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EXIT CHANNELS OF AUTOIONIZATION RESONANCES IN ATOMS*

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ABSTRACT

In many-electron atoms with open shells strong autoionization resonances occur when an electron from an inner, weakly bound subshell is excited. Usually, the resonance state lies above several ionization thresholds and, hence, will decay into more than one exit or continuum channel. Several cases are discussed in which the resonance state is induced by synchrotron radiation, and the exit channels are differentiated and characterized by the analysis of the ejected electrons.

INTRODUCTION

Autoionization resonances studied originally by optical spectroscopy some 50 years ago involved electron excitation from the penultimate electronic level. In this case only one exit channel needed to be considered. Resonances investigated nearly 25 years ago with the aid of synchrotron radiation involved again the penultimate level and, significantly, involved also deeper lying levels, such as the outermost ns levels of the rare-gas atoms. In these cases, two exit channels exist, the $\varepsilon p_{3/2}$ and $\varepsilon p_{1/2}$ channels. However, the use of the photoabsorption technique did not allow one to distinguish the different channels. This situation changed in recent years when, with the advent of the ESSR technique in which electron spectrometry is combined with synchrotron radiation, the various exit channels could be discerned and studied in detail by measuring the variation of the partial cross section, the angular distribution parameter and the spin-polarization parameters over the region of the autoionization resonance.

In this paper, several representative examples of these detailed studies of resonances in atoms will be discussed. Much of the work reported concerns open-shell atoms in which strong intra-shell transitions (involving subshells of the same principal shell) are possible. Two of the important dynamic parameters, the partial photoionization cross section, σ_i, and the photoelectron angular distribution parameter, β_i, are determined in these studies.

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EXPERIMENTAL

An electron spectrometer system containing originally two and most recently three electrostatic electron energy analyzers is used to measure simultaneously at two angles the energy and flux of the photoelectrons ejected from free atoms, including monoatomic metal vapors. Monochromatized synchrotron radiation serves as the excitation source which continuously covers the energy range of interest. Both σ_i and β_i are obtained from the relation

$$I_i \propto \frac{d\sigma_i}{d\Omega} = \frac{\sigma_i}{4\pi}\left(1+\frac{\beta_i}{4}\left(1+3p\cos 2\phi\right)\right)$$

by measuring, respectively, the electron flux I_i at an angle ϕ_m for which $1+3p\cos 2\phi=0$, and at two arbitrary angles, preferably $\phi=0°$ and $90°$. The angle ϕ is referred to the major polarization vector of the synchrotron light. The degree of polarization, p, is usually quite high and ranges from about 90 to 95% in the energy range employed in the present work. Both conventional PES spectra, in which the photoelectron spectrum is obtained at a fixed photon energy and CIS spectra in which the dependence of a constant ionic state on the photon energy is obtained are recorded. While the PES spectra serve the purpose of determining and distinguishing the various possible exit channels, the CIS spectra are especially suited to scan a resonance in fine detail, and continuously, over a given photon energy range.

THE 3d→4p RESONANCE IN GALLIUM

Between 18 and 23 eV a 3d electron can be promoted into the 4p subshell which contains only one electron. Although the excitation does not take place within the same principal shell, the proximity of the nearly empty 4p subshell gives rise to strong transitions to resonance states that lie above three exit channels, namely $\overline{4s}\,{}^1P,\varepsilon\ell$; $\overline{4s}\,{}^3P,\varepsilon\ell$ and $\overline{4p}\,{}^1S,\varepsilon\ell$.

