

Vibrational excitation in photoemission spectroscopy of condensed molecules

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Photoelectron spectra of gas-phase molecules display sharp vibrational structure. The envelope of the spectrum is determined by the Franck-Condon factor. On the other hand, photoelectron spectra of the same molecules, adsorbed or condensed onto metal surfaces show a broad band whose shape resembles the gas-phase Franck-Condon envelope but with no sharp structure. The smearing out of the vibrational structure is usually attributed to lifetime effects or site inhomogeneities. A new mechanism involving intrinsic phonon sidebands in photoemission from condensed molecules is suggested and the details of the theory are worked out. Experimental ultraviolet photoelectron spectra from condensed CO are considered in the light of this theory.

I. GAS-PHASE MOLECULAR SPECTRA

The photoelectron spectra of gas-phase molecules contain many bands due to the ionization from different molecular orbitals. In addition, since the resulting molecular ion can be left in excited vibrational and rotational states, sharp structure corresponding to such excitations appears within each band in the spectrum.¹ Consider the case in which the initial and final molecular states can be written as a product (Born-Oppenheimer approximation):

$$\psi_{i;0} = |N; \epsilon_N\rangle_e |N; \epsilon_v^0\rangle_v$$

and

$$\psi_{f;n} = |N-1, \bar{k}; \epsilon_{N-1}\rangle_e |N-1; \epsilon_v^*\rangle_v,$$

where $|N; \epsilon_N\rangle_e$ and $|N; \epsilon_v^0\rangle_v$ are the N -electron molecular ground-state electronic and vibrational wave functions, respectively; $|N-1; \bar{k}; \epsilon_{N-1}\rangle_e$ is the final-state electronic wave function for the $(N-1)$ -electron molecular ion and photoejected electron with asymptotic wave number \bar{k} , and $|N-1; \epsilon_v^*\rangle_v$ is the final-state molecular-ion vibrational wave function for the ϵ_v^* excited state. From golden-rule perturbation theory, it is easily shown that the energy distribution of the photoejected electrons [due to a perturbation $H' = (e/mc)\vec{p}_{op} \cdot \vec{A}$, with \vec{A} the vector potential of the radiation field] is

$$\begin{aligned} \frac{dj}{d\epsilon} \sim \sum_{\epsilon_{\bar{k},v}^*} \delta(\epsilon - \epsilon_{\bar{k}}) \delta(\epsilon_{\bar{k}} + \epsilon_{N-1} + \epsilon_v^* - \hbar\omega - \epsilon_N - \epsilon_v^0) \\ \times |\langle N-1, \bar{k}; \epsilon_{N-1} | \vec{p}_{op} \cdot \vec{A} | N; \epsilon_N \rangle|^2 \\ \times |\langle N-1; \epsilon_v^* | N; \epsilon_v^0 \rangle|^2, \end{aligned} \quad (1)$$

where ϵ_N and ϵ_{N-1} are the total electronic energies of the molecule and ion (including the possibility of electronic shakeup and thus relaxation energy

shifts^{2,3}) and $\hbar\omega$ is the photon energy. The modules squared overlap integral of the vibrational wave functions is called the Franck-Condon factor and the energy dependence of this factor determines the shape of a given photoionization band *provided the energy of the photoejected electron is sufficiently above threshold that the sudden approximation is valid*⁴ and that the variation with energy over the width of the band (~ 1 eV) of the optical matrix element can be ignored. Then if the zero of energy is defined to be at the adiabatic threshold ($\epsilon_N + \hbar\omega - \epsilon_{N-1} = 0$), the energy distribution is simply

$$\frac{dj}{d\epsilon} \sim \sum_{v^*} \delta(\epsilon + \epsilon_v^*) |\langle N-1; \epsilon_v^* | N; \epsilon_v^0 \rangle|^2 \equiv D_{gas}(\epsilon) \quad (2)$$

and its shape is determined solely by the Franck-Condon factor and the vibrational spectrum. It is implicitly assumed that the rotational bands are so narrow that they just broaden the δ functions a bit.

An extremely comprehensive theory of molecular photoionization has been presented by Cederbaum and Domcke⁵ in which they took advantage of the fact that the hole-vibronic coupling in the gas-phase molecule [which gives rise to the energy distribution of Eq. (2)] is described through the model Hamiltonian:

$$\begin{aligned} H = \sum_{\gamma} \epsilon_{\gamma} c_{\gamma}^{\dagger} c_{\gamma} + \sum_i h\nu_i (b_i^{\dagger} b_i + \frac{1}{2}) \\ + \sum_{i,\gamma} g_{i\gamma} h\nu_i c_{\gamma}^{\dagger} c_{\gamma} (b_i^{\dagger} + b_i), \end{aligned} \quad (3)$$

where the first term is the electron Hamiltonian in second quantized form, ϵ_{γ} is the energy of the γ 'th electronic state, the second term is the vibrational (Boson) Hamiltonian, and the third term

