Temperature-Dependent Photoemission Line Shapes of Physisorbed Xenon

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A model is presented for the temperature dependence of adsorbate photoemission line widths. By approximating the initial and final states as displaced harmonic oscillators, an analytic form for the observed line width is obtained. Comparison with angle-resolved photoemission spectra of xenon on Cu(110) yields excellent agreement.

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Pronounced temperature-dependent photoemission linewidths generally signify an operative vibrational (phonon) broadening or shakeup mechanism.[1] The theoretical and experimental study of this mechanism, in a well-defined layer of xenon physisorbed on Cu(110) over a wide range of temperatures, is the subject of this Letter. This adsorption system was chosen since the interaction potential of a rare-gas atom with a metal surface can be well described by existing theories,[2] and complications due to chemical interaction with the substrate do not arise. Since there are no internal vibrational modes, only the xenon-metal vibration needs to be considered and its low energy [about 2.5 meV (Ref. 3)] justifies the use of certain approximations as outlined below. We find that, by using values for the mean square displacement of Xe atoms and their distance to the substrate and image planes taken from independent experimental determinations, we arrive at a theoretical prediction for the temperature-dependent linewidth which matches the experimental results within the limits of experimental accuracy, *without adjusting any parameters*. The temperature dependence of photoemission linewidths has been previously studied in alkali metals[4] and condensed molecular solids.[5] However, because of the relative complexity of these systems experimental data were treated on a rather empirical basis.

The experiments were carried out in an ultra-high-vacuum angle-resolved photoelectron spectrometer equipped with a helium resonance lamp, an ion gun for crystal cleaning, low-energy electron diffraction (LEED) optics, and a cryostat

sample holder which was cooled with cold He gas, by which the crystal temperature could be varied in the range of 35–200 K[6]; resistive heating was used to anneal the crystal after ion bombardment. The linewidth [full width at half maximum (FWHM)] of the Xe $5p$ levels, which are very intense,[7] were evaluated from spectra recorded at normal emission in many different runs (see inset in Fig. 2 for a sample spectrum). For reasons of intensity only the $m_j = \pm \frac{1}{2}$ component of the $5p_{3/2}$ peak was evaluated. A breakdown of $\vec{k}$ conservation leads to the appearance of shoulders[6] on the Xe $5p$ photoemission peaks in an incommensurate layer; interference with these shoulder peaks was carefully avoided. Since only normal-emission spectra were used for the evaluation, there are no other factors influencing peak shape which could lead to spurious results. HeI light ($h\nu = 21.2$ eV) was used for photoexcitation. Energy resolution was 150 meV. Except for temperatures above 90 K, full monolayer coverage was always maintained, as determined from LEED[8] and angle-resolved photoemission.[7] Temperatures were measured by a calibrated Chromel-Constantan thermocouple spot welded to the crystal. Further details concerning the experimental procedure, as well as the characterization of the xenon layer, are described in Ref. 7.

The origins of phonon-induced photoemission line broadening with respect to the physisorbed Xe are displayed in Fig. 1. The lowest-lying potential-energy curve describing the neutral-Xe-surface interaction is characterized by some equilibrium position z_0 and curvature $d^2V/dz^2|_{z=z_0}$

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$=M\omega^2$. Photoionization creates a quasilocalized positive hole on the Xe which induces a negative screening (image) charge within the substrate. The interaction between the hole and its image provides an additional, attractive term augmenting the neutral curve which results in the Xe$^+$-

metal interaction shown as the upper curve, whose equilibrium distance from the surface is $z^+ < z_0$ and whose curvature is such that ω^+ is not necessarily equal to ω. Within the Franck-Condon picture, the photoelectron energy distribution is given by[9]

$$N'(\epsilon, T) = \sum_{n, m'} \left[\frac{e^{-\epsilon_n/kT}}{Q} \right] |\langle n | m' \rangle|^2 \delta(\epsilon + [\epsilon_{m'} - \epsilon_n] - \epsilon_0), \tag{1}$$

where the sum on n thermally averages over $|n\rangle$, the initial vibrational states of the physisorbed Xe atom, $Q = \sum_n e^{-\epsilon_n/kT}$ is the vibrational partition function, the sum on m' is over all possible final vibrational and dissociative states of the Xe$^+$-metal system, and $\epsilon_0 = \epsilon_+ - \epsilon_a - V_i + h\nu$ with $h\nu$ the photon energy and the other quantities identified in Fig. 1; $\langle n | m' \rangle$ is the overlap integral for the displaced oscillator states, whose modulus squared is the Franck-Condon factor. In the displaced-harmonic-oscillator limit[10] in which $\omega^+ = \omega$ and $T = 0$, Eq. (1) is precisely a Poisson distribution[9]:

