Intrashell Electron-Interaction-Mediated Photoformation of Hollow Atoms near Threshold

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Double photoionization (DPI) of an atom by a single photon is a direct consequence of electron-electron interactions within the atom. We have measured the evolution of the K-shell DPI from threshold up in transition metals by high-resolution x-ray emission spectroscopy of the $K^h\alpha$ hypersatellites, photoexcited by monochromatized synchrotron radiation. The measured evolution of the single-to-double photoionization cross-section ratio with excitation energy was found to be universal. Theoretical fits suggest that near threshold DPI is predominantly a *semiclassical* knockout effect, rather than the purely quantum-mechanical shake-off observed at the infinite photon energy limit.

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The electronic structure of an atom can be largely accounted for assuming each electron to interact with the nucleus independently of all others. A full description, however, requires the inclusion of the interactions among the electrons, a prominent manifestation of which is the atom's DPI by a single photon. The single-particle nature of the photon-electron interaction allows only one electron to be ionized directly by the incoming photon. A second electron can only be ejected because of electron-electron interactions [1]. Decades of intensive research have not, however, succeeded in fully elucidating the mechanism(s) underlying this intuitive understanding. For an infinite-energy photon the sudden approximation accounts well for DPI as a pure shake-off (SO) effect [2]. At lower photon energies DPI becomes a more complex process. Its theoretical description and separation into noninterfering mechanisms [3,4] are still open questions. Two approaches were employed to treat DPI near its energy threshold, E_{th}. A time-dependent perturbation theory [5] successfully describes outer electrons and low-Z atoms, but fails for inner shells and higher-Z atoms [3,6,7]. A many-body diagram expansion [8,9] suggests a knockout (KO) mechanism to dominate near threshold. The only KO calculations to date, for He, agree well with experiment [4,9–11].

K shell DPI forms a K-hollow atom [12], with an empty innermost shell and populated outer shells. Hollow atoms provide insight into atoms very far from equilibrium and into ultrafast dynamics in atoms [13]. They may also yield population inversion and lasing in the hard x-ray regime [14]. The $1s^{-2} \rightarrow 1s^{-1}2p^{-1}$ transition of a $2p$ electron in the presence of the second K vacancy results in the emission of a $K^h\alpha$ hypersatellite (HS) photon, just as the $1s^{-1} \rightarrow 2p^{-1}$ transition of a $2p$ electron causes a conventional $K\alpha$ diagram photon emission. Far above E_{th} the intensity ratio of these two spectra, $R_{K\alpha} = I(K^h\alpha)/I(K\alpha)$, is proportional to the double-to-single K-shell photoionization cross-section ratio, P_{KK}. It provides the most sensitive test for theories of *intrashell* electron-electron interactions. These interactions are particularly important near threshold, where the kinetic energy of the directly ionized electron is low, and it overlaps longer with the atomic electron cloud. Although the near-unique importance of HSs for studying electron-electron interactions, and other atomic effects, has long been recognized [15,16], the HS's low intensity and its fast, $\sim Z^{-4}$, decrease with atomic number Z, rendered $R_{K\alpha}$ measurements very scarce. In particular, the excitation energy E_{ex} dependence of $R_{K\alpha}$ near threshold, where the HS intensities are even lower, has been measured only for low-Z atoms, mostly He [10,17].

We measured the $R_{K\alpha}(E_{\mathrm{ex}})$ evolution from threshold up for the $3d$ transition metals, $23 \leq Z \leq 30$. For all but two (V [7] and Cu [6]), no previous excitation-energy-dependent, near-threshold, measurements are available.

