PHYSICAL REVIEW A VOLUME 38, NUMBER 7 OCTOBER 1, 1988

Photoelectron recapture through post-collision interaction

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(Received 30 June 1988)

In inner-shell photoionization of an atom followed by Auger decay, the Auger electron initially screens the ionic Coulomb field experienced by the photoelectron. A sudden change in screening occurs when the Auger electron overtakes the photoelectron, causing energy transfer from the latter to the former. According to both semiclassical and quantum theories of post-collision interaction, the photoelectron can thus be recaptured by the atom from which it was emitted. This phenomenon has been measured directly with synchrotron radiation, as a function of incident-photon energy, and is found to be in accord with predictions.

In the radiationless decay of an atom that has been photoionized with a photon energy closely above an inner-shell threshold, the Coulomb field of the receding photoelectron perturbs the Auger-electron energy and line shape.[1] This *post-collision interaction* is an intriguing phenomenon that arises from the complex dynamics of many-electron excitations. Both semiclassical[2,3] and relativistic quantum theories[4] of post-collision interaction (PCI) predict the possibility of recapture of the photoelectron under certain circumstances, discussed below.

Experimental evidence for recapture of electrons freed through inelastic scattering was already obtained in 1976 by Van der Wiel, Wight, and Tol.[5] In electron-energy-loss spectra, these workers found that just above the Ar L_2 threshold the sum of Ar^{2+} and Ar^{3+} ion yields failed to account for the total electron energy loss, and ascribed the difference to Ar^+ production by the "shake-down" mechanism.[6] Amusia *et al.*[7] calculated intershell correlations within the random-phase approximation framework and predicted a sharp increase in Ar^+ yield from inelastic electron scattering just above the 2*p* ionization limit of Ar, in qualitative agreement with the results of Van der Wiel *et al.*[5] In his original formulation of the semiclassical theory of PCI, Niehaus[8] calculated the probability of electron recapture during Auger decay after near-threshold inner-shell ionization; in a review of PCI, Schmidt[9] discussed shake-down above the Ar 2*p* threshold and compared the data of Van der Wiel *et al.*[5] with the predictions of Niehaus.[8] This comparison is, however, somewhat unconvincing because a 2*p* excitation cross section is used which increases by a factor of 2 within 2 eV above threshold, thereby already mimicking the observed response.

In their classical paper, Van der Wiel *et al.*[5] already noted that "direct detection of Ar^+ formation in this energy region requires soft x rays," but that the state of synchrotron radiation facilities at that time precluded such an experiment. The first photoionization experiment on this subject with synchrotron radiation was, in fact, not performed until 1984 on the SOR-RING of the University of Tokyo, where Hayaishi *et al.*[10] measured Ar ion yields from photoionization with highly monochromatized incident photons in the vicinity of the 2*p* threshold. These investigators observed Ar^+ being produced "as far as approximately 2 eV above the L_2 threshold" and indicated that "the only possible formation of Ar^+ is . . . due to capture," but did not analyze their results quantitatively in terms of PCI. Presumably, the rather low statistics in these data precluded such an analysis.

Because of the continuing interest in PCI and the critical role that the recapture phenomenon plays for the test of relevant theory, it seemed desirable to make a detailed quantitative comparison of ion yield from near-threshold photoionization with calculated predictions. Here we describe such an experiment.

We measured the partial Ar^+ and Ar^{2+} ion yields from Ar 2*p* photoionization in the threshold region, in analogy with previous studies of the onset of core-electron excitations in atoms, molecules, and solids.[11,12] The experiment was carried out on the HE-TGM II beam line at BESSY.[13] Monochromatized synchrotron radiation passed through the ionization region of a quadrupole mass filter (modified Leybold model Q200). Differential pumping made it possible to raise the pressure in the target region to 10^{-4} Torr of high-purity (99.99%) Ar.

