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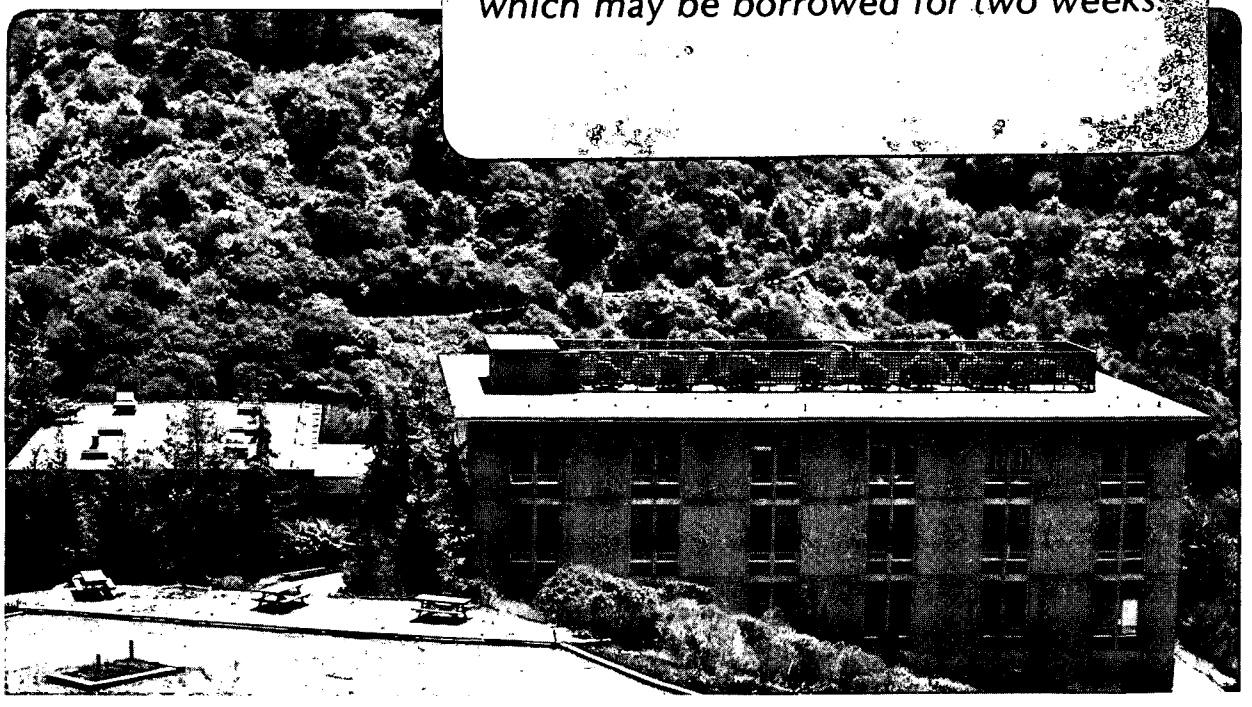

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Observation of Many New Argon Valence Satellites Near Threshold

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Abstract

High resolution photoelectron spectra and zero-volt electron scans were measured following synchrotron radiation excitation of argon, to elucidate the photon energy range between threshold and the Cooper minimum region of the Ar 3s photoline. A number of the "correlation satellite" lines show a dramatic increase of fractional intensity toward threshold, yielding a total of about 40 observed photolines at threshold, of which more than half were not previously observed in photoemission. This effect is interpreted as arising from inelastic scattering of the outgoing photoelectron by the residual ion, yielding high angular momentum ionic states otherwise inaccessible by photoemission.

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Satellite structure in photoelectron spectra is attracting rapidly growing interest, especially since monochromatized synchrotron radiation has made possible the systematic exploration of the photon energy dependence of satellite intensities.[1-4] Special interest has recently focussed on the intensity variation near threshold,[5-7] where satellite transition strengths are directly related to electron correlation effects associated with the photoionization process. A basic problem in the interpretation of satellite spectra is the identification of the dominant correlation effect(s) contributing to the intensity of a given satellite. The energy region near threshold is particularly suited for differentiating among the various electron correlation mechanisms, because they are expected to show different threshold behaviors.