is the interaction between the vibrational modes and the localized hole ($c_\gamma c_\gamma^\dagger$ is nonvanishing only after an electron has been photoejected, leaving behind a hole). The strength of the hole-vibrational coupling is dictated by $g_{i\gamma}$. Knowing $g_{i\gamma}$ is equivalent to knowing the Franck-Condon factors. Roughly speaking, $g_{i\gamma}$ is the ratio of the energy gain of the vibrating atoms due to the time-dependent electric field of the hole divided by the vibrational energy, $h\nu_i$. If one considers the photoionization of a particular orbital γ whose band does not overlap other bands and if it is assumed that the vibrational modes are perfectly harmonic, then it has been shown^{2,5,6} that the photoelectron energy distribution, for a system described by the Hamiltonian of Eq. (3), is

$$D_{\text{gas}}(\epsilon) = e^{-\beta_g} \sum_{n=0}^{\infty} \frac{\beta_g^n}{n!} \delta(\epsilon + nh\nu), \quad (4)$$

where $\beta_g \equiv |g|^2$ and $\epsilon_n^* = nh\nu$ is the n th vibrational excited state. Equation (4) is a Poisson distribution, which in the limit $\beta \gg 1$ is well approximated by a Gaussian with its maximum displaced below the adiabatic threshold energy. This vibrational (or phonon) sideband⁷ is much more intense than the zero-phonon line as β increases beyond unity. A good example of the type of energy distribution I have in mind is the $3a_1$ band in water which to a first approximation can be simulated by Eq. (4) with $\beta_g \approx 5$ and $h\nu \approx 0.1$ eV.⁸ The resulting Franck-Condon envelope is quite Gaussian with a full width at half maximum of approximately 1 eV. In a real experiment, the finite resolution of the energy analyzer broadens the structures in Eq. (4). Thus the observable energy distribution, taken to be the convolution of Eq. (4) with a resolution Gaussian, is

$$D_{\text{gas}}^{\text{obs}}(\epsilon) = \frac{e^{-\beta_g}}{\Delta_r (2\pi)^{1/2}} \sum_{n=0}^{\infty} \frac{\beta_g^n}{n!} \exp\left[-\frac{1}{2} \left(\frac{\epsilon + nh\nu}{\Delta_r}\right)^2\right], \quad (5)$$

where $\Delta_r = E_{\text{FWHM}}/2.35$. Equation (5) has been evaluated for the water $3a_1$ band treating E_{FWHM} parametrically. The resulting spectra are shown in Fig. 1, where it is clear that the vibrational structure cannot be resolved when $E_{\text{FWHM}} \gtrsim h\nu$. Equation (5) provides a good representation of many photoelectron bands¹ although more complicated situations, usually involving coupled modes and anharmonic effects, frequently occur.^{5,8,9}

II. CONDENSED MOLECULAR SPECTRA

In recent years, photoelectron spectroscopy has been used extensively to study the electronic structure of atoms and molecules adsorbed on

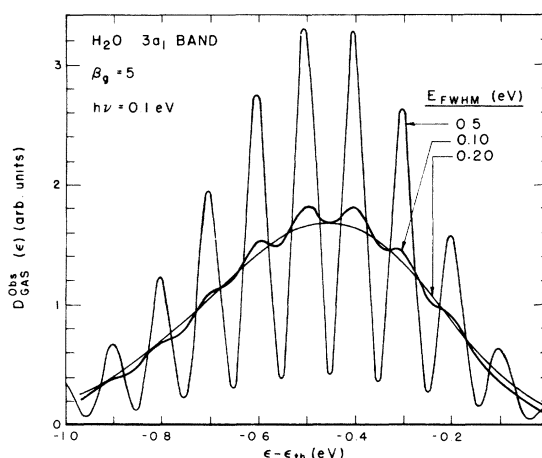


FIG. 1. Approximate photoelectron spectrum for the $3a_1$ band of water vapor calculated from Eq. (5). Resolution E_{FWHM} is treated parametrically. Zero of energy corresponds to the adiabatic threshold energy.

surfaces.¹⁰ Considerable information pertaining to the adsorbate-substrate interaction can be garnered from a meaningful comparison of the gas-phase and adsorbed monolayer spectra.¹¹ The gross differences between these spectra are usually interpreted as some combination of chemical, relaxation, and bonding shifts of the various molecular-orbital bands with respect to one another.¹² Another conspicuous difference is that the easily resolved vibrational structure of gas-phase spectra is washed out and the resulting spectra have shapes sometimes resembling the Franck-Condon envelope.¹³ Various intuitive explanations can be suggested for this. The hole created on the molecule has a finite lifetime before either hopping into the solid or being filled via an interatomic Auger transition from substrate band electrons. In addition, electron-hole pair shakeup,¹⁴ of the type responsible for the Doniach-Šunjić asymmetric photoemission line shape^{4,15} can, in effect, broaden and skew each vibrational line. Lastly, steric inhomogeneities can result in different potentials from site to site.

