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Near Threshold Behavior of Photoelectron Satellite Intensities

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ABSTRACT

The historical background and understanding of photoelectron satellite peaks is reviewed, using He(n), Ne(1s), Ne(2p), Ar(1s), and Ar(3s) as case studies. Threshold studies are emphasized. The classification of electron correlation effects as either "intrinsic" or "dynamic" is recommended.

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I. INTRODUCTION

Satellite peaks in photoelectron spectra tend to evoke one of two common responses. To the investigator studying one-electron properties, or using photoelectron spectroscopy as an analytical tool, a satellite peak is usually either a curiosity or a source of error. From this viewpoint, satellites are acknowledged, then ignored. They are assigned disparaging names, such as "shake-up peaks"--suggesting abnormality--and relegated to the category of phenomena outside the mainstream of science.

At a more fundamental level, of interest to this Conference, photoelectron satellite peaks are assigned to "correlation states", thus acknowledging their origins in the correlated motion of electrons in multielectron systems. We also recognize the intrinsic importance of these satellites, noting that of all observable photoelectron channels, most lead to correlation states in the product ion, in contrast to a very limited number of (intense) channels leading to "main-line" states. Even more important, these satellite transitions contain information about electron correlation that is simply not accessible by other means. We are therefore interested in the extent to which this information can in fact be extracted from spectral data.

This paper is a progress report on our developing understanding of phenomena associated with correlation states in photoelectron spectra, as of mid-1987. The paper is almost entirely phenomenological, as befits the state of the field, with experiment leading theory at this time. We concentrate on the rare gas atoms He, Ne, and Ar, which are in one sense the "simplest" systems, and we focus particularly on near-threshold phenomena, for which considerable progress has recently been made.

The next two sections summarize the level of our understanding of correlation satellite phenomena in 1975 and 1985, respectively. Subsequent sections report recent advances in our knowledge of satellites in He, Ne, and Ar, with different emphases, as is appropriate for these dissimilar atoms. Typically the discussion is set into historical context only to the extent needed to appreciate the significance of threshold or near-threshold findings. In the final Section we draw substantial--and rather optimistic--conclusions about the separability of "intrinsic" and "dynamic" correlation, and about the value of studying correlation-state spectra in general.

II. OUR UNDERSTANDING OF PHOTOELECTRON SATELLITES IN 1975.

The term "shake-up satellites" came into common usage around 1970, by analogy with "shake-off" transitions described earlier by Carlson and co-workers [1,2]. Krause et al. [3] reported 1s correlation states in Ne^+ in 1968, and in 1974 Gelius [4] obtained a textbook quality high-resolution Ne(1s) correlation-state spectrum in which some 13 correlation-state peaks were identified. On the theoretical side, T. Åberg [5] used the sudden approximation and closure to derive expressions relating the energies and intensities of satellites. In this approximation, the photoelectron satellite intensity from a single-configuration initial state of an N-electron atom, $\Psi_o(N)$, to a satellite state $\Psi_j(N-1)$, accompanying the "main-line" transition to obital i, is proportional to

$$I_{ij} = |\langle \Psi_j(N-1) | a_i | \Psi_o(N) \rangle|^2$$

where a_i is an annihilation operator. Based on this approach, extended to include correlation in the initial state, Martin [6] made quantum chemical calculations on both Ne and Ne^+, obtaining correlation-state intensities in good agreement with experiment. Fig. 1 shows how Martin and Shirley illustrated the symmetry between Ne and $Ne^+(1s)$. Thus by 1975 correlation satellites were understood in the high-energy limit as

