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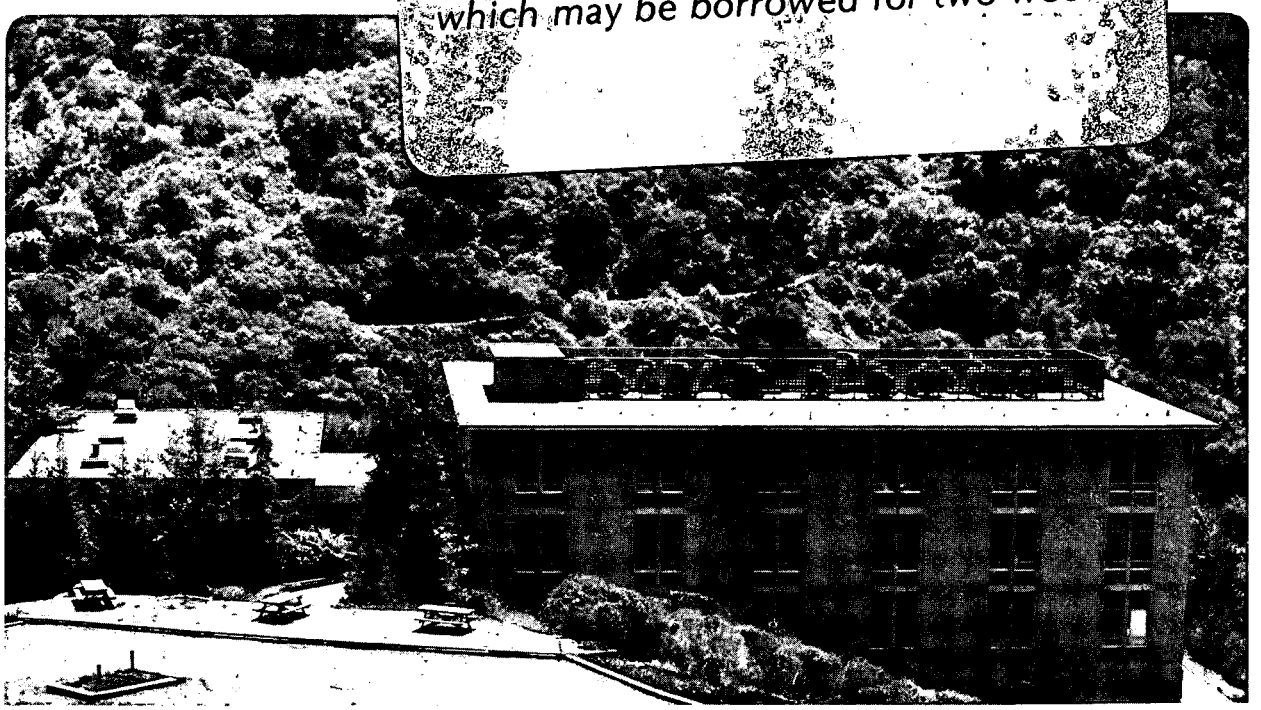

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Orbital-Collapse Effects in Photoemission from Atomic Eu

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Resonant photoelectron spectra of atomic Eu have been measured in the photon-energy ranges of the "4d → 4f" (110-170 eV) and 3d → 4f (1120-1165 eV) excitations. The "4d → 4f" resonance data provide the first determination in a free atom of the decay channels of a "giant resonance" which peaks above its associated threshold. For both inner-shell excitations, decay to Eu^+ main-line configurations is observed, this being the dominant deexcitation process for the "4d → 4f" resonance. The 3d → 4f excitations, however, are characterized by competition between the main-line decay channels and channels corresponding to highly-excited ionic states (satellites). The measured relative partial cross sections indicate that decay after 4d excitation leads predominantly to the 4f manifold, whereas several channels participate in the decay following 3d excitation. The results are interpreted with regard to orbital-collapse phenomena.