It is useful to distinguish between two types of correlations, one nearly independent of the incident photon energy and the other one strongly energy-dependent.[8] The first type is associated with "intrinsic" electron correlation effects in the neutral atom or the ionic core; the main corresponding correlations can be described by configuration interaction in the initial atom and final ion, and they would be present even in the absence of photoemission. Satellite intensities originating from these interactions reflect basically the spatial overlap between different configurations in the initial[9] and final-ionic state,[10] modulated by transition matrix elements. These intensities tend to vary smoothly, and usually slowly, with photon energy.

In contrast, there are also "dynamic" correlations, which exist explicitly through the dynamics of the photoionization process. Dynamic correlations are expected to

affect satellite intensities strongly near threshold, through two mechanisms. First, satellite intensities could rise dramatically very close to threshold through inelastic scattering of the outgoing photoelectron by the ionic potential,[12] because the scattering probability increases with decreasing kinetic energy. Alternatively, that portion of the satellite intensity which arises through the response or "shake" process,[13] in which the passive electron fail to relax completely during photoionization, will decrease near threshold, where the screening potential changes more slowly. The general feasibility of separating correlation mechansisms by distinct threshold behavior has been demonstrated recently for different rare gases[5,6] and molecules.[7] Inelastic scattering near threshold, while predicted for several cases,[14] has been observed only in He,[15] where it is the only possible type of correlation in the final state. The question arises: does this continuum interaction, which is known to affect main line intensities[8] via the coupling of different subshells, also play a role for the satellite structure of larger atoms than helium?

Additional interest in the satellite near-threshold-behavior has been stimulated by recent measurements of satellite cross-section effects observed earlier in main lines, such as autoionizing resonances, shape resonances and Cooper minima.[5,7,2] Such effects, if occurring in the threshold region, could be superimposed on the characteristic satellite intensities, leading to misinterpretations regarding the underlying correlation effects.

The valence subshells of Ar show such phenomena: a pronounced Cooper mini-

mum, final state interactions involving the continuum electron,[8] and the beginning of an orbital collapse.[16] The last leads to strong interactions in the final ionic state, which are assumed to govern the pronounced satellite structure of the 3s photoline.[17] The most prominent peak of this spectrum, $3s^2\ 3p^4\ 3d\ (^2S)$, was the subject of recent studies,[3,4] over a wide energy range. However, none of these studies covered the energy range between the Cooper minimum and threshold.

In this Letter we report the first measurements of increasing satellite peak intensity toward threshold in a system with a nonhydrogenic final ionic state. We observed a dramatic increase in the number of Ar photoelectron satellite lines near threshold, in particular at zero kinetic energy, relative to all previous spectra taken at higher photon energies, including the most recent high resolution spectra. Our results for the $3s^2\ 3p^4\ 3d\ (^2S)$ satellite show a pronounced Cooper minimum in the cross section of this satellite. The behavior of this satellite, despite a shifted Cooper minimum in the satellite channel, appears to be virtually constant down to threshold, as expected theoretically.[8,10]

In this work, the argon valence satellites were studied in the photon energy range 32-100 eV, emphasizing the lower-energy end. The satellite peaks were assigned by comparison with corresponding optical levels.[11] Our data were compared with earlier photoelectron satellite results by selecting some well-separated lines and groups of lines, labeled in order of their binding energies.

The experiments were performed at the Hamburger Synchrotronstrahlungslabor

(HASYLAB) using a toroidal grating monochromator in conjunction with time-of-flight photoelectron analysis and at the Stanford Synchrotron Radiation Laboratory (SSRL) using a plane grating monochromator for a zero-volt electron scan. Both systems have already been described in some detail in earlier publications.[5,6] The time-of-flight system was designed for high resolution and high transmission at low kinetic energies. With small acceleration voltages, the spectrometer, when optimally aligned, has a virtually constant transmission down to approximately 0.5 eV. The overall resolution is about 2% of the kinetic energy of the accelerated electrons. The spectrometer used for the zero-volt electron scan is also based on time-of-flight detection, with an additional extraction field added across the interaction region to enhance the transmission for electrons with 0 eV kinetic energy by three orders of magnitude compared to the faster electrons. The resolution of the zero-volt spectrometer is better than 0.1 eV. Most of the measurements were actually limited by the resolution of the monochromator.