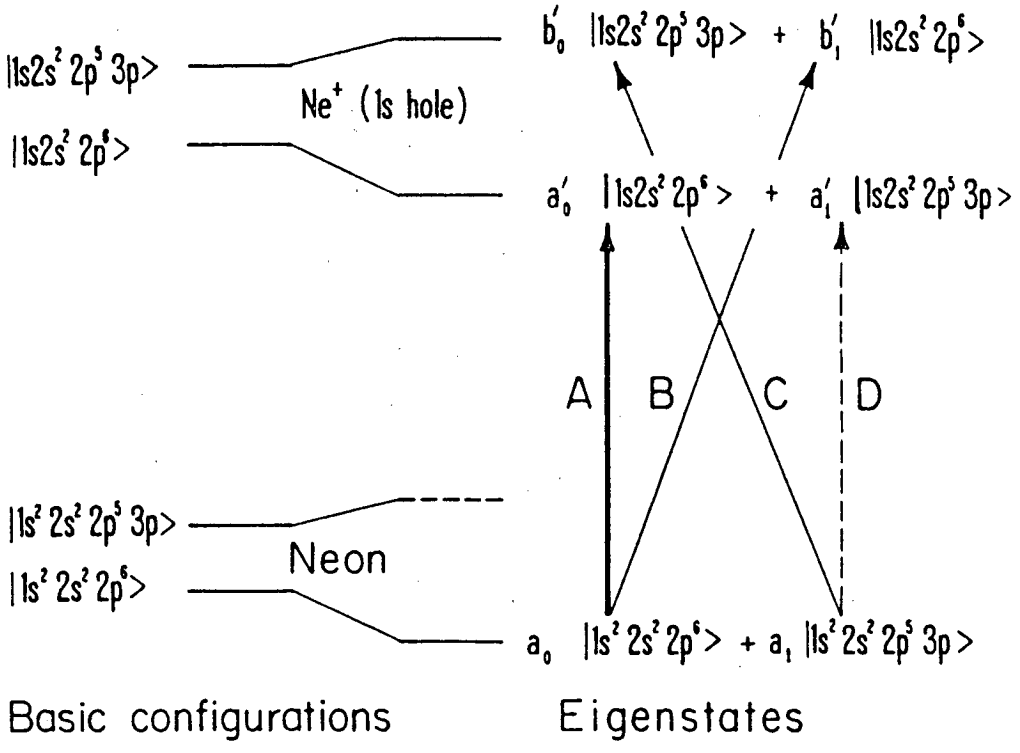

Figure 1. The origin of neon 1s satellites, in "intrinsic" configuration interactions, after Ref. 6.

arising from electron correlation intrinsic in the initial and final states. In fact the terms "ISCI" (for "initial state configuration interaction") and "FISCI" (for "final ionic state configuration interaction") came into usage. In the high energy limit, these were the dominant correlation effects.

Of course it was appreciated that at lower energies, nearer threshold, continuum effects would become important. In the "ISCI-FISCI" scheme, these would be called either "CSCI" (continuum state CI) or "FSCI" (final state CI--an ambiguous designation in which the final state would be presumed to include the continuum electron). More common terms for the same effect are "interchannel coupling" or "continuum-continuum coupling". But in 1975 most photoelectron spectroscopic studies of satellites were carried out at higher energies, where the detailed structure of the continuum was not evident.

Wuilleumier and Krause [7] made an important pioneering contribution in 1974, studying the photon energy dependence of the Ne 2p satellite intensities. Using a series of fixed-energy laboratory x-ray sources, they showed that the (satellite)/(main-line) intensity ratio stayed constant over a wide energy range at high photoelectron kinetic energies ϵ, decreasing at lower energies. They even surmised that this ratio declined to a finite, nonzero value as threshold was approached from above, as shown in Fig. 2. For shake-off intensities a decline to zero at threshold can be argued on phase-space grounds. The argument does not apply to correlation satellites, however, especially in light of the success of the configuration interaction model at high energies. Finally, Wuilleumier and Krause introduced a valuable parameter, the relative energy, ϵ/E_o. Here E_o is the "excitation" energy of the satellite final state relative to the main line.

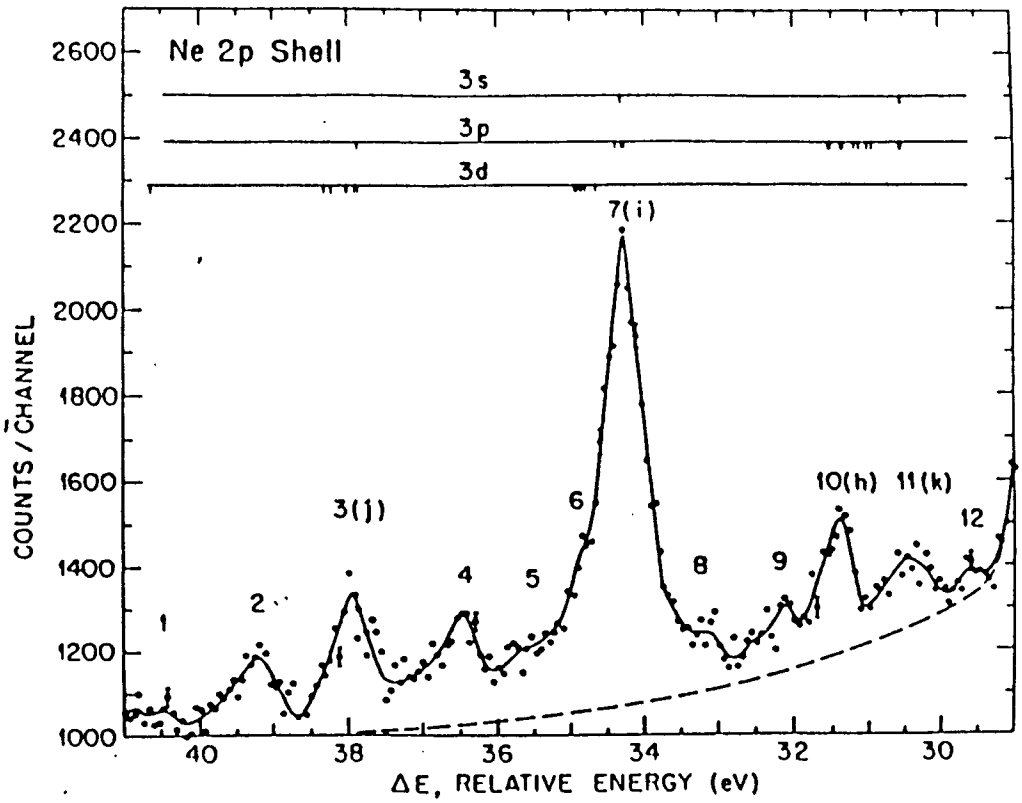

Figure 2. First spectrum of neon 2p satellites, after Ref. 7.

This was the state of affairs for photoelectron correlation satellites in 1975. The high energy intensities were understood, but data near threshold were lacking.