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Inner-shell photoabsorption spectra of atomic transition-metal vapors exhibit "giant resonances" associated with excitations into partially occupied nd or nf subshells.[1] For the rare earths, these resonances ("4d → 4f") have attracted increasing attention in both atomic[2-6] and solid-state physics.[7-17] Different theoretical approaches[18,19] have attributed "4d → 4f" resonances (and giant resonances in general) to an orbital-collapse effect. In some aspects, the resonance effect is similar to shape-resonance phenomena which arise from a centrifugal barrier in the effective potential for the excited electron.[20] Calculations[19,21] have shown that the inner well of this potential becomes deeper as Z (or the effective charge Z_{eff}) increases. As a result, the resonances gradually move closer to and finally below the 4d threshold, as exhibited in the isonuclear sequence Ba, Ba^{+}, Ba^{++}.[5] Similarly, with increasing atomic number the well deepens rapidly, leading to a sudden decrease in both the energy and size of the 4f orbital as it contracts into the inner well over a certain range of Z: hence the term "collapse". This trend also can occur for the same Z if deeper-lying core electrons (e.g. 3d instead of 4d) are excited into the 4f subshell because of the accompanying increase in Z_{eff}. The so-called "4d → 4f" resonant states[22] can be considered as inner-well eigenstates with hybrid character which can behave both like a shape resonance by tunneling through the potential barrier and like a discrete (Feshbach) resonance by autoionizing into neighboring continua.

Direct determination of the decay channels of these inner-shell

resonances, obtained by photoemission studies of the rare earths, provides a very sensitive probe of the effective potential for electrons in the partially filled 4f subshell. In this Letter we report the first such measurements for atomic "4d → 4f" and 3d → 4f excitations. In particular we have studied resonance phenomena in Eu, an element for which the oscillator strength of the "4d → 4f" excitation peaks above the $4d_{5/2}$ ionization threshold. Thus, the "4d → 4f" data yield the first comprehensive results about the relative contributions of autoionization and electronic shape-resonance decay channels to deexcitation of atomic giant resonances. In contrast, the 3d → 4f excitations are discrete transitions lying below their respective 3d ionization limits, thereby making Eu a good candidate for studying orbital-collapse phenomena.

The measurements were made at the Stanford Synchrotron Radiation Laboratory using a time-of-flight (TOF) electron spectrometer described elsewhere.[23] By monitoring the total photoemission intensity at 54.7° relative to the photon polarization vector, we obtained relative total-yield spectra, which allowed an internal calibration of the photon energy (±1 eV) for the "4d → 4f" resonance measurements by comparison with known photoabsorption data.[2] The 3d → 4f energy range was calibrated with a similar uncertainty by measuring a Ne 1s → 3p excitation spectrum. The energy levels relevant to this work are depicted in Fig. 1.

Figure 2 shows total-yield spectra of Eu taken in the photon-energy ranges of the "4d → 4f" and 3d → 4f excitations. Figure 3

shows photoelectron TOF spectra taken at selected photon energies. The TOF spectra in Fig. 3a were taken at $h\nu$=138 eV, on the low-energy side of the "4d → 4f" resonance, which peaks at $h\nu$=141 eV, above the $4d_{5/2}$ threshold at 137 eV. The TOF spectra in Fig. 3b were taken at $h\nu$=1126 eV right on the peak of the $3d_{5/2} \rightarrow 4f$ resonance (top) and at $h\nu$=1120 eV (bottom). The $4d_{5/2,3/2}$ and $3d_{5/2,3/2}$ thresholds (137.5, 142.6, 1131, and 1163 eV, respectively) shown in Fig. 2 were derived from the measured photoelectron kinetic energies.

Several decay channels are available following the 3d and 4d excitations. For the "4d → 4f" resonance, we shall consider two principal types of deexcitation paths, recognizing that their definitions are limited by our incomplete understanding of the decay dynamics of giant resonances.

1) the excited 4d electron experiences an enhancement (via intrachannel tunneling) similar to a shape resonance, resulting in a (main line) Eu^+ $4d^{-1}$ photoemission final state. Connerade[24] has discussed this channel in the context of a shape-independent model.[25]
2) the resonant state decays by autoionization (via interchannel coupling), resulting in Eu^+ configurations corresponding to main lines other than $4d^{-1}$, and their correlation and spin-flip satellites.

For the discrete 3d → 4f resonances, pathway 1 leading to a $3d^{-1}$ final state is energetically inaccessible, and it is convenient to divide the autoionization channels (pathway 2) according to the final

ionic states produced, as follows:

2a) the 4f subshell to which the 3d electron was excited is involved in the decay, resulting in Eu^+ main-line configurations.[26]

2b) the 4f subshell, including the excited 4f electron, remains as a spectator to the decay process, resulting in Eu^+ satellite configurations with eight 4f electrons, which we shall refer to as spectator satellites.[27]

The differentiation of pathways 2a and 2b is possible for the 3d → 4f resonances because the 3d excitation populates the discrete 4f orbital, whereas the 4d electron excited by the "4d → 4f" resonance is placed in a hybrid $\ell=3$ state (not n=4).

