

## Comparison of vibrational broadening in Auger and photoelectron spectroscopy

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Within linear coupling the vibrational broadening of quasiatomic Auger peaks and core photoelectron peaks is approximately equal in ionic crystals, but the Auger broadening is about 3 times that of the core photoelectron broadening for rare-gas atoms physisorbed on metal surfaces.

### INTRODUCTION

Pronounced temperature dependence in photoemission and Auger line-width in solids is generally associated with phonon broadening. The effects are particularly pronounced in ionic crystals,<sup>1-5</sup> where the core hole(s) create extra forces in neighboring ions by direct monopole electrostatic coupling. These forces shift the equilibrium configuration of the system, so that electron emission is accompanied by phonon generation. Fluctuations in the configuration of the system at the instant of emission lead to fluctuations in the numbers of phonons created, and so lead to broadening in electron spectroscopic peaks. More recently Gadzuk *et al.*<sup>6</sup> have shown that gases physisorbed on metals also show strong phonon coupling through fluctuations in the image force with distance from the surface. In metals the phonon coupling is smaller due to the effective screening of the core hole, but broadening of the order of 0.1–0.3 eV may be produced in some cases.<sup>7</sup> Temperature dependence in photoemission linewidths has also been observed in condensed molecular solids.<sup>8</sup>

The purpose of this paper is to compare the phonon broadening for photoemission from localized electron states and for quasiatomic Auger emission. It will be shown that in ionic crystals the vibrational broadening is very similar for the two processes, while for atoms physisorbed on metals the Auger broadening is much larger than in the case of photoemission.

### THEORY

For strong electron-phonon coupling it is possible to adopt the semiclassical configurational coordinate approach. Let us consider first the case of coupling to a single mode of configurational coordinate  $Q$ . The ground-state energy of the system,  $W_g$  may then be specified by

$$W_g = \frac{1}{2}kQ^2, \quad (1)$$

where  $k$  is the effective force constant for an oscillator of effective mass  $m$ . The excited state of the system involving a single core hole (final state of the photoemission process) will then be of the form

$$W^+ = A + \frac{1}{2}k(Q - Q_1)^2, \quad (2)$$

where we have linear coupling; i.e., the excited state has

an equilibrium configuration shifted by  $Q_1$ , but the curvature of the potential-energy function remains the same. The term  $\frac{1}{2}kQ_1^2$  represents the nuclear relaxation energy associated with creation of the core hole.

In the Auger final state a different equilibrium configuration  $Q_2$  will apply, but, within linear coupling, we assume the same  $k$ , which gives

$$W^{++} = B + \frac{1}{2}k(Q - Q_2)^2. \quad (3)$$

The main approximations thus far are the Franck-Condon approximation, neglect of anharmonic terms in the potential curves, and neglect of quadratic terms in the difference energies between the curves.

Photoemission undoubtedly takes place at nuclear configurations around  $Q=0$ , i.e., for normal ground-state configurations. If  $E_{\text{PES}}$  (PES indicates photoelectron spectroscopy) is the kinetic energy of the emitted electrons for incident photon energy  $h\nu$  then

$$h\nu - E_{\text{PES}} = A - kQ_1Q + \frac{1}{2}kQ_1^2. \quad (4)$$

The mean value of the kinetic energy is

$$[E_{\text{PES}}]_{\text{av}} = h\nu - A - \frac{1}{2}kQ_1^2, \quad (5)$$

and the mean-square fluctuation about the mean is

$$[\Delta E_{\text{PES}}^2]_{\text{av}} \equiv [E_{\text{PES}}^2]_{\text{av}} - [E_{\text{PES}}]_{\text{av}}^2 = k^2Q_1^2 \langle Q^2 \rangle, \quad (6)$$

where  $\langle Q^2 \rangle$  is in the appropriate mean value.

