Electron correlation effects in resonant multiphoton ionization of barium

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Angular distributions of energy-resolved photoelectrons and branching ratios for formation of the 6s and 5d configurations of Ba$^+$. Three excited states of barium were prepared and photoionized: (5d 6p)$^1P_1^o$, (5d 6p)$^3D_5^o$, and (6s 6p)$^3P_1^o$. For the (5d 6p)$^1P_1^o$ and (5d 6p)$^3D_5^o$ states, photoelectrons corresponding to the fine-structure levels of the 5d ion core were resolved. For the (6s 6p)$^3P_1^o$ state the photoelectron angular distributions have been measured as functions of the independently variable angle between the polarization vectors of the exciting and ionizing laser radiation pulses. Approximate theoretical expressions based on direct photoionization of the dominant electron configuration of each excited state are generally successful in accounting for the data, but specific discrepancies are noted. Significant intermediate-state interactions are required to account for details of the observations, and some final-state interactions are also implied.

I. INTRODUCTION

In some instances, for example, doubly excited helium atoms, correlation effects can dominate atomic-state properties to the extent that the approximate constants of motion are characteristic of the rotation, bending, and stretching motions of linear triatomic molecules. Significance of the valence pair of electrons, although not necessarily to the extent of moleculelike behavior, has been seen in excited rare-gas anions$^3$ and excited states of the alkaline earths.$^4$ This research is a step in a sequence of experimental studies that is intended to reveal the extent and character of electron correlation in low-lying, excited valence states of quasi-two-electron atoms.

Combined multiphoton-ionization and photoelectron spectroscopy (MPI-PES) has been an effective tool in the study of electron correlation in highly excited states of alkaline earths.$^9,10$ Both angular distributions of photoelectrons and the relative branching ratios to different ion cores are sensitive to the nature and extent of electron correlation. For the MPI-PES process in which a well-defined (excited) state is prepared and photoionized, both intermediate-state and final-state mixing can be important. Intermediate-state mixing of the (5d 7d)$^1D_2$ perturber in the (6s 6p)$^1D_2$ Rydberg-series states in barium resulted in increased 5d-ion-core production in the photoionization process.$^9$ Final-state mixing has been observed in the decay of well-defined autoionizing states.$^9$

This work is part of an investigation of low-lying excited states$^{11}$ and doubly excited bound states of the alkaline earths. Some or all of these states may well show a high degree of correlated electron motion. Multiconfiguration Hartree-Fock calculations have shown extensive mixing in the (6s 6p)$^3P_1^o$ state where the wave function is represented by 0.75(6s 6p)-0.66(5d 6p)-0.04(5d 4f).$^{12}$ Multichannel quantum-defect theory (MQDT) analysis$^3$ of the odd parity, $J=1$ states of barium has shown a mixing angle of $\sim 33^\circ$ connecting the (6snp)$^1P_1^o$ and (5dnp)$^3P_1^o$ channels; the corresponding triplet channels interact with a mixing angle of $\sim 12^\circ$. The bound, even parity, $J=0$ and $J=2$ states of barium are also strongly mixed.$^7,8$ For instance, MQDT analyses indicate that the (6snd)$^1D_2$ and (5ndn)$^1D_2$ channels have a mixing angle of $\sim 21^\circ$ (Ref. 8) and comparable channel mixing is expected for the corresponding continuum states. Indeed, preliminary results from multiconfigurational calculations using core pseudopotentials suggest that the molecular, triatomic description may be appropriate for low-lying excited states and even the ground states of all alkaline earths.$^13$

Our experimental method consists of preparing well-defined bound excited states, photoionizing them, and measuring the angular distributions of the resulting photoelectrons. For excited-state energies less than half of the ionization potential, different laser pulses are used to perform the excitation and the ionization. In this way, for each excited state, a set of photoelectron angular distributions is obtained, each of which is characterized by a single value of the (adjustable) angle $\eta$ between the polarization directions of the two photons (see Fig. 1). An appropriate parametric theoretical expression describes the photoelectron angular distributions; such a curve-fitting procedure has proved very successful for sodium$^{14}$ and lithium.$^{15}$

Previously we reported the photoelectron angular distributions$^{11}$ resulting from the process

$$ (ns^2)^1S_0^o \rightarrow (nsnp)^1P_1^o \rightarrow (ns)^2S_{1/2} + es, d \quad \text{(1)} $$

for the following states: Ca (4s 4p)$^1P_1^o$, Sr (5s 5p)$^1P_0^o$, Sr (5s 5p)$^3P_1^o$, Ba (6s 6p)$^3P_1^o$, and Ba (6s 6p)$^3P_0^o$. The photoelectron angular distributions were successfully reproduced by the theoretical formalism, especially with regard to differences in photoionization of the singlet and triplet states. We found that all (sp)$^3P_1^o$ singlet- and triplet-state photoelectron angular distributions illustrated the same systematic dependence on the angle $\eta$, much of which was predicted by the phenomenological formalism alone. Also, systematic $\eta$-dependent departures from expecta-
tions were observed; the triplet states show greater deviations than the singlets.\textsuperscript{11}