Resonant photoelectron spectroscopy provides the opportunity to measure directly the relative cross sections of the different decay channels listed above. In the "4d → 4f" resonance case, the photoelectron spectrum in Fig. 3a shows the predominance of autoionization (pathway 2) to the 4f final state over autoionization to the other final states observed in the spectrum. Figure 4 shows the partial cross sections for 4d, 4f, 5p, and 6s photoemission in the vicinity of the "4d → 4f" resonance. A similar result for the 4f cross section was obtained from the corresponding constant-initial-state spectrum of Eu metal.[14]

The 4d photoemission cross section measured above 160 eV is found to account for less than 25% of the total photoabsorption cross section. Auger electrons from decay of 4d-hole states were observed

for photon energies near the peak of the giant resonance, providing information on the near-threshold behavior of the 4d cross section. The results in Fig. 4 show that photoemission into the 4d channel (pathway 1) is less likely than decay into the 4f main-line continuum (pathway 2), confirming a calculation by Amusia et al.,[28] as well as indicating that the degree of "partial collapse"[29] of the 4f wavefunction is large. The favored exit channel for the giant resonance is apparently the super-Coster-Kronig-like (sCK) decay[30,31] $4d^9 4f^8 \rightarrow 4d^{10} 4f^6 \epsilon d,g$, leaving the ion in the same final state as reached by 4f photoemission. This behavior is analogous to the decay of the 3p → 3d excitation in atomic Mn.[32] The importance of autoionization decay for the "4d → 4f" resonance demonstrates that photoabsorption spectra of giant resonances are insufficient to test the shape-independent approximation:[17,24] measurements of partial cross sections are required.

Turning to the 3d → 4f excitations, the spectrum in Fig. 3b shows that several of the main-line and spectator-satellite channels are enhanced by autoionization. There is no 3d photoemission peak because the $3d_{5/2}$ resonance lies below threshold. From the binding energies and photon-energy dependences of the emitted electrons compared to the nonresonant spectrum (lower spectrum in Fig. 3b), we propose the following assignments of the peaks in the resonant spectrum. The first two peaks correspond primarily to autoionization into the 4f and 4d main lines, respectively. The third peak contains the $4d^{-2}4f^8$ spectator satellite group and a small contribution from the 4p main

line, whereas the last two features most likely are due to spectator transitions to the $4p^{-1}4d^{-1}4f^{8}$ and $4s^{-1}4d^{-1}4f^{8}$ groups, respectively. The limited resolution of the TOF spectra is insufficient to measure quantitatively the relationship between autoionization into the main-line (pathway 2a) and spectator (pathway 2b) transitions, but it does show qualitatively the competition between the two types of decay channels.

For the $3d_{3/2} \rightarrow 4f$ excitation (TOF spectrum not shown), the $3d_{5/2}$ main-line state also can be reached by autoionization, and in fact this channel accounts for almost half of the total intensity at the $3d_{3/2} \rightarrow 4f$ resonance. We conclude that autoionization to the main n=3,4 photoemission final states contributes considerably to the decay of the $3d \rightarrow 4f$ excitations, especially for the $3d_{3/2}$ spin-orbit component. This result is in good agreement with theoretical predictions for La,[33] and consistent with the asymmetric line-shape of the $3d_{3/2}$ resonance in our total-yield spectrum.

In Fig. 5 we show the partial cross sections of the 4d, 4f, and $3d_{5/2}$ main-line channels and of the $4d^{-2}4f^{8}$ and $4p^{-1}4d^{-1}4f^{8}$ spectator satellites (the "4f peak" includes contributions from the 5s, 5p, and 6s subshells, and the satellites include some 4p and 4s main-line intensity, respectively) in the $3d \rightarrow 4f$ excitation energy range. These results show there is no specially favored decay channel, in contrast to the "$4d \rightarrow 4f$" excitation, but rather that many open channels participate in the decay of the excited states, including significant decay of the $3d_{3/2} \rightarrow 4f$ resonance to the $3d_{5/2}$ channel.

