Excitation-Autoionization Contributions to Electron Impact Ionization

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Experimental measurements of electron impact ionization cross sections for the transition-series ions Ti^{+3}, Zr^{+3}, and Hf^{+3} demonstrate that excitation-autoionization increases the cross sections by more than an order of magnitude over that anticipated for direct ionization. Theoretical predictions of both the energies and approximate magnitudes of these excitation cross sections provide confidence that this important indirect contribution to the total ionization can be estimated for many cases.

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Excitation of an inner-shell electron to a level above the next ionization continuum, followed by autoionization (excitation-autoionization) can in some instances contribute an important part of the total ionization cross section of a species. This was recognized by Goldberg, Dupree, and Allen[1] when considering models of the solar corona. A number of people have since made theoretical estimates[2] of this process and emphasized its importance—particularly for high-charge states. Some workers[3] have incorporated this process into models of high-temperature plasmas, emphasizing theoretical estimates for high-charge states. The effect of excitation-autoionization on ionization cross sections was pointed out by Fox, Hickam, and Kjeldaas[4] in 1953, and their experiments led to extensive experimental activity[5] in the 1960's. However, despite the experimental activity, and the theoretical predictions, there were no experiments which showed the clear dominance of excitation-autoionization over direct ionization until the measurements of Peart and Dolder[6] in 1975 on Ca^+, Sr^+, and Ba^+. They found excitation-autoionization cross sections which were larger than those for direct ionization by factors ranging from 1.5 for Ca^+ to 4 for Ba^+. The work on Li-like ions[7] demonstrates that excitation-autoionization can become more important as the charge state increases. In the experiments and theory presented here, excitation-autoionization is found to be more than an order of magnitude larger than direct ionization. Obviously this process should not be ignored in applications of ionization cross sections, for example, in predictions of ionization equilibrium or ion abundance in astrophysical or fusion plasmas.

The present study is an investigation of the contributions of excitation-autoionization to electron impact ionization in regions of the periodic system where it might be anticipated that these effects should be dominant. In particular, the most favorable cases will involve inner-shell excitations with large oscillator strengths ($f > 1$) for which the autoionizing levels have energies just above the ionization threshold. These conditions are typical of $p \rightarrow d$ transitions of the type $np^6nd^m \rightarrow np^5nd^{m+1}$ in a number of ions of the transition-series elements. The triply ionized fourth-column transition metals, Ti^{+3}, Zr^{+3}, and Hf^{+3}, with $m = 1$ and $n = 3$, 4, and 5, respectively, were deemed tractable cases from both an experimental and a theoretical perspective.

The experimental procedure is that of crossed electron and ion beams described in detail elsewhere.[8] The experimental results for the three ions near the ionization threshold are shown in Fig. 1. The most pronounced feature of the results is the large increase in each of the experimental cross sections just above the ionization threshold. If the prediction using the Lotz formula[9] is taken as a measure of the direct ionization cross section, the enhancements of the cross sections due to the indirect process are factors of about 10 for Ti^{+3} and Hf^{+3} and 20 for Zr^{+3}. The error bars in Fig. 1 are one standard devia-

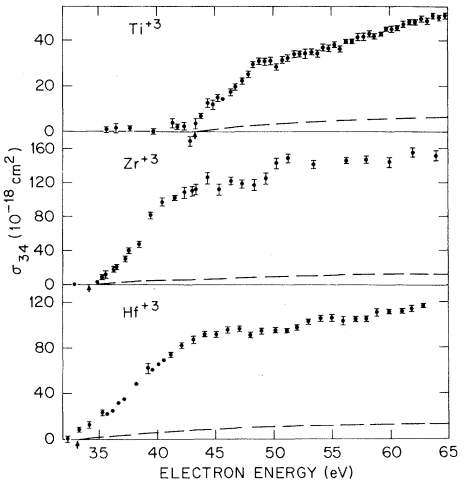

FIG. 1. Experimental results for electron impact ionization of Ti^{+3}, Zr^{+3}, and Hf^{+3}. Error bars are one standard deviation of the mean statistical uncertainty. The dashed line is from the semiempirical formula of Lotz (Ref. 9).

tion of the mean and are representative of the relative uncertainties. The total absolute uncertainty, estimated at high confidence, is less than ±10% for these data.[10] The presence in the beam of appreciable numbers of ions in the $np^6(n+1)s$ metastable state may lead to data for which interpretation is ambiguous. Thus, the region below the ionization threshold was studied in each case to assess the fractional population of the metastable state in the beam. The data indicate <10% metastables for all cases, which will not affect the cross sections significantly.

