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**ELECTRON-CORRELATION SATELLITES IN  
ELECTRON SPECTROSCOPY**

D. A. Shirley, R. L. Martin, B. E. Mills, S. Süzer,  
S. -T. Lee, E. Matthias, and R. A. Rosenberg

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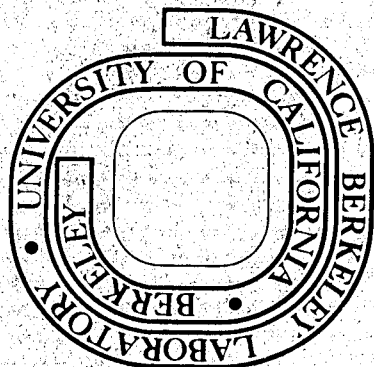
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ELECTRON-CORRELATION SATELLITES  
IN ELECTRON SPECTROSCOPY\*

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I. INTRODUCTION

Ten years ago the photoelectric process was generally regarded as affecting only the active electron appreciably, and multi-electron effects were taken to be of secondary importance. In the ensuing few years both multiplet splitting<sup>1,2</sup> and shake-up<sup>3</sup> had been observed in photoelectron spectra, and the effect of electron correlation on final-state structure had been explained.<sup>2</sup> At the time of the First ISIP Conference, these phenomena were all known but not very well tied together conceptually. Another related phenomenon - relaxation of the passive electrons<sup>4</sup> - was not yet fully appreciated at that time.

Subsequent developments have included the discovery of new phenomena, such as initial-state configuration interaction (ISCI),<sup>5,6</sup> and autoionization in barium,<sup>7,8</sup> as well as refinement in our understanding of the relation between relaxation energy and the presence of "shake-up" satellites. It is now more fully appreciated that "shake-up" states

are not different in principle from "primary" hole states, and that photoelectric transitions to the shake-up states are identical in form to those leading to primary hole states. Another emerging principle is the fact that, because of ISCI, satellites observed in photoemission yield unique information about electron correlations in ground states of atoms and molecules, a finding of general interest outside the field of ISIP. These topics are developed below.

## II. EARLY DEVELOPMENTS ILLUSTRATED BY THE EXAMPLE OF $Mn^{2+}$ .

Perhaps the best single example for discussing satellite structure in photoemission spectra is the 3s, 3p shell of  $Mn^{2+}$ . With the ground-state configuration  $3s^2 3p^6 3d^5$  ( $^6S$ ),  $Mn^{2+}$  is expected to yield  $3s 3p^6 3d^5$  ( $^5S$  and  $^7S$ ) states on 3s photoemission, and  $3s^2 3p^5 3d^5$  ( $^5P$  and  $^7P$ ) states on 3p photoemission. To first approximation the  $^5S: ^7S$  lines would be split by  $(\frac{6}{5})G^2(3s, 3d)$ , by Van Vleck's Theorem,<sup>9</sup> while the relative intensities within each pair of lines ( $^5, ^7S$  and  $^5, ^7P$ ) would be the multiplet ratio 5:7.

The experimental spectra were very surprising at first. The  $^7P$  line stood out clearly, while the  $^5P$  intensity appeared to be distributed over at least three lines<sup>2</sup> (a later higher-resolution spectrum<sup>10</sup> appeared to have at least five lines). This was the first example of a characteristic line's "disappearing" because of being distributed over several final states. A more dramatic recent example has been given by Gelius<sup>11</sup> for the  $4p_{1/2}$  lines of xenon and nearby elements.

Consideration of the  $^5P$  structure of  $Mn^{2+}$  ( $\overline{3p}$ ) or the  $4p_{1/2}$  structure of  $Xe(\overline{4p})$  immediately dispels any illusion that "shake-up" states differ from the primary state, or that one peak must be the "main" peak in

each subshell. Which is the main peak in the Xe(4p<sub>1/2</sub>) spectrum?

Even though the transition intensity is spread over several peaks, the mean energy should be given by a sum rule due to Manne and Åberg.<sup>12</sup> This shows that the mean energy of the photoemission spectrum is given by the one-electron orbital energy,

$$-\epsilon = (\sum_j E_j I_j) / (\sum_j I_j),$$

where the summation is taken over the intensities (I) and energies (E) of the final-state peaks. The sum rule has been approximately confirmed for the Mn<sup>3+</sup>( $\overline{3p}$ ;  $\overline{5p}$ ) lines.<sup>10</sup>

The  $\overline{5s}$  structure of Mn<sup>3+</sup>( $\overline{3s}$ ) was perturbed in a similar, but less dramatic, manner. In this case there was a main line - mostly 3s 3p<sup>6</sup> 3d<sup>5</sup> ( $\overline{5s}$ ), but it lay too low in energy and had too little intensity. Bagus et al.<sup>13</sup> predicted that interaction with the higher configuration 3s<sup>2</sup> 3p<sup>4</sup> 3d<sup>6</sup> ( $\overline{5s}$ ) was responsible both for lowering the energy of the main peak and for draining off intensity. Subsequent experiments confirmed this prediction.<sup>14</sup> Again, the lowest-lying (and most intense)  $\overline{5s}$  line could naively be regarded as the main line and the others as "satellites".