However, enhancement of the satellites shows that autoionization via spectator transitions (pathway 2b) is competitive in the decay of a 3d hole. Our observations of decay to the $4f^{-1}$ state corroborate findings by inverse photoemission[8] (bremsstrahlung enhancement) as well as by direct valence-band photoemission obtained recently for different rare-earth compounds.[16]

In conclusion we have shown that autoionization to main-line configurations is the dominant decay process for the "4d → 4f" resonance in Eu, although this resonance exhibits some shape-resonance "character" as well. The decay of the 3d → 4f resonances shows strong competition between autoionization to main lines and spectator satellites. The populations of the different main-line exit channels change dramatically with the quantum number of the core hole created after excitation to the 4f subshell. This quantitative difference in decay-channel cross sections may be related to the degree to which the vacancy dependence of the double-well potential (as seen very recently for molecules[34]) and thereby the orbital-collapse effect modifies the ℓ=3 excited-state wavefunction. The collapsed 4f wavefunction following 3d → 4f excitation produces a strong autoionizing resonance by virtue of being localized in the inner well of the atomic potential, whereas the ℓ=3 wavefunction populated by the "4d → 4f" excitation may be regarded as "partially collapsed" with enough continuum character to produce some shape-resonance-like decay (pathway 1). A complete understanding of how these differing intermediate-state wavefunctions affect the different decay-channel probabilities will require further

theoretical analysis and experimental studies. Finally, we expect that the decay characteristics observed in Eu also will be found in other rare-earth elements, and that detailed study with higher resolution will yield new insights into inner-shell excitations and giant-resonance phenomena.

Acknowledgements

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26. Because of the difference in spins of the electron excited to the 4f orbital and the "other" seven 4f electrons, the term symbol for the main-line configurations will vary depending on which 4f electron undergoes the decay. However, the present low-resolution results only distinguish among the different configurations.

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Figure Captions

Fig. 1. Energy-level diagram of Eu, indicating the transitions studied. A = autoionization, SR = shape resonance. Some decay channels have been omitted for clarity.

Fig. 2. Total-yield spectra of Eu in the photon-energy ranges of the (a) "4d → 4f" and (b) 3d → 4f resonances.

Fig. 3. TOF photoelectron spectra of Eu vapor taken with photon energies of (a) 138 eV near the "4d → 4f" resonance and (b) 1126 eV at the maximum of the $3d_{5/2}$ spin-orbit component of the 3d → 4f resonance, compared to a nonresonant spectrum at $h\nu$=1120 eV [lower part of (b)]. The insert in (a) shows the presence of spin-flip satellites of the 4f peak.

Fig. 4. Partial cross sections of the 4d (squares, open squares for $4d_{5/2}$ only), 4f (circles), 5p (diamonds), and 6s (triangles) main lines in the vicinity of the "4d → 4f" giant resonance. The solid curves represent two-resonance fits with Beutler-Fano profiles [$q_{eff}(4f)$=1.6, Γ=4.4 eV]. The dotted line represents the shape-resonantly enhanced $4d_{5/2}$ cross section in the shape-independent approximation.

Fig. 5. Partial cross sections of the 4d (triangles), 4f (circles), and $3d_{5/2}$ (stars) main lines, and the $4d^{-2}4f^{8}$ (diamonds) and $4p^{-1}4d^{-1}4f^{8}$ (squares) satellites in the 3d → 4f excitation region. Above the $3d_{5/2}$ threshold, the 4d, 4f, $4d^{-2}4f^{8}$, and $4p^{-1}4d^{-1}4f^{8}$ cross sections have been corrected for appreciable intensity contributions by Auger electrons from decay of the $3d_{5/2}$ hole state.