$$N'(\epsilon) = e^{-\beta} \sum_{m=0}^{\infty} [\beta^m/m!] \delta(\epsilon + m\hbar\omega - \epsilon_0), \tag{2}$$

where

$$\beta = [\lambda/\hbar\omega]^2, \quad \lambda = [\hbar/2M\omega]^{1/2} dV_+/dz \big|_{z = z_0}$$

and as a reasonable first approximation,

$$V_+(z) \simeq V_a(z) - V_{image}(z) + V_i. \tag{3}$$

Furthermore, in the large-β limit expected to be the case for massive Xe (because of the small vibrational frequency), Eq. (2) approaches a Gaussian

$$N'(\epsilon) = \frac{1}{(2\pi)^{1/2}\Delta} \exp\left[-\frac{1}{2}\left(\frac{\epsilon - \epsilon_0 + \beta\hbar\omega}{\Delta} \right)^2 \right], \tag{4}$$

with $\Delta = \beta^{1/2}\hbar\omega$ and the FWHM $W(T) = 2.35\Delta$. Generalization to finite temperature yields[1]

$$W(T) = 2.35\beta^{1/2}\hbar\omega[\coth(\hbar\omega/2kT)]^{1/2}. \tag{5}$$

FIG. 1. Potential-energy curves for atomic and ionic Xe interaction with a surface. The dashed curve, $V_{eff}(z)$ is the effective harmonic potential discussed in the text, $\epsilon_a - \hbar\omega/2$ and $\epsilon_+ - \hbar\omega_+/2$ are atom and adsorbed-ion desorption energies. The structure labeled $|\psi_{in}(Z; T)|^2$ represents the initial-state charge distribution.

Moving on to the actual situation depicted in Fig. 1, a viable strategy for calculating the line shape would be the following: (a) obtain a Xe(atom)-metal interaction from physisorption theory[2]; (b) construct an ion curve by adding an image term such as $V_{image}(z) = e^2/4(z - d_0)$, where d_0 is the effective location of the image plane for finite-density jellium[11]; (c) fit the attractive wells of both curves to harmonic potentials determined in (a) and (b), and with minima displaced by $z_0 - z^+$ with respect to each other; (d) calculate term by term the overlap integrals $\langle n | m' \rangle$, the procedure having been systemized[12] for arbitrary states and frequencies. As a result of the high density of vibrational levels, this could require several hundred such evaluations.

Since the major role of the ionic potential, as far as line shapes are concerned, is contained mainly in the slope[9] within the region $\sim z_0 \pm \bar{u}(T)$ shown in Fig. 1, we introduce an approximation in which the true ion potential, given by Eq. (3), is replaced by an effective harmonic potential with the same frequency as the neutral,[9]

$$V_+(z) \rightarrow V_{eff}(z) = \tfrac{1}{2}\kappa[z - (z_0 - \delta)]^2, \tag{6}$$

in which δ, determined by the requirement that

$$\frac{dV_+(z)}{dz}\bigg|_{z=z_0} = \frac{dV_{\text{eff}}(z)}{dz}\bigg|_{z=z_0},\tag{7}$$

is $\delta = (\lambda/\kappa)[2M\omega/\hbar]^{1/2}$. By using the displaced image potential,

$$\frac{dV_+(z)}{dz}\bigg|_{z=z_0} = \frac{e^2}{4(z_0-d_0)^2},\tag{8}$$

so that

$$\lambda = \frac{e^2}{4(z_0-d_0)^2}\left[\frac{\hbar}{2M\omega}\right]^{1/2}.\tag{9}$$

Insertion of Eq. (9) in Eq. (5) yields the final expression for the linewidth:

$$W(T) = \frac{2.35e^2}{4(z_0-d_0)}\left[\frac{(\hbar/2M\omega)^{1/2}}{(z_0-d_0)}\right]\left[\coth\left(\frac{\hbar\omega}{2kT}\right)\right]^{1/2}$$

$$= \frac{2.35e^2}{4(z_0-d_0)}\left[\frac{\bar{u}(T)}{z_0-d_0}\right],\tag{10}$$

where $\bar{u}(T)$ is the vibrational amplitude of the initial state of the physisorbed Xe atom.