III. THE SITUATION IN 1985: ONE PERSPECTIVE.

A considerable amount of good work was done in this field during the next ten years, but several basic questions about photoelectron satellites remained unanswered. In fact, they remained unformulated. Variable-energy synchrotron radiation sources became widely available, but the focus of interest shifted, understandably, to energy-dependent one-electron properties, continuum resonances, laser excitation, and other more urgent topics. Nevertheless, a limited amount of progress was quietly made on the satellite question.

By 1985, in an invited review talk, [8] the following statements could be made about the evolving understanding of photoelectron satellite peaks:

1. Satellite intensities were understood in the high energy limit (i.e., this was still true). For further understanding, near-threshold data were needed.

2. Three generic models of threshold behavior could be contemplated, at least naively. In the "pure shake-up" model, all satellites would lose intensity as threshold was approached. In the "sudden limit" model, all would retain constant relative intensities. In either case, very little information would be contained in data near threshold.

3. Neither of the above models could fit experiments then newly available [9,10]. A third, generic "state-dependent" model was

proposed, in which each satellite state would be treated separately.

Among the data supporting this conclusion were near-threshold measurements on the Ne K-shell satellites [9] studied earlier by Krause, et al. [3], Gelius [4], and others, and on the Ne 2p satellites [10] reported by Wuilleumier and Krause [7]. In both cases the new measurements extended much closer to threshold than earlier work, thanks to the use of synchrotron radiation. The reduced energy ϵ/E_o introduced by Wuilleumier and Krause [7] was taken as an index of adiabaticity, on the basis that for $\epsilon/E_o \sim 1$ the slowest remaining bound electrons move about as fast as the departing photoelectrons (from the virial theorem, for example). Thus $\epsilon/E_o \gg 1$ could be regarded as the "sudden" and $\epsilon/E_o \ll 1$ as the "adiabatic" regions, respectively. If there is a transition from sudden to adiabatic behavior, it should occur as ϵ/E_o is decreased through unity. The earlier measurements had extended down only to $\epsilon/E_o \sim 2$. The newer results [9,10], reaching as low as $\epsilon/E_o = 0.2$, displayed "near threshold" behavior, with relative intensities varying substantially, and differently from one line to another. Hence the need for a more general "state-dependent" model, in which each state (or each channel) could be treated separately.

A valuable theoretical contribution was made in 1984 by T.D. Thomas [11], who worked out a model for the transition from the adiabatic to the sudden regime. This model should work better for "shake-off" transitions, but it can also serve as a guide to understanding that fraction of a correlation-state transition which really arises through the dynamic "shake-up" process, becoming important for $\epsilon/E_o > 1$.

IV. RECENT ADVANCES IN UNDERSTANDING PHOTOELECTRON SATELLITES NEAR THRESHOLD.

In this Section we summarize recent progress in threshold and near-threshold satellite studies in He, Ne, and Ar. While an attempt is made to cite work by others, the Berkeley and Berlin groups are naturally favored both by choice of subject and by inclusion of unpublished results. Finally, even for this limited scope of material the coverage is uneven because space limitations allow only a summary review of material that has been, or will be, published in more complete form elsewhere. The results are organized below into subsections, according to the atomic shell studied.

A. HELIUM

This atom is unique, for our purposes, in two respects. While several photoelectron satellites are observable, they cannot be resolved beyond the major shells denoted by principal quantum numbers. Also, no correlation is possible in the He^+ final states, which are hydrogenic (one electron). Helium is an important test case because, given the difficulty of ab initio calculations on the dynamics of multielectron systems, it should be the first to yield to truly quantitative interpretation of electron correlation phenomena as elucidated through photoelectron satellite spectra. Indeed, the results thus far are encouraging.

The ready observability of He satellites is illustrated in Fig. 3, taken with a threshold analyzer described by Heimann, et al [12]. In studying helium satellites, the quantities to be measured are the energy-dependent cross-section $\sigma(\epsilon)$ and asymmetry parameter $\beta(\epsilon)$, related by the equation

$$\frac{\sigma(\epsilon,\theta)}{d\Omega} = \frac{\sigma(\epsilon)}{4\pi}\,[1 + \beta(\epsilon)P_2(\cos\theta)]$$