The Manne-Åberg sum rule can be applied to the  $\overline{5s}$  manifold. Alternatively, it is instructive to note that the "main"  $\overline{5s}$  peak experiences some 6 - 8 eV of additional relaxation energy (relative to the Koopmans' Theorem<sup>15</sup> value) by virtue of configuration mixing (and the sum rule). This illustrates the intimate relation between satellite structure and relaxation energy.

In leaving this review section we note an amusing and instructive

analogy between the  $\text{Mn}^{3+}(\overline{3s}; {}^5S)$  and the  $\text{Xe}^+(\overline{4p}, {}^2P_{1/2})$  photoemission spectra. In the  $\text{Mn}^{3+}$  case the two-electron "excitations" that describe the electron correlations in the CI framework are of the type

$$3s^1 3p^6 3d^5 \rightarrow 3s^2 3p^4 3d^6; \text{ i.e., } p^2 \rightarrow sd.$$

In  $\text{Xe}^+$  the excitations are described by increasing all the principal and orbital quantum numbers by one unit,

$$4p^5 4d^{10} 4f^0 \rightarrow 4p^6 4d^8 4f^1; \text{ i.e., } d^2 \rightarrow pf.$$

### III. SHAKE-UP SATELLITES AND ISCI.

The pioneering studies of Carlson and co-workers established the existence of shake-up satellites and identified their basic origins.<sup>3</sup> Their later papers gave perceptive insight into the role played by electron correlation.<sup>16</sup> In fact the shake-up studies in rare gases provide sufficient richness of phenomena to serve as an alternative example of the effects discussed in Section II.

Although the phenomenology of shake-up was well known, the theory of the process was incomplete when we first addressed the problem. In retrospect (and in light of our findings) the most instructive questions that could have been asked about shake-up spectra would have been:

1. Are the shake-up states two-electron excitations reached by a two-step E1-E0 process, or are they in fact exactly the same kind of states as the primary hole states, and reached by a simple dipole (E1) process?
2. Why do computations of shake-up intensities based on Hartree-Fock ground states never give accurate results? Or equivalently, what would happen if the initial and

final states were treated symmetrically?

The answer to (1) is of course that the shake-up satellites arise through simple, one-step electric dipole photoemission processes that are formally identical to those giving rise to the main peaks. This follows from a straight-forward application of the perturbation Hamiltonian

$$\mathcal{H} = \frac{e}{mc} \vec{A} \cdot \sum_i \vec{p}_i \quad (1)$$

to the ground-state N-electron wave function  $\Psi_0(N)$  to yield the final state

$$\Psi_f(N) = \chi_f(1) \sum_n C_{fn} \phi'_n(N-1) \quad (2)$$

Here we have expanded the final state N-electron function into a product of the continuum function for electron 1, viz.  $\chi_f(1)$ , times the N-1 electron eigenstates of the ion, expressed as the product of admixture coefficients  $C_{fn}$  times basis states  $\phi'_n(N-1)$ . This accounts for final-state configuration interaction (FSCI). We have neglected CI involving the continuum state, and antisymmetrization has for simplicity not been indicated explicitly.

In this notation  $f = 0$  denotes the primary hole state, while  $f > 0$  values label the satellite states. In this CI description the two "types" of state differ only in the numerical values of the coefficients  $C_{fn}$ . Any attempt to classify these as two different kinds of states could only arise through confusion of eigenstates  $\Psi_f(N-1)$  with those basis states  $\phi'_n(N-1)$  that form their principal components. Thus in the Ne( $\overline{1s}$ ) case (Fig. 1), the primary hole state would be regarded as  $1s 2s^2 2p^6$



