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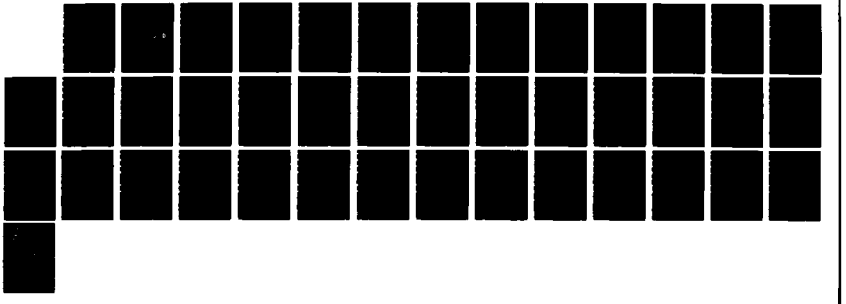

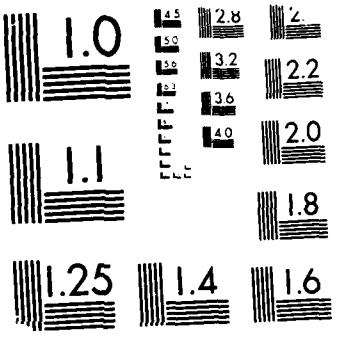


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# Anomalies in the Heat-Capacity Signatures of Submonolayer Adsorbates With Attractive Lateral Interactions

by

Young Sik Kim, Franco Battaglia and Thomas F. George

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The analytic closed form of the heat-capacity signatures previously derived for the McQuistan-Hock (MQH) model of a lattice gas is applied to a various adsorbed systems for which the lateral interaction varies from a few meV to about 300 meV. It is shown that whenever the adsorption system can be described by a two-dimensional gas on which the substrate effects are less important than the adatom-adatom interactions, the computed temperatures at which the heat-capacity signatures display their maximum are in excellent agreement with the experimental measurements.

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# LINE SHAPE OF AN ATOM-CRYSTAL BOND

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## ABSTRACT

The spectral profile for the absorption of infrared laser light by a vibrational bond between a physisorbed atom and a harmonic crystal is calculated. We obtained an analytical expression for the line shape, which includes the finite memory-time effects in the interaction between atomic motion and bulk-atom vibrations. Both the memory in the time regression of the dipole correlation function and the initial correlations are taken into account. It is shown that absorption from a laser with a frequency which is larger than the cutoff frequency $\omega_D$ of the dispersion relation of the crystal can only occur due to a memory in the relaxation process, provided that multiphonon transitions are negligible. We predict a resonance-like line at $\omega_o + \omega_D$ (with $\omega_o$ the unperturbed resonance) for atom-surface bonds with a permanent dipole moment.

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## I. INTRODUCTION

If a crystal is exposed to an atomic vapor, then many atoms will stick to its surface due to the van der Waals interaction. Every atom in the vicinity of the solid experiences an attractive potential, which supports continuum (desorbing) states and bound (adsorbing) states. Transitions from bound to continuum states can be induced by thermal coupling of the vibrational bond with the phonon reservoir of the crystal, or by illumination with a strong infrared laser. With the first mechanism a large desorption rate can be achieved by a sufficient heating of the substrate, whereas in the second process the transition to the continuum is brought about by photon absorption. For these processes the interaction between adsorbate and crystal can be accounted for by relaxation terms in a master equation for the populations of the vibrational levels, where the rate constants are given by the Golden Rule. Dynamical properties of the system are determined by the relative values of these rate constants and by the level structure of the potential. Then the desorption rate as a function of time contains information on the atom-crystal interaction, e.g. the rate constants. Several authors[1-3] applied this technique to evaluate the photodesorption yield as a function of the laser frequency. A far more sensitive method to obtain insight into the details of the dynamical features of adsorbates is by measuring the steady-state low-intensity absorption profile $I(\omega)$ as a function of the probe (laser) frequency $\omega$.[4-6] Then the absorption spectrum will reveal the details of dynamical atom-lattice bonds,[7] surface-modified internal molecular modes,[8] or properties of the interaction between two adspecies.[9] We shall consider a single atom which is adsorbed on a harmonic-lattice crystal, and bounded to the surface by a potential $V(z)$. We neglect lateral motion and indicate the normal to the surface by the z-axis. Then the induced dipole moment $\underline{\mu}(t)$, where t denotes the Heisenberg picture, of the atom-crystal bond must be in the z-direction, and hence

we can write $\underline{\mu}(t) = \mu(t)\underline{e}_z$ with $\mu(t)$ a scalar operator. An infrared laser with intensity $I_L$ (energy per unit of time which passes a unit surface area, perpendicular to the direction of propagation) and polarization $\underline{\epsilon}_L$ is incident on the atomic bond. Since the wavelength of the radiation is much larger than the atom-surface separation, we can adopt the dipole approximation for the interaction between the bond and the external field. Then a general expression for the absorbed energy per unit of time, the absorption profile, reads[10]

$$I(\omega) = I_L|\underline{e}_z\cdot\underline{\epsilon}_L|^2 \frac{\omega}{\epsilon_o \hbar c} \text{Re} \lim_{t\to\infty} \int_0^\infty d\tau\ e^{i\omega\tau} \text{Tr}\rho(t)[\mu(t+\tau),\mu(t)] \quad . \tag{1.1}$$

where $\rho(t)$ is the density operator for the atom, the entire crystal, and the interaction. The appearance of the commutator reflects that the net absorption is a balance between stimulated absorption (the term $\mu(t+\tau)\mu(t)$) and stimulated emission (the term $\mu(t)\mu(t+\tau)$) of photons from and into the laser field.

Transformation of Eq. (1.1) to the Schrödinger picture yields the equivalent expression

$$I(\omega) = I_L|\underline{e}_z\cdot\underline{\epsilon}_L|^2 \frac{\omega}{\epsilon_o \hbar c} \text{Re} \lim_{t\to\infty} \int_0^\infty d\tau\ \text{Tr}\mu e^{i(\omega-L)\tau}[\mu,\rho(t)] \quad . \tag{1.2}$$

Here, the limit $t\to\infty$ only pertains to the density operator $\rho(t)$, and obviously $\rho(t=\infty)$ represents the thermal-equilibrium state of the system. If we write $\sigma$ for an arbitrary density operator, as we shall do throughout the paper, then the Liouvillian L in the exponential in Eq. (1.2) is related to the Hamiltonian H by

$$L\sigma = \hbar^{-1}[H,\sigma] \quad . \tag{1.3}$$

From Eq. (1.2) we notice that the frequency dependence of $I(\omega)$ is governed by the Fourier-Laplace parameter $\omega$ in the transformation of $\exp(-iL\tau)$, and consequently the resonance lines in the profile are situated at the eigenvalues of L. Then we recall that the equation of motion for the density operator is

$$i \frac{d\rho}{dt} = L\rho \quad , \tag{1.4}$$

and therefore the dynamical properties of the system will be displayed in the $\omega$-dependence of $I(\omega)$, even though the system is in a stationary state (for which $\rho(t)$ becomes independent of time). It is not the direct time evolution of $\rho(t)$ which is probed by the laser, but the time-regression operator $\exp(-iL\tau)$ of the dipole correlation functions, as they appear in Eq. (1.1). The significance of a measurement of $I(\omega)$ then relies on the fact that L represents the entire system, rather than only the vibrational bond.