Unlike low-Z atoms, where the Russell-Saunders (LS) angular momentum coupling scheme is valid and the K-shell electrons are only weakly relativistic, for $Z \geq 23$ the coupling becomes intermediate between the LS and the jj schemes, and the K electrons are significantly relativistic. Coupling and relativity sensitively influence the electrons' wave functions and, through the wave functions' overlaps, also the DPI cross sections. For example, the $K^h\alpha_1$ line originates in a transition requiring a spin flip, which is dipole forbidden in the pure LS coupling scheme, and becomes fully allowed only in the jj scheme [6,18]. Thus, its intensity and relative contribution to $R_{K\alpha}$ increase rapidly over the Z range addressed here as the coupling becomes more intermediate. $R_{K\alpha}(E_{\mathrm{ex}})$ measurements should provide, therefore, stringent experimental tests for current theoretical understanding of both effects and their Z variation.

Photoionization by energy-tunable monochromatized synchrotron radiation was used to create the two-vacancy $1s^{-2}$ initial state. Measurements have been carried out at beam lines X25, NSLS, USA, and ID16, ESRF, France. Fully resolved HS spectra were measured by a high-resolution spectrometer using spherically-bent Si and Ge analyzers, operated near back reflection in the Rowland circle geometry. For further experimental and data analysis details see Ref. [6].

The V $K^h\alpha_{1,2}$ HS spectrum, shown in Fig. 1(b), exhibits well-resolved $K^h\alpha_1$ and $K^h\alpha_2$ lines. The very low intensity of the $K^h\alpha_1$ line reflects its being spin-flip forbidden in the LS coupling. Its nonzero intensity is due to the coupling being already slightly intermediate for V. The symmetric shape of $K^h\alpha_2$ implies a pure $1s^{-2} \rightarrow 1s^{-1}2p^{-1}$ HS transition, with no detectable contributions of higher-order spectator transitions. This conclusion is supported by fits employing *ab initio* relativistic Dirac-Fock atomic structure calculations.

The measured vanadium $R_{K\alpha}$ [Fig. 1(a)] demonstrates well the low intensity of HSs. The most outstanding feature, however, is the long energy range, over 8 keV, required to reach saturation. This is particularly striking in comparison with the short saturation range, a few eV only, of the single K electron ionization, the K edge. These differences must reflect different ionization processes. The initial state of the diagram transition, $1s^{-1}$, is created by a direct ionization of a single electron. Its energy range of saturation, ~1 eV, reflects the $1s^{-1}$ vacancy's lifetime. For the two-hole state, $1s^{-2}$, the secondary electron obviously introduces another, much larger, energy scale, the most likely candidate for which is its own binding energy.

To test this hypothesis each of the measured $R_{K\alpha}$ curves [Fig. 2(b)] was scaled as follows. The excess excitation energy above threshold, $\varepsilon = E_{ex} - E_{th}$, was normalized by the secondary electron's binding energy, estimated as $E_B^{sec} = E_{th} - E_K$, where E_K is the neutral atom's $1s$ binding energy (K-edge energy). The curves' intensities were scaled to obtain best agreement. Thus scaled, the curves collapse onto a single curve [Fig. 2(a)], strongly supporting the hypothesis above that the $R_{K\alpha}$ saturation range is determined by the secondary electron's binding energy. This, in turn, implies that DPI is dominated by the electron-electron interaction, rather than by the electron-photon interaction governing the primary-electron photoionization, for which the saturation range is determined by the (much smaller) lifetime width of the directly ionized primary vacancy.

While these results identify the effect dominating the DPI cross-section, they do not point to the specific mechanism for the ejection of the secondary electron, and its Z and E_{ex} dependences. These are still open questions, particularly near threshold and at intermediate- and high-Z atoms, largely because of the scarcity of experimental data. DPI has been successfully accounted for in the infinite photon energy limit ($E_{ex} \gg E_{th}$) as a shake-off (SO) effect [2,3], where the ejection of the directly-ionized electron changes abruptly the atomic field acting on the secondary electron. The secondary electron is, therefore, in an excited state, and has a finite probability of becoming unbound,

