Observation of a collective excitation in the ejected-electron spectra of Yb and Ba

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(Received 29 May 1979)

Ejected-electron spectra of Yb and Ba are presented. In both spectra, structure was seen which is attributable to autoionization to ground *and* excited states of M^+ (M = Ba or Yb), and to Auger decay of highly excited M^{*+} states to the ground state of M^{2+}. In Yb, Auger decay was also observed to populate *excited* states of M^{2+}. Both spectra are strongly affected by a collective resonance in the excitation of a $5p$ electron. For energies above the $5p$ ionization threshold, two-step autoionization to M^{2+} was found to be dominant.

I. INTRODUCTION

Excitation of an atomic electron other than the most loosely bound one, or the simultaneous excitation of two or more electrons, can yield a set of energetically discrete excited states embedded in a continuum. Electron correlation may mix the discrete state with the continuum, leading to eigenstates with sufficient continuum character to produce spontaneous ionization or autoionzation. Spontaneous ionization can also occur following inner-shell ionization, as a result of interactions between singly and doubly charged hole states; autoionization in this case is usually referred to as the Auger effect.[1] Either autoionization or Auger electron spectra contain unique information about electron correlation effects analogous to satellite peaks in photoelectron spectra.[2,3]

Autoionization or ejected-electron spectra can be excited and investigated in a number of ways, including photo-impact,[4] electron-impact,[4] ion-impact,[5] and beam-foil spectroscopy.[6] Because of differences in the modes of excitation and variation of the selection rules, the different types of spectroscopy provide complementary information. A great deal of work has been done on the autoionization of rare gases, but relatively little on atoms of nonvolatile elements, such as metal vapors, in part because of the technical complexities.[7] Recently, we have found that the uv lamp in our photoelectron spectrometer can be used as an electron source. By using it in conjunction with an oven, we can thus readily study the autoionization electron spectra of high-temperature vapors.[7] In this paper we report measurements of the ejected-electron spectra of Yb and Ba following the excitation or ionization of one of the outermost $5p^6$ electrons.

The ejected-electron spectra of the alkaline-earth metals Mg, Ca, and Sr have recently been analyzed.[8-11] In addition, Aleksakhin *et al.* and Melhorn *et al.*[12] have communicated preliminary results on the electron spectrum of Ba. To our knowledge the results given below are the first reported measurements of the ejected-electron spectrum of Yb.

To ascertain the relevant levels which contribute to the autoionization or Auger decay, it is necessary to determine the energies of these levels. For Yb, the primary source of this information comes from the Yb I absorption work of Tracy.[13] These studies show the energies of the optically allowed transitions of the type

$$\mathrm{Yb}(5p^6 4f^{14} 6s^2) \rightarrow \mathrm{Yb}^*(5p^5 4f^{14} nln'l'n''l'')_{J=1}\,.$$

Since all these levels lie in the continuum of Yb II, they may autoionize. The series limits of these lines $[\mathrm{Yb}^+(5p^5 4f^{14} nl)_{J=3/2,1/2}]$ lie in the continuum of Yb III and hence may Auger decay.

The situation in Ba is much more complicated. Recent photoabsorption studies by Connerade *et al.*[14] show the positions of numerous levels of the type $\mathrm{Ba}^*(5p^5 nln'l'n''l'')_{J=1}$, all of which may autoionize. Roig[15] has recently reported the uv-absorption spectrum of Ba II, which gives the positions of many levels of the type $\mathrm{Ba}^+[5p^5 nln'l']$, which may Auger decay; some of these levels serve as series limits in the work of Connerade *et al.*[14] In addition to these photon-impact studies, there have been electron-impact–mass-spectroscopic experiments[16] performed on Ba and Ba^+; these investigations yield complementary results to the photoabsorption work, although they are inherently less sensitive.