These explanations seem less applicable when considering condensed molecular multilayers,¹⁶ which also do not show vibrational structure. There is little evidence to suggest that banding effects occur due to intermolecular electron or hole hopping. This seems quite reasonable since, in general, the small cohesive energy of the constituent molecules in the condensed multilayers (or molecular solid) results from van der Waals rather than chemical bonds. For hole creation in one of the lower-binding-energy molecular-orbital states decay via Auger transitions involving neighboring molecules is both improbable

and often energetically forbidden. In these cases there are no low-lying final states available for an electron which is excited in an intermolecular Auger process. This, of course, suppresses this decay mode. Thus finite hole lifetime broadening should not be an all important factor, although not much broadening is required to wash out the 0.1–0.4 eV structure. Still another fact is that in infrared absorption spectroscopy of chemisorbed or condensed molecules in their electronic ground state, rather sharp vibrational modes are observed which do not differ drastically from the gas-phase results.¹⁷ This suggests that the vibrational properties of the molecules are not significantly perturbed by condensation. With this in mind, it appears that the mechanism responsible for the loss of the vibrational structure is both inherent to the localized-hole-creation process of photoemission and also to the fact that there are neighboring molecules. Within the stated physical conditions of the molecular solid considered here, one of the only remaining broadening mechanisms is phonon excitation (sidebands), which is familiar in photoemission from polar materials.^{18–20} In such cases, discrete electronic states appear broadened and shifted in photoelectron spectra due to the intrinsic production of many (~ 50 in alkali-halide crystals) low-energy ($\sim 10^{-2}$ eV phonons during the sudden switching-on of the localized hole potential.^{4,18,21} The discrete line appears to be a Gaussian, given by the large $\beta \sim 50$ limit of Eq. (4). Note that in this case β is the ratio squared of the hole phonon interaction to the phonon energy. The theoretical approaches to the problem of phonon sidebands in localized hole creation have been well outlined by Mahan.²²

Consider the nature of the vibrational modes in the condensed phase. The ir absorption data¹⁷ indicate that the individual molecular modes are not drastically altered upon condensation. Thus bands of relatively dispersionless vibrational modes (similar to optical modes in ionic crystals) with 0.1–0.5 eV energies occur in almost one-to-one correspondence with the gas-phase modes. In addition, a condensed layer of N molecules contains a band of $3N - 3$ low-energy ($\sim 10^{-2}$ eV) collective modes analogous to acoustical phonons in periodic structures. These arise from the three translational degrees of freedom per molecule in the gas phase which are frozen out by condensation and can be interpreted as collective modes of vibration of a rigid molecule. There is little hybridization between these modes and the intramolecular vibrational modes due to the order of magnitude disparity in their energies.

With the above in mind, I suggest the following chain of events in a photoemission event from a

molecule in a condensed layer. Upon photon absorption by a single molecule, intrinsic molecular vibrational modes are also excited, as in the gas phase. If this was the entire story, then the resulting hole spectral function would be given by Eq. (4) with both β_g and $\hbar\nu$ nearly identical to the gas-phase counterparts. The new feature is that the switching-on of the localized hole potential disturbs the neighboring molecules (most strongly if they possess permanent dipole moments) and this results in the intrinsic excitation of many of the low-energy phonon modes. Consequently, a phonon sideband becomes associated with each of the discrete molecular components in Eq. (4) and in the limit of many phonons, the zero-phonon line has negligible intensity. In this picture, the collective phonon sidebands are also Poisson distributed, as in Eq. (4), but with a still undetermined β . Herein lies the physics problem to be addressed. For an Einstein phonon spectrum, the characteristic Poisson parameter is taken to be

$$\beta_{\text{ph}} = \left\langle \left(\frac{H_{h-\text{ph}}}{\hbar\omega_0} \right)^2 \right\rangle, \quad (6)$$

where $H_{h-\text{ph}}$ is the thermal-averaged coupling interaction between the hole and the phonon system and $\hbar\omega_0$ is the phonon energy. As noted by Pryce,¹⁸ the finite temperature spectral function [a generalization of Eq. (4)] is

$$D(\epsilon, T) = e^{-\beta} \sum_{n=-\infty}^{+\infty} e^{n\theta} I_n \left(\frac{\beta_0}{\sinh\theta} \right) \delta(\epsilon + n\hbar\omega_0),$$

where β and β_0 are the thermal-averaged and zero-temperature coupling, $\theta = \hbar\omega_0/2kT$, and I_n is the n th-order Bessel function of imaginary argument. In the limit of $\beta \gg 1$, this expression tends to a Gaussian, with the thermally averaged Poisson parameter given by Eq. (6).

