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Phonon broadening of x-ray photoemission line shapes in solids and its independence of hole state lifetimes

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Using a simple model we show that the phonon contribution to photoemission line shapes is identical when the hole-state lifetime is either long or short compared to a typical phonon period. The principles are extended to Auger electron, x-ray absorption, and x-ray emission spectroscopies and should also be applicable to other excitation processes in x-ray photoemission. Experimental examples demonstrating these principles are cited.

I. INTRODUCTION

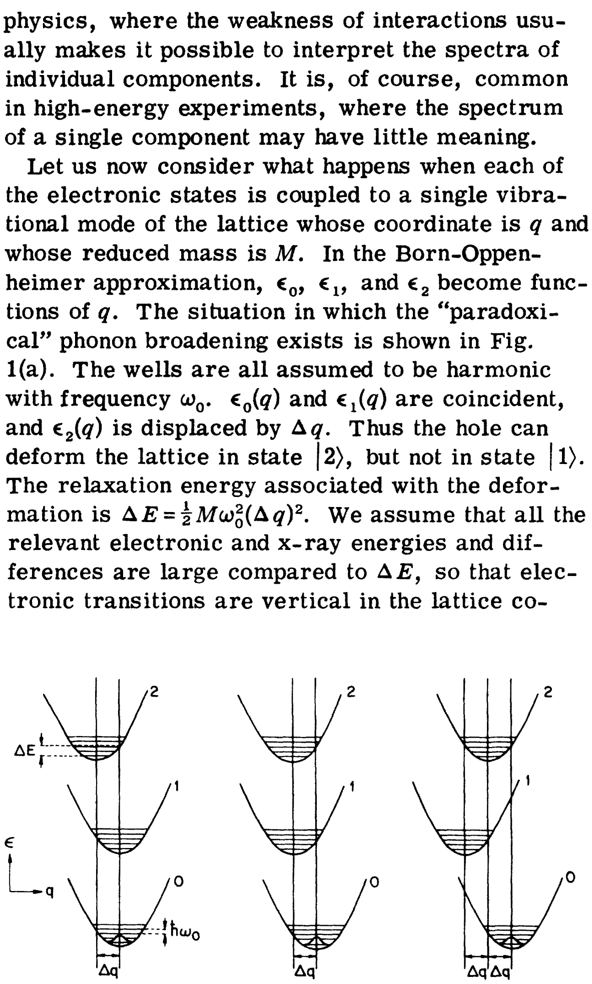
The authors and P. Eisenberger recently presented x-ray photoemission (XPS) spectra for core levels in a series of ionic insulators which displayed substantial and temperature-dependent broadening of the spectral lines.[1] Theoretical estimates based on the simplest model of the coupling of the final-state hole to polar-optical phonons gave good agreement for both the magnitude and temperature dependence of the broadening. The derivation given there assumed a long hole lifetime compared to a typical phonon period. Following the publication of these results, the applicability of the phonon explanation to cases in which the hole lifetime is short compared to a phonon period has been questioned by Sunjić and Lucas.[2] The physical argument supporting their approximate calculation is of the following form: (i) If the Auger or radiative lifetime of the core hole created in the XPS processes is short compared to a phonon period, the quantum state of the lattice cannot be changed in the process. (ii) If phonons are not created or absorbed, there can be no phonon contribution to the XPS linewidth. While (ii) might appear to follow simply from energy conservation, it is in fact not true in all situations. When the initially created hole state is much more strongly coupled to the lattice than the state into which it decays, the fluctuating potential of the lattice zero-point (and thermal) motion can produce phonon broadening of the XPS line *without* creating lattice excitations, and *without* violating energy conservation. In this work, we show, using a simple model, that the phonon broadening of the XPS line is in fact identical in the long- and short-lifetime limits. We then extend our ideas to include the broadening of spectral features in x-ray emission, absorption, and Auger-electron spectroscopies. Finally, we cite experimental examples in each spectroscopy which confirm the validity of these concepts.

After this work was initially submitted for publication, a paper appeared in which certain inconsistent approximations present in the theory given in Ref. 2 are rectified.[3] This improved treatment yields a phonon contribution to the XPS linewidth which is the same in both the long- and short-lifetime limits, in agreement with the result demonstrated here. In addition, it predicts an enhanced phonon contribution in the intermediate case when the lifetime and phonon period are comparable. While the physical origin of this enhancement is obscured within the formalism in Ref. 3, it may be possible to rationalize it in terms of the models considered here. Experimental evidence to verify the existence of a broadening enhancement is considered in Sec. III.