The main purpose of this investigation was to study the structure of the argon valence satellites at energies below the Cooper minimum of the 3s main line, down to threshold. To facilitate comparison of our results with recent work on the valence satellites of Ar, and to identify the problems arising from the Cooper minima in the cross sections right at the beginning, we begin the presentation of our data with the well-known $3s^2\ 3p^4\ 3d\ (^2S)$ "virtual-Auger" satellite. Fig. 1 shows the absolute cross section of this satellite plotted on a kinetic energy scale, together with the data

points of other authors, which were normalized to our 3d cross-section curve. The dashed-dotted curve in Fig. 1 represents this 3s cross-section curve, scaled to the satellite intensity at high kinetic energies. The satellite cross section shows the same qualitative behavior, deviating at low kinetic energies. A simple explanation of this deviation is that the Cooper minimum in the satellite channel occurs at a shifted kinetic energy. Such a shift could be caused by the different overlap of the ionic state in the satellite configuration with the corresponding outgoing electron wave in comparison to the 3s main line. The dashed curve represents the same scaled 3s cross section, shifted by 6 eV to lower kinetic energies. This curve fits the satellite cross section unexpectedly well, even at very low kinetic energies, supporting the idea of a "shifted Cooper minimum" in the satellite channel.

Modulation by this Cooper minimum lowers the near-threshold satellite intensities. However, the "unaffected threshold behavior" of this satellite compared with the 3s main line is virtually constant, as one would expect theoretically. In this example, the Cooper minimum is an additional effect, which may obscure the general threshold behavior of a satellite. Even for a satellite without a Cooper minimum, the (satellite)/(main line) intensity ratio is still affected, though not very close to threshold. To visualize this remaining effect, we have drawn a rough curve (dotted line) for a hypothetical 3s cross section without a Cooper minimum. On dividing this curve by the actual 3s cross section, we obtain a ratio, which shows the general modulating effect of the 3s Cooper minimum on a (satellite)/(main line) branching

ratio.

Fig. 2 shows three selected (satellite)/(3s main line) ratios taken at equal kinetic energy, together with such a tentative ratio curve. This curve is scaled to the respective satellite intensity at high kinetic energy, both as a reminder of the Cooper minimum effect and as a guide to roughly delineate the unaffected near-threshold region. In this near-threshold region we have observed basically two types of behavior. The first is a constant ratio, as shown by satellite 3: $(^1S)4s(^2S)$, which we have also seen in Fig. 1 for satellite 4, which has the same ^2S term symbol in the final ionic state. The second, largely unexpected, is an increasing fractional intensity towards threshold, as shown by satellite 2 ($(^3P)3d(^4D)$, $(^3P)4s(^4P)$). Satellite 1, consisting of two final ionic states $(^1D)3d(^2G)$ and $(^3P)4p(^4P^o)$, is displayed in the uppermost part of Fig. 2. It shows clear indications of resonance enhancement due to autoionization of discrete states (double excitations to 4p5s states around 33.6 eV[18]) into this satellite channel, an effect already observed for He[15] and Ne.[5] However, the enchancement structure for satellite 2 is different from discrete excitations. We propose that this threshold enhancement, which is also shown by other satellites in the Ar valence satellite spectrum, results from inelastic scattering of the outgoing electron in the final state.

To support this interpretation of the observed threshold behavior, we show in Fig. 3 a sequence of three different photoelectron spectra taken in the near-threshold region, together with a zero-volt electron scan. These spectra differ dramatically

from all previous satellite spectra taken at higher photon energies, irrespective of the Cooper minimum in the 3s cross section, both in the number of resolved lines and in their intensity distribution. The zero-volt electron scan shows, in particular, that to almost every optically observed, excited Ar^+ level there corresponds a satellite line. This means that most of the excited Ar^+ configurations interact with the 3s and 3p hole states which are genuinely associated with the Ar valence photoionization process. However, most of these satellite lines disappear relatively quickly with increasing photon energies, although some may be hidden by the limited resolution of the measurements at higher photon energies.