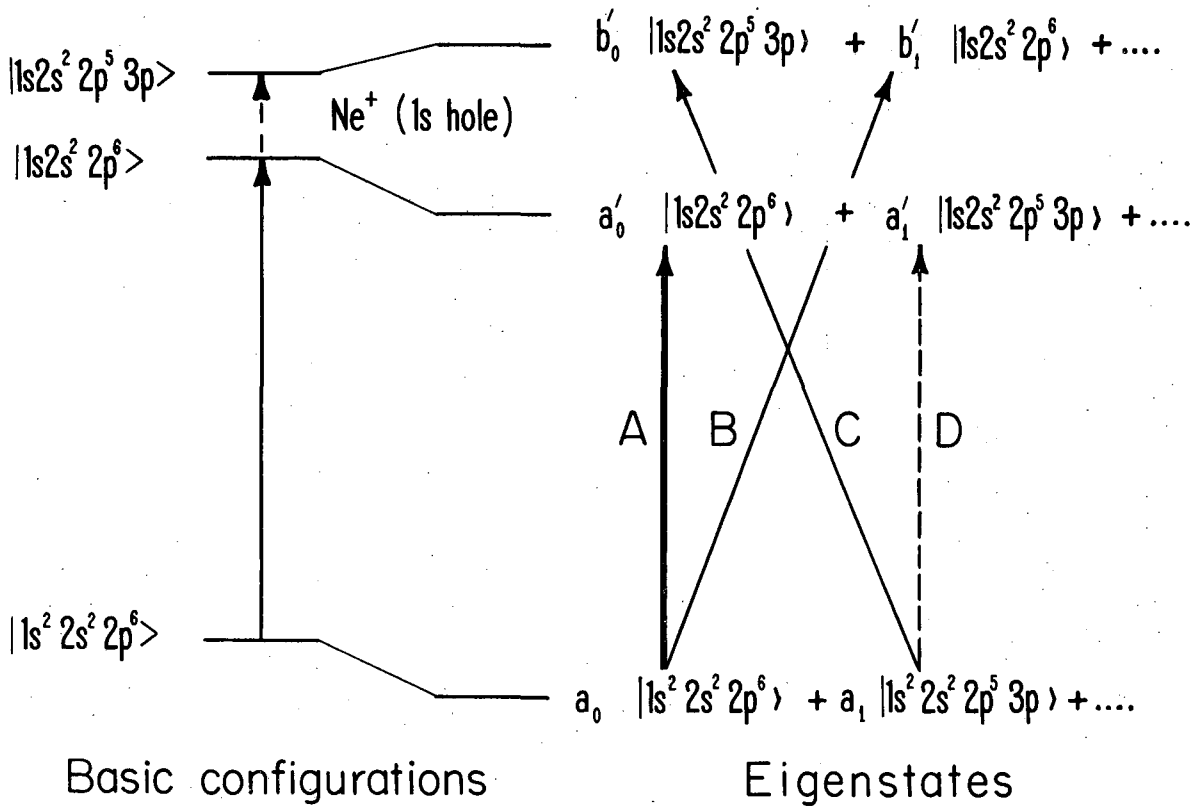


Fig.1 Ne(1s) satellites

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and a shake-up state as  $1s 2s^2 2p^5 3p$ . In fact as Fig. 1 clearly shows, there is no transition - E0 or otherwise - from the main component of the ground state to the  $1s 2s^2 2p^5 3p$  part of the shake-up state. Hence, shake-up is really a misnomer. To state our point a little differently, the composition of the excited states has nothing to do with the photoelectric transition: they are eigenstates of the  $N-1$  electron Hamiltonian, reached with certain probabilities by photoemission from the ground state.

The above answer to question (1) is perhaps well-known to some, but has not been widely appreciated. If it were, the answer to question (2) might have been realized sooner. The problem in computing intensities has stemmed from treating the initial and final states inequivalently. If CI is allowed in the ground state, another channel (C) is opened, leading to computed intensities<sup>17</sup> that agree quite well with experiment,<sup>18</sup> as shown in Table I. Of more general interest than the numerical agreement is the fact that ISIP can be used in this instance to yield insight into electron correlation in the neon ground state. Quantum chemists usually employ rather arcane valence-shell basis functions to account for correlation by minimizing the total energy. The Rydberg-like correlations illustrated in Fig. 1 and Table I hardly affect the total energy but are critically important in fitting transition phenomena such as shake-up spectra. Turning the argument around, the experimental spectra yield rather directly the configuration-interaction composition of the ground state of neon.