## II. HAMILTONIAN

A harmonic crystal can be represented by the Hamiltonian $H_p$ for its phonon field[11]

$$H_p = \sum_{\underset{\sim}{k}s} \hbar\omega_s(\underset{\sim}{k}) a^{\dagger}_{\underset{\sim}{k}s} a_{\underset{\sim}{k}s} \quad , \tag{2.1}$$

in terms of the annihilation ($a_{\underset{\sim}{k}s}$) and creation ($a^{\dagger}_{\underset{\sim}{k}s}$) operators for phonons in the mode $\underset{\sim}{k}s$. Here, $\underset{\sim}{k}$ and s denote the wave vectors and polarizations, respectively, and $\omega_s(\underset{\sim}{k})$ is the dispersion relation. The Hamiltonian for the bounded atom includes a kinetic energy and a potential

$$H_a = -\frac{\hbar}{2m}\frac{d^2}{dz^2} + V(z) \quad , \tag{2.2}$$

with m the mass of the atom. Eigenstates and eigenvalues of $H_a$ can be found easily for a variety of potentials V(z). An important example is the Morse potential, which models the atom-crystal binding quite accurately. Kinetic coupling between the atomic motion and the phonon field is assumed to be dominated by single-phonon interactions, for which the Hamiltonian reads

$$H_{ap} = -(\underset{\sim}{u}\cdot\underset{\sim}{e}_z)\frac{dV}{dz} \quad . \tag{2.3}$$

The operator $\underset{\sim}{u}$ is the displacement of the crystal atom which is closest to the adsorbate. Explicitly[11]

$$\underset{\sim}{u} = \sum_{\underset{\sim}{k}s} \left(\frac{\hbar v}{2MV\omega_s(\underset{\sim}{k})}\right)^{1/2} (a_{\underset{\sim}{k}s} + a^{\dagger}_{-\underset{\sim}{k}s})\underset{\sim}{e}_{\underset{\sim}{k}s} \quad , \tag{2.4}$$

with V and v the volumes of the crystal and a unit cell, respectively, M the mass of a crystal atom, and $\underset{\sim}{e}_{\underset{\sim}{k}s}$ the unit polarization vector of a phonon in the mode $\underset{\sim}{k}s$. The total Hamiltonian then becomes

$$H = H_p + H_a + H_{ap} \quad , \tag{2.5}$$

which determines the Liouvillian L according to Eq. (1.3). Then the density operator $\rho(t)$ of the system follows after solution of Eq. (1.4), and the spectral profile is obtained in evaluating expression (1.2).

## III. RESERVOIR CORRELATION FUNCTION

Due to the many degrees of freedom of the phonon field a direct diagonalization of the Hamiltonian is intractable, so that we have to resort to an approximation. The thermal-equilibrium density operator of the crystal at temperature T is

$$\bar{\rho}_p = (\mathrm{Tr}_p \exp(-H_p/k_B T))^{-1} \exp(-H_p/k_B T) \quad , \tag{3.1}$$

with $k_B$ Boltzmann's constant, and where $\mathrm{Tr}_p$ indicates a trace over the states of the phonon field only. Then the idea is that the large crystal can be regarded as a thermal reservoir, and that its state $\bar{\rho}_p$ is not affected by the presence of the single atom on the surface. The central quantity in standard relaxation theory[12] is the reservoir correlation function

$$f(\tau) = \hbar^{-2} \mathrm{Tr}_p (\underset{\sim}{u} \cdot \underset{\sim}{e}_z) e^{iL_p \tau} (\bar{\rho}_p \underset{\sim}{u} \cdot \underset{\sim}{e}_z) \quad , \tag{3.2}$$

with $L_p \sigma = [H_p, \sigma]/\hbar$. Relaxation constants are then expressed in the Fourier-Laplace transform of $f(\tau)$

$$\tilde{f}(\omega) = \int_0^\infty d\tau \; e^{i\omega\tau} f(\tau) \quad . \tag{3.3}$$

We shall adopt a Debye model for the dispersion relation, which implies

$$\omega_s(\underset{\sim}{k}) = c' k \, H(\omega_D - c' k) \quad , \tag{3.4}$$

in terms of the Debye frequency $\omega_D$, the speed of sound c', and the unit-step function H. Furthermore, we recall the relation

$$\frac{v}{c'^3} = \frac{6\pi^2}{\omega_D^3} \quad , \tag{3.5}$$

expressing that the cutoff frequency $\omega_D$ appears as a consequence of the finiteness of the volume v of a unit cell. Then it is an easy matter to compute $\tilde{f}(\omega)$, and we obtain[13]

$$\tilde{f}(\omega) = \xi \; g(\omega/\omega_D) \tag{3.6}$$

where the overall factor is given by

$$\xi = \frac{3\pi}{2\hbar M\omega_D^2} \quad . \tag{3.7}$$

The dimensionless function $g(\omega/\omega_D)$ which represents the $\omega$-dependence of $\tilde{f}(\omega)$ is found to be

$$g(z) = zH(z)H(1-z) - \frac{i}{\pi}\left(1+z\log\left|1-\frac{1}{z}\right|\right) + \frac{|z|}{e^{\gamma|z|}-1} H(1-|z|)$$

$$+ \frac{i}{\pi} P\int_0^1 dx \, \frac{1}{e^{\gamma x}-1} \times \frac{2zx}{z^2-x^2} \quad , \tag{3.8}$$

which depends parametrically on the temperature through

$$\gamma = \frac{\hbar\omega_D}{k_B T} \quad . \tag{3.9}$$

It will appear that the function g(z) incorporates the refinements of an absorption line in comparison with the standard Lorentzian. A plot of g(z) can be found in Ref. 13.

Two important properties of g(z), which can be deduced from Eq. (3.8), are

$$\text{Re } g(z) = 0 \qquad \text{for} \qquad |z| > 1 \quad , \tag{3.10}$$

$$g(-z) = g(z)^* \qquad \text{for} \qquad T \to \infty \quad . \tag{3.11}$$

Furthermore, g(z) goes to zero very fast for $|z| > 1$. This implies, in view of Eq. (3.3), that $f(\tau)$ has a time width of the order of $1/\omega_D$. In a previous paper[14] we pointed out that this feature prohibits the application of the Markov approximation in the derivation of an equation for the reduced adsorbate density operator $\rho_a(t)$, defined by

$$\rho_a(t) = \text{Tr}_p \rho(t) \quad . \tag{3.12}$$

If only a master equation for the populations of the vibrational states is of interest (as for instance in the desorption problem), then the finite time width of $f(\tau)$ does not have much significance, but for the evaluation of an absorption profile it is of paramount importance that the details of $\tilde{f}(\omega)$ are taken into consideration, as we shall show below.

## IV. DENSITY OPERATOR

Finite memory-time reservoir theory is a complicated mathematical tool, which can be applied to solve Eq. (1.4) for $\rho_a(t)$ and to evaluate steady-state quantum correlation functions, as they appear in Eq. (1.1). Recently we developed the

general theory,[15] and in this paper we apply the formalism to the computation of line shapes of adsorbates.

If we would be able to prepare the adsorbate at time zero in state $\rho_a(0)$, then its state for $t \geq 0$ is given by

$$\tilde{\rho}_a(\omega) = \frac{i}{\omega - L_a + i\Gamma(\omega)} \rho_a(0) \tag{4.1}$$

in the Fourier-Laplace domain. As usual, $L_a$ denotes the commutator with $H_a$, divided by $\hbar$. Coupling to the reservoir is embodied in the relaxation operator $\Gamma(\omega)$, defined by

$$\Gamma(\omega)\sigma_a = \mathrm{Tr}_p L_{ap} \frac{i}{\omega - L_a - L_p} L_{ap}(\sigma_a \bar{\rho}_p) \quad , \tag{4.2}$$

where $\sigma_a$ is an arbitrary adsorbate density operator, and $L_{ap}\rho = [H_{ap}, \rho]/\hbar$. The operator inversion on the right-hand side of Eq. (4.2) might seem awkward, but in Ref. 15 we have shown how to evaluate explicitly the matrix elements of $\Gamma(\omega)$.