Thus, even though Yb has f electrons and therefore more possible final states, the ejected-electron spectrum is much simpler than that of Ba. This simplicity is a manifestation of the dominance of the so-called "giant resonance" for $5p$ excitation. This resonance (nominally $5p^6 6s^2 5d\,^1P_1$) was first predicted by Wendin[17] and later observed by Tracy[13] in the $5p$ absorption spectrum of the lanthanides. As discussed by Connerade and Tracy,[18] the near degeneracy of the $6s$ and $5d$ shells in Ba

and La effectively "shatters" this resonance, and the oscillator strength is spread over many levels.

This paper deals with the various decay channels that may contribute to the observed spectra. Pertinent experimental details are given in Sec. II and results in Sec. III. The results are interpreted for each spectrum in Sec. IV. This interpretation is discussed in Sec. V. Conclusions are given in Sec. VI.

II. EXPERIMENTAL

The electron spectra were recorded using a Perkin-Elmer PS-18 photoelectron spectrometer modified for digital counting and high-temperature studies.[19] The experimental procedures were similar to those employed in photoelectron spectroscopy[3(b)] except that the electron source was provided by the uv lamp operated in the electron mode. The operation and characteristics of a capillary discharge lamp as an electron source have been discussed by Lee *et al.*[7]

The electron spectra were measured with the lamp adjusted to give an optimum compromise of resolution, signal intensity, and signal-to-background ratio.[7] Under these conditions the pressure in the lamp was held between 50 and 100 mTorr and that in the main vacuum chamber was in the low 10^{-5} Torr range. To ascertain that the spectra were independent of the ions present in the lamp, each metal vapor was studied with both He and Ne lamps. The spectra thus obtained were found to be identical except for slight variations in relative peak intensities, which were attributed to lamp fluctuations and variations of the analyzer transmission. The contribution to the spectra due to ionization by (He^+ or Ne^+) ion impact was thus estimated to be negligible. This is further substantiated by the fact that few ions impinged upon the anode of the lamp and subsequently made their way into the ionization chamber to cause ionization.[7] Calibration of the spectra was accomplished by referencing to the photoelectron lines of the metals, Xe, and/or N_2 with the lamp operated simultaneously in both photon and electron modes.[7]

III. RESULTS

The ejected-electron spectra of Yb and Ba are shown in Figs. 1 and 2, respectively. These spectra represent raw data with no smoothing, background subtraction, etc., and were recorded with an energy resolution of (1–2)%. The nonlinear background is a result of the characteristics of the electron source.[7] Due to the complexity of the spectra, only the electron lines with appreciable intensities, i.e., larger than 1% of the most intense line, are identified and numbered in the figures. In many instances, as can be seen in the spectra, the width and profile of an individual line suggests it actually consists of several lines. The energies and relative intensities of the electron lines are collected in Tables I and II. The intensities have been corrected for energy dependence only, and thus carry large uncertainties. They are included primarily for qualitative discussion.

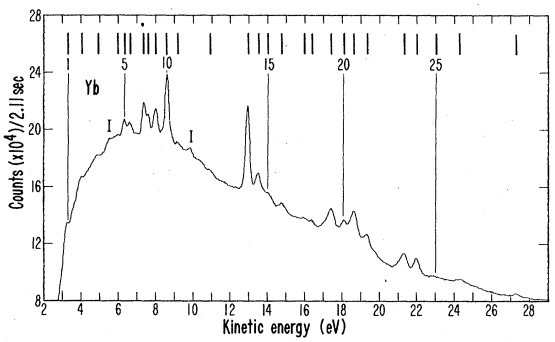

FIG. 1. Ejected-electron spectrum of Yb following excitation or ionization of a $5p$ electron.

