Photoionization of Inner Shells of Excited Atoms: Dominance of Two-Electron Transitions

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Calculations of inner-shell photoionization of excited atoms are performed which demonstrate a general class of states for which ionization plus excitation is the dominant process. The phenomenon is explained in terms of relaxation effects and examples for Li are presented.

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The absorption of electromagnetic radiation by matter is of fundamental significance, as well as of great importance in numerous applications. Owing to the weak coupling of the photon to the electron, through the fine-structure constant, the single-electron process dominates in the photoionization of atoms, molecules, and solids, i.e., one electron is ejected and all other electrons remain in the same state [1]. Of course, it is possible for a second electron to be excited or even ionized, through electron-electron correlation, but the probabilities for these satellite processes have generally been found to be a good deal smaller than the single-electron process [2]. In this Letter, we report on a series of calculations which demonstrate a general class of atomic states for which two-electron photoionization processes dominate, specifically ionization plus excitation.

The calculations were performed in the single-channel multiconfiguration Hartree-Fock (MCHF) approximation using the code of Fischer [3] for the wave functions of the discrete initial excited atomic and the final ionic states. Continuum wave functions, in the MCHF field of the final ionic state, were obtained using our own code [4]. The dipole matrix elements, which can be expressed as a linear combination of products of angular factors, single-electron overlaps between initial- and final-state orbitals, and a single-electron dipole matrix element, were also obtained from our own code [4].

As an example of our results, the situation for photoionization of a $1s$ electron from the $1s^2 3p\ ^2P$ excited state of Li is shown in Fig. 1. The cross sections for leaving the Li^+ ion in $1s2p$, $1s3p$, and $1s4p\ ^{3,1}P$ states are given. The outstanding feature of these results is that the dominant cross section is the $1s^2 3p\ ^2P \rightarrow 1s4p\ ^3P$ channel, which represents ionization plus excitation. This channel is seen to dominate at all of the energies considered. Furthermore, the next-largest cross section is the $1s^2 3p\ ^2P \rightarrow 1s4p\ ^1P$ channel, again ionization plus excitation.

The dominance of these channels can be quantified by looking at the branching ratios, the ratios of the individual cross sections to the total cross section for $1s^2 3p\ ^2P$ photoionization, summed over all of the individual channels. These branching ratios are shown in the panels of Fig. 2 which are broken up into ^3P and ^1P final ionic states to make them more readable. While it is seen that the branching ratios are dependent on energy near threshold, at the higher energies they are virtually constant. At these higher energies, the contribution of the $1s4p\ ^3P$ final state is about 60% of the total and the contribution of $1s4p\ ^1P$ is about 16%. In addition, the contributions of $1s3p\ ^3P$ and $1s2p\ ^3P$ are each about 9%, while the contribution of $1s3p\ ^1P$ is roughly 4% and of $1s2p\ ^1P$ about 2%. Thus, it is clear that our calculations show that there is a 76% probability that the final state contains a $4p$ electron, 13% that it contains a $3p$ electron, and 11% that it contains a $2p$ electron. In other words, when the $1s$ electron is ionized, in only 13% of the transitions does the $3p$ electron remain in the $3p$ state, which is certainly at odds with the notion that the dominant transition is generally a single-electron transition.

In order to explain these results, it is necessary to look at the dominant term in the transition matrix element, which, apart from angular factors, is given by

$$M_{np}(^{1,3}P) = A(^{1,3}P)\langle 1s_i | 1s_f \rangle \langle 3p_i | np_f \rangle \langle 1s_i | r | \epsilon p \rangle \quad (1)$$

for a $1s_i^2 3p_i \rightarrow 1s_f np_f \epsilon p$ transition, where $A(^{1,3}P)$ represents the angular factor. To begin with, the angular factor $A(^3P) = \sqrt{3} A(^1P)$ so that, if the final-state orbitals

