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Photoionization of excited *nf* states in the Cs isoelectronic sequence: A new example of orbital collapse

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Cross sections for the photoionization of excited *nf* states in the Cs isoelectronic sequence show simple monotonic behavior for neutral Cs but considerable structure for the ions due to the collapse of the *nf* orbitals. This is the first demonstration of orbital collapse in highly excited states.

Excited-state photoionization calculations in neutral atoms have revealed a wealth of new phenomenology which arises, fundamentally, because of the spatial extent of the wave function for the discrete excited state.[1,2] Chief examples of these new phenomena are the many zeros that are found in the dipole-matrix elements[3,4] and Cooper minima,[5] far more than are found in ground-state photoionization.[6] The question then arises, how do these zeros behave in going to ionic excited states, i.e., along an isoelectronic sequence. Certainly at high enough nuclear charge Z the situation becomes hydrogenic and extremely simple. However, this evolution is not necessarily monotonic.

In this paper, the photoionization of the excited *nf* states of the Cs isoelectronic sequence is scrutinized. Calculations of *nf* photoionization for the *nf* ($n=4$–9) states of all of the members of the sequence from neutral Cs to Tb^{+10} have been performed employing Hartree-Slater wave functions; the details of the calculation are given elsewhere.[6,7]

The results for neutral Cs are shown in Fig. 1. The salient feature of these results is the simple monotone decreasing behavior of each of the cross sections as a function of energy; no Cooper minima are found. The cross sections are dominated by the $f \rightarrow g$ channel which is almost completely hydrogenic near threshold where most of the oscillator strength is. This is because the discrete *nf* states have quantum defects close to zero, and the continuum *g* states have near-zero phase shifts close to threshold. At higher energies, the εg begins to have appreciable phase shift which implies that the cross section should not be hydrogenic. This is clearly seen in Fig. 1 with the change in slope of each of the cross sections at about 1 Ry; the εg continuum wave has a shape resonance[8] which begins around there.

It might be thought that in going to Ba^+, the next member of the isoelectronic sequence, these cross sections would become even simpler and more hydrogenic. This, however, is not the case. Looking at Fig. 2, the photoionization cross sections of all of the excited *nf* states of Ba^+ show very dramatic Cooper minima.[5] To understand these results, we note that the effective *f*-wave potential (electrostatic attraction plus centrifugal repulsion) is double welled in Cs, but the *nf* states are bound in the outer well.[9] This means that the *nf* wave functions in Cs do not really "feel" the inner well and are essentially hydrogenic as discussed above. Going to Ba^+, however, the added electrostatic attraction causes the *nf* states to "collapse" and to be bound in the inner well, making them nonhydrogenic and giving them each a quantum defect close to unity (except for the 4*f* which becomes a core level). Then,

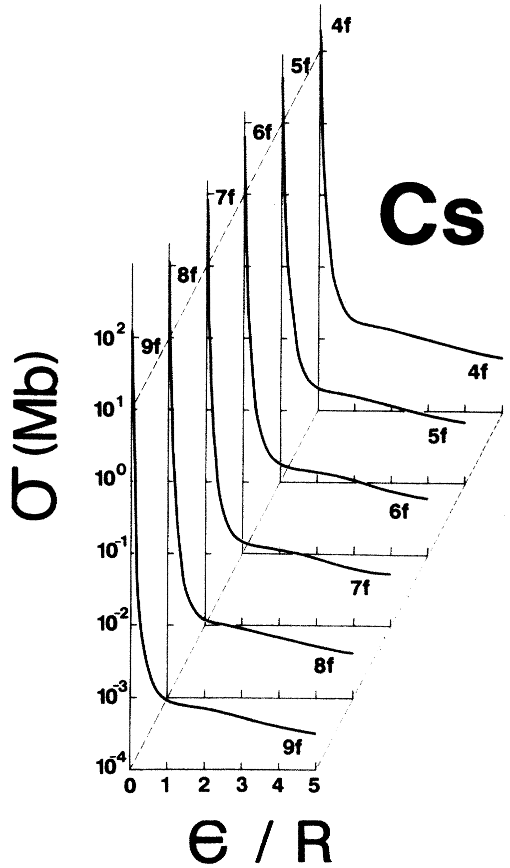

FIG. 1. Photoionization cross sections for the *nf* ($n=4$–9) excited states of neutral Cs shown as a function of photoelectron energy in rydbergs (13.6 eV).