The same approach is applicable to molecular systems. By including initial-state configuration interaction (ISCI) to describe the  $F(1s)$

TABLE I. Ne (1s) CORRELATION-STATE INTENSITIES

State	I (Theory) <sup>a</sup>	I (Expt) <sup>b</sup>
(1s hole)	(100)	(100)
2p → 3p	2.47	3.15(10)
2p → 3p	2.60	3.13(10)
2p → 4p	1.48	2.02(10)
2p → 5p	0.43	0.42(6)
2p → 6p	0.09	~0.15
2p → 4p	0.70	0.96(11)
2p → 5p	0.11	0.17(5)
2p → 6p	0.06	---

a) Ref. 17

b) Ref. 18

shake-up spectrum of the HF molecule, we have again obtained very good agreement with experiment:<sup>19</sup> agreement that was otherwise unavailable (Table II). Thus again shake-up structure yields insight into ground-state correlation.

#### IV. DIRECT OBSERVATION OF ISCI BY PHOTOEMISSION: THE $ns^2$ CASE

If ISCI really leads to substantial admixtures of excited configurations in the ground state, they should be observable directly in photoemission. The Group II metals provide ideal systems in which to study this phenomenon. Berkowitz and co-workers have studied Hg,<sup>6</sup> while our group has studied Ca, Sr, Ba, Zn, Cd, and Hg using a specially-constructed high-temperature probe.<sup>5,20</sup> We shall discuss this subject only briefly because it is not really an inner-shell phenomenon. It does, however, link inner-shell topics in the preceding and following sections.

The essential features of this process are illustrated in Fig. 2 for calcium, which has a nominal electronic configuration [Ar core]  $4s^2$ ;  $^1S$ . In fact, all other  $^1S$  configurations will be admixed into the Ca ground state, yielding a wave function

$$|\psi(^1S)\rangle = a|4s^2\rangle + b|3d^2\rangle + c|4p^2\rangle + d|4s5s\rangle + e|3d4d\rangle + \dots \quad (3)$$

where the argon core has been suppressed in this notation. On photoemission from Ca, the  $Ca^+$  states  $(4p^1; ^2P_{1/2})$ ,  $(4p^1; ^2P_{3/2})$ ,  $(3d^1; ^2D_{3/2})$ ,  $(3d^1; ^2D_{5/2})$ , etc., will be populated. Without ISCI these states would have been inaccessible by one-electron dipole processes from  $4s^2$  alone. All the states of  $Ca^+$  that are accessible from the configurations given in equation (2) were observed experimentally.<sup>20</sup> Again the intensities of the satellite photoemission lines are given by (among other terms)

TABLE II. HF (1s) CORRELATION-STATE INTENSITIES<sup>a</sup>

State No	I (Theory)		I (Expt)
	FSCI only	With ISCI	
(1s hole)	(100)	(100)	(100)
2	1.2	2.0	1.9(3)
3	1.5	3.0	3.0(4)
5	3.6	6.2	5.7(5)
7	0.7	1.2	~1.0
9	2.8	4.1	3.8(5)
10	0.5	0.7	~0.7

a) Ref. 19. States of intensity less than 0.1 are omitted.