As seen from Fig. 1, these channels are clearly separated in the PES Spectrum and, hence, allow the determination of σ_i and β_i through the resonance region for each component. It might be noted that these channels could be further differentiated if it were possible to separate the ^3P multiplet components or if we were to apply a spin-polarization analysis. The interaction of one of the many possible resonance transitions with the direct transitions to the three continua is illustrated in Fig. 2. The photoabsorption spectrum[1] shown along the energy axis is composed of the contribution from the individual exit channels and these contributions. were determined[2], in the CIS mode of operation, by observing the photolines corresponding to each channel over the

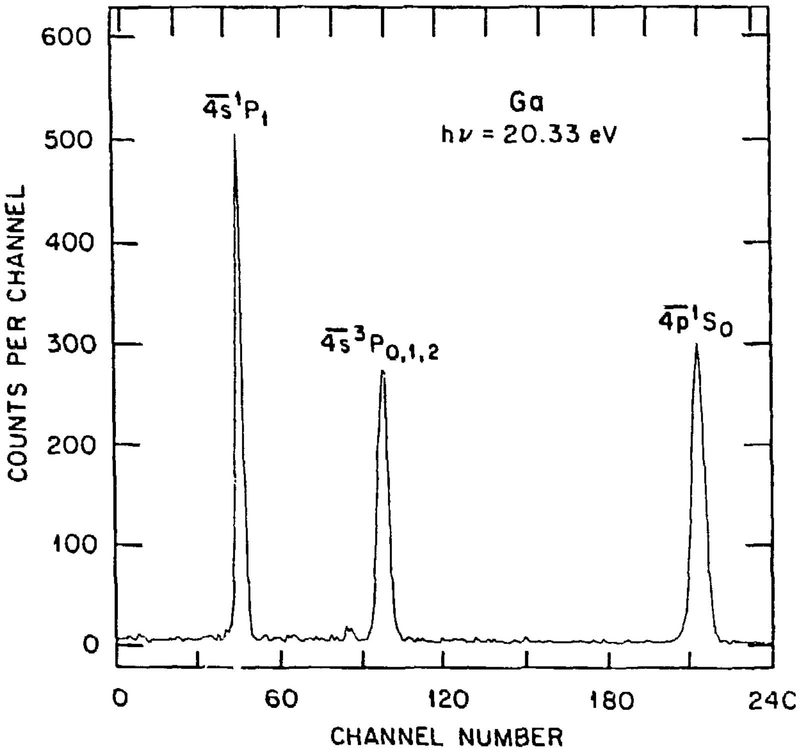

Fig. 1 Photoelectron spectrum of gallium showing the photoelectron lines that are indicative of the available exit channels for the autoionization resonance state occurring at 20.33 eV.

range of the resonance structure. The results are displayed in Fig. 3 and it can be seen that the partial widths follow a pattern similar to that of the total width which, in the absence of strong two-electron transition is virtually identical with the absorption cross section. However, on closer inspection we note that the resonance states that couple the $4p^2$ manifold to a ^3P state preferentially decay into the $\overline{4s}\ ^3P,\varepsilon\ell$ channel, and the states that couple the $4p^2$ to ^1S predominantly decay into the $\overline{4p}$ ^1S, $\varepsilon\ell$ channel. The coupling of $4p^2$ to the open 3d subshell appears to have no discernible relation to the population of the individual exit channels. As the partial widths (σ_i), the β_i parameter shows some characteristic dependence on the coupling of the $4p^2$ manifold: for the ^1S states β shows a small dip at the positions of the resonances, and for the ^3P states β displays a pronounced dip in the $\overline{4p}\,^1S$, $\varepsilon\ell$ exit channel.[2]

The $3d\rightarrow 4p$ resonance is a case where many closely spaced states interact with several continua. As a consequence a theoretical treatment, yet to be undertaken, will have to be quite elaborate.

