Title

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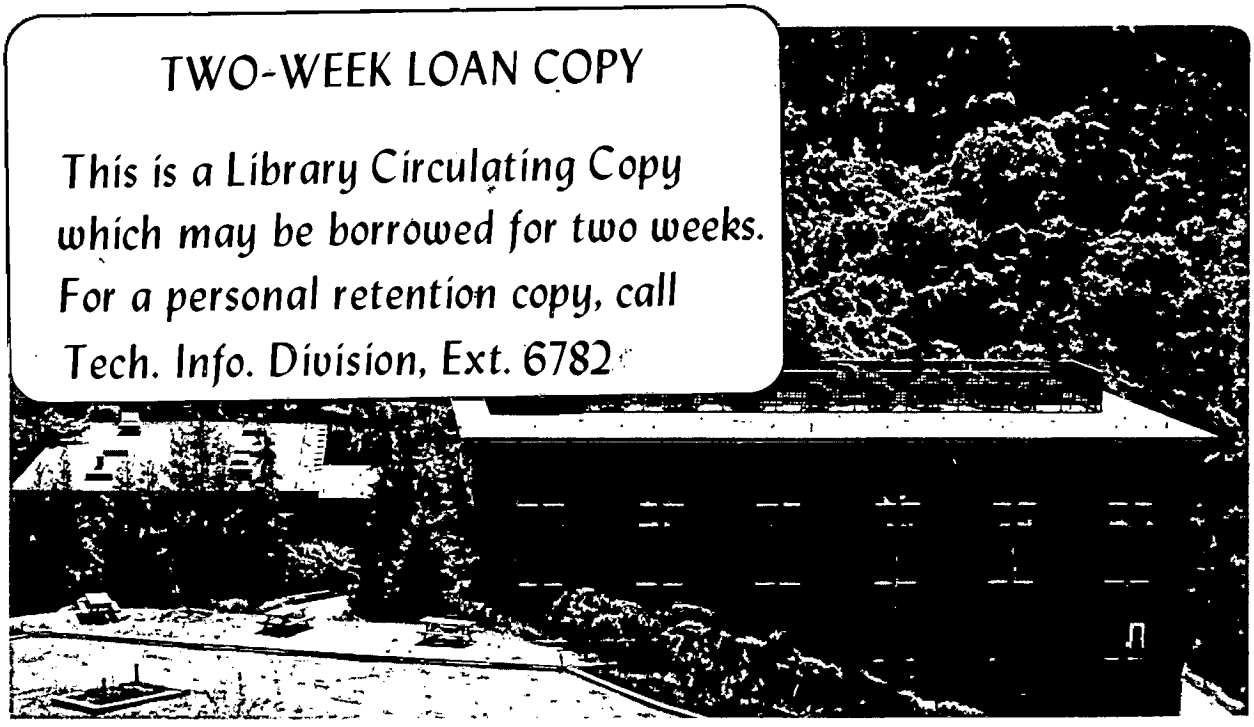

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SELECTIVE RESONANT ENHANCEMENT OF ELECTRON CORRELATION SATELLITES IN ATOMIC BARIUM

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ABSTRACT

Photoelectron spectra from atomic barium were recorded following excitation with synchrotron radiation at selected autoionization resonance energies. The greatly enhanced intensities of peaks arising from certain levels in Ba^+ elucidates the structures of the autoionizing levels and implicates Auger decay as the dominant mode for their interaction with the continuum. Resonance photoelectron spectroscopy shows promise of wide applicability.

The interaction of autoionizing levels with the continuum has received a great deal of attention, following Fano's pioneering work.[1] New interest in this subject has recently been stimulated by the rich satellite structure exhibited in the photoelectron spectrum of Ba vapor upon excitation with 21.22-eV HeI radiation.[2-4] This structure is understood as arising from the fortuitous overlap of the HeI line with an autoionizing level of BaI. Connerade et al.[5] have found many strong absorption peaks in BaI, arising from series based on the 5p ionization thresholds. Each absorption peak arises from a $^1P_1$ state derived from an excited configuration of BaI imbedded in, and admixed with, many BaII continua. Thus, resonant excitation of any absorption peak yields decays into many (BaII + photoelectron) channels, with intensities related to the composition of that particular $^1P_1$ level. Resonance photoelectron spectroscopy, using a tunable-energy photon source, should therefore be capable of generating a whole new class of information about the electronic structure of each autoionizing state. In this Letter we report the first successful application of resonance photoelectron spectroscopy to this system, using synchrotron radiation to excite two selected absorption peaks, at 19.94 eV (621.7 Å) and 21.48 eV (577.3 Å) in BaI. Dramatically different intensity profiles were observed in the two photoelectron spectra, with the 5d and 6d states in BaII being respectively preferred. This first result yields definitive information about the structures and decays of these two resonances, and indicates that resonance photoelectron spectroscopy should have general applicability in elucidating the electronic structure of many-electron systems.

