Strong Angular Correlation of Bound Electrons Revealed by Resonant Two-Color, Three-Photon Ionization of Barium

Oliver C. Mullins, John E. Hunter, III, James S. Keller, and R. Stephen Berry
Department of Chemistry and The James Franck Institute, University of Chicago, Chicago, Illinois 60637
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The $5d7s\,^1D_2$ state of barium was resonantly prepared and photoionized. Branching ratios and photoelectron angular distributions were measured for the $6s$ and $5d$ core states of Ba^+. Strong configuration mixing is indicated for the $5d7s\,^1D_2$ state. The $6s$ core is produced in 43% of the ionization events, and the $5d$-core photoelectron angular distributions show fourth and sixth spherical harmonics in violation of independent-particle predictions.

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Electron correlation can affect and even dominate atomic-state properties. Photon interactions with state-selected excited atoms have been widely used to probe one expression of this, namely configuration mixing, both via emission lifetimes[1-3] and through multiphoton-ionization–photoelectron spectroscopy (MPI-PES).[4-6] MPI-PES of Ba atoms has probed continuum-state interactions by the observation of decays of autoionizing states.[7,8] Bound-state interactions have been observed through the influence of "perturbers" on Rydberg series.[4,5] Our interests[6,9] have been directed toward low-lying states of the quasi-two-electron alkaline earths. The prime question is the extent of valence-shell correlation in these states, and whether they may even exhibit "molecular-like" correlation[10,11] as has been indicated by recent calculations.[12]

Here, we report branching ratios and photoelectron angular distributions for the photoionization of the $5d7s\,^1D_2$ state[13] of barium. In these experiments three ion-core states are energetically accessible—the $6s\,^2S_{1/2}$, $5d\,^2S_{3/2}$, and $5d\,^2D_{5/2}$. We have measured the dependence of both branching ratios and angular distributions on the experimentally adjustable polarization of the $5d7s\,^1D_2$ state. The configuration label of the $5d7s\,^1D_2$ state implies that the photoelectrons for both $5d$ cores should be in p waves, yielding angular distributions of the form $1+\beta P_{20}(\cos\theta)$. This is not at all what we observe for these electrons; we report what is to our knowledge the first observation of electron correlation inducing spherical harmonics above the quadrupole in photoelectron angular distributions, namely the P_{4M} and P_{6M} terms. The broadest significance of this finding is the demonstration of an extreme observable consequence of very strong correlation, in a few-body system well enough understood to be analyzed.

Two-color, three-photon ionization was one experimental method used to probe the $5d7s\,^1D_2$ state. A N_2 laser was used to pump two tunable dyes; the first tuned to 553.7 nm to excite the $6s6p\,^1P_1^\circ$ state, and the second tuned to 635.5 nm to excite from the $6s6p\,^1P_1$ state to the $5d7s\,^1D_2$ state. The relatively powerful 635.5-nm laser pulse which was delayed by ~ 8 ns, a time interval greater than the dye-laser pulse width, was also used to photoionize the $5d7s\,^1D_2$ state. The two collinear laser beams were plane-polarized with an arbitrary known angle η between the axes. The electron signal, maintained linear in laser power, was detected in a plane perpendicular to the laser beams. In other experiments, one-color, three-photon ionization was performed by a resonant two-photon $\lambda = 591.8$ nm excitation of the $5d7s\,^1D_2$ state from the ground state. A third photon from the same laser pulse performed ionization. Time-of-flight analysis separated the different groups of photoelectrons; in the two-color, three-photon experiment electrons corresponding to the fine structure components of the $5d$ core were resolved.

The measured branching ratios to the three cores in our two-color experiments are 43% $6s\,^2S_{1/2}$, 15% $5d\,^2D_{3/2}$, and 42% $5d\,^2D_{5/2}$, with uncertainties of about 4%. No detectable dependence of the branching ratio on η was found. The one-color, three-photon ionization experiment showed a similar large branching to the $6s$ core.

