University of Groningen

Pure dephasing of a vibrational adbond

van Smaalen, Sander; George, Thomas F.

Published in:
Journal of Chemical Physics

DOI:
[10.1063/1.453324](https://doi.org/10.1063/1.453324)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1987

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

van Smaalen, S., & George, T. F. (1987). Pure dephasing of a vibrational adbond. *Journal of Chemical Physics*, 87(12), 7307-7314. <https://doi.org/10.1063/1.453324>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Pure dephasing of a vibrational adbond

Sander van Smaalen, and Thomas F. George

Citation: [The Journal of Chemical Physics](#) **87**, 7307 (1987); doi: 10.1063/1.453324

View online: <https://doi.org/10.1063/1.453324>

View Table of Contents: <http://aip.scitation.org/toc/jcp/87/12>

Published by the [American Institute of Physics](#)

PHYSICS TODAY

WHITEPAPERS

ADVANCED LIGHT CURE ADHESIVES

Take a closer look at what these
environmentally friendly adhesive
systems can do

READ NOW

PRESENTED BY
MASTERBOND
ADHESIVES | SEALANTS | COATINGS

Pure dephasing of a vibrational adbond

Sander van Smaalen

Laboratory of Inorganic Chemistry, Materials Science Center, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Thomas F. George

Departments of Chemistry and Physics and Astronomy, 239 Fronczak Hall, State University of New York at Buffalo, Buffalo, New York 14260

(Received 2 April 1987; accepted 24 August 1987)

A theoretical study of the vibrational relaxation of the adbond between a physisorbed molecule and a crystalline substrate is presented. The bond between the admolecule and the substrate is described as a one-dimensional Morse oscillator. Using standard perturbation theory, expressions for the relaxation of the vibrational adbond due to its interaction with the substrate lattice vibrations are derived. Both energy relaxation and pure dephasing are considered. A numerical evaluation of the resulting expressions for the relaxation constants is given for a Debye spectrum for the phonons and for a surface phonon spectrum. The relative importance of pure dephasing and energy relaxation in determining the absorption linewidth is derived as a function of the fundamental frequency of the active mode.

I. INTRODUCTION

The effects of vibrational excitation of adsorbed molecules by an IR laser has been the subject of many experimental and theoretical studies over the past decade.¹ Primarily, the interest in laser excitation of an adspecies arose because of the prospect of influencing surface chemical reactions² and the prospect of selective laser-induced desorption without heating (i.e., damaging) the substrate.³ Later it was shown that substrate heating via the adsorbate of an otherwise transparent crystal might quite well be the most important process occurring.⁴⁻⁸

Besides using the laser to influence particular processes, it can also be used as an analytical tool. Best known is the measurement of the adsorption line profile and the linewidth. More modern examples are echo experiments and time-resolved transmission spectroscopy. With all these techniques some information can be obtained about the adbond or adsorbate and its interaction with the substrate.

Surface reactions are mainly dependent on the extent to which a particular vibrational mode can be excited and the speed with which relaxation occurs. Processes in which the populations of the vibrational levels are changed, due to an energy exchange with the reservoir, are generally called energy relaxation or T_1 processes.

The adsorption line shape is determined by the Fourier transform of the autocorrelation function of the dipole operator of the adbond. In particular, it involves the time evolution of the off-diagonal elements of the reduced density operator. In the most simplest approximation the adsorption line is a Lorentzian, with a width determined by two processes. The first, inhomogeneous broadening, arises due to inhomogeneities in the environment of the active molecules. For adsorbates, it can have contributions from differences in adsorption sites, roughness of the surface and other causes. Because the magnitude of these irregularities is not well known, inhomogeneous broadening is difficult to analyze in a first principles way. A phenomenological approach was recently given by Gortel *et al.*⁹

The second mechanism, homogeneous broadening, again consists of two parts: energy relaxation (or T_1 processes) and pure dephasing (or T_2^* processes). The latter is the collection of all relaxation terms which contribute to the time evolution of the off-diagonal elements of the density operator, but which do not change the populations. In the simplest approximation the total homogeneous width is given by

$$\frac{1}{T_2} = \frac{2}{T_1} + \frac{1}{T_2^*}. \quad (1.1)$$

Each of these three relaxation times can in principle be determined experimentally. For adsorbates, the energy relaxation time was determined for chemisorbed OH on silica by time-resolved transmission spectroscopy.^{10,11} The same experiments for the lower-frequency adbond mode of physisorbed systems have not been done yet. One problem is the lack of an appropriate laser for these frequencies. Echo experiments give the total dephasing time [Eq. (1.1)]. Together with the previous mentioned time resolved spectroscopy measurements, they can be used to determine the pure dephasing. Finally, simple measurement of the absorption linewidth gives the combination of homogeneous and inhomogeneous broadening. Combined with the result for T_1 and T_2 , it gives the contribution of inhomogeneous broadening.

The question we want to address in this paper is what the relative importance is of energy relaxation and pure dephasing, respectively, to the homogeneous linewidth.

Experimentally, we know from the T_1 measurements by Heilweil *et al.*^{10,11} and previous determinations of the total linewidth¹² that the latter is not due to T_1 processes only. Whether the discrepancy has to be attributed to pure dephasing or to inhomogeneous broadening, cannot be deduced from these experiments. Measurements of the total linewidth for adsorbates have also been done for hydrogen on wolfram,¹³ hydrogen on silicium,¹⁴ and for the internal mode vibration of CO on nickel.¹⁵ Theoretical arguments as well as detailed calculations have been given to show that

these linewidth's are mainly due to pure dephasing.¹⁴⁻¹⁷

All the above indicated experiments and theoretical considerations are about the excitation/relaxation of the vibrational states of a chemical bond, with typically a frequency of 2000 cm^{-1} . Experiments of relaxation of molecules embedded in the solid state suggest that the line broadening is mainly due to pure dephasing. There is no reason to believe this to be different for similar modes of adsorbates.¹⁶ The calculations in this paper will support these conclusions.

However, for physisorbed systems, the adbond mode will have a fundamental frequency in the region $50\text{--}500\text{ cm}^{-1}$, considerably lower than that of a chemical bond. For such low frequencies an experimental analysis is difficult to perform. We are only aware of the measurement of the linewidth of the adbond vibration of CO on nickel.¹⁸ Theoretical analysis has mainly been restricted to energy relaxation.¹⁹⁻²¹ The question we want to answer in this paper is whether for these low-frequency modes pure dephasing still is the most important relaxation process. It will be shown that under certain conditions, dependent on both the adbond and on the details of the reservoir spectrum T_1 and T_2^* processes can become of equal importance, and energy relaxation can even become the more important one.

