the electronic system. H^{v} is assumed to be the Hamiltonian of an harmonic oscillator,

$$H^{v} = \frac{\mu\omega^{2}\xi^{2}}{2} + \frac{\mu\dot{\xi}^{2}}{2} = \hbar\omega[V^{\dagger}V + \frac{1}{2}] \quad , \qquad (8)$$

where μ is the reduced mass of the molecule and $V^{\dagger}$ is the creation operator for a vibrational quantum. H^{rv} is then given by

$$H^{rv} = \delta\xi E = \delta((\frac{\hbar}{2\mu\omega})^{1/2}[V^{\dagger} + V])(-i(\frac{\hbar}{2\varepsilon_{0}U})^{1/2} \sum_{k}\omega_{k}[p^{\dagger}_{k} - p_{k}]) \quad , \qquad (9)$$

where δ is the effective charge carried by the stretching coordinate ξ, E is the electric field, and ε_{0} is the dielectric constant of the vacuum. H^{ev} is given by

$$H^{ev} = V_{a}(\xi)\; a^{\dagger}a + \sum_{b} V_{b}(\xi)b^{\dagger}b - \langle g|\; V_{a}(\xi)\; a^{\dagger}a + \sum_{b} V_{b}(\xi)b^{\dagger}b|g\rangle \quad . \qquad (10)$$

We approximate $V_{a}(\xi)$ by

$$V_{a}(\xi) \simeq \frac{\partial\varepsilon_{a}}{\partial\xi}\,\xi = \frac{\partial\varepsilon_{a}}{\partial\xi}\,(\frac{\hbar}{2\mu\omega})^{1/2}(V^{\dagger} + V) \quad . \qquad (11)$$

III. Kinetic Equation

To compute the evolution of the vibrational state of the molecule, we shall use the Zwanzig projector technique [19]. In this approach, Zwanzig derived an exact kinetic equation for the density operator of one subsystem interacting with another one, which will be named bath subsystem. In our situation the first subsystem will be the internal vibrational mode of the adsorbed diatomic molecule. It interacts with the bath subsystem, which is constituted by two independent subsystems: the laser beam and the electronic system. The interaction Hamiltonian between the vibration and the bath is given by

$$H^I = \left(\frac{\hbar}{2\mu\omega}\right)^{1/2} (V^\dagger + V)\, B \quad , \tag{12}$$

where

$$B = B^e \otimes I_r + B^r \otimes I_e \quad . \tag{13}$$

Here I_r and I_e are, respectively, the identity operator of the radiative and electronic subsystem, $\otimes$ symbolizes the outer product, and

$$B^e = \frac{\partial \varepsilon_a}{\partial \xi} \left(a^\dagger a + \langle g|a^\dagger a|g\rangle\right) \tag{14}$$

$$B^r = -i\delta\left(\frac{\hbar}{2\varepsilon_0 U}\right)^{1/2} \sum_k \omega_k [p_k^\dagger - p_k] \quad . \tag{15}$$

We have removed the dependence of H^{ev} on the electronic degrees of freedom corresponding to the occupation of the molecular orbitals $|b\rangle$. This simplification comes from the fact that these orbitals are not coupled with the electronic orbitals $|S\rangle$ of the metal, which can be verified by computing explicitly the memory kernels in Eq. (24) or (28) below, where no specification on the form of H^I is needed.

The starting operator of the complete system $[\rho(t = 0)]$ is taken to be the outer product of the vibrational $[\rho^v(t = 0)]$ and the bath (ρ^b) density operator,

$$\rho(0) = \rho^v(0) \otimes \rho^b. \tag{16}$$

We assume the vibrational subsystem to be in its ground state at time $t = 0$,

$$\rho^v(0) = |0\rangle\langle 0| \quad . \tag{17}$$

The density operator of the bath subsystem is itself the outer product of the radiative (ρ^r) and electronic (ρ^e) subsystem:

$$\rho^b = \rho^e \otimes \rho^r \quad . \tag{18}$$

The electronic subsystem is taken to remain in its ground state,

$$\rho^e = |g\rangle\langle g| \quad . \tag{19}$$

The density operator of the radiative subsystem corresponds to a statistical superposition of coherent states with different phase [21]. ρ^r is then diagonal in the radiative Hamiltonian eigenstate representation,

$$\rho^r = \sum_{kn} p_{kn} \; |kn\rangle\langle nk| \quad . \tag{20}$$

We note that $\rho^v(0)$, ρ^b, H^v and H^b $(= H^e \quad H^r)$ commute with each other. Furthermore,

$$\mathrm{Tr}_{er}\{H^I \cdot \rho^b\} = \overset{\Rightarrow}{0} \quad , \tag{21}$$

where $\mathrm{Tr}_{er}\{\ \}$ is the trace over all the electronic and radiative states.

To obtain a tractable kinetic equation, we shall invoke the Born approximation [12]. This approximation is valid if the interaction Hamiltonian between the vibrational and bath systems is small in comparison with the Hamiltonians driving their evolutions independently ($H^v >> H^I << H^b$). It then follows from that the kinetic equation can be written as [12]

$$i\hbar\dot{\rho}^v(t) = [H^v, \rho^v(t)] - \frac{i}{\hbar}\int_0^t ds \tag{22}$$

$$\times\ \mathrm{Tr}_{er}\{[H^I, \exp(-iH^v s/\hbar)[H^I(-s), \rho^v(t-s)\otimes\rho^b]\exp(iH^v s/\hbar)]\} \quad ,$$

where the density operator of the vibrational system is defined by $\rho_v(t) = \mathrm{Tr}_{er}\{\rho(t)\}$, and

$$H^I(-s) = \exp(-iH^b s/\hbar)\ H^I\ \exp(iH^b s/\hbar). \tag{23}$$

Equation (23) can be written in terms of the matrix element $\rho^v_{mn}(t)$ ($= \langle m|\rho^v(t)|n\rangle$) simply by multiplying it respectively on the left and by the right with $\langle m|$ and $|n\rangle$. The derivation in the case where $m = n$ is given in Ref. 12. The generalization to the case $m \neq n$ is straightforward. We observe that the integrand in (22) contains a double commutator, corresponding to four terms. To simplify the notation, we shall track explicitly just one of these terms, keeping in mind that the others must be treated in the same way. We then arrive at

$$\dot{\rho}^v_{nm}(t) = -i\omega_{nm}\ \rho^v_{nm}(t) - \frac{1}{\hbar^2}\int_0^t ds\ \{3 \text{ terms} - \sum_{op} \exp(i\omega_{pn}s)$$

$$\times\ \langle H^I_{pm}\ H^I_{no}(-s)\rangle\ \rho^v_{op}(t-s)\} \quad , \tag{24}$$

where

$$H^I_{pm} = \langle p|H^I|m\rangle \quad ,$$

$$\langle\, K \,\rangle = \mathrm{Tr}_{er}\{K\cdot\rho^b\},$$

and

$$\omega_{nm} = (E^v_n - E^v_m)/\hbar = (n - m)\omega \quad .$$

To solve these coupled equations, we transform into the interaction picture by defining

$$\rho^v_{nm}(t) = \tilde{\rho}^v_{nm}(t)\,\exp(-i\omega_{nm}t) \quad . \tag{25}$$