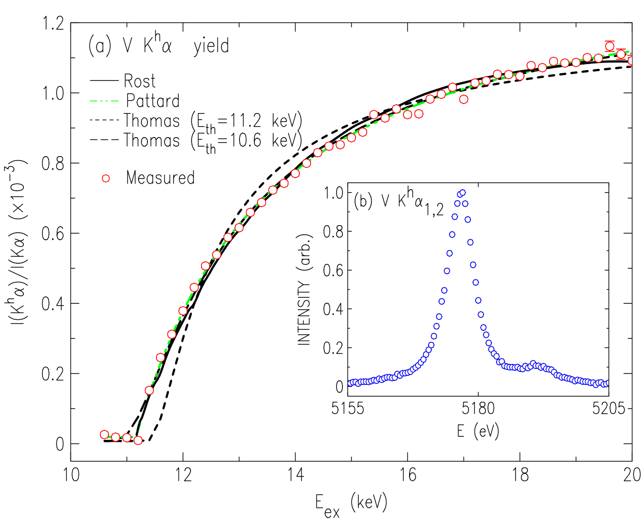

FIG. 1 (color online). (a) HS-to-diagram intensity ratio of V. Thomas's SO model disagrees with the measurements when using the measured threshold, $E_{th} = 11.2$ keV. Rost's KO calculations and Pattard's shape function agree well with the measurements. (b) The $K^h\alpha_{1,2}$ HS spectrum of V, measured at $E_{ex} = 13$ keV. The $K^h\alpha_1$ line's low intensity is discussed in the text. Error bars are smaller than the symbols.

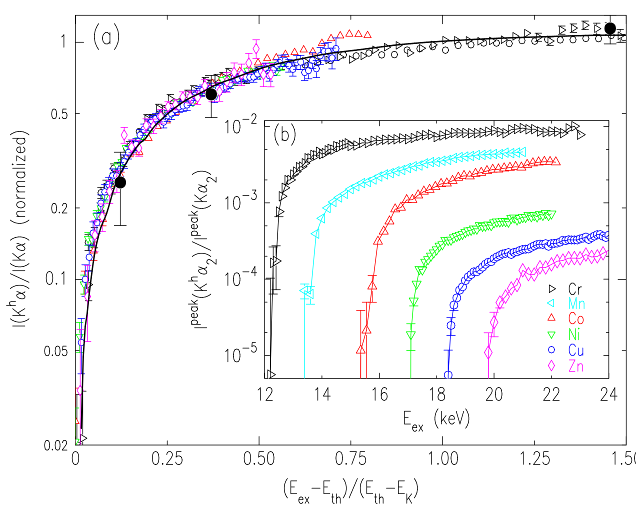

FIG. 2 (color online). (a) Measured HS-to-diagram intensity ratio of the $3d$ transition metals ($Z = 23$–30) (open symbols) and Kanter's Ag ($Z = 47$) results (closed circles), scaled as discussed in the text. Within the error bars of the individual curves, observable also in (b), all curves coincide, and agree well with Rost's KO calculations (black line). (b) The raw measured *peak* intensity ratio curves. Note the logarithmic scale.

i.e., being shaken off the atom. SO theory has been extended to the near-threshold region, where the sudden approximation is invalid, by treating the primary electron's ejection as a time-dependent perturbation on the atomic potential [5]. This yields $R^{SO}_{K\alpha}(E_{ex}) = R_\infty \exp[-m_e(rE_B^{sec})^2/(2\hbar^2\varepsilon)]$, where R_∞, m_e, and r are the saturation R, the electron mass, and the K shell radius. $R^{SO}_{K\alpha}$ fits the measured data well only when $E_{th} = 10.5$ keV, unphysically lower than the measured $E_{th} = (11.22 \pm 0.01)$ keV (Fig. 1, dashed lines). Similar behavior was found for the measured $R_{K\alpha}$ of all other elements studied here. We conclude therefore that the SO contribution near threshold is small, and another mechanism dominates DPI in this region. This conclusion is supported by theory [4] and by the very few extent near-threshold experimental studies, which show that SO accounts well for DPI of outer-shell electrons [19] and of low-Z atoms [20], but fails for K- and L-shell electrons [6,7,21].