Following earlier work,¹⁹⁻²² in the next section we shall present a theory of vibrational relaxation of an adbond, with the lattice vibrations of the substrate as a reservoir. However, we shall retain the terms describing pure dephasing, and we will derive explicit expressions for T_1 and T_2^* . In Secs. IV and V, we shall evaluate these expressions numerically as a function of the fundamental frequency of the adbond vibrational mode. Finally, in Sec. VI, conclusions will be presented.

II. RELAXATION CONSTANTS

Consider a system of an atom or molecule physisorbed on a crystal. It is assumed that the bond between the adsorbate and substrate can be described as a one-dimensional anharmonic oscillator; only vibrations perpendicular to the surface are considered. Excitation of the adbond can be accomplished by laser light in resonance with one pair of vibrational states. Relaxation occurs through the dynamic coupling of the adbond with the lattice vibrations of the substrate. The latter is assumed to act as a thermal bath or reservoir.²³

The potential energy between the adatom and the substrate is given by a one-dimensional potential between the instantaneous position of the adatom z and of the nearest surface atom u_z (Fig. 1),

$$V = V(z - z_0 - u_z). \quad (2.1)$$

The origin is chosen as the average position of the surface atom. The average of the instantaneous displacement u_z is therefore zero. It is assumed that u_z is entirely determined by the lattice vibrations of the substrate (reservoir condition). Then the vibrations of the adatom are described by the Hamiltonian

$$H_a = -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + \langle V(z - z_0 - u_z) \rangle, \quad (2.2)$$

FIG. 1. Schematic drawing of an adsorbed atom at position z above a surface. The nearest surface atom has a time-dependent displacement u perpendicular to the surface.

where m is the mass of the adatom and $\langle \dots \rangle$ denotes the average over the substrate lattice vibrations. The interaction between the adbond and the lattice vibrations is given by

$$H^I = V(z - z_0 - u_z) - \langle V(z - z_0 - u_z) \rangle. \quad (2.3)$$

Furthermore, we denote by H_p and ρ_p^0 , respectively, the Hamiltonian and thermal equilibrium density operator of the harmonic lattice vibrations of the substrate. The eigenfunctions and eigenvalues of the adbond Hamiltonian are defined by

$$H_a |n\rangle = \hbar\omega_n |n\rangle. \quad (2.4)$$

The complete system has the Hamiltonian

$$H = H_0 + H^I = H_a + H_p + H^I. \quad (2.5)$$

The state of this system is described by a density operator ρ , which obeys the equation of motion,

$$\frac{d\rho}{dt} = \frac{i}{\hbar} [H, \rho]. \quad (2.6)$$

Then the adbond can be described by its reduced density operator

$$\sigma(t) = \text{Tr}_p \{ \rho(t) \}, \quad (2.7)$$

where Tr_p denotes the trace over the phonon variables.

Following earlier work,¹⁹⁻²² an approximate expression for the reduced density operator of the adbond can be derived as

$$\begin{aligned} \frac{d\sigma(t)}{dt} = & \frac{1}{i\hbar} [H_a, \sigma(t)] - \frac{1}{\hbar^2} \text{Tr}_p \\ & \times \int_0^\infty dt' [H^I, [\tilde{H}^I(-t'), \rho_p^0 \sigma(t)]] \end{aligned} \quad (2.8)$$

with

$$\tilde{H}^I(-t') = \exp\left(-\frac{i}{\hbar} H_0 t'\right) H^I \exp\left(\frac{i}{\hbar} H_0 t'\right). \quad (2.9)$$

The first term of Eq. (2.8) defines the free evolution of the adbond while, the second term gives the relaxation. A further approximation can be made by neglecting terms on the right-hand side of Eq. (2.8) which oscillate with a frequency different from the free evolution of $\sigma(t)$. Within this approximation, usually denoted as the random-phase approximation (RPA), we obtain for the time derivative of the matrix elements of $\sigma(t)$ between eigenstates of H_a ,

$$\frac{d\sigma_n(t)}{dt} = - \sum_n \Gamma_{nn}^{kk} \sigma_k(t) \quad (2.10)$$

and

$$\frac{d\sigma_{nm}(t)}{dt} = -i\omega_{nm} \sigma_{nm}(t) - \Gamma_{nm}^{nm} \sigma_{nm}(t), \quad (2.11)$$

where $\sigma_{nm}(t) = \langle n | \sigma(t) | m \rangle$, $\sigma_n = \sigma_{nn}$ and $\omega_{nm} = \omega_n$

— ω_m . Let us define

$$a_{nk} = \frac{1}{\hbar^2} \int_0^\infty dt' \{ \langle \tilde{H}_{nk}^I(0) \tilde{H}_{kn}^I(-t') \rangle + \langle \tilde{H}_{nk}^I(-t') \tilde{H}_{kn}^I(0) \rangle \}, \quad (2.12a)$$

$$A_n = \sum_{k \neq n} \frac{1}{\hbar^2} \int_0^\infty dt' \langle \tilde{H}_{nk}^I(0) \tilde{H}_{kn}^I(-t') \rangle, \quad (2.12b)$$

$$F_{nm} = \frac{1}{\hbar^2} \int_0^\infty dt' \{ \langle \tilde{H}_{nn}^I(0) \tilde{H}_{nn}^I(-t') \rangle + \langle \tilde{H}_{mm}^I(-t') \tilde{H}_{mm}^I(0) \rangle - \langle \tilde{H}_{mm}^I(0) \tilde{H}_{nn}^I(-t') \rangle - \langle \tilde{H}_{mm}^I(-t') \tilde{H}_{nn}^I(0) \rangle \}, \quad (2.12c)$$

where $\langle \hat{Q} \rangle = \text{Tr}_p \{ \rho_p^0 \hat{Q} \}$ is the average of $\hat{Q}$ over the phonon reservoir. Then the relaxation constants are given by

$$\Gamma_{nn}^{kk} = -a_{kn} \quad \text{for } n \neq k, \quad (2.13a)$$

$$\Gamma_{nn}^{nn} = (A_n + A_n^*), \quad (2.13b)$$

$$\Gamma_{nm}^{nm} = \text{Re}\{A_n + A_n^* + F_{nm}\}. \quad (2.13c)$$

In the RPA, pure dephasing is given by the diagonal elements of the interaction Hamiltonian. From Eqs. (2.10)–(2.13) it follows that indeed they do not contribute to the time-evolution of the populations. They do influence the coherences, with a rate constant F_{nm} and the added energy relaxation rate constants A_n . A condition for pure dephasing to occur is that F_{nm} is nonzero. As can be deduced from Eq. (2.12c), this means that

$$\tilde{H}_{nn}^I \neq \tilde{H}_{mm}^I \quad \text{for } n \neq m. \quad (2.14)$$