II. THEORETICAL MODEL

The apparent paradox of the breakdown of assertion (ii) can be illustrated by abstracting a few essential elements from the complexity of the actual physical systems of interest. We consider only the electronic ground state $|0\rangle$, the excited hole state $|2\rangle$ produced in photoemission, and a single stable state $|1\rangle$ into which $|2\rangle$ decays. The energies of these states are denoted by $\epsilon_0<\epsilon_1<\epsilon_2$, the energies of the absorbed x ray and the photoelectron by $\hbar\omega_i$ and ϵ_p, respectively, and the decay rate from $|2\rangle$ to $|1\rangle$ by $\gamma/\hbar$. For the sake of argument, we suppose the decay is radiative, and that a photon of energy $\hbar\omega_f$ is emitted in the process. Before considering the effects of lattice coupling, we can illustrate an important point about the use of energy conservation arguments. For the model described, the photoelectron energy spectrum will be a Lorentzian centered at $\epsilon_p=\hbar\omega_i+\epsilon_0-\epsilon_2$, and the decay x-ray spectrum will be a Lorentzian centered at $\hbar\omega_f=\epsilon_2-\epsilon_1$ (this assumes, of course, purely monochromatic incident x rays for photoemission and perfect spectrometer resolution). In the conventional way of describing the photoemission and decay processes *individually*, energy is considered to be conserved within the lifetime uncertainty. However, if we consider the photoemission *and* decay as a *single* process, overall energy must be conserved exactly, since the final state consisting of $\{|1\rangle$ plus photoelectron plus photon$\}$ is stable. Thus, if the spectrum of the sum of the energies of *coincident* photoelectrons and decay x-ray photons were taken, it would be a δ function at $\epsilon_p+\hbar\omega_f=\hbar\omega_i+\epsilon_0-\epsilon_i$. The concept of coincident observation of all the components of the stable final state of an event is not common in condensed-matter physics, where the weakness of interactions usually makes it possible to interpret the spectra of individual components. It is, of course, common in high-energy experiments, where the spectrum of a single component may have little meaning.

Let us now consider what happens when each of the electronic states is coupled to a single vibrational mode of the lattice whose coordinate is q and whose reduced mass is M. In the Born-Oppenheimer approximation, ϵ_0, ϵ_1, and ϵ_2 become functions of q. The situation in which the "paradoxical" phonon broadening exists is shown in Fig. 1(a). The wells are all assumed to be harmonic with frequency ω_0. $\epsilon_0(q)$ and $\epsilon_1(q)$ are coincident, and $\epsilon_2(q)$ is displaced by Δq. Thus the hole can deform the lattice in state $|2\rangle$, but not in state $|1\rangle$. The relaxation energy associated with the deformation is $\Delta E=\frac{1}{2}M\omega_0^2(\Delta q)^2$. We assume that all the relevant electronic and x-ray energies and differences are large compared to ΔE, so that electronic transitions are vertical in the lattice coordinate and the Franck-Condon principle applies (i.e., we are in the "sudden approximation limit" as opposed to the "adiabatic limit").



(a) (b) (c)

FIG. 1. Configuration coordinate diagram of system with three electronic states assuming the Born-Oppenheimer and harmonic approximations. States 0 and 1 are the ground and excited states of the neutral and photoionized system, respectively. State 2 is the excited state of the ionized system which is reached from the ground state in the photoemission process and which decays to 1. Differing couplings to the lattice coordinate q with vibrational frequency ω_0, representing the deformations produced by the core hole (*s*), are indicated in (a), (b), and (c).

If the lifetime of the hole in $|2\rangle$ is long, we can treat that state as the final state and compute the Franck-Condon overlap factors to find the probabilities of reaching various vibrational states from the initial vibrational ground state. (The zero-temperature case is treated here for simplicity since the arguments can be easily generalized for a thermal ensemble.) In the limit when the mean number of vibrational excitations is large, $\bar{n}=\Delta E/\hbar\omega_0\gg 1$, the envelope of these excitation probabilities becomes a Gaussian of full width at half maximum (FWHM) width $\Gamma=2(2\ln 2)^{1/2}(\hbar\omega_0\Delta E)^{1/2}$ as discussed in Ref. 1 and references therein. In this situation, the ensemble of highly excited final states of the vibrational mode can be treated classically. An alternative and much simpler derivation of the Gaussian line shape can then be given. The vertical transition energy $\epsilon_{21}(q)=\epsilon_2(q)-\epsilon_1(q)$ is a linear function of q in the harmonic approximation. Using $\epsilon_{21}(q)$ and the probability distribution for q given by the square of the ground-state harmonic-oscillator wave function, we find exactly the same Gaussian spectrum for the photoelectron as given by the Franck-Condon envelope. We can interpret this semiclassical derivation as a representation of the photoemission event taking random instantaneous snapshots of the fluctuating potential produced by the lattice zero-point motion via the hole-phonon coupling.