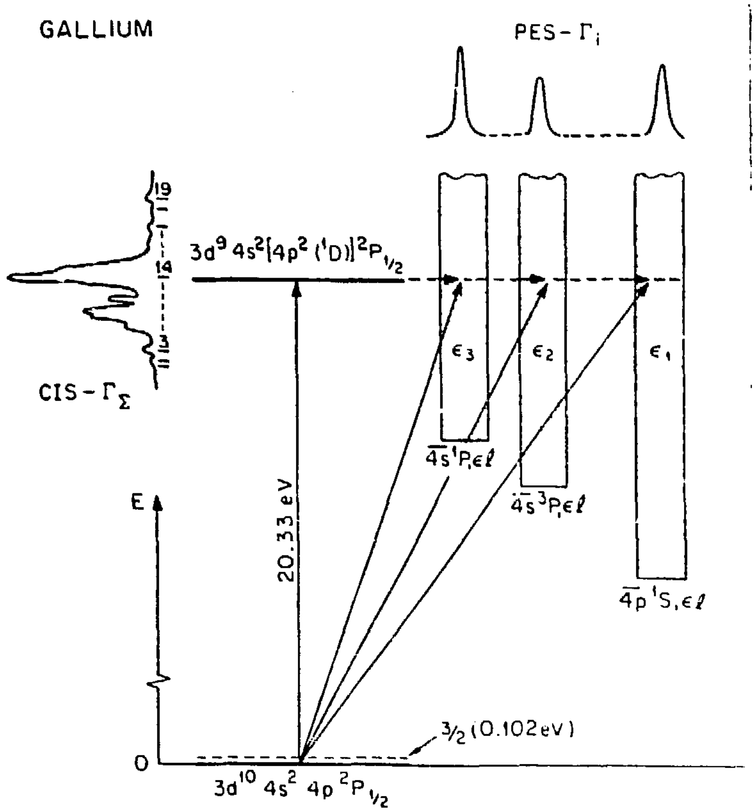

Fig. 2 Schematic of the 3d→4p resonance manifold as seen in absorption and its decay into three exit or continuum channels. The interfering direct photoionization processes are also indicated as well as the final ionic states and the energies ε of the emitted electrons.

THE 4d→5p RESONANCE IN INDIUM

In this element belonging to the same group as gallium strong resonances occur for the same type of excitation. However, as seen from Fig. 4, there is more variation in the individual channels than was observed for Ga (see Fig. 3).[3] At the same time, the coupling of the $5p^2$ manifold has much less effect on the decay characteristics than noted in Ga. For example, peak 10 which is a $5p^2\ ^3D$ resonance state decays into all channels, while in Ga the $^3P,\varepsilon\ell$ channel was preferred. The greater variety in decay paths for In can be attributed to (a) the fact that intermediate coupling prevails imposing less restrictions on the transitions and (b) the presence of many two-electron excitations[4] involving the 5s and 5p electrons close to the positions of 4d→5p excitation.

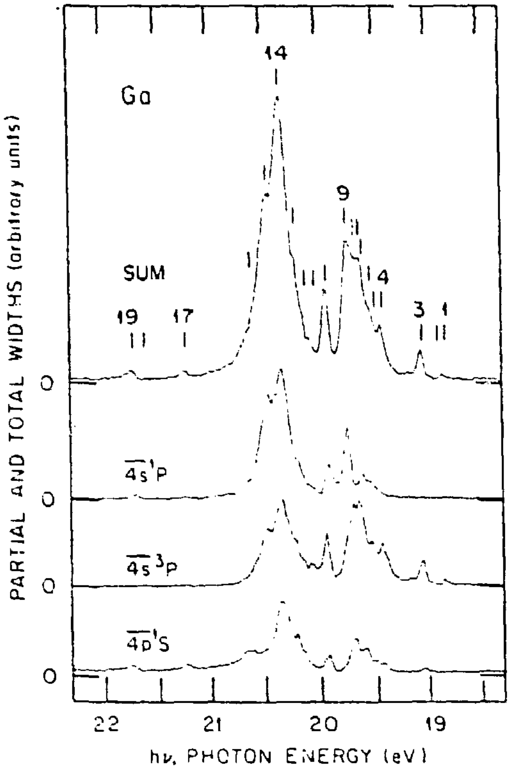

Fig. 3 The partial widths of the decay channels and the total width of the 3d→4p resonance in atomic gallium as recorded in the CIS mode of operation. The top spectrum is virtually identical with the absorption spectrum.