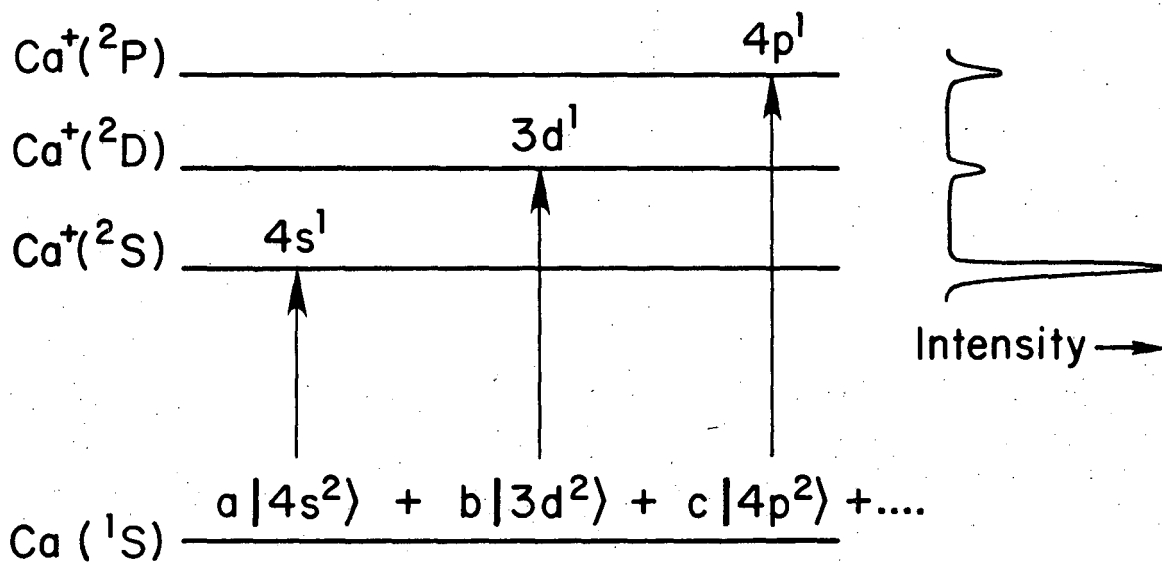


Fig.2 Atomic calcium ISCI

the amplitude coefficients  $a, b, c, \dots$ . With refinement of the interpretation, the photoemission spectrum should provide a sensitive test of CI wave functions.

In the course of this work we accidentally rediscovered resonant autoionization in barium, a process that had been observed by Brehm and Höfler<sup>7</sup> and by Hotop and Mahr,<sup>8</sup> and discussed by Fano.<sup>21</sup> We discuss this topic below.

#### V. AUTOIONIZATION IN Ba AND OTHER $np^6(n+1)s^2$ CASES.

When HeI $\alpha$  (21.22 eV) radiation interacts with atomic barium, it resonantly excites a state such as  $5p^5 6s^2$  ( $ns$  or  $nd$ );  $^1P$  that could be loosely regarded as a Rydberg-like state built on the  $5p^5 6s^2$  continuum threshold. This state mixes, through configuration interaction, with a number of continuum states based on the  $Ba^{++}(5p^6)$  ground state, on  $Ba^+(5p^5 n\ell n'\ell')$  states, and on various  $Ba^+(5p^6 n\ell)$  states. The result is a very complex photoelectron spectrum, in which states of  $Ba^+$  such as  $6f, 8p,$  and  $5g$  are clearly present. Thus Ba is a classic case of "polarization" of the  $5p^6$  shell by configuration interaction with continuum states (CSCI), a third subcategory to be added to ISCI and FSCI (and treated by Fano and Cooper).<sup>22</sup>

The barium case is of course not unique. Many inner shells will possess bound states below its ionization threshold, and consequently should show resonant autoionization. We have concentrated in our recent high-temperature photoemission studies just on the  $5p^6$  shell of atomic vapors in the rare-earth series, using only HeI resonance radiation. Proceeding across the Periodic Table from Ba ( $Z = 56$ ) to Yb ( $Z = 70$ ),

we expect the  $5p^6$  shell to become more tightly bound. This will be a gradual process, however, because the 4f shell, which is filling as Z increases, is quite effective in screening the 5p shell from the increasing nuclear charge. In fact we do not observe evidence of autoionization in Yb. In Eu ( $Z = 63$ ), however, there is still strong evidence of this effect, as shown in Fig. 3. In particular the  $\text{Eu}^+(\text{HeI})$  spectrum shows strong  $^7D$  and  $^9D$  lines, arising from coupling of a 5d electron to the  $(4f^7; ^8S)$  term. This final state could be reached through resonant excitation of a  $\text{Eu}(5p^5 6s^2 5d)$  state admixed with a continuum state based on a  $(5p^6 5d)$  state in  $\text{Eu}^+$  coupled to a free electron.

The use of line photon sources such as HeI is of course not an efficient way of studying autoionization. We have also studied them by electron impact excitation, and shall discuss briefly those aspects which have direct bearing on our photoemission work. The electron impact work was done in the Perkin-Elmer PS-18 photoelectron spectrometer, by operating the lamp as an electron source. We have found that the simple expedient of operating the light source at appropriate low pressures makes it possible to use the plasma in the discharge lamp as an electron gun, and thus we are able to measure autoionization electron spectra excited by low-energy electron impact.

Using the plasma electron source, we have recorded the low energy autoionization electron spectra of Ca, Sr, and Ba under the same conditions as the high temperature photoemission spectra.<sup>20</sup> The spectrum of Ba is shown in Fig. 4. Peak 14 or 15 corresponds to the  $5p^6 6s^2; ^2P_{3/2}$  state and peak 22 to the  $^2P_{1/2}$  state of  $\text{Ba}^+$ .<sup>23</sup> Besides



