

# Photoionization of Ytterbium: 1350–2000 Å\*

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Using a photoionization mass spectrometer, the photoionization efficiency of ytterbium has been measured from 1350–2000 Å. The spectrum is dominated by line structure which tentative analysis indicates is due to the following configurations:  $4f^{14}5dnp$ ,  $4f^{14}6pnd$ ,  $4f^{13}6s^2nd$ , and  $4f^{13}5d6snd$ . The ionization potential derived for Yb I from Rydberg series is  $6.25 \pm 0.01$  eV.

## INTRODUCTION

Meggers and Scribner<sup>1</sup> reported the first description of the emission spectrum of ytterbium. They reported identification of some of the terms in Yb I and Yb II. Meggers and Corliss<sup>2</sup> in 1966 restudied the emission spectrum of ytterbium and reported about 7300 spectral lines belonging to Yb I, Yb II, Yb III, and Yb IV. From extrapolation of the terms identified by Meggers and Scribner, the ionization potential of Yb I was found to be 6.25 eV.<sup>3,4</sup> Zmbov and Margrave<sup>5</sup> using electron-impact techniques measured the ionization potential of ytterbium and found it to be 5.90 eV.

The study reported here gives the photoionization spectrum from 1350–2000 Å. A partial analysis and tentative identification of autoionizing lines have been carried out.

## EXPERIMENT TECHNIQUE

The photoionization mass spectrometer used was essentially that previously described.<sup>6</sup> A ytterbium beam was generated from a radiation-heated tantalum Knudsen cell. The temperature of the Knudsen cell was controlled by regulating the current passing through the heating filament. The photon source was the hydrogen continuum and the hydrogen many-line spectrum generated by a dc discharge. The bandpass used was 3 Å. This bandpass represents a compromise between photon resolution and ion intensity.

The ytterbium sample was obtained from E.S.P.I.<sup>7</sup> and was stated to be 99.9% pure.

## RESULTS AND INTERPRETATION

Figure 1 gives the photoionization efficiency curve of ytterbium in the wavelength region 1350–2000 Å. As is

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<sup>1</sup> W. F. Meggers and B. F. Scribner, *J. Res. Natl. Bur. Std.* **19**, 651 (1937).

<sup>2</sup> W. F. Meggers and C. Corliss, *J. Res. Natl. Bur. Std.* **A70**, 63 (1966).

<sup>3</sup> M. A. El'Yashevich, "Spectra of the Rare Earths," AEC-TR-4403, U.S. AEC Office of Technical Information.

<sup>4</sup> J. Reader and J. Sugar, *J. Opt. Soc. Am.* **56**, 1189 (1966).

<sup>5</sup> K. F. Zmbov and J. L. Margrave, *J. Phys. Chem.* **70**, 3014 (1966).

<sup>6</sup> B. Steiner, C. F. Giese, and M. G. Inghram, *J. Chem. Phys.* **34**, 189 (1961).

<sup>7</sup> Electronic Space Products, Inc., Los Angeles, Calif.

apparent from Fig. 1, the photoionization process is entirely dominated by line structure due to autoionization. Direct ionization to the ground state of Yb II is not observed. The experimental data indicate that throughout the energy range of this study, the direct ionization cross section of Yb I must be down by a factor of at least 100 from the cross section due to autoionization at  $\sim 1800$  Å.

The initial autoionizing lines observed at 1932, 1879, and the very broad line at 1800 Å are interpreted as being due to the  $4f^{14}5d6p$  configuration. The line at 1879 Å interferes with the broad line centered at 1800 Å. If the low-energy wing of this line is attributed partly to the line at 1800 Å, the 1800-Å line can be interpreted as being a symmetrical line.

At wavelengths shorter than 1700 Å, lines from  $4f$  shell excitation appear as well as higher members of the  $4f^{14}5dnp$  configuration. Based primarily upon the behavior of Rydberg denominators, it is possible to make a tentative analysis of the spectrum observed. In this analysis no attempt has been made to determine the Beutler-Fano<sup>8</sup> line-profile parameters. The energy levels given correspond to the maxima of the respective autoionizing line. Higher resolution would be required before a more detailed analysis is justified.

