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Vanishing post-collision interaction during photon-excited Coster-Kronig decay

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In radiationless transitions to atomic inner-shell hole states produced by threshold photoionization, the Auger electron energy is shifted up by post-collision interaction between the two continuum electrons. According to both semiclassical and quantum-mechanical models, this shift is expected to disappear if the photoelectron energy exceeds that of the Auger electron (the "no-passing" effect). This effect, recently observed for a long-lived [$4d$] hole state of Xe, is now also demonstrated for the very fast Xe L_2-L_3N_4 ($J=3$) Coster-Kronig transition, excited with synchrotron radiation.

Post-collision interaction (PCI) during photon-excited radiationless transitions in atomic inner shells represents an interesting aspect of the complex dynamics of electron excitations in many-electron atoms. A hole state is created near threshold, i.e., a slow photoelectron is emitted. The vacancy is filled under emission of a fast Auger electron. In a semiclassical picture, as the photoelectron is passed by the Auger electron, a sudden reduction in screening alters the attractive ionic-core potential experienced by the photoelectron from the Coulombic potential of a charge $+e$ to that of a charge $+2e$. The energy lost by the slow photoelectron in this sudden transition is transferred to the fast Auger electron. The mean energy of the Auger electron distribution is shifted upwards and its shape is distorted.

The semiclassical picture sketched here leads to a reasonably good approximate description of PCI.[1-4] The effect has also been treated in terms of diagrammatic many-body theory,[5,6] resonant-scattering theory,[7-9] and the complex-coordinate approach.[10] A consistent description of the influence of PCI on total and differential inner-shell photoionization cross sections requires relativistic quantum theory.[11]

It has been pointed out by Ogurtsov[12] and by Russek and Mehlhorn[4] that, in terms of the semiclassical model, the time required for the photoelectron to sense the potential change caused by the Auger decay must be taken into account. This aspect of PCI can also be described in terms of relativistic quantum theory based on the resonance-scattering approach:[13] Dynamic screening leads to modification of the quantum-mechanical line-shape formula[11] and the predicted shift. In either model, one is led to expect two consequences: (1) At larger photoelectron energies, the PCI shift and line-shape distortion should be much smaller than previously predicted and (2) the PCI effect in photoexcited Auger transitions should disappear altogether if the energy of the photoelectron exceeds that of the Auger electron; in that case, semiclassically speaking, the Auger electron never passes the photoelectron and no change occurs in the ionic-core potential experienced by the latter.

The no-passing effect was first seen experimentally by Borst and Schmidt[14] in the Xe N_5-$O_{2,3}O_{2,3}$ ($^1S_0$) Auger transition. This involves a very-long-lived initial [$4d$] hole state, of width $\Gamma_i=0.110$ eV, and an Auger energy $\varepsilon_A=29.97$ eV which is large in comparison; the theoretically significant dimensionless parameter ε_A/Γ_i is ~ 272 in this case and the PCI shift near threshold, ~ 0.1 eV.

To test the validity of present theories and seek further experimental verification of the no-passing effect, it is desirable to examine transitions which correspond to other extremes. We have therefore studied the Xe L_2-L_3N_4 ($J=3$) Coster-Kronig transition, which is very fast[15] ($\Gamma_i = 3.06$ eV) and has a relatively low energy[16,17] ($\varepsilon_A \cong 228$ eV; $\varepsilon_A/\Gamma_i \cong 75$) and large PCI shift[16] (~ 3.2 eV near threshold).

The experiment was performed with synchrotron radiation from a 54-pole wiggler operated at 5 kG in the storage ring SPEAR in the Stanford Synchrotron Radiation Laboratory. The electron energy was 3.02 GeV and the current varied from 30 to 60 mA. X rays were focused at grazing incidence by a toroidal mirror and energy selected with a Si(111) $(1,-1)$ double-crystal monochromator. The resultant bandwidth was ~ 0.6 eV at $h\nu \cong 5$ keV. The monochromator crystals were rotated about a common axis by a stepping motor under computer control, with 2000 steps per degree. The x-ray energy scale was calibrated by using the Xe L_2 edge at 5107.0 ± 0.5 eV as a benchmark;[18] details of the calibration procedure are described in a paper by Breinig *et al.*[18]

The focused, monochromatized x-ray beam intersected a jet of Xe gas in the target volume of a double-pass cylindrical-mirror electron-energy analyzer.[16,19] The pressure in the analyzer chamber was maintained at 2.2×10^{-4} Torr. The analyzer pass energy was determined by a set of carefully conditioned mercury batteries.[19] Electrons from the source volume were retarded by hemispherical grids. The retarding potential was programmed by computer through a digital-to-analog converter and voltage amplifier.