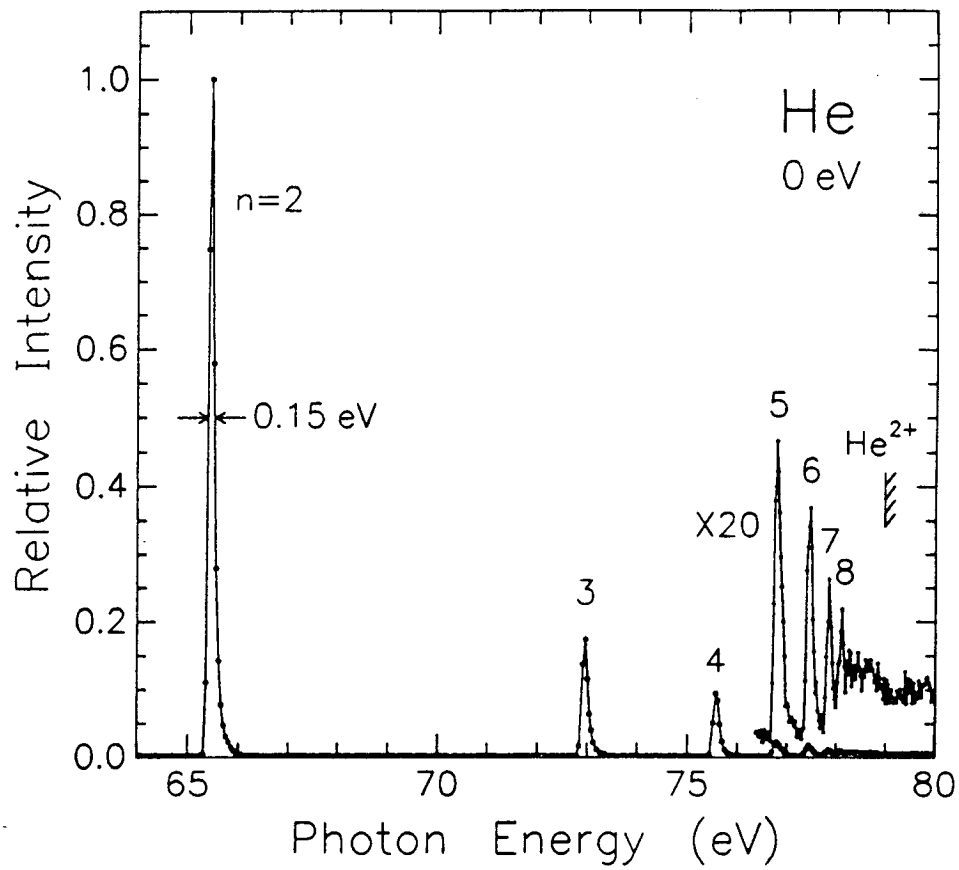

Figure 3. Threshold spectrum of helium satellites, after Ref. 12.

for each peak. The $\sigma(\epsilon)$ and $\beta(\epsilon)$ values can then be used to test theory.

Lindle, et al. [13] summarized the situation for the n = 2 peak as of 1985. Of particular interest is a decrease in $\beta(\epsilon)$ to ~ 0 near threshold, confirming a prediction by Greene [14], based on the SO(4) classification, of increasingly important parity unfavored transition channels.

Later work by Lindle, et al. [15] extended the $\beta(\epsilon)$ studies near threshold to the n = 3 and n = 4 peaks, showing a continuing downward trend in β_n with increasing n, accompanied by $\sigma_n(\epsilon)$ values that increase slowly with decresing ϵ. Threshold measurements [12] now extend this result to n = 6 and support Greene's predictions of β values at threshold, decreasing with increasing n, to values of β = -0.5 or below, as shown in Fig. 4.

B. NEON 2p SATELLITES.

Modern time-of-flight techniques, in concert with variable energy synchrotron radiation, permit the study of Ne 2p satellites at high resolution and good signal-to-noise ratio near threshold. Extension of the measured (satellite)/2p intensity ratio downward by over an order of magnitude relative to the earlier work [7] has allowed exploration of the "adiabatic" region [10] and an approach to the threshold region. Good agreement was found with the results of Wuilleumier and Krause [7] at higher energies. Most notable, however, is the observation of two clearly distinctive energy dependences. For the $Ne^+(^3P)3p(^2P^0)$ final

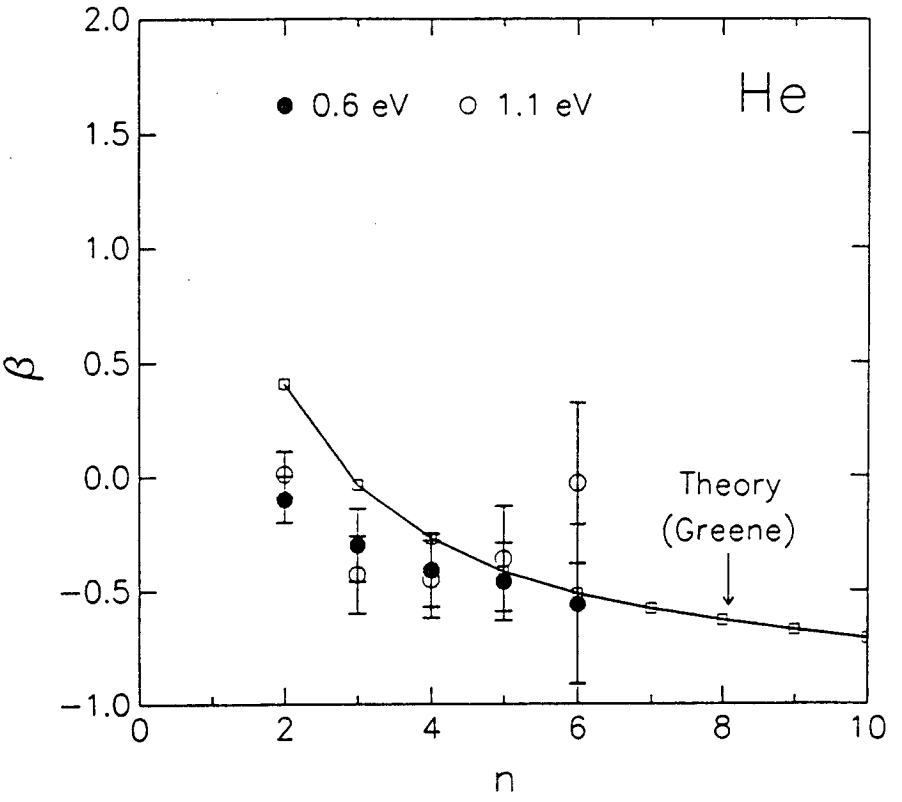

Figure 4. Near-threshold asymmetry parameters of helium satellites, integrated up to 0.6 and 1.1 eV, after Ref. 12 and theoretical threshold values, after Ref. 14.