For example, it can be shown that Eq. (2.14) is not fulfilled when the complete system is described by harmonic oscillators.³⁰ An expression similar to Eq. (2.12c) was given by Burns *et al.*²⁴

In the rest of the paper we shall use the Morse potential for the interaction potential $V(z - z_0 - u_z)$,

$$V_m(z) = D\{\exp(-2\alpha z) - 2\exp(-\alpha z)\}. \quad (2.15)$$

The reasons are that a Morse potential gives a fair description of the van der Waals bond, and that it is to a large extent amenable to analytic evaluation of the expressions. The lattice vibrations are described as a set of harmonic oscillators. Then, following the work of Efrima *et al.*,¹⁹ the correlation functions of the interaction Hamiltonian can be evaluated:

$$\begin{aligned} \langle \tilde{H}_{nm}^I(0) \tilde{H}_{kl}^I(-t') \rangle &= D^2 e^{-2\alpha^2 \langle u^2 \rangle} e^{-i\omega_k t'} \\ &\times B_{nm}^{(2)} B_{kl}^{(2)} \{ \exp(4\alpha^2 \langle u(0)u(-t') \rangle) - 1 \} \\ &+ 4B_{nm}^{(1)} B_{kl}^{(1)} \{ \exp(\alpha^2 \langle u(0)u(-t') \rangle) - 1 \} \\ &- 2B_{nm}^{(2)} B_{kl}^{(1)} \{ \exp(2\alpha^2 \langle u(0)u(-t') \rangle) - 1 \} \\ &- 2B_{nm}^{(1)} B_{kl}^{(2)} \{ \exp(2\alpha^2 \langle u(0)u(-t') \rangle) - 1 \}, \end{aligned} \quad (2.16)$$

where the displacement autocorrelation function is purely determined by the reservoir. $B_{nm}^{(j)}$ is the matrix element of $e^{-j\alpha(z-z_0)}$ between the eigenstates of H_a (see the Appendix).

III. MULTIPHONON CONTRIBUTIONS

The Markov approximation implies a separation of the system in two parts, the reservoir and the subsystem of interest (adbond). Changes in the state of the complete system then have the interpretation of something changing in the adbond accompanied by a change in the reservoir. Within the RPA the time evolution of the reduced density operator of the adbond has a very simple interpretation [Eqs. (2.10) and (2.11)]. Any change of $\sigma(t)$ is accompanied by the creation or destruction of one or more phonons of the substrate.

For the Morse potential and a harmonic lattice, the n -phonon contribution to the relaxation constant is given by the combination of all terms involving the n th power of the autocorrelation function of the surface atom displacement. Each of these terms is singled out easily by expanding the exponential functions in Eq. (2.16). For a Debye spectrum for the phonons, the importance of multiphonon contributions was analyzed by Jedrzejek *et al.*,^{25,26} and up to $n = 2$ by Gortel *et al.*²⁷ These authors considered only the master equation [Eqs. (2.10) and (2.15)], and therefore analyzed only the contributions of the multiphonon contributions to the transition rate constants a_{nk} [Eq. (2.12a)]. It was found that for transitions between vibrational states involving energies less than the Debye frequency, the single-phonon terms dominate. For transitions of energy higher than this Debye frequency, multiphonon terms are also important.

Especially for the motion perpendicular to the surface, i.e., u_z the Debye spectrum is a poor presentation of the density of states (DOS) of the phonon spectrum.²⁸ Recently, the transition rate constants for the vibrational adbond of CO physisorbed on Ni were calculated by Volokitin *et al.*²⁹ using the more realistic surface phonon spectrum due to Black.²⁸ The values they obtained were much lower and in better agreement with experiment than those calculated with the Debye spectrum. Furthermore, it was found that multiphonon terms of high order still give a significant contribution to the rate constants.

Energy relaxation involves a change in energy of the adbond. The transition from level n to level m is accompanied by the creation/annihilation of a phonon, which is depicted in Fig. 2. Multiphonon transitions can be represented by adding one or more virtual adbond levels. Pure dephasing

FIG. 2. The single-phonon and two-phonon contributions to the energy relaxation for the transition from level n to level m , with $\omega_n > \omega_m$. Each arrow denotes the absorption (upwards) or emission (downwards) of a phonon. The energy of each phonon follows from the length of the arrow. The dotted lines indicate virtual adbond levels. I is the single-phonon process, and there are four two-phonon processes indicated by II–V. For the downward transition $n \rightarrow m$, process III is not possible, and for the reverse upward transition, process II does not contribute.

[Eq. (12c)] occurs due to processes in which the populations of the adbond do not change. These can be interpreted as virtual excitations of the adbond, which then returns to its original state. Obviously the minimum number of phonons necessary for such a virtual excitation is two (Fig. 3). Therefore, pure dephasing has only contributions from two-phonon and higher multiphonon processes.

From the notion that pure dephasing is at least a two-phonon process, and from the previous discussion, one expects that pure dephasing will become an important relaxation process whenever the multiphonon contributions to the transition rate constants are important. The analysis in the rest of the paper will support this hypothesis to a large extent, although it will also be found that the intrinsic differences between pure dephasing and energy relaxation do influence their relative importance.

Let us denote the phonon density of states by $\rho(\omega)$, with

$$\int_0^\infty d\omega \rho(\omega) = 1. \quad (3.1)$$

Then, the displacement autocorrelation function is given by

$$\begin{aligned} \langle u(0)u(-t') \rangle &= \frac{\hbar}{2M} \int_0^\infty d\omega \frac{\rho(\omega)}{\omega} \\ &\times \{ [\bar{n}(\omega) + 1] e^{-i\omega t'} + \bar{n}(\omega) e^{i\omega t'} \} \end{aligned} \quad (3.2)$$

with

$$\bar{n}(\omega) = [\exp(\hbar\omega/k_B T) - 1]^{-1}, \quad (3.3)$$

which gives the number of phonons with frequency ω as a function of the temperature T ; k_B is the Boltzmann constant.