Here we report branching ratios in the production of different ion-core states and the angular distributions for energy-resolved photoelectrons produced by resonant excitation with one photon followed by ionization by a second photon (a \textquotedblleft 1+1\textquotedblright process), of the following states of barium: (5\textit{d} 6\textit{p})\textsuperscript{1}P\textsubscript{1}\textsuperscript{0}, (5\textit{d} 6\textit{p})\textsuperscript{1}D\textsubscript{1}\textsuperscript{0}, and (6\textit{s} 6\textit{p})\textsuperscript{1}P\textsubscript{1}\textsuperscript{0}. For the last state only the 5\textit{d}-ion-core photoelectrons are discussed in detail as the 6\textit{s}-ion-core photoelectrons have been described previously.\textsuperscript{11} For the (6\textit{s} 6\textit{p})\textsuperscript{1}P\textsubscript{1}\textsuperscript{0} intermediate state, different laser pulses perform the excitation and ionization so the dependence of the photoelectron angular distributions on the angle \(\eta\) between the directions of polarization of the two photons can be determined (see Fig. 1). Both (5\textit{d} 6\textit{p}) states have excitation energies greater than one-half the ionization potential so the same laser pulse performs excitation and ionization, and \(\eta\) is fixed at zero. For both (5\textit{d} 6\textit{p}) states we resolved photoelectrons from the two fine-structure components—(5\textit{d})\textsuperscript{2}D\textsubscript{5/2} and (5\textit{d})\textsuperscript{2}D\textsubscript{3/2}—of the 5\textit{d}-ion-core state. The branching ratios illustrate the utility of the configurational labels of these states; theoretical expressions dependent on these labels are developed using the irreducible Liouville representation methods. Comparisons and contrasts are described between experimental results and theoretical predictions. Significant intermediate-state interactions and also final-state interactions are suggested, and relativistic effects are seen to be important.

II. EXPERIMENTAL

Most of the details of our method for measuring angular distributions from MPI-PES have been given previously,\textsuperscript{11,14,15} so only those particular to the present experiments will be described here. A Quanta-Ray EXC-1 excimer laser (308 nm; XeCl mix) producing 5-ns pulses was used to pump a homemade tunable dye laser. For the (5\textit{d} 6\textit{p})\textsuperscript{1}P\textsubscript{1}\textsuperscript{0} and (5\textit{d} 6\textit{p})\textsuperscript{1}D\textsubscript{1}\textsuperscript{0} states the same laser pulse performed both the excitation and ionization so the angle \(\eta\) between the polarizations of the exciting and ionizing photons was constrained to be zero. For the (6\textit{s} 6\textit{p})\textsuperscript{1}P\textsubscript{1}\textsuperscript{0} experiments, the 308-nm laser pulse was used for the photoionization step. The polarizations of the two laser beams were rotated synchronously; thus these distributions are characterized by the adjustable angle \(\eta\). In each case the intensities of the laser beams were attenuated until the appropriate linear (or quadratic) dependence of the electron count rate on the laser power was attained. The wavelengths of the transitions to the intermediate states and the corresponding laser dyes (Exciton Corp.) used were (5\textit{d} 6\textit{p})\textsuperscript{1}P\textsubscript{1}\textsuperscript{0} (389 nm, 4,4'-bis-butylcloxy quaterphenyl, or BBQ, in p-dioxane), (5\textit{d} 6\textit{p})\textsuperscript{1}D\textsubscript{1}\textsuperscript{0} (413 nm, 4,4'-diphénylstilbène, or DPS, in p-dioxane), and (6\textit{s} 6\textit{p})\textsuperscript{1}P\textsubscript{1}\textsuperscript{0} (554 nm, Coumarin-540A in ethanol).

With the lasers used to carry out the photoionization processes described here, the excitation energy was always high enough that three states of the ion core were energetically accessible—the (6\textit{s})\textsuperscript{2}S\textsubscript{1/2}, the (5\textit{d})\textsuperscript{2}D\textsubscript{3/2}, and the (5\textit{d})\textsuperscript{2}D\textsubscript{5/2} states of Ba\textsuperscript{+}. The respective energies of the three groups of photoelectrons from photoionization of the various intermediate states were as follows: (5\textit{d} 6\textit{p})\textsuperscript{1}P\textsubscript{1}\textsuperscript{0}, 1.16, 0.56, and 0.46 eV; (5\textit{d} 6\textit{p})\textsuperscript{1}D\textsubscript{1}\textsuperscript{0}, 0.78, 0.18, and 0.084 eV; and (6\textit{s} 6\textit{p})\textsuperscript{1}P\textsubscript{1}\textsuperscript{0}, 1.05, 0.45, and 0.35 eV. Electron energy resolution was accomplished by time-offlight analysis over a 3.8-cm field-free path to the detector. For the states (5\textit{d} 6\textit{p})\textsuperscript{1}P\textsubscript{1}\textsuperscript{0}, (5\textit{d} 6\textit{p})\textsuperscript{1}D\textsubscript{1}\textsuperscript{0}, and (6\textit{s} 6\textit{p})\textsuperscript{1}P\textsubscript{1}\textsuperscript{0}, the time differences between adjacent electron peaks were 26 and 9 ns, 77 and 11 ns, and 33 ns, respectively, where for the last case the two groups of electrons from the 5\textit{d} ion core were not resolved.

