PHYSICAL REVIEW B VOLUME 44, NUMBER 24 15 DECEMBER 1991-II

Inelastic resonance scattering, tunneling, and desorption

J. W. Gadzuk
National Institute of Standards and Technology, Gaithersburg, Maryland 20899

(Received 28 May 1991)

Excitation of a localized oscillator or phonon due to transient charge transfer into and out of electronic states linearly coupled to the oscillator is considered within several different contexts. Specifically, the basic physical content of the mechanisms responsible for phonon broadening in core-level spectroscopy, intramolecular vibrational excitation in resonant electron scattering, phonon excitation in resonant electron tunneling through quantum-well heterostructures, and hot-electron-induced resonant desorption is shown to be similar. Existing exact solutions to the scattering and tunneling problems are here adapted to resonant desorption and numerical consequences—such as excitation and desorption probabilities and translational energy distribution—are obtained. These results and insights are considered in the light of a semiclassical wave-packet-dynamics model, which previously had been developed to account for observed nonthermal, laser-induced desorption in the system NO/Pt(111).

I. INTRODUCTION

The abstract problem of localized-oscillator or boson-field excitation due to a transient driving force provided by electronic transitions, within atomic, molecular, or solid-state systems, has been of great interest in many different areas of physics. Without being exhaustive, one would naturally include such phenomena as optical-absorption line shapes,[1] core-level spectroscopies,[2] intramolecular vibrational sidebands in photoionization[3] and in resonance electron scattering,[4] resonance Raman scattering,[5] stimulated desorption,[6] and inelastic resonant tunneling in quantum-well structures.[7,8]

Recent work on various aspects of resonant electron-induced desorption of atoms and molecules from surfaces has supported the idea that excitation of the adparticle-surface bond, even beyond the bond-breaking level of dissociation or desorption, can be due to the transient forces associated with the resonance state. In particular, experiments showing monochromatized-electron-beam-induced desorption of atomic oxygen from Pd (Ref. 9) and also laser-excited hot-electron-induced desorption of NO from Pt(111) (Ref. 10) have inspired theoretical modeling[11,12] which emphasizes the consequences of temporary ($\sim 10^{-15}$ s) negative (adsorbed) ions on enhanced desorption characteristics.

In nanostructure physics,[13] a problem of intense current interest is inelastic electron tunneling through a quantum well where some sort of electron-phonon coupling exists, but only within the well. The interaction of the tunneling electron with (dispersionless) phonons or localized vibrational modes produces resonant transmission sidebands, as observed in the I-V characteristics of GaAs/$\mathrm{Al}_x\mathrm{Ga}_{1-x}$As resonant-tunneling structures.[14] A number of theoretical models have been constructed[7,8] that are logical extensions of the transient displaced oscillator models developed in spectroscopy[1-3] and resonance scattering.[4]

The objectives of the present paper are manyfold. First we call attention to some inherent parallels between gas-phase resonant electron-molecule scattering, resonant electron-induced desorption, and inelastic resonant electron tunneling in solid-state junctions, at least with regards to the excitation of localized oscillators or bosons. From a broad perspective all of these phenomena involve energy transfer to an oscillator subjected to a transient driving force associated with electron transitions between continuum and localized states or resonances. Selected past treatments of this problem are offered, using as illustrative examples of increasing complexity, the boson excitation experienced in core-level spectroscopies,[2] resonant electron-molecule scattering,[4] and finally, inelastic tunneling in quantum wells.[7,8] Upon making contact with the historical precedents, a recent solvable model of resonant tunneling is adapted to the phenomenon of desorption. To achieve these ends, the paper is structured as follows. Section II presents key physical features of the models used here, ultimately to discuss desorption. First, the wave-packet-dynamics model of resonance stimulated desorption[11,12] is presented. Next the displaced-harmonic-oscillator model for resonant tunneling is put forth and commentary is given on their basic equivalences. The theory is developed in Sec. III, starting first with oscillator excitation in transient core-level events, then in electron scattering, resonant tunneling, and finally in situations leading to desorption. Numerical consequences of the model recently featured by Wingreen, Jacobson, and Wilkins,[7] as might be applicable to desorption, are dealt with in Sec. IV and final discussion is offered in Sec. V.

II. MODELS

A. Wave-packet desorption model

The electronic structure of chemisorbed NO, as relevant to bonding, is characterized by broadened levels as shown in Fig. 1(a). Here it will be assumed that the

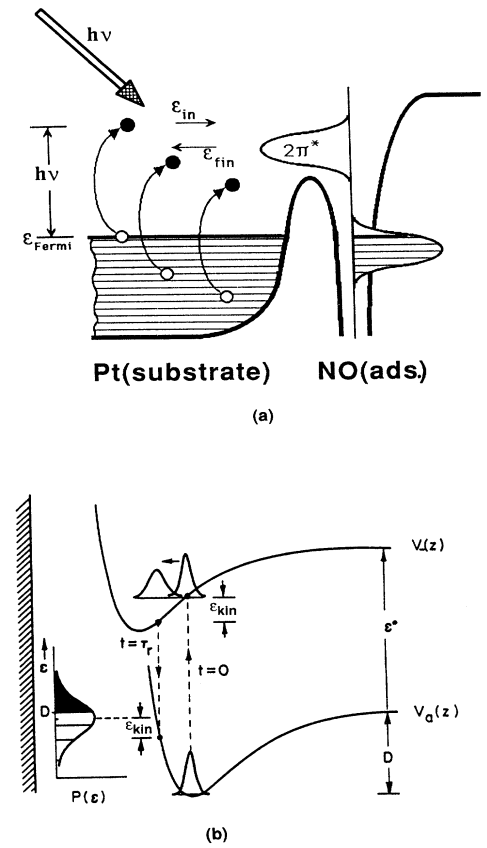


FIG. 1. (a) Energy-level diagram for inelastic hot-electron scattering through $2\pi^*$ shape resonance of adsorbed NO. (b) Potential-energy curves of chemisorbed and negative-ion NO with respect to surface, showing wave-packet propagation throughout the time sequence involving the NO^- $2\pi^*$ resonance. The distribution of final NO states is shown as $P(\varepsilon)$ vs ε.

splitting between the highest occupied (HOMO) and lowest unoccupied (LUMO) NO $2\pi^*$-derived orbital is due to intramolecular Coulomb repulsion between singly and doubly occupied states, as suggested by Johnson and Hulbert[15] on the basis of photoemission and inverse-photoemission spectroscopy.

It has been proposed[11(b)] that the observed nonthermal laser-induced desorption of NO proceeds as follows. Incident radiation with photon energy $h\nu$ creates a distribution of photoexcited electrons with energy ε_{in} in the range $\varepsilon_{Fermi} < \varepsilon_{in} \le (\varepsilon_{Fermi} + h\nu)$, which produces a flux of hot electrons from within the substrate incident upon the adsorbed NO. For those photoexcited electrons resonant with the $2\pi^*$ "level" (or shape resonance), the incident electron with energy ε_{in} may hop onto the adsorbed NO, reside in this resonance for a time τ_R, and then scatter back into an unoccupied conduction-band state with energy $\varepsilon_{fin} \le \varepsilon_{in}$, leaving behind some part of the adsorption system excited with energy $\Delta\varepsilon = \varepsilon_{in} - \varepsilon_{fin}$.

The essential features of the desorption process triggered by resonance electron scattering are pictured in Fig. 1(b). Let the potential-energy function for the NO/Pt(111) system be the attractive potential labeled $V_a(z)$ in Fig. 1(b). When the incident photoexcited electron with kinetic energy ε_{in} is captured in the NO $2\pi^*$ resonance state, an additional image-potential type of attraction is turned on, resulting in the augmented negative ion-surface potential curve shown as $V_-(z)$ in Fig. 1(b). While image attraction corrections provide a highly simplified model for the negative-ion potential, their use has provided intuitively plausible explanations for various stimulated desorption scenarios.[6,11,12,16,17] In any event, the major requirement is only that the intermediate state is one in which forces are applied to the NO^- such that the equilibrium geometries for the two charge states differ. Displaced and "half-truncated" harmonic-oscillator potentials could provide an alternative set of model curves amenable to analytic solution as will be expanded upon in Sec. III D.