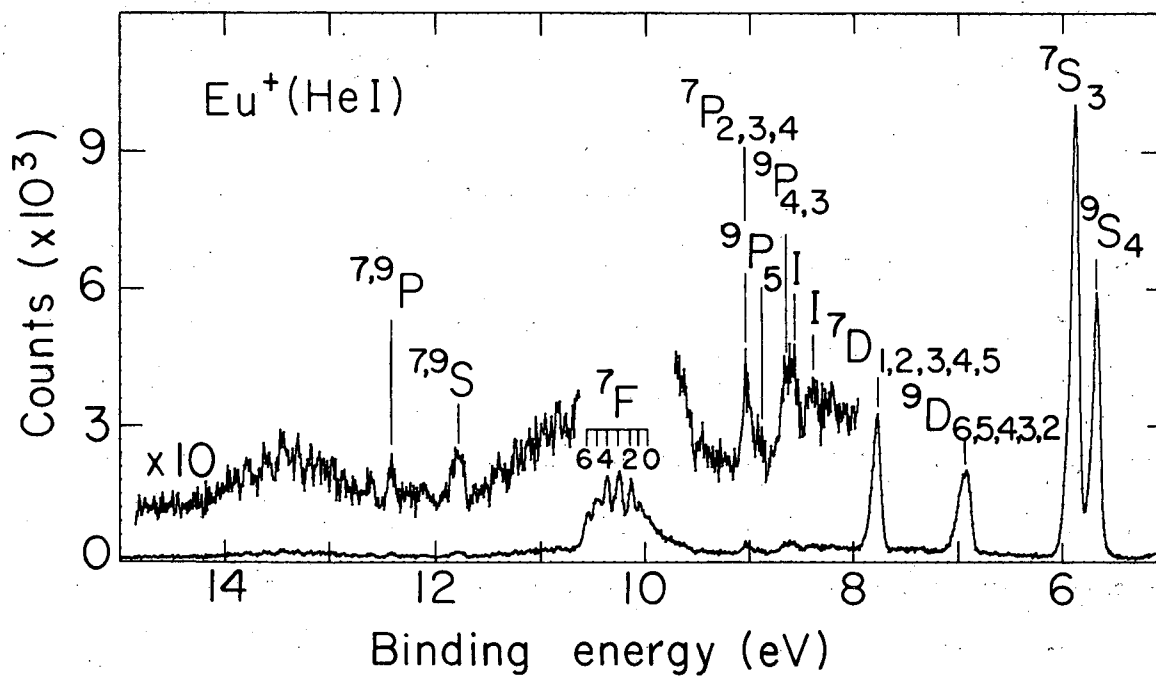


Fig.3 Autoionization in Eu

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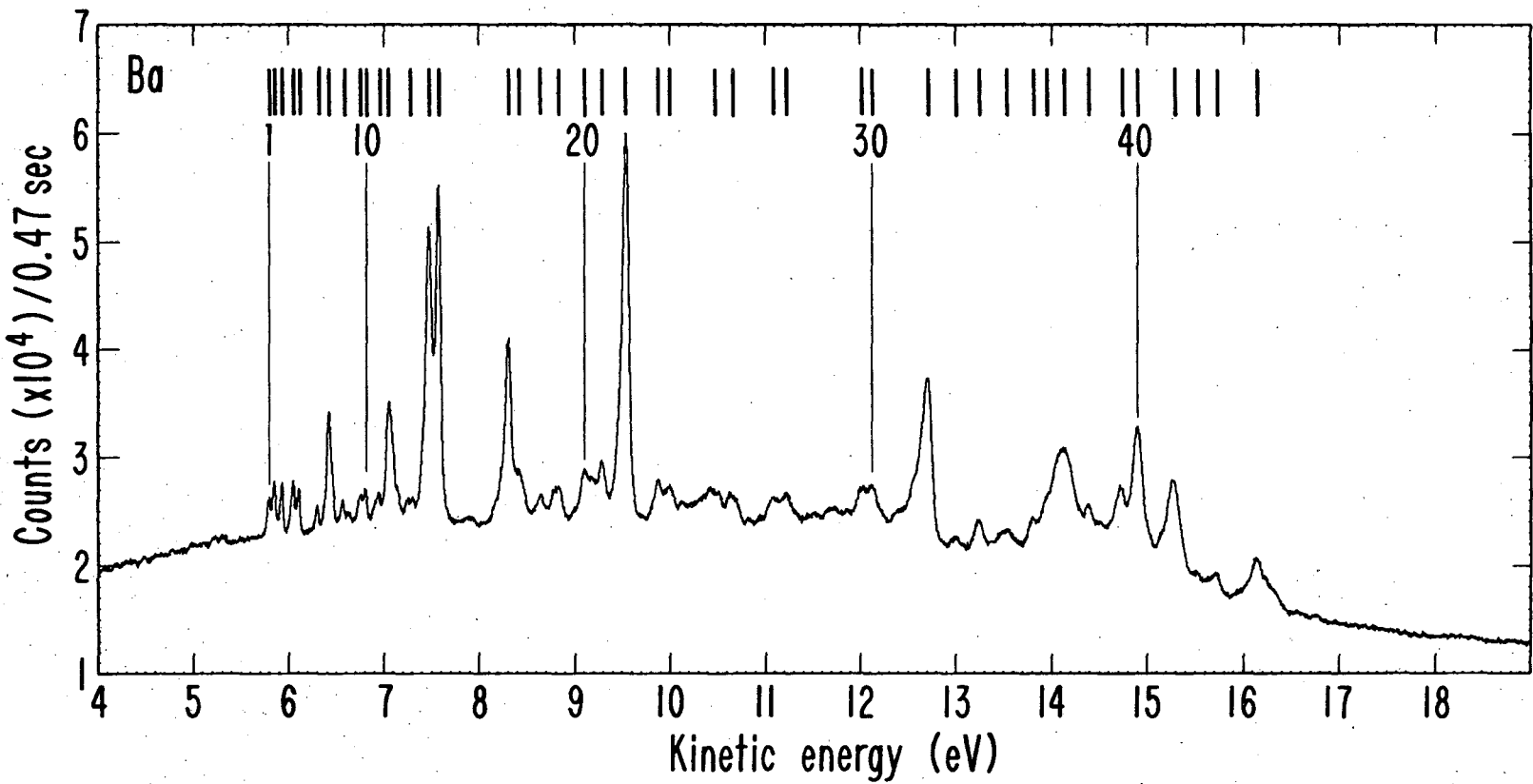


