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Vibrational excitation, hole delocalization, and photoelectron line shapes of molecules

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Certain aspects of hole dynamics in electron spectroscopies of quasilocalized states in the condensed phase define the area of concern in this paper. Of special interest are the possible interference effects between low-energy shakeup satellite (electron-hole pairs, phonons, etc.) production and hole decay processes which determine the observed line shapes. As a specific example, the role and interplay of gas-phase Franck-Condon factors and substrate-induced hole delocalization in determining the photoemission line shape from nonchemisorption bonding-valence orbitals in adsorbed and free-space molecules are considered here. The present theory is discussed in the light of recent theoretical work on phonon broadening and hole decay in core-level x-ray emission, absorption, and photoelectron spectroscopy.

I. INTRODUCTION

Theoretical descriptions of complex dynamical many-body problems are often possible only if the total problem can be regarded as a collection of independent, noninterfering events. Then the algebraic form of a calculated observable quantity is that of a convolution of the theoretical results for each of the assumed-independent events. This procedure is generally valid if the characteristic time scales for each of the processes is different. When the time scales are similar, the complex problem must be regarded as a coherent single entity. An example of such a problem is the subject of this paper. In electron emission (as opposed to absorption) spectroscopies of molecules or solids, a hole is necessarily created, around which there is either electronic or vibrational (phonon) relaxation, or both. Depending upon specifics, a characteristic relaxation time T_R can be identified. In addition, the hole can decay or delocalize within another characteristic time T_D. When $T_R \approx T_D$, the possibility that the relaxation and decay processes mutually interfere must be considered. A possible realization of this condition is the intramolecular vibrational relaxation around a valence orbital hole created in an ultraviolet-photoelectron-spectroscopy (UPS) experiment on a molecule adsorbed on a metal surface. Since the characteristic vibrational times and hole lifetimes are comparable, the interference effects may play a significant part in shaping the photoelectron spectrum.

The theoretical problem of hole decay influences on phonon broadening of core lines in x-ray photoelectron spectroscopy (XPS) of the condensed phase[1] has recently been considered by Šunjić and Lucas[2] (SL) and others.[3-8] The main thrust of the SL hypothesis is that a localized hole which is produced in an XPS event and which lives for a short time relative to an inverse phonon frequency cannot transfer energy to the phonon (or whatever boson) field that is responding to the presence of the created hole. This intuitively appealing idea is then illustrated within a theory in which the effects on the boson field of the hole creation and subsequent decay enter via a phenomenological time-dependent potential acting on the phonons. SL demonstrate that for a short-lived hole, the energy transfer to the phonon system due to the time-dependent field of the hole is reduced by a factor $\sim \omega_0^2/(\omega_0^2+\Delta_h^2)$ relative to that of the infinitely long-lived hole case, where ω_0 is the phonon energy and Δ_h the hole linewidth. SL then assume a one to one correspondence between the hole spectral function and the photoelectron energy distribution (PED) as is usual practice for theories involving infinitely long-lived holes.[9-12] With this assumption, SL then claim that the resulting PED is one in which the phonon broadening is reduced by the previously mentioned energy-transfer factor. Various aspects of the SL theory have been questioned.[5-8] Almbladh and Minnhagen[8] have demonstrated that within a model in which (a) the energy dependence of the hole self-energy can be neglected, (b) the hole has no internal structure, memory, or recoil, and (c) the decay is well described in lowest order in the decay terms, then the resulting PED is the convolution of independent decay and infinitely long-lived phonon broadening functions, thus appearing to vitiate the SL theory. Further comments have appeared concerning both the dangers and/or fallacies in using quasiclassical arguments for the description of quantum-mechanical phenomenon.

Upon further consideration of the SL proposition, it can be seen that their arguments concerning the lifetime quenching of the phonon excitation, as a result of the *total* electron emission and hole decay process, are essentially correct (as will be demonstrated quantum mechanically in Sec. IV). The error was in equating the hole spectral function with the *single*-electron energy distribution. In point of fact, the simplest final state is that with two particles plus the boson field in which one of the particles is the photoelectron and the other either an Auger electron or emitted x ray, depending upon the decay mode. The SL argument gives the (essentially) correct final state of the field (within the limits of their technical approximations) but cannot yield the energies of the individual components of the two-particle final state. This phenomenon has been discussed at some length by Mahan[6] and Almbladh[7] with regards to lifetime quenching of the Franck-Condon shifts displayed between x-ray absorption and emission edges in solids. As noted by Citrin and Hamann,[5] the phonon system can redistribute energy between the absorption (photoelectron) and emission (Auger electron, x ray) products in a way which is independent of the hole lifetime and it is in this way that the photoelectron acquires a phonon broadening, even for short-lived holes. On the other hand, the degree of phonon excitation in the final state depends rather crucially on the hole lifetime (via the SL argument) and this influences the features of the decay product spectrum.[6,7]

The photoionization spectrum from a molecule absorbed on a metal surface presents some new possibilities which are relevant to the general discussion of the previous paragraphs. Specifically, a hole created in a molecular orbital state is "broadened" by (resolvable) intramolecular vibrational excitation on the adparticle. However, due to the presence of the substrate conduction band, the hole can hop or delocalize into the substrate, somewhat analogous to the core-hole decay previously discussed. Still, a number of important differences do exist. First, the delocalization process does not result in a two-particle final state as do the decay processes. Second, the delocalization can be regarded as a conversion of the originally discrete state into either a broadened virtual resonance or equivalently into system eigenstates, normalized over the entire volume of the sample, each with a greater or lesser degree of localization on the adparticle. In the latter representation, one is left with a picture of a localized boson field (intramolecular vibrational modes) scattering and mixing delocalized system hole states. This is in contrast to the more common situation in which a localized hole state scatters delocalized bosons. In the present case, recoil must be dealt with. With these distinctions between the core-hole decay and admolecule delocalization, the arguments and convolution conclusion of Almbladh and Minnhagen[8] do not appear to be applicable here in a straightforward way.

A theoretical study of the just mentioned phenomenon is now presented. In Sec. II, the basic elements of the gas-phase spectroscopies are outlined. The fundamental distinctions between surface emission and absorption experiments, as relevant to vibrational (and relaxation) excitation, are discussed in Sec. III. In the light of the content of Secs. II and III, contact is made with the apparently similar problem of phonon broadening and hole lifetime effects in core-level spectroscopies (x-ray emission, absorption, and photoelectron spectroscopy) of homogeneous solids in Sec. IV. Further discussion of the SL theory and a quantum-mechanical dephasing analog are also given. The distinction between spatial and temporal hole delocalization is elucidated in Secs. IV and V. Expressions for the photoelectron energy distribution from adsorbed molecules then follow which are "lifetime" convolutions (Sec. IV) of gas-phase (Sec. II) spectra, which themselves are renormalized due to the delocalization and recoil effects (Sec. V). The theory is numerically illustrated in Sec. VI, using as examples the nonbonding 1π photoelectron spectra of adsorbed CO and the Voigt line shape. Section VII serves as a finale.

II. GAS-PHASE SPECTROSCOPIES

In both electron energy loss and ultraviolet photoelectron spectroscopy (EELS and UPS) of gas-phase molecules, structure in the electron energy distributions which corresponds to the excitation of various vibrational states is observed.[13–15] If the process involves electronic excitation, then in the Born-Oppenheimer approximation, the intensities of the vibrationally excited states are determined by Franck-Condon factors, that is the modulus square of the overlap integral of the ground-state vibrational wave function $\equiv |0\rangle$ of the electronic ground-state potential with any of the vibrational wave functions $\equiv |x;{}^*\rangle$ of the electronically excited molecule or molecular-ion potentials. The kinetic energy distribution of the detected electrons is given by

$$N_+^0(\epsilon) \sim \sum_x \delta(\epsilon - \epsilon_d + \epsilon_x) |\langle 0|x;{}^*\rangle|^2 , \tag{1}$$

where ϵ_d is the primary electron energy minus the electronic excitation energy in EELS, or is the photon energy minus the electron binding energy in UPS. In either case, relaxation shifts due to intramolecular vibrational effects are *not* to be included in the specification of ϵ_d.