Now consider the case of a short-lived state $|2\rangle$ in Fig. 1(a), which forces us to regard $|2\rangle$ as an intermediate state in the total process of photoemission plus decay. If we contemplate a time-dependent quantum-mechanical formulation of the problem, with the photoemission event at time t and the x-ray decay at t', then only the range $t-t'\lesssim\hbar/\gamma$ will contribute significantly to the integrated amplitude for the total process. The initial ground state of the lattice coordinate q in well 0 will project onto a linear combination of eigenstates of the displaced oscillator in well 2. The phase difference at time t' of the lowest and highest important components of this linear combination is $\bar{n}^{1/2}(t-t')\omega_0$, so if $\bar{n}^{1/2}\hbar\omega_0\ll\gamma$, the linear combination of well 2 eigenstates will not dephase during the times which contribute, and the projection of the lattice-coordinate wave function onto the eigenstates of well 1 in the decay process at t' will be coherent, and give the ground state. This is the formal expression of the intuitive notion that the lattice state cannot change in the limit of sufficiently short hole lifetimes, and it serves to accurately define the term "sufficiently". For the photoelectron the quasiclassical derivation of the fluctuating potential remains unchanged. We expect a distribution of Lorentzian spectra centered at various values $\hbar\omega_i + \epsilon_0(q) - \epsilon_1(q)$ with probabilities given by the square of the lattice ground-state wave function, i.e., a convolution of the Lorentzian lifetime line shape and the Gaussian phonon broadening. The same reasoning can be applied to the decay x ray, and we see that $\hbar\omega_f$ is similarly distributed since $\epsilon_{21}(q)$ is the same linear function as $\epsilon_{20}(q) = \epsilon_2(q) - \epsilon_0(q)$. If we now consider the coincident detection experiment, it is clear that since the photoemission and decay parts of each event occur at *the same q*, the spectrum of the sum

$$\epsilon_p + h\omega_f = h\omega_i - \epsilon_{20}(q) + \epsilon_{21}(q)$$

is q independent and a δ function. *Thus, for a sufficiently short-lived hole state* $|2\rangle$ *and the arrangement of wells in Fig. 1(a), the lattice does not absorb any energy in each event*; *it simply redistributes it between the outgoing electron and photon.*

While we have not treated the case of intermediate lifetimes for $|2\rangle$, it is likely that the simple fluctuating potential picture for the photoemission part of the event should remain valid. The enhanced broadening predicted by Minnhagen in this case[3] could arise from the motion of the coordinate q during the lifetime of state $|2\rangle$, which would introduce an additional distribution for q to be convoluted with the distribution given by the square of the ground-state oscillator wave function. In the time-dependent quantum-mechanical picture, components of the lattice wave function will become partially out of phase while the system is in state $|2\rangle$, and the decay from $|2\rangle$ to $|1\rangle$ will produce excited final states of the lattice as well as the lattice ground state. The extent of the real lattice excitation in this intermediate case will be less than in the the long-lifetime case.

An additional consideration in the intermediate-lifetime case is the rate at which the excited lattice mode dissipates its energy to other phonon modes. In an actual solid this occurs through anharmonic coupling. If the decay from $|2\rangle$ to $|1\rangle$ occurs while the mode is still highly excited, additional broadening of the decay x ray compared to the photoelectron would be expected, while if the excited mode thermalized rapidly, it would not.

The model situation represented by the curves of Fig. 1(a) requires the hole in state $|1\rangle$ to have a much smaller coupling to the lattice than in state $|2\rangle$. This condition would be most commonly encountered in a metal, where the hole in state $|1\rangle$ is completely delocalized. Another common situation is represented in Fig. 1(b), in which the hole-lattice coupling in states $|1\rangle$ and $|2\rangle$ is taken to be the same. This would be expected in an ionic insulator, for example, where a deep hole would typically decay to a higher shell of the same ion. In this case, it is clear that the photoelectron vibrational broadening is the same as for Fig. 1(a), that the lattice is equally excited in the long- and short-lifetime limits, and that the decay x-ray spectrum has no phonon broadening.