For the steady-state line profile we only need the long-time solution of $\rho_a(t)$, which can be found from its Fourier-Laplace transform according to

$$\bar{\rho}_a = \lim_{t \to \infty} \rho_a(t) = \lim_{\omega \to 0} -i\omega \tilde{\rho}_a(\omega) \quad . \tag{4.3}$$

With Eq. (4.1) we then see that $\bar{\rho}_a$ is the solution of

$$(L_a - i\Gamma(0))\bar{\rho}_a = 0 \quad , \tag{4.4}$$

and of course the restictions $\bar{\rho}_a^\dagger = \bar{\rho}_a$, $\mathrm{Tr}_a \bar{\rho}_a = 1$ should be imposed.

In the Markov or zero memory-time approximation, the relaxation operator $\Gamma(\omega)$ acquires a frequency-independent value. It is the $\omega$-dependence of $\Gamma(\omega)$ which reflects the memory in the atom-crystal interaction. In the long-time limit the density operator is determined by $\Gamma(\omega)$ at $\omega = 0$, but this operator is not equal to its Markovian equivalent, as shown elsewhere.[14]

## V. ABSORPTION PROFILE

From Eq. (1.1) we notice that the absorption profile involves quantities as $\mathrm{Tr}\rho(t)\mu(t+\tau)\mu(t)$, which depend on two times, and their evaluation is correspondingly more complicated. In this section we derive a formal expression for $I(\omega)$.

First we introduce a two-time operator

$$D(\tau,t) = e^{-iL\tau}[\mu,\rho(t)] \tag{5.1}$$

and its Fourier-Laplace transform

$$\tilde{D}(\omega,t) = \int_0^\infty d\tau\ e^{i\omega\tau}\ D(\tau,t) \quad , \tag{5.2}$$

where the frequency dependence only refers to the first argument of $D(\tau,t)$. We remark that $D(\tau,t)$ is an operator in the entire atom plus crystal Hilbert space. Comparison of Eqs. (5.1) and (5.2) with Eq. (1.2) shows that the expression for $I(\omega)$ can be cast in the form

$$I(\omega) = I_L\left|\underset{\sim}{e}_z\cdot\underset{\sim}{\epsilon}_L\right|^2 \frac{\omega}{\epsilon_o\hbar c}\ \mathrm{Re}\lim_{t\to\infty}\mathrm{Tr}\mu\tilde{D}(\omega,t) \quad . \tag{5.3}$$

From the fact that the dipole operator $\mu$ acts only on adsorbate states, it follows that

$$\mathrm{Tr}\mu\tilde{D}(\omega,t) = \mathrm{Tr}_a\mu\tilde{D}_a(\omega,t) \quad , \tag{5.4}$$

with $\tilde{D}_a(\omega,t) = \mathrm{Tr}_p\tilde{D}(\omega,t)$, the reduced adsorbate operator.

Then we notice that $D(\tau,t)$ obeys

$$i\,\frac{d}{d\tau}\,D(\tau,t) = L\,D(\tau,t) \quad , \quad \tau \geq 0 \quad , \tag{5.5}$$

as is evident from its definition (5.1). Hence the $\tau$-dependence of $D(\tau,t)$ is governed by the same equation as the one which determines the time evolution of the density operator $\rho(t)$, Eq. (1.4). An important difference is that the initial value for Eq. (5.5) reads

$$D(0,t) = [\mu,\rho(t)] \quad , \tag{5.6}$$

in contrast to the equation for $\rho(t)$, where $\rho(0)$ can be chosen arbitrarily. The time regression of $D(\tau,t)$ on the interval $0 < \tau < \infty$ is identical to the time evolution of $\rho(t)$ on $0 < t < \infty$, and therefore it should be possible to express $\tilde{D}(\omega,t)$ in $\Gamma(\omega)$. Additionally, the initial value $D(0,t)$ depends explicitly on t, via $\rho(t)$, and in a finite memory-time theory this quantity will carry a memory to the time evolution of $\rho(t)$ in the recent past (times smaller than t). Contributions to the line profile which arise due to this mechanism will be referred to as initial correlations. It might seem that in the limit $t \to \infty$ we can replace $\rho(t)$ by $\bar{\rho}_a\bar{\rho}_p$, which would eliminate initial correlations. We shall show that this is not correct in general. In Ref. 15 we have developed a general

method for the evaluation of quantities of the form $\bar{D}_a(\omega, t\to\infty)$. If we apply that theory to the present situation, we find the formal expression for the absorption profile

$$I(\omega) = I_L |\underline{e}_z \cdot \underline{\varepsilon}_L|^2 \frac{\omega}{\epsilon_0 \hbar c} \mathrm{Re}\mathrm{Tr}_a L_X \frac{i}{\omega - L_a + i\Gamma(\omega)} (L_Y - iT(\omega))\bar{\rho}_a \quad , \tag{5.7}$$

where the Liouvillians $L_X$ and $L_Y$

$$L_X \sigma_a = \mu \sigma_a \quad , \tag{5.8}$$

$$L_Y \sigma_a = [\mu, \sigma_a] \quad , \tag{5.9}$$

are introduced in order to simplify the notation. Equation (5.7) is the most condensed and general expression for the absorption profile of an atomic bond on a crystal. We recognize the time regression operator $i/(\omega - L_a + i\Gamma(\omega))$, which is the same indeed as in Eq. (4.1). Initial correlations are accounted for by the frequency-dependent operator $T(\omega)$, which is explicitly

$$T(\omega)\sigma_a = \mathrm{Tr}_p L_{ap} \frac{i}{\omega - L_a - L_p} L_Y \frac{1}{i0^+ - L_a - L_p} L_{ap}(\sigma_a \bar{\rho}_p) \quad . \tag{5.10}$$

Furthermore, we notice that the series of Liouvillians under the trace in Eq. (5.7) act on the stead-state density operator $\bar{\rho}_a$ of the adsorbate, which can be obtained by solving Eq. (4.4).

## VI. MATRIX ELEMENTS OF $\Gamma(\omega)$ AND $T(\omega)$

Eigenvalues and eigenstates of the atomic-bond Hamiltonian $H_a$ from Eq. (2.2) are defined by

$$H_a|p\rangle = \hbar\omega_p|p\rangle \quad , \tag{6.1}$$

and due to the neglect of lateral motion the eigenvalues $\hbar\omega_p$ are non-degenerate. For realistic adsorbate systems there are approximately 25 bound states $|p\rangle$. In this section we expand the various Liouvillians onto the set $\{|p\rangle\}$ of adsorbate bound states.

Without coupling to the reservoir ($\Gamma(\omega) = 0$, $T(\omega) = 0$) the time regression operator is determined by the inverse of $\omega - L_a$, and with Eq. (6.1) we readily find

$$\langle p|((\omega - L_a)\sigma)|q\rangle = (\omega - \Delta_{pq})\langle p|\sigma|q\rangle \quad , \tag{6.2}$$

in terms of the level separations

$$\Delta_{pq} = \omega_p - \omega_q \quad . \tag{6.3}$$

Equation (6.2) relates the matrix elements of $(\omega - L_a)\sigma$ to the matrix elements of $\sigma$ for any adsorbate density operator $\sigma$, and thus Eq. (6.2) implies the matrix representation of the Liouvillian $\omega - L_a$.