### $4f^{14}5dnp$

The  $4f^{14}5dnp$  configuration arises when both  $6s^2$  electrons are excited according to  $\Delta l_1=1$ ,  $\Delta l_2=2$ . The analogous configuration has been observed in barium by Garton and Codling.<sup>9</sup> There are three terms possible for this configuration which preserve  $\Delta J=1$ :  $^3D_1$ ,  $^3P_1$ , and  $^1P_1$ . The  $^3D_1$ ,  $^3P_1$  series have as their limit the  $5d^2D_{3/2}$  level of Yb II. The  $^1P_1$  series has as its limit the  $5d^2D_{5/2}$  level of Yb II. The  $5d^2D_{3/2}$  level lies at  $22\,961\text{ cm}^{-1}$  (2.847 eV)<sup>10</sup> and the  $5d^2D_{5/2}$  level lies at  $24\,333\text{ cm}^{-1}$  (3.017 eV)<sup>10</sup> above the ground state of Yb II.

The very broad peak at 1800 Å is interpreted to be due to the  $5d6p^1P_1$  level. The state is very short lived

<sup>8</sup> U. Fano, *Phys. Rev.* **124**, 1866 (1961); U. Fano and J. W. Cooper, *ibid.* **137**, A1364 (1965).

<sup>9</sup> W. R. S. Garton and K. Codling, *Proc. Roy. Soc. (London)* **75**, 87 (1960).

<sup>10</sup> Dr. William Martin, U.S. Bureau of Standards, Washington (private communication); W. F. Meggers, *J. Res. Natl. Bur. Std.* **71A**, 396 (1967).