IV. INTERPRETATION

Following the electron-impact excitation of one of the outermost corelike electrons in Ba or Yb, there are three possible ways to produce ejected electrons with discrete energies. They are designated e_1, e_2, and e_3 in Fig. 3 and correspond to the following autoionization processes:

$$M^*(5p^5nln'l'n''l'') \rightarrow M^+(5p^6 6s \text{ or } 5p^6nl) + e_1 ,$$

$$M^*(5p^5nln'l'n''l'') \rightarrow M^{*+}(5p^5nln'l') + e_2 ,$$

$$M^{*+}(5p^5nln'l') \rightarrow M^{2+}(5p^6 \text{ or } 5p^6 4f^{13}nl(\text{Yb})) + e_3 .$$

Electrons e_1, e_2, and e_3 lie in different energy regions and can thereby ususlly be distingushed from one another. Generally speaking, e_2-type electrons are of extremely low energy, and the centers of electron groups e_1 and e_3 separated

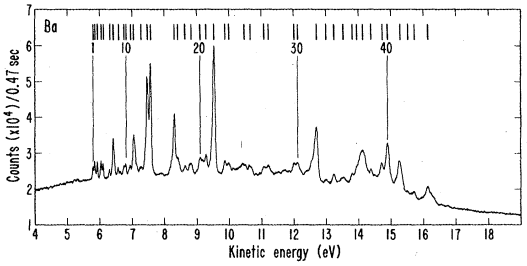

FIG. 2. Ejected-electron spectrum of Ba following excitation or ionization of a $5p$ electron.

by the binding energy of M^+. Due to poor transmission of the analyzer at low energies we were unable to detect e_2 electrons.

This section deals with the possible decay channels which account for the observed spectra. In both spectra, structure was observed which may be attributed to autoionization and Auger decay. Since the Yb spectrum lends itself relatively easily to interpretation, it will be discussed first.

A. Yb ($5p^6 4f^{14} 6s^2$)

1. Autoionization (e_1 electrons, Fig. 3)

The $5p$ absorption spectrum of Yb I below the $(5p^5 6s^2)\,^2P_{3/2}$ threshold is dominated by two intense

TABLE I. Energies, intensities, and state assignments of peaks seen in the ejected electron spectrum of Yb.

No. of peak	Kinetic energy (eV) [a]	Relative intensity [b]	Assignment [c]
1	3.26	26	Yb II $(^2P_{3/2}) \rightarrow [4f^{13}(^2F_{7/2})6P_{3/2}]_{J=2,5}$ (3.23)
2	4.03	21	Yb II $(^2P_{3/2}) \rightarrow [4f^{13}(^2F_{7/2})6P_{1/2}]_{J=3}$ (4.00)
3	4.79	12	
4	5.90	13	
5	6.30	37	Yb II $(^2P_{3/2}) \rightarrow [4f^{13}(^2F_{5/2})5d_{5/2 \text{ or } 3/2}]_{J=4 \text{ or } 1}$ (6.27)
6	6.57	21	Yb II $(^2P_{3/2}) \rightarrow [4f^{13}(^2F_{5/2})5d_{5/2}]_{J=2}$ (6.53)
7	7.33	53	Yb II $(^2P_{3/2}) \rightarrow [4f^{13}(^2F_{5/2})6s_{1/2}]_{J=2,3}$ or $[4f^{13}(^2F_{5/2})5d_{5/2}]_{J=0}$ (7.33)
8	7.56	23	Yb II $(^2P_{3/2}) \rightarrow [4f^{13}(^2F_{7/2})5d_{5/2}]_{J=3,4,5}$ (7.58)
9	7.97	44	Yb II $(^2P_{3/2}) \rightarrow [4f^{13}(^2F_{7/2})5d_{5/2}]_{J=1,2,6}$ (7.99)
10	8.57	100	Yb II $(^2P_{3/2}) \rightarrow [4f^{13}(^2F_{7/2})5d_{3/2}]_{J=3,4}$ (8.59)
11	9.26	5	
12	10.8	5	
13	12.92	93	Yb II $(^2P_{3/2}) \rightarrow 4f^{14}\,^1S_0$ (12.91)
14	13.47	27	Yb II $(^2P_{1/2}) \rightarrow [4f^{13}(^2F_{7/2})5d_{3/2}]_{J=2,3}$ or $[4f^{13}(^2F_{5/2})5d_{5/2}]_{J=0}$ (13.50)
15	14.00	11	
16	14.73	7	Yb I $5p^5(^2P_{3/2})6s^2 7d[1/2]_1 \rightarrow 5p^6 7d\,^2D_{5/2,3/2}$ (14.81)
17	15.98	3	Yb I $5p^5(^2P_{3/2})6s^2 6d[1/2]_1 \rightarrow 5p^6 6d\,^2D_{5/2,3/2}$ (16.00)
18	16.34	3	
19	17.39	29	Yb I $5p^5(^2P_{3/2})6s^2 5d[1/2]_1 \rightarrow 5p^6 4f^{13} 6s^2(^2F_{7/2})$ (17.47)
20	18.09	13	Yb I $5p^5(^2P_{3/2})6s^2 5d[1/2]_1 \rightarrow 5p^6 4f^{13} 6s^2(^2F_{5/2})$ (18.07)
21	18.61	38	Yb I $5p^5(^2P_{3/2})6s^2 5d[3/2]_1 \rightarrow 5p^6 6p(^2P_{1/2})$ (18.62)
22	19.32	16	Yb I $5p^5(^2P_{3/2})6s^2 5d[3/2]_1 \rightarrow 5p^6 4f^{13} 6s^2(^2F_{7/2})$ (19.32)
23	21.30	16	Yb I $5p^5(^2P_{3/2})6s^2 5d[1/2]_1 \rightarrow 5p^6 6s$ (21.38)
24	21.96	15	Yb I $5p^5(^2P_{3/2})6s^2 5d[3/2]_1 \rightarrow 5p^6 6s$ (21.98)
25	22.97	1	
26	24.26	3	Yb I $5p^5(^2P_{3/2})6s^2 7d[1/2]_1 \rightarrow 5p^6 6s\,^2S_{1/2}$ (24.31)
27	27.33	3	Yb I $5p^5(^2P_{1/2})6s^2 5d[3/2]_1 \rightarrow 5p^6 6s$ (27.04)