It is important to establish the relative contributions of bound-state and continuum-state interaction to the branching ratios. The very large branching to the s core is quite unlikely to result from direct scattering of the $5d\epsilon(p,f)$ close-coupled channels into the $6s\epsilon(p,f)$ collision channels,[4,6] but resonances in the continuum can greatly affect branching ratios. There would have to be two resonances fortuitously located to account for the large and similar s-core branching in both the two-color, three-photon and one-color, three-photon ionization experiments which yield continuum states 1162 cm^{-1} apart. Such resonances would have to be $J=3$ resonances; $J=1$ resonances would greatly reduce higher spherical harmonics in the angular distributions (see Fig. 1 and Table I) and $J=2$ resonances cannot be excited for $\eta=0$ because of the Clebsch-Gordan factor $\langle 20|2010\rangle = 0$. Finally, in the energy range of our final state, resonances readily accessible from the $^1D_2$ state by one-photon absorption are expected to be much more widely spaced than

$1200\ \mathrm{cm}^{-1}$. Therefore, we attribute the large $6s$-core branching to intermediate-state interactions in the $5d7s\,{}^1D_2$ state. The dominance of bound-state interactions in determining branching ratios and angular distributions to different ion cores has been observed previously[4–6] in experiments of similar design.

In the production of the s core in photoionization, the photon can be considered to interact with the total orbital angular momentum of the bound state; this process yields a unique final state. Therefore, theoretical angular-distribution expressions can be developed which follow immediately from the term symbol of the state being photoionized,[9] provided that symbol is valid.

We develop parametric theoretical expressions for the angular distributions of photoelectrons from irreducible tensorial forms[14] of a Liouville representation.[15–17] For these three-photon ionization experiments the general form of the angular distribution can be written as

$$\frac{d\sigma}{d\Omega}=\sum_{L\,(\mathrm{even})}^{6}\sum_{M\leq L}^{2} C_{LM}P_{LM}(\cos\theta), \tag{1}$$

where the $P_{LM}(\cos\theta)$ are associated Legendre polynomials and θ is the angle between the momentum vector of the photoelectron and the polarization axis of the ionizing photon. For the distributions corresponding to the $6s$ core, we have included the hyperfine interaction only in the $6s6p\,{}^1P_1^{\circ}$ state.[9] In addition, we approximate the anticipated spin-orbit coupling in the intermediate state and in photoionization by performing a weighted sum of the corresponding singlet- and triplet-distribution expressions. No coherences occur between the singlet and triplet expressions because only the isotropic component of the electron spin contributes to our observations. The corresponding coefficients of Eq. (1) for $6s$-core angular distributions will be published subsequently and are available on request.

The coefficients are parametrized by σ_l and δ_l, respectively the radial integral and the phase shift corresponding to the lth partial wave. We do not allow for spin-multiplicity dependence in these parameters.

Angular distributions for photoelectrons corresponding to the production of the $6s$ ion core were measured as functions of η. Least-squares fits of the distributions to the coefficients of Eq. (1) yield these values of the microscopic parameters: $|\sigma_p/\sigma_f| = 1.38 \pm 0.08$, $|\cos(\delta_p-\delta_f)| = 0.88 \pm 0.02$ with $(\sigma_p/\sigma_f)\cos(\delta_p-\delta_f) > 0$, and the amount of triplet mixing is $(8.9 \pm 4.6)\%$.

The fit of the data to a self-consistent set of parameters is quite good. The triplet mixing of only 9% indicates that the assumption of multiplicity-independent parameters is reasonably sound. The branching ratios and angular distributions corresponding to the $6s$-core production indicate that the $5d7s\,{}^1D_2$ state is a strongly mixed state with a substantial contribution from the $6snd\,{}^1D_2$ channel.