With these definitions, the two-phonon contribution to the pure dephasing rate constant becomes for a Morse poten-

FIG. 3. Multiphonon contributions to pure dephasing. Depicted are both two-phonon processes and one three-phonon process. For the meaning of the symbols see Fig. 2. Note that pure dephasing terms involve only one (real) level of the adbond, and that single-phonon processes are impossible.

tial [Eq. (2.12c)],

$$\begin{aligned} \text{Re}(F_{nm}) &= D^2 e^{-2\alpha^2 \langle u^2 \rangle} \left(\frac{m-n}{k} \right)^2 \frac{4\pi}{\hbar^2} \left(\frac{\alpha^2 \hbar}{2M} \right)^2 \\ &\times \int_0^\infty d\omega \left(\frac{\rho(\omega)}{\omega} \right)^2 \bar{n}(\omega) [\bar{n}(\omega) + 1], \end{aligned} \quad (3.4)$$

where D , α , and k are defined in the Appendix. The imaginary part of the rate constants determines a level shift and will not be considered here.

The energy relaxation contribution to the absorption linewidth of a transition $n \rightarrow m$ is given by $\text{Re}(A_n + A_m^*) = \text{Re}(A_n^* + A_m)$ [Eq. (2.13c)]. $\text{Re}(A_n)$ can be written as [Eq. (2.12)]

$$\text{Re}(A_n) = \frac{1}{2} \sum_{l \neq n} a_{nl}. \quad (3.5)$$

For the latter rate constants the one-phonon contribution is

$$\begin{aligned} a_{nm}^{(1)} &= D^2 e^{-2\alpha^2 \langle u^2 \rangle} (B_{nm}^{(1)})^2 (n-m)^2 \left(1 - \frac{n+m+1}{2k'} \right)^2 \\ &\times \frac{4\pi}{\hbar^2} \left(\frac{\alpha^2 \hbar}{2M} \right) \frac{\rho(|\omega_{nm}|)}{\omega_{nm}} [\bar{n}(\omega_{nm}) + 1]. \end{aligned} \quad (3.6)$$

The two-phonon energy relaxation is given by

$$\begin{aligned} a_{nm}^{(2)} &= D^2 e^{-2\alpha^2 \langle u^2 \rangle} (B_{nm}^{(1)})^2 \left\{ 2 + 8 \left| \frac{n(2k-n-1) - m(2k-m-1)}{2k} \right| \right. \\ &\quad \left. + 8 \left| \frac{n(2k-n-1) - m(2k-m-1)}{2k} \right|^2 \right\} \frac{\pi}{\hbar^2} \left(\frac{\alpha^2 \hbar}{2M} \right)^2 \\ &\times \int_0^\infty d\omega \left(\frac{\rho(\omega)}{\omega} \frac{\rho(-\omega_{mn}-\omega)}{(-\omega_{mn}-\omega)} [\bar{n}(\omega) + 1] [\bar{n}(-\omega_{mn}-\omega) + 1] \right. \\ &\quad + \frac{\rho(\omega)}{\omega} \frac{\rho(\omega_{mn}-\omega)}{(\omega_{mn}-\omega)} \bar{n}(\omega) \bar{n}(\omega_{mn}-\omega) + \frac{\rho(\omega)}{\omega} \frac{\rho(\omega_{mn}+\omega)}{(\omega_{mn}+\omega)} [\bar{n}(\omega) + 1] \bar{n}(\omega_{mn}+\omega) \\ &\quad \left. + \frac{\rho(\omega)}{\omega} \frac{\rho(\omega-\omega_{mn})}{(\omega-\omega_{mn})} \bar{n}(\omega) [\bar{n}(\omega-\omega_{mn}) + 1] \right). \end{aligned} \quad (3.7)$$

The four terms in Eq. (3.7) correspond to the four two-phonon processes denoted by II-V in Fig. 2.

From Eqs. (3.6) and (3.7) we can conclude that the energy relaxation constants strongly depend on the details of the phonon spectrum used. In particular, the single-phonon term is directly proportional to the DOS at the transition

frequency. The pure dephasing constant is less dependent on the phonon spectrum because it involves an integral over the square of $\rho(\omega)$. In the next two sections we shall evaluate the expressions Eqs. (3.4), (3.6), and (3.7) for, respectively, a Debye spectrum and a DOS representing a surface phonon spectrum.

IV. DEBYE SPECTRUM

For a Debye spectrum we have

$$\rho(\omega) = \begin{cases} 3\omega^2/\omega_D^3 & \omega \leq \omega_D \\ 0 & \omega > \omega_D \end{cases} \quad (4.1)$$

Let us define the integral

$$I_D(y) = \int_0^y dx \frac{x^2 e^x}{(e^x - 1)^2} \quad (4.2)$$

Then the two-phonon contribution to the pure dephasing for a Debye phonon spectrum can be written as

$$\begin{aligned} \text{Re}(F_{nm}) &= D^2 e^{-2\alpha^2 \langle u^2 \rangle} \left(\frac{m-n}{k} \right)^2 \left(\frac{\alpha^2}{M} \right) \\ &\times 9\pi \frac{1}{\omega_D^3} \left(\frac{k_B T}{\hbar \omega_D} \right)^3 I_D \left(\frac{\hbar \omega_D}{k_B T} \right). \end{aligned} \quad (4.3)$$

It is easy to show that $I_D(y) = \text{constant} \approx 3.3$ for $(y \rightarrow \infty)$. Then we obtain $\text{Re}(F_{nm}) = O(T^3)$ for $T \rightarrow 0$.