[a] Absolute energy uncertainty of ±0.04 eV.

[b] Corrected for $1/E$ transmission dependence of analyzer—Peak 10 = 100.

[c] Based on the energy levels given in Refs. 13 and 20. The value in parentheses is the optical value from these sources; where more than one final state is indicated, the average value has been given. In addition to the states listed, states of configuration $5p^6 4f^{13} 6s\,5d$ could also contribute to peaks 19–22.

TABLE II. Energies, intensities, and assignments of peaks seen in the ejected-electron spectrum of Ba.

No. of peak	Kinetic energy[a] (eV)	Relative intensity[b]	Observations[c] assignments[d]
1	5.80	28	R } $C_{i,j}$
2	5.85		
3	5.93		
4	6.09	20	R
5	6.10		R
6	6.31	4	R
7	6.43	30	R, C_h
8	6.57	6	R
9	6.76	11	R } C_g
10	6.81		
11	6.95	6	R } C_f
12	7.06	40	R
13	7.29	4	
14	7.48	78	R, C_e
15	7.58	95	R, C_d
16	8.31	53	R, C_c
17	8.41	13	R
18	8.65	19	R
19	8.82		R
20	9.10	14	
21	9.29		R
22	9.55	100	R, $C_{a,b}$
23	9.88	16	R
24	9.99		R, $5p^5 6s^2 5d\,^3P_1 \rightarrow 5p^6 6p\,^2P_{3/2}$ (9.9)
25	10.42	14	
26	10.63		R
27	11.09	15	
28	11.22		R
29	12.00	6	$5p^5 6s^2 5d\,^3P_1 \rightarrow 5p^6 5d\,^2D_{5/2}$ (11.96)
30	12.10	7	R, $5p^5 6s^2 5d\,^3P_1 \rightarrow 5p^6 5d\,^2D_{3/2}$ (12.06)
31	12.71	58	R, $5p^5 6s^2\,^3P_1 \rightarrow 5p^6 6s$ (12.66)
32	13.00	3	R
33	13.25	7	R
34	13.54	5	R
35	13.81	8	R
36	13.96		R
37	14.12	28	R
38	14.39	3	R
39	14.73	10	R
40	14.91	26	R
41	15.27	22	R
42	15.53	1	R

TABLE II. (*Continued*)

No. of peak	Kinetic energy [a] (eV)	Relative intensity [b]	Observations [c] assignments [d]
43	15.72	3	*R*
44	16.14	18	*R*

[a] Absolute energy uncertainty of ±0.09 eV.