How can we explain the qualitative difference between the satellite intensities at threshold and satellite spectra at higher photon energies? The straightforward designation of most of the satellite peaks by optical data[11] shows a large number of final ionic states such as ^2G and ^4F, which cannot be populated directly through photoemission, by invoking correlations only in the ground and final ionic states. To explain the intensities of these satellite states, final-state interactions must be taken into account. In the final state the photoelectron may inelastically scatter on its way out, thereby exciting another electron. In characterizing the energy dependence of these inelastic scattering processes, the relevant energy for most simultaneous excitation and ionization processes is the excess energy necessary for the excitation. A qualitative comparison with the final state interaction in He shows that most of the intensity corresponding $He^+(2p)$ observed near threshold has

already disappeared within one to two units of excess energy. For Ar this means that all satellites associated with a primary 3s hole should lose their intensity comparably over a range of a few eV. This behavior is shown, for example, by satellite 2, having the main configuration $(^1D)3d(^2G)$. This supports the interpretation of the threshold behavior of this satellite as arising through inealstic scattering.

The large overlap between the 3s hole state and the states with a collapsed 3d orbital, which all belong to the same manifold with $n = 3$,[19] is probably responsible for the strength of the observed inelastic scattering processes. However, the strong coupling between the Ar 3s and 3p main lines, especially near threshold,[8] partly obscures the usual distinction between a 3s and a 3p satellite in this region.

In conclusion, we have shown the importance of inelastic scattering processes to the valence satellite structure of argon by studying the threshold and near-threshold behavior of individual satellite lines. The corresponding interpretation of the observed intensity enhancement near threshold is supported by the appearance of many previously unobserved satellite transitions which are not allowed by interactions in the initial and final ionic state alone.

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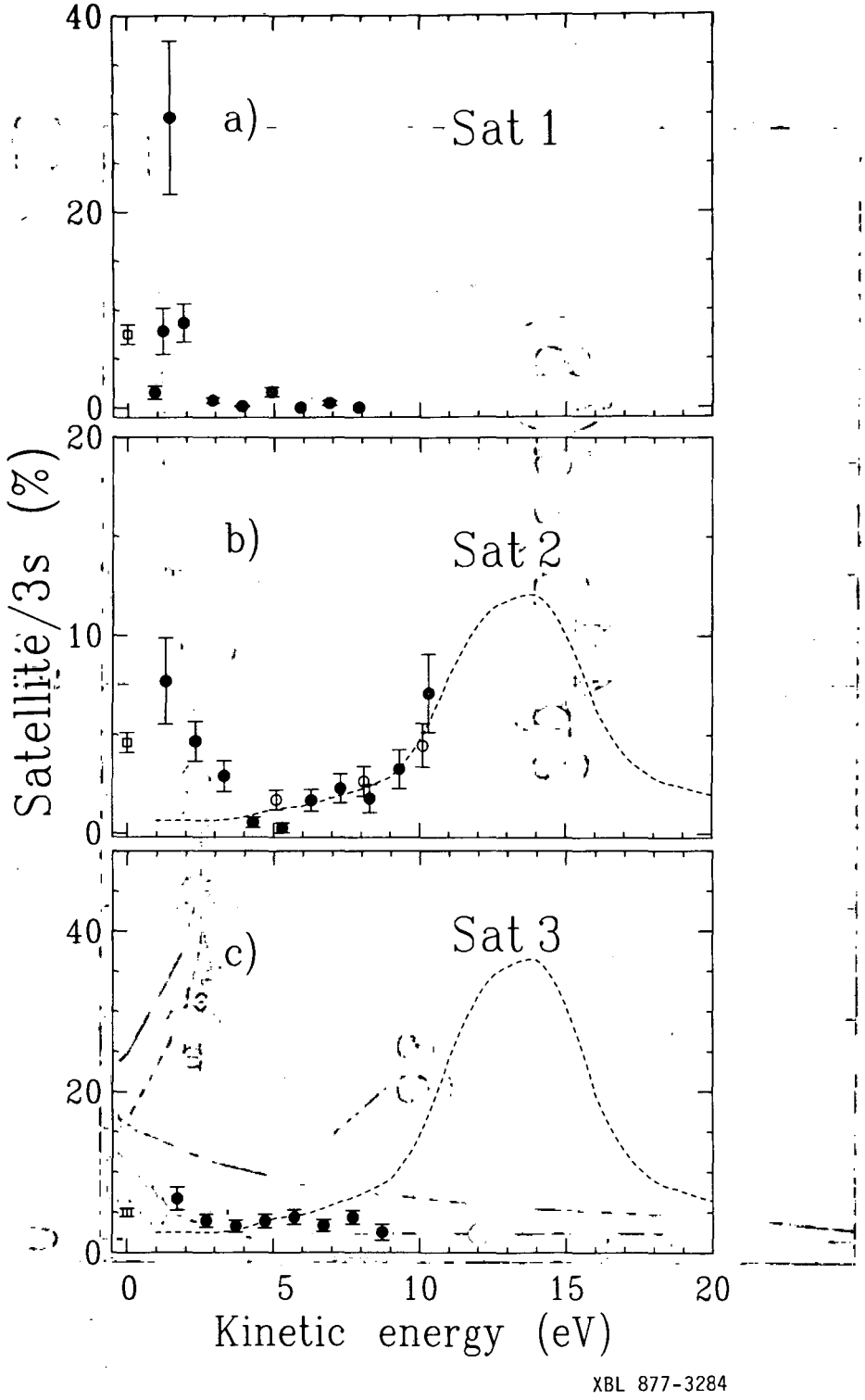