state ("Peak 10"), the intensity ratio (satellite)/2p is essentially energy-independent through the range $0.3 \leq \epsilon/E_o \leq 3$, consistent with the "configuration interaction" model that fits the sudden limit. By contrast, the Ne^+ (^1D)3p($^2P^o$) peak ("peak 7") shows a dramatic decrease as threshold is approached, by a factor of 5 or more. Fig. 5 gives a detailed illustration of this behavior, as reported by Becker, et al [16]. Also shown in this plot is the effect of a resonance near threshold.

This dramatic variation in the energy dependence of the (sat)/2p intensity ratio [10,16], and similar variations to be cited later, provide clear proof that the "general state-dependent" model is essential. Anticipating further data to be presented below, it also appears plausible to envision (sat)/(main-line) ratios as comprised of an energy-independent part and a part that varies (perhaps strongly) with energy. We attribute these to "intrinsic" and "dynamic" correlations, respectively. Here, <u>intrinsic</u> correlations are simply attributes of the initial atomic and final ionic states. They are present independent of the photoelectric transition, and are only weakly energy dependent. <u>Dynamic</u> correlations, on the other hand, owe their existence to the dynamic interaction of the leaving photoelectron with the ionic potential. They can be expected to vary strongly with ϵ/E_o.

Careful study of the Ne 2p satellites down to, and at, threshold, support this formulation. In particular there is substantial variation in both $\sigma(\epsilon)$ and $\beta(\epsilon)$ over several satellites for $\epsilon/E_o \leq 1$ [10], and in particular some satellites show anomalously large intensities right at threshold [12]. Finally, the average threshold value of the orbital angular momentum ℓ in the ionic final state Ne^+ ($1s^2 2s^2 2p^4$ $n\ell$) increases

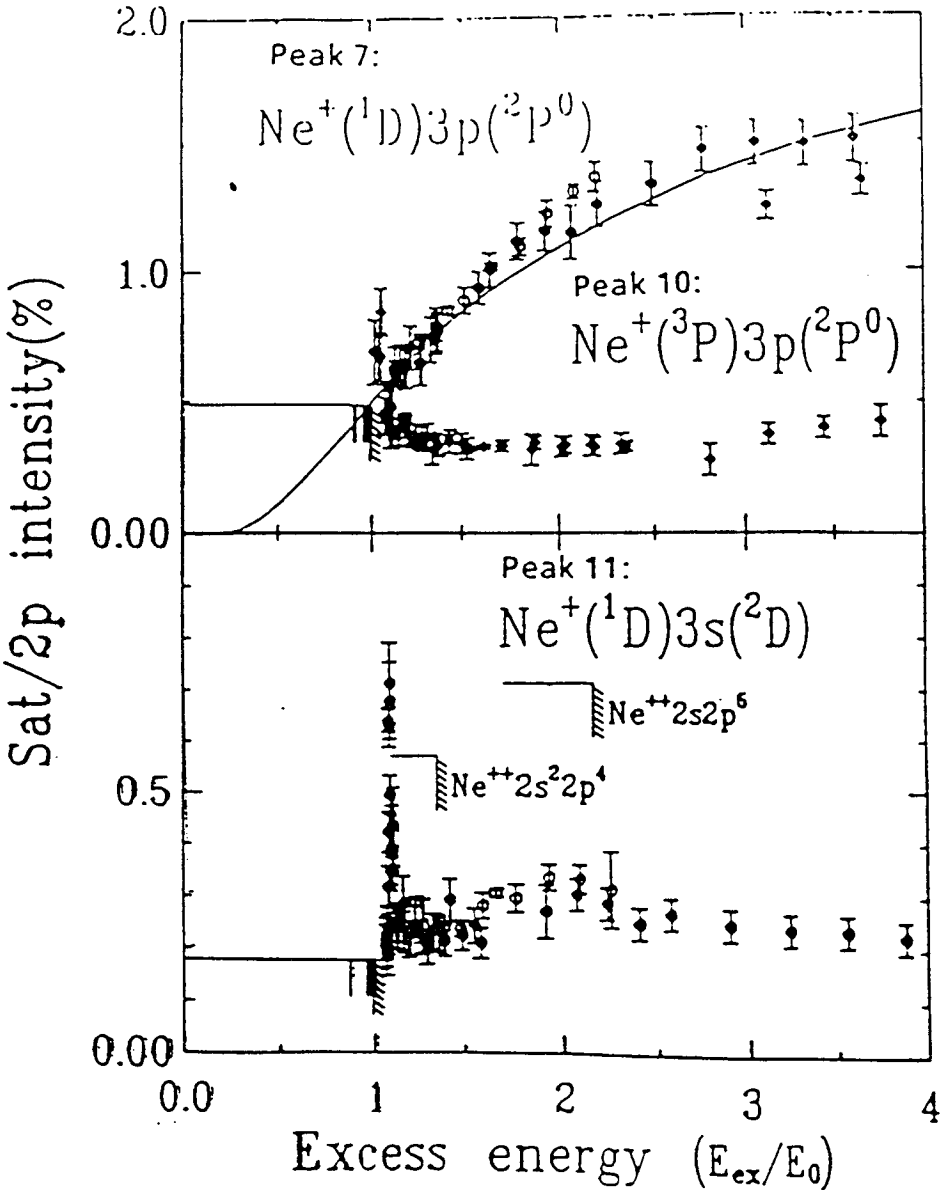

Figure 5. Near threshold 2p satellite intensities, after Ref. 16.

rapidly with n, in agreement to Greene's theory for helium [14]. This is strong evidence for highly correlated electron-electron motion at threshold, between the photoelectron and the remaining valence electrons, leading to the latter being recoupled and left in high angular momentum states.