A variable-energy photon source was provided by the 8° beam line at Stanford Synchrotron Radiation Laboratory (SSRL), which, in conjunction with a 1570 Å thick Aℓ window, passed radiation in the energy range 17 eV < hν < 34 eV. A high-temperature oven operated at 840° ± 20°C yielded Ba vapor in an effusive atomic beam at a particle density of 10^{13} cm^{-3}. Irradiation with the photon beam yielded a counting rate of 5-35 sec^{-1} in a specially designed time-of-flight (TOF) electron analyzer oriented at the "magic angle," $\theta = 54.7^{\circ}$ relative to the electric vector of the >97% polarized photon beam.[6] The TOF analyzer, described in detail elsewhere,[7] consisted of a mu-metal shielded 28.5 cm drift tube, a microchannel plate, and a retarding grid which was operated at a 5-volt bias. The TOF analyzer utilized the unique pulse structure of the storage ring at SSRL (300 psec pulse duration (FWHM), 780 nsec repetition period) to obtain photoelectron spectra that were unaffected by fluctuations in synchrotron beam current and sample number density, with very high efficiency and excellent signal-to-noise ratios. All of these features were essential for the success of the experiment.

A total electron-yield spectrum of atomic barium between 700 Å and 490 Å is shown in Fig. 1. All the major features of the absorption spectrum of Connerade et al.[5] are present. While quantitative comparison of intensities is not yet feasible because of uncertainties in efficiency factors and background levels in our experiment, the relative intensities of the main peaks in the absorption and excitation spectra are at least roughly comparable, implying that most of the absorbed photons lead to ionization.

Photoelectron spectra were collected at several peak positions in Fig. 1: we report results for the two wavelengths indicated, 621.7 Å and 577.3 Å. An uncertainty of ± 0.7 Å was introduced by the SSRL monochromator, and the total band pass was 2.5 Å.

Photoemission from BaI to BaII can occur through both direct and resonant processes, illustrated in Fig. 2. For clarity we discuss direct processes first.

The photoionization cross-section for an N-electron atom in initial state g going to a final ionic state f by emitting a photoelectron of energy ε and angular momentum ℓ is proportional to the square of a matrix element

$$\sigma_{gj} \propto \left| \langle g | \sum_{\mu=1}^{N} \vec{A} \cdot \vec{p}_{\mu} | f, \varepsilon\ell \rangle \right|^2 \qquad (1)$$

Here, $\vec{A}$ is the vector potential and μ is the electron index. For the BaI ground state.

$$\begin{aligned} |g\rangle \cong & - 0.9603 |[\mathrm{Xe}]\, 6s^2;\ {}^1S_o\rangle - 0.2539 |[\mathrm{Xe}]\, 6p^2;\ {}^1S_o\rangle \\ & + 0.0207 |[\mathrm{Xe}]\, 6p^2;\ {}^3P_o\rangle + 0.1134 |[\mathrm{Xe}]\, 5d^2;\ {}^1S_o\rangle \\ & - 0.0032 |[\mathrm{Xe}]\, 5d^2;\ {}^3P_o\rangle \end{aligned} \qquad (2)$$

according to multiconfigurational Dirac-Fock calculations by Rose et al.[8] Here [Xe] represents the xenon core configuration. Direct photoemission leads primarily to the $^1P_1$ final state $|f, \varepsilon\ell\rangle = |[\mathrm{Xe}]\, 6s;\ {}^2S, \varepsilon p\rangle$.