When state $|2\rangle$ has $\epsilon_2 < 2$ keV, nonradiative Auger electron emission is considerably more probable than radiative decay.[4] In this case, state $|1\rangle$ is a two-hole state, and three possibilities can be envisioned for the lattice mode wells. If both holes are delocalized in $|1\rangle$, Fig. 1(a) should apply, while if one hole remains on the initially excited atom, we should have Fig. 1(b). In both these cases, the discussion in the preceding paragraphs applies with "Auger electron" substituted for "decay x ray". If both holes remain on the initially excited atom, however, a greater displacement of the well minimum will occur, as shown in Fig. 1(c). If the harmonic approximation is still assumed here, the displacement is just $2\Delta q$. The short-lifetime limit is easily analyzed in this situation according to the previously applied principles. We find that the photoelectron has the usual phonon broadening, the Auger electron has an equal broadening (neglecting anharmonicity), and the sum of the two energies measured in coincidence has a distribution of twice this width, consistent with leaving the lattice in a more-highly excited state. For longer lifetimes, the photoelectron width remains unchanged. The Auger width, however, depends on the previously mentioned rate of equilibration of the relevant lattice mode. If the excitation energy deposited in the initial photoemission process dissipates (thermalizes) and it reaches its displaced ground state before the Auger decay, a width equal to that in the short-lifetime limit is obtained. However, if the Auger decay occurs while the mode is still highly excited, a considerably larger width is expected.

While we have so far restricted our discussion to x-ray photoemission, it is easy to apply parallel arguments to x-ray absorption spectra for the types of situations modeled in Figs. 1(a) and (b). In Fig. 1(a), consider the spectrum of x-rays $\hbar\omega_i$ absorbed in excitation from $|0\rangle$ to $|2\rangle$, $|2\rangle$ now being an overall neutral excited state. It is clear from our previous arguments that a Gaussian phonon broadening of the absorption line must occur. If $|2\rangle$ is long lived, lattice excitations will be created, the decay photon $\hbar\omega_f$ (from decay to either $|1\rangle$ or $|0\rangle$) will be phonon broadened, and in the case of decay to $|0\rangle$, the center of the emission spectrum will be Stokes shifted relative to that of the absorption spectrum of $\hbar\omega_i$. If the lifetime of

$|2\rangle$ is longer than the lattice phonon period but short compared to the thermalization time, additional broadening of $\hbar\omega_f$ will occur as discussed above. In the case when $|2\rangle$ is short lived, no lattice excitation will occur and there will be no Stokes shift. There will be phonon broadening of both the absorption and emission spectra, however, with coincident absorbed and emitted photons having identical energies. In Fig. 1(b), the absorption spectrum of $\hbar\omega_i$ will be broadened as in 1(a) independent of the lifetime of $|2\rangle$. The emission spectrum of $\hbar\omega_f$ will be unbroadened and unshifted from $\hbar\omega_i$ in both lifetime limits.

III. EXPERIMENTAL RESULTS

We now cite some examples of experimental results which illustrate the general principles discussed above. The selected examples involve both polar and nonpolar solids and are merely intended to be representative. The principles apply equally well to gases and surface species whose photoemission spectra exhibit vibrational structure (in the former systems individual vibrational states can sometimes be resolved). Also, while only XPS data is cited for photoemission, the principles apply as well to ultraviolet photoemission line shapes in all the above mentioned systems.