[b] Corrected for $1/E$ transmission of analyzer. Peak 22 = 100.

[c] *R* indicates a Ba II energy level observed by Roig (Ref. 15) that is capable of producing an Auger electron of this energy. C_S indicates series limits observed by Connerade *et al.* (Ref. 14) which could also result in the same Auger decay; the *s* subscript indicates the series in Ref. 14.

[d] Assignments based on the optical values from Refs. 14 and 33; optical value is in parentheses.

peaks at excitation energies (E_a) of 27.63 and 28.23 eV. Tracy has assigned these peaks to the $5p^5(^2P_{3/2})4f^{14}6s^25d(1/2)_1$ and $5p^5(^2P_{3/2})4f^{14}6s^25d(3/2)_1$ levels of Yb I.[13] Autoionization of these two states to the ground state of Yb II ($5p^64f^{14}6s^2S_{1/2}$) will give rise to two electron peaks at energies E_e of $E_a - E_b(6s)$, where $E_b(6s)$ is the binding energy of a 6*s* electron (6.25 eV).[20] These energies correspond to peaks 23 and 24 in Fig. 1. In addition, it is possible for these levels to autoionize to excited states of Yb II such as $5p^64f^{13}6s^2\,^2F_{7/2,5/2}$, $5p^64f^{14}5d\,^2D_{5/2,3/2}$, and $5p^64f^{14}6p\,^2P_{3/2,1/2}$. Such transitions account for the observed intensity between 17 and 20 eV in Fig. 1. It is also possible to identify some of the less intense peaks in Fig. 1 with weaker features observed in the absorption spectrum. These assignments are summarized in Table I.

In the region between the $5p^5\,^2P_{3/2}$ and $^2P_{1/2}$ threshold lies the so-called "giant resonance" $5p^5(^2P_{1/2})6s^25d(3/2)_1$ (33.29 eV, 1.4-eV FWHM).[13] Decay

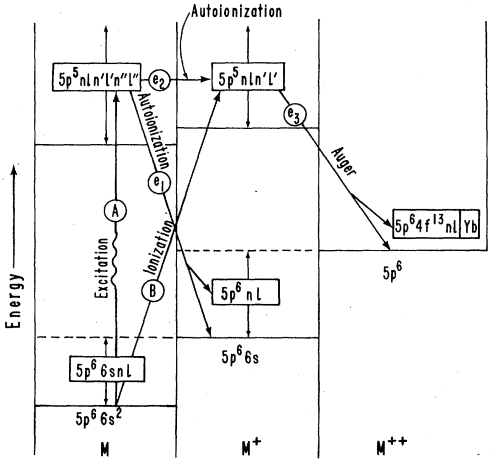

FIG. 3. Energy-level diagram depicting the various excitation and decay channels discussed in the text, M = Yb ($5p^64f^{14}6s^2$) or Ba ($5p^66s^2$).

of this state to the ground state of Yb II should yield an e_1 electron of energy 27.04 eV. Since the resonance is so broad, it is possible that the weak feature (peak 27) at 27.33 eV is a result of this decay. Since the absorption peak is so intense, it seems surprising that the corresponding electron is so weak. However, other experimental evidence suggests the reason for this is that the "giant resonance" decays primarily to the Yb II ($5p^56s^2\,^2P_{3/2}$) state, with release of an e_2 electron. This state then Auger decays to ground and excited states of Yb III. The reasoning for this will become clearer in Sec. IV A 2.