The satellites $|[\text{Xe}]\,6p;\ ^2P_{1/2,3/2},\ \varepsilon s \text{ or } \varepsilon d\rangle$ and $|[\text{Xe}]\,5d;\ ^2D_{3/2,5/2},\ \varepsilon p \text{ or } \varepsilon f\rangle$ can also be populated directly by excitation of the small $6p^2$ and $5d^2$ components of g (see Eq. (2)), but in much lower intensity. This result was obtained in the direct photoemission spectrum of BaI excited by the 16.85 eV line of NeI.[4]

Resonance photoelectron emission occurs via the resonant excitation of an intermediate highly excited state of BaI which can autoionize to various states in BaII. This process, also illustrated in Fig. 2, should be describable in terms of the detailed electronic structure of the autoionizing states, compared with the BaII final states. Each resonance should have its own "signature" in the form of its photoelectron spectrum, with the intensities of peaks (corresponding to states in BaII) giving a rather direct description of the parent state's structure. If the intensity patterns are sufficiently pronounced, it should be possible to draw strong conclusions about the structures of the autoionizing states even without a detailed theoretical model of this process, which is as yet unavailable. In fact, the spectra presented below show very dramatic intensity variations.

The resonance photoelectron spectra are shown in Fig. 3. The resonances that were selected correspond to the first two members of the Rydberg series "d" in the notation of Connerade et al.[5] They assigned these peaks as

$$[\{5p^5 5d;\ ^3D)6s\ ^2D_{3/2}\}5d]^o_{J=1} \qquad (622.9\ \text{Å})$$

and

$$[\{5p^5 5d;\ ^3D)6s\ ^2D_{3/2}\}6d]^o_{J=1} \qquad (577.1\ \text{Å})$$

We shall abbreviate these as $\Phi(5d)$ and $\Phi(6d)$, respectively.

Both spectra in Fig. 3 have some contributions from direct photoemission. These can be separated out qualitatively, following the discussion below Eq. (2), which concluded that the direct process yields a strong 6s peak and weaker 6p and 5d peaks. The upper spectrum in Fig. 3 deviates strongly from this pattern in that the 5d peak is the highest peak in the spectrum; the same is true for the 6d peak in the lower panel. A simple interpretation of these results is that the $\Phi(nd)$ states Auger-decay via the Coster-Kronig transition $5p^5 5d6s \rightarrow 5p^6 + e^-$, with the nd electron playing a "spectator" role. In fact this is only the most obvious one of several decay channels that participate in these transitions. For clarity and brevity we shall not attempt a more complete interpretation here, but this result serves to illustrate the value of the resonance photoemission method. We note that the $\Phi(5d)$ resonance spectrum (upper panel, Fig. 3) is relatively free of extraneous peaks, in contrast to the $\Phi(6d)$ spectrum (lower panel). This could be because the $\Phi(5d)$ state is really simpler; more likely it is a consequence of exciting other resonances in the neighborhood of 577 Å in the lower spectrum at the resolution of our experiment: both the results of Connerade et al.[5] and the peak shapes in Fig. 1 would support this interpretation.

With the insight provided by these results, we can now identify the same mechanism in the photoelectron spectrum of BaI excited by the 584 Å HeI_α line.[4] No compelling reason could be given for the sudden increase in intensity of the peak at 14.22 eV "binding energy" (peak 10 in Ref. 4),[9] which corresponds to the $5p^6 11s$ state in BaII.

However, Connerade et al.[5] have assigned the absorption line at 584.3 Å to excitation of an 11s electron. In light of this assignment and the present results, it seems very probable that the sudden intensity in peak 10 of Ref. 4 is in fact another manifestation of the phenomenon shown here in Fig. 3. Although Connerade et al. did not specify the core configuration of this state, we note that large contributions from configurations such as $4p^5 5d^2 11s$ and $5p^5 5d6d\ 11s$ would also explain the large intensities of the BaII $5p^6 5d$ and $5p^6 6d$ peaks in the HeI spectrum.

