The Spectra of Na II, III, and IV in the Extreme Ultraviolet

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New lines of Na II, III and IV have been found and classified in the region between 434,000 and 242,000 cm^{-1}.

INTRODUCTION

THE spectrum of Na II in the near ultraviolet has been classified by Frisch[1] in a recent article, who also gives a list of references to previous work on this spectrum. In the extreme ultraviolet region Bowen[2] and Edlen and Ericson[3] have observed the resonance lines 372.065A and 376.350A.[3] The spectrum of Na III (fluorine-like) has been studied by Edlen and Ericson[4] and Mack and Sawyer.[5] The lines corresponding to the $2s-2p$ transitions are the only lines recorded by these investigators for this ion. Both Edlen and Ericson[4] and Mack and Sawyer[5] predict a PP° group of Na IV in the region of 244,000 cm^{-1}. This group had been found and identified previously by Gale and Hoag of this laboratory, but had not been published. The observation of this group and of other lines in this region, which might be attributed to sodium, caused Professor Gale to suggest the present problem to the author.

GENERAL PROCEDURE

The source was a high potential vacuum spark, (*hot spark*).[6] This took place between hollow aluminum electrodes stuffed with metallic sodium which had first been rolled in nickel gauze. It was found that when the pressure in the discharge chamber was below 10^{-4} cm of Hg and the electrodes were separated about 1.5 mm, the vacuum gap (source) would not break down below 40,000 volts. The maximum voltage of the high potential source was above 100,000 volts. The primary circuit of the transformer was automatically made and broken by a very quick acting switch twenty-two times each minute, the duration of the sparks being from one-twentieth to one-tenth seconds each. The total time required for an exposure was from two to four hours.

The vacuum spectrograph used in this investigation was the one designed by Hoag,[7] with a few changes. The grating was glass, instead of speculum, with 1500 lines to the inch. The plate holder accommodated 2×18 inch plates

[1] R. Frisch, Zeits. f. Physik **70**, 498 (1931).
[2] I. S. Bowen, Phys. Rev. **23**, 1 (1924).
[3] B. Edlen and A. Ericson, Comptes Rendus **190**, 116 (1930).
[4] B. Edlen and A. Ericson, Comptes Rendus **190**, 173 (1930).
[5] J. E. Mack and R. A. Sawyer, Phys. Rev. **35**, 299 (1930).
[6] I. S. Bowen, J.O.S.A. **13**, 89 (1927).
[7] B. Hoag, Astrophys. J. **66**, 225 (1927).

and was so arranged that it could be raised to allow three exposures on one plate without removing it from the vacuum. Very thin glass Schumann plates, made by Hilger and Company, were used.

In reducing the plates a linear dispersion was assumed between the Al IV line of 160.073A[8] and the O III line at 599.598A,[9] error curves were then plotted by the aid of intermediate standards (O III 266.992,[10] Na II 372.065,[3] Na III 380.091[4] and O III 525.795A).[9] These error curves were found to be extremely smooth for all plates.