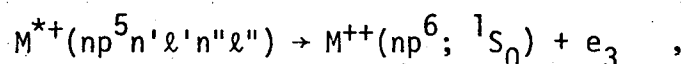
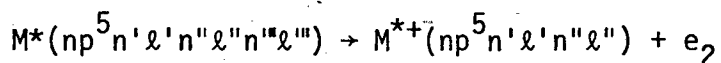
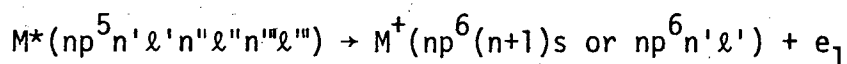
Fig.4 Autoionization electron spectrum of Ba

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these intense primary lines, there are in the spectrum a number of "satellites" with comparable intensities. The electron spectra of Ca and Sr show similar behavior. It is interesting to note that the three intense peaks associated with double autoionization in the HeI photoelectron spectrum of Ba,<sup>7,8</sup> corresponding to peaks 1, 2, and 3 in Fig. 4, have relatively small intensities in the electron spectrum.

Following the electron impact excitation of one of the outermost core-like electrons in Ca, Sr, or Ba, there are three possible ways to produce ejected electrons with discrete energies. They are designated  $e_1$ ,  $e_2$ , and  $e_3$  in Fig. 5 and correspond to the following autoionization processes:



where  $n = 3, 4,$  and  $5$  for Ca, Sr, and Ba respectively. Electrons  $e_1$ ,  $e_2$ , and  $e_3$  lie in different energy regions, and as such, they can usually be distinguished from one another. Generally speaking,  $e_2$ -type electrons are of extremely low energy, and the centers of the electron groups  $e_1$  and  $e_3$  are separated by the binding energy of  $M^+$ . From simple estimates of energies, we have found that the  $e_3$  electrons must contribute predominantly to the observed electron spectra of Ca, Sr, and Ba.

There are two ways by which  $M^{*+}(np^5 n' \ell' n'' \ell'')$  states can be populated (Fig. 5), i.e., via excitation (A) and subsequent autoioniza-