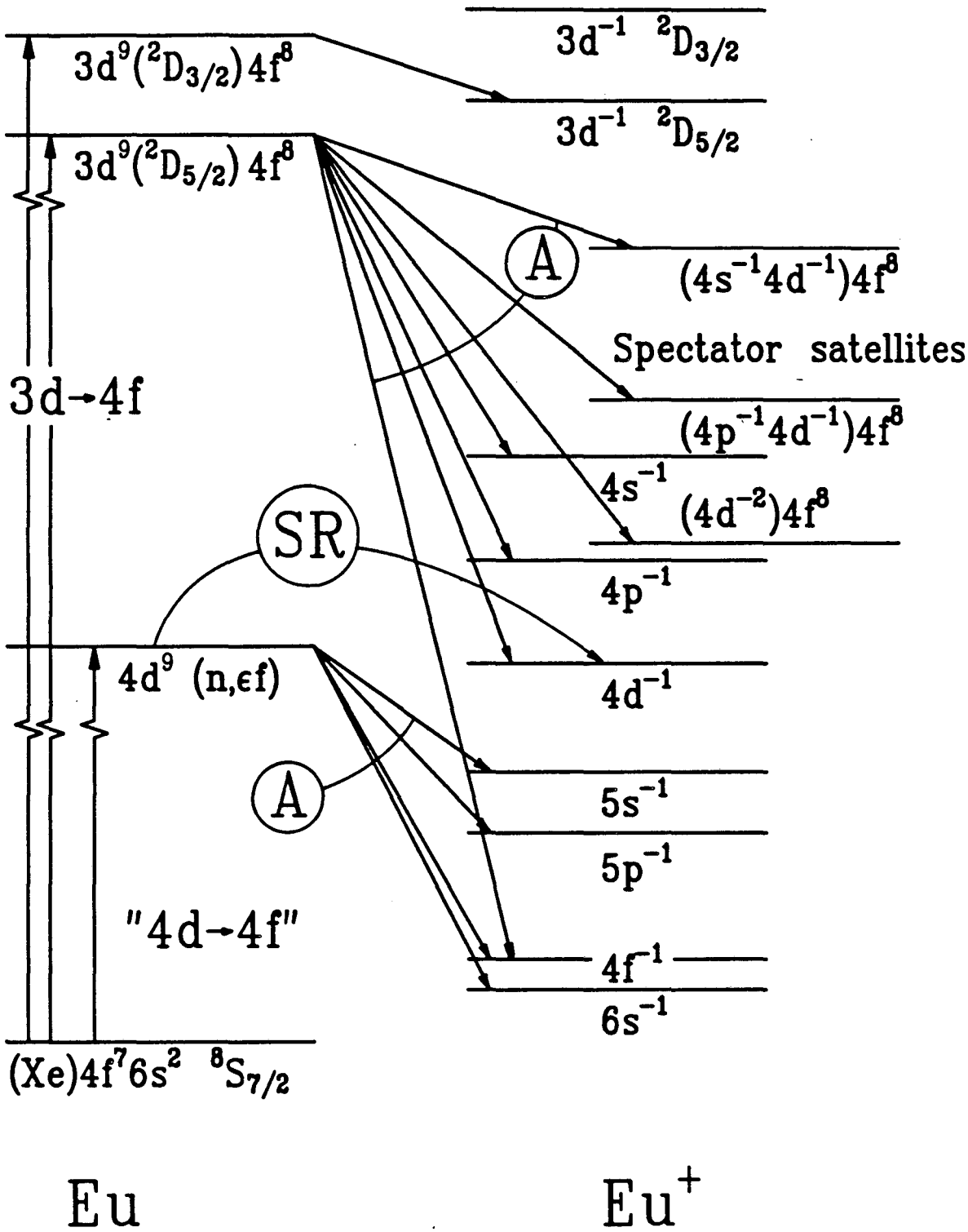

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Figure 1

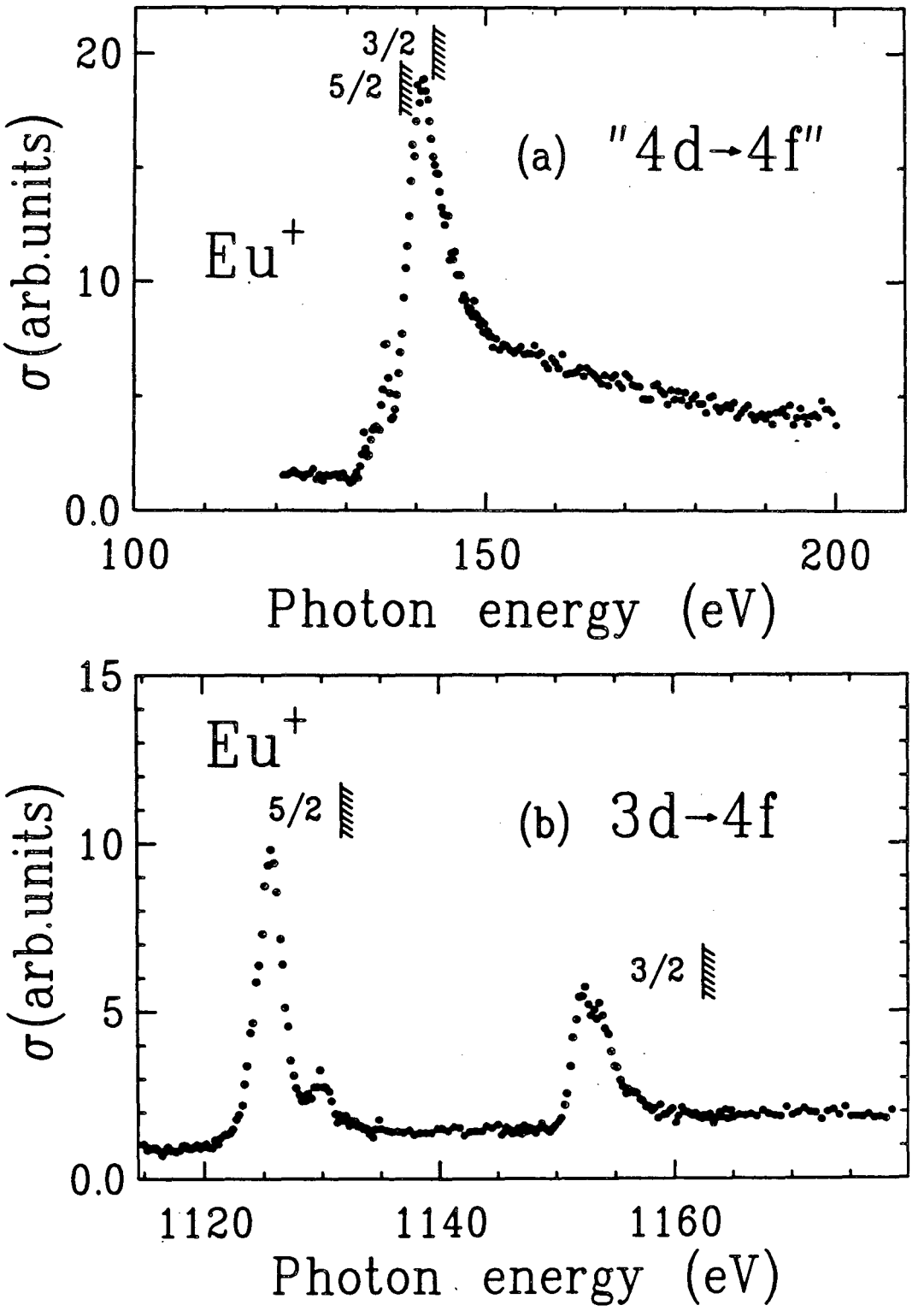