To proceed, a model for the condensed layer must be adopted. Rather arbitrarily, although not in conflict with intuition, assume that the molecules separated by a distance R are periodically arranged with either ferro- or antiferroelectric ordering of their permanent dipole moments, which are oriented along the z axis. No conclusions will be made here, however, which require long-range order. The resulting model I consider is shown in Fig. 2. A localized point hole is created on the central molecule at center 0 during the photoemission process. (It would not be difficult to allow for a spatially extended hole.) This hole or point charge interacts with the array of dipoles via a sum of pairwise interactions

$$V_{\text{int}} = \sum_i V_{d-h}(\vec{R}_i), \quad (7a)$$

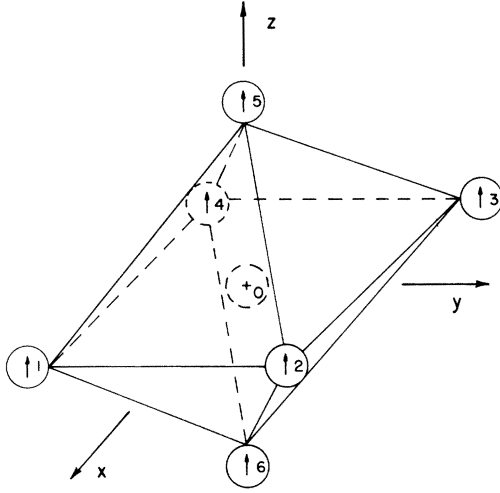


FIG. 2. Octahedral cage model for the localized hole created on the molecule at site 0. Only molecules at sites 0, 5, and 6 are displaced due to the hole-dipole interaction.

with

$$V_{d-h}(\vec{R}_i) = e\mu_i(\cos\theta_i)/R_i^2, \quad (7b)$$

where μ_i is the permanent dipole associated with the molecule at center i (which differs at most only in sign from site to site). Expanding \vec{R}_i about the equilibrium point \vec{R}_{i0} and retaining terms linear in molecular displacements, the interaction, Eq. (7a) is

$$V_{int} \simeq \sum_i [V_{d-h}(\vec{R}_{i0}) + \delta\vec{u}_i \cdot \vec{\nabla}_{d-h}(\vec{R})|_{\vec{R}=\vec{R}_{i0}} + \dots]. \quad (8)$$

The first term gives rise to a rigid shifting or renormalization of the energy scale but not to any phonon excitation and thus will be disregarded. A typical gradient term is

$$\vec{\nabla} V_{d-h}(\vec{R}_i) = \hat{i}_r \left(\frac{-2e\mu_i \cos\theta_i}{R_{i0}^3} \right) + \hat{i}_\theta \frac{e\mu_i}{R_{i0}^3} \sin\theta_i. \quad (9)$$

If I include only nearest-neighbor dipole-hole interactions, Eqs. (8) and (9) when applied to the geometrical model of Fig. 1, lead to the hole-phonon interaction

$$H_{h-ph} \simeq (\delta u_6^x - \delta u_5^x) \frac{2e\mu}{R^3} + (\delta u_1^\theta + \delta u_2^\theta + \delta u_3^\theta + \delta u_4^\theta) e\mu/R^3 - \delta u_0^r 4e\mu/R^3, \quad (10)$$

where δu^r is a displacement in the radial direction when $\theta = 0$ or π and δu_i^θ are essentially hindered rotations of the four molecules in the $x-y$ plane.

On the basis of simple electrostatics it can be seen that the hole coupling to the translational modes of 5 and 6 is much greater than to the hindered rotational (or librational) modes of 1-4 and thus by far the dominant channel for energy transfer to the phonon system is through the displacement of 0, 5, and 6. Consequently the θ displacements will henceforth be dropped. Note that the interaction of the dipole moments on 5 and 6 with the hole on 0 also causes a displacement δu_0^r of the molecule upon which the hole is localized. The displacements of the individual molecules can be expressed by the following coherent sum of phonons²²:

$$\delta\vec{u}_i = \frac{1}{\sqrt{N}} \sum_{\vec{q},j} \left(\frac{\hbar}{2M\omega_{\vec{q},j}} \right)^{1/2} \hat{\epsilon}_{\vec{q},j} \times (a_{\vec{q},j}^- e^{i\vec{q} \cdot \vec{R}_i} + a_{\vec{q},j}^+ e^{-i\vec{q} \cdot \vec{R}_i}), \quad (11)$$

where N is the total number of molecules, $\hat{\epsilon}_{\vec{q},j}$ is the polarization vector of a phonon in the j th mode with wave vector \vec{q} , and $a_{\vec{q},j}^-$, $a_{\vec{q},j}^+$ are the annihilation and creation operators. Referring to Fig. 2, the lattice positions for the present model are $\vec{R}_5 = R\hat{i}_x$, $\vec{R}_6 = -R\hat{i}_x$, and $\vec{R}_0 = 0$. For this geometry, Eqs. (10) and (11) can be brought to the form

$$H_{h-ph} = -\frac{4e\mu}{R^3} \frac{1}{\sqrt{N}} \sum_{\vec{q},j} \left(\frac{\hbar}{2M\omega_{\vec{q},j}} \right)^{1/2} (\hat{\epsilon}_{\vec{q},j} \cdot \hat{i}_x) \times [a_{\vec{q},j}^- (1 + i \sin q_x R) + a_{\vec{q},j}^+ (1 - i \sin q_x R)]. \quad (12)$$