The gas-phase photoelectron spectra show a rich variety of forms, depending upon R_0, the equilibrium nuclear separation and the slope of the potential-energy curve for the excited molecular-ion (hole state) with respect to the ground state, as in Fig. 1. Ionization of a lone-pair electron in the AB diatomic molecule leaves R_0 relatively unchanged, in which

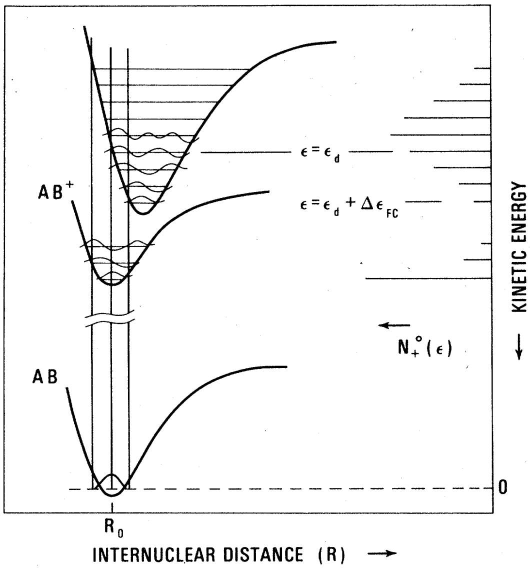

FIG. 1. Potential-energy diagrams illustrating some possible configurations which result in the photoionization spectra shown on the right. Note that the energy scale, in terms of photoelectron kinetic energy, increases from top to bottom. (From Rabalais, Ref. 14).

case little intrinsic vibrational excitation appears (such as in the 4σ or 5σ peaks of CO), whereas ionization from a bonding orbital (such as the 3σ or 1π orbitals of CO) causes the nuclei to separate ($R_0^+ > R_0^{\text{neutral}}$) and $|0\rangle$ projects onto many of the excited vibrational states of the molecular ion. Consequently a large number of vibrational features appear in the spectrum. The point of maximum kinetic energy, often referred to as the adiabatic threshold or "zero-phonon line", is shifted by some amount $\equiv \Delta\epsilon_{FC}$ called the Franck-Condon (FC) shift above ϵ_d. In addition, a band of discrete "satellite" lines appear below the zero-phonon line with intensities depending upon the FC factors. It is not unusual for both the shifts and bandwidth to be as large as ~ 1 eV. The maximum intensity in the band does not have to coincide with either $\epsilon_d+\Delta\epsilon_{FC}$ or ϵ_d.

Within a linear displaced harmonic oscillator model of the vibrational field, and in the limit in which nonadiabatic coupling between the electronic and vibrational motion can be neglected, Eq. (1) leads to a Poisson distribution for the photoelectron spectrum[15]

$$N_+^0(\epsilon)=e^{-\beta}\sum_{n=0}^{\infty}\left[\frac{\beta^n}{n!}\right]\delta(\epsilon-\epsilon_d-\beta\omega_0+n\,\omega_0)$$

$$\rightarrow \lim_{\beta>>0}\frac{1}{(2\pi)^{1/2}\Delta}\exp\left[-\frac{1}{2}\left[\frac{\epsilon-\epsilon_d}{\Delta}\right]^2\right], \qquad (2)$$

where $\beta=\Delta\epsilon_{FC}/\omega_0$, $\Delta=\beta^{1/2}\omega_0$, and ω_0 is the intramolecular vibrational energy. From Eq. (2), it is apparent that $N_+^0(\epsilon)_{\max}$ occurs at $\epsilon=\epsilon_d$ only in the large β limit. For CO 1π, $\beta\simeq 2.5$ and $\omega_0\simeq 0.2$ eV so $\Delta\epsilon_{FC}\simeq 0.5$ eV. (Similar effects in x-ray absorption and emission edges have recently been discussed by Mahan[6] and Almbladh.[7])

Before moving to adsorbed molecules, note that unless one incorporates the FC factors into photoionization theories, as discussed at great length by Cederbaum and Domcke,[15] it is not apparent that electron binding energies obtained from molecular cluster calculations can be directly compared with observed photoionization spectra to an accuracy better than the vibrational bandwidth.

III. ABSORPTION VERSUS EMISSION FOR ADSORBATES

What are the new features which must be considered when doing vibrational spectroscopy on adsorbed molecules? The experimental facts are that in absorption spectroscopies (infrared and EELS), the vibrational modes still remain fairly sharp and similar to those for the gas phase whereas in emission spectroscopies (UPS and XPS), not only are the individual intramolecular vibrations washed out, but also additional broadening upon the FC envelopes appears.[16,17] The distinctions between the absorption and emission spectroscopies are shown in real space in the top part and in energy space in the bottom part of Fig. 2. For both cases, the adsorbed molecular

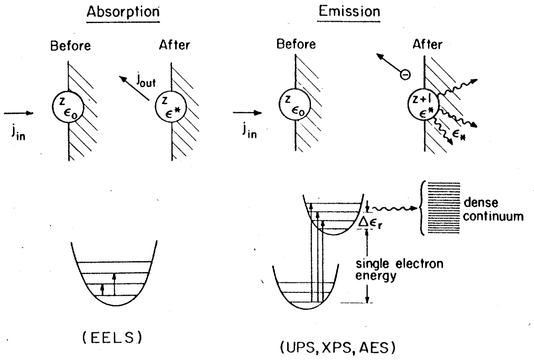

FIG. 2. Schematic illustration of the distinctions between absorption and emission processes, both in terms of "real"-space (top) and potential-energy (bottom) diagrams. The circles represent localized surface complexes and the symbols within, the state of the complex before or after the process. Absorption is characterized by transitions within the electronic ground-state energy surface whereas emission requires transitions to an excited-state surface. The excited state can be coupled to a dense continuum of other states, reached by either shakeup not included in the potential-energy curves or by radiative decay for instance. The coupling is represented by the wavy pointing line.

complex is represented by the circle and the substrate by the crosshatched area. For absorption, a beam is incident on the chemisorption complex (charge Z, energy ϵ_0), weakly coupled to the indented substrate. Upon scattering, the complex remains in the charge state Z but is now excited to some ϵ^*. Since any interaction with the substrate is necessarily of Coulombic origin, and since the monopole value of the complex does not change, the excited state complex remains weakly coupled to the substrate. Hence the gas phase and adsorbed spectra remain reasonably similar. Vibrational transitions on the electronic ground-state potential surface, shown on the bottom left (as in EELS) are typical of this process. Things are quite different in emission. Upon ejection of an electron from the chemisorbed complex, the charge state changes by one, thus turning on a strong coupling with the substrate. This shows up as a time varying field crossing the boundary which delivers energy to the elementary excitations (electron-hole pairs, bulk or surface plasmons) of the substrate. Thus new host-induced shakeup satellites and relaxation shifts are possible. In addition, electron transfer across the boundary, from substrate to ion, is possible which reduces the localization lifetime of the hole state. It is the observable consequences of this latter possibility which we will consider here. In the language of theoretical chemistry,[18] the hole state (unlike the neutral ground state) coupling to a dense continuum (provided by the substrate), as shown in the lower right of Fig. 2, is the source of any fundamental differences between absorption and emission spectroscopies of vibrational excitations.

IV. DEEP HOLES, PHONONS, AND DECAY

Šunjić and Lucas[2] recently raised the question (within the context of phonon broadening of core lines in XPS from alkali halides[1]), how can a relatively slow vibrational field (phonons with $\omega_0 \sim 10^{-2}$ eV) respond to the field of a localized hole created in a photoejection process, if the hole lifetime (due to radiative or Auger decay) is short relative to the vibrational period ($\Delta_{\text{hole}} \simeq 1$ eV)? The theoretical alternatives reduced to two possibilities: (a) Treat the hole as infinitely long lived, calculate the phonon excitations [Eq. (2)] and then convolve the results with a lifetime Lorentzian.[5–8] (b) Renormalize the hole-phonon coupling [which showed up in their theory as the replacement of β by $\beta_{\text{renorm}} = [\omega_0^2/(\omega_0^2+\Delta_h^2)] \times \beta$ in Eq. (2)] to account for the finite lifetimes.