With all this in mind, desorption is imagined to proceed as follows. Upon capture of the incident electron in the $2\pi^*$ orbital, the wave-packet characterizing the nuclear motion of the adsorbed NO suddenly finds itself as a nonstationary state on $V_-(z)$, as in a Franck-Condon transition, and thus accelerates inward towards the surface. After a time interval τ_R, the negative-ion resonance lifetime, the moving, displaced, and distorted wave packet is returned to $V_a(z)$, again as a Franck-Condon transition, but this time involving the projection of a moving initial-state wave packet onto both the discrete bound and continuum desorptive states of $V_a(z)$. As is apparent from Fig. 1(b), the dynamics on $V_-(z)$, the intermediate-state potential-energy curve, can easily lead to electron-assisted desorption represented by the area under the filled-in region of the (extremely τ_R-dependent) final-state distributions labeled $P(\varepsilon)$, if $h\nu$ is large enough for ε to exceed D, the desorption energy. This model has been quantified using the Gaussian wave-packet propagation techniques developed by Heller[18] and the results presented in analytic form in the so-called short-time limit.[11,12]

B. Inelastic resonant-tunneling model

Recently the phenomenon of resonant tunneling, treated in some detail many years ago within the context of field-emission spectroscopy,[19] has been discussed in terms of the model Hamiltonian

$$H = H_{el} + H_{ph} + H_{int} , \tag{1a}$$

with

$$H_{el} \equiv \varepsilon_a c^\dagger c + \sum_{\kappa,\alpha} \varepsilon_{\kappa\alpha} c^\dagger_{\kappa\alpha} c_{\kappa\alpha} + \sum_{\kappa,\alpha} V_{\kappa\alpha,a} (c^\dagger_{\kappa\alpha} c + c^\dagger c_{\kappa\alpha}) , \tag{1b}$$

$$H_{ph} = \hbar\omega_0 b^\dagger b , \tag{1c}$$

$$H_{int} = \lambda_0 c^\dagger c (b + b^\dagger) , \tag{1d}$$

which is sometimes called a local polaron model.[20] Equation (1) describes a system in which a discrete localized electronic state [eigenvalue equal to ε_a, Fermion operators $(c^\dagger, c)$] is coupled via a set of matrix elements $V_{\kappa\alpha,a}$ to a number of electronic continua specified by index α, with eigenvalues $\varepsilon_{\kappa\alpha}$ and operators $c_{\kappa\alpha}^{\dagger}, c_{\kappa\alpha}$. This electronic system is in contact with a dispersionless boson field described by the harmonic-oscillator Hamiltonian, Eq. (1c), which is linearly displaced according to the perturbation, Eq. (1d), when ε_a, the localized electronic state, is occupied. In physical terms, the force provided by the time-dependent occupation of the state $[n_a(t)=\langle c^{\dagger}(t_+)c(t)\rangle]$ can leave the field or oscillator excited and it is this possibility which has led to observable consequences of the "transient local polaron model".

The tunnel junction shown in Fig. 2 is conveniently characterized by this Hamiltonian with the sums on α restricted to two terms, in which $\alpha=l(r)$ refers to the continuum of electron-band states in the left (right) electrodes. With the electrodes biased by $\Delta\mu$ as indicated in Fig. 2, inelastic tunneling proceeds in the following way. A flux of electrons in the left-hand electrode is incident upon the barrier, some of which are transferred by the $V_{\kappa l,\alpha}$ term in $H_{\rm el}$ into the quantum well, particularly when the bias is such that ε_a, the resonant level of the well, is tuned to the Fermi level of the left electrode. Upon entering the well in which the boson or vibrational system is in its ground state (at $T=0$), $c^{\dagger}c$, the occupation number changes from 0 to 1, and the interaction term $H_{\rm int}$, which is linear in boson operators, and thus oscillator displacement is switched on. Subsequent time evolution of the oscillator occurs under the action of the displaced harmonic-oscillator potential until $V_{\kappa r,a}$ transfers the electron from the quantum well into an unoccupied band state within the right-hand electrode. As a result of this transfer, $c^{\dagger}c=0$, the oscillator potential returns to its original form, and the oscillator is now in a distribution of excited states due to the forcing of the transient linear perturbation [just as in Fig. 1(b)]. The total amount of energy left in the vibrational system is balanced by the energy loss of the electron which has tunneled, which in turn has an upper bound equal to $\Delta\mu$, the applied bias. The inelastic tunneling characteristics for such a junction, in the wide-band limit with energy-independent $V_{\kappa\alpha,a}$, have been given an exact analytic solution by Wingreen, Jacobson, and Wilkins[7] which shall be discussed in Secs. III C and then III D in the context of desorption.

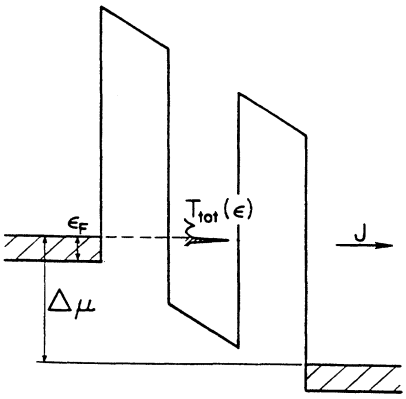


FIG. 2. Schematic of a resonant-tunneling structure carrying current J between two doped contacts with Fermi energies ε_F. The current as a function of bias $\Delta\mu$ depends on the interacting transmission spectrum $T_{\rm tot}(\varepsilon)$, an example of which is sketched in the well (Ref. 7).

C. Equivalences

The basic similarities between the wave-packet model presented in Sec. II A and the resonant-tunneling model of Sec. II B, at least from the point of view of dynamics and oscillator excitation due to electron scattering and/or tunneling are by now probably apparent.[12] The molecular potential in Fig. 1(a) and the quantum well in Fig. 2 play the same role, specific system details influencing only the numerical values of the parameters $\hbar\omega_0$, ε_a, $V_{\kappa\alpha,a}$, and λ_0 in Eq. (1), but not the essential physics. Furthermore, the biased electrodes serves the same function in the junction as does the photoexcited substrate in the desorption experiment, namely providing both an incident flux of high-energy electrons (the left electrode) and a continuum of unoccupied lower-energy states (the right electrode) into which the incident electron can inelastically scatter. The maximum possible energy transfer to the oscillator is $h\nu$ or $\Delta\mu$ in the two equivalent systems.

III. THEORY

For present purposes, the essential issue which a theory of inelastic resonance scattering or tunneling through a localized (either molecular or quantum well) electronic state must address is determination of the probability per event that an incident electron with energy ε_i scatters into a final state of energy ε_f, the difference in energy, $\Delta\varepsilon=\varepsilon_i-\varepsilon_f$, remaining in the phonon or oscillator system. Historically related problems have been nicely dealt with both in gas-phase resonance electron scattering from molecules[4] and in solid-state core-level spectroscopies.[2,21] In electron scattering, the energy of the incident and the scattered particle are monitored, not just their difference. This fact gives rise to an added degree of complexity over the core-level theories in which the core hole has no internal degree of freedom other than whether or not it exists. It is informative to proceed from simple to complex and this rule dictates the unfolding of this theory section.