The yield of singly and doubly ionized Ar atoms was recorded as a function of the energy of the incident photons. Results are shown in Fig. 1, which includes a total photon absorption curve[14] for comparison. This latter curve shows structure due to various 2*p*-electron excitations. The L_2 and L_3 ionization thresholds, separated by spin-orbit splitting of 2.03 eV,[15] are indicated by vertical lines in Fig. 1. Pronounced peaks below each ionization threshold are caused by excitation of core electrons to

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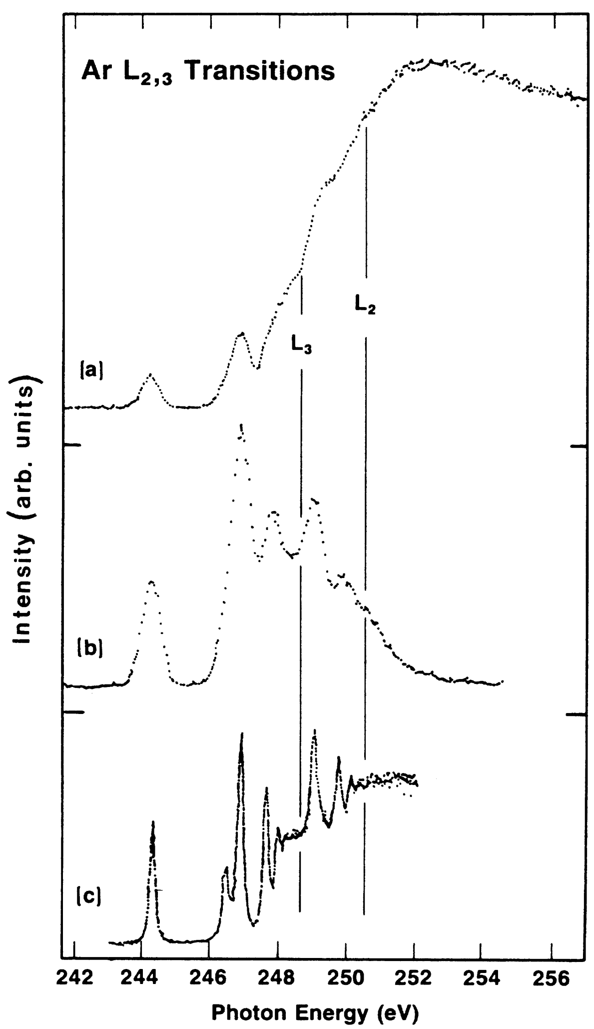

FIG. 1. Ion yield and total photoabsorption spectrum of Ar, as a function of incident-photon energy, showing the onset of the 2*p*-electron excitations. (a) Yield of Ar^{2+} ions; (b) yield of Ar^+ ions; (c) absorption spectrum (from Ref. 14). Vertical lines indicate L_3 and L_2 ionization thresholds.

Rydberg states; two series have previously been identified, converging to the respective ionization limits.[15] Both of these Rydberg series are seen here as well in the partial ion-yield curves.

Of central importance for the present study is the fact that the yield of singly charged Ar^+ ions exhibits a pronounced gradual decrease in the range of ~2–3 eV above the 2*p* ionization threshold, whereas the Ar^{2+} ion yield exhibits a complementary increase in this photon energy range. These steady variations in the partial ion yields cannot be understood in terms of a single-particle model, but can be seen to arise from post-collision interaction in the Auger decay of the 2*p* core hole, as described below.

The mechanisms through which the primary ions can be produced in this experiment are as follows. (i) Singly charged Ar^+ ions can arise from (a) direct photoionization of an outer 3*p* or 3*s* valence electron, (b) radiationless deexcitation of a core-electron Rydberg state[16] (autoionization), or (c) photoionization of a 2*p* electron followed by fluorescent decay of the 2*p* hole. (ii) Doubly charged Ar^{2+} ions, on the other hand, can be produced by (a) outer valence-electron ionization accompanied by shake-off, (b) shake-off accompanying decay of a Rydberg state, or (c) Auger decay of the core hole left from 2*p*-electron photoionization. Auger cascades from that level are energetically forbidden.

