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Author
Lindle, D.W.

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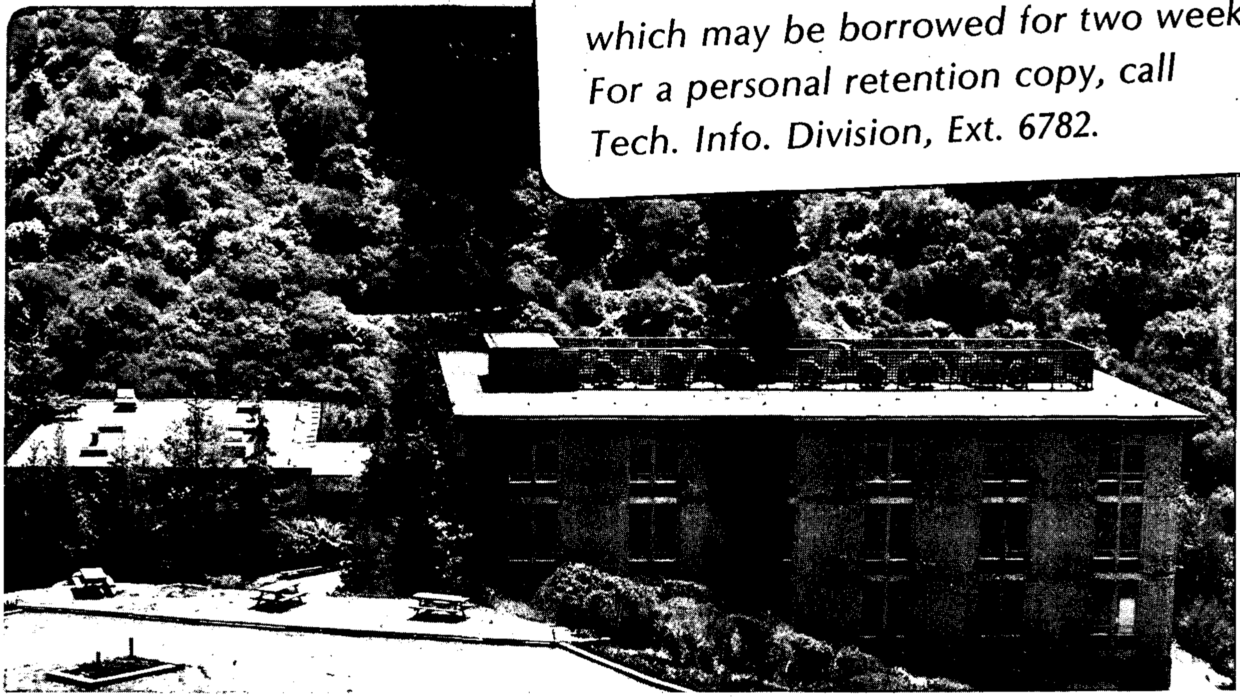

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PHOTOEMISSION FROM THE 3d SUBSHELL OF ATOMIC Kr

D.W. Lindle, P.H. Kobrin,* C.M. Truesdale,† P.A. Heimann,
T.A. Ferrett, U. Becker,‡ H.G. Kerkhoff,‡ and D.A. Shirley

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemistry
University of California
Berkeley, California 94720

Angular-distribution asymmetry parameters are presented for Kr 3d photoemission using photon energies from 100 to 600 eV. The asymmetry parameter fell below the Hartree-Fock-theory prediction at high photon energies, and showed resonant interchannel-coupling effects near the 3p threshold. The summed intensity of 4p → np satellites relative to the 3d main line was found to decrease with photon energy in the range 180 to 270 eV, and the average asymmetry parameter for these shake-up states showed a marked increase over the same energy range.

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*Present address: Department of Chemistry, Pennsylvania State University, University Park, PA 16802.

†Present address: Research and Development Division, Corning Glass Works, Corning, NY 14831.

‡Permanent address: Fachbereich Physik, Technische Universität Berlin, 1000 Berlin 12, West Germany.