A. Core-level spectroscopy

It is interesting to consider first a demonstration of the boson or oscillator excitation that occurs in a core-level process involving recoiless-hole creation and subsequent decay. The physical picture implied by Eq. (1) (plus an additional excitation term which creates the initial core hole) is one in which the oscillator system (phonons, plasmons, bosonized electron-hole pairs, etc.) is subjected to a driving force that is proportional to the time-dependent core-hole population (equal to one minus the electron occupation). When the effects of the $V_{\kappa\alpha,a}$ coupling of the discrete core state to the continuum can be represented by an exponential decay,[2(c)] then the problem of oscillator excitation embodied in Eq. (1) is equivalent to that of a forced classical harmonic oscillator subjected to the time-dependent perturbation

$$H_{\rm int}(z,t)=zf(t)\ , \tag{2a}$$

where, by comparison with Eq. (1d), the driving force is

$$f(t)=\lambda_0\Theta(t)e^{-\gamma t/\hbar}(2m\omega_0/\hbar)^{1/2} \tag{2b}$$

and z and m are the oscillator position and mass, respectively.[22] It is easily demonstrated that the energy gain to the oscillator is $\Delta\varepsilon_{\rm class}=|f(\omega_0)|^2/2m$ with $f(\omega_0)$ the ω_0 Fourier component of the forcing function.[23] For $f(t)$ given by Eq. (2b) the energy gain is

$$\Delta\varepsilon_{\rm class}=\lambda_0^2\hbar\omega_0/[(\hbar\omega_0)^2+\gamma^2]\ , \tag{3}$$

as implied in a proposal due to Šunjić and Lucas[24] (SL) which has subsequently received considerable attention.[2(c),(3b),21,25]

The correspondence principle provides the connection between the energy gain of the forced classical harmonic oscillator, as specified here by Eq. (3), and the vibrational excitation probability distribution of the equivalent quantum-mechanical harmonic oscillator subjected to the same forcing function. In terms of the parameter

$$\beta_\gamma\equiv\Delta\varepsilon_{\rm class}/\hbar\omega_0=\beta\{\omega_0^2/[\omega_0^2+(\gamma/\hbar)^2]\} \tag{4}$$

with

$$\beta\equiv(\lambda_0/\hbar\omega_0)^2 \tag{5a}$$

and

$$\Delta\varepsilon_r\equiv\lambda_0^2/\hbar\omega_0=\beta\hbar\omega_0\ , \tag{5b}$$

it is well established[26] that the excited-state distribution for $0\rightarrow n$ vibrational transitions induced by a separable perturbation, such as Eq. (2a), is

$$P_\gamma(\varepsilon)=e^{-\beta_\gamma}\sum_{n=0}^{\infty}(\beta_\gamma^n/n!)\delta(\varepsilon-n\hbar\omega_0)\ , \tag{6a}$$

a Poisson distribution. Furthermore, when $\beta_\gamma\gg1$, the discrete Poisson distribution is well approximated by a continuous Gaussian,

$$\frac{dP_\gamma}{d\varepsilon}=\frac{1}{\Delta_\gamma\sqrt{2\pi}}\exp\left[-\frac{1}{2}\left[\frac{\varepsilon-\beta_\gamma\hbar\omega_0}{\Delta_\gamma}\right]^2\right]\ , \tag{6b}$$

where $\Delta_\gamma=\beta_\gamma^{1/2}\hbar\omega_0$. Equations (3) or (4)–(6) clearly demonstrate that the degree of excitation is a sensitive function of τ_R, the lifetime of the core hole, as embodied in the parameter $\gamma\equiv\hbar/\tau_R$, with respect to an oscillator period. For a short-lived hole, $\gamma/\hbar\gg\omega_0$. Thus $\Delta\varepsilon_{\rm class}/\hbar\omega_0\rightarrow0$ and the oscillator remains in its ground state. In the other extreme of a long-lived hole, $\gamma/\hbar\ll\omega_0$ and thus $\beta_\gamma\sim\beta$ so the distribution of oscillator excited states is Poisson with characteristic parameters of a permanently displaced oscillator, in other words a Franck-Condon distribution. From a dynamics point of view, the initial step-function displacement implied a sudden transition, hence the Franck-Condon distribution followed by the slow, therefore adiabatic, return to the original oscillator configuration, as governed by the exponential decay.

B. Resonance electron-molecule scattering

A new level of complexity arises for processes in which light electrons rather than transient but infinitely massive core holes drive the oscillator or phonon system. Due to the fact that electrons can recoil, the entangled dynamics of the electron coupled to the oscillator must be maintained in the theoretical construction, and this requires considerations beyond the simple forced-oscillator model. Within the context of gas-phase resonance-electron scattering from small molecules, this problem was treated by Herzenberg and co-workers in terms of the so-called boomerang model.[4(a)] The problem was later reformulated by Domcke and Cederbaum (DC) explicitly within the model specified by Eq. (1) and a compact analytic solution was provided.[4(b)] For purely resonant scattering in which the discrete-state–continuum interaction is independent of oscillator extension, as for example Eq. (1b), DC have shown that the $0\rightarrow n$ vibrational excitation cross section for an electron with incident kinetic energy equal to ε_i can be expressed as

$$\sigma_n(\varepsilon_i)\sim\varepsilon_i^{-1}\Gamma(\varepsilon_i)\Gamma(\varepsilon_f)\left|\sum_{m=0}^{\infty}\frac{\langle n|\tilde{m}\rangle\langle\tilde{m}|0\rangle}{\varepsilon_i-\tilde{\varepsilon}_m-\Lambda_{mm}(\varepsilon_i)+(i/2)\Gamma_{mm}(\varepsilon_i)}\right|^2 \tag{7}$$

with $\tilde{\varepsilon}_m=\varepsilon_a-\Delta\varepsilon_r+m\hbar\omega_0$. An effective non-Hermitian energy operator $\Sigma=\Lambda-i\Gamma/2$, which accounts for the role of the discrete-state–continuum coupling on the oscillator dynamics, has been incorporated into Eq. (7) as diagonal matrix elements in the basis which diagonalizes the intermediate-state displaced-oscillator Hamiltonian equal to $H_{\rm ph}+H_{\rm int}$. In other words,

$$\Sigma_{mm'}(\varepsilon_i)=\langle\tilde{m}|\Sigma(\varepsilon_i-H_{\rm ph})|\tilde{m}'\rangle=\sum_{j=0}^{\infty}\langle\tilde{m}|j\rangle\Sigma(\varepsilon_i-j\hbar\omega_0)\langle j|\tilde{m}'\rangle \tag{8}$$

has been taken to be nonzero only when $m=m'$.[27] Also in Eq. (7), $\Gamma(\varepsilon_{i(f)})/\hbar$ is the electron transition rate at the initial (final) energy into (out of) the quasidiscrete resonance state and $\langle n|\tilde{m}\rangle$, etc., are vibrational overlap integrals where $|\tilde{m}\rangle$ denotes vibrational states of the temporary negative ion and $|n\rangle$ those of the neutral molecule. Using standard formulas for the displaced oscillator overlap integrals or Franck-Condon factors[26(b)] and taking both Λ_{mm} and Γ_{mm} as energy-independent constants, DC's expression for the excitation cross section, which follows from Eq. (7), can be worked into the equivalent form

$$\sigma(\varepsilon_f,\varepsilon_i)\sim\varepsilon_i^{-1}\Gamma(\varepsilon_f)\Gamma(\varepsilon_i)e^{-2\beta}\sum_{n=0}^{\infty}\frac{\beta^n}{n!}\delta(\varepsilon_i-\varepsilon_f-n\hbar\omega_0)\left|\sum_{m=0}^{\infty}\frac{A_{n,m}}{\varepsilon_i-(\varepsilon_a'-\Delta\varepsilon_r)-m\hbar\omega+i\Gamma/2}\right|^2 , \tag{9}$$

$$A_{n,m}=\begin{cases}(-1)^{n-m}L_m^{n-m}(\beta) & \text{for } m\le n\\ \beta^{m-n}(n!/m!)L_m^{m-n}(\beta) & \text{for } m\ge n ,\end{cases}$$