2. *Auger decay (e_3 electrons, Fig. 3)*

Decay of the Yb II $5p^54f^{14}6s^2\,^2P_{3/2}$ (31.350 eV) state to the ground state of Yb III $5p^64f^{14}\,^1S_0$ (18.44 eV)[20] yields an electron of 12.91 eV kinetic energy. This corresponds to the intense peak (13) in the electron spectrum. It is also possible to identify decay to excited configurations of Yb III, such as $4f^{13}6s$, $4f^{13}5d$, and $4f^{13}6p$. Using the Yb III energy levels given by Martin *et al.*,[20] we have assigned most of the lower-energy features to this process. This information is summarized in Table I.

We note the absence of a peak corresponding to the transition

$$5p^54f^{14}6s^2\,^2P_{1/2} \rightarrow 5p^64f^{14}\,^1S_0,$$

which should appear at 19.08 eV. Peak 14 at 13.47 eV may be assigned to the $5p^54f^{14}6s^2\,^2P_{1/2}$ state decaying to the $5p^64f^{13}6s$ level.[20] However, the intensities of these peaks are much smaller than one would expect if the $5p^56s^2\,^2P_{3/2}$ and $^2P_{1/2}$ levels were populated statistically. Statistical behavior would be expected, in the absence of relativistic effects, if direct ionization (path *B*, Fig. 3) were the dominant mechanism by which the $^2P_{3/2}$ and $^2P_{1/2}$ states were populated. Since the spin-orbit splitting in Yb is large, one cannot neglect relativistic effects. However, it seems unlikely that such a mechanism

could account for the total lack of structure attributable to $5p^5 4f^{14} 6s^2\,{}^2P_{1/2}$ decay. Consequently, excitation (path A, Fig. 3) followed by autoionization with ejection of e_2 electrons appears to be the dominant path.

The behavior has been observed to a lesser extent in the lighter alkaline earth metals Sr and Ca $[np^6(n+1)s^2]$ and 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 that the corresponding arguments do not apply to Mg, where $3s$ and $3d$ shells are involved. However, the proposed two-step mechanism could explain the total absence of autoionization structure observed by Pejcev *et al.*[8(b)] corresponding to the intense 213.50-Å transition $(2s^2 2p^6 3s^2 \rightarrow 2s^2 2p^5 3p^2 3d)$ in Mg I.[21] This state lies above *both* the $2p^5\,{}^2P_{3/2}$ and ${}^2P_{1/2}$ limits. Thus, it appears that this state preferentially populates the ${}^2P_{3/2,1/2}$ levels, which subsequently decay to the ground state of Mg III. This explanation is consistent with both the statistical population of the ${}^2P_{3/2}$ and ${}^2P_{1/2}$ levels and the lack of autoionization structure. In Ca the collapsed nd levels begin to provide states in between the ${}^2P_{3/2}$ and ${}^2P_{1/2}$ limits that make indirect population of the ${}^2P_{3/2}$ level more probable. As one proceeds from Mg to Ba, the effect becomes more pronounced,[8-12] and at Yb there is little if any direct population of the $5p^6 6s^2\,{}^2P_{3/2}$ state.

Such behavior is reasonable in light of the huge oscillator strength observed by Tracy for the giant resonance in Yb I.[13] It was noted above that the branching ratio for autoionization of this state to the ground state of Yb II was almost negligible. The only other nonradiative decay channel of this level is autoionization to the $5p^5 4f^{14} 6s^2\,{}^2P_{3/2}$ level. Auger decay of this state leads to most of the observed low-energy peaks in the spectrum.