Substitution of Eq. (4.1) in Eq. (3.6) gives for the single-phonon energy relaxation

$$\begin{aligned} a_{nm}^{(1)} &= D^2 e^{-2\alpha^2 \langle u^2 \rangle} (B_{nm}^{(1)})^2 (n-m)^2 \left(1 - \frac{n+m+1}{2k} \right) \\ &\times \left(\frac{\alpha^2}{M} \right) \frac{6\pi}{\hbar \omega_D^3} \omega_{nm} [1 + n(\omega_{nm})] \end{aligned} \quad (4.4)$$

for $\omega \leq \omega_D$. For $\omega > \omega_D$ we have $a_{nm}^{(1)} = 0$. The two-phonon contribution is [Eq. (3.7)]

$$\begin{aligned} a_{nm}^{(2)} &= D^2 e^{-2\alpha^2 \langle u^2 \rangle} (B_{nm}^{(1)})^2 \left(\frac{\alpha^2}{M} \right)^2 \frac{9\pi}{4\omega_D^3} E \left(\frac{\hbar \omega_D}{k_B T}, \frac{\hbar \omega_{nm}}{k_B T} \right) \\ &\times \left\{ 2 + 8 \left| \frac{n(2k-n-1) - m(2k-m-1)}{2k} \right| \right. \\ &\left. + 8 \left(\frac{n(2k-n-1) - m(2k-m-1)}{2k} \right)^2 \right\}. \end{aligned} \quad (4.5)$$

The expression for the integral E depends on the values of ω_D and ω_{nm} . For $|\omega_{nm}| > 2\omega_D$ we have

$$E(x_D; x_{nm}) = 0, \quad (4.6a)$$

For $2\omega_D \geq \omega_{nm} \geq \omega_D$,

$$\begin{aligned} E(x_D; x_{nm}) &= \int_{(x_{nm}-x_D)}^{x_D} dx x(x_{nm}-x) \frac{e^{x_{nm}}}{(e^x - 1)(e^{x_{nm}-x} - 1)}, \end{aligned} \quad (4.6b)$$

and for $\omega_D \geq \omega_{nm} \geq 0$,

$$\begin{aligned} E(x_D; x_{nm}) &= \int_0^{x_{nm}} dx x(x_{nm}-x) \frac{e^{x_{nm}}}{(e^x - 1)(e^{x_{nm}-x} - 1)} \\ &+ 2 \int_{x_{nm}}^{x_D} dx x(x-x_{nm}) \frac{e^x}{(e^x - 1)(e^{x-x_{nm}} - 1)}, \end{aligned} \quad (4.6c)$$

with similar expressions for $\omega_{nm} < 0$.

For $T \rightarrow 0$, $x_D^{-3} E(x_D, x_{nm})$ converges to a limiting value. This means that at low temperature all n -phonon contributions to the energy relaxation remain finite. Therefore, in the

limit $T \rightarrow 0$, energy relaxation will always dominate pure dephasing.

We are interested in an estimate of the different contributions to the total relaxation rate Eq. (2.13c). In order to do this we shall use values for the parameters which represent realistic systems like Ar/KCl and CO/Ni. That is, we use a number of adbond levels $k = 25$. Different systems, i.e., with a different fundamental frequency, are then represented by choosing different values for both α and D , such that $k = 25$. The values for μ and M are taken in accordance with the system CO/Cu.²⁶ In the low-temperature limit, $x_D < 1$, the energy relaxation rate constant $\text{Re}(A_1 + A_0)$ for the $1 \rightarrow 0$ transition can be approximated by $\frac{1}{2}a_{10}$. Also, for the $1 \rightarrow 0$ transition ($n, m \ll k$), the n, m -dependent factors have a simple approximate expression. With these substitutions and approximations, the relaxation constants become

$$F_{10}^{(2)} = D^2 e^{-2\alpha^2 \langle u^2 \rangle} \left(\frac{1}{k} \right)^2 \frac{9\pi}{\omega_D^3} \left(\frac{\alpha^2}{M} \right)^2 \frac{3.3}{x_D^3}, \quad (4.7a)$$

$$\begin{aligned} \text{Re}(A_1^{(1)} + A_0^{(1)}) &\approx \frac{1}{2} a_{10}^{(1)} = D^2 e^{-2\alpha^2 \langle u^2 \rangle} \frac{1}{2k} \frac{6\pi}{\omega_D} \frac{\alpha^2}{M} \frac{\omega_{10}}{\hbar}. \end{aligned} \quad (4.7b)$$

For $2\omega_D \geq \omega_{10} \geq \omega_D$ we have

$$\begin{aligned} \text{Re}(A_1^{(2)} + A_0^{(2)}) &\approx \frac{1}{2} a_{10}^{(2)} = D^2 e^{-2\alpha^2 \langle u^2 \rangle} \frac{1}{2k} \frac{9\pi}{\omega_D^3} \left(\frac{\alpha^2}{M} \right)^2 \frac{9}{8} \\ &\times \left[\left(\frac{x_{10}}{x_D} \right)^2 \left(2 - \frac{x_{10}}{x_D} \right) - \frac{1}{3} \left(2 - \frac{x_{10}}{x_D} \right)^3 \right] \end{aligned} \quad (4.7c)$$

and for $\omega_D \geq \omega_{10} \geq \omega$,

$$\begin{aligned} \text{Re}(A_1^{(2)} + A_0^{(2)}) &= D^2 e^{-2\alpha^2 \langle u^2 \rangle} \frac{1}{2k} \frac{9\pi}{\omega_D^3} \left(\frac{\alpha^2}{M} \right)^2 \frac{9}{12} \left(\frac{X_{10}}{X_d} \right)^3. \end{aligned} \quad (4.7d)$$

It is noted that for $\omega_{10} > \omega_D$, $a_{10}^{(1)} = 0$, and that for $\omega_{10} > 2\omega_D$, $a_{10}^{(2)} = 0$, but that the pure dephasing constant is only weakly dependent on the fundamental frequency.

From Eqs. (4.7) the following estimates of the relative importance of the various contributions at low temperature can be made for $0 < \omega_{10} < \omega_D$:

$$\frac{F_{10}^{(2)}}{\frac{1}{2} a_{10}^{(1)}} \neq \frac{1}{30} \frac{1}{x_D^3}, \quad (4.8a)$$

$$\frac{F_{10}^{(2)}}{\frac{1}{2} a_{10}^{(2)}} = \frac{1}{3} \frac{1}{x_{nm}^{(3)}}. \quad (4.8b)$$

For $\omega_D < \omega_{10} < 2\omega_D$, the single-phonon energy relaxation is identically zero, but Eq. (4.8b) remains valid.

From Eqs. (4.8), it follows that, for a Debye spectrum, the pure dephasing rate constant is much smaller than the single-phonon energy relaxation, and of about the same magnitude as the two-phonon energy relaxation. The two-phonon contribution to the energy relaxation is much smaller than the single-phonon term, and the three-phonon term will again be an order of magnitude smaller than the

two-phonon term. Therefore, when compared to three-phonon or higher-order terms in the energy relaxation rate constant, the pure dephasing will be the most important relaxation process.

