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Photoionization of the Ba $6snl\,^1L$ states

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The photoionization cross sections of the singly excited Ba states $6snl\,^1L$ with $n=5$–9 and $l=0$–2 have been calculated in the Hartree-Slater approximation over a broad energy range. Our results establish some systematic trends of these cross sections as functions of photon energy and the quantum numbers n and l. Our data for $6s5d$ extend previous preliminary predictions to higher photon energies and agree very well with recent measurements, in the energy range where channel coupling and autoionizing transitions are not important. Comparison is also made with a calculation carried out within the local-density random-phase approximation.

INTRODUCTION

During the past few years there has been an increased interest in the photoionization of *excited* atomic states. The available measurements and calculations on the photoionization cross sections of such states have been limited mostly to alkali-metal atoms, usually because they present fewer theoretical and experimental problems in their treatment. In spite of this simplicity, agreement between experiment and theory is not always good and the best accord is usually achieved by semiempirical calculations. The ground and excited states of barium, an alkaline-earth atom, have attracted extensive experimental and theoretical attention as examples of states with a high level of configuration interactions and of electron correlations in general. In particular, the photoionization of the $4d$ subshell has been measured and calculated by various researchers.[1–6] Its complications stem from the yet unfilled $4f$ subshell which, however, "collapses" inside the centrifugal barrier in a relaxed $4d^9 5s^2 5p^6$ core as well as in the ground state of the Ba^+ ion and in elements heavier or equal in weight to La.[3] In addition, it was found[7] that for the Ba ground state and for photon energies of 21.2 eV, about 90% of the $6s$ photoionizations are accompanied by a strong excitation or even ionization of the other $6s$ electron.[8]

With the availability of lasers as high-intensity light sources, a number of experiments were performed on the photoionization of excited atoms. The experiments either combine two lasers, one for substantially populating the excited state and the other for photoionization,[9–11] or use one laser for excitation and synchrotron radiation for photoionization.[4,12,13]

This investigator has recently carried out calculations of excited cesium states with considerable success.[14] The present paper represents an extension of that work and an attempt to evaluate the suitability of the Hartree-Slater approximation[15] in treating the photoionization of excited alkaline-earth atoms, using the unusual case of Ba as an example.

In calculating the atomic wave functions for the initial and final states we use the Hartree-Slater (HS) approximation[15,16] to obtain the atomic potential, which is consequently kept the same for the initial and final state, i.e., we also employ the "frozen-core" approximation. The latter is usually a minor approximation when outer electrons are removed by the photoionization process. We realize, however, that since the initial state is an *excited* one, we ought to use the appropriate self-consistent field of this excited state, rather than the ground-state potential tabulated by Herman and Skillman.[15] The Schrödinger equation is solved in the usual fashion[17] to obtain the initial- and final-state electronic wave functions, which are then used to calculate the transition matrix elements and the photoionization cross sections. In all cases we used the experimental wavelengths from Moore's tables,[18] or from more recent experimental determinations.[19]

RESULTS AND DISCUSSION

Figures 1–3 present our calculated photoionization cross sections for the $6sns\,^1S$, $6snp\,^1P$, and $6snd\,^1D$ states, respectively, with the nl excited electron being ionized. The calculation for the corresponding (allowed) triplet states yields cross sections differing by less than 10%. Within the present Hartree-Slater approximation, the differences occur mainly because of the use of different threshold energies for the two spin states. This effectively shifts the two curves, with respect to one another, by the threshold energy difference, usually less than half an eV. In addition, because the photoionization cross section[17]

$$\sigma_\gamma(E) = \tfrac{4}{3}\pi^2 a_0^2\,\alpha\omega\,|\langle \gamma E \| D \| i\rangle|^2$$

of an initial state $|i\rangle$ resulting in the state $|\gamma E\rangle$ is directly proportional to the photon energy ω, the threshold energy difference also changes the *absolute* cross-section values for the same photoelectron energies. These differences are most important at threshold and quickly become insignificant with increasing photon energy.

All the $6sns$ photoionization cross sections exhibit a Cooper minimum[20] near threshold. Apart from the region of the minimum, the curves remain relatively flat over a wide range of energy, albeit the absolute cross-section values are rather small. From the bunching of the curves in Fig. 1, we can infer that the core relaxation, essentially that of the $6s$ electron, is mostly taking place in going from $6s^2$ to the $6s7s$ configuration. Further relaxation is more gradual and less dramatic. This effect can also be seen directly from Table I, where we tabulate the expectation value $\langle r\rangle$ for the pertinent orbitals and configurations. The visual effect of Fig. 1 is slightly misleading since the $6s^2$ photoionization is twice as big as it would have been if the two $6s$ electrons were not equivalent. Thus, in comparing their general behavior, the $6sns$, $n>6$, curves should be compared to the

TABLE I. Expectation values $\langle r \rangle$ for outer orbitals of the $6snl$ configurations of Ba, as predicted by the relaxed Hartree-Slater approximation (in a.u.).