C. ARGON K-SHELL SATELLITES.

This example is included to illustrate the special advantages afforded by comparison of satellite excitation phenomena accompanying core-level excitation: i.e., the possiblities of x-ray and Auger analyses, which give supportive or complementary information.

Deslattes, et al. [17] reported relative $K\beta'$ and $K\beta_V$ x-ray satellite intensites, relative to the $K\beta_{1,3}$ line, for Ar excited by synchrotron radiation. The $K\beta_V$ intensity in particular showed a well-defined gradual decrease in relative energy as threshold was approached

from above, as expected for x-ray de-excitation following an energy-dependent "shake" process.

Armen, et al. [18] studied the (photon) energy-dependent Auger spectrum following excitation of Ar with synchrotron radiation. Electron peaks associated with "diagram" lines, "shake-up" lines (correlation satellites), and "shake-off" transitions to Ar^{2+} states were all observed and studied through a broad photon energy range. The shake-off intensity fell gradually to zero near threshold and was measured quite definitively, in good agreement with the x-ray results [17]. The "shake-up" peak, which included several unresolved components, also decreased at threshold.

Although both of these measurements provide good indications of the energy dependence of correlation phenomena, a direct measurement of single photoelectron channels is still needed. This measurement was provided initially by Kobrin, et al [9], and more accurate results have subsequently been obtained. A 25 eV satellite of the Ar K line was observed, in agreement with a prediction by Dyall [19] for a [1s 3p] 4p state. The relative satellite intensity was constant down to about ϵ = 50 eV (ϵ/E_o = 2), below which it fell off smoothly, apparently toward a finite value at threshold. Thus both intrinsic and dynamic correlations appear to be present.

D. THE ARGON 3S SATELLITES

Correlation of inner-valence shells is a recurrent phenomenon in atoms and molecules, for which the Ar 3s case can be considered the prototype. The common theme in this correlation is that final ionic states produced by ionization of an inner valence orbital electron are strongly mixed through correlation with higher energy ionic states formed by additional pairwise correlation of two electrons from an outer valence shell. Four well known examples are [20-22]

$$Mn^+(3s3p^63d^5) \rightarrow Mn^+(3s^23p^43d^6)$$

$$Ar^+(3s3p^6) \rightarrow Ar^+(3s^23p^43d)$$

$$Xe(4p^54d^{10}) \rightarrow Xe^+(4p^64d^84f)$$

$$SnS(1\sigma^22\sigma^23\sigma^21\pi^4) \rightarrow SnS^+(2\sigma^1 CI \text{ states})$$

In each case the diagonal energy price is reduced by partial cancellation of the energy cost of promoting one member of the pair and demoting the other. The angular momentum conditions (i.e., same symmetry) are satisfied by recoupling within the opened outer valence shell, and with the promoted electron. As a result, inner valence shell correlation tends to be strong throughout these otherwise very different examples.

The Ar 3s satellites were first reported by Spears, et al. [21], in 1974, as three partially resolved peaks, designated by a $3s^23p^4(^1D)$ core plus a 3d, 4p, or 4d electron: e.g., $Ar^+3s^23p^4(^1D)3d^2S$. These designations refer, of course, to the principal configurations in highly correlated states. It is notable that, in this original high photon energy (x-ray) photoelectron spectrum, only three peaks were present in substantial intensity. This was consistent with subsequent quantum chemical calculations for "intrinsic" correlation satellites, based on configuration interaction [23]. In this experiment, there were no satellite peaks with binding energy below about 38 eV. Other subsequent studies at x-ray excitation energies gave similar results.

In 1985, Adam, et al. [24] reported a synchrotron radiation study in which, by using photon energies not far above the Ar 3s threshold, they succeeded in producing quite a different photoelectron satellite spectrum. Three satellite peaks appeared below 38 eV, in higher

intensity than those above 38 eV, in the $h\nu$ = 43 eV spectrum. In the new satellites the p^4 core has recoupled to 3p as well as ^1D. "Dynamic" as well as "intrinsic" correlation would be needed to explain the new results.

Interest in this subject has grown very rapidly. Earlier this year, Svensson, et al. [25] reported a high resolution x-ray ($h\nu$ = 1487 eV) photoelectron spectrum of the Ar 3s region. Eleven peaks were noted, and the spectrum was in good overall agreement with the earlier work of Spears, et al. [21], with most of the spectral intensity falling above 38 eV binding energy. An adjacent paper by Kossmann, et al. [26] reported a low energy ($h\nu$ = 77 eV) photoelectron spectrum, also with high electron energy resolution, with even more peaks [13]. The satellite intensity pattern was similar, but substantially more intensity fell below 38 eV, as Adam, et al. had also noted [24] at even lower photon energy. This additional intensity fell in states of symmetry different than the main line (^2S), again supporting dynamic, in addition to intrinsic, correlations at low photon energies.