Defining $G(\vec{q}) \equiv 1 + i \sin q_x R$, the thermal averaging

$$\begin{aligned} \langle H_{h-ph}^2 \rangle &\sim \langle (Ga + G^*a^\dagger)(Ga + G^*a^\dagger) \rangle \\ &= |G|^2 [1 + 2n(\omega_{\vec{q},j})] \\ &= |G|^2 \coth(\hbar\omega_{\vec{q},j}/2kT), \end{aligned}$$

where

$$a_{\vec{q},j}^- a_{\vec{q},j}^+ = n(\omega_{\vec{q},j}) = (e^{\hbar\omega_{\vec{q},j}/2kT} - 1)^{-1}$$

is the number operator for the particular mode. Using this result with Eq. (12), the mean-squared hole-phonon coupling is

$$\begin{aligned} \langle H_{h-ph}^2 \rangle &= \left(\frac{e\mu}{R^2} \right) \frac{16}{R^2} \frac{1}{N} \sum_{\vec{q},j} \left(\frac{\hbar}{2M\omega_{\vec{q},j}} \right) (\hat{\epsilon}_{\vec{q},j} \cdot \hat{i}_x)^2 \\ &\quad \times (1 + \sin^2 q_x R) \coth \left(\frac{\hbar\omega_{\vec{q},j}}{2kT} \right). \end{aligned} \quad (13)$$

If it is assumed that the phonon spectrum is isotropic and in addition that the transverse and longitudinal dispersion relations are identical, then the sum on j is greatly simplified. For one trans-

verse mode, $\hat{\epsilon}_{\vec{q},t} \cdot \hat{i}_z = \sin\theta$ and for the other, $\hat{\epsilon}_{\vec{q},t} \cdot \hat{i}_z = 0$. For the longitudinal mode, $\hat{\epsilon}_{\vec{q},t} \cdot \hat{i}_z = \cos\theta$. Thus

$$\sum_j (\hat{\epsilon}_{\vec{q},j} \cdot \hat{i}_z)^2 = \cos^2\theta + \sin^2\theta = 1$$

and Eq. (13) reduce to

$$\langle H_{\hbar\text{-ph}}^2 \rangle = \left(\frac{e\mu}{R^2} \right) \frac{16}{R^2} \frac{1}{N} \sum_{\vec{q}} \frac{\hbar}{2M\omega_q} (1 + \sin^2 q_z R) \times \coth(\hbar\omega_q/2kT). \quad (14)$$

Independent of the phonon dispersion law, the sum on \vec{q} (if the $\sin^2 q_z R$ term is neglected) is N times the mean-square displacement of a molecule in the lattice about its equilibrium position. The \sin^2 term will, of course, be smaller and for Einstein phonons, is $\frac{1}{2}$ the leading one. All likely alternatives fall between $\frac{1}{2}$ and 1. Using the Einstein result, Eq. (14) is simply

$$\langle H_{\hbar\text{-ph}}^2 \rangle \simeq 24 \left(\frac{e\mu}{R^2} \right)^2 \frac{\langle \delta u(T)^2 \rangle}{R^2}, \quad (15)$$

where the mean-square displacement is

$$\langle \delta u_E(T)^2 \rangle = (\hbar/2M\omega_0) \coth(\hbar\omega_0/2kT).$$

Finally the major result from Eqs. (6) and (15) is the Poisson parameter characterizing the intrinsic hole-phonon excitation spectrum:

$$\beta_{\text{ph}} \simeq 24 \left(\frac{e\mu}{R^2 \hbar\omega_0} \right)^2 \frac{\langle \delta u(T)^2 \rangle}{R^2}, \quad (16)$$

a rather simple expression. Nevertheless it is felt that the principal physics has been dealt with although details could be sharpened up. Upon rearrangement, the structure of Eq. (16) and its relationship to the physical mechanisms are quite transparent. The term $(2e\mu/R^3)^2 \times \langle \delta u^2 \rangle$ is the square of a force on a molecule times its likely displacement which is the mean-square energy picked up by the oscillators. Dividing by $\hbar\omega_0$ gives the number of quanta. The remaining factor of 6 arises from the number of molecules and relative strengths of each displacement [four from Eq. (10)] times the coherence factor [1.5 from the discussion after Eq. (14)].