Fig. 1(a), $|2\rangle$ *long lived; Fig. 1(b),* $|2\rangle$ *short lived; Fig. 1(c),* $|2\rangle$ *short lived (x-ray photoemission):* In the following examples we compare different hole-state lifetimes in the same material with the corresponding phonon period. The production and decay of Mg 1*s*, 2*s*, and 2*p* holes in MgO can be represented by the three different configuration diagrams shown in Fig. 1. A Mg 1*s* hole decays primarily via intra-atomic Mg *KLL* Auger transitions[4] and is represented by Fig. 1(c). A Mg 2*s* hole in MgO decays mainly by interatomic Coster-Kronig transitions,[5] i.e., $\mathrm{Mg}(L_1)\mathrm{Mg}(L_{2,3})\mathrm{O}(L)$, so the comparatively delocalized nature of the hole in the oxygen-derived conduction band with respect to the localized Mg 2*p* hole implies that Fig. 1(b) is most appropriate. A Mg 2*p* hole in MgO is filled almost solely by interatomic Auger transitions[5] of the type $\mathrm{Mg}(L_{2,3})\mathrm{O}(L)\mathrm{O}(L)$, and this final state is best described by Fig. 1(a). For our purposes here we assert that the Mg 1*s*, 2*s*, and 2*p* lifetimes in MgO are all comparable to the lifetimes in Mg metal[6,7]; these lifetime widths in Mg have been determined from XPS measurements[8] to be 0.35 ± 0.03, 0.45 ± 0.03, and 0.03 ± 0.02 eV, respectively.[8,9] All three hole-state lifetime widths are considerably smaller than the FWHM phonon broadening at 300 °K, $\Gamma_{\mathrm{ph}} = 1.61 \pm 0.10$ eV.[9-11] Most significantly, the phonon broadening is the same for all three levels within experimental error. In MgO the longitudinal optical phonon energy $\hbar\omega_{\mathrm{LO}} = 0.092$ eV,[12] i.e., *larger* than the 2*p*, and *smaller* than the 1*s* and 2*s* lifetime widths. Thus the Mg(1*s*, 2*s*) and 2*p* levels are identically broadened independent of the fact that their lifetimes are, respectively, short and long compared with the lattice phonon period.

Fig. 1(b), $|2\rangle$ *short lived (x-ray photoemission and x-ray emission):* Both the Cu 1*s* and 2*p* holes in Cu and CuO decay to final states which, for the case of x-ray emission (Cu $K\alpha$ or Cu $L\beta$), are described by Fig. 1(b). Their lifetimes in the metal and the oxide are virtually identical.[6,13] The Cu $K\alpha_1$ ($1s - 2p_{3/2}$) x-ray widths in Cu and CuO at FWHM (including a small instrumental contribution) are 2.39 ± 0.10 and 2.42 ± 0.10 eV,[6] respectively, in good agreement with the widths calculated assuming just lifetime broadening.[6] The respective XPS Cu $2p_{3/2}$ linewidths of 0.74 ± 0.06 and 2.42 ± 0.11 eV,[6,9] however, are very different in these two materials because of their different hole-phonon coupling strengths.[14] These results clearly show the presence of significant phonon broadening in the XPS data and the absence of such broadening in the x-ray emission spectra involving transitions between deep (similar) core levels.

Fig. 1(c), $|2\rangle$ *short lived (x-ray photoemission and Auger emission):* The lifetime width of a Na 1*s* hole in either Na or NaI is determined primarily by Na *KLL* transitions and so Fig. 1(c) is most appropriate. From XPS measurements in Na, the Na 1*s* lifetime width is found to be 0.30 ± 0.03 eV.[8,9] This value is much larger than the LO phonon energy in NaI, $\hbar\omega_{\mathrm{LO}} < 0.026$ eV,[12] so the phonon-broadening contribution to the Auger and XPS linewidths should be the same if the lattice were strictly harmonic. The XPS phonon broadening at 500 °K in NaI is measured to be $\Gamma_{\mathrm{ph}} = 1.16 \pm 0.09$ eV, while that for the Na *KLL* (^1D) Auger electrons is 1.51 ± 0.2 eV.[9-11,15] The difference in phonon widths is interpreted as evidence for anharmonicity and for possible coupling to other lattice modes in the doubly ionized final state.