The configurational assignment of $5d7s$ for the ${}^1D_2$ state results in several predictions concerning the photoionization process leaving Ba^+ in a $5d$ level. This configurational label implies that $5d$-core photoelectron angular distributions should be dominated by an η-independent, large (~ 2) value of the coefficient C_{20} and that the coefficients $C_{2M\neq 0}$, C_{4M}, and C_{6M} should be nearly zero. If the $5d7s$ configuration dominates, only significant spin-orbit coupling in the photoionization step (but not spin-orbit coupling in the bound state) could appreciably reduce the expected magnitude of C_{20} much below 2; however, s-core data indicate that spin-orbit coupling in the photoionization step is small. These predictions concerning angular distributions are independent of the fine-structure component of the $5d$ core and of the electron orbital and spin angular-momentum coupling scheme assumed for the final state.

Typical angular distributions corresponding to the production of the $5d\,{}^2D_{3/2}$ and $5d\,{}^2D_{5/2}$ cores are shown in Fig. 1. These distributions directly contradict the predictions based on dominance of the $5d7s$ configuration label. The angular distributions show very appreciable fourth spherical harmonics and even the sixth harmonic appears to be significant and η dependent. Table I lists the coefficients for the Legendre polynomials for $\eta = 0°$ and $90°$ angular distributions [for which Eq. (1) can be simplified to $\sum_{L\,(\mathrm{even})}^{6} C_{L0} \times P_{L0}$] corresponding to all three cores. Additionally, the coefficients C_{20} are considerably smaller than 2; in fact, for the distributions corresponding to $\eta = 0°$ for the $5d\,{}^2D_{3/2}$ core, $C_{20} \sim 0$. Furthermore, these angular distributions show a very large η dependence. Clearly, the $5d$-core angular distributions are not dominated by a large, constant $C_{20}P_{20}(\cos\theta)$ term perturbed by higher harmonics and weak η dependence. That is, the $5d7s$ configurational label is totally inadequate as a guide to properties of the observed photoelectron angular distributions. The only evidence obtained here which is even consistent with the expected[18] jj-coupled $5d7s$ character of the bound state is the larger branching to the $5d\,{}^2D_{5/2}$ core than to the $5d\,{}^2D_{3/2}$ core and the somewhat smaller range of values of the coefficients C_{20} for the $5d\,{}^2D_{5/2}$ core.

In spite of its previous successes concerning MPI-PES, a multichannel quantum-defect theory (MQDT) analysis[18] resulted in predictions contradictory to our findings: The $5d7s\,{}^1D_2$ state was stated to be dominantly ($\sim 90\%$) a jj-coupled pure $5d7s$ configurational state. The inaccurate predictions of this analysis presumably reflect the necessity of arbitrarily constraining a large number of free parameters in the theoretical analysis and the shortcomings of MQDT analyses for low-lying states.

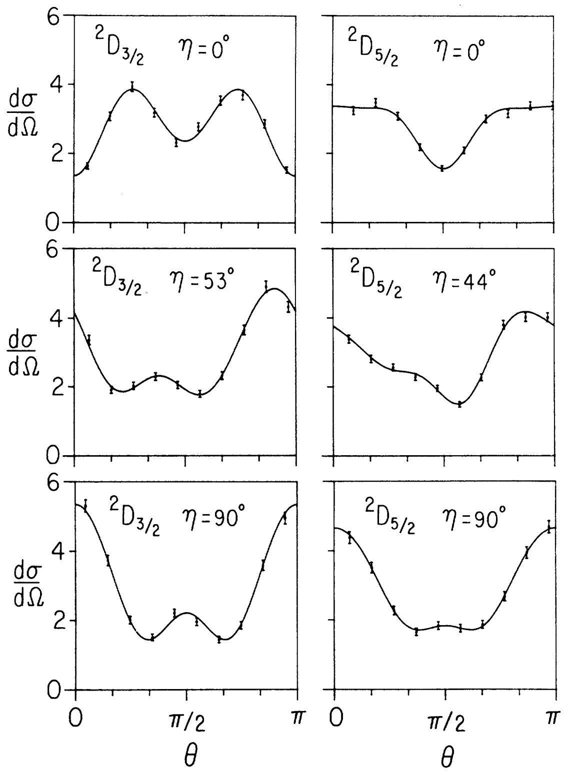

FIG. 1. Photoelectron angular distributions corresponding to the process

$$6s^2\,{}^1S_0 \xrightarrow{\nu_1} 6s6p\,{}^1P_1^\circ \xrightarrow{\nu_2} 5d7s\,{}^1D_2 \xrightarrow{\nu_2} 5d\,{}^2D_{3/2,5/2}+\epsilon$$