In order to assign numbers to the ratio $\langle \delta u(T)^2 \rangle / R^2$, I use both the empirical melting temperature $\equiv T_m$ of the condensed layer and the Lindemann melting criterion.²³ This law states that melting takes place when the root-mean-square vibration of a molecule is roughly $\frac{1}{8}$ the intermolecular spacing R . With the Einstein relation for the mean-square displacement,

$$\frac{\langle \delta u(T)^2 \rangle}{\langle \delta u(T_m)^2 \rangle} = \frac{\coth(\hbar\omega_0/2kT)}{\coth(\hbar\omega_0/2kT_m)} \equiv R(T, T_m).$$

The Lindemann criterion then yields

$$\frac{\langle \delta u(T)^2 \rangle}{R^2} = \frac{\langle \delta u(T_m)^2 \rangle}{R^2} R(T, T_m) = \frac{R(T, T_m)}{64},$$

and thus Eq. (16) can be written

$$\beta_{\text{ph}} \simeq \frac{3}{8} \left(\frac{e\mu}{R^2 \hbar\omega_0} \right)^2 \frac{\coth(\hbar\omega_0/2kT)}{\coth(\hbar\omega_0/2kT_m)}, \quad (17)$$

which is a convenient form to work with.

In the limit of large β , the Poisson distribution $D_n = e^{-\beta_{\text{ph}}} \beta_{\text{ph}}^n / n!$ is well approximated by a Gaussian²⁴

$$D_n \approx \frac{1}{(2\pi\beta_{\text{ph}})^{1/2}} \exp\left(-\frac{(\beta_{\text{ph}} - n)^2}{2\beta_{\text{ph}}}\right)$$

or with $n = \epsilon/\hbar\omega_0$:

$$D(\epsilon) = \frac{1}{\Delta_{\text{ph}}(2\pi)^{1/2}} \exp\left(-\frac{(\epsilon + \beta_{\text{ph}} \hbar\omega_0)^2}{2\Delta_{\text{ph}}^2}\right), \quad (18)$$

where $E_{\text{FWHM}} = 2.35 \Delta_{\text{ph}} = 2.35 \beta_{\text{ph}}^{1/2} \hbar\omega_0$ and the sign convention for energy, introduced in Sec. I, has been used. The observable condensed molecular photoemission spectrum is then the convolution of Eqs. (4) and (18):

$$D_{\text{con}}^{\text{obs}}(\epsilon) = \frac{e^{-\beta_g}}{\Delta_{\text{ph}}(2\pi)^{1/2}} \times \sum_{n=0}^{\infty} \frac{\beta_g^n}{n!} \exp\left[-\frac{1}{2} \left(\frac{\epsilon + n\hbar\nu + \beta_{\text{ph}} \hbar\omega_0}{\Delta_{\text{ph}}} \right)^2\right]. \quad (19)$$

If resolution limitations are also to be included, then Δ_{ph} should be replaced by $(\Delta_{\text{ph}}^2 + \Delta_r^2)^{1/2}$.

III. RESULTS

One of the most popular adsorbed or condensed molecular systems that has been studied with photoelectron spectroscopy is CO on transition-metal substrates.²⁵ Cederbaum, Domcke, von Niessen, and Brenig¹³ have presented a detailed theoretical interpretation of the ultraviolet photoemission spectrum for *chemisorbed* CO on Ni in which the gas-phase spectrum is broadened by a 1-eV Gaussian in order to obtain a line shape that can be compared with experiment. Since the CO was chemisorbed, strong interactions with the substrate would be expected to provide mechanisms for the 1 eV width.

The photoionization spectrum from the CO 1π orbital is a good example to consider. Equation (5) with $\beta_g = 2.45$, $\hbar\nu = 0.2$ eV, and $\Delta_r = 0.05$ eV, tolerably reproduces the experimental gas-phase results.

Now consider the condensed phase. The melting temperature of condensed CO is sufficiently low, that at $T = 77$ K, the ratio of temperature \coth 's

is near unity. The permanent dipole of CO is $\mu \sim 0.1$ D. Taking $R \sim 1.5\text{--}2$ Å and $\hbar\omega_0 \approx 10^{-2}$ eV, the number of phonons in the sideband, from Eq. (17), falls within the range $\beta_{\text{ph}}^{\text{CO}} \approx 20\text{--}60$ which is quite reasonable based on past experience. Letting $T_m \approx 80$ °K, Eq. (19) has been evaluated with various values for $\beta_{\text{ph}}^{\text{CO}}$ in this range and with a span of resolution parameters Δ_r . The results are shown in Fig. 3. Several points are noteworthy. For a given Δ_r , both the peak maximum and envelope shape are quite sensitive to the value of $\beta_{\text{ph}}^{\text{CO}}$. In fact the maximum in a spectrum is displaced below the adiabatic threshold energy by as much as 0.5 eV owing to the phonon sidebands.^{36(a)} It is difficult to assign a specific value to β_{ph} since it varies from 20 to 60 as R varies between 1.5 and 2.0 Å. Thus I cannot give a definitive answer to the question of whether vibrational structure can be resolved in photoemission from condensed layers of CO. From Fig. 3 it is observed that even with perfect