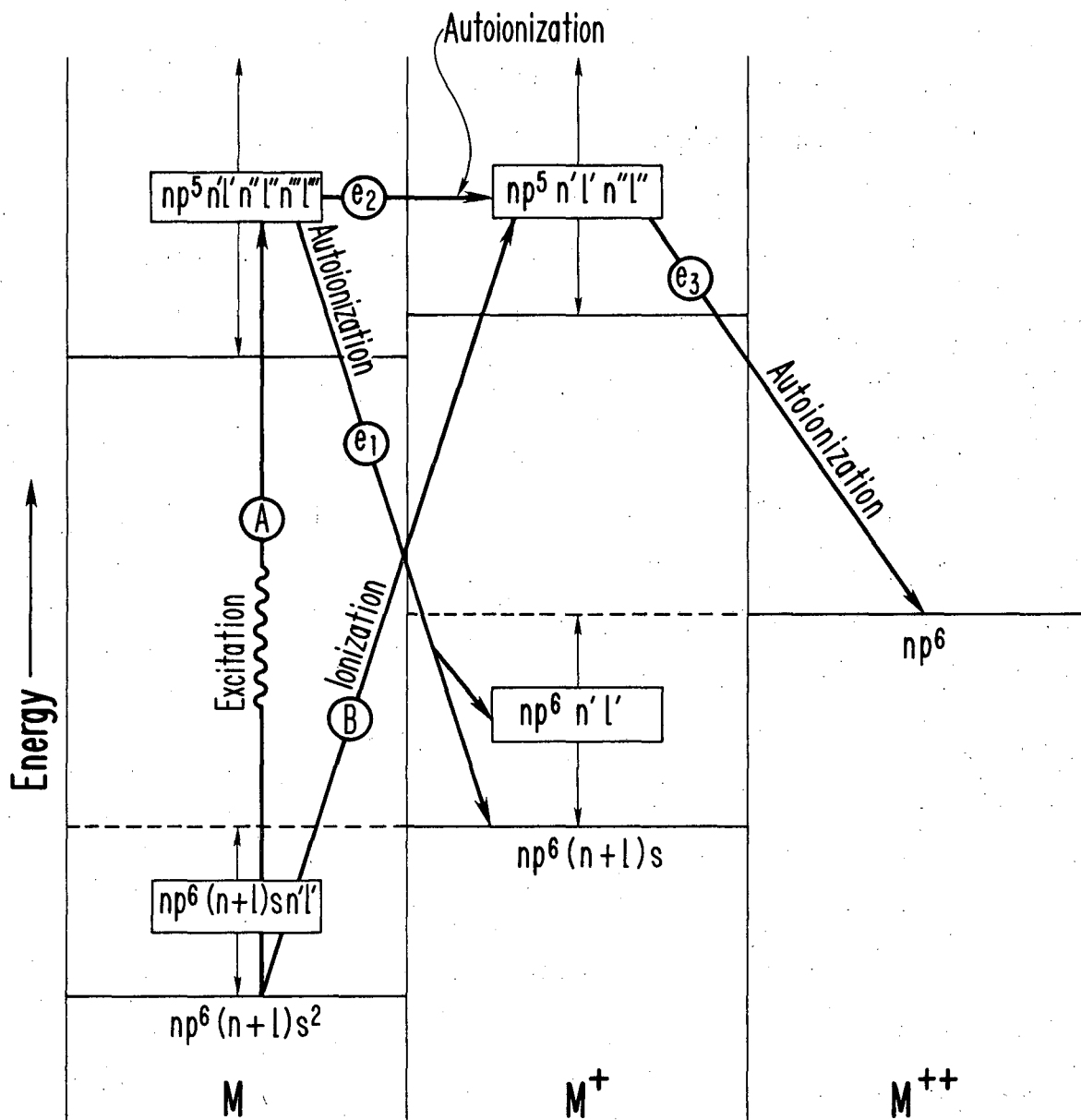


Fig.5 Autoionization in M; M=Ca, Sr or Ba

tion ( $e_2$ ) or by direct ionization (B). If process B is the major contributor to  $M^{*+}$  states, the resulting electron spectrum should be dominated by the s-o doublets of  $M^{*+}(np^5(n+1)s^2; 2p_{1/2,3/2})$ , with the "satellite" states appearing in small intensities. This is certainly not the situation in Ba (Fig. 4). In contrast, the observed spectrum is expected if Ba  $^{*+}$  states are reached predominantly through excitation and subsequent autoionization. Consequently, the s-o  $5p^{-1}$  partners are not observed in statistical ratio in Ba, and a large number of satellites with appreciable intensities are present. Similar arguments and conclusion also apply to Ca and Sr.

The reason that autoionization rather than direct ionization is mainly responsible for the population of  $M^{*+}$  states is due to the collapse (or near degeneracy) of the nd into the (n+1)s shell as a result of np excitation or ionization. We note, however, the corresponding arguments do not apply to Mg, where 3s and 3d shells are involved, and consequently autoionization  $e_2$  is not readily allowed on energy grounds. Therefore, the low energy electron spectrum of Mg<sup>24</sup> is dominated by the  $2p^5 3s^2$  autoionizing states as expected from direct ionization (B).

A great deal of work needs to be done before a complete picture of inner-shell autoionization becomes available. It is already clear, however, that far from being simple and stable, inner shells of atoms can when properly excited yield valuable, detailed information about many-electron phenomena.

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