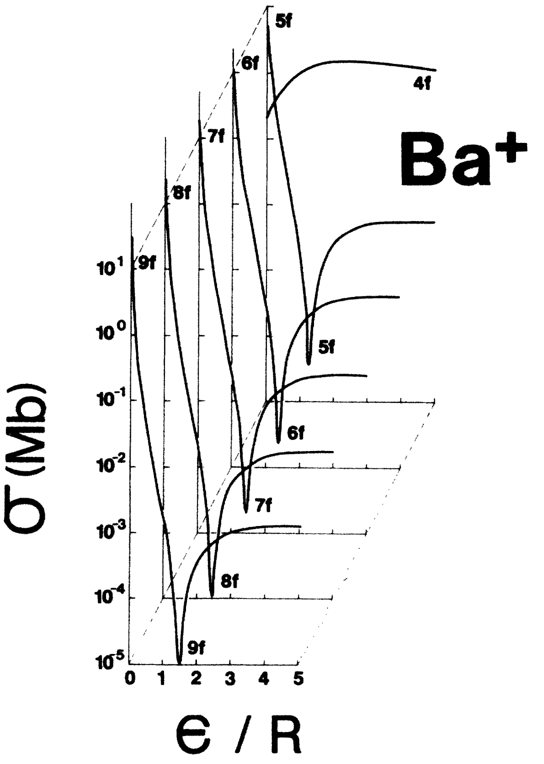

FIG. 2. Photoionization cross sections for the nf ($n=4$–9) excited states of Ba$^+$ (which is isoelectronic to Cs) shown as a function of photoelectron energy in rydbergs (13.6 eV).

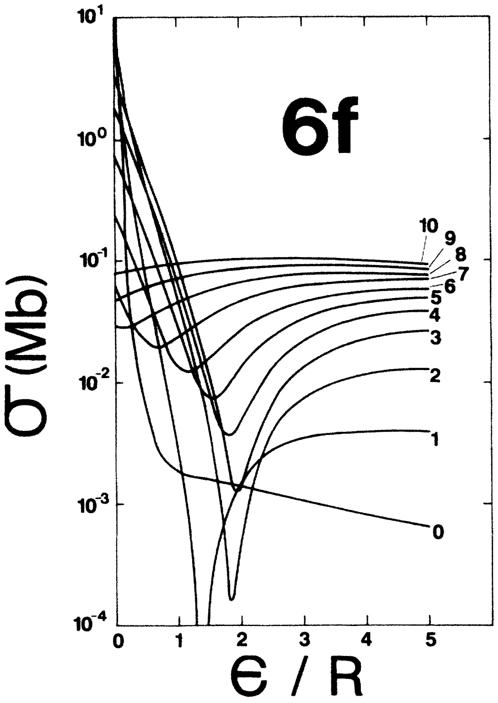

FIG. 3. Photoionization cross sections for the $6f$ excited states of the first 11 members of the Cs isoelectronic sequence as a function of photoelectron energy in rydbergs (13.6 eV). Each curve is labeled by the charge of the ion, i.e., 0 refers to neutral Cs, 1 to Ba$^+$, 2 to La^{+2}, etc.

since the continuum g states still have near-zero phase shifts near threshold, there is a relative phase-shift difference between initial and final states in the $nf \rightarrow \varepsilon g$ transitions in Ba$^+$ of about π. From previous work,[1-4] this difference implies a Cooper minimum in each, as seen in Fig. 2.