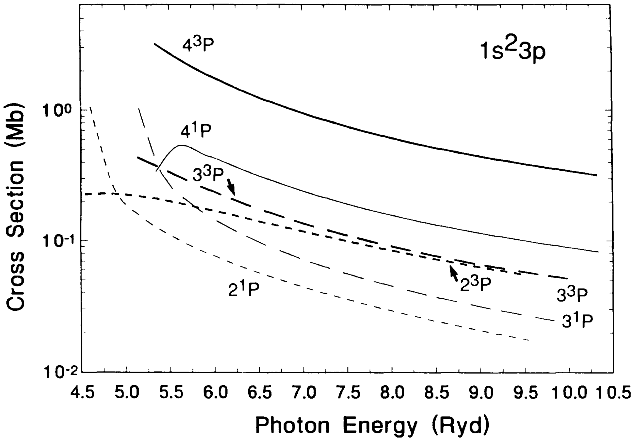

FIG. 1. Photoionization cross sections calculated for $1s$ ionization from the Li $1s^2 3p$ excited state to various $n\,^3P$ and $n\,^1P$ states of the Li^+ ion vs photon energy. The curves are our dipole-length results which are in good agreement with dipole velocity (not shown).

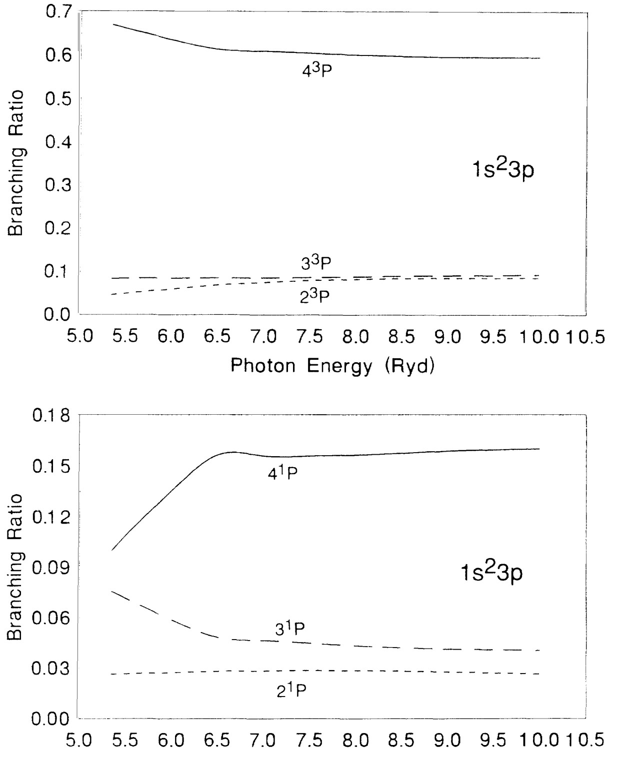

FIG. 2. Branching ratios for individual $n\,^3P$ (upper panel) and $n\,^1P$ (lower panel) final states of Li^+ arising from $1s$ photoionization of the $1s^23p\ ^2P$ excited state of Li. Each curve represents the given cross section over the total.

were the same in both states, the triplet cross sections would be a factor of 3 larger than those of the singlets; this explains why the triplet cross sections are much larger than the singlets ones.

More importantly, however, the only significant change in the dominant term in the matrix element, with changing n of the np_f electron, comes from the overlap term in Eq. (1), $\langle 3p_i|np_f\rangle$. The cross section, then, is proportional to the square of this overlap term. Our calculations show that for the ^3P final states, the squares of this overlap factor are 0.089, 0.107, and 0.759 for $2p$, $3p$, and $4p$ final states, respectively, while for the ^1P's, the results are 0.090, 0.162, and 0.718, respectively. The fact that the $\langle 3p_i|4p_f\rangle$ overlaps are by far the largest means that the cross sections for $1s4p$ final states are the largest, thus explaining the higher-energy results shown in Figs. 1 and 2.