The present results are consistent with arguments presented by Fano and Cooper,[10] and with the formalism developed by Davis and Feldkamp,[11] which was used to explain the absorption spectra of atomic Mn.[12,13] Similar arguments have also been invoked to explain electron energy loss[14] and photoemission[15] spectra of Ni metal. Wendin[16] has applied many body techniques and arrived at similar conclusions in regard to resonances in satellite structure. Population of satellite levels via autoionization has also been noted in the photoemission spectra of Xe and Kr,[17] and ejected electron spectra of Mg,[18] Ca,[19] Sr,[20] and of Ba and Yb.[21] Analysis of these spectra also implies that Auger decay is a preferred channel for autoionization. With resonance photoemission now shown to be a feasible technique that yields large intensity changes, we can expect many applications in the elucidation of autoionization phenomena.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Figure 1. Total electron yield spectrum of atomic Ba. The data have been smoothed with a spline fitting routine.

Figure 2. Simplified energy-level diagram of relevant levels in BaI and BaII. Direct photoemission is denoted by slanted solid line and resonant photoemission by vertical solid lines, with favored channels shown by double lines. Minor channels are indicated schematically by dashed lines. Not drawn to scale.

Figure 3. Photoelectron spectra of atomic Ba taken at two autoionizing resonances. The assignments are from Ref. 5. The background has been subtracted and the data smoothed with a spline-fitting routine.