where

$$L_n^{\alpha}(\beta)=\sum_{j=0}^{n}(-1)^j\left[\begin{matrix}n+\alpha\\ n-j\end{matrix}\right]\beta^j\Big/j!$$

are generalized Laguerre polynomials and $\varepsilon_a'\equiv\varepsilon_a+\Lambda$ Although DC do carry out a proper evaluation of $\Sigma_{mm}'(\varepsilon_i)$ given by Eq. (8) in terms of a continued-fraction expression and recursion relations appropriate to a tridiagonal system,[20,28] the major features of the resonance-scattering event are more transparent with the approximate solution expressed in Eq. (9). Basically the partial inelastic scattering cross section is the product of incident electron penetration into the molecule $[=\Gamma(\varepsilon_i)]$ multiplied by a measure of its resonance with the vibrationally renormalized quasibound state (the energy denominator or propagator), weighted by Poisson factors (or equivalently by vibrational overlap integrals) and interference terms, ultimately multiplied by the transition rate out of the molecule for an electron with final-state energy $\varepsilon_f=\varepsilon_i-n\hbar\omega_0$. The general form of the energy-dependent resonance cross section is one showing a series of resonance peaks, more or less equally spaced $\hbar\omega_0$ apart, each with a width determined by Γ, the inverse resonance lifetime, and all within a "Poissonian" or Gaussian envelope characterized by the electron-vibrator β parameter. This picture has been quite successful in providing an intuitively clear account of gas-phase inelastic electron-scattering data.[29]

C. Resonant electron tunneling

Next consider oscillator excitation experienced in resonant electron tunneling through a quantum well. The basic phenomenon is very similar to vibrational excitation in resonance scattering, the distinctions mainly appearing in matters of detail such as spherical versus planar symmetry or few versus tens of angstroms characteristic length scales, issues which arise only when actually *computing* the $V_{\kappa,a}$ matrix elements between localized and continuum states (as opposed to the customary procedure of just *assigning* a value).[30]

Wingreen, Jacobson, and Wilkins (WJW) have presented a comprehensive and readable analysis of inelastic resonant tunneling in junction structures characterized by the Hamiltonian of Eq. (1) and have obtained the tunneling equivalent of the inelastic cross section, the probability for inelastic transmission and/or reflection of an incident electron of energy ε_i into a state with energy ε_f. WJW refer to these quantities, in the junction case, as a transmission (reflection) matrix equal to $T(\varepsilon_f,\varepsilon_i)$ $[R(\varepsilon_f,\varepsilon_i)]$. For systems described by Eq. (1) in the wide-band limit and with $V_{\kappa r,a}$ and $V_{\kappa l,a}$ taken to be energy independent, the exact solutions for the transmission and thus by unitarity, the reflection matrices are

$$T(\varepsilon_f,\varepsilon_i)=\Gamma_l\Gamma_r e^{-2\beta}\sum_{n=0}^{\infty}\frac{\beta^n}{n!}\delta(\varepsilon_i-\varepsilon_f-n\hbar\omega_0)\times\left|\sum_{m=0}^{\infty}\sum_{j=0}^{n}\frac{B_{n,m,j}}{\varepsilon_i-(\varepsilon_a'-\Delta\varepsilon_r)-(m+j)\hbar\omega_0+i\Gamma/2}\right|^2 , \tag{10a}$$

where

$$B_{n,m,j}\equiv(-1)^j\left[\begin{matrix}n\\ j\end{matrix}\right]\beta^m\Big/m!$$

and

$$\begin{aligned}R(\varepsilon_f,\varepsilon_i)=&\left[\frac{\Gamma_l}{\Gamma_r}\right]T(\varepsilon_f,\varepsilon_i)\\ &+\delta(\varepsilon_f-\varepsilon_i)\{1+2\Gamma_l\mathrm{Im}[G_a(\varepsilon_i)]\}\\ \equiv&R_{\text{inel}}(\varepsilon_f,\varepsilon_i)+R_{\text{elastic}}(\varepsilon_i)\end{aligned} \tag{10b}$$

with the following clarification. The resonance widths

$$\Gamma_{l\,(r)}(\varepsilon)=2\pi\sum_{\kappa}|V_{\kappa l\,(\kappa r),\,a}|^2\delta(\varepsilon-\varepsilon_{\kappa l\,(\kappa r)})$$

are due to elastic coupling between the localized state and the left or right continua and the total width $\Gamma=\Gamma_l+\Gamma_r$. As in Eq. (9), a real self-energy shift, given as the Hilbert transform of $\Gamma(\varepsilon)$, has been incorporated into a renormalized localized eigenvalue $\varepsilon_a'\equiv\varepsilon_a+\Delta$. The weak-energy dependencies of both Γ and Δ have been neglected in Eqs. (10). The electron-phonon interaction strength appears through the dimensionless parameter β and the "relaxation energy" $\Delta\varepsilon_r$ given by Eqs. (5a) and (5b), respectively. The reflection matrix, Eq. 10(b), has been expressed in terms of an inelastic and elastic component, the latter given in terms of $G_a(\varepsilon_i)$, the Green's function of the resonant site including electron-phonon interactions.

A crucial quantity of importance in the case of adsorbate resonances is the total inelastic reflection probability for an incident electron with energy ε_i,

$$
\begin{aligned}
R^{\text{tot}}_{\text{inel}}(\varepsilon_i) &= \int d\varepsilon_f R_{\text{inel}}(\varepsilon_f,\varepsilon_i) \\
&= \Gamma_l^2 e^{-2\beta} \sum_{n=0}^{\infty} \frac{\beta^n}{n!} \left| \sum_{m=0}^{\infty} \sum_{j=0}^{n} f_{n,m,j}(\varepsilon_i,\Gamma) \right|^2 \\
&\equiv \sum_{n=0}^{\infty} R_n(\varepsilon_i;\beta,\Gamma_l,\Gamma)
\end{aligned}
\tag{11}
$$

with $f_{n,m,j} \equiv B_{n,m,j}$ divided by the denominator from Eq. (10a). WJW have provided the sum rule

$$\int d\varepsilon_i \int d\varepsilon_f T(\varepsilon_f,\varepsilon_i) = 2\pi\Gamma_l\Gamma_r/\Gamma \ ,$$

which with Eqs. (10b) and (11) implies that

$$\frac{1}{2\pi\Gamma_l}\int d\varepsilon_i R^{\text{tot}}_{\text{inel}}(\varepsilon_i) = 1 \ . \tag{12}$$

Equations (11) and (12) will be particularly useful for processes involving an incident electron flux distributed uniformly in energy over the "width" of the phonon-induced resonance.

When considering either a molecule adsorbed at a solid-vacuum interface or a quantum well located close to the left electrode, then $\Gamma_l \gg \Gamma_r$, in which case $\Gamma_{\text{tot}} \simeq \Gamma_l$ in Eqs. (10) and (11), the role of the right electrode is negligible, and $T^{\text{tot}}(\varepsilon_{in}) \approx 0$ (i.e., all electrons are reflected).

Finally, one is invited to note the similarity (and differences) in algebraic structure between the electron-scattering cross section [Eq. (9)] and the tunneling transmission matrix [Eq. (10)]. The obvious similarities follow from the near identity in physical content of the two phenomena. The major difference here, the "j-summed" contribution in the intermediate-state denominator of Eq. (10) but not in Eq. (9), is due to the fact that only a simplified form for $\Sigma_{mm'}(\varepsilon_i)$, Eq. (8), has been retained in Eq. (9). This is not intended to imply any significant difference in the physics of the two situations.