After some simple algebra, we end up with

$$\dot{\tilde{\rho}}^v_{nm}(t) = -\frac{1}{\hbar^2}\,\{3 \text{ terms} - \sum_{op}\exp[i(\omega_{po} + \omega_{nm})t]\int_0^t ds\,\exp(i\omega_{on}s)$$

$$\times\, \langle H^I_{pm}\; H^I_{no}(-s)\rangle\tilde{\rho}^v_{op}(t-s)\} \quad . \tag{26}$$

Without any interaction ($H^I = \overset{\Rightarrow}{0}$), the quantities $\tilde{\rho}_{op}(t - s)$ are constant. With $H^I \neq \overset{\Rightarrow}{0}$, they are expected to vary only on a time scale much greater than the oscillation period of the vibration. Thus the only terms in the sum "$\sum_{op}$" which give rise to a variation of $\tilde{\rho}^v_{nm}(t)$ during a period corresponding to several oscillations are the ones verifying

$$\omega_{po} + \omega_{nm} = 0 \quad \text{or} \quad p = m - n + o \quad . \tag{27}$$

Neglecting all the others, we can write the following kinetic equation where we use $\langle H^I_{ij}(-s)\; H^I_{k\ell}\rangle = \langle H^I_{k\ell}\; H^I_{ij}(-s)\rangle^*$, $\tilde{\rho}^v_{ij} = \tilde{\rho}^v_{ji}{}^*$, $H^I_{k\ell} = H^I_{\ell k}$:

$$\dot{\tilde{\rho}}^v_{nm}(t) = -\frac{1}{\hbar^2}\int_0^t ds$$

$$\times \sum_{o} \{\exp(i\omega_{no}s) \langle H^{I}_{no}\, H^{I}_{on}(-s)\rangle\, \tilde{\rho}^{v}_{nm}(t-s)$$

$$+ [\exp(i\omega_{mo}s) \langle H^{I}_{mo}\, H^{I}_{om}(-s)\rangle\, \tilde{\rho}^{v}_{nm}(t-s)]^{*}\}$$

$$- \sum_{o} \{\exp(i\omega_{on}s) \langle H^{I}_{(m-n)+o,m}\, H^{I}_{no}(-s)\rangle\, \tilde{\rho}^{v}_{o,(m-n)+o}(t-s)$$

$$+ [\exp(i\omega_{om}s) \langle H^{I}_{(n-m)+o,n}\, H^{I}_{m,o}(-s)\rangle\, \tilde{\rho}_{o,(n-m)+o}(t-s)]^{*}\} \quad . \qquad (28)$$

The above equation gives us the following result: only the elements of the vibrational density matrix which belong to the same diagonal ($\tilde{\rho}_{ij}$ with $|j - i|$ = constant) are coupled in the kinetic equation. More generally, even for an highly anharmonic vibration it is easy to see that the diagonal elements of $\rho^{v}(t)$ evolve independently from the others [put $m = n$ in Eqs. (26), (27) and (28)]. The importance of this result will be emphasized in Section VII. In our situation, further simplifications can be made. Using (12) we find that $\langle H^{I}_{(m-n)+o,m}\, H^{I}_{no}(-s)\rangle$ is different from zero only if $o = n \pm 1$. In the case where $o = n + 1$, it is equal to $\frac{\hbar}{2\mu\omega}\,[(m+1)(n+1)]^{1/2} \times D(-s)$, where $D(-s)$ is defined as

$$D(-s) \equiv \langle B\, B(-s)\rangle \quad . \qquad (29)$$

The kinetic equation can then be written as

$$\dot{\tilde{\rho}}^{v}_{nm}(t) = -\frac{1}{2\hbar\mu\omega}\int_{0}^{t} ds\, \{((n+1)\exp(-i\omega s)\, D(-s)\, \tilde{\rho}^{v}_{nm}(t-s)$$

$$+ n \exp(i\omega s)\, D(-s)\, \tilde{\rho}^{v}_{nm}(t-s))$$

$$+ (m+1)[\exp(-i\omega s)\, D(-s)\, \tilde{\rho}^{v}_{nm}(t-s)]^{*}$$

$$+ m[\exp(i\omega s)\, D(-s)\tilde{\rho}^{v}_{nm}(t-s)]^{*}\}$$

$$- \{([(n+1)(m+1)]^{1/2} \exp(i\omega s)\, D(-s)) + \text{c.c.}\}\, \tilde{\rho}^{v}_{n+1,m+1}(t-s)$$

$$- \{(\sqrt{mn}\, \exp(-i\omega s)\, D(-s)) + \text{c.c.}\}\tilde{\rho}^{v}_{n-1,m-1}(t-s) \quad . \qquad (30)$$

The kinetic equation for the diagonal elements is

$$\dot{P}_n(t) = - \frac{1}{\hbar\mu\omega} \,\mathrm{Re}\int_0^t ds\, \{(n+1)\exp(-i\omega s) + n\exp(i\omega s)\}\, D(-s)\, P_n(t-s)$$

$$- (n+1)\exp(i\omega s)\, D(-s)\, P_{n+1}(t-s)$$

$$- n\exp(-i\omega s)\, D(-s)\, P_{n-1}(t-s) \quad , \qquad (31)$$

where $P_n(t) = \tilde{\rho}^{v}_{nn}(t) = \rho^{v}_{nn}(t)$. A last simplification comes from the fact that

$$\langle B^e \rangle_e = \langle B^r \rangle_r = \vec{0} \quad , \qquad (32)$$

where $\langle K \rangle_e = \mathrm{Tr}_e\{K \cdot \rho^e\}$, and $\mathrm{Tr}_e\{\ \}$ is the trace over all the electronic states (with a similar definition for $\langle\ \rangle_r$).

The memory kernel then splits into two parts, one related to the interaction between the molecule and the laser, the other related to the interaction between the molecule and the substrate [22],

$$D(-s) = D^e(-s) + D^r(-s) \quad , \qquad (33)$$

where $D^e(-s) = \langle B^e\ B^e(-s) \rangle_e$, with a similar definition for $D^r(-s)$. Because at time $t = 0$ the nondiagonal elements of the vibrational density matrix are equal to zero, they will remain zero at all times. We are not interested in their evolution anyway, because the mean vibrational energy does not depend on them.