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Figure 2

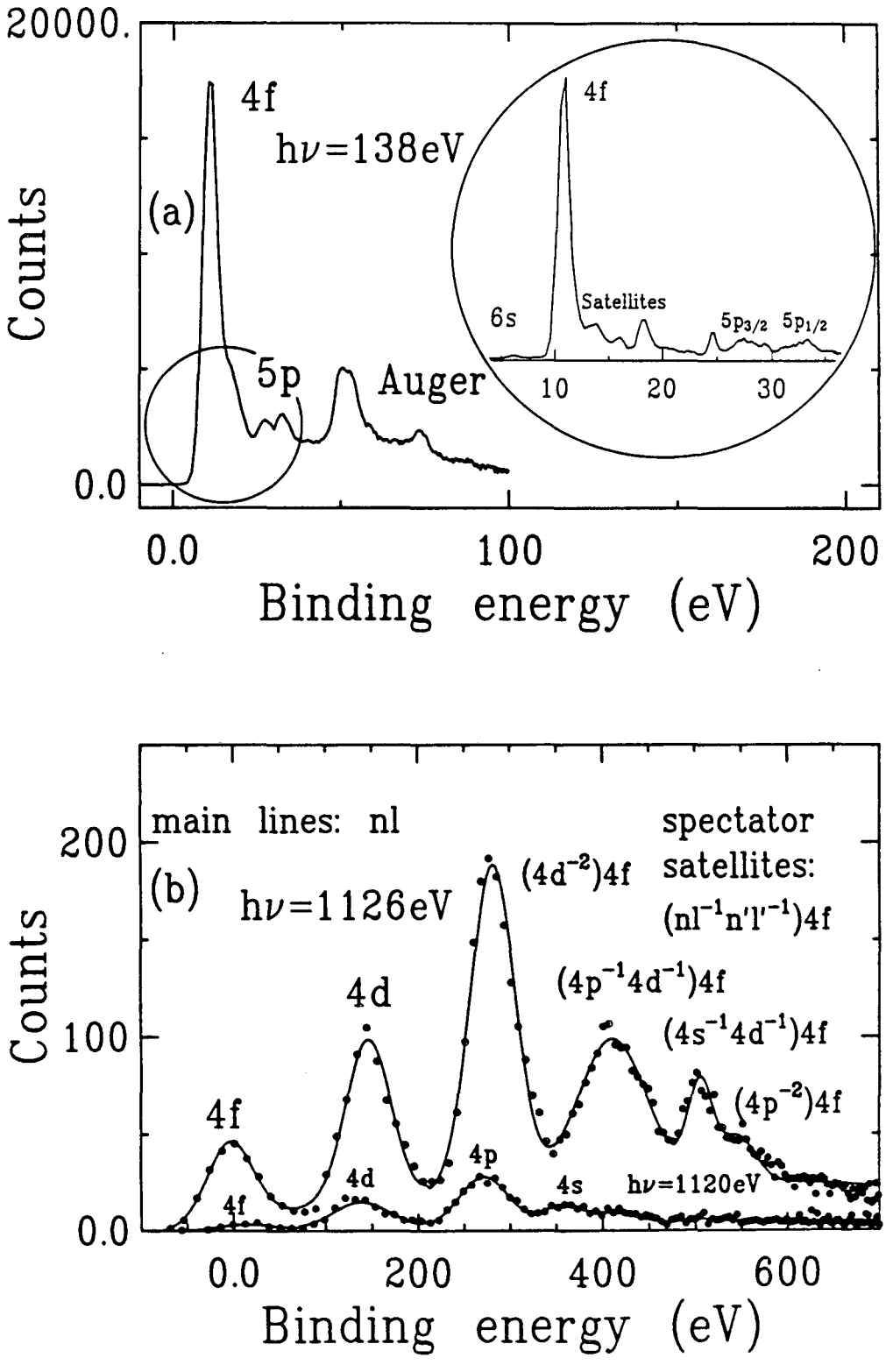

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