D. Desorption

A venerable model for a bound molecular system, such as an atom or molecule adsorbed on a surface, is a harmonic oscillator truncated on one side.[31] While this model can be misleading when considering kinetic processes which in real life involve "ladder climbing" up a progressively softer potential well, it is much more meaningful for addressing bound-to-"predissociative" continuum Franck-Condon transitions of the type considered here.[32] This is illustrated in Fig. 3. As discussed in Sec. II A, vibrational excitation and/or desorption on such a system of potential curves can be considered as a sequence of Franck-Condon-like transitions, in which the initial vibrational ground state on the equilibrium adsorption potential-energy curve associated with H_{ph} is projected onto a coherent superposition of displaced oscillator eigenstates of $H_{\text{ph}}+H_{\text{int}}$. The wave packet formed from this superposition state propagates for a time duration τ_R before returning to the potential energy, curve of H_{ph}, but now displaced from the well minimum.[33] In the case of the full harmonic potential, the probability that the nth vibrational state is excited is expressed as

$$
\begin{aligned}
P_n(\tau_R) &= \left| \sum_{m=0}^{\infty} \langle n|\tilde{m}\rangle e^{-i\varepsilon_{\tilde{m}}\tau_R} \langle \tilde{m}|0\rangle \right|^2 \\
&\equiv |\langle n|\phi_{\text{fin}}(\tau_R)\rangle|^2 \ ,
\end{aligned}
\tag{13}
$$

for step-function switching on and off of the intermediate-state potential.[34] The reader is referred to the Appendix for further discussion. From a real-time point of view, the "down" Franck-Condon transition puts the moving wave packet on the inner wall of H_{ph} and thus the distribution given by Eq. (13) should be little affected by whether the oscillator well is truncated or not on the outer side, at least not until after the time delay exceeds $\sim\frac{1}{2}$ an oscillator period.

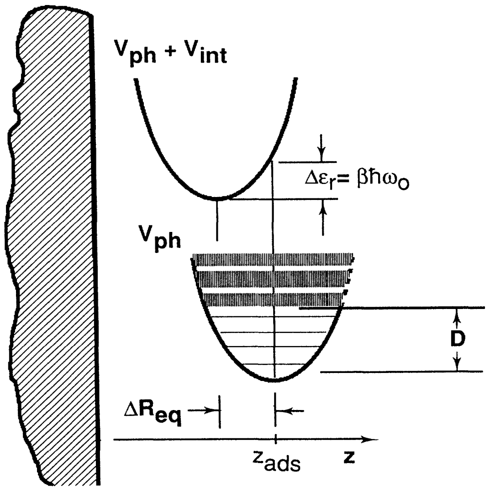


FIG. 3. Potential-energy curves for resonant desorption, analogous to the process shown in Fig. 1(b), but here with half-truncated harmonic-oscillator potential for the adsorption bond. The predissociative and/or predesorbtive states of the oscillator, those with energy greater than D, are here symbolized by the broadened levels. In this figure, $n_d = 4$.

For desorption to be possible as a result of not only the sharp switching implicit in Eq. (13), but more importantly, as a result of inelastic electron scattering, the target oscillator must be left excited with energy equal to or in excess of D, the desorption energy. Within the context of the model discussed in Sec. III C, the desorption probability per resonance event for a hot electron with energy ε_i is given by an expression like Eq. (11), but including only those values of $n \geq n_d$ where n_d is the smallest integer greater than $D/\hbar\omega_0$. The desorption probability is thus

$$P_{\text{des}}(\varepsilon_i) = \sum_{n=n_d}^{\infty} R_n(\varepsilon_i;\beta,\Gamma_l,\Gamma) \ . \tag{14}$$

The translational energy distribution of the desorbed molecules is taken as

$$\frac{dN}{d\varepsilon}(\varepsilon;\varepsilon_i{:}\beta,\Gamma,D)\sim\sum_{n=n_d}^{\infty}\frac{1}{\pi}\frac{\Delta_\omega}{[\varepsilon-(n\hbar\omega-D)]^2+\Delta_\omega^2}\times\varepsilon^{\eta}R_n(\varepsilon_i;\beta,\Gamma) \qquad (15)$$

where the "picket fence" discrete δ function spectrum of oscillator states in excess of energy D have been given a predissociative width $\Delta_\omega \approx \hbar\omega_0$. The value of the exponent η depends upon the geometry and other details of the experimental configuration. For comparison with experimental results, this (essentially) one-dimensional number density energy distribution, $dN/d\varepsilon$, must be transformed to a three-dimensional representation to properly account for phase space factors.[35] Comparison to specific laboratory results will require additional transformations from the experimental observables (i.e., time- and/or velocity-dependent product densities) to the predicted energy distributions. For the NIST experiments in which a number density distribution of desorbed molecules is measured in the time-of-flight apparatus,[10,11(b)] $\eta=\frac{1}{2}$ is appropriate.

For the sake of completeness, note that when the oscillator excited-state distribution is given by the continuous Gaussian of Eq. (6b), then the dissociation or desorption probability is

$$P_{\mathrm{des}}^{\gamma}=\int_D^{\infty}\frac{dP_\gamma}{d\varepsilon}d\varepsilon=\tfrac{1}{2}\left[1-\mathrm{erf}\left[\frac{D-\beta_\gamma\hbar\omega_0}{\sqrt{2}\Delta_\gamma}\right]\right], \qquad (16)$$

which is a convenient limiting case.

IV. RESULTS AND COMMENTARY

Numerical consequences of the various models of oscillator excitation due to transient forces are presented here. Although special emphasis is placed on inelastic resonance scattering and tunneling as relevant to a hot-electron-induced desorption scenario,[11(b),12] the results are more general, owing to the generic nature of the model Hamiltonian, Eq. (1), which is at the heart of this study.

First, the *total* inelastic reflection probability inferred from Eqs. (5), (10), and (11) has been calculated as a function of incident electron energy (with respect to an energy zero at the renormalized adsorbate resonance energy, i.e., $\varepsilon_a'=0$) treating the resonance width Γ and the vibrational coupling constant β parametrically. Some results are displayed in Fig. 4(a). This shows the total inelastic scattering probability independent of the final-state electron energy or equivalently, of the energy transferred to the oscillator. The complementary desorption probabilities per scattered electron with incident energy ε_i obtained from Eq. (14), again with several values of Γ, β, and now desorption energy D, are shown in Fig. 4(b). The labeled energies (Γ, D, and explicitly ε_i) are given in units of $\hbar\omega_0$. It is apparent in all the plots of Fig. 4 that the coupling of the vibrational modes to the localized resonance serves to spread out the energy range of the effective resonance, due to what would be called phonon sidebands or vibrational Franck-Condon features in other fields. The price to be paid is that the maximum values of R_{inel}, the inelastic reflection probability, and as a result P_{desorb}, the desorption probability, are significantly reduced as β increases. This is to be expected on the basis of sum rules such as Eq. (12) which say that the vibrational coupling redistributes, but does not enhance or diminish, the spectral weight associated with the resonance.[2,7] Equation (9), the cross-section expression of Domcke and Cederbaum, has been evaluated as an equality and the quantity $\int \varepsilon_i \sigma(\varepsilon_f,\varepsilon_i)d\varepsilon_f$ as a function of ε_i was found to be numerically indistinguishable from the results of WJW, obtained from Eqs. (10) and (11). Apparently the approximations implicit in proceeding from Eqs. (7) to (9) are of limited numerical consequences, at least in the region of parameter space under study here. This is fortunate as the slightly more compact algebraic structure of Eq. (9) compared with Eq. (10) will be useful later.

Next, the desorption probability as a function of desorption energy (in integral multiples of $\hbar\omega_0$) with labeled values for Γ, β, and ε_i is depicted in Fig. 5 for incident energy exactly on (the $\beta=0$) resonance. A general point which should be noted from Figs. 4(b) and (5) is the obvious finding that, all other things being equal, P_{des} is smallest for adsorbates with the largest binding or desorption energy. On the other hand, comparison of Figs. 5(a) and 5(b) shows an effect when all other things are *not* equal, namely when the vibrational coupling constant is changed. For systems with low D, small β coupling produces a greater desorption probability then does large β coupling. However, large β is enormously more effective for systems with larger desorption energies.