In the photon-energy region immediately above the L_2 ionization threshold, the total absorption cross section is essentially constant [Fig. 1(c)]. Any change in the partial ion yields in this energy range therefore reflects a change in the branching ratios of the various channels that lead to the formation of these ions. The cross sections for outer valence excitations are known to exhibit Fano profiles due to interchannel coupling and interference effects that occur largely in the region of the Rydberg excitations below the core ionization threshold. It is highly unlikely that these effects account for the change in ion branching ratio above the L_2 and L_3 thresholds, because the total valence-electron photoionization cross section is quite small and the core-electron excitations occur at much higher energies than the valence excitations.

We are left with secondary processes in the decay of a 2*p* hole as the cause for the change in ion branching ratio. The ratio between fluorescent and Auger decay of the core hole is not expected to vary with incident-photon energy in this range, and the fluorescent channel is so weak ($\sim 2\times 10^{-4}$ of the total hole-state width[17]) that it cannot possibly account for the observed changes in ion yield. The Auger channel must therefore be responsible for the change in $[Ar^+]/[Ar^{2+}]$ ion branching ratio with excitation energy. We proceed to show how post-collision interaction (PCI) can bring about the observed effect.

An intuitive and quite accurate picture of PCI is provided by the semiclassical model of Russek and Mehlhorn.[3] We consider an atomic electron that is originally bound with energy $-E_B$ and is ionized under absorption of a photon of energy ω.[18] The energy with which the photoelectron recedes from the singly charged residual ion is $E=\omega-E_B=\frac{1}{2}v^2-1/r$. The inner-shell vacancy left by the photoelectron is filled under emission of a fast Auger electron that overtakes the photoelectron at R (Fig. 2). At this point, the potential seen by the photoelectron changes suddenly from $-1/r$ to $-2/r$, and the electron consequently loses energy $1/R$ that is transferred to the Auger electron. It follows that the photoelectron will be recaptured and become bound again if $1/R \gtrsim E$, i.e., if the Auger electron catches the photoelectron at a distance $R \lesssim (\omega-E_B)^{-1}$.

Let the photoelectron be emitted at time $t=0$ from its bound-state radius R_S; it reaches R at a time $t=T=\int_{R_S}^{R} dr/v$, where $v=[2(E+1/r)]^{1/2}$.[3] It takes the Auger electron a time interval T' to move from its bound-state position R_A to R; we have $T'=\int_{R_A}^{R} dr/v_A$, with $v_A=[2(E_A+2/r]^{1/2}$, where E_A is the "diagram" energy of the Auger electron, in the absence of any PCI shift. The time at which the Auger electron reaches R is the sum of T' and the lifetime τ of the core hole. In order for the photoelectron to become bound, we must have $T'+\tau < T$, i.e., the hole must decay in a time no longer than $\tau=T-T'$. The mean life of the hole is the reciprocal of

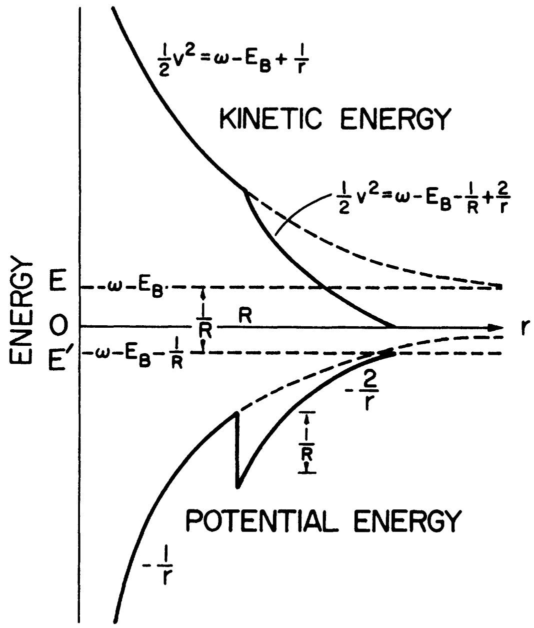

FIG. 2. Schematic energy diagram illustrating post-collision interaction. The total energy of the photoelectron is E before and E' after the Auger decay.