For Auger emission there are various possibilities according to whether the core lifetime is much less than, comparable with, or much longer than a typical lattice vibration period. Usually the core lifetime is much less than  $10^{-13}$  sec so that the Auger emission process takes place in the same configuration as the photoemission process; then the phonon broadening reflects ground-state configurations, as in photoemission. This is the only case that will be dealt with here, but similar results can be obtained for the long-lifetime regime. The mean Auger energy  $[E_{\text{AES}}]_{\text{av}}$  (AES represents Auger electron spectroscopy) is then

$$[E_{\text{AES}}]_{\text{av}} = A - B + \frac{1}{2}k(Q_1^2 - Q_2^2), \quad (7)$$

and the mean-square fluctuations about the mean is given by

$$[\Delta E_{\text{AES}}^2]_{\text{av}} \equiv [E_{\text{AES}}^2]_{\text{av}} - [E_{\text{AES}}]_{\text{av}}^2 = (F_1 - F_2)^2 \langle Q^2 \rangle, \quad (8)$$

where  $F_1 = kQ_1$  and  $F_2 = kQ_2$  are the generalized forces on the unperturbed oscillator of generalized coordinate  $Q$ , leading to equilibrium shifts  $Q_1$  and  $Q_2$ , respectively (Fig. 1). Using

$$\langle Q^2 \rangle = \frac{\hbar}{2m\omega} \coth \left[ \frac{\hbar\omega}{2k_B T} \right], \quad (9)$$

where  $\omega$  is the normal mode frequency, we obtain

$$[\Delta E_{\text{PES}}^2]_{\text{av}} = \frac{\hbar F_1^2}{2m\omega} \coth \left[ \frac{\hbar\omega}{2k_B T} \right], \quad (10a)$$

$$[\Delta E_{\text{AES}}^2]_{\text{av}} = \frac{\hbar(F_1 - F_2)^2}{2m\omega} \coth \left[ \frac{\hbar\omega}{2k_B T} \right], \quad (10b)$$

which reduce to

$$[\Delta E_{\text{PES}}^2]_{\text{av}} = \frac{F_1^2 k_B T}{m\omega^2} \quad (10a')$$

and

$$[\Delta E_{\text{AES}}^2]_{\text{av}} = \frac{(F_1 - F_2)^2 k_B T}{m\omega^2} \quad (10b')$$

for  $k_B T \gg \hbar\omega$ .

The full width at half maximum (FWHM) for the x-ray photoelectron spectroscopy (XPS) and AES profiles would then be given by

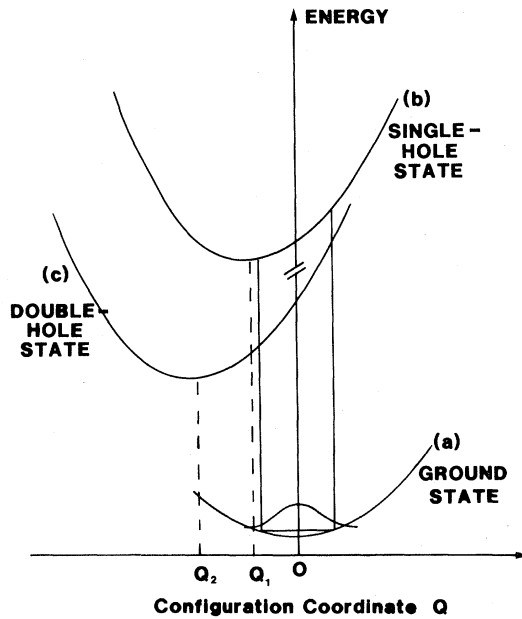


FIG. 1. Schematic configurational coordinate diagram for (a) the ground state, (b) the single-hole final state of the core-hole photoemission process with equilibrium configuration shifted by  $Q_1$ , and (c) the double-hole final state of the Auger process with equilibrium configuration shifted by  $Q_2$ . Depending on the system  $Q_1$  and  $Q_2$  may be positive or negative.

$$\left. \begin{array}{l} \Delta E_{\text{PES}} \\ \Delta E_{\text{AES}} \end{array} \right\} = 2.35 \times \left\{ \begin{array}{l} ([\Delta E_{\text{PES}}^2]_{\text{av}})^{1/2} \\ ([\Delta E_{\text{AES}}^2]_{\text{av}})^{1/2} \end{array} \right., \quad (11)$$

if this was the only significant broadening mechanism.