Brion, et al. [27] have also reported a similar study, with spectral results in essential agreement with those of Kossmann, et al. [26].

All of the published photoemission work on Ar 3s emphasizes the need for a detailed study of the energy dependence of satellite intensities near threshold. Such a study has now been carried out, with dramatic and unexpected results. Becker, et al. studied the threshold and near threshold photoelectron spectra of Ar 3s satellites, including a 90 meV FWHM resolution threshold spectrum due to Heimann [28]. Some 40 lines were observed at threshold, corresponding to states with symmetry designations of angular momenta as large as ^2G and ^4F, in contrast to ^2S only expected for final states excited through intrinsic correlations and having the same ^2S symmetry as the main line hole states, ($3s3p^6;\,^2S$). Figure 6 shows the threshold spectrum [28].

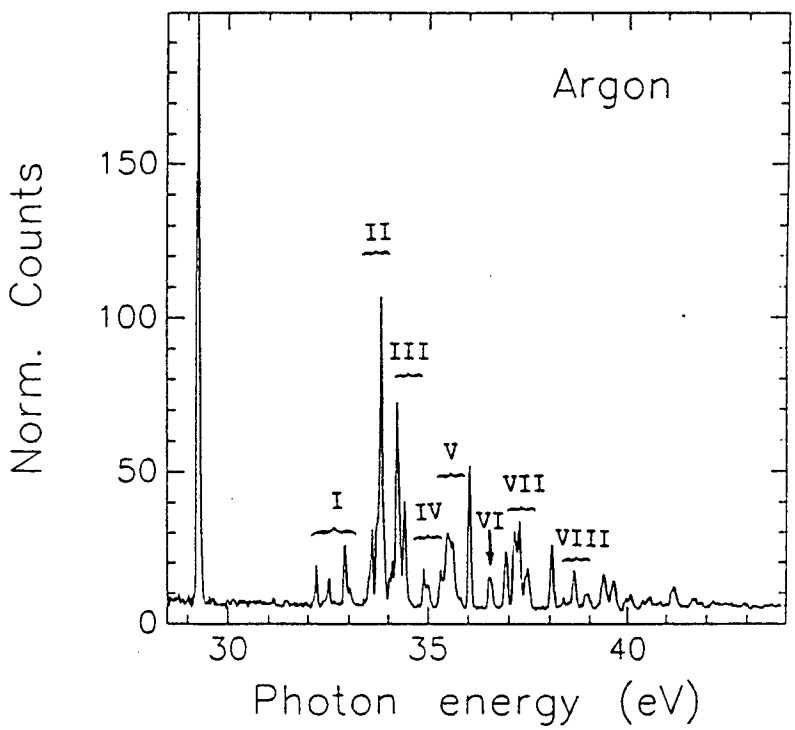

Figure 6. Argon 3s line at (29.3 eV) and satellite lines, at threshold, after Ref. 28. Satellite groups are labelled by Roman numerals for Fig. 7.

Many of the satellites shown in Fig. 6 had not been observed previously in photoemission spectra. Indeed, Becker, et al. found that the intensities of these new threshold peaks decreased rapidly above threshold: they could be regarded as "threshold resonances". This behavior is displayed, mostly for groups, in Fig. 7. Clearly this new type of behavior--a rapid <u>increase</u> of satellite intensity with decreasing energy toward threshold--is a "dynamic" correlation effect, but exactly opposite to the characteristic decrease shown for the "shake-up" mechanism!

How do "threshold resonances" arise? Becker, et al. have examined this question in more detail than can be given here, concluding that the origin is inelastic scattering of the outgoing photoelectron in the more general context of interchannel coupling [29,30]. An intuitive picture of this phenomenon can be described by thinking of a highly-correlated