The interaction region of the laser beams and the atomic barium beam is located at the center of two concentric copper spheres with screens to allow passage of the photoelectrons to the channeltron detector. The outer sphere was held at ground; the inner sphere was held at \(\sim 45\) V. A somewhat more negative potential was applied to a screen in front of the channeltron, thereby preventing electron transmission except during the application of a positive pulse to the channeltron screen. This pulse, triggered by a photodiode and adjusted to the appropriate width and delay using a pulse generator, allowed selective observation of the desired group of electrons.

III. THEORY

We measure the angular distribution of photoelectrons in a plane perpendicular to the propagation direction of the collinear, plane-polarized exciting and ionizing laser pulses. The angle between the photon polarization directions is \(\eta\) (see Fig. 1); \(\eta=0\) for a one-color two-photon ionization experiment.

Irreducible density-matrix methods\textsuperscript{16} in the Liouville representation\textsuperscript{17,18} are used to obtain photoelectron angular distribution equations.\textsuperscript{11,14,15} The extended Wigner-Eckart theorem\textsuperscript{16,18} gives the following angular distribution expression with the subscript \(L\) indicating the Liouville representation:
\[
\frac{d\sigma}{d\Omega} = \sum_{\text{all}} \langle \mathcal{E} (\Omega) | (l_f' j_f' j_p J M) L (l_f j_f j_p j_0, j_c j_a, 0, J) | | S | | (j_a j_a 0, 0, (11) P_1, (11) P_2, J) L (j_a j_a 0, 0, (11) P_1, (11) P_2, J M | \rho \rangle_L ,
\]

(2)

where \( l_f \) (\( l_f' \)) and \( s_f \) are the orbital and spin angular momenta of the continuum electron, respectively; \( j_c \) and \( j_a \) are the angular momenta of the final ionic core and the initial atomic state. The ket \( | \rho \rangle \) is the initial density state and the bra \( \langle \mathcal{E} (\Omega) | \) is the electron detector operator. We have included the multipole moments \( P_1 \) and \( P_2 \) of the exciting and ionizing photons in the initial density matrix but the results of photon absorption are included in the composite scalar scattering operator \( S \). Here, we have neglected the hyperfine interaction because it is not among the most important corrections in the following single-configurational analyses.

The multiple moments which can contribute to the photoelectron angular distributions are those which survive the projection of the initial density state onto the detector operator. Generally for our plane-polarized two-photon ionization of isotropic atoms, as depicted in Fig. 1, the angular distribution expression is given by

\[
\frac{d\sigma}{d\Omega} = C_{00} P_{00} + C_{20} P_{20} + C_{21} P_{21} + C_{22} P_{22} + C_{40} P_{40} \\
+ C_{41} P_{41} + C_{42} P_{42} ,
\]

(3)

where \( P_{LM} \) represents the associated Legendre polynomials with argument \( \cos \theta \), \( \theta \) is the angle between the polarization vector of the ionizing radiation and the momentum vector \( k_e \) of the photoelectron. For the special case \( \eta = 0 \) the general angular distribution expression [Eq. (3)] reduces to

\[
\langle l_f' j_f' j_p, l_f, j_f, j_p, j_0, J, S | | j_a, j_a 0, (11) P_1, (11) P_2, J \rangle 
\]

\[
= \sum_{l_f j_f} \left[ l_f, l_f', p_1, p_2 \right]^{1/2} \left[ p_1, j_p, j_p' \right]^{1/2} \left[ 1, j_f, j_f' \right]^{1/2} \left[ 0, p_1, p_1 \right]^{1/2} \langle l_f | R | (11) l_f' \rangle \langle (11) l_f' | R^* | l_f' \rangle ,
\]

(6)

where \( \langle l_f | R | (11) l_f' \rangle \) is the reduced matrix element of Hilbert space and \( [l_1, l_2] = (2l_1 + 1)(2l_2 + 1) \), etc.; \( j_p \) (\( j_p' \)) is the total angular momentum of the \( p \) electron. With appropriate detector operators, this expression reduces to a simpler form [Eq. (7)] if the fine-structure levels are unresolved or equivalently if an incoherent sum over the core angular momenta \( j_c \) is performed:

\[
\langle l_f' j_f' j_p, l_f, j_f, j_p, j_0, J, S | | j_a, j_a 0, (11) P_1, (11) P_2, J \rangle 
\]

\[
= [l_f, l_f', p_1, p_2]^{1/2} [p_1]^{1/2} [L] \left[ 1, L, 1 \right] \left[ 1, L, 1 \right] \langle l_f | R | (11) l_f' \rangle \langle (11) l_f' | R^* | l_f' \rangle .
\]