Translational energy distributions obtained by evaluation of Eq. (15) are shown in Fig. 6 where n_d, β, and Γ are varied parametrically in Figs. 6(a)–6(c), respectively. It is apparent that the general "shape" of the distributions, unlike their relative magnitudes which have been normalized away, is fairly insensitive to parameter variations in the chosen range. Still, the peak of the distribution moves to higher energies with increasing oscillator displacement which results from larger β and/or intermediate-state lifetime $\tau_R(\sim\hbar/\Gamma)$. Obviously one could be seriously misled if this apparent "heating" was interpreted in terms of some equilibrium thermal effect.

An important message to be gleaned from Figs. 4–6 is that there is more excitation to the oscillator for the longer-lived resonances, those with the narrowest widths. The physical basis for this has been spelled out in detail, both in Sec. III A and elsewhere,[6(b),11,12,32] where it has been stressed that the intermediate-state potential, the displaced oscillator here, must exist long enough for "consequential" motion to occur over it. This is clearly illustrated in Fig. 7. The ratio $\beta_\gamma/\beta=\Delta\varepsilon_{\mathrm{class}}/\beta\hbar\omega_0$ vs $\omega_0\tau_R$, obtained from Eq. (5), is shown in Fig. 7 as the thick curve. The associated analytic desorption probability from Eqs. (5) and (16), is also displayed in Figs. 7(a) and 7(b) as a function of $\omega_0\tau_R$, treating β and D parametrically as labeled. Here the implications of the lifetime on physical observables, such as the oscillator excitation and desorption probabilities, are clear.

Finally it is informative to examine the resonance lifetime dependence of the total desorption probability obtained from the DC-WJW model, which is

$$P_{\text{des}}(\tau_R)=\frac{1}{2\pi\Gamma_l}\sum_{n=n_d}^{\infty}\int d\varepsilon_i R_n(\varepsilon_i;\beta,\Gamma_l,\Gamma)\ . \tag{17}$$

This is of more than pedagogical interest since laser-excited hot-electron-induced desorption is initiated by an incident flux of substrate electrons upon the adsorbed molecule, fairly uniformly distributed in energy across the resonance.[11(b)] Integration on ε_i, as in Eq. (17), is an attempt to account for this aspect of the laser experiments. To proceed, we take advantage of the numerical identity between the results based on the DC expression, Eq. (9), and the WJW expressions to make the replacement

$$R_n(\varepsilon_i;\beta,\Gamma_l,\Gamma)\Longrightarrow\Gamma^2 e^{-2\beta}(\beta^n/n!)\left|\sum_m \frac{A_{n,m}}{\varepsilon_i-\bar{\varepsilon}_m+i\Gamma/2}\right|^2 \tag{18}$$

with $\bar{\varepsilon}_m\equiv\varepsilon_a'-\Delta\varepsilon_r+m\hbar\omega_0$. Inserting Eq. (18) into Eq. (17) and carrying out the integration, the total desorption

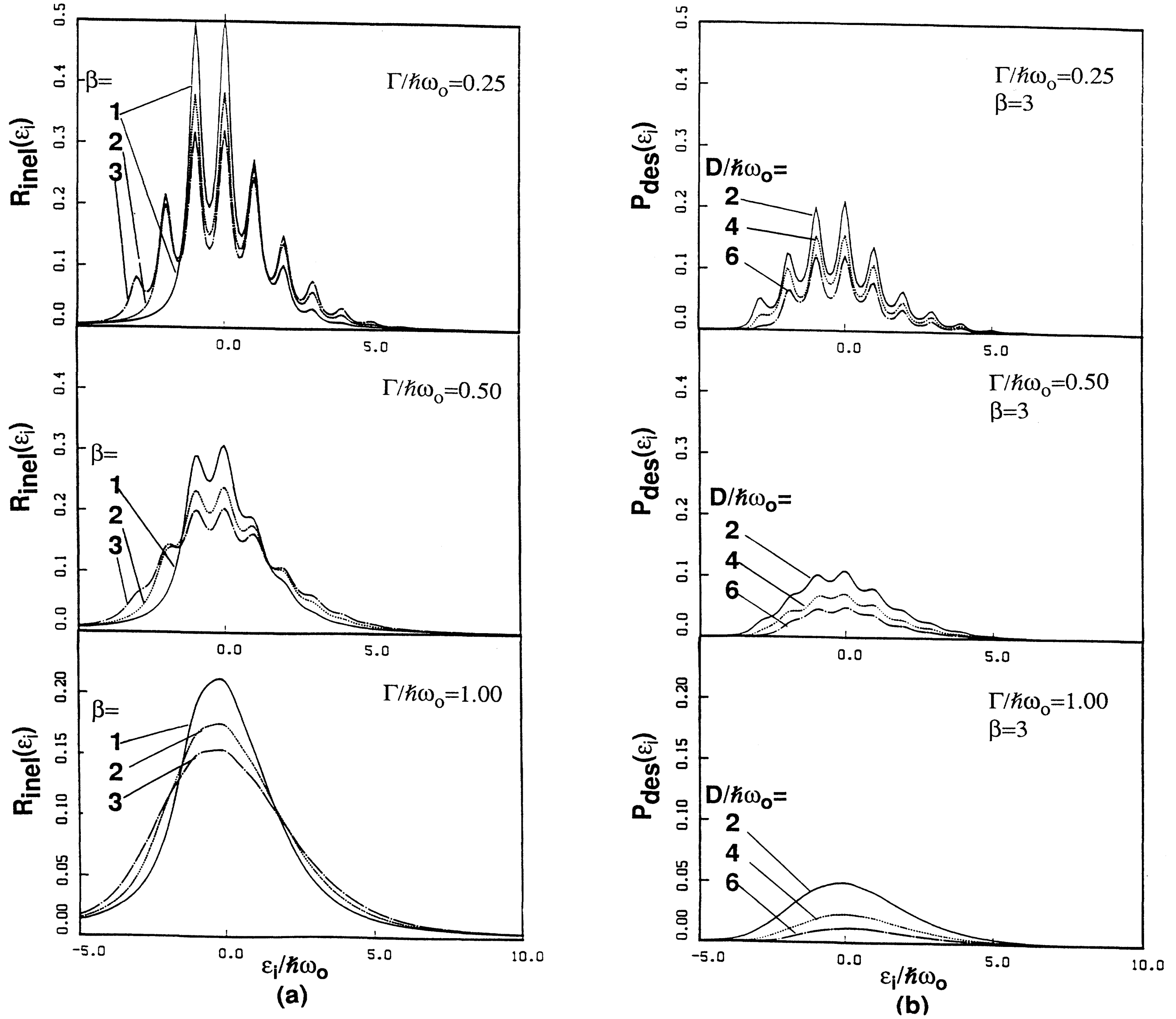
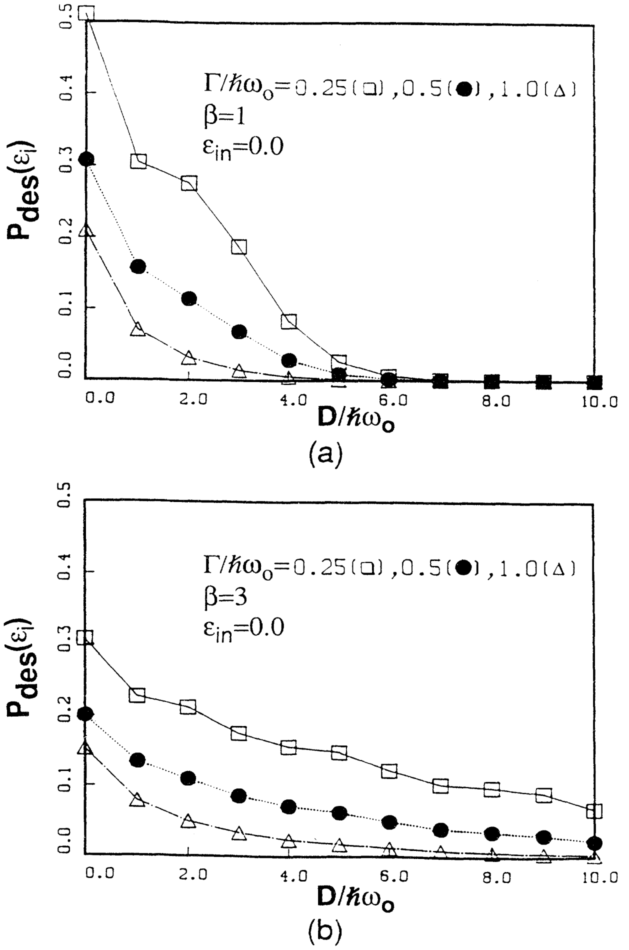