The coupling between the crystal-atom motion and the adsorbate motion is established by the Hamiltonian $H_{ap}$ of Eq. (2.3), which has the adbond part

$$S = \frac{dV}{dz} \quad . \tag{6.4}$$

Matrix elements of this Hermitian operator will be denoted by

$$S_{pq} = \langle p|S|q\rangle = S^*_{qp} \quad . \tag{6.5}$$

Similarly we denote the matrix elements of $\mu$ by $\mu_{pq} = \langle p|\mu|q\rangle = \mu^*_{qp}$. In case of a Morse potential explicit expressions for $S_{pq}$ and $\mu_{pq}$ can be derived, with an integral due to Rosen.[16] Furthermore, we remark that for any potential $V(z)$ the diagonal matrix elements of its derivative vanish with respect to the eigenstates of $H_a$, e.g.,[17]

$$S_{pp} = 0 \quad . \tag{6.6}$$

The permanent dipole moments $\mu_{pp}$ of level $|p\rangle$, however, are finite in general.

With the methods of Ref. 15 we can evaluate the matrix elements of $\Gamma(\omega)$, as defined in Eq. (4.2), with respect to the basis set $\{|p\rangle\}$. The results is

$$\langle p|\{\Gamma(\omega)\sigma\}|q\rangle = \sum_{ab} \{\tilde{f}(\Delta_{qa}+\omega)S_{pa}S_{ab}\langle b|\sigma|q\rangle + \tilde{f}^*(\Delta_{pa}-\omega)S^*_{qa}S^*_{ab}\langle p|\sigma|b\rangle$$

$$- (\tilde{f}(\Delta_{bp}+\omega)S_{pa}S_{bq} + \tilde{f}^*(\Delta_{aq}-\omega)S^*_{qb}S^*_{ap})\langle a|\sigma|b\rangle\} \quad , \tag{6.7}$$

in terms of the matrix elements of S and the reservoir correlation function $\tilde{f}(\omega)$ from Section III. It appears that the frequency dependence of $\Gamma(\omega)$ enters as a shift of the level separations $\Delta_{pq}$ in the arguments of the correlation function.

The initial correlation operator $T(\omega)$ from Eq. (5.10) involves the inversion of two Liouvillians. After laborous computations we obtain

$$\langle p|(T(\omega)\sigma)|q\rangle = \sum_{abc} \frac{\mu_{bc}}{\Delta_{cb}+\omega} \{(\bar{f}(\Delta_{qc})-\bar{f}(\Delta_{qb}+\omega))S_{pb}S_{ca}\langle a|\sigma|q\rangle$$

$$- (\bar{f}^*(\Delta_{cq}) - \bar{f}^*(\Delta_{bq}-\omega))S_{pb}S_{aq}\langle c|\sigma|a\rangle$$

$$+ (\bar{f}(\Delta_{bp})-\bar{f}(\Delta_{cp}+\omega))S_{cq}S_{pa}\langle a|\sigma|b\rangle$$

$$- (\bar{f}^*(\Delta_{pb})-\bar{f}^*(\Delta_{pc}-\omega))S_{cq}S_{ab}\langle p|\sigma|a\rangle\}$$

$$- \sum_{abc} \frac{\mu_{pc}}{\Delta_{cp}+\omega} \{(\bar{f}(\Delta_{ac}) - \bar{f}(\Delta_{ap}+\omega))S_{aq}S_{cb}\langle b|\sigma|a\rangle$$

$$- (\bar{f}^*(\Delta_{ca}) - \bar{f}^*(\Delta_{pa}-\omega))S_{aq}S_{ba}\langle c|\sigma|b\rangle\}$$

$$- \sum_{abc} \frac{\mu_{bq}}{\Delta_{qb}+\omega} \{\bar{f}(\Delta_{ba}) - \bar{f}(\Delta_{qa}+\omega))S_{pa}S_{ac}\langle c|\sigma|b\rangle$$

$$- (\bar{f}^*(\Delta_{ab}) - \bar{f}^*(\Delta_{aq}-\omega))S_{pa}S_{cb}\langle a|\sigma|c\rangle\} \quad . \tag{6.8}$$

Again, the frequency depenence enters as a shift of the arguments in $\bar{f}(\Delta_{ab})$, but in addition overall factors $(\Delta_{ab}+\omega)^{-1}$ appear. Furthermore, we see that $T(\omega)$ depends on the matrix elements of the dipole operator.

## VII. TWO STATES

With the matrix representations of the various Liouvillians it is straightforward to evaluate $I(\omega)$ from Eq. (5.7) for any configuration of levels, or, for any potential $V(z)$. The profile $I(\omega)$ will exhibit many overlapping lines at the adsorbate resonances $\Delta_{ab}$. In order to disentangle the contributions to

$I(\omega)$ from the different transitions, and to elucidate the significance of initial correlations, we elaborate on the situation where the potential supports only two bound states. Let us denote these states by $|2\rangle$, $|1\rangle$, with the convention that $\omega_o \quad \omega_2 - \omega_1 > 0$. From Eq. (6.5) it follows that $S_{11} = S_{22} = 0$, and therefore the only non-vanishing matrix element of dV/dz is

$$S_o = \langle 1|S|2\rangle \quad , \tag{7.1}$$

which will be assumed to be real (as for a Morse potential).

From Eqs. (6.2) and (6.7) we find the matrix representation of $\omega - L_a + i\Gamma(\omega)$. On the basis $|2\rangle\langle 2|$, $|1\rangle\langle 1|$, $|2\rangle\langle 1|$, $|1\rangle\langle 2|$ this becomes

$$\omega - L_a + i\Gamma(\omega) =$$

$$\begin{pmatrix} \omega+ip(\omega) & -iq(\omega) & 0 & 0 \\ -ip(\omega) & \omega+iq(\omega) & 0 & 0 \\ 0 & 0 & \omega-\omega_o+i\eta(\omega) & -i\eta(\omega) \\ 0 & 0 & -i\eta(\omega) & \omega+\omega_o+i\eta(\omega) \end{pmatrix} \quad , \tag{7.2}$$

in terms of the parameter functions

$$p(\omega) = S_o^2(\bar{f}(\omega_o+\omega) + \bar{f}^*(\omega_o-\omega)) \quad , \tag{7.3}$$

$$q(\omega) = S_o^2(\bar{f}(-\omega_o+\omega) + \bar{f}^*(-\omega_o-\omega)) \quad , \tag{7.4}$$

$$\eta(\omega) = S_o^2(\bar{f}(\omega) + \bar{f}^*(-\omega)) \quad . \tag{7.5}$$

Inversion of the matrix (7.2) then yields the resolvent for $\tilde{\rho}_a(\omega)$, Eq. (4.1), and a Fourier-Laplace inverse of the result gives $\rho_a(t)$. Recalling the complicated frequency dependence of $\bar{f}(\omega)$, Section III, shows that an evaluation of $\rho_a(t)$ in the transient regime $0 < t < \infty$ is evidently impossible, unless numerical methods are applied.