(7)
Because $\eta=0$ the general expression Eq. (4) applies. Equation (6) yields the coefficients for the $j_e=\frac{1}{2}$ core and

\[ j_e=\frac{1}{2} \text{ core photoelectrons} \text{ and Eq. (7) yields the corresponding coefficients for the (fine-structure) unresolved photoelectrons, all for the photoionization of the } (5d6p)^2P^+_1 \text{ state:} \]

\[
\begin{align*}
(5d)^2D_{3/2}^0 & \quad C_{00} = -\frac{1}{50} \sigma_2^2 + \frac{19}{125} \sigma_4^2 \\
(5d)^2D_{5/2}^0 & \quad C_{00} = \frac{1}{25} \sigma_2^2 + \frac{17}{350} \sigma_4^2 \\
5d & \quad C_{00} = \frac{1}{10} \sigma_2^2 + \frac{11}{50} \sigma_4^2 \\
(5d)^2D_{3/2}^0 & \quad C_{20} = -\frac{6}{53} \sigma_2 \sigma_4 \cos(d_2 - d_3) + \frac{1}{2} \sigma_4^2 \\
(5d)^2D_{5/2}^0 & \quad C_{20} = -\frac{4}{23} \sigma_2 \sigma_4 \cos(d_2 - d_3) + \frac{1}{14} \sigma_4^2 \\
5d & \quad C_{20} = -\frac{2}{5} \sigma_2 \sigma_4 \cos(d_2 - d_3) + \frac{1}{14} \sigma_4^2 \\
(5d)^2D_{3/2}^0 & \quad C_{40} = -\frac{48}{375} \sigma_2^2 \\
(5d)^2D_{5/2}^0 & \quad C_{40} = \frac{18}{625} \sigma_2^2 \\
5d & \quad C_{40} = -\frac{6}{175} \sigma_2^2.
\end{align*}
\]

From the same equations, the corresponding coefficients for photoelectrons leaving the $j_e=\frac{1}{2}$ and $\frac{3}{2}$ cores and for the (fine-structure) unresolved 5d-ion-core photoelectrons due to photoionization of the $(5d6p)^2D^+_1$ state are obtained:

\[
\begin{align*}
(5d)^2D_{3/2}^0 & \quad C_{00} = \frac{1}{50} \sigma_2^2 + \frac{33}{125} \sigma_4^2 \\
(5d)^2D_{5/2}^0 & \quad C_{00} = \frac{1}{75} \sigma_2^2 + \frac{57}{350} \sigma_4^2 \\
5d & \quad C_{00} = \frac{1}{30} \sigma_2^2 + \frac{13}{150} \sigma_4^2 \\
(5d)^2D_{3/2}^0 & \quad C_{20} = -\frac{2}{23} \sigma_2 \sigma_4 \cos(d_2 - d_3) + \frac{1}{2} \sigma_4^2 \\
(5d)^2D_{5/2}^0 & \quad C_{20} = -\frac{4}{23} \sigma_2 \sigma_4 \cos(d_2 - d_3) + \frac{1}{42} \sigma_4^2 \\
5d & \quad C_{20} = -\frac{2}{73} \sigma_2 \sigma_4 \cos(d_2 - d_3) + \frac{1}{2} \sigma_4^2 \\
(5d)^2D_{3/2}^0 & \quad C_{40} = -\frac{516}{375} \sigma_2^2 \\
(5d)^2D_{5/2}^0 & \quad C_{40} = \frac{878}{375} \sigma_2^2 \\
5d & \quad C_{40} = -\frac{6}{175} \sigma_2^2.
\end{align*}
\]

The breakdown of the independent-particle model is clearly indicated just from the appearance of Ba$^+$ in its 5d state, in the photoionization of the $(6s6p)^1P^+_1$ state of barium. Either admixture of the 5d6p configuration (or others) in the intermediate $1P^+_1$ state or intra-atomic electron scattering in the final state would account qualitatively for the Ba$^+$ 5d ions. That is, both intermediate- and final-state mixing can contribute to the presence of a product arising, apparently, from two-electron excitation. The angular distributions of photoelectrons associated with the 5d ion core are relatively structureless, so a unique quantitative analysis is quite difficult. Nevertheless, insight can be gained by examining the consequences of intermediate-state mixing. For the process

\[
(6s^2)^1S_0 \rightarrow (6s6p + 5d6p)^1P^+_1 \rightarrow (5d)^2D^+_1 + e^-d
\]

the reduced matrix element for the direct photoionization of the $(5d6p)$ configuration is

\[
\langle (l_f|l_f'J,(2200,J)||S||(J_dJ_d)0,(11)P_1,(11)P_2,J) = [l_f,l_f',P_1,P_2]^{1/2} \begin{pmatrix}
1 & 1 & P_1 \\
1 & 1 & P_2 \\
3[P_1]^{1/2} & l_f & l_f' & J \\
2 & 1 & 1 \\
2 & 1 & 1 \\
0 & P_1 & P_1
\end{pmatrix}
\]

\]

In accordance with our qualitative examination of process (10) we do not list the explicit form of the coefficients for Eq. (3) but we will discuss Eq. (11) in Sec. V.