FIG. 4. (a) (Left) Total inelastic reflection probability vs incident energy [Eq. (11)] for assigned Γ and with $\beta=1,2,3$ (from maximum to minimum curve). (b) (Right) Desorption probability vs energy [Eq. (14)] for $\beta=3$, parametric Γ, and $D=2,4,6$ (maximum to minimum). Note scale change for $\Gamma=1$ figures (bottom).

probability is compactly given by

$$P_{\text{des}}(\tau_R)=e^{-2\beta}\sum_{n=n_d}^{\infty}(\beta^n/n!)\sum_{m,m'}\frac{A_{n,m}A_{n,m'}}{1+r^2(m-m')^2} \tag{19}$$

with $r\equiv\hbar\omega_0/\Gamma=\omega_0\tau_R$. Equation (19) is intriguingly related to some past theories of inelastic resonance scattering based on the sudden-switching model characterized by Eq. (13); this is discussed further in the Appendix.[34] Some numerical implications of Eq. (19) are displayed in Figs. 8(a)–8(c), where $P_{\text{des}}(\tau_R)$ is shown as a function of τ_R, for set D and a family of β values. These results are in harmony with the ideas developed in terms of semiclassical wave-packet dynamics,[11] the illustrative example of the forced harmonic oscillator of Sec. III A and Fig. 7, and hopefully, one's intuitive expectations. Succinctly summarized, Fig. 8 shows that longer-lived resonances show larger desorption yields, saturating at a value that is a monotonically increasing function of the oscillator displacement of the intermediate state, as embodied in the value of β.



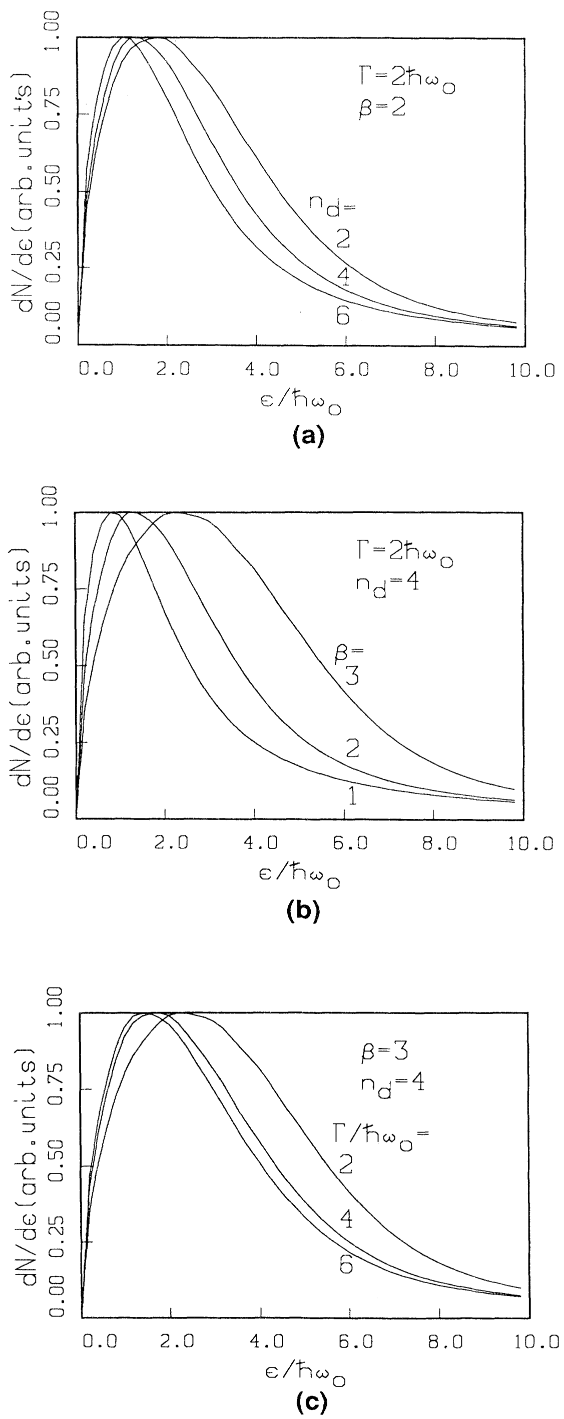
(a)

(b)

FIG. 5. Desorption probability vs desorption energy with $\Gamma=0.25, 0.50, 1.00$, $\varepsilon_{\text{in}}=0.0$, and (a) $\beta=1$, (b) $\beta=3$.

V. SUMMARY

The general problem of phonon and/or vibrational excitation occurring in a resonant scattering, tunneling, or hot-electron-induced desorption event involving gas-



(a)

(b)

(c)

FIG. 6. Normalized translational kinetic-energy distribution of desorbed molecules from Eq. (15), with specified system parameters. Figure 6(a), 6(b), and 6(c) show the systematic variation with parametric $n_d(=D/\hbar\omega_0)$, β, and Γ, respectively.

phase and adsorbed molecules or quantum wells has been considered. In all these cases, the common feature is based on temporary trapping of an incident electron flux within the scattering region. The nonequilibrium forces imposed on the nuclear system (vibrational or phonon modes) for the life of the resonance result in a distribution of vibrationally excited states when the system is returned to its original electronic ground state. While the consequences of bound-to-bound transitions are observable mainly in the electron-energy-loss spectrum, bound-to-continuum transitions are also possible, resulting in both molecular dissociation and desorption. For the harmonic systems considered here, the magnitude of the vibrational excitation depends both upon the displacement of the intermediate-state oscillator from the ground state, as embodied in the parameters λ_0 and thus β, and also upon the lifetime of the resonance state with respect to the inverse oscillator frequency. The implications of the model were demonstrated for a variety of realizations, which also helped provide a proper historical perspective.

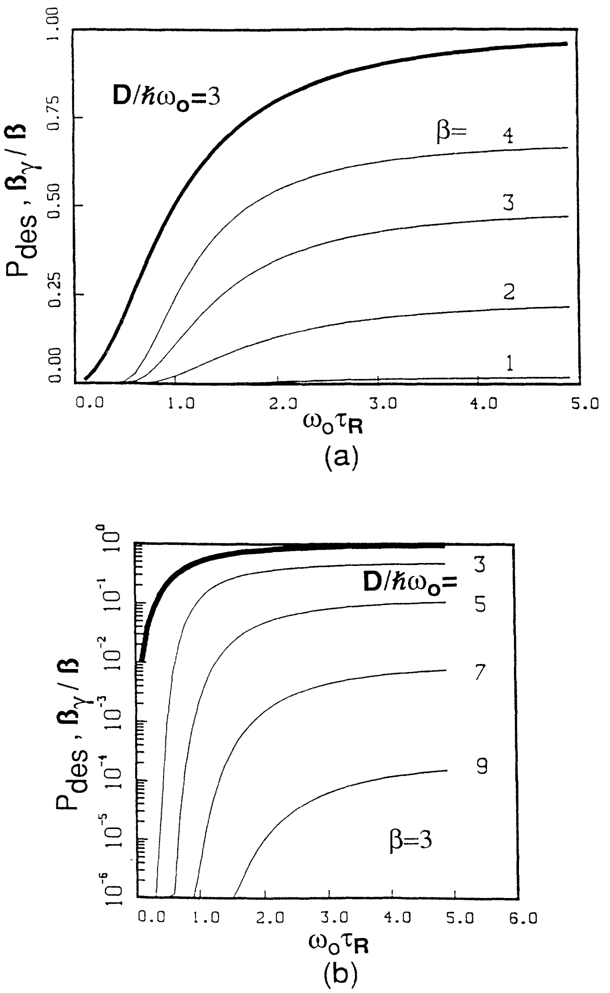


FIG. 7. β_γ/β (heavy curve) and desorption probability (light curves) as a function of τ_R, the resonance lifetime $(x\omega_0)$, obtained from the analytic expressions, Eqs. (4) and (16). (a) $D=3$, $\beta=1,2,3,4$; (b) $\beta=3$, $D=3,5,7,9$.