IV. Computation of the Memory Kernel

Let us first compute the part of the memory kernel due to H^{ev}. From (13), (23) and (33), we obtain

$$D^e(-s) = \left(\frac{\partial\varepsilon_a}{\partial\xi}\right)^2 \langle g|(a^\dagger a - \langle g|a^\dagger a|g\rangle)\exp(-iH^e s/\hbar)$$

$$\times\ (a^\dagger a - \langle g|a^\dagger a|g\rangle)\exp(iH^e s/\hbar)|g\rangle \quad . \tag{34}$$

Using (6) and its Hermitian conjugate, we can transform this into

$$D^e(-s) = \left(\frac{\partial\varepsilon_a}{\alpha\xi}\right)^2 \sum_{\varepsilon_\alpha < \varepsilon_f} \sum_{\varepsilon_\beta > \varepsilon_f} |\langle a|\alpha\rangle|^2\ |\langle a|\beta\rangle|^2 \exp[-(\varepsilon_\alpha - \varepsilon_\beta)s/\hbar] \quad . \tag{35}$$

This formula has been derived previously by Persson [10]. The new feature which we shall introduce is a generalization to all vibrational transitions, the justification of the Markov approximation, and the formula (39) which is not clearly established in [10].

Replacing the sum by an integral,

$$\sum \rightarrow \int d\varepsilon\ \rho(\varepsilon) \quad , \qquad \rho(\varepsilon)|\langle a|\alpha\rangle|^2 \rightarrow \rho_a(\varepsilon) \quad ,$$

we obtain

$$D^e(-s) = \left(\frac{\partial\varepsilon_a}{\partial\xi}\right)^2 \int_0^{\varepsilon_f} d\varepsilon_\alpha \int_{\varepsilon_f}^{\infty} d\varepsilon_\beta\ \rho_a(\varepsilon_\alpha)\ \rho_a(\varepsilon_\beta)\ \exp[-i(\varepsilon_\beta - \varepsilon_\alpha)s/\hbar] \quad , \tag{36}$$

where $\rho_a(\varepsilon)$ is the density of states of the orbital $|a\rangle$. If we assume that the width of $\rho_a(\varepsilon)$ is on the order of 1eV [23], then $D^e(-s)$ vanishes for s $>> \hbar/1\mathrm{eV} \simeq 10^{-15}$ s. During such a short time, the system cannot evolve, and $D^e(-s)$ may be integrated over s assuming $P_n(t-s) \simeq P_n(t)$ in (31), which is the Markov approximation. From [10], we have

$$\mathrm{Re} \int_0^t ds\ \exp(i\omega s)\ D^e(-s) \simeq \pi\hbar^2\omega\ \rho_a^2(\varepsilon_f)\left(\frac{\partial\varepsilon_a}{\partial\xi}\right)^2 \quad .$$

$$\mathrm{Re}\int_0^t ds\ \exp(-i\omega s)\ D^e(-s) = 0 \quad . \tag{37}$$

Taking into account the fact that the orbital $|a>$ is fourfold degenerate [10], we end up with a rate of transition from the vibrational state n to m equal to

$$R^e_{nm} = \frac{\pi\hbar}{4\mu}\,(n\ \delta_{n,m+1})\sigma^2 \quad , \tag{38}$$

where $\sigma = \frac{\partial\varepsilon_\alpha}{\partial\xi}\ \rho_a(\varepsilon_f)$.

As shown in [10], σ may be determined experimentally. It is the derivative of the number of electrons in the orbital $|a>$ with respect to the stretching amplitude. Persson assumed that the difference between the dipole moment of the adsorbed (D_a) and free (D_f) molecule is due to this charge transfer. Then, the effective charge (δ) associated with the stretching of the adsorbed molecule is equal to $\delta = (\delta^+ + \bar{e}d\sigma)$, where δ^+ is the effective charge associated with the stretching of the free molecule, $\bar{e}$ is the charge of one electron, and d is the mean distance separating the electron in the orbital $|a>$ from the metal surface. Using the fact that the transition dipole moment of the free and adsorbed molecule are, respectively,

$$D_f = \delta^+\left(\frac{\hbar}{2\mu\omega}\right)^{1/2} \quad \text{and} \quad D_a = \delta\left(\frac{\hbar}{2\mu\omega}\right)^{1/2} \quad ,$$

we can estimate σ to be

$$\sigma = \frac{D_a - D_f}{\bar{e}d}\left(\frac{2\mu\omega}{\hbar}\right)^{1/2} \quad . \tag{39}$$

We now compute the part of the memory kernel due to H^{rv}. Some simple algebra leads to

$$D^r(-s) = \frac{\hbar\delta^2}{2\epsilon_0 U} \sum_k \omega_k \{\langle p_k^\dagger p_k\rangle \exp(-i\omega_k s) + (\langle p_k^\dagger\, p_k\rangle + 1)\exp(i\omega_k s)\} \ . \quad (40)$$

By taking U large enough, we may replace the sum by an integral

$$\sum_k \rightarrow \frac{U^{1/3}}{2\pi c} \int_0^\infty d\omega_L \quad , \qquad \langle p_k^\dagger\, p_k\rangle \rightarrow n(\omega_L) \quad ,$$

where c is the speed of light.

We also neglect the term "(+1)exp($-i\omega_k s$), which gives the damping of the vibrational level due to the vacuum fluctuations of the electric field. Finally, we assume the spectral intensity of the laser to be a Lorentzian centered around ω,

$$n(\omega_L) = N \frac{\Gamma_L}{\pi[\Gamma_L{}^2 + (\omega - \omega_L)^2]} \quad , \qquad (41)$$

where Γ_L is the spectral linewidth of the laser and N is the density of photons. Because $n(\omega_L)$ vanishes quickly when ω_L is different from ω, we may replace ω_k in (40) by ω. The intensity of the laser is given by:

$$I = \frac{c\epsilon_0}{\delta^2} D^r(0) = \frac{\hbar\omega N}{\pi U^{2/3}} \quad . \qquad (42)$$

Finally, we obtain from Eqs. (40)-(42)

$$D^r(-s) = \frac{I\delta^2}{2c\epsilon_0} \int_0^\infty d\omega_L \frac{\Gamma_L[\exp(i\omega_L s) + \exp(-i\omega_L s)]}{\pi[\Gamma_L{}^2 + (\omega - \omega_L)^2]}$$

or

$$D^r(-s) = \frac{I\delta^2}{2c\epsilon_0} e^{-\Gamma_L s} [\exp(i\omega s) + \exp(-i\omega s)] \quad . \qquad (43)$$