THE 5p→5d RESONANCE IN YTTERBIUM

Ytterbium is a closed-shell atom, but the presence of the empty 5d subshell close to the 6s and 4f levels produces strong resonances involving the indirect 5p→5d transition and the direct $4f \rightarrow \varepsilon \ell$ and $6s \rightarrow \varepsilon p$ transitions. The structure observed[5] in the three main exit channels is plotted in Fig. 5. Further structure occurs between 32 and 38 eV. However, since much of this range lies above the $5p_{3/2}$ ionization threshold and above the two-electron ionization limit, additional channels of the Auger type open up. Preliminary data[5] reveal the presence of these channels, so that the three channels shown in Fig. 5 will account for only part of the photoabsorption cross section reported earlier.[6]

THE 3p→3d RESONANCE IN MANGANESE

Transition series elements are subject to pronounced resonance features which may occur at rather high energies, up to nearly 200 eV, and which extend over a wide energy range. Transitions will take place from p to d levels and from d to f levels within the same principal shell. This implies that the otherwise smooth behavior of the dynamic properties will be

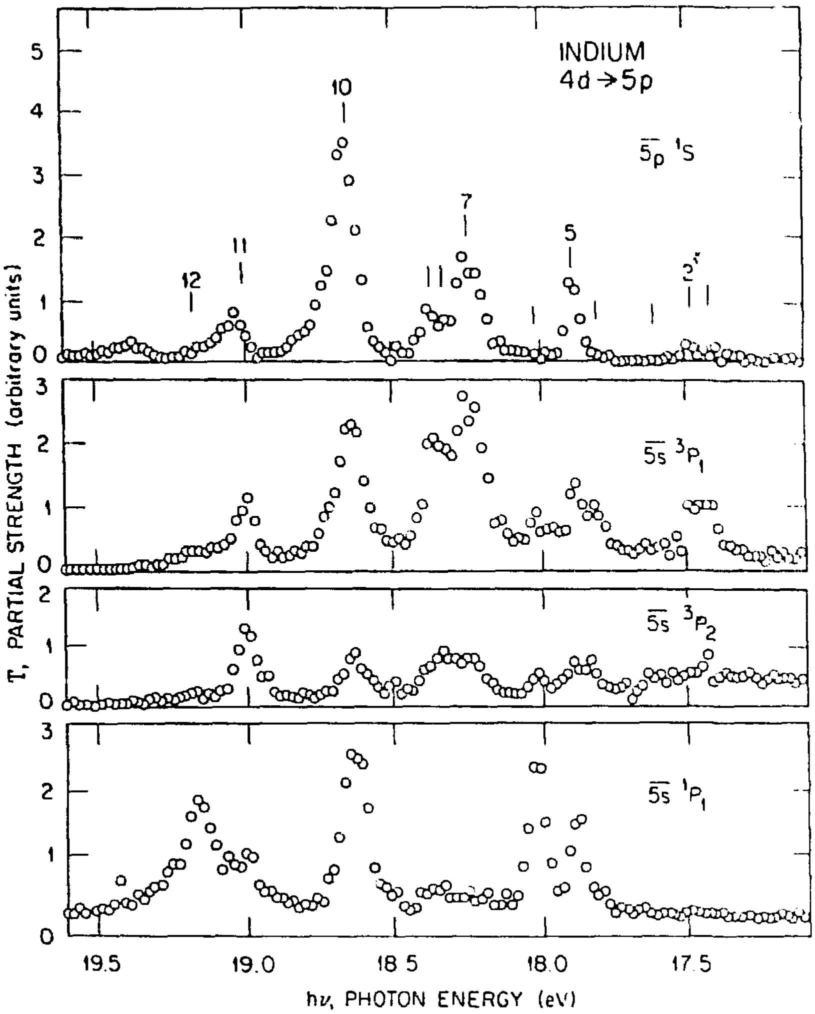

Fig. 4 The partial strengths or widths of the decay channels over the 4d→5p resonance in In as recorded in the CIS mode of operation.

strongly disturbed in many elements of the Periodic Table. One of the best studied elements is Mn and an overall representation[7] of the behavior of σ_i and β_i is shown in Fig. 6. At the resonance all exit channels can be seen to be strongly enhanced including the two-electron channels, the satellite lines which are due to 3d ionization together with either 4s or 3d electron excitation. Theoretical calculations[8] of the resonance properties are in good agreement with experiment for the 3d channel and in fair agreement with the weaker 4s channel. However, no calculations exist so far for the ionization-with-excitation channels.