Calculations of the energy levels and eigenvectors were performed with use of a multiconfiguration atomic structure program furnished to us by Cowan.[11] The values of the average energies of each configuration as well as the necessary electrostatic and spin-orbit parameters were calculated with use of center-of-gravity Hartree-Fock wave functions with relativistic modifications[12] (HFR). In calculating the energy levels within a configuration, Hartree-Fock electrostatic parameters were adjusted for the effects of correlation[11]; in this case a scaling factor of 0.80 was selected to match the experimental levels[13] for the bound states of $V^{+4}(3p^53d^2)$.

For the calculation of the total ionization cross sections, the excitation-autoionization and direct ionization were assumed to take place independently. In this case

$$\sigma_{\text{total}} = \sigma_{\text{ion}} + \sum_i \sigma_{\text{excit}}{}^i B_i{}^A,$$

where σ_{ion} is the cross section due to the direct ionization process, σ_{excit} is the excitation cross section for a transition to the autoionizing level i, and $B_i{}^A$ is the branching ratio for autoionization from the level i. The Lotz formula[9] was used to estimate the magnitude of the direct ionization process (the scaled Coulomb-Born result[14] is approximately 15% lower than Lotz near the maximum). The excitation cross sections were calculated in a nonunitarized distorted-wave approximation. Because of the complexity of the calculations for configurations of the type np^5nd^{m+1}, the preliminary results reported here retain only the direct dipole term in the interaction between the scattered electron and the ion. The target state wave functions were calculated with use of the HFR method, and the distorted-wave continuum functions were determined with use of a Hartree potential plus the semiclassical exchange approximation of Riley and Truhlar.[15] The branching ratios were calculated with use of a method similar to that reported in Cowan and Mann.[2]

The experimental and theoretical results for Ti^{+3} in the energy region near the ionization threshold are shown in Fig. 2. Two structures centered around 44.5 and 47.5 eV are apparent in the data. These dominant features are identified as excitation-autoionization due to the $3p^53d^2$-$[0.72(^3F)+0.69(^1G)]^2F$ term at 44.5 eV (calculated energy) and the experimentally unresolved terms $3p^53d^2[0.87(^3P)+0.39(^1D)+0.31(^1S)]^2P$ at 48.0 eV and $3p^53d^2[0.85(^3F)+0.34(^3P)+0.41(^1D)]^2D$ at 49.1 eV. The positions of the calculated terms agree with the experimental features to within the calculational or experimental uncertainties. The comparison between experiment and theory for the $4p^64d \rightarrow 4p^54d^2$ transition in Zr^{+3} and the $5p^64f^{14}5d \rightarrow 5p^54f^{14}5d^2$ in Hf^{+3} is similar to the results shown here for Ti^{+3}. The factor of 2.5 discrepancy between the theoretical and experimental cross sections may have a number of causes. Nonunitarity and the neglect of exchange may account for the largest part of the discrepancy. However, configuration mixing is also significant; as an example, mixing between the ground state $3p^63d$ and $3p^43d^3$ reduces the oscillator strength of the transitions to the autoionizing levels of $3p^53d^2$ by about 20%. Additional interactions with the $3p^53d^2$ configuration may also be important.

As seen in Fig. 1, the experimental cross sections continue to rise at energies beyond the highest terms of np^5nd^2. This is believed to be due

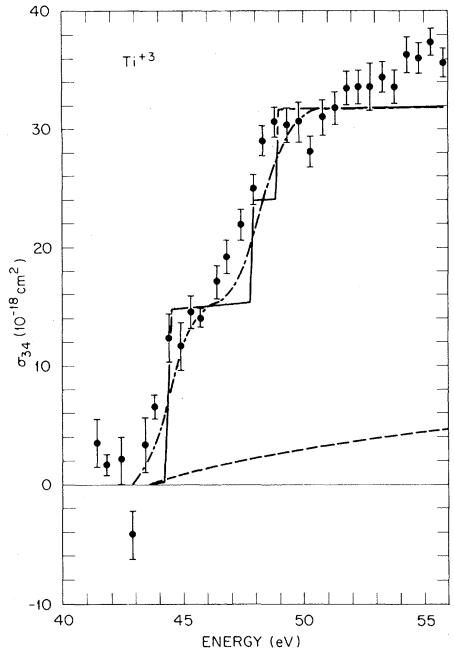

FIG. 2. Detail of Ti^{+3} cross section. The solid line is the theoretical prediction divided by 2.5. The dot-dashed line is the solid curve convoluted with a 2-eV full width at half maximum Gaussian, chosen to simulate the electron-energy spread. The dashed line is from the semiempirical formula of Lotz (Ref. 9).