as a function of the angle η between the polarization directions of the collinear laser beams. The solid curves represent least-squares fits by Eq. (1). The indivdual curves are normalized to the same number of total counts. The three curves on the left-hand side correspond to the production of the $j=\frac{3}{2}$ ion core; those on the right-hand correspond to the production of the $j=\frac{5}{2}$ ion core.

Generally, the photoelectron angular distributions corresponding to the $5d$ core are qualitatively consistent with a substantial contribution of $5dnd$ character to the $5d7s\,{}^1D_2$ state. Because the "nd" electron has nonzero angular momentum, alignment information of the intermediate state persists to reflect itself in the photoelectron angular distributions. Thus, any $5dnd$ character of the ${}^1D_2$ bound state would give rise to η dependence, to spherical harmonics higher than the second, and to values of C_{20} smaller than 2 for angular distributions corresponding to the $5d$ core. The strong mixing found for the $5d7s\,{}^1D_2$ state is consistent with observations that singlet states tend to be more strongly mixed than triplets.[6,19,20]

Previously, the *non*appearance of η dependence or of spherical harmonics higher than $L=2$ in photoelectron angular distributions was reported for the photoionization of the $6s6p\,{}^1P_1^\circ$ state leaving the Ba^+ in the $5d$ state.[6] These results were attributed to bound-state electron correlation. Here, we have found unexpected η dependence and spherical harmonics higher than 2 for $5d$-core angular distributions from "$7s$" photoionization. With the inclusion of strong correlation in the picture, the results fall into a plausible, interpretable pattern.

A general feature seen here is that larger j values of the core are accompanied by smaller contributions of higher spherical harmonics in the photoelectron angular distributions. Table I and Fig. 1 illustrate this effect. Cores with larger j values compete more effectively in the redistribution and sharing of alignment produced by photoabsorption so that the corresponding photoelectrons exhibit less spatial anisotropy. Similarly, reduction of higher harmonics in photoelectron angular distributions has been attributed to angular-momentum exchange between the core and the ionized electron.[4]

Our MPI-PES investigation indicates that the $5d7s\,{}^1D_2$ state is strongly mixed. It is likely that other

TABLE I. The least-squares values of the coefficients for the Legendre polynomial $1+C_{20}P_{20}+C_{40}P_{40}+C_{60}P_{60}$ obtained from fitting of the $\eta=0°$ and 90° angular distributions for the three ion-core states in the photoionization of the $5d7s\,{}^1D_2$ state.

Ion core	η	C_{20}	C_{40}	C_{60}
$6s\,{}^2S_{1/2}$	0°	−0.10 ±0.12	−1.20 ±0.12	0.70 ±0.02
	90°	−1.44 ±0.05	1.29 ±0.08	−0.66 ±0.02
$5d\,{}^2D_{3/2}$	0°	0.04 ±0.04	−0.59 ±0.06	0.01 ±0.08
	90°	0.69 ±0.04	0.80 ±0.05	−0.11 ±0.06
$5d\,{}^2D_{5/2}$	0°	0.51 ±0.04	−0.32 ±0.03	0.11 ±0.04
	90°	0.75 ±0.10	0.33 ±0.03	−0.05 ±0.06

low-lying states will also exhibit mixing to the extent that no single configuration label aptly describes the state. It is important to determine whether any other classification scheme (such as the molecular picture) can be found which provides a significantly better predictive model.

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