Figure 3

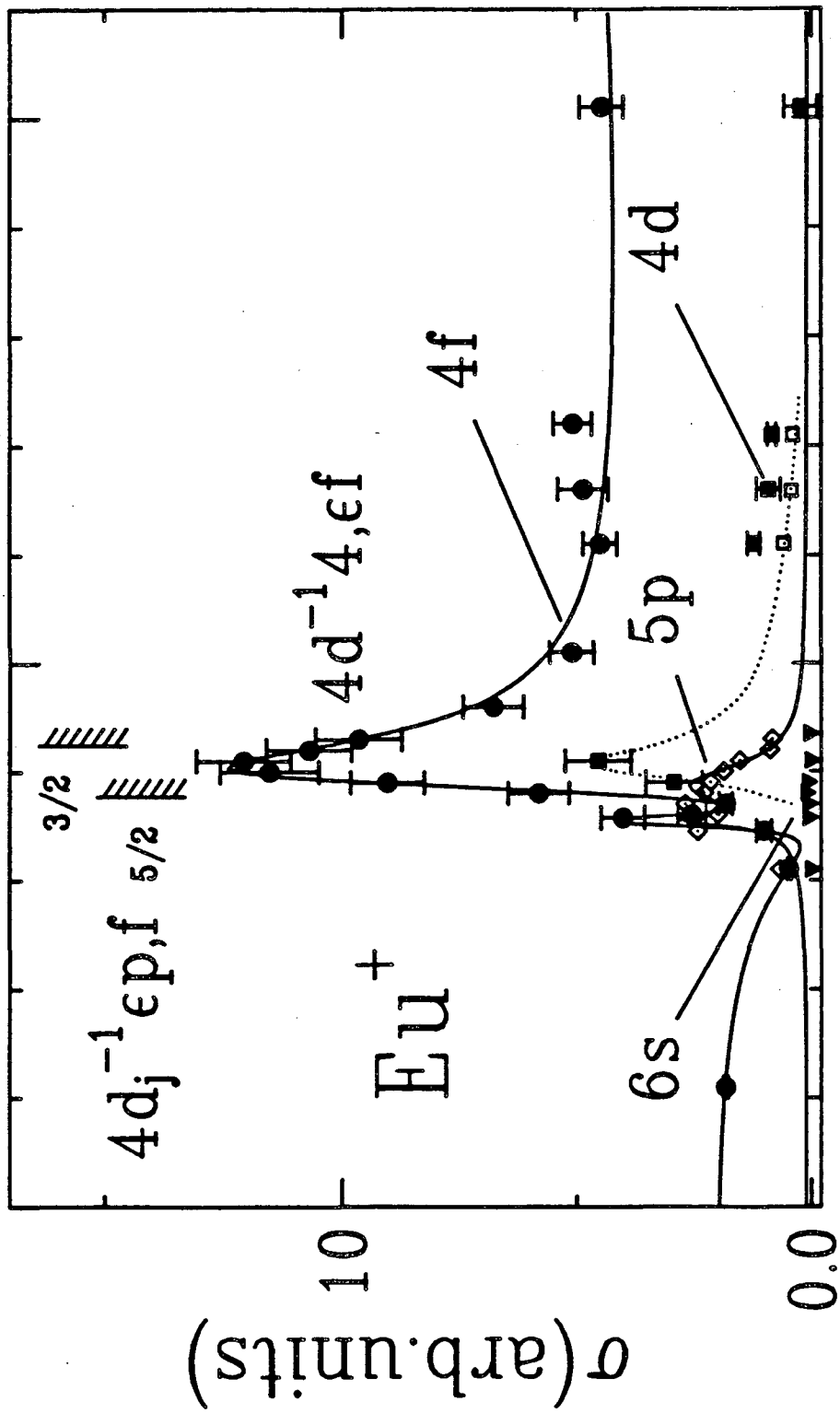

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Figure 4