The Xe L_2-L_3N_4 Coster-Kronig peak was recorded (Fig. 1) as excited by incident x rays of eight different energies, ranging from 5153 to 6007 eV, i.e., from 46 to 900 eV in excess of the Xe L_2 binding energy. This range of E_{exc} thus bracketed the Coster-Kronig electron energy at which the no-passing effect is expected to set in. At each x-ray energy, several Coster-Kronig spectra were measured and later combined. Typical peak counting rates were ~ 10–20 Hz, with signal-to-background ratios from 0.4 to 0.5 (Fig. 1).

The energy of the L_2-L_3N_4 diagram-peak centroid was determined, as a function of photon excess energy E_{exc}, by means of a least-χ^2 procedure[20] applied with an appropriate fitting function. The spectrum measured at $h\nu = 5204$ eV, which contained the best statistics, was used to establish a fitting function that allowed for three independent peaks: The diagram line, a shake-up–shake-off peak that produces a low-energy shoulder on the diagram peak (see Fig. 1), and a high-energy satellite of undetermined origin. Each peak was represented by a Pearson-VII function[19] of variable width, center, and height, of a shape that could be varied continuously from Lorentzian to Gaussian. A standard fitting function was then derived by removing parameters through the introduction of physically realistic constraints. The three peaks thus were fixed in widths and relative separations in the standard fitting function that was used to determine the diagram-line centroids at the various photon excess energies. The result is displayed in Fig. 2. Other reasonable fitting functions derived in a similar manner yielded statistically equivalent results; in particular, the high-energy satellite does not affect the outcome of the analysis.

The quantity of interest is the PCI shift $\Delta(E_{\text{exc}})$, which is the (positive) energy shift of the centroid of the L_2-L_3N_4 ($J=3$) Coster-Kronig diagram line when the transition is excited by photoionization with x rays of energy E_{exc} in excess of the Xe L_2 binding energy. The shift is with reference to the asymptotic energy ε_A of the Auger (or Coster-Kronig) electrons observed in the high-energy limit $E_{\text{exc}} \to \infty$. The energy ε_A is obtained when there is complete relaxation of the atom between excitation and deexcitation (the "two-step" model applies); this characteristic energy depends only on the atomic energy levels[21]

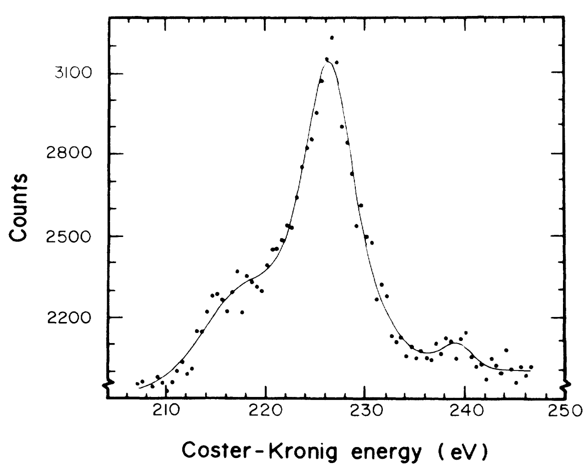

FIG. 1. Measured spectrum of L_2-L_3N_4 Coster-Kronig electrons emitted following $2p_{1/2}$-shell ionization of Xe atoms with 5204-eV photons.

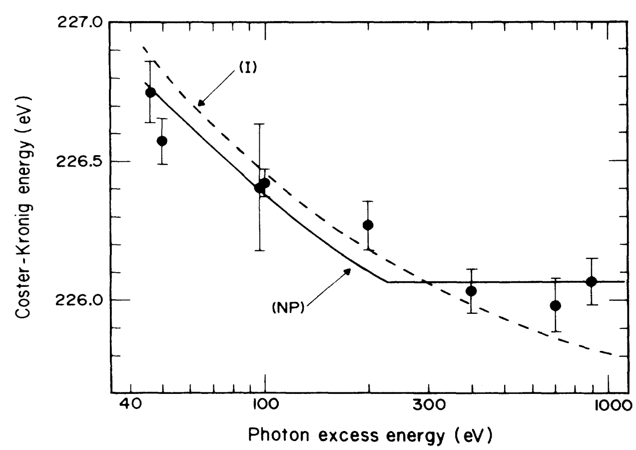

FIG. 2. Measured Xe L_2-L_3N_4 ($J=3$) Coster-Kronig electron energies (dots with error bars) as a function of incident-photon excess energy over the L_2 ionization potential. The broken curve (I) represents the prediction of the simple shake-down theory according to Ref. 11; the solid curve (NP), calculated according to the semiclassical formula of Ref. 4, includes the no-passing effect that causes the PCI shift to vanish at $E_{\text{exc}} = \varepsilon_A$.

and is independent of the mode of primary excitation. In the present experiment, the electron-energy scale floated by an undetermined offset and ε_A was determined by a simple least-squares fit of the data to the appropriate PCI model.