The idea of intermediate-state lifetime quenching of the vibrational excitation was demonstrated in the most straightforward way using the Šunjić-Lucas forced oscillator model for phonon excitation in condensed-matter

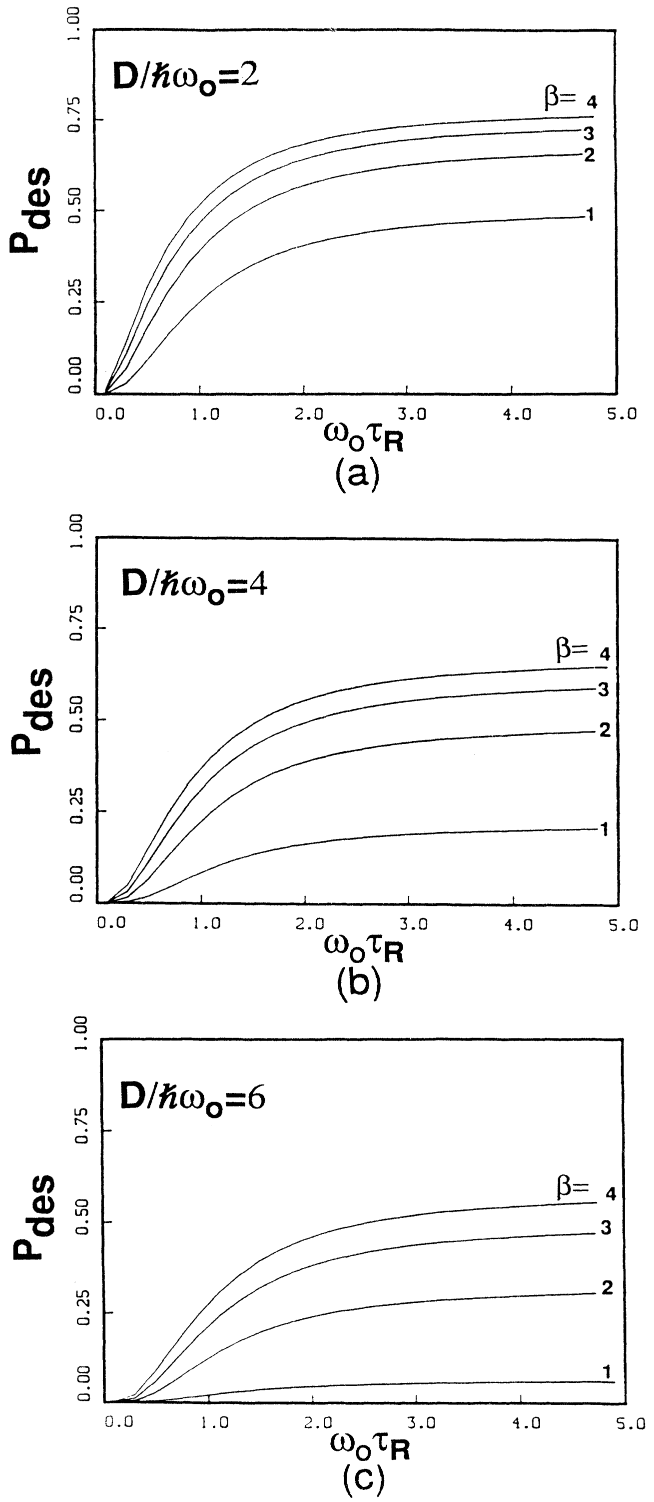


FIG. 8. Desorption probability as a function of τ_R, resonance lifetime $(x\omega_0)$ from Eq. (19), with $\beta=1$, 2, 3, and 4 and $n_d=(D/\hbar\omega_0)=$ (a) 2, (b) 4, (c) 6.

core-level spectroscopy.[24] The analytic solution to the boomerang model[4(a)] for electron-molecule resonance scattering due to Domcke and Cederbaum[4(b)] incorporated electron dynamics into the problem beyond the simple potential switching experienced in the transient hole effect of SL. More recent applications of the model to the problem of inelastic resonant tunneling (and reflection) through (from) quantum-well structures have been considered here with special emphasis on the presentation of Wingreen, Jacobson, and Wilkins.[7] The relationship to the electron-scattering work of CD has been demonstrated.

Going beyond the generic problem of oscillator excitation in electron scattering and/or tunneling, the implications of such excitation to the current problem of hot-electron-induced desorption has been worked out.[10] Not surprisingly, the results presented here for theoretical desorption characteristics obtained from the exactly solvable displaced-oscillator model support the insights and conclusions based upon time-dependent wave-packet dynamics.[11]

Although the present truncated, displaced-harmonic-oscillator model cannot be pushed too far in terms of quantitative significance, that is the price one pays for analytic solutions to complex problems. Nonetheless, the additional insights provided and the sense of unity with other areas of physics which is achieved, hopefully make this an acceptable price.

APPENDIX

The phenomenon of intramolecular vibrational excitation probabilities in resonance electron-energy-loss spectroscopy of physisorbed diatomic molecules has previously been addressed in terms of the sudden-switching model leading to excitation probabilities given by Eq. (13).[34] No electron dynamics appears within this formulation. The main feature of this model follows from the coherent m sum over paths connecting $|0\rangle$ with $|n\rangle$, leading to the interference effects responsible for the intermediate-state lifetime dependence of the excitation probabilities. For situations in which the initially prepared state decays according to some distribution of lifetimes, $P_N(\tau_r)$ should be averaged over all values of τ_R, weighted by the probability that the intermediate state still exists at the given moment.[2(c)] Hence with Eq. (13) and the assumption of an exponential decay law,

$$\langle P_n\rangle = \int_0^\infty \frac{dt}{\tau_R}\exp(-t/\tau_R)P_n(t)$$

$$= \sum_{m,m'} \frac{f(n,\tilde{m})f^*(n,\tilde{m}')}{1+(\omega_0\tau_R)^2(m-m')^2} \tag{A1}$$

with $f(n,\tilde{m})\equiv\langle n|\tilde{m}\rangle\langle\tilde{m}|0\rangle$. Referring to the arguments invoked to proceed from Eqs. (7) to (9), it can be seen that

$$f(n,\tilde{m})=\exp(-\beta)(\beta^n/n!)^{1/2}A_{n,m}\ .$$

Thus the excitation probabilities implied by Eq. (19) and those given by the "exponentially averaged, sudden-switching" result, Eq. (A1), are identical. In other words, the DC-WJW solution, when averaged over all initial- and final-electron energies (consistent with energy conservation), is equivalent to the sudden-switching model in which the electron energies do not appear explicitly, only implicitly through the energy dependence of the resonance lifetime or time delay $\tau_R=\hbar\partial\delta/\partial\varepsilon$, where δ is the phase shift of the dominant partial wave characterizing the shape resonance.[36]

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