We tentatively suggest the knockout (KO) mechanism [4,9,10] to dominate DPI near threshold. Here the primary photoelectron knocks out the secondary electron, billiards-like, on its way out. Thus, KO reflects *post*-photoabsorption (final-state) correlations. By contrast, in the frozen-atom or sudden-approximation SO effect the electrons are ejected abruptly, with the atom frozen in its preabsorption state. SO reflects, therefore, *pre*-photoabsorption (initial state) electron correlations within the atom. Indeed, in a Feynman diagram representation the electron-electron interaction precedes the photoionization in a SO process, while the order is reversed in a KO process [4,22]. Rost *et al.* [4,9] employed the different nature of the SO and KO processes to separate the contribution of the quasiclassical KO to the DPI cross section from that of the purely quantum-mechanical SO. The KO contribution was calculated for He only [4]. However, in our higher-Z range the K shell is already well separated from the outer shells, rendering its DPI similar to that of the two-electron He. We scaled, therefore, the calculated He KO curve as discussed above to allow a comparison with the measured $R_{K\alpha}(E_{ex})$. As Fig. 1 (solid line) demonstrates, good agreement was obtained between the scaled and measured curves over the full E_{ex} range measured, supporting the suggestion that KO, rather than SO, dominates DPI near threshold. This suggestion holds also for all other elements studied here, as demonstrated in Fig. 2(a) by the good agreement of the scaled KO (solid line) and measured $R_{K\alpha}$ (symbols) curves. It is likely to hold also for higher-Z atoms, as implied by the good agreement of the Ag ($Z = 47$) measurements of Kanter *et al.* [3] with the universal curve in Fig. 2(a). While likely, definite conclusions regarding the domination of KO near threshold, as suggested here, will have to await further theoretical work (e.g., Rost-type calculations for our Z range).

Pattard [23] proposed an analytic shape function for $R_{K\alpha}$ which satisfies the Wannier law near threshold [24] and the Bethe-Born theory [23] at high energies: $R^{shape}_{K\alpha} \propto \varepsilon^\alpha(\varepsilon + E_0)^\beta/(\varepsilon + E_1)^{\alpha+\beta}$. $\alpha = 1.056$ is the Wannier threshold exponent, β depends on the ionizing projectile ($\beta = 1$ for charged particles and $\beta = 7/2$ for photons), and E_1, E_0 are fit parameters. As Fig. 1(a) demonstrates, $R^{shape}_{K\alpha}$ fits the measured $R_{K\alpha}$ very well. Moreover, while for He and Li^+ $E_0 \approx 2E_1$ [23], we find $E_0 = E_1$ for all elements studied here. This yields a simpler $R^{shape}_{K\alpha} \propto (1 + E_1/\varepsilon)^{-\alpha}$, independent of the nature of the exciting projectile (β), and requiring only a single energy scale, E_1. The different behavior may reflect the strong Z dependence of the effects of relativity, or a valence vs core difference.

The y-axis scale factors of Fig. 2(a) and the known shape of the KO curve allow deriving the saturation values $R^{sat}_{K\alpha}$ of $R_{K\alpha}(E_{ex})$. These yield the double-to-single K-shell photoionization cross-section ratio, $P_{KK} = (\omega_K/\omega_{KK})R^{sat}_{K\alpha}$, where ω_K and ω_{KK} are the (nearly equal [16]) fluorescence yields of the singly and the doubly ionized K shell. An extensive review of previous P_{KK} results is outside the scope of this paper. Representative previous experimental and theoretical results are shown however in Fig. 3. Our P_{KK} values agree reasonably well with the (fewer-element) measurements of Ahopelto [25], the most complete previous single-measurement set available for our Z range. Since our P_{KK} values were obtained using the KO curve, this agreement further supports our tentative suggestion of the KO domination near threshold. Figure 3 also shows that experiment is tenfold underestimated by the theoretical nonrelativistic pure SO prediction [26] (dash-dot line). Semiempirical scaling theories [27,28] (dash line), based on the SO-predicted Z^{-2} dependence of R^{sat}, improve somewhat the agreement, but still leave a sixfold gap.