Recent photoemission measurements of the 4d and 4f subshells of Xe,[1,2] Hg,[3] and I in CH_3I[4] have exhibited pronounced oscillations in the energy-dependences of angular distributions caused by interaction of the photoelectron with a centrifugal barrier in the atomic potential. We report here measurements that indicate similar effects for the Kr 3d asymmetry parameter, although no centrifugal barrier is present for atomic Kr because of the smaller Coulomb attraction in this lower-Z element.[5] This result is explained by considering the shape of the atomic potential as a result of the strong centrifugal repulsion near the nucleus.[5] Also included are results illustrating the importance of multi-electron effects: interchannel coupling of the 3d and 3p subshells, and production of satellites of the 3d main line. For the satellites, relative intensities and asymmetry parameters are presented which show significant changes with photon energy.

All of the measurements were made with photons from Beam Line III-1 at the Stanford Synchrotron Radiation Laboratory and the double-angle time-of-flight (DATOF) method.[2,6,7] The ultra-high vacuum monochromator was protected by a 1500Å thick Al window from the $\sim 10^{-5}$ torr pressure in the experimental chamber. The photon beam intersected an effusive gas jet at the interaction region viewed by the apertures of two TOF detectors, allowing measurement of photoelectron intensities at two angles and nearly all energies simultaneously.

Yang's theorem[8] defines the differential cross section, $d\sigma/d\Omega$, for photoionization of a randomly oriented sample by linearly polarized radiation in the dipole approximation as

$$\frac{d\sigma(h\nu)}{d\Omega} = \frac{\sigma(h\nu)}{4\pi}[1 + \beta(h\nu)P_2(\cos\theta)] , \qquad (1)$$

where θ is the angle between the momentum vector of the ejected electron and the polarization vector of the incident radiation, $P_2(\cos\theta)$ is the second Legendre polynomial, and σ and β are the cross section and angular-distribution asymmetry parameter, respectively, for the photoionization process under study. In this work we assume the validity of the dipole approximation, and the effect of incomplete (~98%[2]) linear polarization is taken adequately into account by the calibration procedure described in Ref. 6.

Simultaneous measurement of the relative intensities of two photoelectron peaks at θ=54.7°, for which $P_2(\cos\theta)$ vanishes, yields branching-ratio data that are independent of variations in photon flux and gas pressure. Measurement at one additional angle (θ=0°) yields values of β that are also independent of these changes. The methods for extracting these values from the TOF spectra are described in detail in Refs. 2 and 6. We estimate systematic errors to be ±10% for branching ratios and ±0.10 for asymmetry parameters. At certain photon-energy settings of the monochromator, a component of second-order radiation (energy of 2hν) was large enough to produce peaks in our spectra, primarily second-order peaks of Kr 3d photoionization. Because the β measurements are independent of the photon flux, we were able to extend our β_{3d} results to higher photon energies using this second-order radiation.

A TOF spectrum of Kr taken at 224 eV photon energy is shown in Fig. 1. This spectrum is dominated by features associated with 3d subshell photoionization; the unresolved 3d photoemission lines with binding energies of 93.7 eV ($4d_{5/2}$) and 94.9 eV ($4d_{3/2}$),[9] a satellite peak of the 3d line, mostly composed of 4p → 5p shake-up states (~114 eV binding energy[10]), and all of the Auger features below 60 eV kinetic energy. Evidence of 3p ionization (thresholds at 214.4 and 222.2 eV[9]) is apparent with the $M_{2,3}M_{4,5}N$ Auger peak. The remaining high-energy peaks result from photoionization of the valence subshells and from photoemission induced by higher-order components of the synchrotron radiation.

Figure 2 displays the measured asymmetry parameters for 3d photoionization along with previous measurements by Krause[11] and Carlson et al.[12] At low energies, we observe excellent agreement with the earlier data,[12] whereas the earlier higher-energy results[11] are systematically higher than the present data. Comparison with Hartree-Fock velocity (HF-V)[13] and relativistic random-phase approximation (RRPA)[14] calculations also is made in Fig. 2. The theoretical curves nearly coincide from threshold to 125 eV, both showing good agreement with the experimental results. Above 200 eV, the HF-V calculation overestimates the asymmetry parameter measured here, but agrees rather well with the earlier measurements.[11] The minimum in β_{3d} at 115-120 eV can be ascribed to an interaction of the photoelectron in the εf channel with the repulsive part of the atomic potential.[5,15] Near threshold, the centrifugal repulsion experienced by an $\ell=3$ continuum wavefunction inhibits the ϵf channel. As the energy increases, this channel rapidly dominates the photoionization process, inducing a subsequent change in the asymmetry parameter.[16] The concurrence of the theoretical results with the experimental measurements at low energy confirms this interpretation, as well as indicating that Kr 3d photoionization is described adequately by a one-electron model.

