Resonant Photoemission in Atomic Calcium: A Test Case for Atomic Theory

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We have observed a multitude of resonance phenomena in the photoelectron spectrum of atomic calcium excited in the $3p$ threshold region. Their detailed interpretation needs extensive theoretical insight; nevertheless, we distinguish some systematic connections between resonant intermediate levels and final-state photoelectron distributions. Finally, the lowest $3p$-ionization threshold, at 30.8 eV, is measured here, for the first time, from Auger lines observable only under resonant excitation conditions.

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In this Letter, we report on the problem of identifying intermediate excited states in resonant photoemission studies. One of the major results of the present work is the development of photoelectron satellite behavior as one goes from compact (strongly localized) to diffuse (Rydberg-type) *one-electron* excitations, i.e., switches from autoionization to Auger dominated decays, and when one goes from one-electron excitations to *double* or even *triple* excitations.

In our experiment, we combined electron spectrometry with synchrotron radiation to measure continuously, in the photon-energy region below and above the $3p$-ionization thresholds of atomic calcium, the electrons emitted in the direct photoionization processes and in the autoionization or Auger decays of intermediate $3p$ excited states. In the various exit channels, the residual Ca^+ $3p^6nl$ ion can be left in the ground state ($nl=4s$) or in excited states, producing numerous satellite lines ($nl=3d$, $4p$, $5s$, $4d$, $5p$, ...). Previous work in the field has mostly demonstrated the qualitative importance of resonant photoemission,[1,2] or studied in detail the influence of one specific resonance on an autoionizing intermediate state in the main exit channels.[3-8] A recent analysis of the main and satellite exit channels was made in a closely related case, the $5p$ excitation in barium,[9] over a narrow autoionization region.

Atomic calcium was chosen for this work because it is the simplest example of a closed-shell atomic system which shows a full range of many-body effects,[10,11] e.g., (i) strong induced field effects due to a large dynamic polarizability of the $3p$ subshell; (ii) contraction of the outermost shell charge distribution with change of configuration (collapse) upon core ionization of the type $3p^54s^2 \rightarrow 3p^53d^2, 3p^54s3d$, leading to large shakeup and shakedown satellite structures on, respectively, the high and low binding-energy side of the $3p$ main lines; (iii) Auger decay $3p^54s^2 \rightarrow 3p^6\epsilon l$ following the creation of a hole in the first inner shell; (iv) post-collision interaction effects under the condition of threshold excitation. The great advantage with Ca, compared to Ba, is that it is sufficiently simple to provide a proving ground for atomic many-body theory. From the experimental data, one can actually extract a number of reasonably clear-cut cases that can be compared with theoretical model calculations.

We used our previously described apparatus at the ACO synchrotron radiation facility[12] to measure, with a cylindrical mirror analyzer, the electrons emitted at the magic angle of 54°44′ in the interaction of a monochromatic photon beam[13] with a beam of Ca atoms. Calcium was evaporated from a resistively heated stainless-steel oven at about 800 K. Electron spectra were systematically recorded every 0.1 eV between 26 eV and 40 eV, with a bandpass of 0.08 eV (every 0.03 eV at some selected resonances). This method of obtaining the data provides more accurate results than the use of the constant-ionic-state (CIS) analysis[8] when a large number of exit channels have to be simultaneously investigated, especially when some of them are relatively weak.

Figure 1 shows a typical photoelectron spectrum, obtained at a photon energy of 31.99 eV, with the following main features: (a) a main $3p^64s$ line; (b) $3p^6nl$ satellite lines converging towards the $3p^6$ double-ionization threshold; (c) Auger lines above the $3p^6$ threshold. The spectrum is excited via a