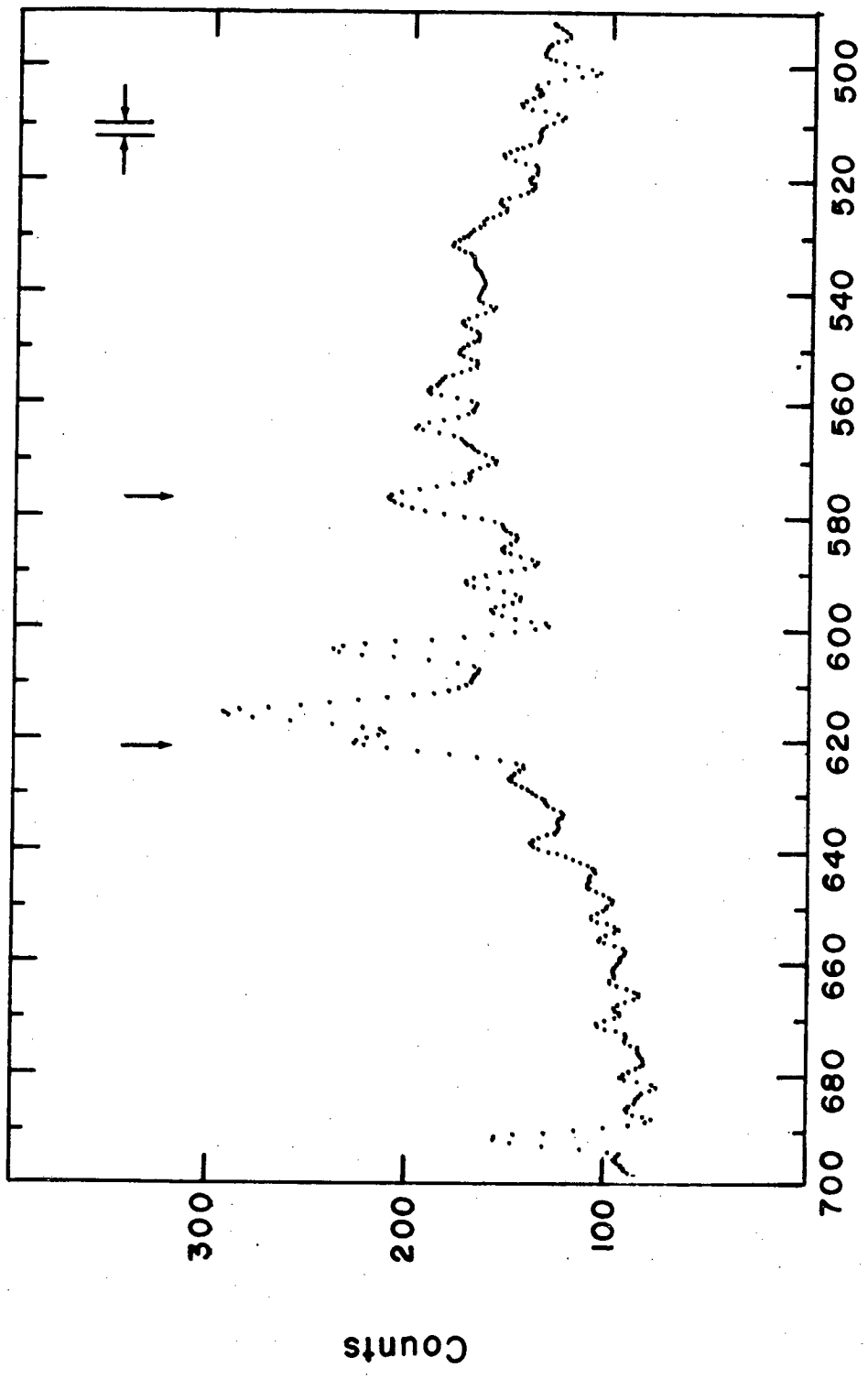

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Figure 1

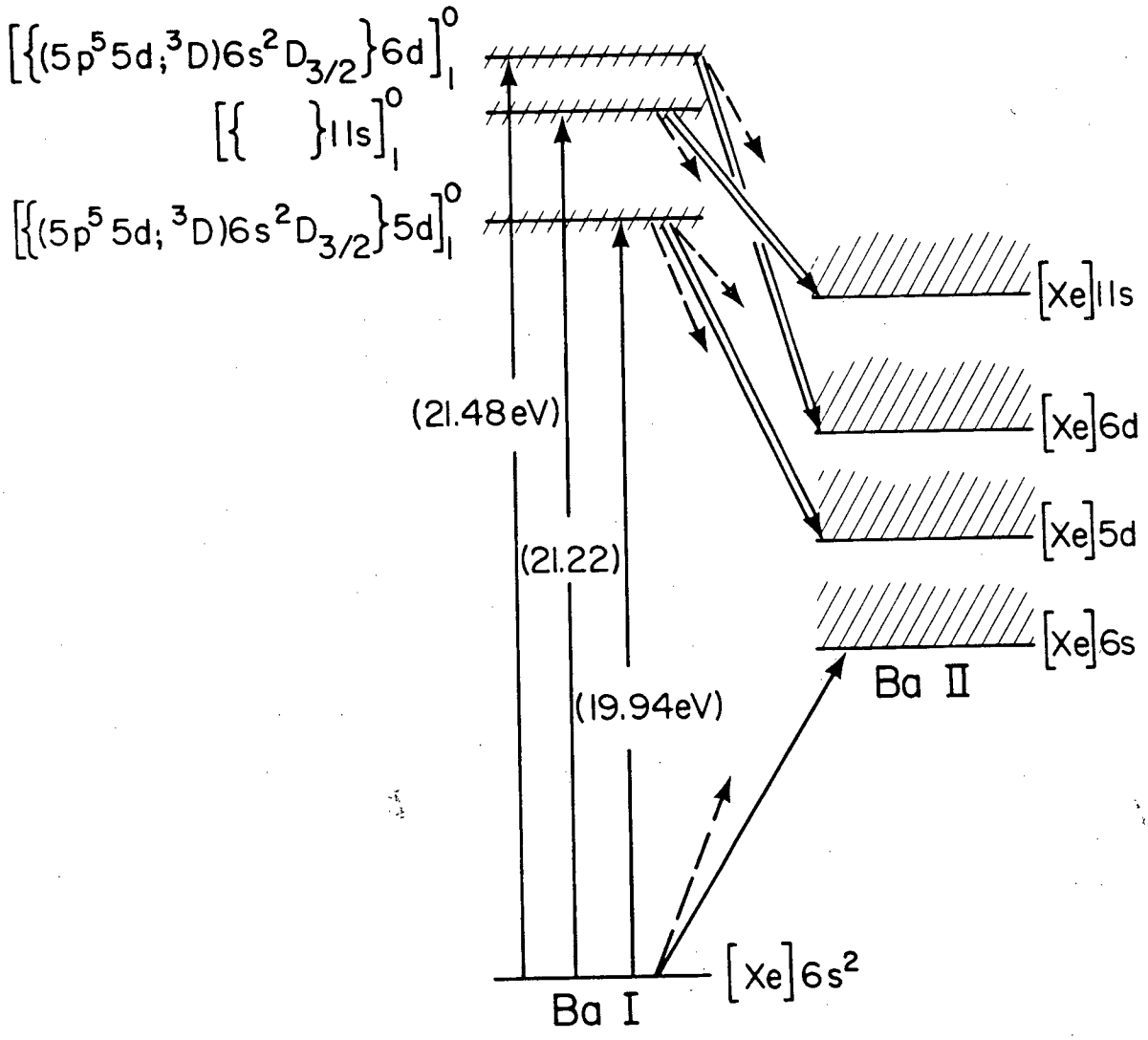

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Figure 2