**IV. DATA ANALYSIS**

Table I lists the branching ratios to the 6s- and 5d-ion-core states in the photoionization of the $(5d6p)^1P^+_1$, $(5d6p)^3D^+_1$, and $(6s6p)^1P^+_1$ states of barium; in the first two cases the photoelectrons from the fine-structure doublet of the 5d ion core were resolved.

For the $(5d6p)$ photoionization experiments $\eta=0$ so the general expression describing the photoelectron angular distributions is given by Eq. (4). Figure 2 shows the photoelectron angular distributions for the photoionization of the $(5d6p)^1P^+_1$ state [Figs. 2(a) and 2(c)] and of the $(5d6p)^3D^+_1$ state [Figs. 2(b) and 2(d)]. Figures 2(a) and 2(b) correspond to the production of the $(5d)^2D_{5/2}$ ion core state and Figs. 2(c) and 2(d) correspond to the production of the $(5d)^2D_{3/2}$ ion core state. The solid curves represent least-squares fits of the individual curves to the general expression Eq. (4). The dashed curves represent the best simultaneous fit of both the $(5d)^2D_{3/2}$ and $(5d)^2D_{5/2}$ data to the configurational models for the $(5d6p)^1P^+_1$ and $(5d6p)^3D^+_1$ states. For the configurational model the coefficients for Eq. (4) are given by Eq. (8) for the $(5d6p)^1P^+_1$ state and by Eq. (9) for the $(5d6p)^3D^+_1$ state. Table II lists the coefficients corresponding to a polynomial analysis using Eq. (4) with unconstrained coefficients for the angular distributions shown in Fig. 2. Also listed in Table II are the values of the parameters corresponding to the configurational analysis: $\sigma_d/\sigma_d$—the ratio of radial matrix elements, $\cos(d_2 - d_3)$—the cosine of the relative phase shifts for the $s$ and $d$ partial waves, and the sign of their product. In the photoionization of the $(5d6p)^3D^+_1$ state the photoelectrons corresponding to the $(5d)^2D_{3/2}$ ion state were produced with an excess energy of only 84 meV. This very low excess energy made it difficult to measure the angular distributions and also may introduce uncertainty into the branching ratio. Accordingly, in Tables I and II we have as-
Table I. Branching ratios to the (6s)²S_{1/2} and (5d)²D_{3/2,5/2} states of Ba⁺ in the photoionization of the (5d 6p)³P_{1/2}^0, (5d 6p)³D_{3/2}^0, and (6s 6p)³P_{1/2}^0 states of Ba.

<table>
<thead>
<tr>
<th>State</th>
<th>s core</th>
<th>d core</th>
<th>²D_{1/2}</th>
<th>²D_{3/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5d 6p)³P_{1/2}^0</td>
<td>7</td>
<td>93</td>
<td>49</td>
<td>51</td>
</tr>
<tr>
<td>(5d 6p)³D_{3/2}^0</td>
<td>4</td>
<td>96</td>
<td>88</td>
<td>12(±12%)^b</td>
</tr>
<tr>
<td>(6s 6p)³P_{1/2}^0</td>
<td>83</td>
<td>17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^a Typical error is roughly ±3%.
^b We list a substantially larger error for the very low energy photoelectrons (84 meV) and of course errors for all branching percentages for the (5d 6p)³D_{3/2}^0 state must be adjusted accordingly.

signed large uncertainties to the corresponding parameters.

Figure 3 compares the photoelectron angular distributions for the 5d-ion-core photoelectrons (solid curves) and the 6s-ion-core photoelectrons (dashed curves) in the photoionization of the (6s 6p)³P_{1/2}^0 state of barium. The solid curves representing the 5d-ion-core photoelectron angular distributions were obtained by a least-squares fit to the general expression Eq. (3), but we do not list the corre-
sponding coefficients because of the inherent error in a six-parameter fit of relatively structureless (ten-channel) angular distributions. The dashed curves describing the s-core data result from a theoretical analysis described elsewhere.11

Figure 4 shows the photoelectron angular distributions corresponding to the production of the 6s ion core state for the photoionization of the following states of barium: (a) (5d 6p)³D_{3/2}^0; (b) (6s 6p)³P_{1/2}^0; (c) (5d 6p)³P_{3/2}^0; and (d) (6s 6p)³P_{3/2}^0. The asymmetry of the data shown in the (6s 6p)³P_{1/2}^0 curve results because η = 172° (as opposed to 180°). The solid curves of Figs. 4(a)−4(c) represent least-squares fits to the data based on Eq. (4), and the solid curve of Fig. 4(d) is a simulation of the expected angular distribution based on the data shown for η = 172° as well as on other measurements.11 The corresponding parameters for the (η = 0) 6s-ion-core angular distributions are listed in Table III.