V. SURFACE PHONON SPECTRUM

In the model used in this paper, the coupling between the adbond and the phonon reservoir is mediated by the motion of the surface atom perpendicular to the surface. Especially for this direction of the motion, the theoretical calculations of Black²⁸ for a Ni(111) surface show a large difference in the spectrum of the surface phonons compared to that of the bulk phonons. The most prominent characteristic of this spectrum is that the DOS consists of a single peak at frequency $\omega_0 = 24.2$ THz. Besides this peak, there is some extra den-

sity in the tails between frequencies of 60 and 300 cm^{-1} (as visible in the picture given by Black). We want to evaluate the expressions for the relaxation constants for such a phonon density of states. In order to do this, we approximate the calculated spectrum by the simple analytical form

$$\rho(\omega) = (\ln 2/2\omega_0^2\Delta) \omega^2 \exp(-|\omega_0 - \omega| \ln 2/\Delta), \quad (5.1)$$

where $\Delta = 1.45$ THz $= \frac{1}{2}$ FWHM. The ω^2 dependence is chosen in order to obtain the correct limiting behavior for $\omega \rightarrow 0$; the exponential gives a reasonable representation of the spectrum calculated by Black.

Again, we consider the $1 \rightarrow 0$ transition in the low-temperature limit. Substitution of the DOS [Eq. (5.1)] into Eqs. (3.4), (3.6), and (3.7) gives the required rate constants. After rearrangement they become

$$\frac{1}{\omega_0} \text{Re}(a_{nm}^{(1)}) = \left(\frac{\omega_{nm}}{\omega_0}\right)^4 \left(\frac{\pi}{M}\right) \left(\frac{\omega_0}{\Delta}\right) \exp\left(-\ln 2 \left|1 - \frac{\omega_{nm}}{\omega_0}\right| \frac{\omega_0}{\Delta}\right) \times 2\pi \ln 2 (B_{nm}^{(1)})^2 \left(1 - \frac{n+m+1}{2k}\right)^2 \frac{k^4}{[|n-m|(2k-n-m-1)]^3}, \quad (5.2)$$

$$\frac{1}{\omega_0} \text{Re}(a_{nm}^2) = \left(\frac{\omega_{nm}}{\omega_0}\right)^4 \left(\frac{\pi}{M}\right)^2 \left(\frac{\omega_0}{\Delta}\right)^2 I_S \left(\frac{\omega_{nm}}{\omega_0}\right) (B_{nm}^{(1)})^2 \frac{1}{2} \pi [\ln(2)]^2 \left(\frac{k}{|n-m|(2k-n-m-1)}\right)^2 \times \left\{1 + 2 \left(\frac{k}{|n-m|(2k-n-m-1)}\right) + \left(\frac{k}{|n-m|(2k-n-m-1)}\right)^2\right\}, \quad (5.3)$$

$$\frac{1}{\omega_0} \text{Re}(F_{nm}) = \left(\frac{\omega_{nm}}{\omega_0}\right)^4 \left(\frac{\mu}{M}\right)^2 \left(\frac{\omega_0}{\Delta}\right)^2 \pi (\ln 2)^2 \frac{k^2}{(2k-m-n-1)^4 (m-n)^2} \times \int_0^\infty dz z^2 \exp\left(-\frac{2 \ln 2 |1 - z\omega_0|}{\Delta}\right) \left[\exp\left(\frac{z\hbar\omega_0}{k_B T}\right) - 1\right]^{-1} - \left[1 - \exp\left(-\frac{z\hbar\omega_0}{k_B T}\right)\right]^{-1}, \quad (5.4)$$

where $z = \omega/\omega_0$, and $I_S(\omega_{nm}/\omega_0)$ is given by

$$I_S(x) = \frac{1}{6} x^3 \exp[-\ln 2 (2-x)\omega_0/\Delta] \quad (5.5a)$$

for $x \leq 1$, and

$$I_S(x) = \left\{2x \left(\frac{\Delta}{\omega_0 2 \ln 2}\right)^2 - 4 \left(\frac{\Delta}{\omega_0 2 \ln 2}\right)^3\right\} \exp\left[\frac{-\ln(2)x\omega_0}{\Delta}\right] + \left\{2(x-1) \left(\frac{\Delta}{\omega_0 2 \ln 2}\right) - 4 \left(\frac{\Delta}{\omega_0 2 \ln 2}\right)^3 - 2|x-2| \left(\frac{\Delta}{\omega_0 2 \ln 2}\right)^2 \pm \left(\frac{2}{3} - x + \frac{1}{6} x^3\right)\right\} \exp\left(\frac{-\ln 2 |2-x|\omega_0}{\Delta}\right) \quad (5.5b)$$

for $x \geq 1$. The plus sign applies for $x \geq 2$ and the minus sign for $1 \leq x \leq 2$ ($x = \omega_{nm}/\omega_0$). It follows that the energy relaxation rate constants are, in this low-temperature approximation, independent of the temperature. Pure dephasing is strongly temperature dependent, through the exponential functions.

The Morse potential parameters representing some real physisorbed systems are such that the number of levels k is more or less constant.²⁶ To compare the energy relaxation and pure dephasing, we plot in Fig. 4 the relaxation constants as a function of the fundamental frequency ω_{10} of the vibrational adbond. The constants defining the adbond (k, μ, M) are the same as those used in Sec. IV.

All quantities are given in units of the characteristic fre-

quency ω_0 of the phonon spectrum. We see that, as expected, the n -phonon energy relaxation rate constant has a maximum at frequency $n\omega_0$. For $\omega_{10} \neq \omega_0$ it decreases exponentially with $|\omega_{10} - \omega_0|$. The pure dephasing constant is much less dependent on the transition frequency. The largest effect is due to the increase of $d^2 V(z - z_0)/dz^2|_{z=z_0}$ with increasing ω_{10} , and not to a resonance effect as for the energy relaxation.