Fortunately, the absorption profile depends only on the steady-state density operator $\rho_a(t = \infty)$, which obeys Eq. (4.4). With the matrix representation (7.2) this equation is easily solved, with result

$$\bar{\rho}_a = |2>n_2<2| + |1>n_1<1| \quad . \tag{7.6}$$

The steady-state level populations are

$$n_2 = \frac{q(0)}{p(0) + q(0)} \quad , \quad n_1 = \frac{p(0)}{p(0) + q(0)} \quad , \tag{7.7}$$

and Eq. (7.6) expresses that the coherence $<1|\bar{\rho}_a|2>$ vanishes, as usual in thermal equilibrium. From the definitions of p(0) and q(0) in Eqs. (7.3) and (7.4) we see that the factor $S_o^2$ drops out, and hence the populations are completely determined by the reservoir correlation function $\bar{f}(\omega)$, at the resonance $\omega = \omega_o$. With Eq. (3.6) we then find that the dependence on $\xi$ also disappears, so that $n_2$ and $n_1$ are determined by g(z), which has only the temperature as parameter. Explicitly,

$$n_2 = \frac{\mathrm{Re}\ g(-\omega_o/\omega_D)}{\mathrm{Re}(g(\omega_o/\omega_D) + g(-\omega_o/\omega_D))} \quad , \tag{7.8}$$

$$n_1 = \frac{\mathrm{Re}\ g(\omega_o/\omega_D)}{\mathrm{Re}(g(\omega_o/\omega_D) + g(-\omega_o/\omega_D))} \quad , \tag{7.9}$$

which contain only the real parts of the correlation functions. Then it follows from Eq. (3.10) that for $\omega_o > \omega_D$ the level populations are undetermined. This is a consequence of the fact that we restricted the atom-crystal interaction to single-phonon couplings.

## VIII. INITIAL CORRELATION OPERATOR

For a two-state system the initial correlation operator $T(\omega)$ is a $4 \times 4$ matrix, but its general representation, as it follows from Eq. (6.8), is still cumbersome. For the evaluation of the spectrum $I(\omega)$, however, we only need to know the result of its action on $\bar{\rho}_a$, as can be seen from Eq. (5.7). Since $\bar{\rho}_a$ has only two non-vanishing matrix elements, rather than four, this simplifies the situation. On the same basis as the representation (7.2), we then find

$$T(\omega)\bar{\rho}_a = \begin{pmatrix} x(\omega) \\ -x(\omega) \\ y(\omega) \\ -y(\omega) \end{pmatrix} , \tag{8.1}$$

with

$$x(\omega) = \frac{S_o^2}{\omega}(\mu_{11}-\mu_{22})$$

$$\times \{n_2(\bar{f}(\omega_o) - \bar{f}(\omega_o+\omega) - \bar{f}^*(\omega_o) + \bar{f}^*(\omega_o-\omega))$$

$$+ n_1(\bar{f}(-\omega_o) - \bar{f}(-\omega_o+\omega) - \bar{f}^*(-\omega_o) + \bar{f}^*(-\omega_o-\omega))\} , \tag{8.2}$$

$$y(\omega) = \frac{2S_o^2}{\omega_o^2-\omega^2}\,\mu_{21}$$

$$\times \{n_2((\bar{f}(\omega_o) - \bar{f}(\omega))(\omega_o+\omega) + (\bar{f}^*(\omega_o) - \bar{f}^*(-\omega))(\omega-\omega_o))$$

$$+ n_1((\bar{f}(-\omega_o) - \bar{f}(\omega))(\omega_o-\omega) + (\bar{f}^*(-\omega) - \bar{f}^*(-\omega_o))(\omega+\omega_o))\} \quad . \qquad (8.3)$$

The right-most factor in Eq. (5.7) is $(L_Y - iT(\omega))\bar{\rho}_a$, and therefore the relative significance of the initial correlations follows from a comparison of $T(\omega)\bar{\rho}_a$ with $L_Y\bar{\rho}_a$. With Eq. (5.9) we find

$$L_Y\bar{\rho}_a = \mu_{21}(n_1-n_2)\begin{pmatrix}0\\0\\1\\-1\end{pmatrix} \quad . \qquad (8.4)$$

The most important difference is that $L_Y\bar{\rho}_a$ only depends on the transition dipole matrix element $\mu_{21}$, whereas $T(\omega)$ acquires a contribution from the permanent dipole moments of the two levels (terms proportional to $x(\omega)$). Furthermore, $T(\omega)$ is proportional to $S_o^2$ (the strength of the interaction between the vibrating atom and the crystal), whereas $L_Y\bar{\rho}_a$ is independent of this parameter.

## IX. LINE SHAPE

An absorption profiel for a two-state system is called a line shape, because it singles out a specific transition of the vibrational bond. With the matrix representations of the previous sections we are now able to construct the line shape $I(\omega)$ by simple matrix operations. First we define the dimensionless line shape $\bar{I}(\omega)$ by

$$\bar{I}(\omega) = I(\omega)\{I_p(\epsilon_o\hbar c)^{-1}|\underline{e}_z\cdot\underline{\epsilon}_L|^2\mu_{21}^2\}^{-1} \quad , \tag{9.1}$$

in order to suppress irrelevant overall factors. Then we write $\bar{I}(\omega)$ as a sum of two contributions

$$\bar{I}(\omega) = \bar{I}(\omega)_{reg} + \bar{I}(\omega)_{in} \quad , \tag{9.2}$$

where $\bar{I}(\omega)_{reg}$ comes from the term $L_Y\bar{\rho}_a$ (regression part) and $\bar{I}(\omega)_{in}$ represent the initial-correlation contribution. It appears that $\bar{I}(\omega)$ can be expressed entirely in the parameters

$$a = \xi S_o^2 \quad , \tag{9.3}$$

$$m = \left(\frac{\mu_{22}-\mu_{11}}{\mu_{21}}\right)^2 \quad . \tag{9.4}$$

Here, a equals the half width at half maximum if the line would be approximated by a Lorentzian, and in the case $T = 0$, $\omega_o = \frac{1}{2}\omega_D$, and m measures the relative importance of the permanent dipole moments in comparison with the transition dipole moment. We finally obtain

$$\bar{I}(\omega)_{reg} = 2\omega\omega_o(n_1-n_2)\ \mathrm{Re}\ \frac{i}{D(\omega)_{coh}} \quad , \tag{9.5}$$

$$\bar{I}(\omega)_{in} = 2\omega\omega_o\ \mathrm{Re}\left\{\frac{i}{D(\omega)_{coh}}\,\phi(\omega) - \frac{m}{D(\omega)_{pop}}\,\psi(\omega)\right\} \quad , \tag{9.6}$$

in terms of the auxiliary functions

$$D(\omega)_{coh} = \omega^2 - \omega_o^2 + 2i\omega\eta(\omega) \quad , \tag{9.7}$$

$$D(\omega)_{pop} = \omega(\omega+i(p(\omega)+q(\omega))) \quad , \tag{9.8}$$

$$\phi(\omega) = -2ia\{n_2(\frac{g(\hat{\omega}_o)-g(\hat{\omega})}{\omega_o-\omega} + \frac{g^*(-\hat{\omega})-g^*(\hat{\omega}_o)}{\omega+\omega_o})$$

$$+ n_1(\frac{g(-\hat{\omega}_o)-g(\hat{\omega})}{\omega_o+\omega} - \frac{g^*(-\hat{\omega}_o)-g^*(-\hat{\omega})}{\omega_o-\omega})\} \quad , \tag{9.9}$$

$$\psi(\omega) = \frac{a}{2\omega_o}\{n_2(g(\hat{\omega}_o) - g(\hat{\omega}_o+\hat{\omega}) - g^*(\hat{\omega}_o) + g^*(\hat{\omega}_o-\hat{\omega}))$$

$$+ n_1(g(-\hat{\omega}_o) - g(-\hat{\omega}_o+\hat{\omega}) - g^*(-\hat{\omega}_o) + g^*(-\hat{\omega}_o-\hat{\omega}))\} \quad , \tag{9.10}$$

with $\hat{\omega} = \omega/\omega_D$ the frequency in units of $\omega_D$. The two $D(\omega)$ functions are the determinants of the two submatrices in Eq. (7.2), and the subscripts coh and pop refer to the subspaces of coherences ($|2\rangle\langle 1|$ , $|1\rangle\langle 2|$) and populations ($|2\rangle\langle 2|$ , $|1\rangle\langle 1|$), respectively. The above sequence of formulas determines the shape of a single absorption line, where $\omega_o$, a, $\gamma$ and m are the only arbitrary parameters (if we take $\omega_D$ as the frequency unit). For a specified potential V(z) we can express $\omega_o$, a and m in properties of this potential, and $\gamma$ is simply the temperature of the crystal.