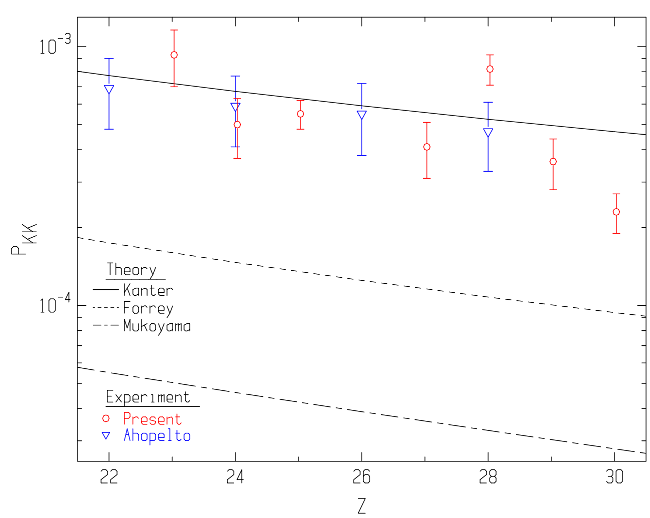

FIG. 3 (color online). Double-to-single K-shell photoionization cross-section ratio, P_{KK}, from our (circles), and previous (triangle) measurements. The theoretical SO (dash-dot line) and semiempirical power-law (solid and dash lines) curves are discussed in the text.

The empirically-fitted $Z^{-1.61}$ curve of Kanter *et al.* [3,29] (solid line) agrees well with experiment. This curve reflects not only a large KO contribution even at saturation, high above threshold, but also shows that as Z increases, the KO-to-SO contribution ratio *at saturation* increases as $\sim\sqrt{Z}$ [3].

In conclusion, we have shown here that the near-threshold evolution of DPI is universal not just for light atoms, but also for the relativistic K shells of heavier $23 \leq Z \leq 30$ atoms. The scaling leading to this universality implies that near threshold DPI is dominated by electron-electron interactions. A classical (rather than quantum-mechanical) knockout process, reflecting *post*-photoabsorption electron-electron correlations, is tentatively suggested to dominate the near-threshold DPI process. The P_{KK} values derived from our measurements support these conclusions. The agreement of our results with the Rost model, based on noninterfering KO and SO channels, supports, *in general*, Feinberg's approach [30], which also assumes no such interference, but not the MBPT result [8] which finds such interference to be important. However, this point will have to be examined more carefully, considering the different nature and excitation modes of the calculations of Rost (quasiclassical, photoexcitation) and Feinberg (quantum mechanical, β-decay).

Since the energies of all inner-shell electrons in our Z range depend sensitively on relativity, the collapse of the different-Z $R_{K\alpha}(E_{\mathrm{ex}})$ curves onto a single curve upon scaling the excess energy by the secondary electron's binding energy, E_B^{sec}, implies that relativity influences $R_{K\alpha}(E_{\mathrm{ex}})$ mostly through the E_B^{sec} dependence. However, the lack of detailed *ab initio* theoretical calculations for atoms other than He does not allow one to separate out the specific relativistic, coupling, and other contributions, and their variation with Z. Theoretical KO calculations for atoms heavier than He, and $R_{K\alpha}(E_{\mathrm{ex}})$ measurements for higher-Z atoms, both very challenging, are clearly called for to elucidate the physics underlying the DPI mechanisms, and to resolve the individual contribution of each effect.

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