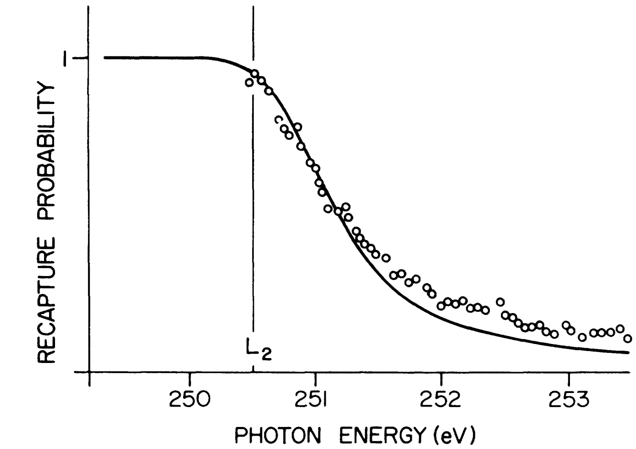

FIG. 3. Measured Ar^+ yield above the L_2 photoionization threshold [from Fig. 1(b)] (dots) and calculated photoelectron recapture probability (solid curve), as functions of incident-photon energy.

the hole-state width Γ, hence the probability that the hole decays in a time τ is

$$P(\tau)=\int_0^{\tau}\exp(-t'\Gamma)dt' . \quad (1)$$

The recapture probability given by Eq. (1) is not significantly affected by the differences between the energies of the six Auger transitions that can fill an Ar L_2 hole; the probability is primarily a function of the incident-photon energy ω and the width Γ of the L_2 hole state.

In Fig. 3 we compare the observed Ar^+ yield above the L_2 ionization threshold [Fig. 1(b)] with the calculated recapture probability for $\Gamma = 0.185$ eV as a function of ω. This $2p$ core hole width was estimated from the measured width of the lowest Rydberg peak ($2p_{3/2} \rightarrow 4s$) in Fig. 1(c), corrected for the monochromator resolution of 0.1 eV.[8] The monochromator resolution in the present experiment was 0.34 eV, as determined from the measured width of the same absorption peak in Fig. 1(b). A quantitative comparison becomes possible by setting the calculated recapture probability equal to unity below threshold, folding the monochromator resolution into the calculated results, and scaling the data so that they coincide with the calculated curve at threshold (Fig. 3). Agreement between the calculation and experimental data is seen to be very good, thus providing further support for current PCI theory.[3,4,19]

In a fully quantum-mechanical treatment of PCI, the ionic charge seen by the photoelectron is reinterpreted on the basis of asymptotic properties of the continuum wave function pertaining to the two outgoing electrons.[4] This procedure has been shown[4] to be consistent with the semiclassical model[3] used in the present analysis, which hinges upon the time required for the Auger electron to overtake the photoelectron.[20] Agreement between the predictions of the two models, which offhand appears surprising, is thus explained.[4]

We gratefully acknowledge illuminating discussions with T. Åberg. One of us (W.E.) would like to thank the staff of BESSY for their hospitality. At the University of Oregon, this work was supported in part through U.S. Air Force Office of Scientific Research Grant No. AFOSR-87-0026 and National Science Foundation Grant No. PHY-85-16788.

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[19]The predicted recapture probability is sensitive to the $2p$ core-hole width Γ. If instead of $\Gamma = 0.185$ eV we choose $\Gamma = 0.116$ eV [G. C. King and F. H. Read, in *Atomic Inner-Shell Physics,* edited by B. Crasemann (Plenum, New York, 1985), p. 317], the calculated recapture probability is reduced in comparison with that shown in Fig. 3, by approximately a factor of $\frac{1}{2}$ at 252–253 eV photon energy.

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