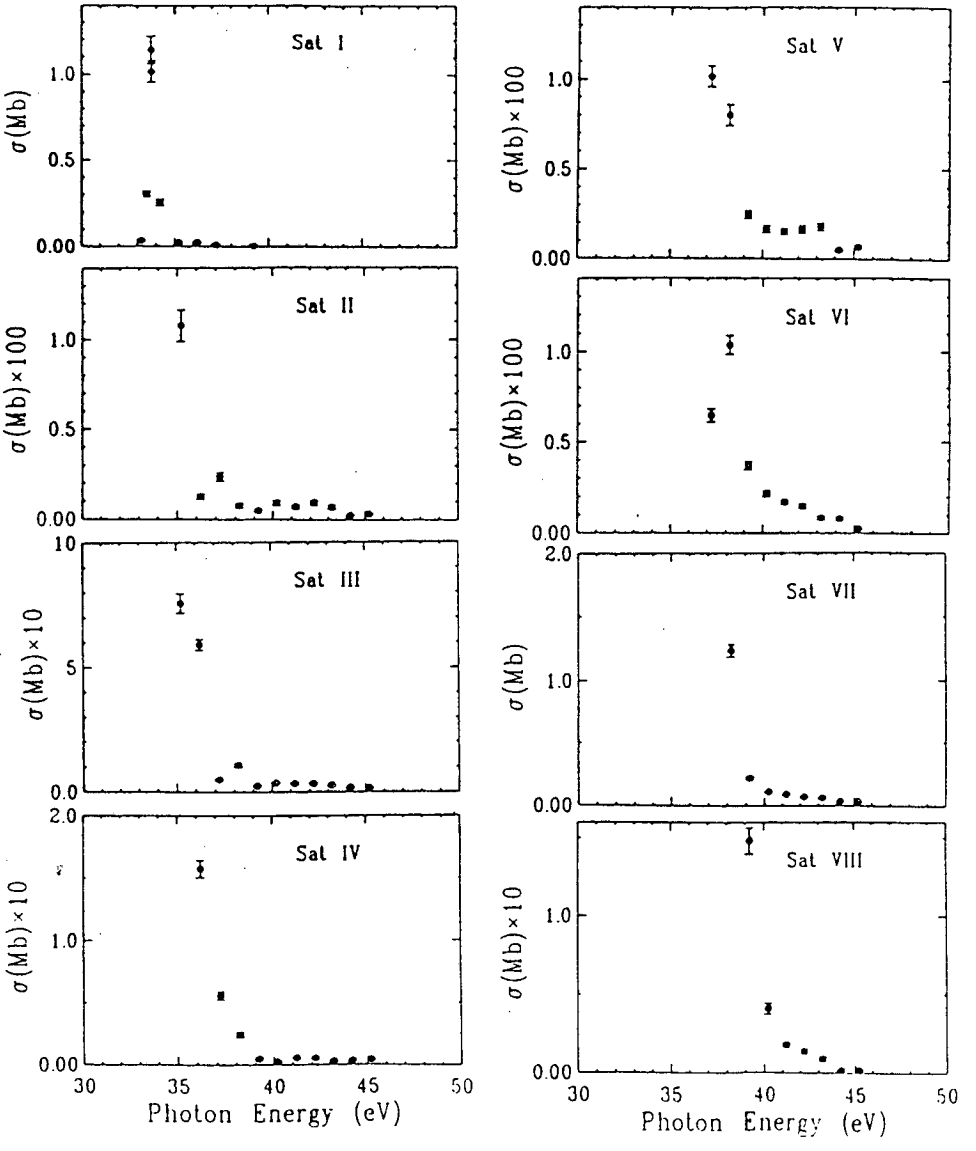

Figure 7. Ar 3s satellite intensities near threshold showing rapid decrease. See Fig. 6 and Ref. 28.

18-electron system Ar^* (= Ar + hν) in which the excitation energy hν raises ground-state Ar to an excited-state energy range (Ar^*) where the total energy is equal to that of several states Ar^+_i + e$^-$(ϵ_i). The energy balance condition is hν = E_i + ϵ_i, wher E_i is the energy of state i in Ar^+. Near threshold, hν ~ E_i and ϵ_i ~ 0. Continuum-continuum interchannel coupling is strong, of the inelastic scattering cross-section large, near threshold. A remarkable feature of this dynamic correlation mechanism is that every state in Ar^+ appears to be accessible through threshold excitation. Clearly many possibilities exist for expanding our understanding of correlations through the study of such threshold phenomena.

V. SUMMARY

Our understanding of photoelectron satellites, and the underlying correlation phenomena, has made rapid progress recently. In 1975, "shake-up" and "configuration interaction" descriptions of satellite intensities both had some support, and in the sudden limit the latter appeared quantitatively adequate in at least one case.

By 1985, the availability of synchrotron radiation had facilitated near-threshold studies of $\sigma(\epsilon)$ and $\beta(\epsilon)$. The results clearly showed that no single simple mechanism could adequately describe near-threshold behavior. Instead, each channel appeared to possess its own, perhaps unique, behavior. A more general, state-dependent theory was needed.

Since 1985 the amount and quality of information available on photoelectron satellites has increased rapidly, mainly because of synchrotron radiation usage and threshold studies. For example, helium satellites show threshold β(n) values decreasing to β ~ -0.5 at n = 6, as predicted by Greene, and essentially energy independent $\sigma_n(\epsilon)$ for n = 2-6.

Neon 2p satellites clearly show varying behavior near threshold, in both $\sigma(\epsilon)$ and $\beta(\epsilon)$. In particular, some peaks display energy-independent intensities, while the intensities of others decrease by substantial factors ($\geq$ 2) as threshold is approached, consonant with configuration interaction theory and "shake-up" theory, respectively. Some peaks show very high intensity right at threshold.

The Ar K-shell features are corroborated near threshold by x-ray and Auger studies. Direct measurements of photoelectron satellite intensities show a decline through the "sudden-to-adiabatic" transition region, to an apparently nonzero value at threshold.

The Ar 3s satellites received the most attention and yielded the biggest surprises. Low energy photoelectron spectra, near the 3s threshold, showed more, and different, peaks than the high-energy spectra. Dramatically different behavior was discovered at threshold, where many peaks, corresponding apparently to every Ar^+ state, were observed. They decreased rapidly in intensity with increasing photon energy. "Inelastic scattering", a special "threshold resonance" form of interchannel coupling, was suggested as the mechanism for this phenomenon, which attests to strong electron correlation near threshold. From this behavior and the Ne 2p results, the concepts of "intrinsic" and "dynamic" electron correlation effects emerged, replacing the earlier concepts of the "adiabatic" and "sudden" limits.

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