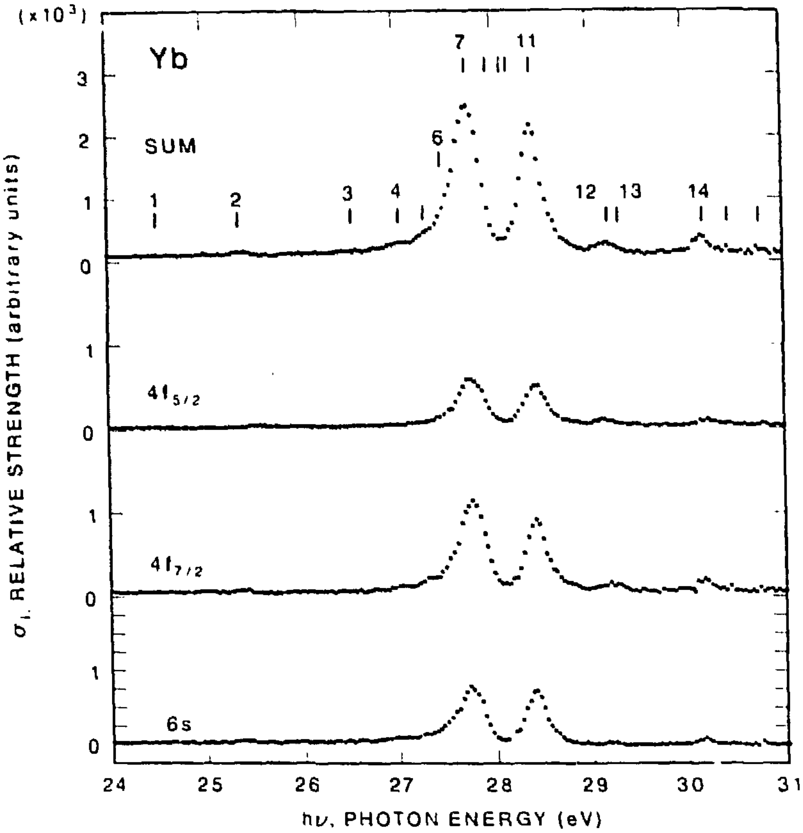

Fig. 5 The partial and total strengths of the decay channels over the 5p→5d resonance in Yb.

THE RESONANCES IN LEAD

In a heavy element like lead with many subshells in the outer regions of the atom many resonance states can be reached from different subshells and these states can, in turn, decay into many exit channels. Resonances have been observed by us for 5d→6p and 6s→np excitations. The 6s→np resonance is of particular interest, because the decay of the $np_{3/2}$, n=7,8,... states converging to the $^4P_{1/2}$ limit leads to a positive contribution, a peak, in the $\overline{6p}\ ^2P_{3/2}$, εℓ channel and to a negative contribution, a window, in the other possible channel, $\overline{6p}^2P_{1/2}$,εℓ. These contributions are of the same magnitude and hence, cancel in a photoabsorption spectrum which measures only the sum of the contributions.[9] In contrast to the $np_{3/2}$ states, the $np_{1/2}$ states exhibit positive contributions in both exit channels. A theoretical treatment of these closely related resonances that differ so greatly from one another is still outstanding.