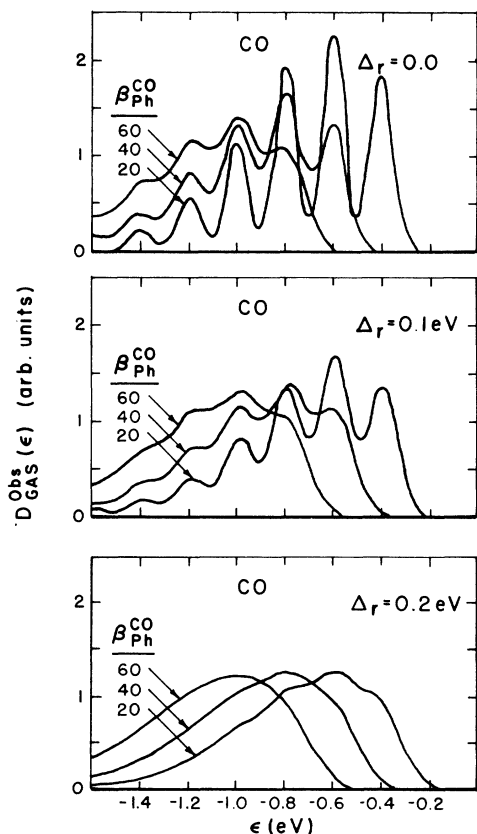


FIG. 3. Approximate photoelectron spectra for the 1π orbital of condensed CO, calculated from Eq. (19). Resolution parameter $\Delta_r = E_{\text{FWHM}}/2.35 = 0.0, 0.1,$ and 0.2 eV in each of the three panels, respectively. Within each panel, the hole-dipole coupling parameter $\beta_{\text{ph}}^{\text{CO}} = 20, 40,$ and $60,$ as labeled. Zero of energy corresponds to the adiabatic threshold energy.

resolution ($\Delta_r = 0$), the structure is almost all gone for $\beta_{\text{ph}}^{\text{CO}} = 60$ and this is not an extreme or unrealistic limit.

Even though the present results do not allow for definitive conclusions, some useful guidelines for the experimentalist in search of molecularlike vibrational structure do emerge from this study. From Eq. (17), it is seen that choosing a molecule with a very small dipole moment would be advisable if one wants to see vibrations; for instance, homonuclear diatomics such as H_2 or N_2 or linear molecules such as CO_2 ($\mu = 0$) if they can be condensed without dissociating. Another tack would be to condense larger molecules so that R is large and thus β_{ph} small. Lastly, one should look at molecular bands in which $\hbar\nu$ is relatively large. By these criteria, the $3a_1$ condensed water band should not display vibrational structure since the dipole moment is large ($\mu \approx 1.78$ D) and $\hbar\nu \approx 0.1$ eV is small.

With regards to the experimental situation in general, most surface photoemission experiments have been performed with energy resolution $\sim 0.2\text{--}0.3$ eV which by itself rules out the vibrational structure. In addition, most experiments have been on chemisorbed monolayers, rather than condensed multilayers, so that lifetime and substrate pair shakeup broadening dominate. Photoemission studies of condensed hydrocarbons and H_2O on Ni,^{16(a)} MoS_2 ,^{16(b)} and W,^{16(c)} as well as N_2 , N_2O , NO , and NO_2 on Ni,^{16(d)} do not reveal any vibrational fine structure although this could be due to resolution limitations. In any event, the presently existing data are not in conflict with the main point of this paper.^{20(b)}

IV. CONCLUSIONS

Phonon sidebands produced in photoemission from condensed polar molecules broaden the gas-phase spectra to such an extent that individual molecular vibrational modes may not be resolved unless some unusual properties characterize the condensed layer. Since this conclusion follows from a simple model calculation in which the principal result, Eq. (24), is extremely sensitive to the choice of parameters $\hbar\omega_0$ and R and also to the hole-phonon coupling scheme (nearest neighbors only in a dipole aligned condensed phase), not much stress is placed on conclusions based on the absolute numbers obtained here. Nonetheless, the basic point that collective-phonon-mode sidebands broaden the individual molecular vibrational levels in a photoemission experiment remains perfectly valid independent of the model parameters and it is just a question of degree. The physically reasonable model presented here sug-

gests that the broadening is comparable with the molecular vibrational energies, if the molecule possesses a permanent dipole moment $\mu \gtrsim 0.1$ D. Higher multipole-hole interactions are undoubtedly small enough to be ignored. The crucial experimental test of these ideas will most easily be carried out on condensed CO ($\mu \sim 0.1$ D) and N₂ ($\mu = 0$) with the spectra obtained at very low temperatures and with good resolution ($\ll 0.2$ eV). CO is marginal, whereas N₂ should show vibrational structure if phonons are the only broadening mechanism. Thus experiments on these two systems (or any two isoelectronic molecules, one polar and the other not) should provide a means for isolating the degree of broadening due to phonons as opposed to other mechanisms.

Ideally, the definitive test is the $\coth(\hbar\omega/2kT)$ temperature dependence of the bandwidth. Unfortunately such experiments are technically difficult, if not impossible, since the layers condense only at very low (≈ 80 K) temperatures. Thus the range of temperature variation which is de-

sirable for such a test is unattainable.