The quantity $D^r(-s)$ does not vanish before s is larger than Γ_L^{-1}. Γ_L^{-1} is the temporal coherence of the electric field and may be larger than the characteristic time of the evolution of the probabilities $P_n(t)$, in which case the Markov approximation is not applicable. Furthermore, we may not then neglect the temporal coherence of the stretching position $\xi(t)$. To take this into account, we replace $\pm\,\omega$ in (31) by $\pm\omega + i\Gamma_v$. Γ_v^{-1} is the temporal coherence of $\xi(t)$ and is given by

$$\Gamma_v = R^e_{10} = \frac{\pi\hbar\sigma^2}{4\mu} \quad . \tag{44}$$

V. Equation of Evolution and Property of the Steady State

By neglecting the integrals

$$\int_0^t ds\, \exp(\pm i2\omega s)\, \exp(-\Gamma s)\, P_n(t-s) \quad ,$$

we can express the kinetic equation (31) in the simple form

$$\dot{\vec{P}}(t) = \frac{\pi\hbar\sigma^2}{4\mu}\, \overset{\Rightarrow}{D}\, \vec{P}(t) + \frac{\delta^2 I \overset{\Rightarrow}{E}}{2\hbar\omega\mu c\varepsilon_0} \int_0^t ds\, \exp(-\Gamma s)\, \vec{P}(t-s) \quad , \tag{45}$$

where $\Gamma = \Gamma_L + \Gamma_v$, $\vec{P}(t)$ is the vector $(P_0(t), P_1(t) \ldots)$, $\overset{\Rightarrow}{D}$ is the matrix

$$\begin{pmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 & 0 \\ 0 & 0 & -2 & 3 & 0 \\ 0 & 0 & 0 & -n & (n+1) \\ & & & \ddots & \end{pmatrix} \quad ,$$

and $\overset{\Rightarrow}{E}$ is given by

$$\begin{pmatrix} -1 & 1 & 0 & 0 & 0 \\ 1 & -3 & 2 & 0 & 0 \\ 0 & 2 & -5 & 3 & 0 \\ 0 & 0 & n & -(2n+1) & (n+1) \\ & & & & \ddots \end{pmatrix} .$$

In the steady state, $\dot{P}(t)$ is zero and $\vec{P}(t-s)$ is equal to $\vec{P}(t)$, such that (45) becomes

$$\dot{\vec{P}}(t) = \alpha[\overset{\Rightarrow}{D} + \beta\overset{\Rightarrow}{E}]\,\vec{P}(t) = \vec{0} \tag{46}$$

with $\alpha = \frac{\pi\hbar\sigma^2}{4\mu}$ and $\beta = \frac{2\delta^2 I}{\pi\hbar^2\omega\Gamma\sigma^2 c\varepsilon_0}$.

In fact, by eliminating "$= \vec{0}$" on the far right-hand side of Eq. (46), we obtain the kinetic equation within the Markov approximation. In the steady state, the probabilities P_n^s are given by

$$P_{n+1}^s = [(2v+1)\beta + v]\,P_n^s - \beta n P_{n-1}^s \quad . \tag{47}$$

This kind of equation admits only one normalized solution [24], given by

$$P_n^s = \left(\frac{\beta}{1+\beta}\right)^n \frac{1}{1+\beta} \quad . \tag{48}$$

The mean number of vibrational quanta is given by

$$\langle n\rangle = \sum_{n=0}^{\infty} nP_n^s = \beta \quad . \tag{49}$$

The power dissipated into the metal is given by the scalar product between $\alpha\overset{\Rightarrow}{D}\vec{P}^s$ and $(0,\hbar\omega,2\hbar\omega,\ldots)$, which is equal to

$$\text{Power} = |-\alpha\beta\hbar\omega| = \frac{\delta^2 I}{2\mu c\varepsilon_0\Gamma}\ \text{molecule}^{-1} \quad . \tag{50}$$

To know how many times it takes to the system to reach the steady state, we must integrate Eq. (45) numerically. This leads to the iterative equation

$$P_n(t+\Delta t) = P_n(t) + \Delta t\cdot\alpha\{[-nP_n(t) + (n+1)\, P_{n+1}(t)] + \beta\Gamma \int_0^t ds\, \exp(-\Gamma s)[nP_{n-1}(t-s) + (n+1)P_{n+1}(t-s) - (2n+1)P_n(t-s)]\} \quad . \tag{51}$$

To iterate this equation to arbitrary t, we need not know all the history, $P_n(t-s)$, of the system since,

$$\int_0^{t+\Delta T} ds\, \exp(-\Gamma s)P_n(t+\Delta t-s) \simeq e_n^{-\Gamma\Delta t}[\Delta t\cdot P_n(t+\Delta t) + \int_0^t ds\, \exp(-\Gamma s)P_n(t-s)] \quad . \tag{52}$$

When the anharmonicity of the vibration is high, the laser can only couple the two lowest vibrational levels. The interaction between the molecule and the metal entails a vibrational transition to just the lower level. Then the populations of the levels containing more than one quantum will decay rapidly to zero (α^{-1} ~ lifetime). Furthermore, if at $t = 0$ these levels are not occupied, they will remain empty all the time. In that situation, our problem reduces to a two-level system, and the kinetic equation reduces to

$$\dot{\vec{P}}^a(t) = \alpha[\begin{pmatrix} 0 & 1 \\ 0 & -1 \end{pmatrix}\dot{\vec{P}}^a(t) + \beta\Gamma\begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix} \int_0^t ds\, \exp(-\Gamma s)\, \vec{P}^a(t-s)] \quad . \tag{53}$$

Here $\alpha\beta\Gamma = \Omega^2/2$, where Ω is the Rabi frequency defined by

$$\Omega^2 = \frac{2I}{c\epsilon_0}|\langle 1|M|0\rangle|^2/\hbar^2 \quad ,$$

where $M = \delta\xi$ is the dipole moment operator, and $\vec{P}^a(t) = (P_0^a(t), P_1^a(t))$. At the steady state, the population of the upper level and the power dissipated into the metal are given by

$$P_1^a = \frac{\beta}{2\beta + 1} = \frac{\Omega^2}{2\Omega^2 + 2\alpha\Gamma} \tag{54}$$

$$\text{P}\overset{a}{\text{o}}\text{wer} = \frac{\hbar\omega\alpha\beta}{2\beta + 1}\ \text{molecule}^{-1} \quad . \tag{55}$$

These results are formally equivalent to those obtained by van Smaalen, Arnoldus and George (see Section VI of Reference 16), who transformed to dressed states to compute the laser heating of a transparent crystal via adsorbed atoms. They accounted for the detuning, Δ, between the frequency of the laser and the vibration, and they neglected the lifetime α^{-1} and the laser width Γ_L. In any event, by taking the high laser intensity limit, we end up with the same saturation power

$$\text{P}\overset{a}{\text{o}}\text{wer}^{\text{sat}} = \frac{\hbar\omega\alpha}{2}\ \text{molecule}^{-1} \quad . \tag{56}$$

Comparing (54) and (55) to (49) and (50), we observe that the only new feature introduced by the anharmonicity is the saturation factor $(2\beta + 1)^{-1}$, so that the effect of the anharmonicity is negligible if $\beta \ll 1$.

The kinetic equation (53) can be rewritten in terms of the population inversion as

$$[\dot{P}_1^a(t) - \dot{P}_0^a(t)] = -2\alpha P_1^a(t) - \Omega^2 \int_0^t ds\, \exp(-\Gamma s)\, [P_1^a(t-s) - P_0^a(t-s)] \quad . \tag{57}$$

On a time scale shorter than Γ^{-1}, we can describe analytically the behavior of the population inversion. Neglecting the term $-2\alpha P_1^a$ and estimating $\exp(-\Gamma s)$ as unity, we can write the solution of (57) as

$$[P_1^a(t) - P_0^a(t)] = - \cos(\Omega t) \quad . \tag{58}$$

Here we have taken the initial conditions to be $P_0^a(0) = 1$ and $P_1^a(0) = 0$. This is the Rabi oscillation, and such behavior cannot be revealed using the Markov approximation. This oscillation will damp on a time scale of Γ^{-1} to reach the steady state defined in (54) and (55).