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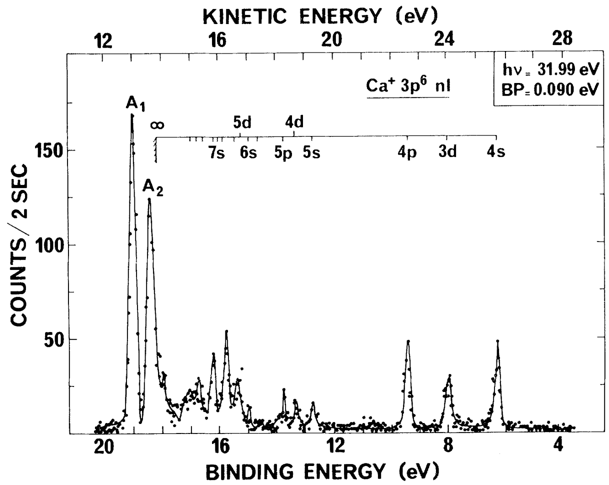

FIG. 1. Spectrum of electrons ejected from atomic calcium by 31.99-eV photons. At this energy, the intermediate $3p^5 4s^2\,{}^2P_{3/2}5s\,[\frac{3}{2}]_1$ state is formed via a *single*-electron excitation, according to the photon absorption data (Ref. 14). A_1 and A_2 are two Auger lines observable only at low photon energy, just above threshold. A_1 corresponds to the lowest $3p$-ionization limit at 30.8 eV binding energy involving $4s \rightarrow 3d$ rearrangement.

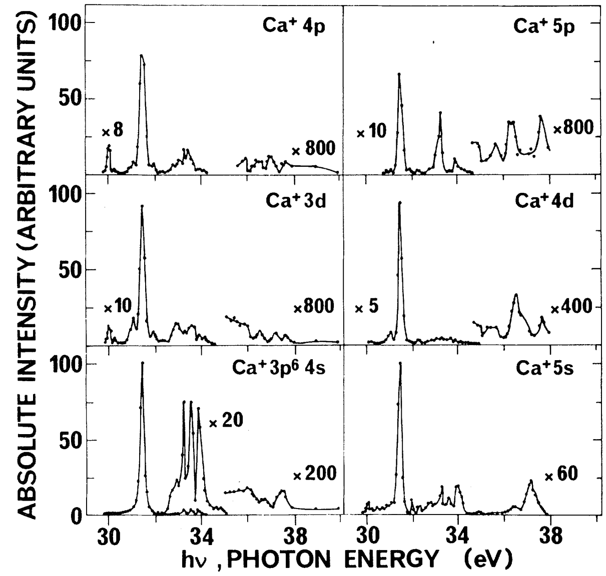

FIG. 2. Relative cross sections of the main $(4s)$ and of five satellite $(3d,\ 4p,\ 5s,\ 4d,\ 5p)$ $3p^6nl$ exit channels. The two main $3p$ thresholds are at 34.33 eV $(3p^5 4s^2\,{}^2P_{3/2})$ and 34.67 eV $(3p^5 4s^2\,{}^2P_{1/2})$.

weak, sharp $3p^5 4s^2 5s$ resonance, but nevertheless a whole distribution of satellites is resonantly excited. This appears to be the rule rather than the exception. Only in very special situations does a resonance excitation branch to a particular excited level of the final ionic system.

Figure 2 presents the variation of the partial photoionization cross sections as a function of the photon energy for six exit channels. Similar data have been obtained for the $5p$ photoionization of Ba.[9] However, for the discussion of our results, we are very much aided by the absorption spectrum of Ca vapor and the classification by Mansfield and Newson,[14] which allows us to identify the resonant satellite signature of different intermediate resonances, while, in the case of Ba, such an identification was limited by the complexity of the photoabsorption spectrum.

Broadly speaking, we may distinguish between three distinct modes of decay of a *single-electron* excitation, $h\nu + \mathrm{Ca} \rightarrow \mathrm{Ca}(3p^5 4s^2 nl)$.