Their work stimulated quite some discussion in the literature.[3–8] The current view seems to favor alternative (a) which provides a theoretical picture in agreement with experiment.[1]

Since the SL proposition does have an intuitive appeal, it seems desirable to examine it more deeply in order to understand where the pitfalls lie. The essence of their idea is contained in the following argument. For an infinitely long-lived hole, the phonons respond to an instantaneously switched on potential $V_{\text{hole}}(t) = V_0\theta(t)$ whose (imaginary part of the) Fourier transform is $V_{\text{hole}}(\omega) \sim V_0/i\omega$. On the other hand, for a decaying hole

$$V^{\Delta}_{\text{hole}}(t) = V_0\theta(t)e^{-\Delta_h t} ,$$

$$V^{\Delta}_{\text{hole}}(\omega) \sim V_0/(i\omega - \Delta_h) ,$$

which is much smaller than $V_{\text{hole}}(\omega)$ when $\Delta_h >> \omega$. Since the *net* lattice excitation (at frequency ω) is due to the driving force of the ωth Fourier component of the time-dependent hole potential, little excitation will occur for short-lived holes.

The basic consequences of these semiclassical ideas can also be reproduced on a strictly quantum-mechanical model in the following way. Suppose that a harmonic oscillator system, initially in the ground state $|0,0\rangle$ of the electronic ground-state potential suddenly finds itself in the potential of some excited electronic state, say a molecular-ion state as in photoionization, at time $t=0$. Then within the Franck-Condon limit (vertical transitions and no relative phase changes due to the process of switching on the new potential[9(b),19]) the ensuing time-dependent wave function of the oscillator can most easily be expressed as a coherent sum of oscillator eigenstates of the ionic potential, that is

$$\psi(t>0) = \sum_i \langle i^*|00\rangle e^{i\epsilon_i^* t}\psi_{i^*} , \tag{3}$$

where $\langle i^*|00\rangle$ is the overlap integral of the ground-state oscillator wave function with the ith excited ion oscillator state with energy ϵ_i^*. If after a time $t=1/\gamma$, the system returns to its electronic ground state (by a decay process for instance) then it becomes most convenient to describe the subsequent time evolution of the oscillator in terms of the set ψ_{j0}, the electronic ground-state oscillator functions. Consequently

$$\psi(t>1/\gamma) = \sum_j \langle j0|\psi(t=1/\gamma)\rangle e^{i\epsilon_j^0(t-1/\gamma)}\psi_{j0} ,$$

which with $\psi(t=1/\gamma)$ given by Eq. (3) can be written

$$\psi(t>1/\gamma) = \sum_{i,j} \langle j0|i^*\rangle \langle i^*|00\rangle e^{i(\epsilon_i^* - \epsilon_j^0)/\gamma} e^{i\epsilon_j^0 t}\psi_{j0} . \tag{4}$$

The probability that the oscillator ends up in the jth excited state, as a result of the entire process, is given by

$$P_{j'} = \lim_{t \to \infty} |\langle j'0|\psi(t)\rangle|^2$$

and with Eq. (4)

$$P_{j'} = |\sum_i \langle j'0|i^*\rangle e^{i\epsilon_i^*/\gamma} \langle i^*|00\rangle|^2 \, . \tag{5}$$

Equation (5) gives a transparent picture of the chain of events. Upon initial excitation, $|00\rangle$ is projected onto the set of excited oscillator states $|i^*\rangle$. Each component of the state vector acquires a different amount of phase while in the intermediate excited state and it is this dephasing which depends on the time spent in the intermediate state before the circuit is completed back to the electronic ground state. If the lifetime of the "intermediate" ionic state is sufficient to allow dephasing, then a net transfer of energy to the oscillator system results and it is this phenomenon which is more or less reproduced by the SL model.

Two interesting and general limits are obtained from Eq. (5). For hole lifetimes that are short relative to oscillator frequencies $\epsilon_i^*; << \gamma$, $e^{i\epsilon_i^*/\gamma} \approx 1$ (no dephasing),

$$P_{j'}(\gamma \to \infty) = |\langle j'0|00\rangle|^2 = \delta_{j',0} \, ,$$

and the oscillator does not excite throughout the roundtrip. In the other extreme of long-lived holes ($\epsilon_i^* >> \gamma$), the phase factor in Eq. (5) is rapidly fluctuating in sign, tending to average out to zero the off-diagonal terms in the coherent sum on intermediate states, leaving

$$P_{j'}(\gamma \to 0) = \sum_i |\langle j'0|i^*\rangle|^2 |\langle i^*|00\rangle|^2 \, ,$$

which is just a sum of probabilities over the various incoherent paths proceeding from the initial ground state $|00\rangle$ to a specified final state $|j'0\rangle$, given that an intermediate dephasing step is made in one of the ionic states $|i^*\rangle$. These results are completely independent of the details of the oscillator potentials (harmonic or not, eigenvalue structure of either state, etc.). Nonetheless, they show that the degree of oscillator excitation, due to the *total* process of hole creation and annihilation, does depend crucially on the magnitude of the hole lifetime relative to the oscillator frequency. In this sense, the classical model is not as misleading as some have suggested.

Unfortunately the link between the oscillator excitation probability or decaying hole spectral function and the photoelectron spectrum is not straightforward. SL assumed that they were proportional. This was the fundamental flaw in their argument. In its simplest form, the decaying hole spectral function is proportional to some two-particle energy distribution, that of the photoelectron plus decay product, and some additional theoretical inputs are required in order to separate this into individual components. The reader is referred to the physically illuminating discussion of Citrin and Hamann[5] and the equally illuminating but more mathematical treatments of Mahan,[6] Almbladh,[7] and Minnhagen[8] for possible resolutions of this problem. The central idea is that the initial state core electron experiences a fluctuating potential due to the thermal and zero-point motion of the surrounding atoms and it is an averaging over the possible initial state configurations (expressible in phonon coordinates) which produces the major, but lifetime-independent, phonon broadening of the core-level XPS lines. Hence a convolution of a decay function with a lifetime-independent phonon-broadening function produces an acceptable representation of the XPS line shape.

V. UPS OF ADSORBED MOLECULES

In UPS of adsorbed molecules, observed widths of valence orbitals (after considerations of FC broadening) are typically of order 1 eV compared to vibrational energies of order 0.1 eV. Thus the hole lives on the molecule for a short time relative to the intramolecular vibrational period and the considerations of the last few paragraphs should be germane. Note, however, that the *differential* observed widths of lone pairs versus intramolecular bonding orbitals have been discussed in terms of Lorentzian-convolved FC envelopes.[16,17] The implications of the ideas outlined in Secs. I–IV, as they apply to the valence orbital UPS line shapes, will now be worked out. To effect this end, the section will be subdivided into parts dealing with (A) the model Hamiltonian, (B) the hole spectral function, (C) coupling constant renormalization, (D) hole recoil, and (E) the union of items A–D.

A. Model Hamiltonian

It is well established that the problem of a decaying hole linearly coupled to a boson field is compactly represented by the model Hamiltonian[8]

$$H = H_a + H_c + H_D + H_b \, , \tag{6a}$$

with

$$H_a = \epsilon_a c_a^\dagger c_a \, , \tag{6b}$$

$$H_c = \sum_j \epsilon_j c_j^\dagger c_j \, , \tag{6c}$$

$$H_D = \sum_j (V_{aj} c_j^\dagger c_a + V_{aj}^* c_j c_a^\dagger) \, , \tag{6d}$$

$$H_b = \omega_0 b^\dagger b + \lambda_0 c_a c_a^\dagger (b + b^\dagger) \, . \tag{6e}$$

In Eq. (6), ϵ_a, c_a, and $c_a^\dagger$ are the localized electron eigenvalues and fermion operators; ϵ_j, c_j, and $c_j^\dagger$, are the unperturbed continuum energies and operators to which the discrete localized state is coupled with strength V_{aj}; and ω_0, b, and $b^\dagger$ are the same quantities for the bosons which are linearly coupled (in the gas phase where $V_{aj}=0$) with strength λ_0 to hole states.