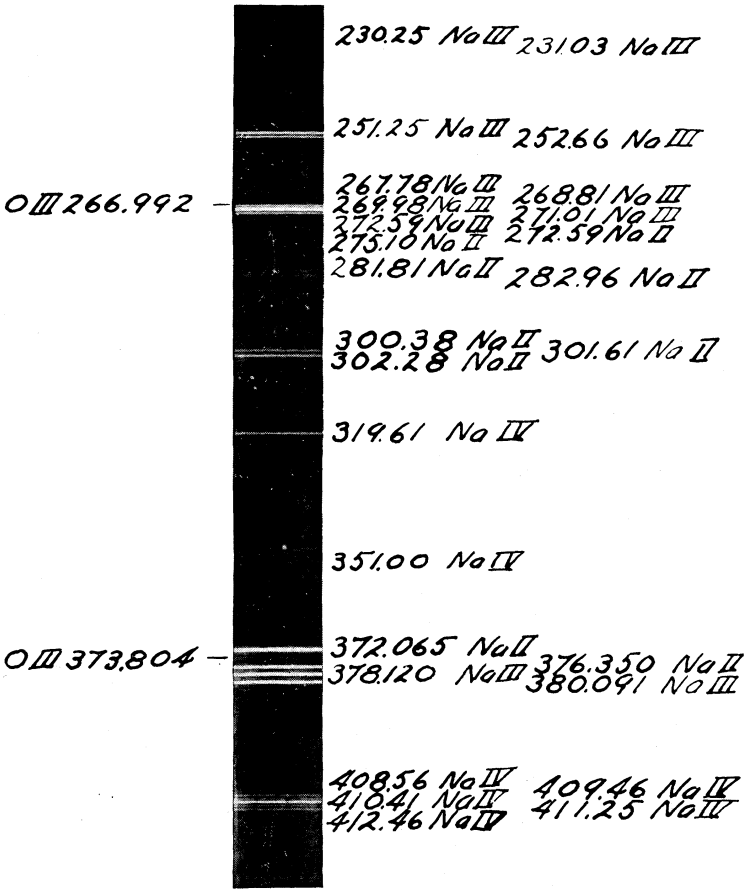

Fig. 1. Typical spectrogram.

With a very narrow slit and the pressure in the discharge chamber below 10^{-4} cm of Hg (as observed with an ionization gauge) plates were easily obtained which were free from fog and weak gas lines. Under these conditions

[8] J. Soderqvist and B. Edlen, Zeits. f. Physik **69**, 356 (1931).

[9] From a list of standard oxygen wave-lengths furnished through the courtesy of Dr. Bengt Edlen of Uppsala.

[10] A. Ericson and B. Edlen, Zeits. f. Physik **59**, 659 (1930).

only the prominent oxygen, carbon and aluminum lines appeared as impurities, which were used as standards in reducing the plates.

Na II (NEON-LIKE)

In the region investigated one would expect to find, besides the prominent resonence transitions $s^2p^6\ {}^1S_0 - s^2p^5 3s\ {}^3P_1,\ {}^1P_1$, transitions from two or three of the three $3d$ levels with $J=1$ and possibly from higher s orbits than the $3s$.

It was found possible to form two series formulas of the type

$$\nu = \nu_0 - 4R/(m+\mu+\alpha/m)^2 \text{ where } m = 1, 2, 3, \cdots$$

whose limits differed by the same amount (in cm^{-1}) as the separation of the ground terms of Na III ($s^2p^5\ {}^2P_{1/2,3/2}$). In addition to the three pairs of transitions used in forming these series formulas a fourth pair and possibly a fifth pair were found. (The latter was later found to fit better into the term scheme of Na III.) The levels thus found correspond to the ms_2 and ms_4 levels of neon as given by Paschen,[11] whose limits are ${}^2P^\circ_{1/2}$ and ${}^2P^\circ_{3/2}$, respectively. From the value of the latter limit 47.068 volts has been obtained as the ionization potential of Na II. The lines resulting from transitions from these levels to the ground term $s^2p^6\ {}^1S_0$ can be seen easily on the plates (Fig. 1 typical). They are given in Table I and II and are shown diagrammatically in Fig. 2a.

TABLE I. *Observed and calculated transitions of Na II.*

I	λ (obs.)	ν (cm^{-1})	Config. and Terms	ν (calc.†)
6	376.350[3]	265710	$s^2p^6\ {}^1S_0 - s^2p^5 3s\ {}^3P_1{}^\circ(s_4)$	265710
10	372.065[3]	268770	$s^2p^6\ {}^1S_0 - s^2p^5 3s\ {}^1P_1{}^\circ(s_2)$	268770
0	302.28	330830	$s^2p^6\ {}^1S_0 - s^2p^5 4s\ (s_4)$	330945
3	301.61	331540	$s^2p^6\ {}^1S_0 - s^2p^5 3d\ Z_{11}$	331502[1]
			$4s\ (s_2)$	332811
2	300.38	332910	$s^2p^6\ {}^1S_0 - s^2p^5$	
			$3d\ Z_2$	333050[1]
1	282.96	353260	$s^2p^6\ {}^1S_0 - s^2p^5 5s\ (s_4)$	353283
1	281.81	354850	$s^2p^6\ {}^1S_0 - s^2p^5 5s\ (s_2)$	354854
0	275.10	363500	$s^2p^6\ {}^1S_0 - s^2p^5 6s\ (s_4)$	363510
0	273.99	364960	$s^2p^6\ {}^1S_0 - s^2p^5 6s\ (s_2)$	364888
(0	271.01	369000	$s^2p^6\ {}^1S_0 - s^2p^5 7s\ (s_4)$	369028)*
(0	269.98	370400	$s^2p^6\ {}^1S_0 - s^2p^5 7s\ (s_2)$	370459)*