	$6sns$		$6snp$		$6snd$	
n	$6s$	ns	$6s$	np	$6s$	nd
5	...	...	...	...	5.328	3.230
6	4.879	4.879	4.663	6.396	4.314	11.530
7	4.305	11.259	4.254	13.673	4.227	20.747
8	4.213	20.188	4.188	24.011	4.187	33.220
9	4.186	31.901	4.177	36.961		

$6s^2$ one, reduced by a factor of 2.

Figure 2 shows that, in contrast to the $6sns$ states, the $6snp$ photoionization cross sections show no Cooper minima in the energy range studied. As a result, they have their largest values at threshold, from which they fall quickly by about three orders of magnitude before their slope becomes less steep and they behave more like the $6sns$ states. Here again we obtain a visual representation of the relaxation effects, which are seen to be gradual with no abrupt changes.

Figure 3 presents a more dramatic picture than either one of Figs. 1 or 2. The $6snd$ photoionization cross sections are seen to fall with almost constant slope, the one displayed by the $6snp$ cross sections at their intermediate-value regions. Whereas the $6snd$, $n = 6$–8, cross sections all have a Cooper minimum very close to threshold, $6s5d$ cross section does not exhibit one in that region. The $6s5d$ cross section *does* have a minimum, however, around 110 eV (not shown in the picture). Near threshold, and hardly seen in the scale of Fig. 3, the $6s5d$ curve exhibits a maximum, evidence that the Cooper minimum has moved to the discrete spectrum. The dramatic difference between $5d$ and the other nd curves is the over one order of magnitude difference in their absolute values. This is not so much a result of the $6s$ relaxation as the result of the $5d$ orbital "collapse" within the d-wave centrifugal barrier. As is well known, the $5d$ shell is not occupied in the ground-state configuration of any atom of the periodic system with $Z < 57$ (i.e., it first happens in La), exactly because of the height of the centrifugal barrier.[3,21] As we clearly see from Table I, the $5d$ orbital lies mainly within that barrier and is actually more compact than the $6s$ orbital. However, the situation is again inverted for higher-n d orbitals, which spend most of their time outside the barrier, as is obvious from the numbers in Table I.

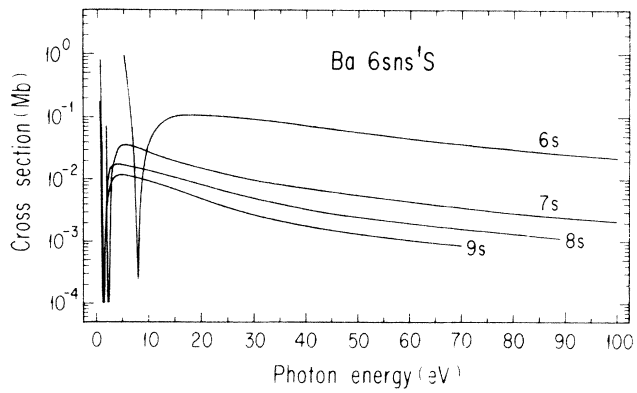

FIG. 1. Photoionization cross sections for the Ba $6sns\,^1S$ states.

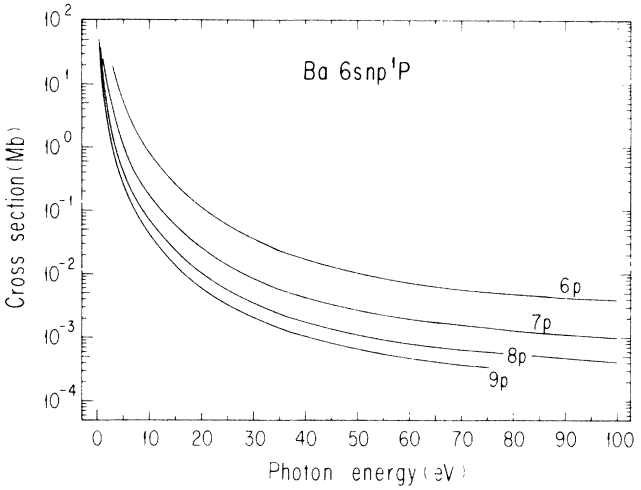

FIG. 2. Photoionization cross sections for the Ba $6snp\,^1P$ states.

Therefore, the relative position and behavior of the curves in Fig. 3 should not be surprising, but is an elegant illustration of the interplay between the effects of orbital relaxation and "collapse."