Almbladh and Minnhagen have emphasized,[8] after Anderson[20] and Fano,[21] that the unitary transformations

$$c_a = \sum_n v(\tilde{\epsilon}_n) d_n \,, \tag{7a}$$

$$c_j = \sum_n u(\tilde{\epsilon}_n, \epsilon_j) d_n \,, \tag{7b}$$

diagonalize

$$H_a + H_c + H_D \rightarrow \sum_n \tilde{\epsilon}_n d_n^\dagger d_n \equiv H_n \,,$$

when

$$v(\tilde{\epsilon}_n) = [B_a(\tilde{\epsilon}_n)/\rho(\tilde{\epsilon}_n)]^{1/2} \,, \tag{8a}$$

with

$$B_a(\tilde{\epsilon}_n) = \frac{1}{\pi} \frac{\Gamma(\tilde{\epsilon}_n)}{[\tilde{\epsilon}_n - \epsilon_a - \Delta(\tilde{\epsilon}_n)]^2 + \Gamma^2(\tilde{\epsilon}_n)} \,, \tag{8b}$$

$$\Delta(\tilde{\epsilon}_n) = \mathrm{P} \int \frac{|V_{aj}|^2}{\tilde{\epsilon}_n - \epsilon_j} \rho_c(\epsilon_j) \, d\epsilon_j \,, \tag{8c}$$

$$\Gamma(\tilde{\epsilon}_n) = \pi \rho_c(\tilde{\epsilon}_n) \langle |V_{aj}|^2 \rangle \tag{8d}$$

and

$$\rho(\tilde{\epsilon}_n) \simeq B_a(\tilde{\epsilon}_n) + \rho_c(\tilde{\epsilon}_n) \,. \tag{8e}$$

Here $\rho_c(\epsilon_j)$ and $\rho(\tilde{\epsilon}_n)$ are the unperturbed and perturbed continua density of states in the vicinity of the adsorbate, $\langle |V_{aj}|^2 \rangle$ is an "averaged" coupling term, and $u(\tilde{\epsilon}_n, \epsilon_j)$ is not needed here. The simple virtual-level model is appropriate when Δ and Γ are slowly varying with $\tilde{\epsilon}_n$, in which case $B_a(\tilde{\epsilon}_n)$ is a Lorentzian.

In the core-hole decay problem, $H_c + H_D$ describe the final state continua of an x ray plus valence-band hole (radiative decay) or Auger electron plus two valence-band holes [for core-valence-valence Auger transitions which are the only ones consistent with the form for H_b given in Eq. (6e)] and the coupling of these continua with the localized hole. Things are somewhat different for hole delocalization due to hopping or (solid-state band effects). In this case H_D coherently transfers the hole between the localized site a and any other site within the solid, if j is a band state index. This possibility converts the discrete localized state into a broadened resonance or virtual state if $|V_{aj}|$ is reasonably small compared to the bandwidth and does not vary significantly with j, and if ϵ_a lies well within the band.[20] However only one hole exists throughout the entire process. The valence-electron structures of many adsorption systems are described quite nicely by the virtual-level model.[22] As specific examples, we would include the valence electrons in ionic alkali chemisorption and neutral-rare-gas physisorption as well as nonbonding molecular orbitals in chemisorbed molecules such as the 1π for CO on Ni. Recall that the gas-phase photoelectron spectra of 1π CO is rich in vibrational structure, due to H_b induced-boson excitation. It is in cases like this, where both H_D and H_b must be considered, that interest arises.

Taking advantage of the prediagonalization transformations Eq. (7), the full Hamiltonian of Eq. (6) can be written equivalently

$$H = \sum_n \tilde{\epsilon}_n d_n^\dagger d_n + \omega_0 b^\dagger b + \sum_{n',n''} \lambda_{n',n''} d_{n'} d_{n''}^\dagger (b + b^\dagger)$$

$$\equiv H_n + H_b' \,. \tag{9}$$

In this form the theoretical problem has been transformed into the determination of a new V_{aj}-dependent renormalized coupling constant $\lambda_{n'n''}$ which permits off-diagonal hole scattering by the localized bosons. A similar philosophy has been adopted in certain aspects of polaron theory but with attention focused on the boson renormalization of the hopping parameter V_{aj}, rather than the hopping parameter renormalization of the boson coupling constant.[23] In either case a "band narrowing" effect results.

B. Hole spectral function

For photoionization events ending in one-particle final states (i.e., no Auger or radiative decay) the photoemission energy distribution resulting from ionization of the ϵ_a level (in the sudden limit) is proportional to the hole spectral function[3–5,8,9,15]

$$N_+(\omega) = \int_{-\infty}^{+\infty} \frac{dt}{2\pi} e^{i\omega t} \langle c_a^\dagger(0) c_a(t) \rangle \,, \tag{10}$$

with $c_a(t) = e^{iHt} c_a e^{-iHt}$ and the expectation value is taken over the exact no-hole ground state. It is a standard exercise[9,15] to show that for $H = H_a + H_b$, Eqs. (6) and (10) lead directly to the independent boson model (IBM) spectrum given by Eq. (2) with $\beta = (\lambda_0/\omega_0)^2$. For cases in which a decay particle is produced through the action of H_D, the general correspondence between the hole spectral function, Eq. (10), and the one-electron photoemission energy distribution is not clear, as detailed in the discussion of SL theory. Under the limiting (but widely applicable) conditions imposed by Almbladh and Minnhagen,[8] the photoemission energy distribution is given as the convolution of Eq. (10) for $H = H_a + H_b$, with a lifetime Lorentzian whose parameters are determined by $H_c + H_d$.

In the present case of hole delocalization as opposed to decay, only one electron is produced and thus a one-to-one correspondence between the hole spectral function and the photoelectron energy distribution (PED) (subject to the usual limitations) exists. The photoelectron spectrum resulting from ionization of the ϵ_a state is obtained from the Green's function

$$g_a(t) = i\langle c_a^\dagger(0)c_a(t)\rangle \simeq \sum_n |v(\tilde{\epsilon}_n)|^2 \langle d_n^\dagger(0)d_n(t)\rangle \ , \tag{11}$$

where the c_a operators have been expressed in terms of the prediagonalized d_n operators through Eq. (7a) and only diagonal terms have been retained (as discussed elsewhere[24]) to facilitate comparisons with local density of states[25] changes due to simple Lorentzian broadening in the $\lambda_0=0$ limit. The time dependence of $d_n(t)$ is now more conveniently expressed through the Eq. (9) version of the system Hamiltonian. In the d representation, Eqs. (9) and (11) yield

$$g_a(t) = \sum_n |v(\tilde{\epsilon}_n)|^2 e^{-i\tilde{\epsilon}_n t}\langle 0|d_n^\dagger e^{iH_b' t} d_n|0\rangle \ . \tag{12}$$

Since both $\lambda_{n',n''}$ and also $v(\tilde{\epsilon}_{n'})$ which appear in H_b' or Eqs. (9) and (12) depend upon V_{aj}, details of the hole delocalization process enter into the hole-boson coupling in a nontrivial manner, one which cannot be described by a simple convolution of noninterfering events. This conclusion is independent of the specific technical approximations one chooses to reduce Eq. (12) to a computationally tractable form. For completeness we note that the appropriate hole Green's function for the free-space molecule, in analogy with Eq. (12), is

$$g_a^0(t) = e^{-i\epsilon_a t}\langle 0|c_a^\dagger e^{iH_b t} c_a|0\rangle \ , \tag{13}$$

with H_b given by Eq. (6e).

C. Coupling-constant renormalization

The coupling between the hole and the vibrational modes of the molecule is Coulombic and thus can be obtained from the electrostatic energy

$$\Delta E \equiv \frac{1}{2}\int \phi_{\text{hole}}(\vec{r})\rho_{\text{nuc}}(\vec{r})\, d^3r \ , \tag{14}$$

where $\phi_{\text{hole}}(\vec{r})$ is the electrostatic potential at $\vec{r}$ due to the hole charge distribution and $\rho_{\text{nuc}}(\vec{r})$ is the nuclear charge distribution (ion cores plus electrons rigidly tied to the nuclear motion). For a free-space molecule, the charge distribution associated with a hole wave function $\psi_a(\vec{r})$ is $\rho_{\text{hole}}(\vec{r}) = |\psi_a(\vec{r})|^2$ so Eq. (14) can be written

$$\Delta E = \frac{1}{2}\int |\psi_a(\vec{r}\,')|^2 \frac{e^2}{|\vec{r}-\vec{r}\,'|}\rho_{\text{nuc}}(\vec{r})\, d^3r\, d^3r' \ . \tag{15}$$

The nuclear charge distribution is well approximated by a sum of point charges at the instantaneous position $\vec{r}_i$ of each nuclei, that is

$$\rho_{\text{nuc}}(\vec{r}) = \sum_i \delta^{(3)}(\vec{r}-\vec{r}_i) \ .$$

Thus Eq. (15) reduces to

$$\Delta E = \frac{1}{2}\sum_i e^2 \int \frac{|\psi_a(\vec{r}\,')|^2}{|\vec{r}_i-\vec{r}\,'|}\, d^3r' \equiv \sum_i \Delta E_i \ . \tag{16}$$