Generalizing to  $N$  coordinates  $Q_i$  of frequency  $\omega_i$  with generalized forces  $F_1^i$  and  $F_2^i$ , respectively, we have

$$[\Delta E_{\text{PES}}^2]_{\text{av}} = \hbar \sum_{i=1}^N \frac{(F_1^i)^2}{2\omega_i} \coth \left[ \frac{\hbar\omega_i}{2k_B T} \right], \quad (12a)$$

and

$$[\Delta E_{\text{AES}}^2]_{\text{av}} = \hbar \sum_{i=1}^N \frac{(F_1^i - F_2^i)^2}{2\omega_i} \coth \left[ \frac{\hbar\omega_i}{2k_B T} \right]. \quad (12b)$$

Here  $Q_i$  has been normalized so that the kinetic energy in the  $i$ th mode is  $\frac{1}{2}\dot{Q}_i^2$ . The displacement of the  $i$ th atom  $\Delta \vec{r}_i$  from its equilibrium position may be expressed as

$$\Delta \vec{r}_i = \sum_t \vec{a}_i^t Q_t, \quad (13)$$

where  $\vec{a}_i^t$  is the normalized eigenvector for the displacement of the  $i$ th atom in the  $t$ th normal mode.

#### APPLICATION TO IONIC CRYSTALS

Let us now compare the behavior of Eqs. (10a) and (10b) for the case of localized holes ionic crystals and rare gases physisorbed on metal surfaces. In the ionic crystal the generalized forces  $F_1^i$  and  $F_2^i$  are related to the monopole Coulomb forces between the single or double hole and ions in the crystal lattice. For a point-ion model the magnitude of the force on the  $i$ th ion at distance  $\vec{r}_i$  from the localized core hole is

$$\vec{\mathcal{F}}_n^i = \frac{nZ_i e^2}{4\pi\epsilon_0 r_i^2} \hat{r} \quad (14a)$$

where  $n$  is the number of core holes ( $n=1,2$ ), and  $Z_i$  is the ionic charge (of sign + or -). If electronic polarization is taken into consideration, the core Coulomb forces will be reduced due to additional dipolar potentials and, within a continuum local-field model, will approximately be given by

$$\vec{\mathcal{F}}_n^i = \frac{nZ_i e^2}{4\pi\epsilon_0 \epsilon_\infty r_i^2} \hat{r} \quad (14b)$$

where  $\epsilon_\infty$  is the high-frequency dielectric constant. Devey<sup>9</sup> has shown this to be a good approximation especially beyond first neighbors. For a set of displacements  $\Delta \vec{r}_i$  the generalized force for the  $t$ th normal mode will be

$$F_n^t = \sum_i \vec{\mathcal{F}}_n^i \cdot \vec{a}_i^t.$$

Different authors have adopted different approximations in the derivation of  $F_n^t$ . Citrin *et al.*<sup>3</sup> assume coupling only to the long-wavelength longitudinal-optic mode in the manner of Huang and Rhys<sup>10</sup>; Matthew<sup>1</sup> and Matthew and Devey<sup>2</sup> adopt the Einstein approximation, while Mahan<sup>4</sup> has evolved a multimode approximation. From the point of view of this paper we are only concerned with

how  $F_n^t$  scales with  $n$ . Provided that the electronic polarization in the system is linear, all the terms in  $F_n^t$  vary linearly with  $n$ , so that within the linear approximations of (i) linear electron-phonon coupling and (ii) linear dielectric response,

$$|F_i^t| = |F_1^t - F_2^t| \quad \text{for all } t,$$

i.e.,

$$[\Delta E_{\text{PES}}^2]_{\text{av}} = [\Delta E_{\text{AES}}^2]_{\text{av}}.$$