VI. Numerical Results

In this section we adopt the numerical data listed in Table I, which correspond to carbon monoxide molecule adsorbed on a copper surface. The laser characteristics correspond to an infrared beam emanating from an optical parametric oscillator pumped by a YAG laser. This beam is focused to obtain a section of 1 mm^2 and strikes the surface with a small grazing angle of incidence.

From (39) and (46), we obtain [10]

$$\alpha = \Gamma_v = 6.4 \times 10^{11}\ s^{-1} \quad . \tag{59}$$

Since the temporal coherence of the position $\xi(t)$ ($\Gamma_v^{-1} = 1.5 \times 10^{-12}$ s) is much smaller than the temporal coherence of the laser electric field ($\Gamma_L^{-1} > 10^{-11}$ s), we may make the estimation

$$\Gamma = \Gamma_v + \Gamma_L \simeq \Gamma_v = \alpha \quad . \tag{60}$$

With this condition, the mean number of vibrational quanta is inversely proportional to the square of α. This reflects the fact that this number is limited by the rate of damping of the vibrational energy into the metal, as well as by the broadening in energy of the vibrational levels. The broadening decreases the absorption efficiency of the quasi monochromatic laser beam. This does not occur if the linewidth of the laser is greater than the width of the vibrational levels, in which case

$$\Gamma = \Gamma_v + \Gamma_L \simeq \Gamma_L \quad . \tag{61}$$

Adopting the numerical data of Table I, and using Eq. (49), we obtain the mean number of vibrational quanta at the steady state to be

$$\langle n \rangle = \beta = 0.03 \quad . \tag{62}$$

The power transmitted from the laser beam to the surface is calculated from Eq. (50) to be

$$\text{Power} = 7 \times 10^{-10} \text{ J s}^{-1} \text{ molecule}^{-1} \quad . \tag{63}$$

From (50) and (60), we observe that the power is inversely proportional to α, due to the fact that Γ_L is much smaller than Γ_v. If the interaction between the molecule and the substrate is less important, we have a situation where Γ_L is much larger than Γ_v, in which case the power is independent of α, where α measures the strength of the interaction between the molecule and the substrate. This holds if the hypothesis of harmonicity remains valid, which means that β, the mean number of vibrational quanta in the steady state, is not too high, say less than 0.1. The region where our model fails depends on the laser characteristics and is given by

$$\log(\frac{\alpha}{\Gamma_L}) < \log(\frac{5\delta^2 I}{\hbar\omega\Gamma_L^2\mu c\varepsilon_0}) \quad , \tag{64}$$

where we have assumed $\alpha \ll \Gamma_L$. This is illustrated in Fig. 1.

To estimate the time τ necessary to reach this steady state, we compute the evolution of the populations of the vibrational levels using (51) and (52). We adopt the initial conditions $P_n(0) = \delta_{n,0}$. The evolution of the mean number of vibrational quanta and the occupation probabilities of the three lowest levels are shown in Figs. 2 and 3 for two different values of β. The populations of the vibrational levels in the steady state for β equal to 1 are presented in Fig. 4, here we take the steady state to be achieved when the mean number of vibrational quanta reaches 90% of its exact value in the steady state. τ does not depend noticeably on β and is estimated to be

$$\tau \doteq 4\alpha^{-1} \doteq 5.6 \times 10^{-12}\ \mathrm{s} \quad . \tag{65}$$

This small value indicates that the mean number of vibrational quanta will follow the instantaneous intensity of the laser since the intensity varies on a time scale of the order of 10^{-9} s. In Fig. 5, we show the evolution of the mean number of vibrational quanta both with and without the Markov approximation. We observe that this approximation overestimates the rate of evolution of the system and gives τ equal to 2.3 α^{-1}.

VII. Conclusions

We have derived a simple kinetic equation for the populations of the vibrational levels of a diatomic molecule adsorbed on a metal. The molecule interacts with the electronic degrees of freedom of the metal and an infrared laser beam. This equation can readily be solved and is valid for all laser linewidths, infrared absorption widths of the adsorbed molecule, and time scales. It has been shown that, to compute the evolution of the populations, the Markov approximation is not valid if the temporal coherence of the laser field is greater than the time scale during which the populations are changing. This failure was observed earlier by Beri and George [22].

Our kinetic equation corresponds exactly to the one obtained using the random-phase approximation. The use of this simplification has entailed the neglect of the nondiagonal elements of the density matrix to compute its evolution, and this approximation has remained questionable in the case of the interaction between a laser and a molecule [12]. It has been used extensively, either implicitly in application of the golden rule [14], or explicitly [13,22]. Our theoretical development proves that this approximation leads to the correct kinetic equation for the populations of the vibrational levels. This conclusion should emphasize the validity of some theoretical predictions already given in the literature.

Our results also show the equivalence of the steady-state properties computed using the golden rule [14], the random-phase approximation [12,22], the Markov approximation [13], the transformation to dressed-states technique [15-17], or the Zwanzig projector technique. In the specific situation considered in the previous section, the probability of finding an adsorbed molecule in its first-excited vibrational level is 0.03, which suggests that resonant excitation of a molecule adsorbed on a metal surface could provide a means of laser-enhanced surface reactions.

Acknowledgments

This research was supported by the Fonds National de la Recherche Scientifique of Belgium, Le Ministère Belge de la Politique Scientifique (S.P.P.S., Bruxelles), the Office of Naval Research, the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract F49620-86-C-0009, and the National Science Foundation under Grant CHE-8519053. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon. We want to thank Dr. H. F. Arnoldus and Dr. S. van Smaalen for helpful discussions and for a critical reading of the manuscript. AP thanks the State University of New York at Buffalo for its hospitality during his visit in February-March 1986, when much of this research was carried out.

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Table I: Data used in numerical calculations.

Characteristics of the Adsorbate

System considered: CO adsorbed on Cu [3]

$D_f = 0.1$ Debye

$D_a = 0.22$ Debye

$\omega = 2100 \text{ cm}^{-1} \simeq 4 \times 10^{14} \text{ s}^{-1}$ [8]

$d = 7.8 \; 10^{-11}$ m [10]

To account for the screening of the electric field by the electronic polarizability of the adsorbed molecule, we adopt $\delta = 0.6 \, \bar{e}$ [25].

Characteristics of the Laser Beam

pulse duration: 15×10^{-9} s

pulse energy: 10^{-2} J

beam cross section: 10^{-6} m^2

surface enhancement of the intensity by constructive interference between the incident and reflected beam: ~ 4 [20]

mean intensity: ~ $3 \times 10^{12} \text{ J m}^{-2} \text{ s}^{-1}$

laser width: $\Delta\omega_L < 1 \text{ cm}^{-1} \simeq 3 \times 10^{10} \text{ s}^{-1}$

Figure Captions

1. Dependence of the power dissipated into the metal on the strength (α) of the interaction between the admolecule and the substrate, where

$$\text{Power}_{\max} = \lim_{\alpha\to 0} \text{Power}(\alpha) = \frac{\delta^2 I}{2\Gamma_L \mu c \epsilon_0} .$$

The region where the hypothesis of harmonicity fails is darkened with points.