For stretch modes in diatomic molecules $\vec{r}_i$ can be regarded as the relative nuclear coordinate and the sum on i reduces to a single term. Expanding $\vec{r}_i$ about the equilibrium positions,

$$\vec{r}_i = \vec{r}_{i0} + \vec{u}, \quad \text{with } \vec{u} = \left[\frac{\hbar}{2M\omega_0}\right]^{1/2}(b+b^\dagger)\hat{\epsilon}$$

the normal-mode displacement operator, M the reduced mass, and $\hat{\epsilon}$ a unit vector in the normal-mode direction,

$$\Delta E = \Delta E(\vec{r}_i)\big|_{\vec{r}_i=\vec{r}_{i0}} + \vec{u}\cdot\frac{d}{d\vec{r}_i}E(\vec{r}_i)\big|_{\vec{r}_i=\vec{r}_{i0}} + \dots \ . \tag{17}$$

The first term on the right-hand side in Eq. (17) is just a rigid shift which plays no role in the dynamical behavior. Writing the displacement vector $\vec{u}$ in terms of the b operators, comparison of Eqs. (6e), (16), and (17) shows that the hole-boson coupling constant λ_0, for the free molecule, is identically

$$\lambda_0 = \frac{e^2}{2}\left[\frac{\hbar}{2M\omega_0}\right]^{1/2}\left[\hat{\epsilon}\cdot\frac{d}{d\vec{r}_i}\int\frac{|\psi_a(\vec{r}\,')|^2}{|\vec{r}_i-\vec{r}\,'|}\, d^3r'\right]\bigg|_{\vec{r}_i=\vec{r}_{i0}} \tag{18}$$

Proceeding to the molecule weakly coupled to the substrate, we note that in real space, the unitary transformations, Eqs. (7a) and (7b) have the effect of mixing the (*assumed* complete and mutually orthonormal) set of metal states $\psi_j(\vec{r})$ and the molecule state $\psi_a(\vec{r})$ resulting in new system wave functions

$$\psi_n(\vec{r}) = \eta[v(\tilde{\epsilon}_n)\psi_a(\vec{r}) + \sum_j u(\tilde{\epsilon}_n,\epsilon_j)\psi_j(\vec{r})] \ , \tag{19}$$

which form the basis for the d representation. Specification of the normalization constant η requires further considerations. From orthonormality,

$$\langle n|n\rangle = 1 = |\eta|^2[|v(\tilde{\epsilon}_n)|^2 + \sum_j |u(\tilde{\epsilon}_n,\epsilon_j)|^2] \ . \tag{20}$$

If the substrate is regarded as a free-electron metal, $u(\tilde{\epsilon}_n,\epsilon_j)$ is slowly varying with j,[20] and thus

$$\begin{aligned}\sum_j |u|^2 &\simeq |\bar{u}|^2\Omega\int_{k_l}^{k_u}\frac{d^3k}{(2\pi)^3}\\ &= |\bar{u}|^2\Omega\left[\frac{k_u^3-k_l^3}{6\pi^2}\right] >> |v(\tilde{\epsilon}_n)|^2 \ ,\end{aligned} \tag{21}$$

where $\bar{u}$ is an average value of $u(\tilde{\epsilon}_n, \epsilon_j)$ within the relevant volume of k space bounded by k_u and k_l, and Ω is the substrate normalization volume. Letting $k_l = 0$ and $k_u = k_F$ the Fermi wave number which are reasonable limits and setting $|\bar{u}|^2 = 1$ which says that there is a one-to-one correspondence between perturbed and unperturbed continua states,[21] the normalization constant obtained from Eqs. (20) and (21) is

$$\eta \simeq (n_s \Omega)^{-1/2} , \tag{22}$$

where $n_s = k_F^3/2\pi^2$ is the free-electron density in the solid. This form for the normalization constant is a result of some technical approximations which do not affect any qualitative conclusions.

In order to evaluate the Green's function, Eq. (12), describing the time evolution of the adsorbed molecule hole, the coupling constant $\lambda_{n',n''}$ in Eq. (9) must be specified. This characterizes possibly off-diagonal mixing of the delocalized d states by the localized vibrational field. Proceeding as in the derivation of λ_0 given by Eq. (18), the nondiagonal hole charge density from Eqs. (19) and (22) is

$$\rho_{\text{hole}}^{n',n''}(\vec{r}) = \frac{1}{n_s \Omega} \Big\{ v(\tilde{\epsilon}_{n'}) v^*(\tilde{\epsilon}_{n''}) |\psi_a(\vec{r})|^2 + \sum_j [v(\tilde{\epsilon}_{n'}) u^*(\tilde{\epsilon}_{n''}, \epsilon_j) \psi_a(\vec{r}) \psi_j(\vec{r}) + \text{c.c.}]$$
$$+ \sum_{j,j'} [u(\tilde{\epsilon}_{n'}, \epsilon_j) u^*(\tilde{\epsilon}_{n''}, \epsilon_{j'}) \psi_j(\vec{r}\,') \psi_{j'}^*(\vec{r}) + \text{c.c.}] \Big\} , \tag{23}$$

where c.c. stands for complex conjugate. Due to the much larger overlap of $\rho_{\text{nuc}}(\vec{r})$ with $|\psi_a(\vec{r})|^2$ compared to that with $\psi_a(\vec{r})\psi_j^*(\vec{r})$ or $|\psi_j(\vec{r})|^2$, by far the dominant contribution when $\rho_{\text{hole}}^{n',n''}(\vec{r})$ from Eq. (23) is inserted into Eq. (15) comes from the first term on the right-hand side. Within the constraint that the second and third terms can be neglected, the energy integral analogous to Eq. (16) is

$$\Delta E^{n',n''} \simeq \left[\frac{1}{n_s \Omega} v(\tilde{\epsilon}_{n'}) v^*(\tilde{\epsilon}_{n''}) \right] \times \frac{1}{2} \sum_i e^2 \int \frac{|\psi_a(\vec{r}\,')|^2}{|\vec{r}_i - \vec{r}\,'|^2} d^3 r' , \tag{24}$$

which is identical to the free-space molecule result multiplied by the vibrationally independent "delocalization term" in brackets. Mapping of the integral in Eq. (24) onto the expression for the coupling constant λ_0 [Eq. (18)] has already been carried out. Consequently the d-representation coupling constant $\lambda_{n',n''}$ which follows from Eq. (24) is

$$\lambda_{n',n''} \simeq \frac{1}{n_s \Omega} v(\tilde{\epsilon}_{n'}) v^*(\tilde{\epsilon}_{n''}) \lambda_0 . \tag{25}$$

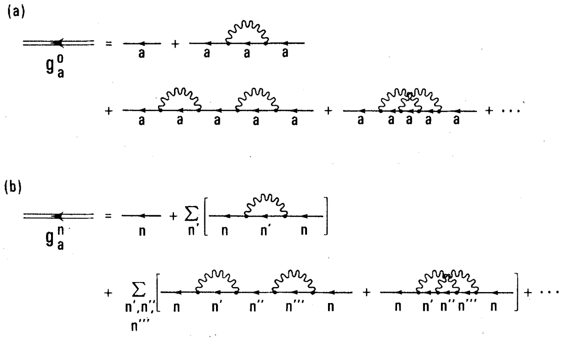

FIG. 3. Diagrammatic representation of hole propagation in a renormalizing boson field. (a) Stationary (core) hole with no internal structure, thus no recoil. Consequently all hole lines represent the same state. (b) Delocalized hole which can scatter into various intermediate states. Hence the sum on possible intermediate state.

D. Hole recoil

The distinction must now be recognized between the dynamics of a nonstationary localized core hole and that of stationary extended d_n states, interacting with the localized boson field, and the ways in which each characteristic behavior is incorporated in either Eq. (6) and Eq. (13) or Eqs. (9), (12), and (25), respectively. If the exponential in the rigid core-hole propagator Eq. (13) is written as an expansion, then each term can be represented diagramatically as in Fig. 3(a). The point to be stressed is that although the bare hole propagator is renormalized by the boson self-energy processes, each hole-boson vertex is characterized by the same hole propagator entering and leaving. This is due to the lack of any dynamical degrees of freedom in the hole, other than the two states, which in an anthropomorphic sense are existence or death,[26] with no options on the "quality of life". There is no way for the hole to record the fact that it interacted with the bosons, or vice versa, hence the name independent-boson model. For each c_a state entering the vertex, there is only one possible state leaving.