It is to be expected that the maxima in $a_{10}^{(n)}$ will gradually decrease with increasing n . Then, for transition frequencies larger than $n\omega_0$ with n on the order 3 or 4, pure dephasing will become a more important process than energy relaxation. A notable difference with the Debye spectrum is that

FIG. 4. The logarithm of the various n -phonon contributions to the relaxation constants vs the fundamental frequency of the vibration. The low-temperature approximation is used [Eqs. (5.2)–(5.4)]. All quantities are given in units of the characteristic frequency of the surface phonon spectrum. The pure dephasing $F_{10}^{(2)}$ is plotted for two values of the temperature. Note that the low-temperature approximation does not make sense for $\omega_{10}/\omega_0 < k_B T / \hbar \omega_0$.

the single-phonon and two-phonon contributions to the energy relaxation are still larger than the pure dephasing even if $\omega_{10} > n\omega_0$ ($n = 1, 2$, respectively). For the Debye spectrum the n -phonon term is exactly zero for $\omega_{10} > n\omega_D$. This is due to $\rho(\omega)$ now being nonzero for $\omega > \omega_0$. Therefore, the precise behavior of $a_{10}^{(n)}$ for $\omega_{10} > n\omega_0$ depends strongly on the exact form of $\rho(\omega)$. Since the difference between the calculated spectrum²⁸ and a Lorentzian peak (used here) or, for example, a Gaussian function cannot be seen for $\omega \geq 2\omega_0$, the values of the n -phonon relaxation constants beyond $\omega_{10} = (n + 1)\omega_0$ are not reliable, and no conclusion should be drawn regarding their behavior at those frequencies.

VI. DISCUSSION

It is well known that pure dephasing is a relaxation process which is due to anharmonicities in the system. In the model used in this paper, anharmonicity is introduced in the active mode (vibrational adbond), and its magnitude is fixed by the choice of a Morse potential to represent this bond. Another approach can be to take into account the anharmonicity in lattice vibrations.³⁰ We assume that this can be neglected with respect to the effect of the adbond anharmonicity. Therefore, it should be kept in mind that the calculations presented here and elsewhere^{17,31} give values for the pure dephasing constants which can be strongly model dependent. Energy relaxation is already present in a harmonic system and does not change dramatically upon introducing anharmonicity.

It is found that for low temperature the pure dephasing constant goes to zero as T^3 ($T \rightarrow 0$) [Eqs. (4.7) and (5.4); see also Ref. 17]. Apparently this result does not depend on the details of the phonon spectrum. It does depend on the kind of relaxation process studied, i.e., on the form of the coupling between the active mode and lattice vibrations. This can be compared to the results of Skinner and Hsu who find a T^7 dependence for the relaxation of the electronic excitation of a molecule embedded in a crystal.³¹

The calculations presented in Secs. III–V clearly show that resonance is an important effect in determining the magnitude of the energy relaxation rate constants [Eqs. (3.6) and (3.7)]. The n -phonon contribution is large whenever all phonons involved are of a frequency at which the DOS is large. For the Debye spectrum this means that the n -phonon term has a maximum for the transition frequency smaller but of the order $n\omega_D$. For $\omega_{10} > n\omega_D$, that term is identically zero. For the surface phonon spectrum, each n -phonon term in the rate constant has a maximum at $n\omega_0$ and decreases strongly for $|\omega_{10} - n\omega_0| \neq 0$. The results also show that on going to a higher multiphonon process, the maximum value of the relaxation constant decreases with increasing n (see also Refs. 25–27).

The lowest-order contribution to the pure dephasing is a two-phonon process. Because it involves only a single adbond level, the resonance effect is now that the largest contribution to the relaxation constant comes from virtual excitations with frequency ω_0 . Since there are no other restrictions on the position of the virtual level, the relaxation constant will hardly depend on the fundamental frequency. Its magnitude should therefore be of the order of the two-phonon energy relaxation term at its maximum. On the other hand, it will roughly be lower by a factor of $\bar{n}(\omega_0)$ than this term, because it also involves the absorption of a phonon. It is this factor which introduces the strong temperature dependence of the pure dephasing (Fig. 4).

This analysis shows that at high temperatures, where $\bar{n}(\omega_D)$ or $\bar{n}(\omega_0) > 1$, the two-phonon pure dephasing term will be of the order of the maximum value of the two-phonon energy relaxation term. For lower temperature [$\bar{n}(\omega_0)$, $\bar{n}(\omega_D) < 1$], the two-phonon pure dephasing will be somewhat smaller. Then, one expects pure dephasing to be the most important relaxation process when the transition frequency of the active mode is much larger than the characteristic frequency (ω_0 or ω_D) of the phonon reservoir. This is in accordance with the result of Gadzuk and Luntz¹⁶ and Hutchinson and George,¹⁷ who considered the relaxation of an internal vibrational mode of an adsorbed molecule. Although the coupling mechanism is different there, the conclusions are also valid for the relaxation of an electronic excitation.³¹ However, for the low-frequency adbond vibrations of a physisorbed molecule, the energy relaxation is mainly due to single-phonon and/or two-phonon contributions. Then energy relaxation will give the largest contribution.

ACKNOWLEDGMENTS

This research was supported by the Office of Naval Research and the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract No.

F49620-86-C-0009. The United States Government is authorized to reproduce and distribute reprints notwithstanding any copyright notation hereon. The research of S. van Smaalen has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences.

APPENDIX: MATRIX ELEMENT $B_{nm}^{(j)}$

The Morse potential is given by

$$V_m(z - z_0) = D \{ \exp[-2\alpha(z - z_0)] - 2 \exp[-\alpha(z - z_0)] \}. \quad (\text{A1})$$

Averaging $V(z - z_0 - u)$ over the lattice vibrations (i.e., over u) results again in a Morse potential,

$$\langle V_m(z - z_0 - u) \rangle = V'_m(z - z'_0), \quad (\text{A2})$$

with renormalized parameters

$$\begin{aligned} D' &= D \exp(-\alpha^2 \langle u^2 \rangle), \\ \alpha' &= \alpha, \\ z'_0 &= z_0 + \frac{3}{2} \alpha \langle u^2 \rangle. \end{aligned} \quad (\text{A3})$$

The adbond Hamiltonian is defined with the renormalized Morse potential as potential energy. Let us denote its discrete eigenfunctions by $|n\rangle$. Then the corresponding eigenvalues are

$$E_n = -\frac{\hbar^2 \alpha'^2}{2\mu} (k - n + \frac{1}{2})^2, \quad (\text{A4})$$

where

$$k = \frac{(2\mu D')^{1/2}}{\hbar \alpha}. \quad (\text{A5})$$

The integer part of k represents the number of bound states. From Eq. (A4) one directly obtains the fundamental frequency

$$\omega_{10} = \frac{\hbar^2 \alpha'^2}{\mu} (k - 1). \quad (\text{A6})$$

The following matrix elements can be calculated as^{19,32}

$$\begin{aligned} B_{nm}^{(1)} &= \langle n | e^{-\alpha(z - z'_0)} | m \rangle \\ &= \frac{1}{2k} \left\{ \frac{(2k - 2n - 1)(2k - 2m - 1)}{n!m! \Gamma(2k - n) \Gamma(2k - m)} \right\}^{1/2} \\ &\quad \times \Gamma(n + 1) \Gamma(2k - m), \end{aligned} \quad (\text{A7})$$

$$\begin{aligned} B_{nm}^{(2)} &= \langle n | \exp(-2\alpha(z - z'_0)) | m \rangle \\ &= B_{nm}^{(1)} \left(\frac{n(2k - n - 1) - m(2k - m - 1) + 2k}{2k} \right), \end{aligned} \quad (\text{A8})$$

both for $n > (m - 1)$.