2. Evolution of the occupation probabilities of the three lowest vibrational levels, $P_0(t)$, $P_1(t)$ and $P_3(t)$, and of the mean number of vibrational quanta, $\langle n\rangle$, for $\beta = 1$.

3. Same as Fig. 2, with $\beta = 0.01$.

4. Occupation probabilities of the vibrational levels at the steady state for $\beta = 1$.

5. Evolution of the mean number of vibrational quanta under the Markov approximation ($\langle n\rangle_M$) and without this approximation ($\langle n\rangle_{nonM}$) for $\beta =$ 0.01

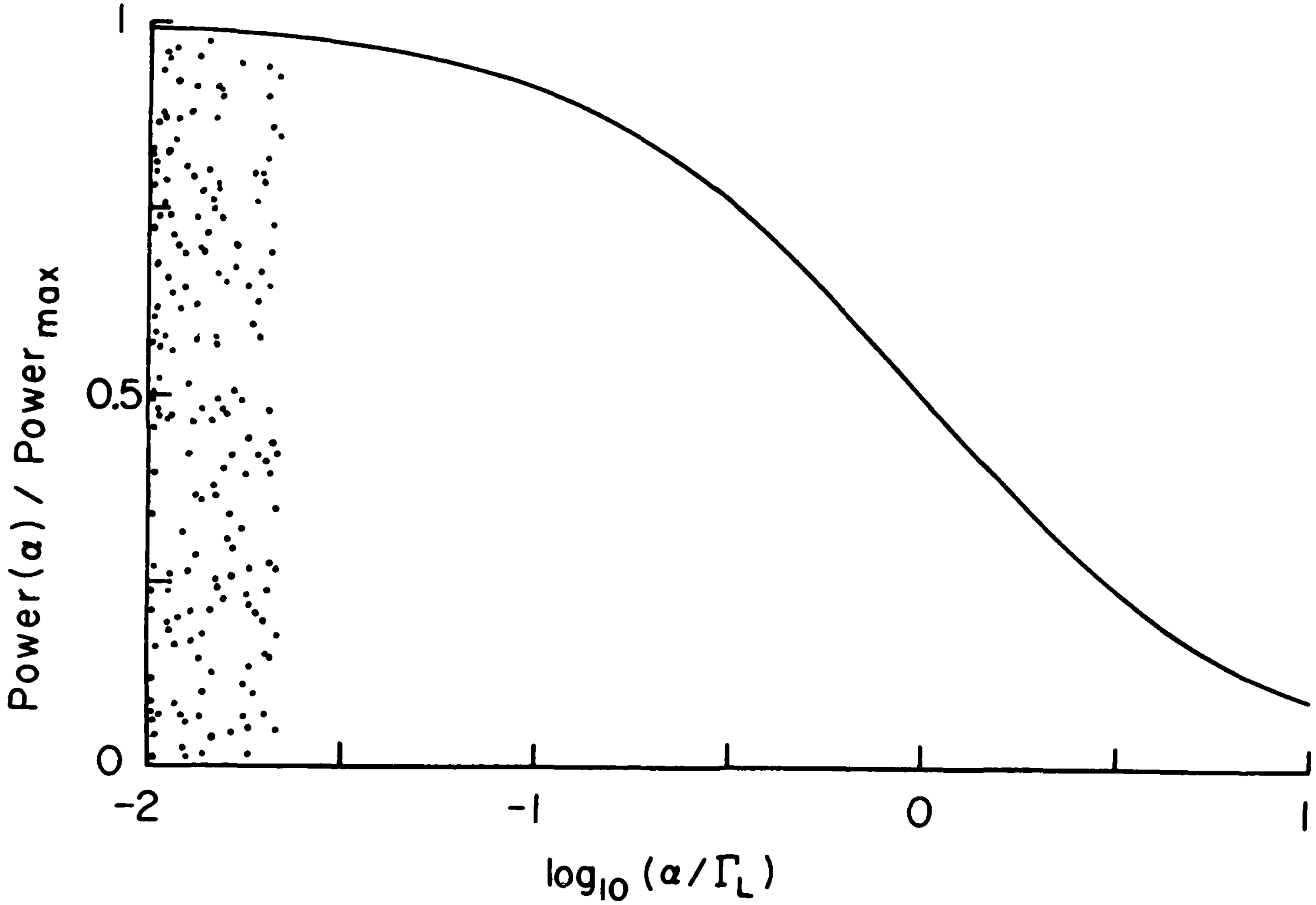
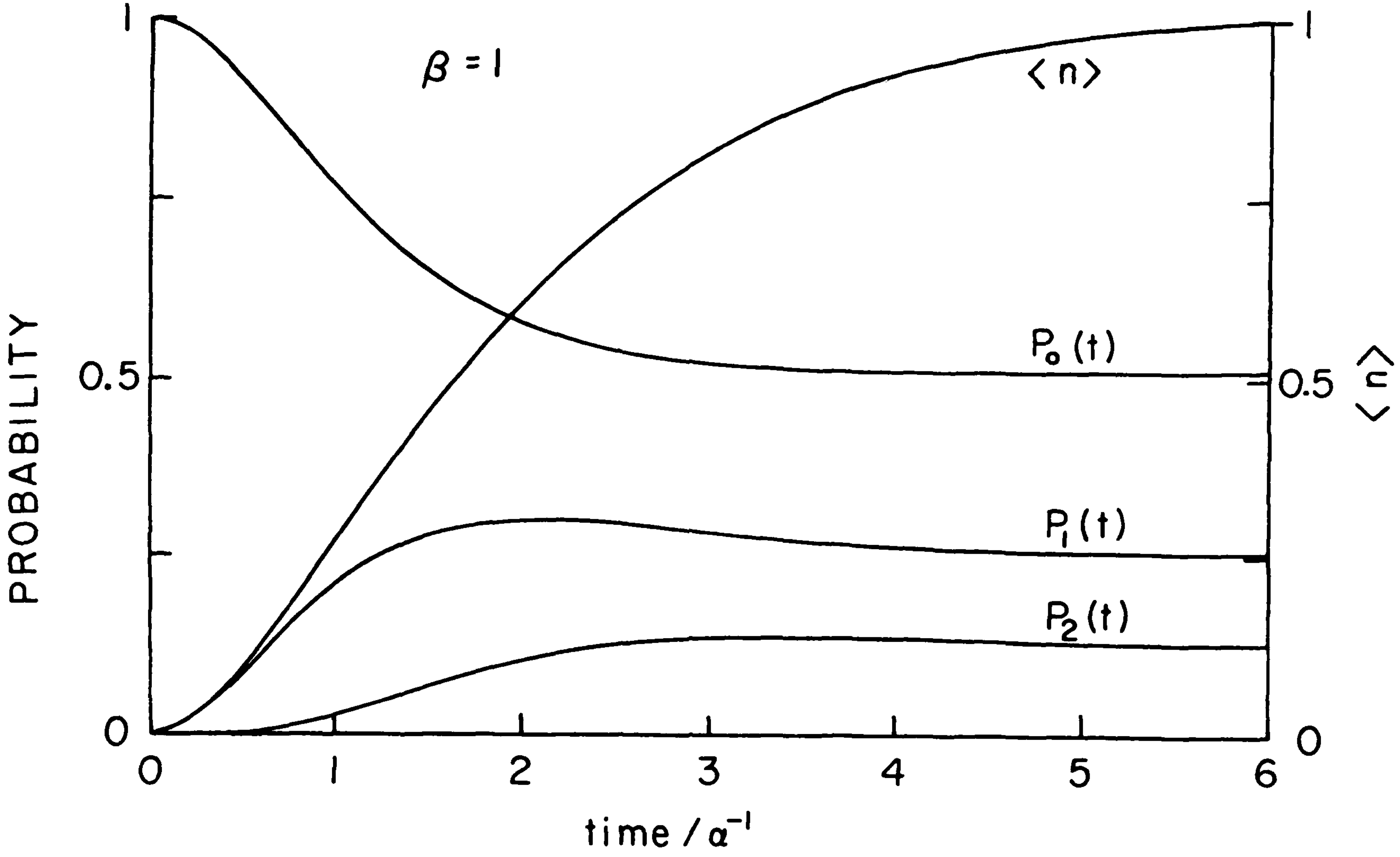