* Probably Na III.

† Calculated ν obtained from the following formulas:

$ms_2 \cdots \nu = 382800 - 4R/(m+0.963845-0.001872/m)^2$

$ms_4 \cdots \nu = 381430 - 4R/(m+0.949650-0.002057/m)^2$

in which $m = 1, 2, 3, \cdots$.

Of the three $3d$ levels with $J=1$ one should have the limit $s^2p^5\ {}^2P^\circ_{1/2}$ and the other two the limit $s^2p^5\ {}^2P^\circ_{3/2}$, of the latter two only the transition to the ground term from one of them is observed. This level is calculated to be 331,540 cm^{-1} above the ground term, and corresponds, within experimental error, to the Z_{11} term of Frisch.[1] The other $3d$ ($J=1$, ${}^2P^\circ_{1/2}$ limit) falls too close to the $4s(s_2)$ level to be resolved, it would correspond to the Z_2 term of Frisch.

[11] Paschen-Goetz, Seriengesetze (1922).

The transition from this level to the ground term is evident only from the fact that the line classified as the $^1S_0-4s(s_2)$ transition is unusually wide for a line of that intensity. The $4s(s_2)$ and $4s(s_4)$ levels correspond to the Z_3 and

TABLE II. *Term values of Na II.*

Config.	Term	Term Value (cm^{-1})	Limit
s^2p^6	$^1S_0$	0	
s^2p^53s	$^3P_1(s_4)$	265710	$^2P^\circ_{3/2}$
s^2p^53s	$^1P_1$ (s_2)	268770	$^2P^\circ_{1/2}$
s^2p^54s	(s_4)	330830	$^2P^\circ_{3/2}$
s^2p^53d	Z_{11}	331540	$^2P^\circ_{3/2}$
s^2p^54s (and $3d$)	(s_2) and Z_2	332910	$^2P^\circ_{1/2}$
s^2p^55s	(s_4)	353260	$^2P^\circ_{3/2}$
s^2P^55s	(s_2)	354850	$^2P^\circ_{1/2}$
s^2p^56s	(s_4)	363500	$^2P^\circ_{3/2}$
s^2p^56s	(s_2)	364960	$^2P^\circ_{1/2}$
s^2p^57s	(s_4)	369000	$^2P^\circ_{3/2}$
s^2p^57s	(s_2)	370400	$^2P^\circ_{1/2}$