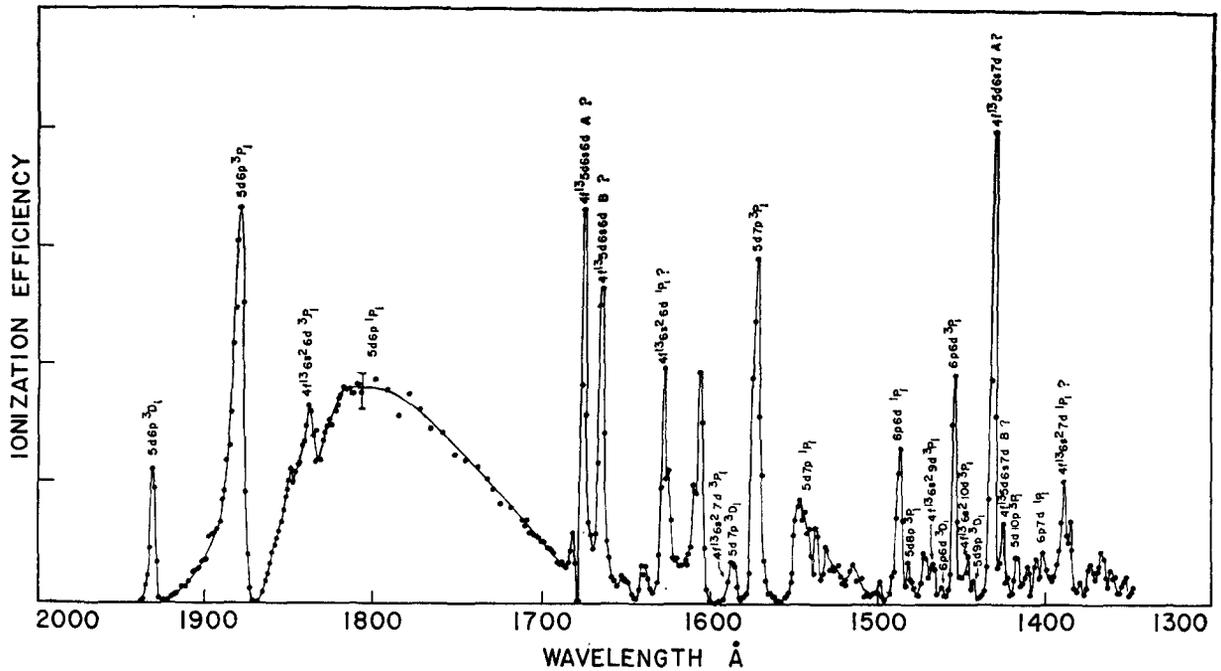


FIG. 1. Photoionization efficiency curve of ytterbium from 1350 to 2000 Å. The vertical scale is in arbitrary units.

( $\sim 10^{-15}$  sec) and has the largest total intensity of any line observed. This is consistent with the level assigned. This peak and its second member at  $\sim 1550$  Å are the only two resolvable members of this series. The less well-defined line at 1550 Å is also broad and is modulated by structure of uncertain origin. It seems unlikely that the line at  $\sim 1800$  Å could be the  $5d7p^1P_1$  since this would imply that the  $5d6p^1P_1$  level lies very low.

The first member of the  $5dnp^3P_1$  series lies at 1879 Å. The lines identified as higher members of this series are shown in Table I. The first member of the  $5dnp^3D_1$  series lies at 1932 Å and the second member at 1586 Å. The only other resolved term of the  $5dnp^3D_1$  series is at 1442 Å. These results are also tabulated in Table I.

TABLE I.  $5dnp$  series.

$E$ (eV)	$\lambda_{vac}$	Identifi- cation	Rydberg denominator
$^3P_15dnp$ limit 9.097 eV			
6.599	1879	$5d6p$	2.33
7.891	1571	$5d7p$	3.35
8.377	1480	$5d8p$	4.34
...	...	...	...
8.755	1416	$5d10p$	6.30
$^3D_15dnp$ limit 9.097 eV			
6.418	1932	$5d6p$	2.25
7.817	1586	$5d7p$	3.26
Unresolved			
8.600	1442	$5d9p$	5.22

These results for the  $5dnp$  configuration in ytterbium are very much like those reported for barium by Garton and Codling.<sup>9</sup> This comparison lends some weight to the interpretation given here.

#### $4f^{14}6pnd$

This configuration has the same first terms as the  $4f^{14}5dnp$  configuration. The series from this configuration, however, go to the  $4f^{14}6p$  level of Yb II. The  $6p^2P_{3/2}$  level of Yb II lies at  $30\,392.3\text{ cm}^{-1}$  (3.768 eV)<sup>3</sup> and the  $6p^2P_{1/2}$  level lies at  $27\,061.9\text{ cm}^{-1}$  (3.355 eV).<sup>3</sup> The  $6pnd^1P_1$  series has as a limit the  $6p^2P_{1/2}$  level of Yb II and the  $6pnd^3P_1$ ,  $^3D_1$  series have as their limit the  $6p^2P_{3/2}$  level of Yb II. The results and tentative identification of these lines are given in Table II.

TABLE II.  $6pnd$  series.

$E$ (eV)	$\lambda_{vac}$	Identifi- cation	Rydberg denominator
$^1P_16pnd$ limit 9.605 eV			
Unresolved			
8.345	1486	$6p6d$	3.28
8.852	1400	$6p7d$	4.25
$^3P_16pnd$ limit 10.018 eV			
6.599	1879	$6p5d$	1.99
8.529	1454	$6p6d$	3.02
$^3D_16pnd$ limit 10.018 eV			
6.418	1932	$6p5d$	1.95
8.470?	1464	$6p6d$	2.96