A very recent investigation of the Ba $6s5d$ photoionization was carried out by Bizau *et al.*[13] over an unprecedented experimental energy range for any *excited*-state photoionization. In addition, Ref. 13 presents a calculation by Wendin, within the local-density random-phase approximation (LDRPA). Thus, we have a broad energy range over which to compare their results with our present and older preliminary calculations.[22] This comparison is shown in Fig. 4. Before further commenting on the figure, we should point out that our calculation does not include the effects of autoionization, which result in lines being superimposed over the continuous background,[23] or channel interaction effects. We could conceivably include such effects in our calculations, but this is not presently done, and our results are predictions about the shape and absolute magnitude of the "background." From Fig. 4 it is clear that, in their specified region of validity, our Hartree-Slater calculations are not only in excellent agreement with the experiment, but also outperform the considerably more sophisticated

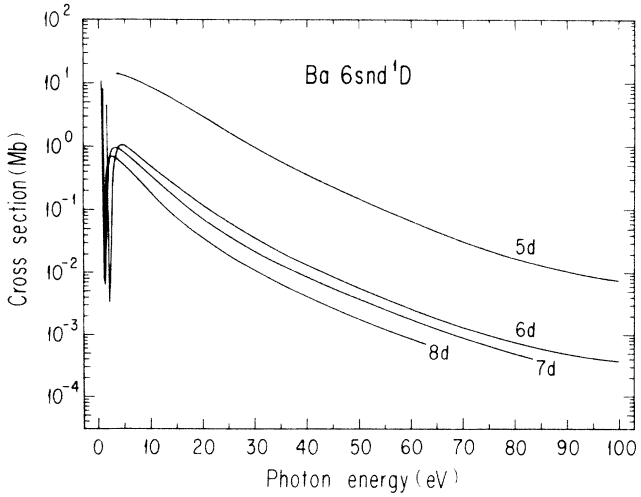

FIG. 3. Photoionization cross sections for the Ba $6snd\,^1D$ states.

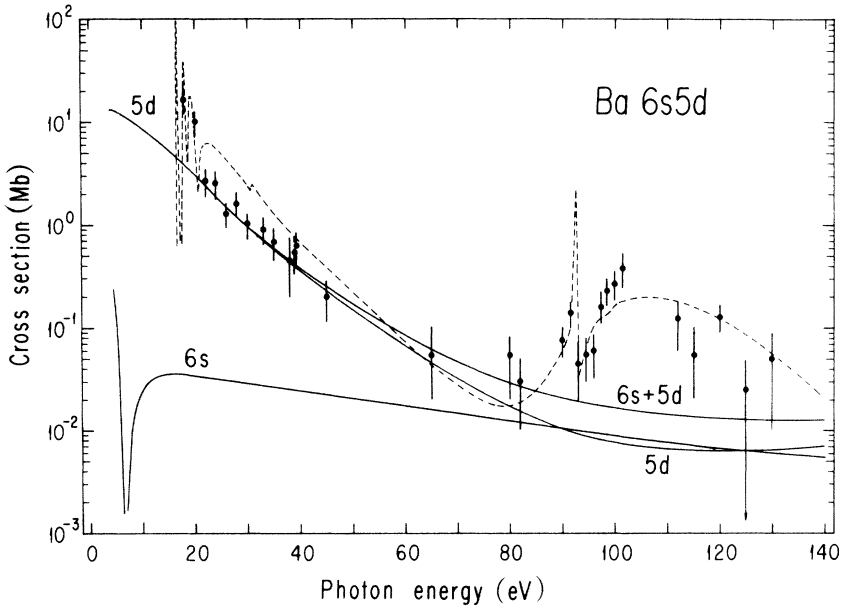

FIG. 4. Ba $6s5d$ photoionization cross section as function of the photon wavelength: solid curve, present Hartree-Slater calculations; dashed line, the LDRPA results from Ref. 13; ♦, absolute experimental data from Ref. 13. The labels on our theoretical curves indicate which orbital is photoionized in each case.

LDRPA calculations. This better agreement may be a fortuitous result, but it appears to us not likely so, given the fact that the absolute value and relative curve shape are in excellent agreement over a 60-eV photon energy range ($h\nu = 20$–80 eV) for cross-section values spanning three orders of magnitude. The experimentally observed cross-section enhancement above ~ 90 eV coincides with the opening of the $4d^{10}$ subshell and results from channel coupling, nicely reproduced by the LDRPA calculation.[13]

Overall, it appears that the Hartree-Slater approximation can yield dependable photoionization cross sections for excited states of different atomic species, especially away from threshold.

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