The single-electron picture seems to break down near 210 eV. The 3d asymmetry parameter experiences a resonance effect apparently associated with the onset of 3p ionization. Because this feature appears below the $3p_{3/2}$ ionization threshold at 214.4 eV, we assign this interchannel interaction as autoionization of a Rydberg level(s) involving excitation of a 3p electron. Three such levels have been observed in absorption,[17] the resonances at 210.7 eV (3p → 5s) and 213.2 eV (3p → 6s,4d) being the likely candidates for the effect observed here.

The sum of the intensities of the 3<u>d</u>4<u>p</u>np satellites relative to the 3d main line is shown in the top of Fig. 3. The 4p → np satellites were unresolved in the TOF spectra: thus the results in Fig. 3 represent values for all of these peaks combined. Very little is known about the energy-dependent behavior of satellite intensities.[18] Empirically, Wuilleumier and Krause[19] have plotted satellite relative intensities against a reduced-energy parameter, ϵ/E_0, where ϵ is the kinetic energy of the satellite photoelectron, and E_0 is the satellite excitation energy (i.e. the binding energy of the satellite less the binding energy of the main line). For the Kr 3d4pnp satellites, E_0 is approximately 20 eV, and the reduced-energy region covered by the measurements in Fig. 3 is $3.5 \leq \varepsilon/E_0 \leq 8.2$. At the upper end of this range, one suspects the high-energy or sudden limit to be reached.[19] Our high-energy value of 7.8(6)%, an average of our results above 210 eV, agrees very well with an Al Kα measurement[20] of 8(1)% for the sum of the 4p → np satellites, but disagrees with a higher-resolution Mg Kα measurement[10] of 11.7% for these same transitions. The latter value is in better agreement with the theoretical sudden-limit result[10] of 10.6%. However, because both of the earlier measurements did not take the asymmetry parameter into account, they must be interpreted with caution. At lower energies we find the relative intensity to be larger than our high-energy value, illustrating that other processes besides shake-up may become important for lower values of the reduced energy. We note that the 3d main line cross section is decreasing in this energy range, as determined from absorption measurements[21] and the fact that 3d subshell absorption dominates at these energies (see Fig. 1).

Even less is known about the energy dependence of satellite asymmetry parameters. As a first approximation, one might expect that the satellite β will mimic the asymmetry parameter of the main line. Comparison of the 3d4pnp asymmetry-parameter results in Fig. 3 to β_{3d} (Fig. 2) shows that both β parameters increase in this energy range, but the slope for the satellite asymmetry parameter is about a factor of 2 larger than for β_{3d}. An explanation for this intriguing result is not possible within the context of energy-independent shake-up calculations.

For photon energies between 225 and 285 eV, evidence of 3p photoionization appeared in our spectra in the form of an $M_{2,3}M_{4,5}N$ Auger feature. These Auger transitions have been found to contribute approximately 50% to the decay of 3p vacancy states.[22] Consequently, we can estimate that 3p subshell absorption accounts for about 10% of the total absorption cross section in this energy range. The 3p photoemission peak itself was discernible for energies from 275 to 285 eV. The 3p asymmetry parameter was determined to be 0.26(8) at these energies, lower than the HF-V result[13] of 0.5, but nearly the same as β_{3d} in this photon-energy range. A similar result has been observed for the I 4p and 4d subshells in CH_3I.[4] In that work, recourse was made to strong many-electron interactions in the I 4p subshell in an attempt to understand this phenomenon. Ohno and Wendin[23] have discussed the same types of effects for the Kr 3p subshell. The asymmetry parameter for the $M_{2,3}M_{4,5}N$ Auger feature was found to be 0.0(1). Likewise, the asymmetry parameters for the $M_{4,5}NN$ Auger peaks were found to be approximately zero over the energy range studied.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Fig. 1. TOF photoelectron spectrum of Kr at a photon energy of 224 eV and with $\theta=0^\circ$. All of the features below 60 eV are $M_{4,5}NN$ Auger lines. The 3d satellite includes all of the 4p → np shake-up transitions. The peaks to the right of the 3d main line arise from valence photoionization and from photoemission induced by second- and higher-order components of the incident radiation.