Performing the same expansion on Eqs. (12) and (25), the equivalent diagrammatic representation is shown in Fig. 3(b). The significant point here is that the interaction term

$$H'=\sum_{n,n'}\lambda_{n,n'}d_n d_{n'}^{\dagger}(b+b^{\dagger})$$

permits scattering of the incoming n hole into any of a large number of n' states and this is what is meant by recoil. Thus the hole-boson scattering at some time t depends upon the history for all times $t'<t$ since it is only in this way that one can ascertain which hole state enters the vertex at t. The action of H' on the bare states can be viewed as a vibrationally induced mixing or hybridization amongst them. Rigorous treatment of this complex problem is at least equivalent to a Kondo theory[27] and thus is beyond the scope of this study.

A reasonable mean-field approximation can be introduced which retains the features of the recoil phenomenon essential to the qualitatively correct description of the present problem. Setting

$$\sum_{n',n''}\lambda_{n',n''}d_{n'}d_{n''}^{\dagger}\simeq fN\sum_{n'}\lambda_{n',n'}d_{n'}d_{n'}^{\dagger}\ , \tag{26}$$

the following interpretation is offered. For an incident hole state n', the boson interaction can scatter into any of the N other continuum states n''. Thus the sum on n'' is replaced by a multiplicative factor N and the n'' index replaced by n'. The memory or recoil effect is thus dealt with in an average sense. However, each scattering most likely couples only those states within an energy $\pm\omega_0$ of the incident hole energy which is a fraction $f\simeq\omega_0/\Gamma$ of the available hole states with significant amplitude on the adatom.[28] Obviously this physical argument is reasonable only when $\omega_0<\Gamma$, which is the case in physically realistic systems. For model calculations, f will be taken to be unity if $\omega_0>\Gamma$ implying random and complete dynamical mixing in this limit. Finally, the nondiagonal hole-boson interaction in Eq. (9) which follows from Eqs. (25) and (26) is

$$H_{\text{int}}\simeq\sum_{n'}f|v(\tilde{\epsilon}_{n'})|^2\lambda_0 d_{n'}d_{n'}^{\dagger}(b+b^{\dagger}) \tag{27}$$

upon noting that $N/\Omega=n_s$.

E. Final result

Proceeding to a final working expression for the hole spectral function and thus PED is now straightforward. When Eq. (27) is inserted in Eq. (12), the only surviving term in the n' sum is for $n'=n$. Thus, H_b can be replaced by

$$H_b'=\omega_0 b^{\dagger}b+f|v(\tilde{\epsilon}_n)|^2\lambda_0 d_n d_n^{\dagger}(b+b^{\dagger})\ , \tag{28}$$

where it is apparent that the hole delocalization has led to a renormalized boson coupling. The matrix elements in Eq. (12) are identical with the IBM model in which $\lambda'(\tilde{\epsilon}_n)\equiv f|v(\tilde{\epsilon}_n)|^2\lambda_0$ is substituted for λ_0. Equations (8a), (8b), (8e), (10), (11), (12), and (28), together with the replacement $\sum_n\rightarrow\int\rho(\tilde{\epsilon}_n)\,d\,\tilde{\epsilon}_n$, result in the following "renormalized-convolution" expression for the hole spectral function:

$$N_+(\omega)=\int d\,\tilde{\epsilon}_n\,B_a(\tilde{\epsilon}_n)N_+^0(\omega-\tilde{\epsilon}_n;\lambda'(\tilde{\epsilon}_n))\ , \tag{29a}$$

or explicitly

$$N_+(\omega)=\sum_{m=0}^{\infty}\int d\,\tilde{\epsilon}_n\,B_a(\tilde{\epsilon}_n)e^{-\beta(\tilde{\epsilon}_n)}\left(\frac{\beta^m(\tilde{\epsilon}_n)}{m!}\right)\delta(\omega-\tilde{\epsilon}_n-\beta(\tilde{\epsilon}_n)\omega_0+m\,\omega_0) \tag{29b}$$

$$=\sum_{m=0}^{\infty}\frac{B_a(\tilde{\epsilon}_n)e^{-\beta(\tilde{\epsilon}_n)}[\beta^m(\tilde{\epsilon}_n)/m!]}{\omega_0|\,d\beta\,(\tilde{\epsilon}_n)/d\,\tilde{\epsilon}_n|}\Bigg|_{\tilde{\epsilon}_n=\omega-\beta(\tilde{\epsilon}_n)\omega_0+m\,\omega_0}\ , \tag{29c}$$

where $\tilde{\epsilon}_n$ in Eq. (29c) is to be determined self-consistently. A useful approximation giving an upper limit to the renormalized boson coupling (and thus a *lower limit* to any observable effects due to renormalization) is $\lambda'(\tilde{\epsilon}_n)\simeq\lambda'(\tilde{\epsilon}_n=\epsilon_a+\Delta(\epsilon_a))$ in Eq. (29a). This implies that all states within the broadened resonance couple to the bosons with identical strength, specified at the resonance maximum. Then Eq. (29b) reduces to

$$N_+(\omega)\simeq\sum_{m=0}^{\infty}B_a(\omega-\beta_r\omega_0+m\,\omega_0)e^{-\beta_r}(\beta_r^m/m!) \tag{30a}$$

where at resonance, from Eqs. (8a), (8b), and (8e),

$$v^2(\epsilon_r)=[1+\pi\Gamma(\epsilon_r)\rho_c(\epsilon_r)]^{-1}\ , \tag{30b}$$

so

$$\beta_r=f^2v^4(\epsilon_r)\frac{\lambda_0^2}{\omega_0^2}=\lim_{\omega_0<\Gamma}\beta_0\left(\frac{\omega_0^2}{\Gamma^2}\right)v^4(\epsilon_r)\ . \tag{30c}$$

Equations (30a)–(30c) constitute the final result. Before moving to a specific example, note that a "typical" adsorption situation is characterized by $2\Gamma(\epsilon_r)\simeq1$ eV, $\rho_c(\epsilon_r)\sim0.25$ states/eV, and $\omega_0\simeq0.2$

eV, so the delocalization factor $f^2v^4 \simeq 0.1-0.2$ which considerably reduces the Franck-Condon broadening of the line, but at the expense of "lifetime broadening". It is also interesting to note the similarity between $f^2=\omega_0^2/\Gamma^2$ factor in Eq. (30c), obtained from microscopic (albeit qualitative) quantum-mechanical considerations, and the SL renormalization which is $\omega_0^2/(\Delta_h^2+\omega_0^2)^2 \simeq |V_{\mathrm{hole}}(\omega)|^2$.

Finally attention is called to another related problem which depends crucially upon interference effects between a boson field response to a switch on hole charge and the subsequent temporal evolution of this initially localized charge. The substrate electron relaxation response to a suddenly created core hole on an adsorbed atom or molecule belongs to this generic class of events. Here surface plasmons are the boson quanta and the "unfilled atomic orbital" screening process, in which a hole is transferred from the adparticle to the substrate, is the delocalization mechanism. Various aspects of this response have been explored in quite some detail recently[10–12] and the interested reader is referred to these works for further details.

VI. TWO EXAMPLES

Some numerical consequences of the theory just outlined are now demonstrated through two specific examples.

A. Adsorbed CO 1π photoemission line shapes

Photoemission studies of CO adsorbed on transition-metal surfaces are very popular.[17,29] For valence orbital ($4\sigma, 1\pi, 5\sigma$) emission, two or three pieces of structure are usually observed in the photoelectron energy distribution. The nonbonding O lone-pair 4σ orbital emission appears as a bump roughly 10–12 eV below the substrate Fermi level. The chemisorption bonding *C* lone-pair 5σ orbital and the nonbonding (to substrate) 1π orbitals show up sometimes resolvable,[16,17] sometimes not,[29] in the 6–10 eV (below the Fermi level) range. In spite of the fact that intramolecular vibrational structure has not been observed,[4,15a,16,29] there have been some suggestions that the relative widths of the various peaks may bear some relation to the widths of the free-space Franck-Condon envelopes of the particular orbitals in question.[17] The present purpose is not to comment on those observations but to note that the state of the art of surface photoemission is advancing to the point where meaningful questions, whose answers are revealed through subtle changes in high-resolution line shapes, can be asked with a reasonable expectation that these questions will not go unanswered for long. Witness the dramatic evolution, from an esoteric many-body fantasy[23,30] to a routine laboratory analytic technique,[31] of the core-level asymmetries associated with XPS line shapes. (This is not to imply that the careful execution of the actual experiments is easy, only that the *meaningful* interpretation of *high-quality* data can be done without having to justify the theoretical underpinnings of the interpretation on a case by case basis.)