V. RESULTS AND DISCUSSION

Several symptoms of the breakdown of the independent-particle model have been observed in these two-photon ionization experiments. The one-photon excitations of the ground state to the doubly excited (5d 6p)³P_{1/2}^0 and (5d 6p)³D_{3/2}^0 states are forbidden within the independent-particle model (and are spin forbidden as well). In the photoionization step, branching paths corresponding to two-electron excitations were observed for the (5d 6p)³P_{1/2}^0, (5d 6p)³D_{3/2}^0, and (6s 6p)³P_{1/2}^0 states of barium. In photoionization the two-electron excitation paths compete with the one-electron excitations; only the latter are consistent with the independent-particle model. Our measured branching ratios are largely independent of the different degeneracies of the s and d ion cores. Such weak dependence is due here to the forms of the appropriate detector and projection operators. We observed significantly larger branching into the 5d core channel from the (6s 6p)³P_{1/2}^0 state (17%) than branching into the 6s core channel from either the (5d 6p)³P_{1/2}^0 state (7%) or the (5d 6p)³D_{3/2}^0 state (4%). This observation is consistent with the finding that, for the alkaline earths, the J = 1 odd-particle singlet channels appear to be more strongly mixed with one another than the triplet channels.1 Even though we observe a substantial breakdown of the independent-particle model in our photoionization experiments, the utility of the configuration label is evident in that it
TABLE II. The least-squares-fit values for the Legendre polynomial Eq. (4) are listed as functions of the particular photoionized state and the ion core populated. Also listed are the configurational analysis parameters \( \sigma_s/\sigma_d \)—the ratio of the radial matrix elements, \( \cos(\delta_s - \delta_d) \)—the cosine of the relative phase shift, and the sign of their product for the \( s \) and \( d \) partial waves. Values of these parameters were obtained by simultaneous fit of the \( (5d)^2D_{3/2} \) and \( (5d)^2D_{5/2} \) distributions using Eq. (8) for the \( ^2P \) state and Eq. (9) for the \( ^2D \) state.

<table>
<thead>
<tr>
<th>State photoionized</th>
<th>Ion core</th>
<th>Polynomial analysis</th>
<th>Configurational analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (5d \ 6p)^3P_1 )</td>
<td>( (5d)^2D_{3/2} )</td>
<td>( P_{20} )</td>
<td>( P_{40} )</td>
</tr>
<tr>
<td>( (5d \ 6p)^3P_1 )</td>
<td>( (5d)^2D_{3/2} )</td>
<td>1.48±0.03</td>
<td>-0.10±0.04</td>
</tr>
<tr>
<td>( (5d \ 6p)^3P_1 )</td>
<td>( (5d)^2D_{3/2} )</td>
<td>0.55±0.03</td>
<td>-0.08±0.04</td>
</tr>
</tbody>
</table>

FIG. 3. Photoelectron angular distributions resulting from the processes \( (6s^2)^1S_{0} \rightarrow (6s \ 6p)^1P_1^0 \rightarrow (5d)^2S_{1/2} + es, d \) (dashed curves) and \( (6s^2)^1S_{0} \rightarrow (6s \ 6p)^1P_1^0 \rightarrow (5d)^2D_{1/2,3/2} + es, d \) (solid curves) for different values of \( \eta \): (a) 26° (dashed), 29° (solid); (b) 65° (dashed), 59° (solid); (c) 97° (dashed), 97° (solid); (d) 136° (dashed), 134° (solid). See Fig. 1 for definitions of \( \theta \) and \( \eta \).

FIG. 4. Photoelectron angular distributions corresponding to the process \( (6s^2)^1S_{0} \rightarrow (5d \ 6p)^1P_1^0 \rightarrow (6s)^2S_{1/2} + es, d \) for various bound excited states of Ba: (a) \( (5d \ 6p)^3D_1^0 \); (b) \( (6s \ 6p)^3P_1^0 \), \( (5d \ 6p)^3P_1^0 \), \( (5d \ 6p)^3P_1^0 \), \( (6s \ 6p)^3P_1^0 \); (d) \( (6s \ 6p)^3P_1^0 \). For (a), (b), and (c) \( \eta=0' \) and the solid curves represent least-squares fits to the data; the solid curve of (d) is a simulation of the expected angular distribution for \( \eta=0' \) based on the data shown for \( \eta=172' \) as well as on other measurements.
TABLE III. Analyses of the angular distributions corresponding to the production of the 6s ion core for $\eta=0$ are listed. Least-squares-fit values for the Legendre polynomial Eq. (4) are listed for the (5d 6p)$^3D^+_1$, (6s 6p)$^3P^+_1$, and (5d 6p)$^3P^+_1$ states. Reliable estimates of the corresponding parameters for the (6s 6p)$^3P^+_1$ state are also given.

<table>
<thead>
<tr>
<th>State photoionized</th>
<th>$P_{20}$</th>
<th>$P_{40}$</th>
<th>$P_{60}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5d 6p)$^3D^+_1$</td>
<td>0.87±0.10</td>
<td>0.06±0.08</td>
<td>1</td>
</tr>
<tr>
<td>(6s 6p)$^3P^+_1$</td>
<td>2.27±0.02</td>
<td>1.45±0.05</td>
<td>1</td>
</tr>
<tr>
<td>(5d 6p)$^3P^+_1$</td>
<td>0.38±0.09</td>
<td>−0.44±0.06</td>
<td>1</td>
</tr>
<tr>
<td>(6s 6p)$^3P^+_1$</td>
<td>0.61±0.05</td>
<td>−0.81±0.06</td>
<td>1</td>
</tr>
</tbody>
</table>

*\(\eta=0\) parameters estimated from $\eta=172^\circ$ data shown in Fig. 4(d) and other data (Ref. 11).