Fig. 1(a), $|2\rangle$ *short and intermediate lived (x-ray photoemission, x-ray absorption, and x-ray emission):* Production and annihilation of Na 2*p*, and Li 1*s* holes in their respective metals are best described by Fig. 1(a) because these states decay primarily to double vacancy final states that are delocalized within the conduction band. From XPS measurements the lifetime widths at FWHM are 0.02 ± 0.02 eV for Na 2*p*,[8,9] and 0.04 ± 0.03 eV for Li 1*s*.[16] The effective Debye phonon cutoff energies $\hbar\omega_D$ can be approximated by the metal Debye temperatures ($\hbar\omega_D \simeq \Theta_D$) and are 0.013 and 0.035 eV for Na and Li, respectively.[17] Thus within the experimental uncertainties it appears that the lifetimes are comparable to the effective phonon periods and that we are in the intermediate regime. We can test whether there is an enhanced XPS linewidth broadening as predicted by Minnhagen[3] by performing the following test. From the temperature dependence of XPS linewidth[8,16] and x-ray absorption[18-20] edge measurements, it is possible to determine empirical Debye phonon cutoff energies.[8] These in turn can be compared with the phonon cutoff energies approximated by the respective Debye temperatures.[17] The empirical $\hbar\omega_D$ values for Na and Li are, respectively, 0.010 ± 0.003 and 0.027 ± 0.003 eV.[8] The Li results are clearly smaller than the corresponding Debye-temperature values[17] and suggest the possible presence of an enhancement effect.[3] Additional evidence to support this effect is seen by comparing the Stokes-shift energy of 0.18 ± 0.04 eV, observed[21] between emission[22] and absorption[20] K-edge measurements, with the larger value of 0.30 ± 0.04 eV calculated from the expressions by Hedin and Rosengren[25] using our empirically determined value for $\hbar\omega_D$.[8] The Na result, on the other hand, suggests that such an enhanced broadening effect is *not* present. This is further supported by the essentially equivalent phonon broadening measured for the Na $2s$ level[8] whose lifetime width is clearly shorter than $\hbar\omega_D$. Why there appears to be enhancment in Li and none in Na cannot be explained by Minnhagen's calculations. The most likely explanation may simply be that qualitatively the effect is there, but that quantitatively it is overestimated. Further study is required to answer this point.

From the above discussions and experimental results, we see that, contrary to the suggestion by Šunjić and Lucas,[2] even in the limit of very short hole-state lifetimes there is no difficulty in representing the lifetime and phonon broadening contributions of photoemission line shapes by a simple convolution of Gaussian and Lorentzian functions. It should be noted that the one experimental result cited by Šunjić and Lucas, in which they claim that vibrational broadening of physisorbed molecules disappears, is misquoted. The actual experimental observation[26] is that there is indeed appreciable vibrational broadening from photoemission of physisorbed molecules, but because of the large number of closely spaced levels in the physisorbed system, the individual vibrational structure (ordinarily observable in the gas phase) is unresolved.

Šunjić and Lucas raise an additional point which will also be clarified here. On the one hand, they suggest that the alkali-halide films in Ref. 1 might have been sufficiently thin to significantly alter the eigenfrequencies of the long-wavelength optical phonons[12] used to calculate[1] the phonon broadening. On the other hand, they argue that if more recent estimates of escape depths of electrons in alkali halides are used,[27] ~50 Å, there would be broadening due to the inhomogeneous energy distributions of the outgoing electrons, thus explaining the large observed linewidths. We point out here, however, that the latter arguments obviate the validity of the former. The estimated film thicknesses quoted in Ref. 1 were based on average escape depths of ~20 Å for both substrate and halide solids,[28,29] so the more recent halide escape-depth values[27] imply film thicknesses that were actually much larger than originally quoted. The LO-phonon modes are therefore bulklike and the need for invoking an alternative broadening mechanism, which may indeed be present to some unknown degree, does not appear to be necessary.

Finally, we mention that so long as the sudden approximation is valid, the principles discussed above for phonons should be entirely applicable to line-shape modifications due to coupling to other excitations in XPS. The core-hole lifetime should manifest itself strictly as a Lorentzian convolution with the spectral distribution of the excitation process itself. Thus the electron-hole pair effects in XPS core-electron spectra in metals are observed to be completely independent of the core-hole lifetime.[16,30] Similarly, plasmon satellites of short-lived hole states are observed[16,30] to be broader than those generated by longer-lived states simply as predicted by Lorentzian convolution.

Note added in proof: C. O. Almbladh (unpublished) has very recently considered the intermediate lifetime case using a different theoretical formalism. He confirms the long- and short-lifetime results reported here and the enhanced broadening as discussed by Minnhagen, but finds that the range of ratios of lifetime to phonon period in which the enhancement is significant is considerably narrower than that found by Minnhagen. This result helps explain the absence of observable enhanced broadening in Na since the Na $2p$ lifetime width is sufficiently short with respect to $\hbar\omega_D$ so as to reduce the enhancement.

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[9] The error bars represent all cumulative errors of data precision and removal of instrumental contributions, and thus indicates the accuracy of the quoted mean values.

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[13] This statement is certainly valid for the Cu 2*p* and 1*s* holes since their lifetimes are primarily determined by intra-atomic Auger transitions which are insensitive to chemical environment.

[14] The XPS Cu 2*p* linewidths in CuO should be somewhat broadened due to multiplet splitting, but from the Cu 3*s* splittings this effect is negligible compared to the phonon contribution.

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