This means that the phonon broadening is approximately the same for core PES and quasiatomic Auger emission. This equality in the respective phonon broadenings is in sharp contrast to the nuclear relaxation energies for the final states of PES and AES processes, which scale quadratically with  $n$ ; this leads to much larger electronic relaxation shifts in quasiatomic AES than in core PES. The effect has been discussed in some detail for the case of ionic crystals by Kowalczyk *et al.*<sup>11</sup> and Matthew,<sup>12</sup> and the PES and AES energies are consistent with such a scaling to first order. However, these nuclear relaxation energy differences are not reflected in the phonon broadening. Citrin *et al.*<sup>3</sup> have noted comparable temperature dependence of breadths in AES and PES, but no detailed analysis has been made.

#### APPLICATION TO PHYSISORBED RARE GASES

In the model of electron-phonon coupling of rare-gas atoms physisorbed on metals developed by Gadzuk *et al.*,<sup>6</sup> it is argued that the main coupling will be to the Einstein-type oscillation of the rare-gas atom itself, weakly bound as it is to the crystal surface. The creation of  $n$  core holes on the rare-gas atom is accompanied by image screening at the surface. Reverting to the one-mode model of Eqs. (1)–(10) we have

$$F_n = \frac{1}{4\pi\epsilon_0} \frac{n^2 e^2}{4d^2}, \quad (15)$$

where  $d$  is the distance of the rare-gas atom from the crystal surface. Equations (10a) and (15) with  $n=1$  correspond exactly to the theory of Gadzuk *et al.*<sup>6</sup> for PES broadening, but, since the image forces scale quadratically with  $n$  we now have

$$[\Delta E_{\text{AES}}^2]_{\text{av}} = 9[\Delta E_{\text{PES}}^2]_{\text{av}}, \quad (16)$$

i.e., if the phonon broadening were dominant the Auger FWHM would be 3 times the PES FWHM. For Xe on Cu(110) the FWHM of the  $5p$  photoemission peak<sup>6</sup> is

$$W_{\text{PES}}(T) = (0.04 + 0.0019T)^{1/2}$$

in units of eV, where the first term corresponds to the lifetime-broadening component, while the second term is the phonon-broadening term in its high-temperature-limit form. The theory presented here predicts that for an Auger transition such as  $N_{45}O_{23}O_{23}$  or  $M_{45}N_{45}N_{45}$  each multiplet component will be broadened as

$$W_{\text{AES}}(T) = (\alpha^2 + 0.017T)^{1/2}$$

in units of eV, where  $\alpha$  is the sum of the lifetime broadenings of initial and final states. No definitive comparison of PES and AES breadths has yet been made, but Kaindl *et al.*<sup>13</sup> find broadening  $\sim 1$  eV for  $N_{45}O_{23}O_{23}$  transitions in Xe on Pd at a temperature in excess of 40 K. The lifetime broadening of the initial  $N_{45}$  state is small,<sup>14</sup> but systematic temperature variation has not been attempted in order to isolate the phonon-broadening component. Nuttall and Gallon<sup>15</sup> have observed  $L_{23}M_{23}M_{23}$  Auger peaks of Ar on Ag at low coverage with FWHM  $\sim 2$  eV (a figure substantially larger than the initial-state lifetime broadening). Probably the best system on which to test the theory developed here would be the  $M_{45}N_{45}N_{45}$  spectrum of Xe adsorbed on a convenient metal, e.g., W. Here the Auger transition is unambiguously atomlike, and a limited number of final-state multiplets have large intensity; accurate thermal broadening parameters should readily be deducible after deconvoluting instrumental broadening, lifetime broadening, and other temperature-independent components. Kaindl *et al.*<sup>13</sup> have already confirmed that for adsorbed rare-gas atoms the shift of the AES peak is approximately 3 times that of the PES peak due to the scaling of the electronic relaxation energy with number of core holes. This paper predicts that the respective breadth components are similarly related.