But why should the overlaps favor the $3p \to 4p$ so strongly? To understand this point, note that a reasonably high excited state of Li is virtually completely screened by the $1s^2$ core. Thus, the excited electron "sees" a charge of 1. Similarly, in the Li^+ ion, the excited electron sees a charge of 2, so that the $3p_f$ of the final state is considerably more compact than the $3p_i$ of the initial state. Thus, the principal overlap of the $3p_i$ wave function is with $4p_f$ which, owing to the increased charge it sees, occupies the same region of space as the $3p_i$.

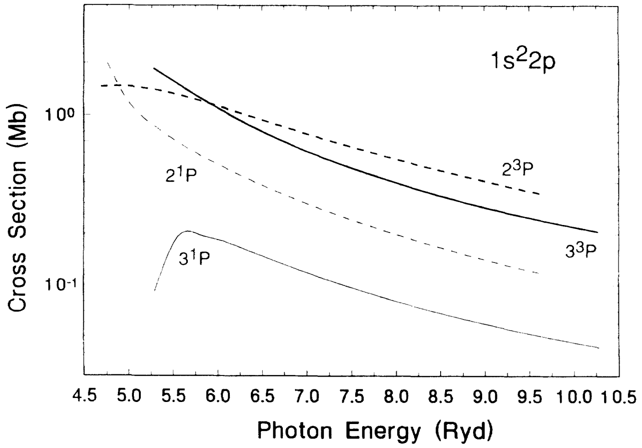

FIG. 3. Photoionization cross sections calculated for $1s$ ionization from the Li $1s^22p$ excited state to various $n\,^3P$ and $n\,^1P$ states of the Li^+ ion vs photon energy. The curves are our dipole-length results which are in good agreement with dipole velocity (not shown). The $4p$ final states are omitted because their cross sections are extremely small.

The effect is quite dramatic when the initial-state excited electron sees a charge of 1 and the final-state excited electron sees a charge of 2, so that the effective charge changes by a factor of 2. For lower excited states, or the ground state, where the wave function of the outermost shell penetrates the core, the removal of an inner-shell electron still changes the effective charge by 1, but the change is nowhere near a factor of 2. This is why this effect does not generally occur for ground or low excited states. As an example the results for $1s$ photoionization from the $1s^22p$ state of Li are shown in Fig. 3, where it is seen that the largest cross section is to the $1s2p\ ^3P$ state of Li^+; in other words, only a single-electron transition.

From the above discussion, it is clear that this effect is not peculiar to excited p electrons; it will be in evidence for any angular momentum. It is also clear that, although results have been presented for Li, these two-electron transitions will dominate the photoionization in inner-shell photoionization of excited states of atoms throughout the periodic spectrum.

Note that, up to this point, we have only discussed the cross sections away from threshold. Near threshold the branching ratios become extremely energy dependent, as was seen in Fig. 2. In brief, in the threshold region correlation effects are more important and terms other than the type given in Eq. (1) contribute appreciably to the dipole matrix element. These terms drop off in importance quite rapidly with increasing energy, giving rise to the energy dependence seen. A more complete discussion of the energy dependence of the cross sections will be presented elsewhere.

From the explanation of this effect, it is evident that the ionization mechanism does not have to be a photon. Inner-shell ionization of excited atoms by fast electrons or protons should exhibit this same effect. Furthermore, it should be in evidence for multiphoton ionization of an inner shell of a highly excited atom. In fact, a recent experiment on excited Ba appears to show this multielectron effect [5]. Autoionization of excited states should also exhibit this phenomenon and it has already been seen experimentally for core-excited argon [6]. Thus, we are dealing with an extremely general phenomenon.

Finally, note that the primary problem in understanding atoms is understanding the details of the correlation among atomic electrons. For most atomic processes, the effect of correlation is a relatively small perturbation on the dominant transition mechanism, i.e., satellite lines in photoelectron spectroscopy. In this Letter, however, we have described a general class of states which exist for all multielectron atoms and exhibit dominant multielectron transitions under the action of a single-particle operator, transitions characteristic of correlation. Thus, with the emergence of the technology to create and ionize inner shells of such excited states [7], we have a new "laboratory" to study multielectron transitions.

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