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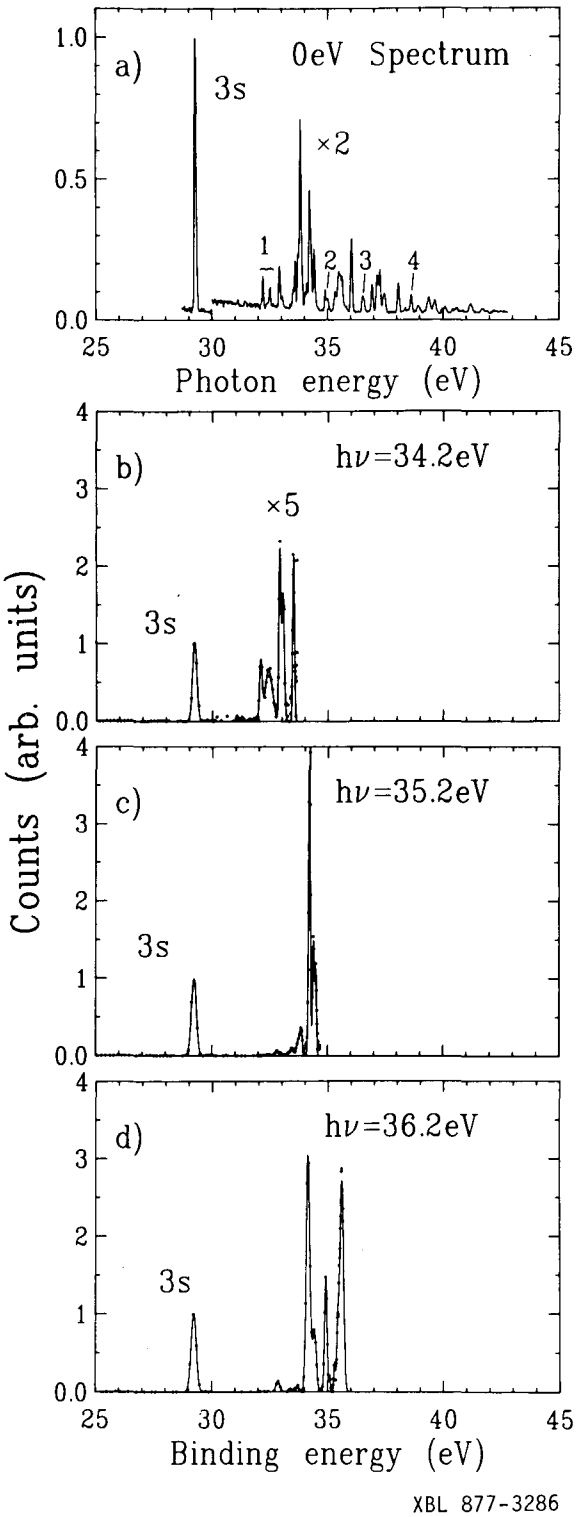
Figure 2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0eV Spectrum
3s
×2
1
2
3
4
Photon energy (eV)
b)
hν=34.2eV
×5
3s
c)
hν=35.2eV
3s
d)
hν=36.2eV
3s
Counts (arb. units)
Binding energy (eV)
XBL 877-3286

Figure 3

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