Autoionization much stronger than Auger decay:

$$3p^5 4s^2 nl \rightarrow 3p^6 4s\,\epsilon l'.$$

The resonance decays mainly to the $4s$ ionization channel. The signature of this type of resonance is that the entire $3p^6nl$ ionic final-state distribution resonates as a whole. There is no resonant behavior in the satellite to main-line intensity ratio. This behavior is obtained if the electron(nl)–hole$(3p)$ wave functions strongly overlap, which really applies only to a single case, the strong $3p^5 3d 4s^2\,{}^1P$ resonance at 31.41 eV (see Fig. 2).[15]

Autoionization and Auger decay having similar probabilities:

$$3p^5 4s^2 nl \rightarrow 3p^6 4s\,\epsilon l'$$

comparable to

$$3p^5 4s^2 nl \rightarrow 3p^6 4s^0 n'l'\epsilon l''.$$

This situation occurs if the excited nl electron and the $4s$ valence electrons have comparable overlaps with the $3p$ core hole, and it applies to an intermediate range of excitations well below the $3p^5 4s^2$-ionization thresholds (34.33 and 34.67 eV). The signature in this region is that the branching ratio of $3p^6nl$ satellites to the main $3p^6 4s$ line varies dramatically while the $4s$ main line still shows strong resonance behavior.

Auger decay much more important than autoionization:

$$3p^5 4s^2 nl \rightarrow 3p^6 4s^0 n'l'\epsilon l''.$$

The core hole then Auger decays long before recombination has time to occur. The resonance therefore branches mainly to ionic excited states represented by $3p^6n'l'$ satellites, and there is only a weak resonance in the $4s$ main line. The process is sometimes described in terms of the resonantly excited electron (nl) being a *spectator*, but it must be emphasized that this concept is *not valid in general:* The change in potential from the intermediate to the final state spreads the intermediate nl level over a range of final $n'l'$ levels. With regard to which excited (nl) levels have weak wave-function overlap (weak recombination rate) with the $3p$ core-hole level, there are two major possibilities: (i) $nl=5s$ (Fig. 1), $6s$, . . . , leading to prominent resonances in a number of low-lying satellites; (ii) nl highly excited, approaching the ionization limit: This results in prominent resonances in groups of highly excited satellites. However, since Auger decay dominates, close to threshold one necessarily enters a region where highly excited levels (nl) merge into a quasicontinuum. Consequently, one cannot observe resonances in individual satellites.

In order to observe really dramatic resonances in one or two low-lying satellites, and only weakly resonant behavior of the $4s$ mainline, we have to probe *doubly* or *triply* excited resonances. The most spectacular resonance we have found so far is a resonance in the $5s$ satellite at an excitation energy around 37 eV, i.e., well above the main $3p^54s^2$ thresholds (Fig. 3). We propose that we are dealing with a *doubly* excited resonance: $h\nu + \mathrm{Ca} \rightarrow 3p^53d4s5s$, representing a $4s \rightarrow 5s$ shakeup satellite to the $3p^53d4s^2$ *absorption* resonance. Again, the autoionization process must dominate: $3p^53d4s5s \rightarrow 3p^65s$, but, this time, the process leads with the largest probability to the $3p^65s$ satellite configuration. Figure 2 shows that there is a large resonance in the $5s$ satellite, while the $4s$ main line rather shows an antiresonance (dip) in this region. One should note that, even in this case, the $5s$ electron does not remain a spectator: There is, relatively speaking, also a prominent resonance in the $6s$ satellite.

Our final example (Fig. 4) is very special. Firstly, it involves a *triply* excited intermediate resonance at $h\nu = 29.98$ eV:[14] $h\nu + \mathrm{Ca} \rightarrow 3p^53d^3 + 3p^53d4p^2$, and, secondly, the photon energy is below the lowest $3p$-ionization threshold. The decay of the in-

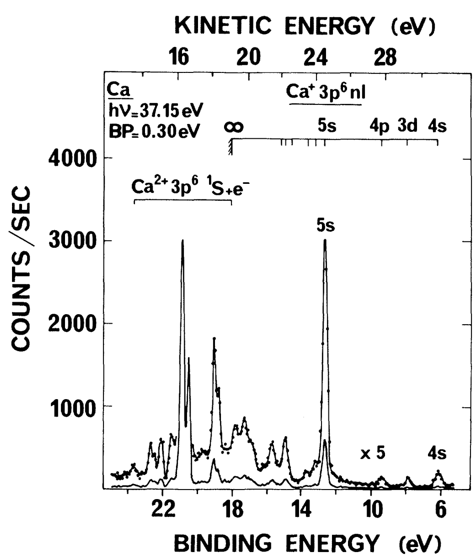

FIG. 3. Spectrum of electrons ejected from atomic calcium by 37.15-eV photons. The proposed intermediate state $3p^53d4s5s$ is excited via a *two-electron* transition. The Auger spectrum ($Ca^{2+}\ 3p^6\,{}^1S + e^-$) is the mirror image of the $3p$ photoelectron lines, not shown in the figure.