Correctly predicts the dominant ion core branching for all three cases (see Table I).

Previously, we were successful in analyzing photoelectron angular distributions from the photoionization of five (sp)$^1P^+_1$ and (sp)$^3P^+_1$ states of calcium, strontium, and barium. However, this analysis did not necessitate consideration of electron configurations. In fact, a parametric configurational analysis is almost precluded for production of the s ion core in the photoionization of (sp) states. We are able to employ configurational models to describe the angular distribution of photoelectrons associated with the 5d ion core.

The photoionization process which yields various ion cores is not a direct probe of the configurational expansion coefficients of the bound state because the branching ratios depend on the cross section for photoionization of each different configuration as well as on the amplitude of each configuration. If a direct photoionization process dominates the production of the 5d ion core then an analysis based on a single configuration may represent a reasonable first approximation.

Using the (5d 6p) configuration to represent the $^3P^+_1$ and $^3D^+_1$ states and assuming that the photoionization event is a direct process in which the photon operates only on the orbital angular momentum of the 6p electron, we obtain the photoelectron angular distribution coefficients given in Eqs. (8) and (9), respectively. One theoretical prediction is that only the (5d 6p)$^3D^+_1\rightarrow$(5d)$^2D^3_1/2+e_d$ photon-electron angular distributions should have a large, negative coefficient for the $P_{40}$ term; in fact, this is what the data show (Fig. 2). These (normalized) angular distributions are described by two parameters so it is quite significant that there is agreement between theory and experiment for one of the parameters, the coefficient of the $P_{40}$ term. The magnitude and sign of the $P_{20}$ coefficient cannot be predicted without calculation of the radial integrals and of the phase shifts for the s and d partial waves; this is true in general and is not dependent on our model.

By using the least-squares-fit values of the parameter $|\alpha_s/\alpha_d|$ in the $P_{90}$ coefficients of Eqs. (8) and (9), branching percentages to the (5d)$^2D^3_1/2$ and (5d)$^2D^3_3/2$ ion-core states can be obtained. The (parametric) theoretical values versus the experimental values for the (5d 6p)$^3P^+_1$ and (5d 6p)$^3D^+_1$ states are 61%:39% theory, 49%:51% experimental, and 71%:29% theory, 88%:12% experimental, respectively. In spite of the quantitative discrepancies, the relative trend in the branching ratios is predicted.

Some important, general characteristics of the angular distributions of photoelectrons corresponding to the 5d ion core from the photoionization of the (5d 6p) states are understandable in terms of a single-configurational analysis. However, it is quite clear from Fig. 2 that the data are not accurately reproduced by the single-configuration model. One distinct difference between experiment and the model’s prediction is the relative anisotropy in the (5d 6p)$^3P^+_1$ curves for the (5d)$^2D^3_1/2$ and (5d)$^2D^3_3/2$ ion core production. The theoretical form predicts very similar anisotropies for these curves regardless of the parameter values; the experimental curves show substantially greater anisotropy for the (5d)$^2D^3_3/2$ curve. The ion core and the photoelectron compete for the anisotropy which results from absorption of linearly polarized photons. In general, larger $j$ values compete more effectively for the anisotropy so the photoelectron angular distributions correspond to larger final-state angular momenta of the ion core are flatter. Both (5d 6p)$^3P^+_1$ and (5d 6p)$^3D^+_1$ data sets illustrate this effect while the single-configurational model for the (5d 6p)$^3P^+_1$ photoionization does not. Projection into the (5d 6p) configuration of the $^3P^+_1$ state produces a rather isotropic orbital component of the p electron (considering that the 5d ion core is unobserved) so the photoelectron angular distributions are dependent primarily on the polarization of the second photon and hence independent of the $j$ value of the core [see Eq. (6)]. We can show, by including an L (total orbital angular momentum) or j dependence in the photoionization step of the (5d 6p)$^3P^+_1$ state, that the anisotropy for the (5d)$^2D^3_3/2$ case may be larger than for the (5d)$^2D^3_1/2$ case (We shall not prove this here because the resulting expressions contain a large number of parameters and the angular momentum algebra is rather complicated.)