Finally note that the broadening mechanism proposed here does not overrule other and abundant mechanisms such as vibrational dephasing^{26(e)} and hole lifetime effects.²⁷⁻³⁰ By focusing on weakly condensed molecular layers, lifetime effects should be minimized. On the other hand, there can be no question that for chemisorbed monolayers (which most experiments have been performed on) lifetime effects are all important, providing a broadening of the order of 1 eV, and there should be no possibility of resolving the vibrational structure.

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- ^(a) However, the adiabatic threshold energy is displaced upwards by roughly the same amount. Thus sum rule requirements that the mean energy in the spectrum is independent of the vibrational excitation are satisfied. I am grateful to Dr. L. Cederbaum for helpful comments on this point. ^(b) F. J. Himpsel, N. Schwenter, and E. E. Koch, *Phys. Status Solidi B* **71**, 615 (1975) have performed uv photoemission experiments from solid N₂ and O₂. The slopes of their spectra are quite similar to Franck-Condon envelopes, but since their resolution was ~0.2 - 0.3 eV, intramolecular vibrational structure was not resolved.
- ²⁷M. Sunjie and A. Lucas, *Chem. Phys. Lett.* **42**, 462 (1976) and J. W. Gadzuk (unpublished) argue that since the time dependence of the photoexcited hole charge density is $n(t) = \theta(t) \exp(-\gamma t/\hbar)$ with γ the hole level width, the Fourier transform goes as $(\omega - i\gamma/\hbar)^{-1}$ and thus the modulus squared hole-boson coupling β_{ph} should be multiplied by $(\hbar\omega_0)^2/[(\hbar\omega_0)^2 + \gamma^2]$. With $\hbar\omega_0 = 10^{-2}$ eV and $\gamma \sim 10^{-1}$ eV, this reduces β_{ph} to 1% of the $\gamma=0$ value. Physically this says that a suddenly switched-on hole that lives for only a small fraction of a vibrational period cannot transfer much energy to the low-energy (long-time response) phonon modes since the hole is not present by the time it takes the phonons to respond.
- ²⁸D. R. Hamann and P. H. Citrin (private communication) argue that the hole lifetime can be treated adequately by convolving the $\gamma=0$ phonon spectrum, obtained from Eqs. (17) and (19), with a lifetime Lorentzian, in contradiction with the picture discussed in Ref. 27. Although it is puzzling that the physical situation discussed in Ref. 27 is incorrect, according to Hamann and Citrin, their philosophy appears to be implicitly adopted in the theory of the Doniach-Sunjić asymmetric x-ray photoemission line shape (Refs. 4 and 15). In this theory the effects of short-hole lifetimes on the long-time (low-energy electron-hole pair shakeup) response of a boson field are included by simply performing a convolution of the $\gamma=0$ pair shakeup spectrum with the lifetime Lorentzian. The resulting line shapes are in good agreement with experimental observations. In any event, an unresolved dichotomy exists between the arguments in Ref. 27 and those in x-ray photoemission spectroscopy (XPS) line-shape theory. Not knowing the resolution of this problem, I have restricted considerations in this paper to physical situations in which $\gamma \rightarrow 0$ and have thus sidestepped this interesting question.
- ²⁹ Recently an end to the dichotomy expressed in Refs. 27 and 28 has evolved from discussions with Citrin, Hamann, and Sunjić. In fact, both arguments are correct when applied to the appropriate problems. As an example, considered by Sunjić and Lucas, take the XPS linewidth for a K 2p electron from a halide of K. The inverse lifetime of a 2p hole is 0.23 eV according to Citrin *et al.* (Ref. 19). However, this is the lifetime with respect to the hole moving from the L to the M shell where it still remains localized on the source atom. As long as the size of the M hole is much less than the minimum phonon wavelength, the electrostatic part of the hole-phonon coupling constant changes insignificantly. Thus the phonon system is not influenced by this Auger transition. But it is this transition which gives rise to the 0.23 eV width. Once the hole bubbles up to the highest-energy core level, the only remaining non radiative transition possible is an $M_{45}-V-V$ (V =valence) transition which is much slower than the core transitions (≤ 0.01 eV). It is this transition which determines the lifetime for the hole to remain localized on the source atom and not the 0.23 eV lifetime. The ~0.01 eV level width is that one which enters the Sunjić-Lucas "hole vertex correction." The end result is that the coupling constant should be modified, as outlined in Ref. 27, but with γ determined by the $M_{45}-V-V$ transition rate. The resulting spectrum should then be convolved with a 0.23 eV Lorentzian as outlined in Ref. 28.
- ³⁰ Recently, Minnhagen (unpublished) has completed a diagrammatic many-body theory of phonon effects in XPS line shapes and finds the same vertex corrections discussed in Ref. 27. Again γ determined by the hole localization time rather than the Auger decay time for the hole to move amongst subshell levels is, as mentioned in Ref. 29, the appropriate width.