Substitution of $D(\omega)_{coh}$ into Eq. (9.5) and removal of the real part yields

$$\bar{I}(\omega)_{reg} = \frac{4(n_1-n_2)\omega_o\omega^2 Re\eta(\omega)}{\{\omega_o^2-\omega^2+2\omega Im\eta(\omega)\}^2 + 4\omega^2(Re\eta(\omega))^2} \quad . \tag{9.11}$$

From the definition (7.5) of $\eta(\omega)$ and the property (3.10) of the reservoir correlation function, it follows that $\mathrm{Re}\eta(\omega) = 0$ for $\omega > \omega_D$, and consequently

$$\bar{I}(\omega)_{reg} = 0 \quad , \quad \text{for } \omega > \omega_D \quad . \tag{9.12}$$

Therefore, absorption for $\omega > \omega_D$ can only be a result of nonvanishing initial correlations.

## X. APPROXIMATIONS

Before we discuss the relevance of the finite memory-time in the time regression of dipole correlation functions and the importance of the inclusion of initial correlations, we summarize the results from earlier theories. A most obvious approximation would be the factorization

$$\lim_{t\to\infty} D(0,t) = [\mu,\bar{\rho}_a]\bar{\rho}_p \tag{10.1}$$

of the initial condition for the time-regression equation (5.5). It can be shown[15] that this implies $T(\omega) = 0$, and consequently $\bar{I}(\omega)_{in} = 0$, so that $\bar{I}(\omega)$ is approximated by $\bar{I}(\omega)_{reg}$.

A more rigorous simplification is the Markov approximation, in which any memory effect is discarded. First this implies the factorization (10.1), where a memory of $\rho(t)$ to its recent past is neglected. Secondly, we adopt a memoryless description of the time regression, which yields a frequency-independent relaxation operator $\Gamma_m$. The Markovian equivalent of the matrix (7.2) reads[18]

$$\omega - L_a + i\Gamma_m =$$

$$\begin{pmatrix} \omega+ip(0) & -iq(0) & 0 & 0 \\ -ip(0) & \omega+iq(0) & 0 & 0 \\ 0 & 0 & \omega-\omega_o+i\eta(\omega_o) & -i\eta^*(\omega_o) \\ 0 & 0 & -i\eta(\omega_o) & \omega+\omega_o+i\eta^*(\omega_o) \end{pmatrix} . \qquad (10.2)$$

In the left-top submatrix, the parameter functions $p(\omega)$ and $q(\omega)$ are replaced by their values at $\omega = 0$. Since the steady-state level populations $n_1$ and $n_2$ are determined by $\Gamma(0)$, we conclude that $n_1$ and $n_2$ are unaffected by this approximation. In the right-bottom submatrix the functions $\eta(\omega)$ are now evaluated at the resonance frequency $\omega_o$, rather than at the laser frequency $\omega$, and furthermore, the functions $\eta(\omega_o)$ in the fourth column are now complex-conjugated. In this approximation the line shape is found to be

$$\bar{I}(\omega)_m = \frac{4(n_1-n_2)\omega_o\omega^2 \mathrm{Re}\eta(\omega_o)}{\{\omega_o^2-\omega^2+2\omega_o \mathrm{Im}\eta(\omega_o)\}^2 + 4\omega^2(\mathrm{Re}\eta(\omega_o))^2} , \qquad (10.3)$$

which greatly resembles $\bar{I}(\omega)_{reg}$ from Eq. (9.11). The most important difference is that we now find $\mathrm{Re}\eta(\omega_o)$ in the numerator, rather than $\mathrm{Re}\eta(\omega)$, which implies that $\bar{I}(\omega)_m$ is finite for $\omega > \omega_D$.

In the most simple theory of relaxation (which leads to a master equation for the time evolution of the populations), we furthermore neglect any coupling between coherences and populations, and between coherences which evolve with a different frequency in a free evolution (no coupling to the reservoir). This approximation is usually called the secular approximation, and it is equivalent to the neglect of terms which oscillate fast on a time scale 1/a (Eq. (9.3)).

Then we replace the off-diagonal matrix elements $-i\eta(\omega_o)$ and $-i\eta^*(\omega_o)$ in Eq. (10.2) by zero, which gives for the line shape (s = secular)

$$\bar{I}(\omega)_s = \omega_o(n_1-n_2)\ \mathrm{Re}\ \frac{i}{\omega-\omega_o+i\eta(\omega_o)} \quad . \tag{10.4}$$

We obtain the standard Lorentzian, which has its maximum at $\omega = \omega_o + \mathrm{Im}\eta(\omega_o)$, and has a half-width at half-maximum equal to $\mathrm{Re}\eta(\omega_o)$.

It is easy to verify that the three approximations yield the same value for $\bar{I}(\omega)$ at the resonance frequency $\omega_o$, e.g.,

$$\bar{I}(\omega_o)_{reg} = \bar{I}(\omega_o)_m = \bar{I}(\omega_o)_s = \omega_o(n_1-n_2)\mathrm{Re}\ \frac{1}{\eta(\omega_o)} \quad . \tag{10.5}$$

Conversely, this implies that the successive refinements will have a major significance in the line wings only, which is illustrated in Fig. 1.

## XI. RESULTS

The line shape $\bar{I}(\omega)$ is composed of two contributions, which are drawn separately in Fig. 2 for a specific set of parameters. We notice that the initial correlation part is not small, and that it takes on both positive and negative values. A considerable increase of the absorption is found in the line center and the red wing, whereas the blue wing is only slightly modified, both in comparison with the line shape $\bar{I}(\omega)_{reg}$ (the best approximation so far). Due to the neglect of permanent dipole moments in this case (m = 0), we find a sharp edge at $\omega = \omega_D$, and a vanishing absorption for $\omega > \omega_D$. Of course, multiphonon processes would also give rise to absorption at $\omega > \omega_D$, but these contributions are assumed to be small. The cutoff can be understood from the fact that a photon absorption from the laser gives rise to a transition $|1\rangle \rightarrow |2\rangle$ of the adsorbate. Energy

conservation then implies that this process must be followed by a single-phonon emission into the crystal, under a decay $|2> \rightarrow |1>$ of the adsorbate bond. In a Debye model there are no phonon modes available for $\omega > \omega_D$, and therefore this process cannot occur.

A remarkable profile arises if we allow the atomic bond to have a permanent dipole moment ($m \neq 0$), which is illustrated in Fig. 3. For $\omega < \omega_D$ the value of m has hardly any significance, but above the cutoff frequency we now find a finite absorption if $m \neq 0$. We observe a peak at $\omega = \omega_o + \omega_D$, a smooth background for $\omega_D < \omega < \omega_o + \omega_D$. How can this be understood? First we remember that a low-intensity profile is a balance between the stimulated absorption and emission rates for single-photon transitions. Hence the phenomenon cannot be attributed to multiphoton processes. Then we recall that we restricted ourselves to a model of single-phonon interactions, which rules out multiphonon processes. Third, a positive $\bar{I}(\omega)$ corresponds to a photon absorption. A positive $\bar{I}(\omega)$ in the range $\omega > \omega_D > \omega_o$ can then only be found from the following energy-conserving process. Initially the adsorbate is in its lower state $|1>$. Absorption of a photon then excites the system to a virtual level with energy $\hbar\omega$ above the energy of state $|1>$, and subsequently this state decays to $|2>$, accompanied by the emission of a phonon with frequency $\omega - \omega_o$. The second transition can only occur if $\omega - \omega_o < \omega_D$, or $\omega < \omega_o + \omega_D$. This explains why $\bar{I}(\omega)$ vanishes identically for $\omega > \omega_o + \omega_D$, and can be finite for $\omega_D < \omega < \omega_o + \omega_D$.