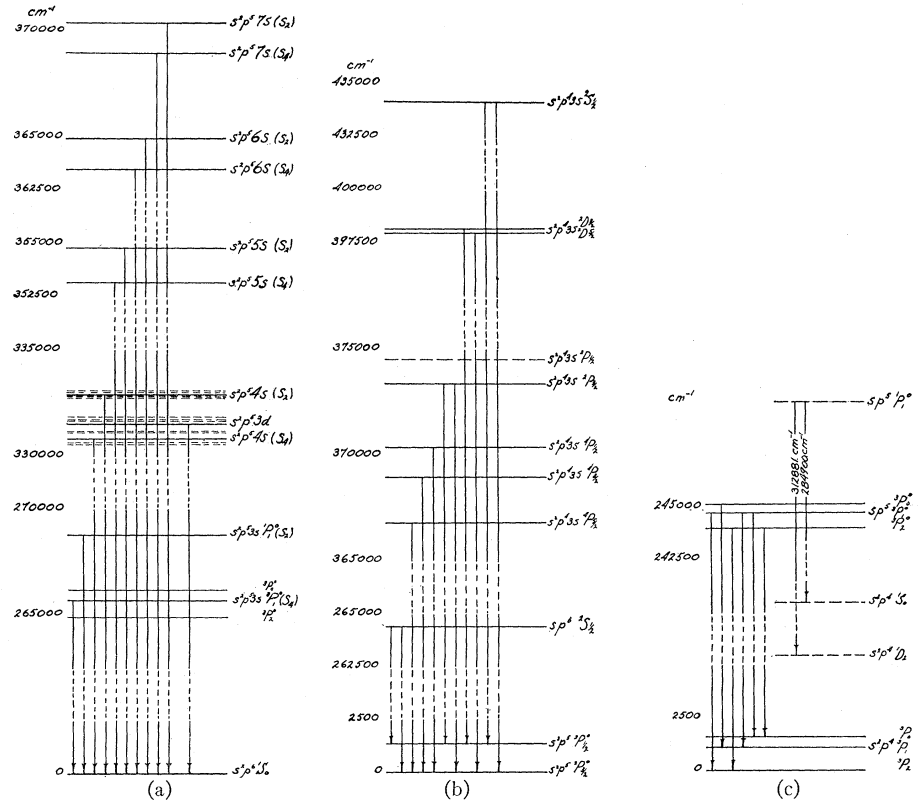

Fig. 2. Term schemes for Na II, Na III, and Na IV for transitions in the far ultraviolet.

Z_{14} levels of Frisch. The other $4s$ and $3d$ terms, which have been calculated from Frisch's values, are indicated by dotted lines in Fig. 2(a) and are given the following J values; $Z_{1,5,8,10,15}$ $J=2$, $Z_{4,9,12}$ $J=3$, Z_{13} $J=4$ and $Z_{6,7}$ $J=0$.

The levels in Fig. 2(a) between 335,000 and 330,000 cm^{-1} are Z_1 to Z_{16} reading down, $Z_{8,9}$ are indicated as one level.

Na III (FLUORINE-LIKE)

In addition to the previously observed transitions $2s-2p$ reported by Edlen and Ericson[4] and Mack and Sawyer,[5] lines have been found which can be classified as $s^2p^5-s^2p^43s$ transitions. These are given in Table III, shown diagrammatically in Fig. 2(b) and the term values are given in Table IV.

TABLE III. *Observed transitions of Na III.*

I	λ	ν (cm^{-1})	Config. and Terms
6	380.091[4]	263095	$s^2p^5\ {}^2P^\circ_{1/2}-sp^6\ {}^2S_{1/2}$
8	378.120[4]	264466	$s^2p^5\ {}^2P^\circ_{3/2}-sp^6\ {}^2S_{1/2}$
0	272.59	366840	$s^2p^5\ {}^2P^\circ_{3/2}-s^2p^43s\ {}^4P_{5/2}$
0*	271.01	369000	$s^2p^5\ {}^2P^\circ_{3/2}-s^2p^43s\ {}^4P_{3/2}$
0*	269.98	370400	$s^2p^5\ {}^2P^\circ_{3/2}-s^2p^43s\ {}^4P_{1/2}$
2	268.81	372060	$s^2p^5\ {}^2P^\circ_{1/2}-s^2p^43s\ {}^2P_{3/2}$
6	267.78	373430	$s^2p^5\ {}^2P^\circ_{3/2}-s^2p^43s\ {}^2P_{3/2}$
		374600[t]	$s^2p^5\ {}^2P^\circ_{3/2}-s^2p^43s\ {}^2P_{1/2}$
2	252.26	396410	$s^2p^5\ {}^2P^\circ_{1/2}-s^2p^43s\ {}^2D_{3/2}$
5	251.25	398010	$s^2p^5\ {}^2P^\circ_{3/2}-s^2p^43s\ {}^2D_{5/2,3/2}$
1	231.03	432840	$s^2p^5\ {}^2P^\circ_{1/2}-s^2p^43s\ {}^2S_{1/2}$
2	230.25	434210	$s^2p^5\ {}^2P^\circ_{3/2}-s^2p^43s\ {}^2S_{1/2}$

* Possibly Na II.
[t] Masked by O III line 266.992A.