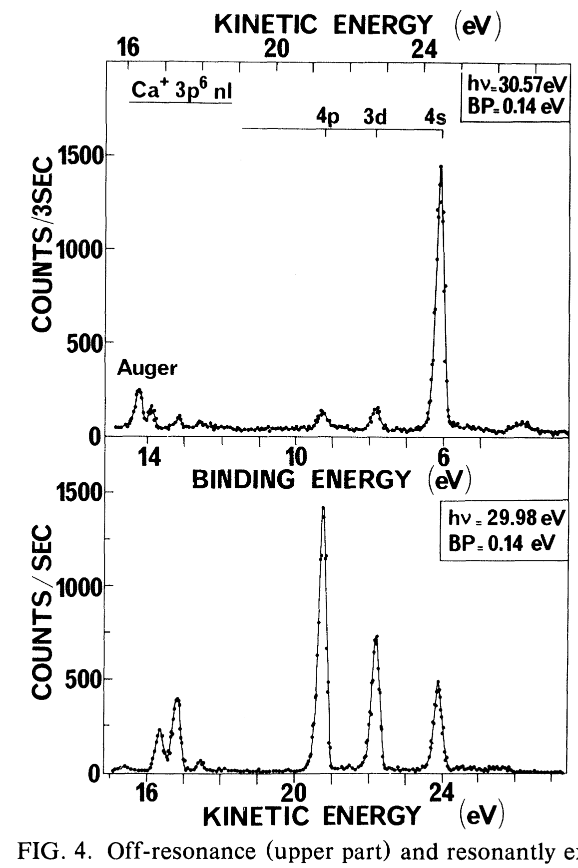

FIG. 4. Off-resonance (upper part) and resonantly excited (lower part) electron spectra from atomic calcium. The off-resonance spectrum shows the weak intensity of the $3p^63d$ and $3p^64p$ satellite lines, arising from initial state configuration interaction. The spectrum at 29.98 eV is produced via a *triply* excited intermediate $3p^5(3d^3\,{}^2P)\,{}^3P_1$ state, according to Ref. 14. In both spectra, the counting rate is the same for the $4s$ main line.

termediate resonance to lowest order necessarily leads to the $3p^63d$ or $3p^64p$ satellite configurations. The coupling to higher satellites, as well as the main $4s$ line, is quite weak. This appears very clearly in Fig. 4, and also in Fig. 2, where the $3p^63d$ and $4p$ satellites show prominent resonance enhancements,[16] while the main $4s$ line rather shows a dip or an oscillatory behavior.

In conclusion, we have demonstrated that photoelectron spectroscopy is a powerful tool for studying the dynamics of resonant excitation and decay processes, taking the example of atomic calcium in the $3p$ threshold region. In general, any given intermediate $3p$ resonance will lead to resonant enhancement of large groups of photoelectron lines, the distribution of which characterizes the intermediate state. Only in exceptional cases does a resonance appear only in one or two specific satellite lines. We finally note that resonant excitation was essential for being able to observe, via the Auger spectrum, the lowest $3p$-ionization limit at 30.8 eV.

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[15]Similar behavior was found by Korbrin *et al.* (Ref. 9) for barium: The $(5p^56s^2\,{}^2P_{3/2})5d\,{}^1P$ resonance at 617.8 Å decays mainly to the $5p^66s$ channel.

[16]Analogous satellite $(5p^65d, 6p)$ resonances were observed in barium (Ref. 9). However, the intermediate level was proposed to be $(5p^55d\,{}^3D)6s\,{}^2D_{5/2}5d$, i.e., a double excitation.