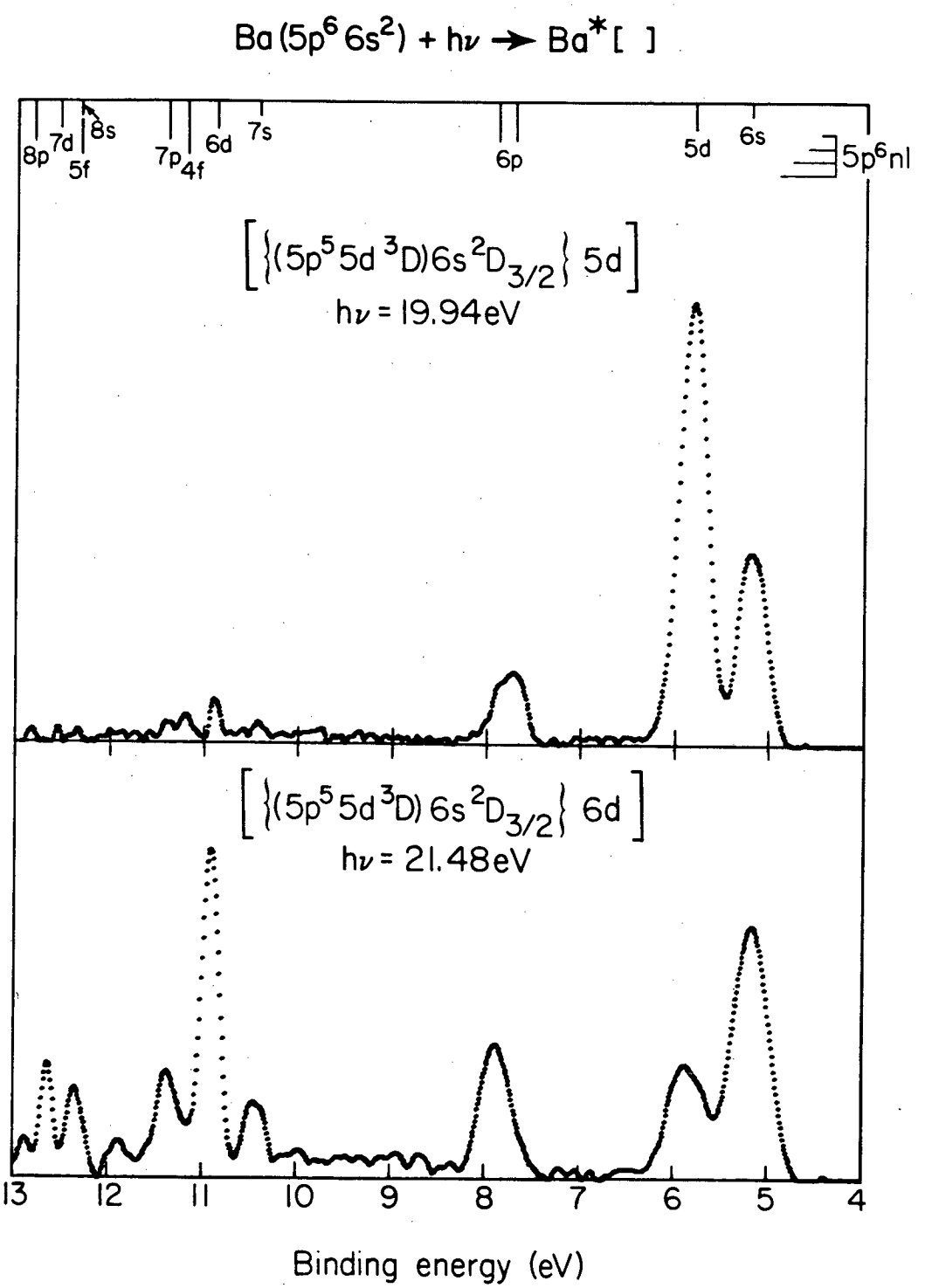

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Figure 3

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