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AUTOIONIZATION IN THE PHOTOELECTRON SPECTRA OF Ba

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In earlier papers, we reported direct observation of initial-state configuration interactions in atomic Cd[1] and Pb[2]. We have also observed similar phenomena in the alkaline earths Ca, Sr, and Ba and the Group IIB elements Zn and Hg[3]. Among these metals Ba differs distinctly in showing strong electron correlation effects in both initial and final states. This communication gives a preliminary account of the dramatic correlation effects manifested in the photoelectron spectra of atomic Ba.

During the course of our work the HeI photoelectron spectrum of Ba was independently reported twice by other workers[4,5]. The results of these studies are summarized as follows:

1. The HeI spectrum[4,5] showed a number of excited-state peaks of Ba^+ with intensities comparable to that of the 6s state.

2. The spectrum[4,5] showed pronounced peaks of high intensity in the binding energy region 14.2-15.2 eV. These peaks were believed to be the Ba^+ states $5p^6nl$, with n around 11.

3. Above the double ionization threshold (15.215 eV) of Ba, two groups of three peaks[5] each were detected at electron kinetic energies ca. 5.9 and 0.1 eV. The low-energy group was attributed to the ejection of a $5p_{3/2}$ electron via autoionization. The Ba^+ ion thus formed underwent Auger decay to the ground state of Ba^{++}, giving rise to the three intense peaks at 5.9 eV and accounting for the formation of ca. 90% of the abundant Ba^{++} found in the mass spectrum.

Within the independent-electron approximation, the observed excited Ba^+ states are forbidden, and above the Ba^{++} threshold discrete peaks are not to be expected. Fano[6] as well as Brehm and Höfler[4] proposed several arguments to rationalize the unusual spectrum. We have measured the HeI and NeI photoelectron spectra of Ba. By comparing the two, we have found rather direct evidence that autoionization is the main cause of the peculiar photoelectron spectrum.

The HeI and NeI spectra of Ba are depicted in Fig. 1, with the peak assignments labelled. The experimental setup has been reported previously[2]. The HeI spectrum of Ba is in very good agreement with that of Hotop and Mahr[5], but because of better statistics we were able to detect several additional peaks in the region 12.8-14.2 eV (Fig. 1). In the NeI spectrum most of the high energy peaks are absent, and we observe satellite peaks corresponding only to 5d, 6p, 7s, 6d and 4f states of Ba^+, with much lower total cross sections and different relative intensities than in the HeI spectrum. The peaks labelled S_1, S_2 and S_3 are believed to arise from excitation by satellite lines of NeI radiation (see below).

The disappearance of the rich satellite structure in the NeI spectrum offers compelling evidence that autoionization processes are occuring in the HeI spectrum, and constitute the major source of the strong single and double ionization. It appears that an excited state of Ba—e.g. one of the $5p^5 6s^2$ (ns or nd) ^1P states—absorbs the HeIα(21.22 eV) radiation resonantly. 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 latter must have the form $(Ba^{+}5p^6 n\ell)(\varepsilon l')$. Two types of configuration can be formed from states above the Ba^{++} threshold, however. The first type involves two continuum electrons; i.e., $(Ba^{++}5p^6)(\varepsilon l)(\varepsilon' l')$. The second consists of a discrete Ba^{+} 5p-hole state imbedded in the Ba^{++} continuum; e.g., $(Ba^{+}5p^5 n\ell n'\ell')(\varepsilon l'')$. The oscillator strength of the resonant transition will be shared among these continuum states. Resonant absorption and autoionization gives rise to the various features observed in the photoelectron spectrum. The $Ba^{+}(5p^6 n\ell)$ lines are produced directly via autoionization of the $(Ba^{+}5p^6 n\ell)(\varepsilon l')$ states and detected as peaks through the kinetic energy of the continuum electron. The $Ba^{++}5p^6$ state is formed by double autoionization of the two continuum electrons from $(Ba^{++}5p^6)(\varepsilon l)(\varepsilon' l')$, yielding a continuous electron distribution at energies beyond the Ba^{++} threshold i.e., at kinetic energies below ca. 6 eV. This Ba^{++} state may also be reached from $(Ba^{+}5p^5 n\ell n'\ell')(\varepsilon l'')$, by a two-step autoionization-Auger process, yielding the two sets of discrete peaks reported by Hotop and Mahr.

By contrast, the relatively weak intensity of the satellite structure in the NeI (16.85,16.67 eV) spectrum, and the proximity in energy of these states (5d, 6p, 7s, 6d and 4f) to the ground state of Ba^{+} tend to suggest that they are predominantly due to initial-state configuration interaction as in Cd[1], Hg [7]and Pb[2]. Similar phenomena have been found[3] in Ca and Sr, the chemical analogs of Ba, in both HeI and NeI spectra. However, we cannot preclude contributions from shake-up[8] and configuration interaction between various final continuum states.

The peaks marked S_1, S_2 and S_3 in the NeI spectrum cannot be assigned to any states of Ba^{+} resulting from excitation by the NeI 16.85/16.67 eV doublet. The possibility of impurities has been carefully checked and can be ruled out. We tentatively attribute these peaks to ionization by those satellite lines of NeI radiation that have energies ranging from 19.69 to 21.11 eV[9] and intensities less than 1% of the main lines. The unusually intense photoelectron peaks due to these lines are again an indication of autoionization.