Fig. 1



PROBABILITY
1
0.5
0
$\beta = 1$
$\langle n \rangle$
$P_o(t)$
$P_1(t)$
$P_2(t)$
0.5
0
1
$\langle n \rangle$
0
1
2
3
4
5
6
time / α^{-1}

Fig. 2

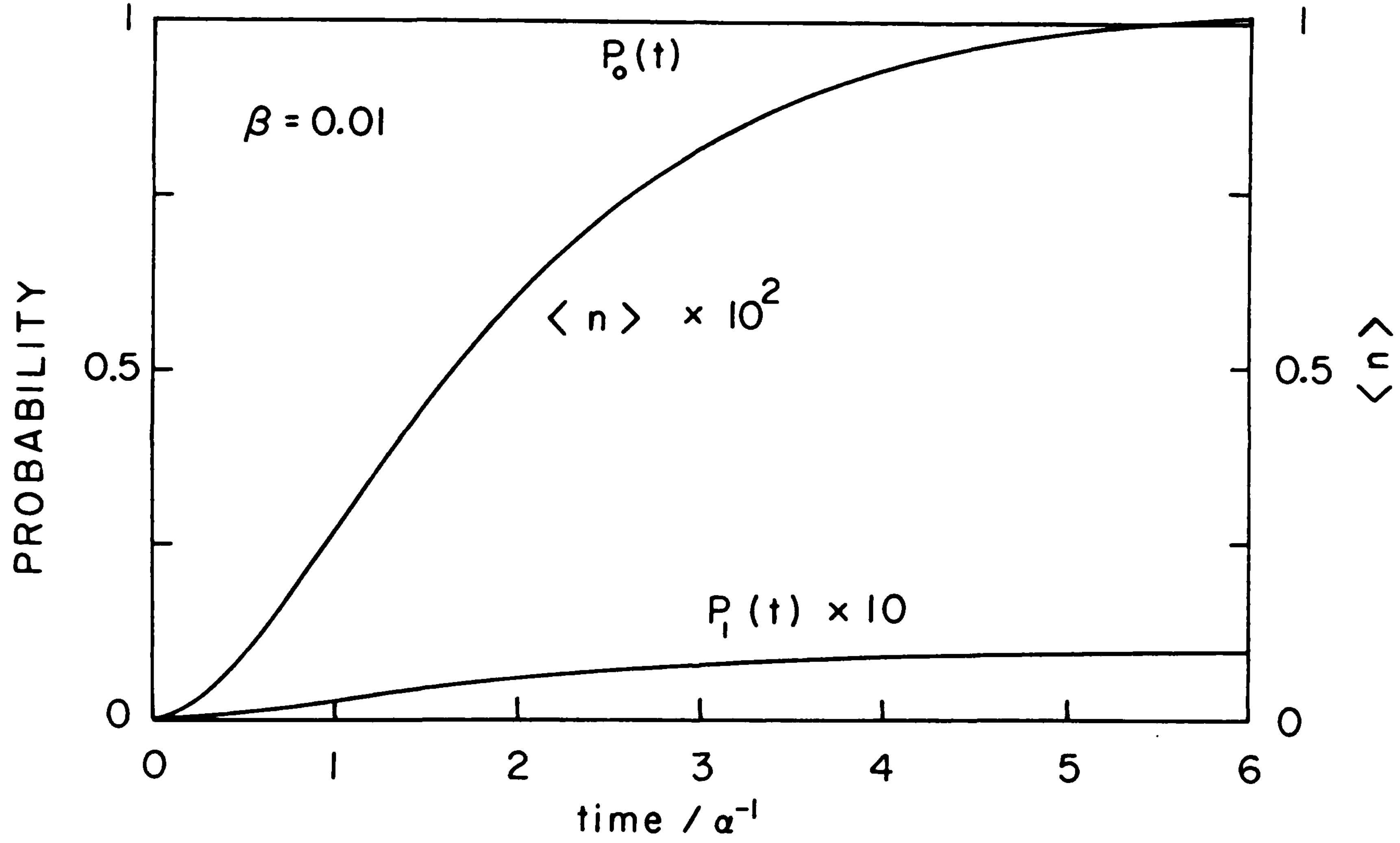

PROBABILITY
1
0.5
0
0
1
2
3
4
5
6
time / α^{-1}
1
0.5
0
$\langle n \rangle$
$P_o(t)$
$\beta = 0.01$
$\langle n \rangle \times 10^2$
$P_1(t) \times 10$