As already mentioned, the free-space CO 1π band displays a series of vibrational lines fitting within an ~ 0.75 eV wide envelope. Ignoring rotational broadening, the gas-phase spectrum is tolerably reproduced by Eq. (2) with the choice $\beta=\lambda^2/\omega_0^2=2.45$ and $\omega_0=0.2$ eV.[4,15] The theoretical adsorbed CO 1π spectrum is given by Eqs. (8b) and (30a)–(30c) where the influence of the substrate enters through the assignment of numerical values for $\rho_c(\epsilon_r)$ and $\Gamma(\epsilon_r)$. A not unreasonable[32] $\rho_c \sim 0.25$ states/eV has been taken to represent the *s*-band part of the continuum with which the 1π orbital is degenerate. The resonance width $\Gamma(\epsilon_r)$ is treated parametrically. The calculated results are shown in Fig. 4 where in Fig. 4(a), the low value of $\Gamma=0.05$ eV (and thus $f=1$) was chosen to illustrate the slightly modified free space spectrum. In Fig. 4(b), spectra obtained with the "typical" value of $\Gamma=0.25$ eV and "extreme" limit of $\Gamma=0.5$ eV are depicted. In both figures, the full (dashed) curve is the renormalized (unrenormalized, $f^{1/2}v=1$) spectrum. The dot-dashed curves in Fig. 4(b) are the Lorentzian resonance shapes neglecting vibrational excitation. All curves are properly normalized with respect to each other.

The first striking feature of these results is the absence of any visible dramatic change due to the renormalization. In part this is due to a "Catch 22"-like situation. The vibrational structure dominates the spectrum only for long-lived holes where $\Gamma \ll \omega_0$. But in this region the renormalization factor is close to unity and thus the vibrational spectrum is well approximated by that of the free-space molecule. In the other limit $\Gamma > \omega_0$ which is typical of current experimental configurations, hole delocalization significantly alters the vibrational spectrum. But in this limit the total spectrum is dominated by the lifetime Lorentzian. The vibrational bands reshape and broaden the Lorentzian somewhat, but in a way that decreases with increasing Γ. Thus the renormalization correction becomes visibly significant only in the region where the corrected vibrational spectrum exerts diminishing influences on the total spectrum. This is illustrated more strikingly in Fig. 5 where the renormalized (but nonconvolved) Poisson distribution $N_+^0(\omega;\lambda'(\tilde{\epsilon}_n=\epsilon_r\equiv 0))$ obtained from Eqs. (29) and (30) is drawn, treating $\Gamma(\epsilon_r)$ parametrically. Indeed one can see the general shifting and compression of the vibrational spectrum towards the $\omega=0$ point with increasing $\Gamma(\epsilon_r)$. However, as noted, the dramatic changes are masked by the Lorentzian

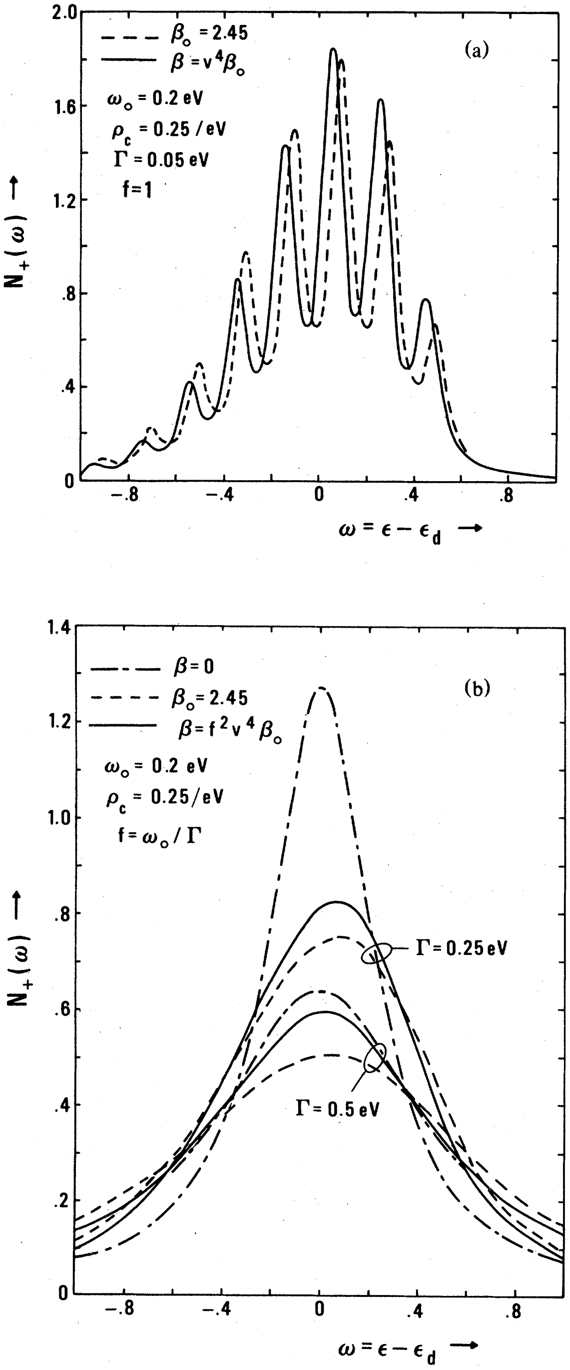

FIG. 4. Hole spectral function and thus photoelectron energy distribution for ionization from the 1π orbital of adsorbed CO. The gas-phase result, convolved with an appropriate Lorentzian, is shown as the dashed curve and the renormalized result, from Eq. (30), by the full curve. (a) $\Gamma = 0.05$ eV; (b) $\Gamma = 0.25$ and 0.50 eV. Here the hole spectral function, neglecting vibrational broadening, is also shown as the dot-dash curve.

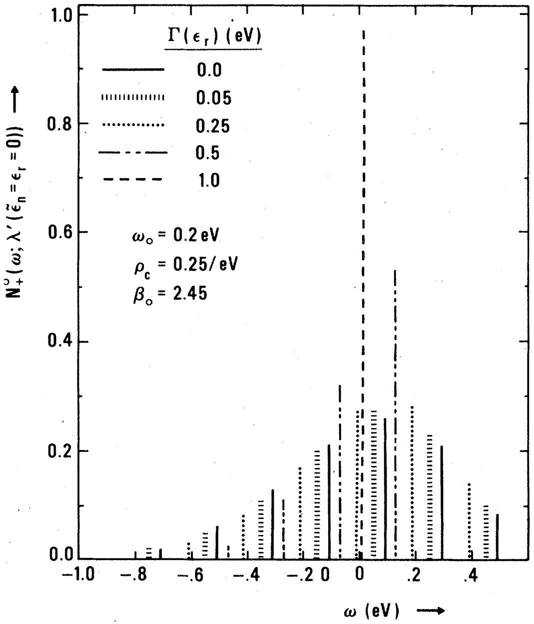

FIG. 5. Renormalized Poisson vibrational spectrum, $N_+^0(\omega;\lambda'(\bar\epsilon_n = \epsilon_n = 0))$ vs ω treating $\Gamma(\epsilon_r)$ and thus the renormalization factor $f^{1/2}v$ parametrically.

broadening in the observable spectrum. Nonetheless it has been quite instructive to arrive at this conclusion via theoretical considerations on a microscopic model.

On the positive side, clear systematics can be seen in these results. In all cases, the reduced β tends to concentrate more of the spectral weight near the line center which effectively narrows the observable level width.[23] Recall also that the approximation in which $\lambda'(\bar\epsilon_n)$ is set equal to its largest possible value, for a given set of parameters, minimizes the effects of coupling constant renormalization. This is the approximation that has been invoked here which allows tedious evaluation of Eq. (29) to be replaced by straightforward calculation of Eq. (30). The true line shape lies somewhere between the full [Eq. (30)] and the dot-dashed pure Lorentzian curves in Fig. 4(b), probably closer to the renormalized curve.