Fig. 2. Angular-distribution asymmetry parameter for Kr 3d photoemission. Solid circles are the present results, open circles and X's are from Refs. 12 and 11, respectively. The curve represents both RRPA (Ref. 14) and HF-V (Ref. 13) calculations, after the RRPA curve is shifted 9 eV to lower energy to coincide with the experimental threshold. The two calculations nearly agree for photon energies from threshold to 125 eV, at which point the RRPA curve stops.

Fig. 3. Intensity relative to the 3d main line (top) and asymmetry parameter (bottom) for the Kr $3\underline{d}4\underline{p}np$ satellites. All of the 4p → np satellites were unresolved and are included in these results.

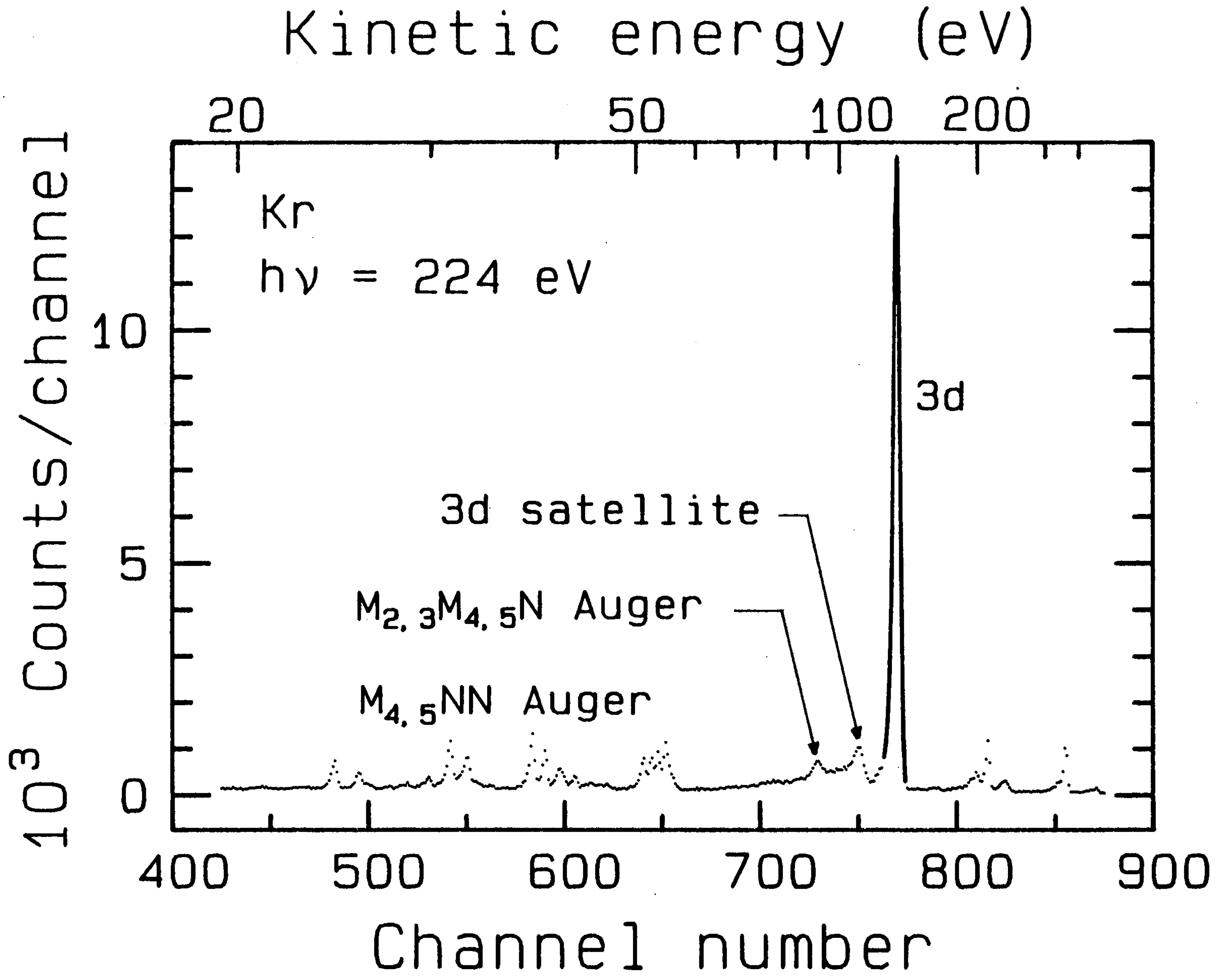

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Figure 1

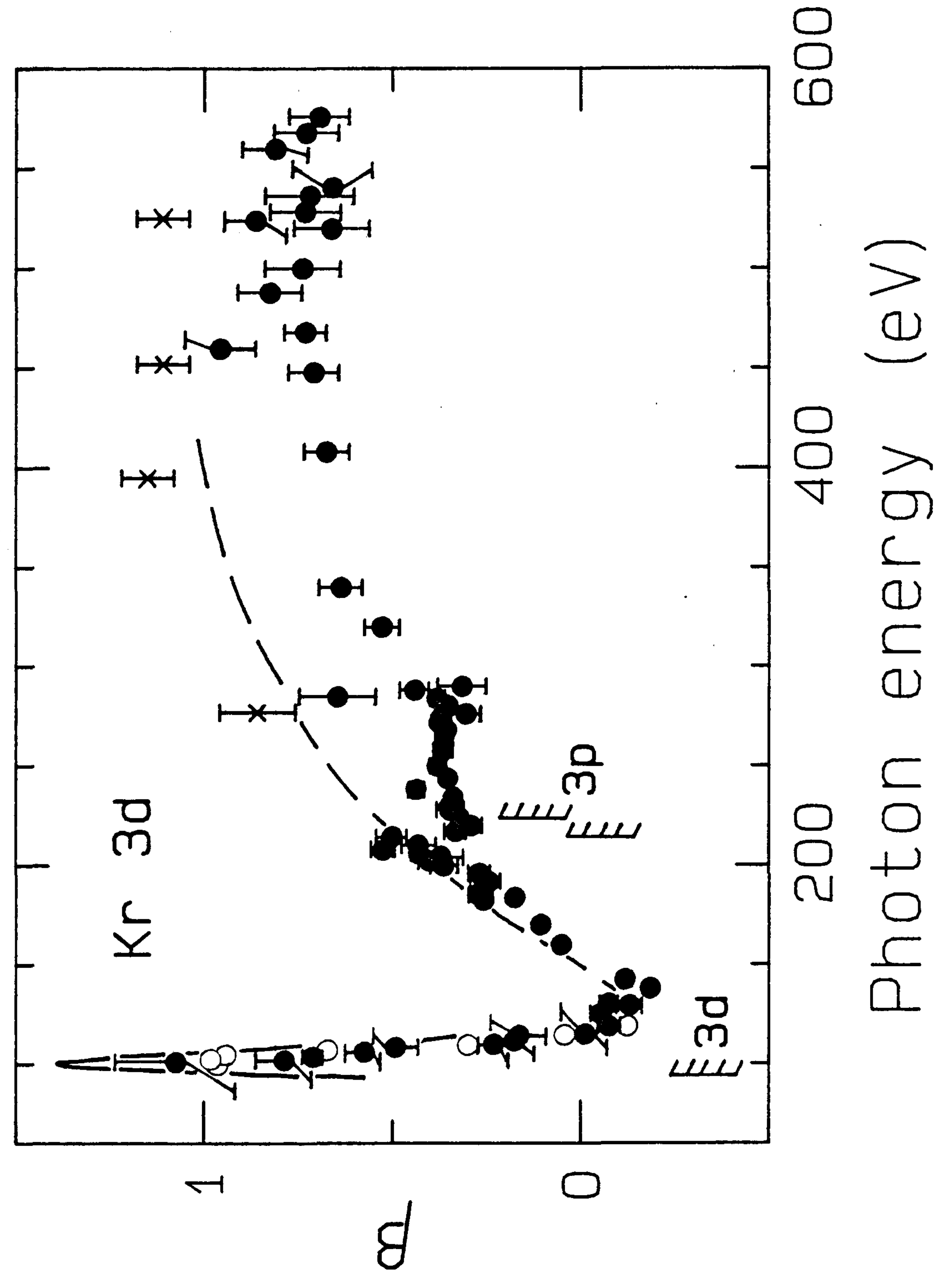

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Figure 2

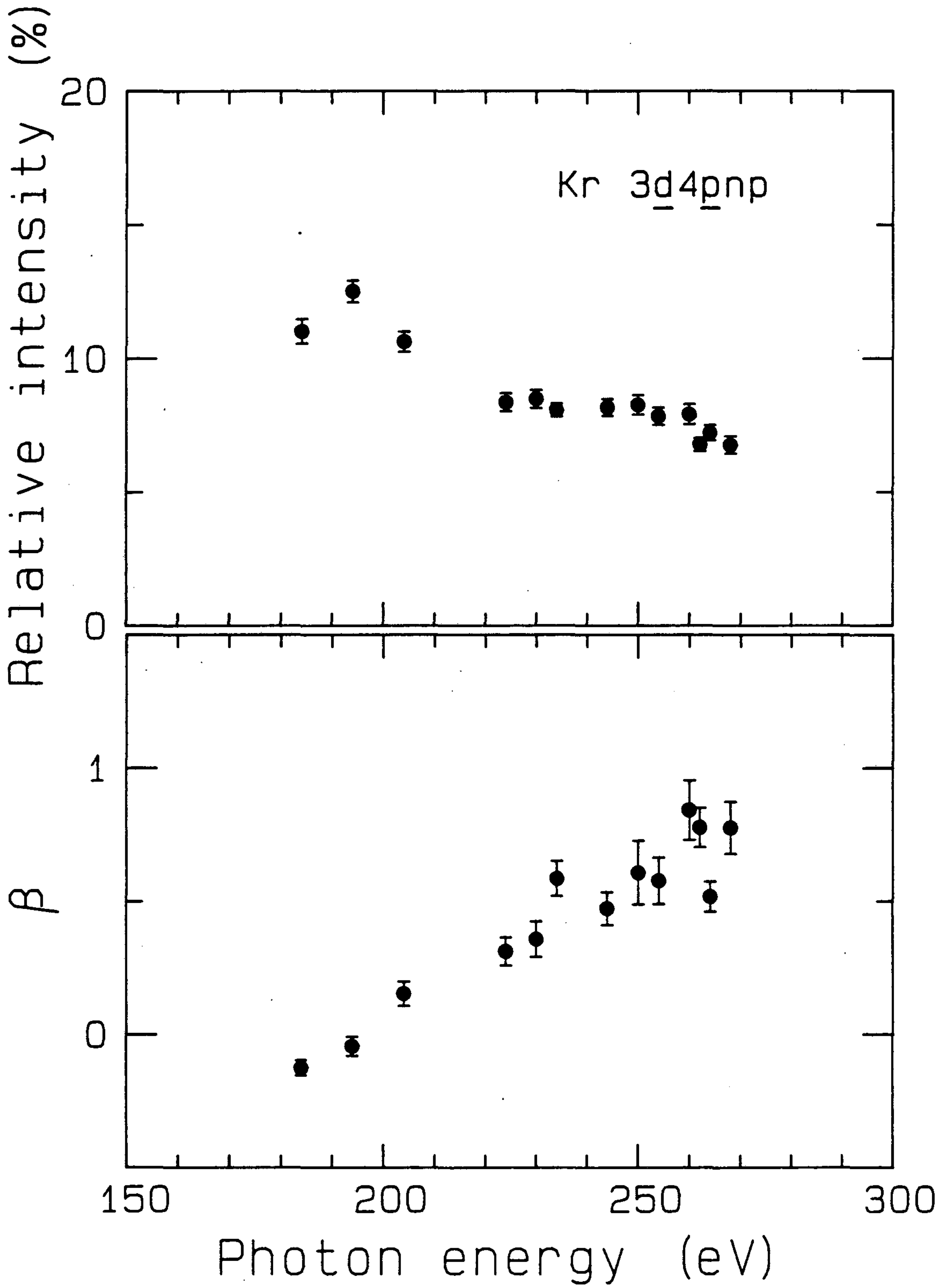

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Figure 3

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720