The production of the 5d ion core (17%) in the photoionization of (6s 6p)$^3P^+_1$ state is formally a two-electron excitation and thus indicates a breakdown of the independent-particle model, either in the intermediate or final state and perhaps both. The corresponding angular distributions are characterized by several distinct features (see Fig. 3): they are $\eta$ independent, relatively flat, and have their maximum at $\theta=90^\circ$. These angular distributions can be represented roughly by $d\sigma/d\Omega \sim P_{90} + \beta P_{20}$ (where $\beta$ is the asymmetry parameter) as opposed to the general expression Eq. (3). This implies photoionization of an isotropic electron in the intermediate state; we therefore consider the extreme case in which all mixing occurs in the intermediate state [process (10)]. The correspond-
ing angular momentum algebra is given in Eq. (11). The salient feature is that the Wigner 9-j symbol representing projection into the (5d 6p) configurational component of the intermediate state has the effect of reducing the anisotropy of the p electron by a factor of 10 compared to that of the (6s 6p) configuration. Thus, the projection into the (5d 6p) configuration produces a nearly isotropic p electron similar to the (5d 6p)\(^3\)P\(_1^o\) model described earlier, and very little \(\eta\) dependence would be expected in the angular distributions. We do not list detailed results of this approximate model (only intermediate-state interaction) because the principal feature of \(\eta\) independence is seen directly in the data. With intermediate-state projection into the 5d-containing configuration, the anisotropy of the ionizing photon is transferred to the continuum electron so flat angular distributions are not generally expected. However, flattened distributions are consistent with the maxima at \(\theta=90^\circ\) indicating partial cancellation of terms in the \(C_{20}\) coefficient.

The occurrence of 5d-ion-core production in the photoionization of the (6s 6p) state can also result from final-state mixing. This process can be considered as an inelastic (half) scattering of a relatively high-energy continuum electron and the 6s ion core producing a lower-energy continuum electron and the 5d ion core. In this scattering process much of the anisotropy of the continuum electron is transferred to the 5d ion core so the photoelectron angular distributions are considerably flattened, but the anisotropy which remains is \(\eta\) dependent. The \(\eta\) independence of the 5d-ion-core photoelectron angular distributions implies that intermediate-state mixing is important in the production of the 5d ion core in the photoionization of the (6s 6p)\(^1\)P\(_1^o\) state. Additionally, the relatively structureless distributions are consistent with some contribution to the 5d-ion-core production from final-state interaction.

The photoionization of the (5d 6p)\(^3\)P\(_1^o\) and (5d 6p)\(^3\)D\(_1^o\) states results in the production of the 6s ion core in the amounts 7% and 4%, respectively; the rest of the events lead to the 5d-ion-core production. In the absence of spin-orbit mixing in the intermediate state and in the photoionization step, these photoelectron angular distributions (where \(\eta=0\)) must be described by the \(l=2, m=\pm 1\) continuum wave, that is, by the \(d_{2s}\) wave\(^{11}\) which has nodes at \(\theta=0^\circ\) and \(90^\circ\). In the formation of a state by a photon which is described by the \(|JM_f=10\rangle\) angular momentum state, the orientation of the orbital (\(L\)) and spin (\(S\)) angular momenta are given by the Clebsch-Gordan terms \(|10\rangle LM_f SM_f\rangle\) where \(M_f\) represents the projection of angular momentum \(i\). Thus for formation of the \(^3P\(_1^o\) state by a \(|10\rangle\) photon, the effective orbital angular momentum state is \(|1\pm 1\rangle\) because \(|10\rangle 1010\rangle=0\). In the photoionization by a second \(|10\rangle\) photon \(M_f\) remains equal to \(\pm 1\), so for production of the ion core in its \(s\) state, the continuum electron is the \(d_{1s}\) wave. In the formation of the \(^3D\(_1^o\) state by a \(|10\rangle\) photon, the orbital description includes the \(|2\pm 1\rangle\) and the \(|20\rangle\) angular momentum states. In the photoionization of the \(^3D\(_1^o\) state with a \(|10\rangle\) photon, only a \(d\) wave is formed; and because the Clebsch-Gordan term \(|20\rangle 1010\rangle=0\), the resulting \(d\) wave is also the \(d_{1s}\) wave.
wave production is quite large. This reasoning applies to the configurational analyses of the \((5d\,6p)^3P^\pi\) and \((5d\,6p)^3D^\pi\) states (see Table II) and to the intermediate-state mixing analysis of the \(5d\)-ion-core production in the photoionization of the \((6s\,6p)^3P^\pi\) state. In all three cases the ratio \(\alpha_e/\alpha_d \sim 3.5\), which is very large and probably indicates inadequacies of the respective models. Thus, the magnitude of the apparent \(s\)-wave production can be used to indicate the accuracy of the model in describing the photoionization process.

VI. SUMMARY

The measurement of branching ratios to different ion cores and of the photoelectron angular distributions is a step toward determining the nature and extent of electron correlation effects in bound and continuum states. We find that some of the features of the photoionization data can be understood in terms of a direct photoionization process acting upon a single configuration, but as expected, such an oversimplified model has only limited predictive ability. The significant impact of intermediate-state mixing on our experimental observations is clearly indicated.

When comparing angular distributions corresponding to the production of the same final ion-core state by the photoionization of different intermediate states, we find that photoelectrons which represent the dominant branching tend to have more anisotropic angular distributions. For the \((5d\,6p)^3P^\pi\) and \((5d\,6p)^3D^\pi\) states resolution of the ion fine-structure levels in MPI-PEES was achieved and for the \((6s\,6p)^3P^\pi\) state variable-\(\eta\) MPI-PEES was applied; these experimental methods combined with the theoretical methods of the irreducible Liouville representation constitute a powerful probe of electron dynamics in the photoionization process.

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