Also seen in Fig. 2 is the fact that the minimum moves out in energy somewhat with increasing principal quantum number n. This is due to two separate effects. The first is that the nf quantum defects increase slightly with increasing n, thus increasing the phase-shift difference and moving the minimum towards higher energy. In addition, it is known that the portion of the matrix element generated in the inner (nonhydrogenic) region always mitigates against zeros in the continuum and tends to move them closer to (or below) threshold. This "inner effect" is greater for the lower nf states since a greater proportion of their matrix elements is generated in the inner region; thus, the inner effect also tends to make the minima in the higher nf states occur at higher energy.

Going further along the isoelectronic sequence produces changes, but none so dramatic as the change in going from Cs to Ba$^+$. As an example, the cross sections for $6f$ are given in Fig. 3 for the entire sequence from neutral Cs to Tb^{10+}. Here we see that the minimum moves out from Ba$^+$ to La^{2+}, remains the same for Ce^{3+}, and then starts moving in with increasing Z until it moves below threshold. Note that, even for Tb^{10+}, the highest member of the isoelectronic sequence considered, the cross section is still not monotone decreasing from threshold; the effects of the zero below threshold are still evident. This general behavior is simply explained. The $f \rightarrow g$ phase-shift difference maximizes at 1.09 (in units of π) for Ce^{3+} and decreases for higher Z, the value being 0.71 for Tb^{10+}. This indicates that the minimum should be furthest out in energy for Ce^{3+} and move in for higher Z. Furthermore, the phase-shift difference of 0.71 for Tb^{10+} is greater than 0.5 and, thus, a minimum should appear here as well. These

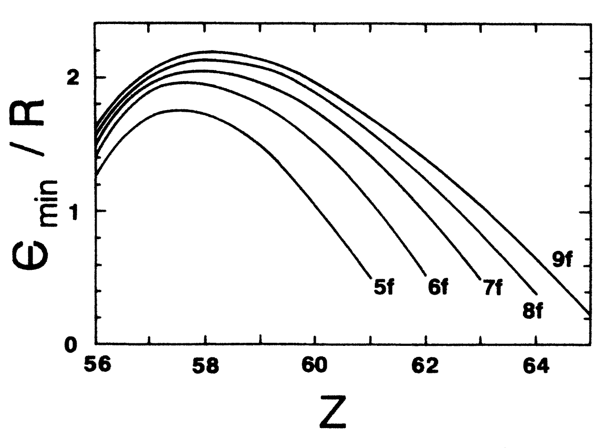

FIG. 4. Locus of zeros in the $nf \rightarrow \varepsilon g$, ($n=5$–9) dipole matrix elements showing photoelectron energy in rydbergs (13.6 eV) against nuclear charge Z. The termination of a curve indicates that the zero lies below threshold for the next higher Z.

arguments are modified by the existence of the inner effect discussed above. The part of the dipole-matrix element generated in the inner, nonhydrogenic region certainly increases with increasing Z as the wave functions become more compact. Since the inner region mitigates against zeros, the zeros move into the discrete region more rapidly than the phase-shift analysis would suggest.

If this explanation concerning the inner effect is, in fact, correct, it should be evident in looking at different principal quantum numbers n since the higher n, the smaller portion of the matrix element, results from the inner region so minima should move out with increasing n; this was seen for Ba^+ discussed above. More generally, the locus of $nf \to \varepsilon g$ zeros for $n=5-9$ is shown in Fig. 4. From this figure it is quite clear that the minima move out, as a function of n, in *all* cases. Since the phase-shift difference, which determines the matrix element in the outer (hydrogenic) region, is virtually the same for all n, the only difference can be the inner effect which not only pulls the lower-n minima in, but also causes the minima from differing n to move below threshold at different values of z, as indicated in Fig. 4.

In summary, we have presented a case of excited-state photoionization which is very simple in the neutral system, but acquires rich structure in going to ions along the Cs isoelectronic sequence due to the collapse of the excited nf wave functions. Despite the fact that the calculations are simple and no experiment exists to verify this aspect of orbital collapse, it is expected that the results presented provide at least a qualitative (if not better) view of reality, since they depend most sensitively on the phase shifts and quantum defects whose accuracy is reasonably good, especially for ions.[10,11]

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