Fig. 3

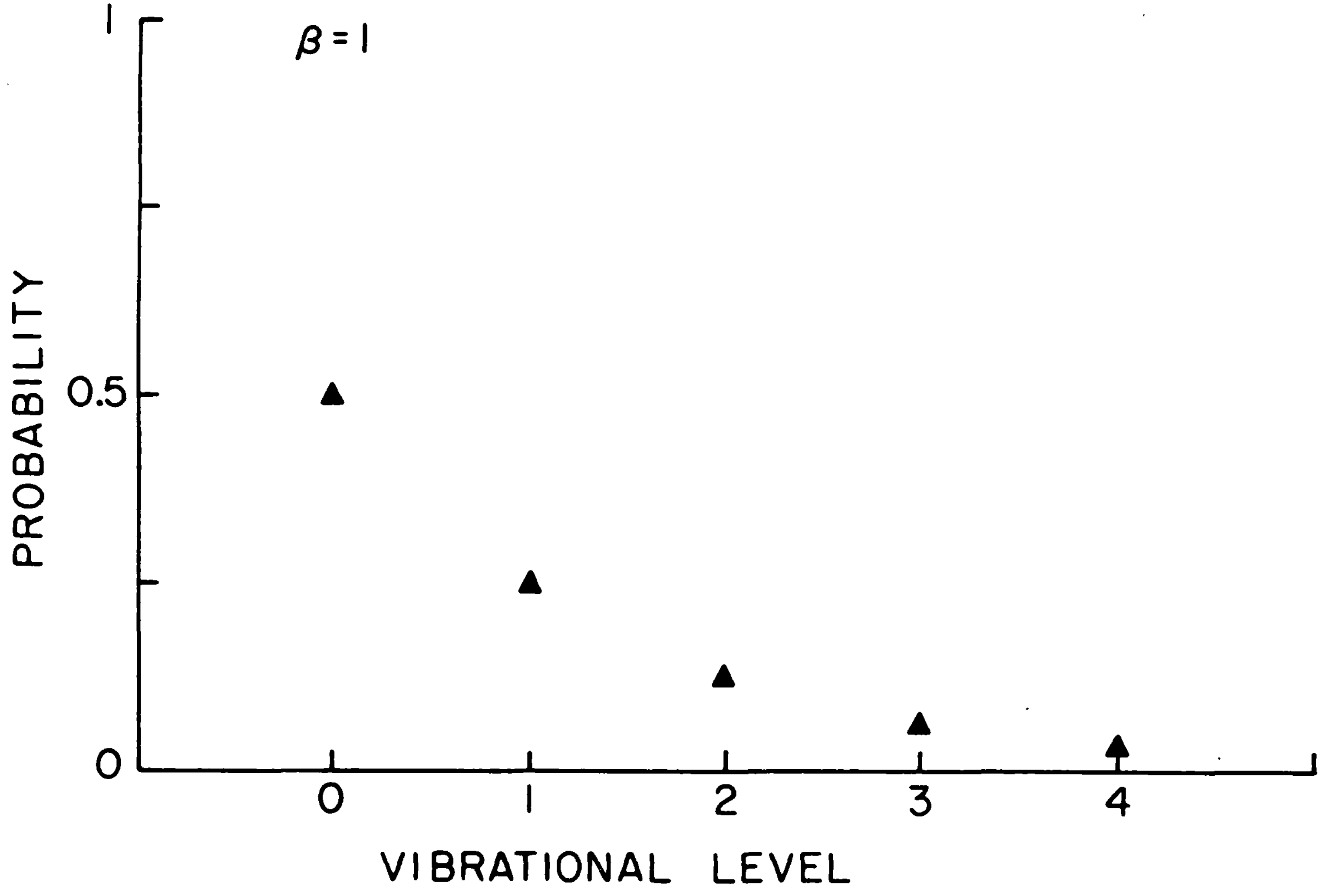


Fig. 4

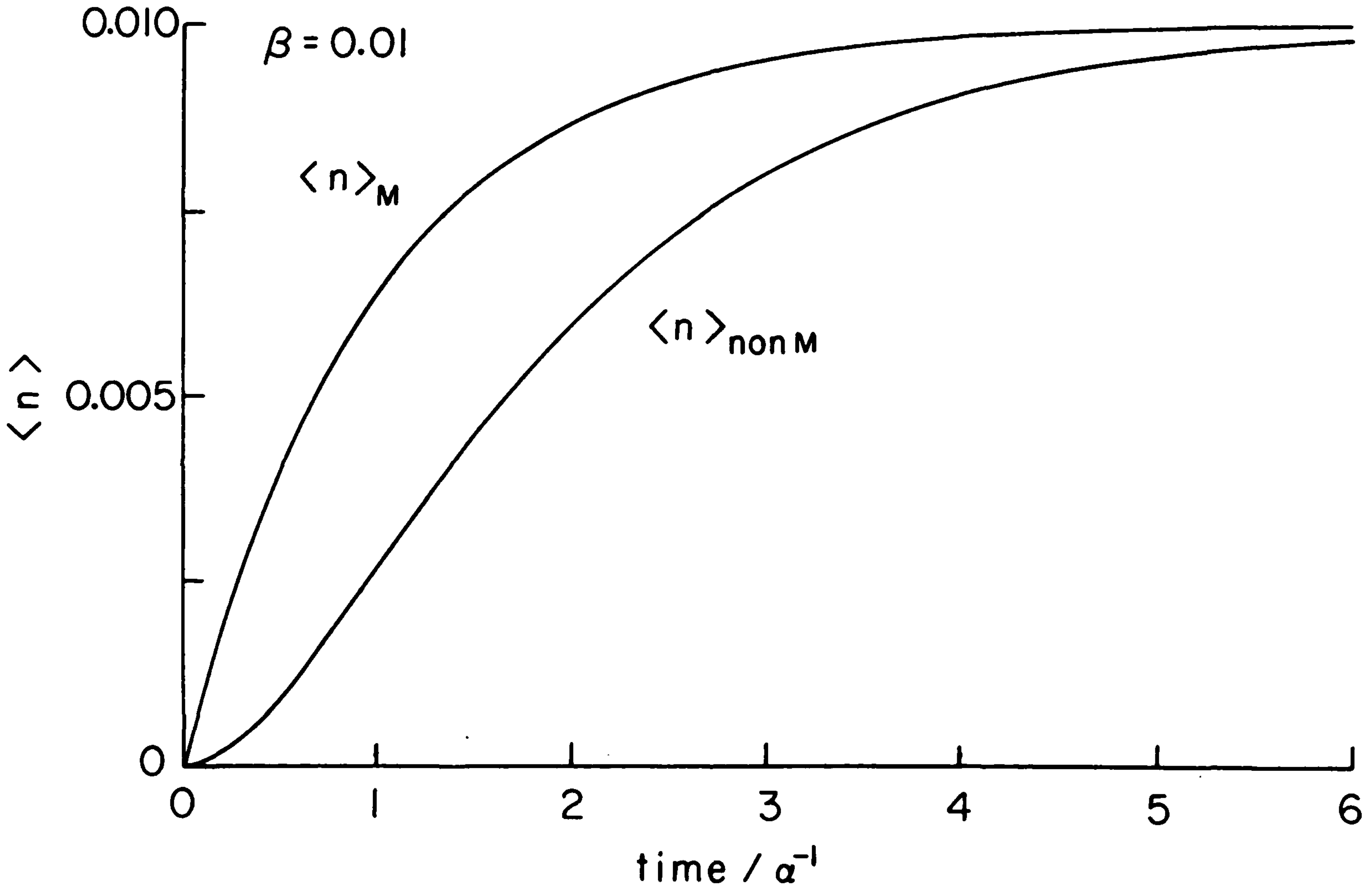

$\beta = 0.01$
$\langle n \rangle_M$
$\langle n \rangle_{non\,M}$
$\langle n \rangle$
0.010
0.005
0
0
1
2
3
4
5
6
time / α^{-1}

Fig. 5

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