Tracy commented on this aspect of the giant resonance in Yb.[13] Hansen[22] and Connerade *et al.*[23] invoked a similar two-step autoionization process to explain the double ionization anomaly in Ba I when excited with He I radiation.[24] Analogous behavior has been noted in the ejected-electron spectrum of Na, where the Na^* $[2p^5 3s(^1P)nl]$ levels appear to decay preferentially to the Na^+ $[2p^5 3s\,(^3P)] + e_2$ continuum rather than Na^+ $(2p^6\,{}^1S) + e_1$.[25]

B. Ba $(5p^6 6s^2)$

1. Autoionization

As mentioned previously, the Ba I $5p$ absorption spectrum is immensely complex. In order to assign this spectrum, Connerade *et al.*[14] grouped the lines into 12 series. The series limits were found from levels observed in the $5p$ absorption spectrum of Ba II.[15] The lowest of these autoionizing levels, and one of the most intense, lies at 17.87 eV above the ground state. Autoionization of this state to the ground state of Ba II yields an e_1 electron with 12.66 eV kinetic energy, coinciding with peak 31 in Fig. 2. It is also possible to identify peaks corresponding to decay of this level to specific excited states of Ba II; i.e., $5p^6 5d\,{}^2D_{5/2,3/2}$ and $5p^6 6p\,{}^2P_{3/2,1/2}$. The $5p^6 6p\,{}^2P_{1/2}$ state is not identified in our spectrum; however, it does appear clearly in the work of Aleksaksin *et al.*[26] The relative intensities of these satellites is in qualitative agreement with recent photoemission work on Ba I.[27]

We also believe that the intense peaks at higher energies than peak 31 are due to autoionization to the ground state of Ba II. According to the absorption data of Roig,[15] it is also possible to identify most of these lines with Auger transitions (see Table II). The assignment of these peaks to autoionization is supported by the fact that peaks 22–30 are of relatively low intensity and thus are probably due to some second-order process (such as the satellite lines mentioned earlier). The abrupt rise in intensity at peak 31 implies that a new channel has opened. Since peak 31 has been identified as a primary autoionizing transition, the implication is that the other strong higher-energy peaks occur via this mechanism. This type of "two-region" behavior was seen earlier in the spectrum of Yb and has also been observed in Ca (Ref. 9) and Sr (Ref. 10). Aleksakhin *et al.*[11] invoked similar reasoning in their discussion of Ba. Unfortunately, the relatively poor electron-energy resolution and the large density of autoionizing states in this region[14] $(19 < h\nu < 22$ eV) preludes assignment of the lines in the corresponding electron spectrum $(14 < E < 17$ eV) to individual autoionizing transitions.

2. Auger decay

Based on energy considerations, it seems likely that most of the peaks 1–22 are due to Auger transitions. All of these peaks are also seen in the electron-impact work of Melhorn *et al.*[12] who used 2-keV electrons for excitation. They reported binding energies for the $5p^6 6s^2\,{}^2P_{3/2}$ and ${}^2P_{1/2}$ states of 22.75(5) and 24.76(2) eV, in good agreement with our values based on the positions of peaks 15 and 22 [22.79(9) and 24.76(9) eV]. As mentioned earlier, the assignment of these states is nominal since the near degeneracy of the $5d$ levels effectively "smears out" these states as is indicated by the large number of peaks (states) in this region.

Peaks 1–3 appeared as very intense structure in the He I photoelectron spectrum of Ba.[28] At that time it was postulated that path A (Fig. 3) was the

primary mechanism by which the $5p^5nln'l'$ states were populated. These states lie at ~15.8 eV above the ground state of Ba II. This is the same energy as the first autoionizing threshold observed by Peart *et al.*[16(b)] in electron-impact–mass-spectroscopic studies of Ba^+. Multiconfigurational Hartree-Fock calculations by Hansen[29] assigned these levels to the $5p^55d(^3P)6s\,^2P$ configuration, and they are the lowest-lying autoionizing levels for Ba II. This conclusion is supported by multiconfigurational Dirac-Fock calculations of Connerade *et al.*[23] Roig observed weak structure as low as 14.7 eV, but his spectrum was complicated by excitation from the metastable $5p^65d\,^2D_{5/2,3/2}$ levels.[15]

Thus, the first peaks in the ejected-electron spectrum come at energies corresponding to the first possible Auger states in Ba II. Most of the other peaks, 4–22, are due to Auger decay of higher-lying levels. In order for these states to be populated via autoionization of Ba I (step A, Fig. 3), autoionizing levels with $E_a > 21.0$ eV are required. Decay of these levels to the *ground* state of Ba II would yield electrons with $E_e > 15.8$ eV. It is interesting to note that the ejected-electron spectrum shows very little intensity after this threshold. This implies, as noted earlier in Yb, that once the Auger channel becomes energetically possible, the Ba I $5p^5nln'l'n''l''$ levels preferentially populate these Ba II $5p^5nln'l'$ states (e_2 electrons) at the expense of the Ba II $5p^6nl$ states (e_1 electrons).