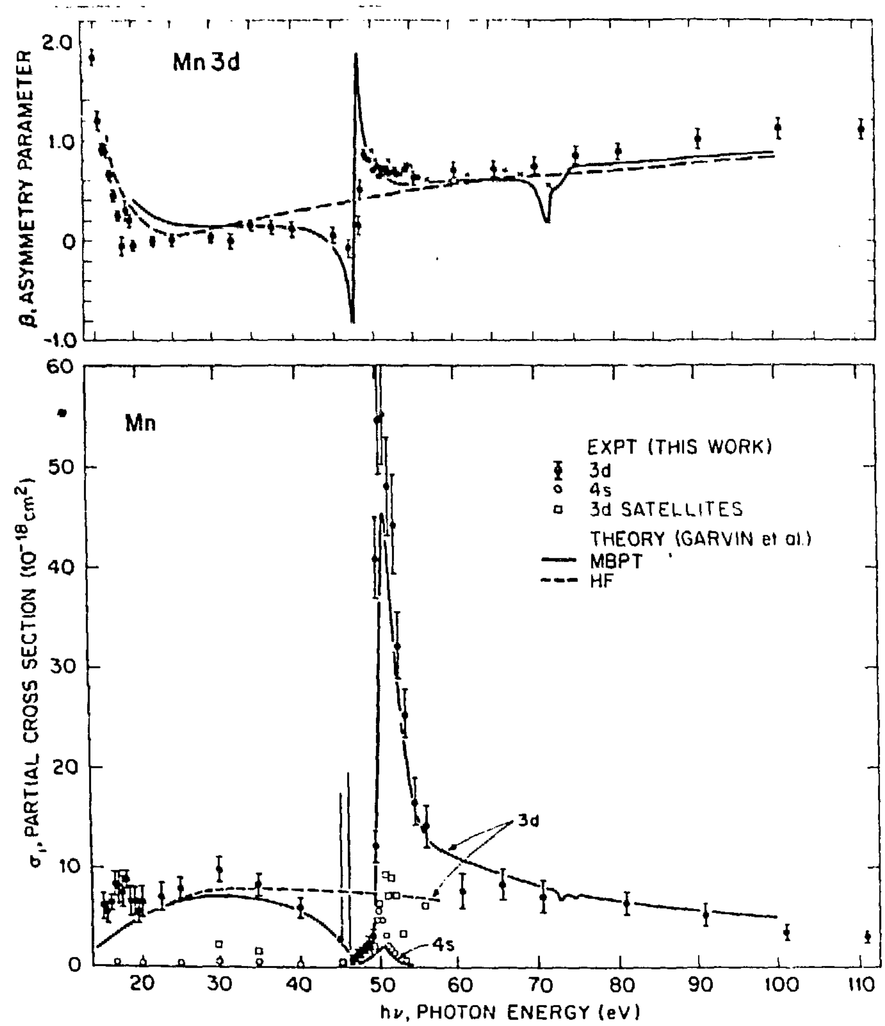

Fig. 6 The behavior of σ and β for different exit channels in the region of the 3p→3d resonance in Mn.

FINAL REMARKS

Autoionization resonances have now been studied in a number of atoms, many of them open-shell atoms, and they have been characterized by their partial strengths and β parameters as observed in ESSR experiments of the available exit channels. A great variety in the behavior of the dynamic parameters has been seen. So far no overall systematics have evolved. Theoretical calculations are still lacking in many instances. The situation appears to be more complex than it was for the related, but simpler case of Auger transitions in the early phases of the study of the Auger effect when the simple hydrogenic model could provide some guidance for the transitions between inner shells.

As we penetrate deeper into the shell structure, electrons from deeper lying shells are excited and more exit channels become accessible. In the transition region between the classical autoionization region and the classical Auger effect region, the radiationless decay of resonance states can involve single-electron exit channels as described in this paper and two-electron exit channels that are of the Auger type. Both types of continuum channels couple not only to the resonance states but also to each other and it will be of interest to determine the degree of coupling between the various channels. A few pilot studies, theoretical and experimental, have been made in this region. A detailed study was carried out for Xe,[10] in which the effects of $4d \rightarrow np$ resonances were delineated for the Auger ionization channels and the 5s and 5p photoionization channels. More work in this area is needed and will doubtless be done in the future.

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