## XII. CONCLUSIONS

We performed very detailed calculations on the optical spectral profile and line shapes of physisorbed atoms on the surface of a harmonic crystal. Coupling of the atomic motion to the phonon field of the crystal provides the relaxation mechanism for the evolution of the adsorbate vibrational states towards thermal

equilibrium. Since the amplitude correlation function of a substrate atom has a finite decay time, the time evolution of the reduced adsorbate density operator exhibits a memory effect. The absorption profile is determined by dipole correlation functions, depending on two times. We identified two different aspects of the memory, which were called regression and initial correlation. A general finite memory-time reservoir theory was applied for the evaluation of the line shape.

It appeared that the properties of the reservoir could be accounted for by a single dimensionless function g(z), which has only the dimensionless temperature $\gamma$ as parameter (apart from a scaling factor $\xi$). The other parameters of the line shape are the resonance frequency $\omega_o$ of the uncoupled adsorbate, the interaction-strength parameter a (frequency, related to line width), and the permanent-dipole parameter m (dimensionless). From our analytical expression for the line shape we showed that any absorption above the Debye frequency can only be a consequence of nonvanishing initial correlations (in the single-phonon approximation). It was exemplified (Fig. 3) that $\bar{I}(\omega)$ is finite indeed for $\omega > \omega_D$, provided that the transition has a permanent dipole moment (as is the case for a Morse potential).

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FIGURE CAPTIONS

Fig. 1. Secular (a), Markov (b) and regression (c) approximation of $\bar{I}(\omega)$ as a function of $\hat{\omega} = \omega/\omega_D$, and for $\omega_o = 0.65 \times \omega_D$ (dotted line), $a = 0.4 \times \omega_D$, $\gamma = 10$ (low temperature) and $m = 0$. Curve a is a Lorentzian around $\omega_o + \mathrm{Im}\eta(\omega_o)$, but for the present parameters the line shift is negligible ($\mathrm{Im}\eta(\omega_o) = -0.011$). As predicted in Eq. (10.5), the value of $\bar{I}(\omega_o)$ is the same for the three curves. The secular approximation gives a finite absorption for $\omega \leq 0$, whereas the improved results, curves b and c, give a vanishing absorption for $\omega \to 0$. In the blue wing, however, curves a and b remain finite, but the most refined theory gives $\bar{I}(\omega) = 0$ for $\omega > \omega_D$.

Fig. 2. Curve a and b are $\bar{I}(\omega)_{reg}$ and $\bar{I}(\omega)_{in}$, respectively, for the same parameters as in Fig. 1. Their sum, curve c, is $\bar{I}(\omega)$, which is calculated with the present theory. Comparison of curves a and c shows the significance of the improvement. Note also the considerable red shift of the line with respect to the resonance frequency $\omega_o$.

Fig. 3. Curve a is the same as curve c from Fig. 2 ($m = 0$), and for curve b we took the dipole-moment parameter m equal to 0.7. The nonzero value of m appears to have no importance at all for $\omega < \omega_D$, but for $\omega > \omega_D$ only the profile b remains finite. As pointed out in the text, the absorption for $\omega > \omega_D$ is entirely due to the initial correlations.