This explanation is also consistent with the relatively large ratio (R) of Ba^+ to Ba^+ ions induced by He I radiation (21.2 eV); $R = 2.4(6)$,[24] as compared to that induced by Ne I radiation (16.8 eV), $R = 0.25(5)$,[24] as well as the ratio induced by He metastables,[30] $2\,^3S$ (19.8 eV), $R = 0.010(5)$, and $2\,^1S$ (20.6 eV), $R = 0.018(6)$. The He I radiation coincides with an autoionizing level *above* the first $(5p)^{-1}$ threshold, while the Ne I radiation is both off resonance and below this threshold. While there are a number of strong autoionizing states capable of being populated by the He metastables, they all lie *below* the first $(5p)^{-1}$ threshold.

Because the e_2 electrons populating the Ba II $5p^5nln'l'$ are very low in energy, it is possible that some of the Auger decay is influenced by postcollisional interaction effects.[31] It is not possible to assess the magnitude of the effect in the spectra presented here; it may be responsible for shifting some of the Auger peaks in energy and causing them to be asymmetric.

V. DISCUSSION

In this section we present qualitative reasons why the two-step mechanism becomes preferred when energetically possible. The matrix element governing the decay rate of an autoionizing state, ϕ_a, is given by $\langle \phi_a | 1/r_{12} | \phi_i, \epsilon l \rangle$ (Ref. 32), where ϕ_i represents the wave function of the ionic state and ϵl that of the continuum electron of energy ϵ and angular momentum l. Let us consider decay of the giant resonance in Yb. In this case $\phi_a = 5p^5(^2P_{1/2})6s^25d(3/2)_1$ (suppressing the filled f shell). The first step in the two-step ionization process involves decay to $\phi_i = 5p^5(^2P_{3/2})6s^2$ which then decays to the doubly charged ion. For single ionization, $\phi_i = 5p^6nl$. Upon examination of the matrix element, it seems evident that the greatest overlap will occur for $\phi_i = 5p^5(^2P_{3/2})6s^2$. Therefore, any autoionizing levels lying above the first $(5p)^{-1}$ level should preferentially decay in a two-step manner.

VI. CONCLUSIONS

Ejected-electron spectra of Ba and Yb have been presented. These are the first such spectra of Yb. Analysis of the spectra shows autoionization to both ground and excited states of M^+ ($5p^6nl$), Auger decay to the ground state of M^{2+} ($5p^6$), and for Yb, Auger decay to excited states of M^{2+} ($5p^6 4f^{13}nl$). The evidence indicates that autoionization to the ground and excited states of M^+ ($5p^6nl$) is only appreciable below the first $(5p)^{-1}$ ionization threshold. Above this level, autoionization proceeds primarily in a two-step manner: first, to the highly excited M^+ $5p^5nln'l'$ states and then Auger decay to the ground state(s) of M^{2+}.

If this hypothesis is correct, then mass-spectroscopic studies done at some of the stronger Ba I autoionizing resonances above the first $(5p)^{-1}$ threshold should yield an even larger ratio of M^{2+} to M^+ than the value of 2.4(6) observed by Brehm and Bucher using He I radiation[24] (this is a relatively weak resonance in the absorption spectrum). This effect should be especially dramatic at the energy of the giant resonance in Yb I.[13] In order to characterize this process further, studies using variable energy electrons and photons are required. We have recently begun such work on Ba, using synchrotron radiation.

ACKNOWLEDGMENT

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under Contract No. W-7405-Eng-48.

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