$4f^{13}6s^2nd?$

Meggers<sup>10</sup> observed transitions in Yb I which he identified as due to  $4f^{13}6s^25d-4f^{14}6s^2$  transitions, the lowest of which is about 2.85 eV in energy. The series formed by the  $4f^{13}6s^2nd$  configuration would have as their limit the  $4f^{13}6s^2\ ^2F_{5/2}$  or  $4f^{13}6s^2\ ^2F_{7/2}$  level of Yb II. This inverted doublet in Yb II has energies of 3.914 and 2.655 eV above the ground state of Yb II.<sup>10</sup> Preserving  $\Delta J=1$  we have the following possible series:

$$^2F_{7/2}+d_{5/2} = (\frac{7}{2}, \frac{5}{2})_1,$$

$$^2F_{5/2}+d_{5/2} = (\frac{5}{2}, \frac{5}{2})_1,$$

$$^2F_{5/2}+d_{3/2} = (\frac{5}{2}, \frac{3}{2})_1.$$

Hence, there could be two series going to the  $^2F_{5/2}$  limit and one going to the  $^2F_{7/2}$  limit.

The most intense line expected would be that corresponding to a  $^1P_1$  term.  $4f^{13}6s^2nd^1P_1$  series would go to the  $^2F_{5/2}$  limit in Yb II. Two terms that we have tentatively identified as belonging to this series are shown in Table III.

A series going to the lower limit, i.e., the  $^2F_{7/2}$ , is tentatively identified in Table III. It is labeled  $^3P_1$  for identification only, and cannot be considered to be a confirmed notation.

$4f^{13}6s5dnd$

Many possible series arise out of this configuration and go to various levels of the  $4f^{13}6s5d$  configuration of Yb II. With the present data it is impossible to make any identification of these series. The results are shown in Table IV and must be considered no more than very speculative.

TABLE III.  $4f^{13}6s^2nd$  series.

<i>E</i> (eV)	$\lambda_{vac}$	Identifi- cation	Rydberg denomi- nator
$^1P_14f^{13}6s^2nd$ limit 10.614 eV			
7.615	1628	$4f^{13}6s^26d$	2.31
8.930	1388	$4f^{13}6s^27d$	3.32
$^3P_14f^{13}6s^2nd$ limit 8.905 eV			
6.752	1836	$4f^{13}6s^26d$	2.51
7.795?	1590	$4f^{13}6s^27d$	3.50
Unresolved			
8.449	1467	$4f^{13}6s^29d$	5.45
8.576	1446	$4f^{13}6s^210d$	6.42

TABLE IV.  $4f^{13}5d6snd$  series.

Limit 9.815 eV $4f^{13}5d6snd$ Limit $^3[1\frac{1}{2}]J=[1\frac{1}{2}]$ Yb II			
A series			
<i>E</i> (eV)	$\lambda_{vac}$	Identifi- cation	Rydberg denomi- nator
7.406	1674	$4f^{13}5d6s5d?$	2.38
8.667	1430	$4f^{13}5d6s6d?$	3.44
B series			
7.452	1664	$4f^{13}5d6s5d?$	2.40
8.700?	1425	$4f^{13}5d6s6d?$	3.49

IONIZATION POTENTIAL

The ionization potential of Yb I can be derived by taking the limit of any of the Rydberg series observed and subtracting the known corresponding excitation energy of the limit level in Yb II.<sup>10</sup> The value of the ionization potential of Yb I obtained in this manner from the two series of the  $5dnp$  configuration is  $9.097 - 2.847 = 6.25$  eV. This value for the ionization potential of Yb I is consistent with the series limits of the other less well-identified Rydberg series identified here. An estimated error on this derived value for the ionization potential is  $\pm 0.01$  eV.

CONCLUSIONS

While many of the classifications suggested here are tentative the main features of the spectrum seem clear. The dominating lines are those from the  $4f^{14}5dnp$  configuration and the  $4f^{14}6pnd$  configuration. The excitations involving  $4f$  electrons are in some cases intense and contribute to the complexity of the spectrum. The classification of the lines observed into various Rydberg series represents a self-consistent analysis of the data based primarily upon the behavior of Rydberg denominators.

Alternate analysis of this spectrum may be possible; however, any interpretation must be consistent with the experimental data.

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