B. Large-β limit: Voigt profiles

The role of the delocalization renormalization can be nicely illustrated, in general terms, for cases in which β is sufficiently large that the discrete Poisson distribution is well represented by the continuous Gaussian, as given in Eq. (2). In this limit, Eqs. (2), (8), and (29), together with the previously discussed approximation on $\lambda'(\tilde{\epsilon}_n)$ can be cast into the form

$$N_+(\omega) = \frac{1}{(2\pi)^{1/2}\Delta} H(a,x) \ ,$$

with

$$H(a,x) \equiv \frac{a}{\pi} \int_{-\infty}^{+\infty} \frac{e^{-y^2} dy}{a^2 + (x-y)^2} \ , \tag{31}$$

$$a^2 \equiv \frac{\Gamma^2}{2\Delta^2} = \frac{\Gamma^2}{2f^2 v^4 \beta_0 \omega_0^2}$$

and

$$x^2 = \omega^2/2\Delta^2 \ .$$

The line shape given by $H(a,x)$ is known as a Voigt profile, about which much has been written and tabulated.[33,34] Spectral lines in many astrophysical situations are well described by this profile, usually in the small a limit where the natural linewidth (Γ) is much smaller than the Doppler width (Δ). Realistic examples for our situation are just the reverse.

The most interesting feature of this line shape which is pertinent to the point of this paper is the variation of the linewidth as a function of Δ, Γ, and the renormalization factor $f^{1/2}v$. The dimensionless halfwidth w is defined by $H(a,w) = \frac{1}{2}H(a,0)$. Armstrong[34] has discussed a number of analytic approximations for $w = w(a)$. That one due to Danos and Geschwind,[35] $w \simeq (\ln 2 + a^2)^{1/2}$ gives the correct large and small a asymptotic limits and is acceptable for present purposes, throughout the entire parameter space. Defining $R \equiv \beta_0\omega_0^2/\Gamma^2$, the full width at half maximum of Eq. (31) which follows from the Danos-Geschwind form is

$$\Delta E(f^{1/2}v)/2\Gamma = (1.386 f^2 v^4 R + 1)^{1/2} \ . \tag{32}$$

The ratio of the renormalized to unrenormalized ($f^{1/2}v = 1$) widths from Eq. (32), as a function of $f^{1/2}v$ and parametric R are shown in Fig. 6. It is apparent that considerable line narrowing can occur, especially when the Gaussian (vibrational) broadening is the dominant mechanism ($R >> 1$). In actual fact however large R usually follows from small Γ and small Γ usually implies $f^{1/2}v$ near unity, concentrating the action in the upper right-hand corner of Fig. 6 where the line narrowing is in the 10–20% range. This is the Catch-22 phenomenon previously alluded to. Still an observable effect is predicted.

As an example, consider the CO 1π line shape within the Gaussian approximation. Using the parameters from Sec. V, for $\Gamma = 0.25$ or 0.5 eV, $f^{1/2}v = 0.817$ or 0.54 and $R = 1.57$ or 0.392, respectively. In either case, the results in Fig. 6 yield

$$\Delta E(f^{1/2}v)/\Delta E(f^{1/2}v = 1) \simeq 0.8$$

which should be observable, if not dramatic.

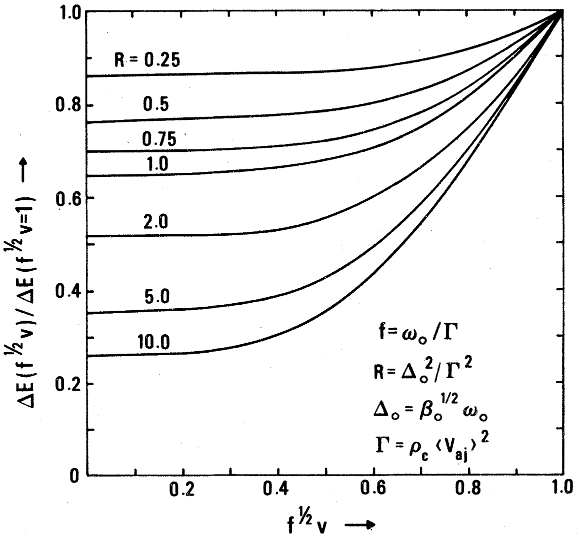

FIG. 6. Ratio of renormalized to unrenormalized full width at half maximum for large β, Voigt line shape as a function of the renormalization factor $f^{1/2}v$. The ratio of the Gaussian vibrational to Lorentzian lifetime widths is treated parametrically.

VII. SUMMARY

Similarities and differences between absorption and emission electron spectroscopies of free space versus adsorbed molecules have been considered in this paper. Charge fluctuations in emission spectroscopies of adsorbates introduce a strong final state coupling between the resulting molecular ion and the substrate which drastically alters the gas-phase electron spectrum. On the other hand such effects are not present in absorption spectroscopies so meaningful comparisons between free space and adsorbed molecule spectra are possible.

Next, attention was focused on the microscopic mechanisms responsible for the substrate-induced modifications of the gas-phase emission spectra. The most obvious was simple "lifetime broadening" due to molecular hole delocalization into the substrate. More interesting in principle were the interferences between the hole delocalization and intramolecular vibrational shakeup processes whose description requires a theory beyond that of a simple convolution of independent processes. The delocalization-vibrational interference phenomenon was considered in the light of recent discussions pertaining to hole decay-phonon interferences in core-level XPS from solids. Fundamental distinctions between the two were noted when they existed.[36]

The final results for the hole spectral function and thus photoelectron energy distribution were presented in a form which looked like a convolution theory, but with some important differences; namely, that the hole-vibrational coupling constant appearing in the Poisson distribution of the independent-boson model was effectively reduced or renormalized due to the delocalization process. Numerical examples illustrating this effect were given. Specifically the photoemission line shape for hole creation in the 1π orbital of adsorbed CO and for any system in which the number of phonons produced is large were calculated for a realistic range of parameters. Although the interference effects which were the key issue in this study did not lead to dramatic modifications in the anticipated line shapes, the modifications are probably large enough to be observed in careful high-resolution photoemission studies. This is not to be interpreted pessimistically, for past experience has shown that most phonon-induced changes to an electron emission spectrum are small but rewardingly detectable. Hopefully the present example is no exception to this rule.

Finally we take cognizance of some ideas presented here which may have implications beyond the study of photoelectron line shapes. Originally it was thought that a certain symmetry should exist between the theory of *localized hole* excitation of *delocalized bosons,* as occurs in core-level XPS, and *delocalized hole* excitation of *localized bosons,* as in adsorbed molecule valence level spectroscopy. This notion was encouraged through consideration of the basic equation for the coupling constant, Eq. (14), in which the relevant properties of the hole and boson appear as a product, suggesting that the final results might be independent of which entity is localized and which is delocalized. As has been demonstrated in this study, there is another effect which does distinguish between the two possibilities. Recoil or localized vibrational mixing of delocalized hole states occurs in valence orbital but not core-level phenomena, owing to the lack of any memory mechanism (other than off or on) in the core state. It seems possible that the localized coupling of extended states via intramolecular vibrations of adsorbed molecules could have other interesting consequences.

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[28] It could be argued that a more appropriate choice would be $f = \omega_0/W$ where W is of order the substrate bandwidth or Fermi energy. It is felt that this choice is either irrelevant or inappropriate for the following reasons. Suppose we picked this assignment. Then one should be less cavalier in proceeding from Eqs. (21) to (22). Rather than replacing $k_u^3 - k_l^3$ by k_f^3, thus obtaining a quantity $\sim n_s$, one would require a quantity which is a measure of the substrate density in the region of the admolecule. This density is appreciable only for those substrate states degenerate with the virtual level which is $\sim \Gamma/W$ times n_s. With these choices, the interaction term is proportional to $(\omega_0/W)N/(\Gamma/W)n_s\Omega = \omega_0/\Gamma$, as in Eq. (27), and the f question is irrelevant. Furthermore it seems counter intuitive that the renormalization should be a strong function of W, provided $W > \Gamma$, as no additional physics accompanies the widening of the band. Thus the above f choice also seems inappropriate.

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[36] The reader should also study the very enlightening series of papers by Cini, who addressed somewhat similar problems from a new point of view. See M. Cini, Solid State Commun. 20, 605 (1976); 24, 681 (1977); Phys. Rev. B 17, 2486 (1978); and Surf. Sci. 79, 589 (1979).