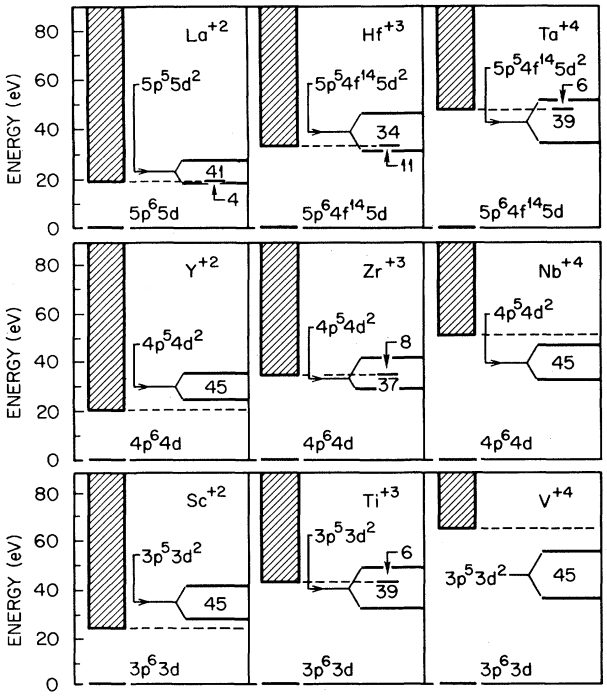

FIG. 3. Energy level structure of np^5nd^2 relative to the ionization limit for several transition metals. The number of levels above and below the respective ionization threshold is indicated for each case. Hatched region indicates the ionization continuum for the next higher ionization state.

to transitions to autoionizing levels of configurations such as $np^5nd(n+1)p$, $np^5nd(n+1)d$, and $nsnp^6nd^2$, which do lie in the appropriate energy ranges.

A theoretical survey of the energy levels of the np^5nd^{m+1} configurations has been performed for ions of the transition-series elements. An example for np^5nd^2 is shown in Fig. 3. As the charge state increases, the ionization potential increases more rapidly than the energy of the levels of np^5nd^2 so that they become bound and cannot autoionize. In general, the $np^6nd^m \rightarrow np^5nd^{m+1}$ transitions will not contribute to ionization cross sections for ions with charge state greater than +4. However, in order to determine the contributions of such transitions to ionization, a detailed calculation is required, and no general scaling appears possible. In the case of Ti^{+3}, for example, there are only six of the 45 levels which autoionize; yet nearly all of the oscillator strength lies in these six levels which accounts for the large effects seen here.

The present study demonstrates that excitation-autoionization can completely dominate the ionization processes and certainly cannot be neglected. Although many of the transitions of importance are quite complex, it is possible to predict where the indirect process should dominate and to estimate the magnitude of such effects.

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[10]Systematic uncertainties judged to have a possible correlation were added linearly after which a quadrature sum of systematic uncertainties was made. One-sided systematic uncertainties were added linearly to the resultant quadrature sum. The total absolute uncertainty estimated at high confidence level is less than $\pm 10\%$ for these data.

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Electron Correlation and Kellman-Herrick Quantization in Doubly Excited Helium

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Conditional probability distributions based on accurate wave functions for He** confirm the proposal that electron correlation in doubly excited atoms leads to quantization like that of a linear triatomic molecule.

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Kellman and Herrich have proposed recently[1-4] that the quantization in some states of doubly excited helium is much more like that of a linear triatomic molecule than of the atomic shell model. Basing their inference primarily on the energy levels in approximate O(4) symmetry derived from a broken $O(4)\times O(4)$ symmetry of two hydrogenlike electrons, they suggest that the approximate constants of the motion of states normally designated by configurations $(nln'l')$ correspond to the rotational and vibrational motions of a linear ABA molecule. Configuration mixing is considerable in these states, so that the orbital angular momentum of each electron is in no way a good constant of the motion; i.e., a "solar system" model is a poor model for states of He** with $n_1 = n_2$.

However until the proposal of Kellman and Herrick, we had no physical picture to supplant that of orbiting electrons, each with nearly constant angular momentum. Their new molecular model offers a conceptual picture dramatically different from anything previously accepted as a description of electrons in an atom. (Moleculelike models had occasionally been proposed[5] but never with a logical or quantitative basis comparable to or related to that of Refs. 1–4.) The arguments given by Kellman and Herrick are persuasive, but their model overturns our traditional conceptions at such a deep level that we are immediately obliged to put that model to test. If their suggestion survives such a test, it opens the possibility for identifying hitherto unexplored commonalities of microscopic few-body systems generally, including molecules, nuclei, and possibly even hadrons.