#### EXTENSION TO QUADRATIC COUPLING

The predictions discussed thus far have depended on linear response both in electron-phonon coupling and in dielectric response. Quadratic coupling in the electron-phonon interaction for color centers in ionic crystals has been considered, for example, by Matthew and Hart-Davis,<sup>16</sup> and for the ionic crystal case the effects will be small both in PES and AES. On the other hand, weakly bound rare-gas atoms suffer a very violent change in potential when the core-hole image charge interaction is switched on. The ion will be strongly attracted to the surface, and its inward relaxation will be eventually controlled by repulsive overlap forces. Similarly, the curvature of the potential well will drastically change.

Let us extend the one-mode model to take into account quadratic effects in the electron-phonon interaction such that the (0,1,2) -hole systems are characterized by spring constants  $(k, k', k'')$ . For PES

$$[E_{\text{PES}}]_{\text{av}} = h\nu - A - \frac{1}{2}k'Q_1^2 + \frac{1}{2}(k - k')\langle Q^2 \rangle \quad (17)$$

and

$$[\Delta E_{\text{PES}}^2]_{\text{av}} = F_1^2 \langle Q^2 \rangle + \frac{1}{2}(k - k')^2 \langle Q^2 \rangle^2, \quad (18)$$

where for Gaussian fluctuations  $\langle Q^4 \rangle = 3\langle Q^2 \rangle^2$ .

Now  $k$  is small, and so  $k' \sim -(e^2/4\pi\epsilon_0)(1/2d^3)$ . From the data of Gadzuk *et al.*<sup>6</sup> the additional temperature-dependent shift in  $[E_{\text{PES}}]_{\text{av}}$  is  $\sim 10^{-2}$  eV at 100 K, and the fractional correction to the FWHM is of order 0.01. For AES the effects will be marginally bigger, but the overall conclusions of the linear electron-phonon coupling model should be valid. Somewhat more suspect are the estimates of  $F_1$  and  $F_2$ , based on linear response of the metal electron system. The true self-consistent electronic response

may be markedly nonlinear, but this will enhance rather than diminish the differences between electron-phonon coupling in AES and PES.

### DISCUSSION

It is important to understand the origin of the different scaling of PES and AES breadths for ionic crystals and rare-gas atoms adsorbed on metals. In ionic crystals the main electron-phonon coupling arises from monopole electrostatic forces between the core-hole charge  $n$  and the ions in the crystal; dielectric response reduces the effective field at ion sites and so the magnitude of the force. However, the forces still scale linearly in the number of core holes  $n$ . There will be additional forces between core holes and dipoles induced on neighboring ions; although these are proportional to  $n^2$ , they are much smaller than the monopole forces. For physisorbed rare-gas atoms the core hole can only couple through induced charges, and the force between atoms containing a core hole or core holes will now scale mainly as  $n^2$ . The electrons in the metal are much more responsive than the electrons in the ionic crystal, so that the induced forces are larger than for ionic crystals. Although the phonon broadening in core-hole spectra of these physisorbed systems may be somewhat smaller than for ionic crystals, it is readily measurable and

should show the strong differences between PES and AES discussed here.

### CONCLUSIONS

In summary, it has been shown that, assuming linear electron-phonon coupling and linear electronic relaxation, the vibrational broadening in core-hole photoelectron spectroscopy and quasiatomic Auger spectra of ionic crystals will be, to a good approximation, the same, but that the vibrational broadening of Auger electron energy distributions for rare-gas atoms physisorbed on metals will be 3 times that for core-photoelectron peaks. These predictions are not inconsistent with the limited data currently available, but more detailed experimental studies of XPS and AES breadths are necessary to test the model presented here.

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