The Ba 5p binding energies are believed to lie in the 21-25 eV range[10], so that NeI satellite and HeIα radiation can excite the associated closely-spaced Rydberg levels resonantly, leading to autoionization. TRe HeIβ line (23.08 eV) might be expected to lead to similar phenomena. In fact the Ba^+5d(HeIβ) peak is more intense than the Ba^+6s(HeIβ) peak, supporting this expectation. This leads us to speculate that the peaks between 14.2-15.2 eV are formed in the same manner as are the three peaks around 15.3 eV; i.e., formation of Ba^{++} through two-step ionization, except by resonant absorption of HeIβ radiation.

The present interpretation of the photoelectron spectra of Ba is tentative. Further experimental verification is required. A detailed report of our experimental results on Ba vapor will be given later.

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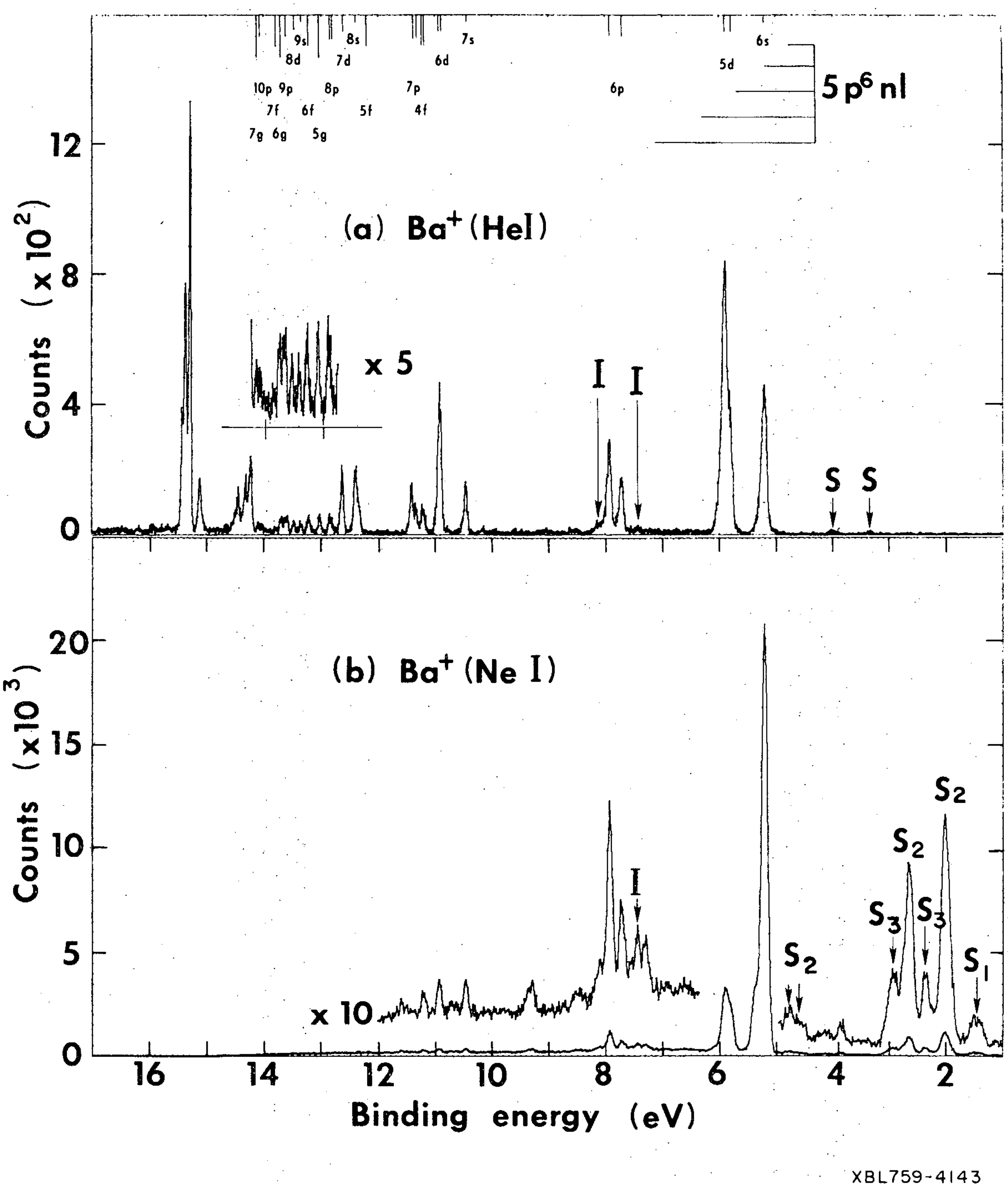
Figure Caption

Fig. 1 (a) HeI photoelectron spectrum of Ba; (b) NeI photoelectron spectrum of Ba. In both spectra the peaks marked I are due to inelastically scattered electrons from the intense peaks in exciting the neutral Ba to the lowest ^1P state, i.e., $5p^6 6s^2 (^1S) \longrightarrow 5p^6 6s6p (^1P)$. Those marked S are due to excitations by the satellite lines of HeI and NeI radiation. Unidentified peaks in the NeI spectrum may be due to excitation by NeII radiation.



9s
8s
7s
6s
8d
7d
6d
5d
10p
9p
8p
7p
6p
5p^{6}nl
7f
6f
5f
4f
7g
6g
5g
(a) Ba$^+$(HeI)
Counts (x 10^2)
12
8
4
0
x 5
I
I
S
S
(b) Ba$^+$(Ne I)
Counts (x10^3)
20
15
10
5
0
I
S$_2$
S$_2$
S$_3$
S$_3$
S$_2$
S$_1$
x 10
16
14
12
10
8
6
4
2
Binding energy (eV)
XBL759-4143

Fig. 1