The final-state width in the L_2-L_3N_4 transition is[15] $\Gamma_f = \Gamma\ (L_3N_4) \cong \Gamma(L_3) = 2.82$ eV, i.e., almost as large as the initial-state width. The asymmetry in the Coster-Kronig line shape consequently is very small, and the electron-spectrometer transmission function renders the distortion undetectable. We therefore limited ourselves to studying the peak centroid energy as a function of photon energy excess. For the comparison of theory with experiment, calculated line shapes were convoluted with the final-state Lorentzian and with the electron-spectrometer window function, taken to be a Gaussian with $\sigma = 1.15$ eV.

The experimental results are compared with two theoretical models, the first of which (denoted by I) does not include the no-passing effect and the second of which (labeled NP) does. For the first (shake-down) model, which does not take into account the interaction between photoelectron and Auger electron in the final state, we have used our analytic quantum-mechanical formula[11] with a change of unit charge in the potential experienced by the outgoing photoelectron. In the range of E_{exc} considered here, this formula leads to essentially the same line shape and shift predicted by the Niehaus model[3] if the stationary-phase approximation is not invoked, or by the model of Helenelund *et al.*[2]

For the second model (NP), which takes account of the time required for the Auger electron to overtake the photoelectron, we invoke the semiclassical formula of Russek and Mehlhorn.[4] The model involves the distances from the nucleus at which the photoelectrons and Coster-Kronig electrons originate; for these we have used average distances $\langle r \rangle$ from Hartree-Fock ground-state wave functions.[22] The unshifted Coster-Kronig electron energy was taken to be $\varepsilon_A = 228$ eV in the calculation of the relative shift; this approximation does not significantly affect the fitting procedure.

The fit of the predictions from the two theories to the experimental data is included in Fig. 2. For the NP model, which includes the no-passing effect, the reduced χ^2 is 1.32 and the fitted asymptotic Coster-Kronig energy is $\varepsilon_A = 226.07 \pm 0.03$ eV. For the shake-down model I, in which the no-passing effect is not included, we have $\chi^2 = 3.55$ and $\varepsilon_A = 225.50 \pm 0.03$ eV. The residuals for the two fits are illustrated in Fig. 3. For model I, a definite systematic deviation from experiment is noted, and only 75% of the data points fall within $\pm 2\sigma$ of the theoretical curve. The residual plot for the NP model, on the other hand, shows random deviations about zero, and all data points fall within $\pm 2\sigma$ of the theoretical prediction.

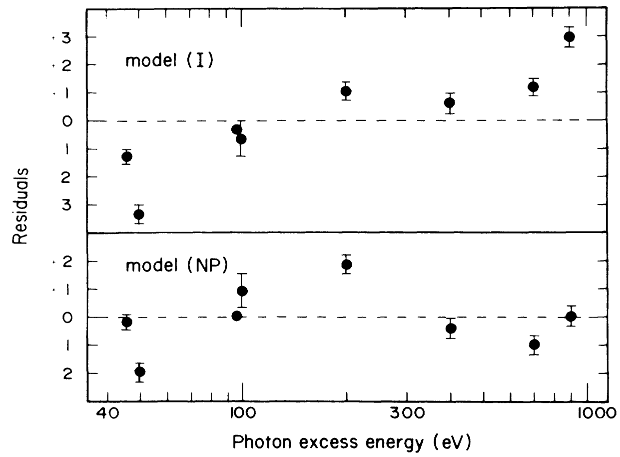

FIG. 3. Plot of residuals of the fits of curves (I) and (NP) in Fig. 2 to the experimental data. For each point, the difference between the measured value and the final fitted curve is normalized by the standard deviation associated with that point. The error bars associated with each residual now reflect the uncertainty in the fitted value of ε_A, which for either model is $\sigma(\varepsilon_A) = 0.028$ eV.

We conclude that the no-passing effect clearly manifests itself in this case of an exceedingly fast, low-energy Coster-Kronig transition. If the time required for the Coster-Kronig electron to catch up and pass the photoelectron is not taken into account (model I), the final observed energy of the secondary electron is overestimated; in the present case, the shift is overestimated by 0.5 eV for $E_{\text{exc}} \cong \varepsilon_A$. The Russek-Mehlhorn semiclassical model[4] fits the present data well. It will be shown elsewhere[13] that the fully quantum-mechanical theory also adequately accounts for the no-passing effect once dynamic screening is included.

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