The configuration s^2p^4ns theoretically yields inverted ${}^4P_{1/2,3/2,5/2}$, ${}^2P_{1/2,3/2}$ terms with limit at $s^2p^4\ {}^3P$; ${}^2D_{3/2,5/2}$ terms with limit at $s^2p^4\ {}^1D_2$; and a ${}^2S_{1/2}$ term with limit at $s^2p^4\ {}^1S_0$. Lines are found which are considered to

TABLE IV. *Term values of Na III.*

Config.	Term	Term Value (cm^{-1})	Limit
s^2p^5	${}^2P^\circ_{3/2}$	0	
s^2p^5	${}^2P^\circ_{1/2}$	1370	
$s\ p^6$	${}^2S_{1/2}$	264460	
s^2p^43s	${}^4P_{5/2}$	366840	${}^3P$
s^2p^43s	${}^4P_{3/2}$	369000	${}^3P$
s^2p^43s	${}^4P_{1/2}$	370400	${}^3P$
s^2p^43s	${}^2P_{3/2}$	373430	${}^3P$
s^2p^43s	${}^2P_{1/2}$	[t]374600?	${}^3P$
s^2p^43s	${}^2D_{5/2}$	398010	${}^1D$
s^2p^43s	${}^2D_{3/2}$	398230	${}^1D$
s^2p^43s	${}^2S_{1/2}$	434210	${}^1S$

[t] Masked by O III line 266.992A.

come from all these levels, for $n=3$, except from the ${}^2P_{1/2}$ level, and these levels fit well into a Moseley diagram with the same terms of other members of this isoelectronic sequence (F I[12] and Ne II[13]).

The transitions from the ${}^2P_{1/2}$ level to the ${}^2P^\circ_{3/2,1/2}$ levels are assumed to be masked by the prominent O III line at 266.992A and the line corresponding to the transition ${}^2P^\circ_{3/2}-{}^2P_{3/2}$ of Na III respectively. The relative position

[12] H. Dingle, Proc. Roy. Soc. **A117,** 411 (1927).
[13] T. L. deBruin and C. J. Bakker, Zeits. f. Physik **69,** 19 (1931).

of this $^2P_{1/2}$ level on this assumption is indicated by a dotted line in Fig. 2(b).

The lines here identified as corresponding to the transitions between the $^4P_{1/2,3/2}$ and the $^2P^\circ_{3/2}$ levels possibly may be the fifth members of the ms_2 and ms_4 series of Na II, but it seems more likely that they belong to Na III.

Na IV (OXYGEN-LIKE)

The PP° group at 244,000 cm^{-1} that had been found and identified as that of Na IV on photographs taken by Gale and Hoag,[14] during their investigation of multiply ionized lithium, was obtained on nearly all the plates taken during this investigation. The central line was not resolved, which made it difficult to determine exactly the position of the $^3P_1$ and $^3P_0{}^\circ$ levels.

In addition to the triplet levels there should be a $^1D_2$ and a $^1S_0$ level for the configuration s^2p^4, and a $^1P_1$ level for the configuration sp^5. Lines have been found which probably correspond to the allowed transitions between these levels, and these transitions fit well into a Moseley diagram with the same transitions of Ne III given by Boyce and Compton.[15] The actual position of these levels can not be given from the results obtained, but it is possible to place them roughly from the information obtained from the positions of the ^4P, ^2P, ^2D, and ^2S levels of Na III. This has been done in Fig. 2(c).