Fig. 1

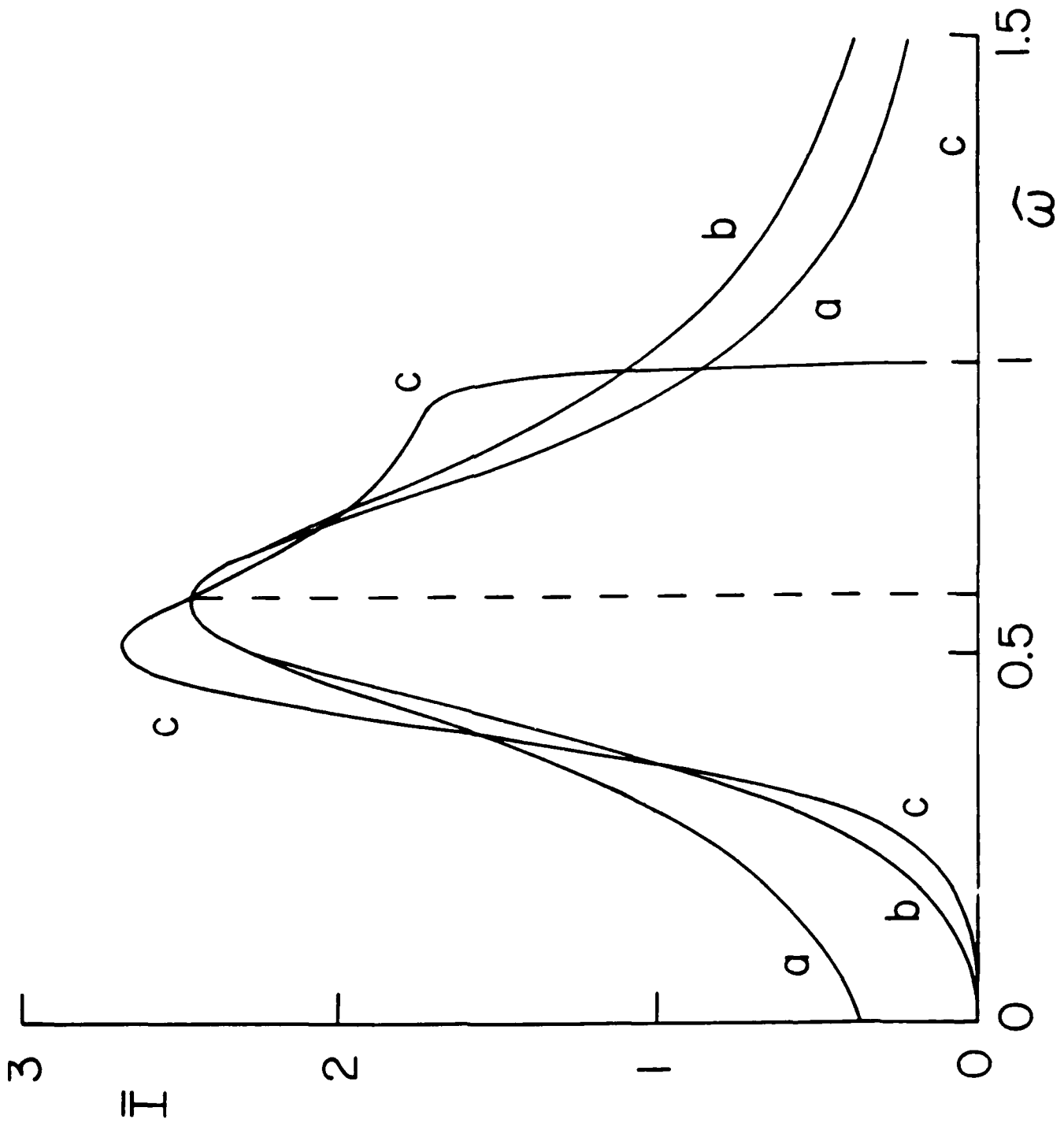


Fig. 2

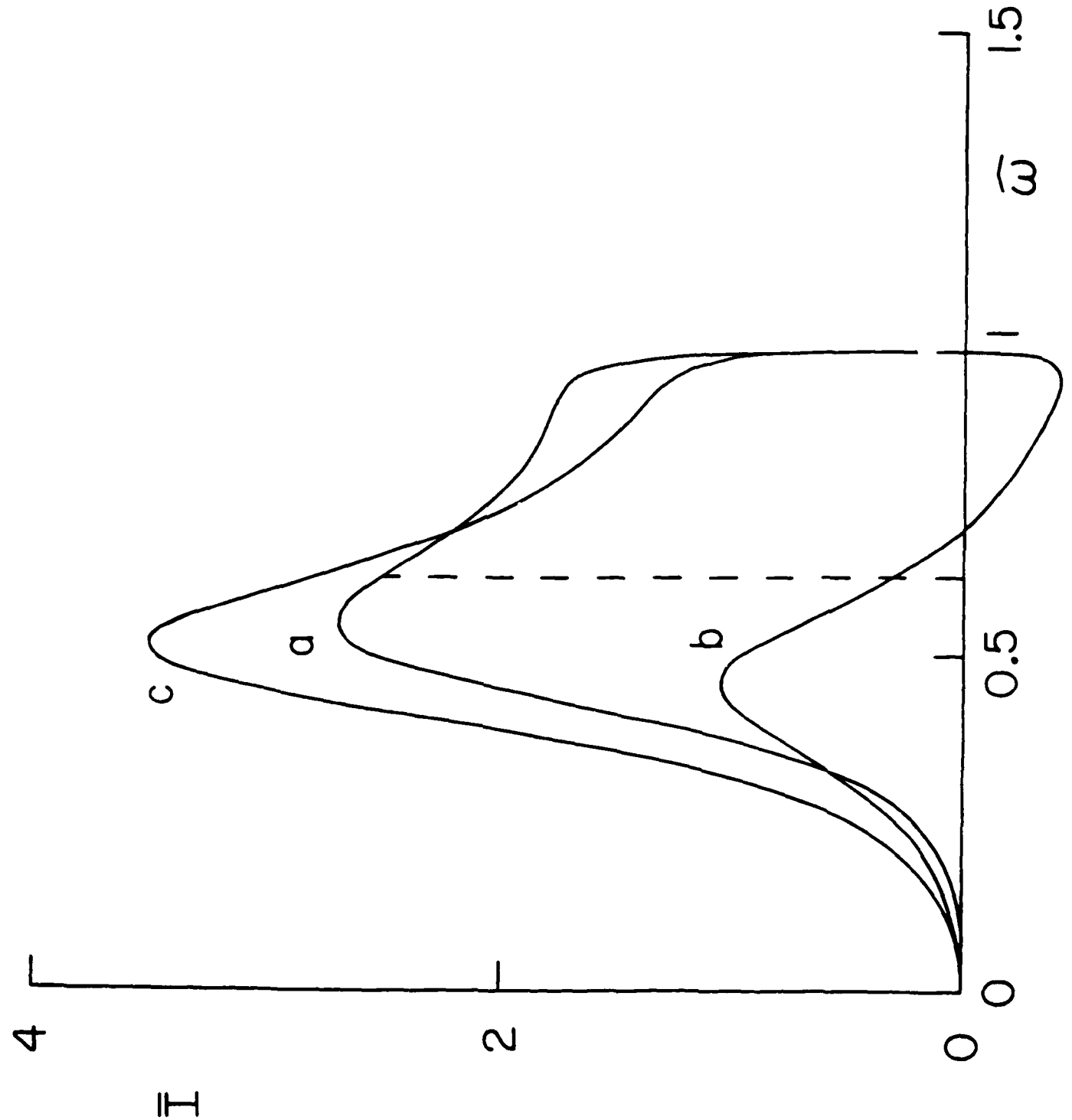
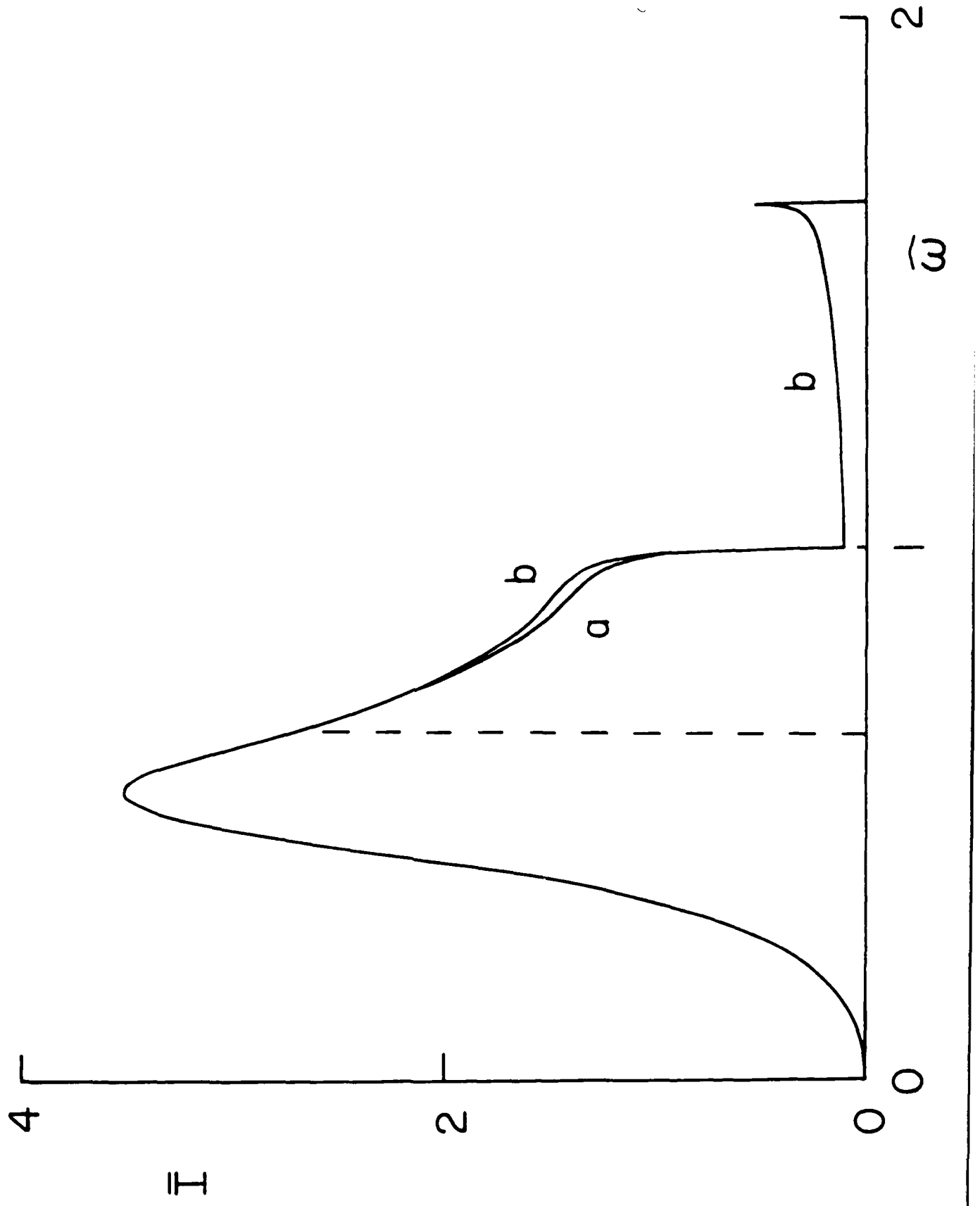


Fig. 3



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