Equation (10) may be handled in two ways. In either case one first requires values for z_0 and d_0, either from theory or experiment. For Xe on $r_s = 2$ jellium, Lang[2c] estimates that $z_0 \simeq 5$ bohrs, $d_0 \simeq 1.6$ bohrs, and thus $e^2/4(z_0-d_0) \simeq 2$ eV which is consistent with values obtained from LEED[13] (for z_0) and ultraviolet photoelectron spectroscopy[14] (for image shifts). Alternatively and preferably, the second form of Eq. (10) can take advantage of vibrational amplitudes inferred from LEED-determined[13] surface Debye-Waller factors.

For the system Xe on Ag(111), which should be similar to Xe on Cu(110) as far as linewidths are concerned, Unguris and co-workers have determined $\bar{u}^2T = (2.9\pm0.6)\times10^{-4}$ Å^2/K from LEED beam profile analyses. With use of these values, Eq. (10) is

$$W(T) = 0.044\ T^{1/2}\ \text{eV}\tag{11}$$

with T in degrees Kelvin.

In order to compare our observations with Eqs. (10) and (11), we follow Salaneck et al.[5] who studied photoemission linewidths in condensed layers of isopropyl benzene, and assume that the observed linewidth is given by

$$W_{\text{obs}}(T) = [W_{\text{other}}^2 + W(T)^2]^{1/2},\tag{12}$$

where W_{other} includes temperature-independent broadening mechanisms such as experimental resolution and hole "lifetime" effects,[15] which
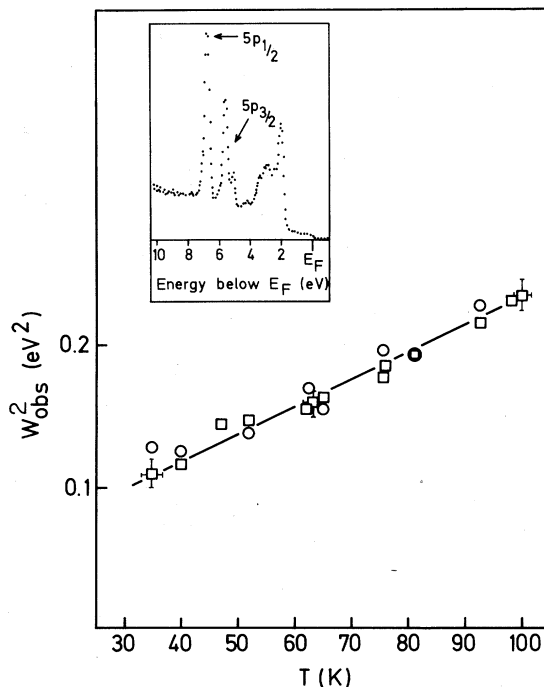

FIG. 2. Square of the linewidth W_{obs} vs layer temperature T of the Xe $5p_{1/2}$ (squares) and $5p_{3/2}$ (circles) photoemission peaks for a Xe layer adsorbed on Cu(110); a sample spectrum, recorded in normal emission, is shown in the inset.

have been discussed in great detail by Citrin, Wertheim, and Baer for alkali metals.[4]

A comparison of the theoretical values for the linewidth with our experimental data is shown in Fig. 2. The solid line represents Eq. (12), where the value of $W_{\text{obs}}(T=0)$, corresponding to the best fit, is 0.2 eV. This value gives a reasonable estimate of the sum of instrumental resolution and hole-lifetime effects.[7] The data points are shown as squares for the $5p_{1/2}$ peak and circles for the $5p_{3/2}$ peak with experimental accuracy indicated by error bars. The level of agreement between theory and experiment is most encouraging, particularly since the quantities required for an evaluation of Eq. (12) are derived from either experimental data or recent calculations,[2c] with no extraneous "free parameters" involved.

Explicit therefore, the final expression for the temperature dependence of the Xe $5p$ photoemission peaks FWHM is

$$W_{\text{obs}}(T) = (0.04 + 0.0019T)^{1/2}\ \text{eV}.\tag{13}$$

In summary, we have presented a theoretical model which gives the temperature dependence

of the photoemission linewidths for rare-gas atoms adsorbed on a metal surface. The effect arises from the temperature-dependent weighting of the Franck-Condon factors between the initial (atomic) and final (ionic) adsorbate vibrational states. These have been explicitly evaluated within the displaced-harmonic-oscillator limit,[9] and an analysis of data for the $5p_{1/2}$ and $5p_{3/2}$ levels of Xe adsorbed on Cu(110) has been performed, yielding excellent agreement between theory and experiment.

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