TABLE V. *Observed transitions of Na IV.*

I	λ	ν (cm^{-1})	Config. and Terms
3	412.46	242448	$s^2p^4\ ^3P_1-sp^5\ ^3P^\circ_2$
2	411.25	243161	$s^2p^4\ ^3P_0-sp^5\ ^3P^\circ_1$
6	410.41	243654	$s^2p^4\ ^3P_{2,1}-sp^5\ ^3P^\circ_{2,1}$
2	409.46	244224	$s^2p^4\ ^3P_1-sp^5\ ^3P^\circ_0$
3	408.56	244762	$s^2p^4\ ^3P_2-sp^5\ ^3P^\circ_1$
0	351.00	284900	$s^2p^4\ ^1S_0-sp^5\ ^1P^\circ_1$
3	319.61	312880	$s^2p^4\ ^1D_2-sp^5\ ^1P^\circ_1$

TABLE VI. *Term values of Na IV.*

Config.	Terms	Term Values (cm^{-1})
s^2p^4	$^3P_2$	0
s^2p^4	$^3P_1$	1110
s^2p^4	$^3P_0$	1600
s^2p^4	$^1D_2$	A
s^2p^4	$^1S_0$	$A+27980$
sp^5	$^3P^\circ_2$	244050
sp^5	$^3P^\circ_1$	244760
sp^5	$^3P^\circ_0$	245330
sp^5	$^1P^\circ_1$	$A+312880$

In conclusion the author wishes to express his appreciation to Dean Gale for suggesting the problem and for his helpful encouragement throughout the investigation, and to Professor R. S. Mulliken for his advice in the analysis.

Note added in proof: J. Soderqvest, Zeits. f. Physik **76,** 316 (1932), gives an analysis of the Na III spectrum which agrees well with the results given above.

[14] H. G. Gale and B. Hoag, Phys. Rev. **37,** 1703 (1931).

[15] J. C. Boyce and K. T. Compton, Proc. Nat. Acad. Sci. **15,** 656 (1929).

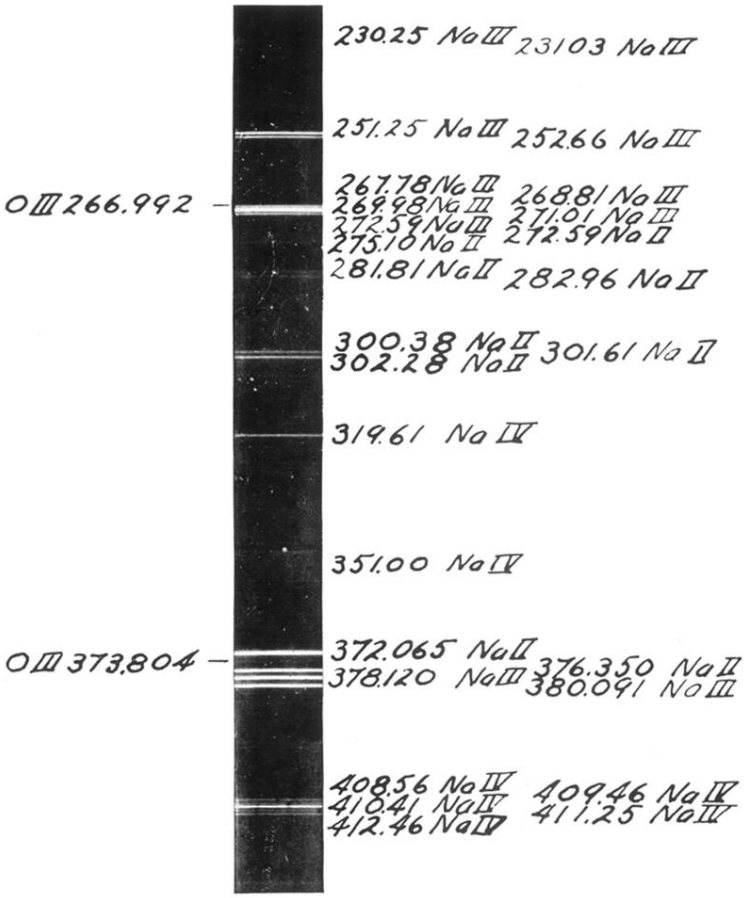

Fig. 1. Typical spectrogram.