We need the matrix elements of the interaction Hamiltonian [Eq. (2.12)]. Substitution of the explicit form of H^I [Eq. (2.3)] shows that this involves matrix elements of $\exp[-j\alpha(z - z_0)]$, for $j = 1, 2$. That is, we need matrix elements of both terms of the Morse potential [Eq. (A1)] between the eigenstates of the renormalized Morse potential [Eqs. (A2) and (A3)]. We note that $\exp[-j\alpha(z - z_0)] = \exp[-j\alpha(z - z'_0)] \exp[-j\alpha(z'_0 - z_0)]$, and that

$(z'_0 - z_0) = \frac{3}{2} \alpha \langle u^2 \rangle$ is constant. Then from Eqs. (A7) and (A8) we immediately obtain the result

$$B_{nm}^{(j)} = \langle n | \exp(-j\alpha(z - z_0)) | m \rangle = e^{-j\frac{3}{2}\alpha^2 \langle u^2 \rangle} B_{nm}^{(j)} \quad (\text{A9})$$

with $j = 1, 2$.

This result was used in the evaluation of Eq. (2.16). We stress that the correction so obtained [Eq. (A9) vs Eqs. (A7) and (A8)] is of the same order of magnitude as the corrections obtained directly from using the renormalized Morse potential instead of $V_m(z - z_0)$ itself in H_a .

¹T. J. Chuang, Surf. Sci. Rep. 3, 1 (1983).

²M. S. Djidjoev, R. V. Khokhlov, A. V. Kiselev, V. I. Lygin, V. A. Namiot, A. I. Osipov, V. I. Panchenko, and B. I. Provotorov, in *Tunable Lasers and Applications*, edited by A. Moordadian, T. Jaeger, and P. Stokseth (Springer, Berlin, 1976), p. 100ff.

³M. S. Slutsky and T. F. George, Chem. Phys. Lett. 57, 474 (1978).

⁴J. Heidberg, H. Stein, and E. Riehl, Phys. Rev. Lett. 49, 666 (1982).

⁵I. Hussla, H. Seki, T. J. Chuang, Z. W. Gortel, H. J. Kreuzer, and P. Piercy, Phys. Rev. B 32, 3489 (1985).

⁶K. Veeken, P. A. M. van der Heide, L. M. ten Dam, A. R. de Vroomen, and J. Reuss, Surf. Sci. 166, 1 (1986).

⁷Z. W. Gortel, H. J. Kreuzer, P. Piercy, and R. Teshima, Phys. Rev. B 28, 2119 (1983).

⁸S. van Smaalen, H. F. Arnoldus, and T. F. George, Phys. Rev. B 35, 1142 (1987).

⁹Z. W. Gortel, P. Piercy, R. Teshima, and H. J. Kreuzer, Surf. Sci. 165, L12 (1986).

¹⁰E. J. Heilweil, M. P. Casassa, R. R. Cavanagh, and J. C. Stephenson, J. Chem. Phys. 82, 5216 (1985).

¹¹E. J. Heilweil, M. P. Casassa, R. R. Cavanagh, and J. C. Stephenson, J. Chem. Phys. 85, 5004 (1986).

¹²H. P. Boehm and H. Knözinger, in *Catalysis: Science and Technology*, edited by J. R. Anderson and M. Boudart (Springer, Berlin, 1983).

¹³Y. J. Chabal and A. J. Sievers, Phys. Rev. B 24, 2921 (1981).

¹⁴J. C. Tully, Y. J. Chabal, K. Raghavachari, J. M. Bowman, and R. R. Lucchese, Phys. Rev. B 31, 1184 (1985).

¹⁵B. N. J. Persson and R. Ryberg, Phys. Rev. Lett. 54, 2119 (1985).

¹⁶J. W. Gadzuk and A. C. Luntz, Surf. Sci. 144, 429 (1984).

¹⁷M. Hutchinson and T. F. George, Chem. Phys. Lett. 124, 211 (1986).

¹⁸S. Chiang, R. G. Tobin, P. L. Richards, and P. A. Thiel, Phys. Rev. Lett. 52, 648 (1984).

¹⁹S. Efrima, C. Jedrzejek, K. F. Freed, E. Hood, and H. Metiu, J. Chem. Phys. 79, 2436 (1983).

²⁰B. Fain and S. H. Lin, Surf. Sci. 147, 497 (1984).

²¹H. F. Arnoldus, S. van Smaalen, and T. F. George, Phys. Rev. B 34, 6902 (1986).

²²Z. W. Gortel, H. J. Kreuzer, P. Piercy, and R. Teshima, Phys. Rev. B 27, 5066 (1983).

²³W. H. Louisell, *Quantum Statistical Properties of Radiation* (Wiley, New York, 1973).

²⁴M. J. Burns, W. K. Liu, and A. H. Zewail, in *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems*, Vol. 4, edited by V. M. Agranovich and R. M. Hochstrasser, Modern Problems in Condensed Matter Sciences (North-Holland, Amsterdam, 1983), p. 305ff.

²⁵C. Jedrzejek, K. F. Freed, S. Efrima, and H. Metiu, Chem. Phys. Lett. 74, 227 (1981).

²⁶E. Hood, C. Jedrzejek, K. F. Freed, and H. Metiu, J. Chem. Phys. 81, 3277 (1984).

²⁷Z. W. Gortel, H. J. Kreuzer, and R. Teshima, Phys. Rev. B 22, 512 (1980).

²⁸J. E. Black, Surf. Sci. 105, 59 (1981).

²⁹A. I. Volokitin, D. M. Braun, and V. M. Yakovlev, Surf. Sci. 172, 31 (1986).

³⁰W. H. Hesselink and D. A. Wiersma in Ref. 24, p. 249.

³¹J. L. Skinner and D. Hsu, Adv. Chem. Phys. 65, 1 (1986).

³²J. A. Beswick and J. Jortner, J. Chem. Phys. 68, 2277 (1978).