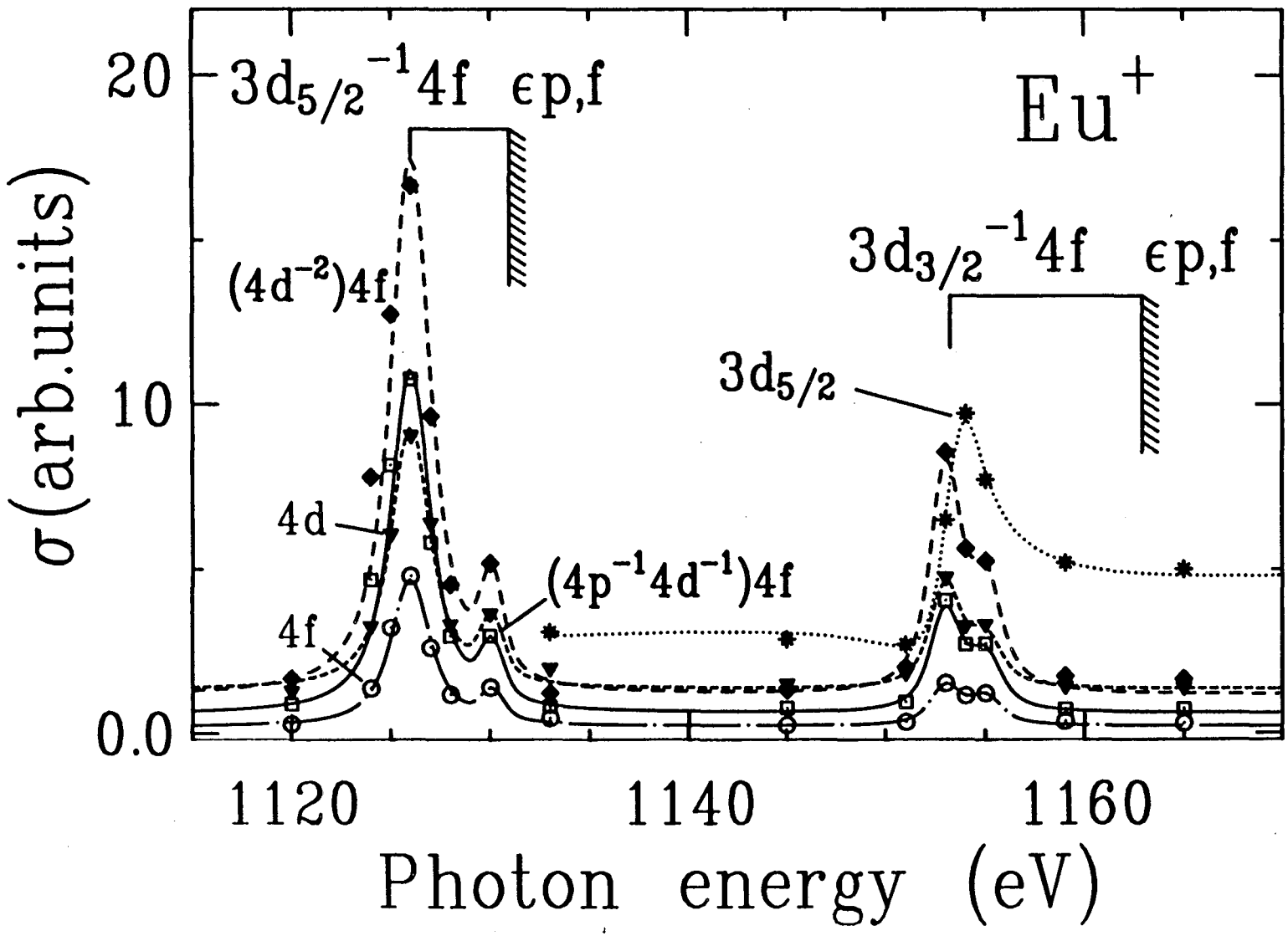

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Figure 5

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