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$\lambda\lambda$ 3100—2750 之間的鈉分子吸收光譜

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一九四七年辛哈發表的鈉分子光譜的工作報告，在表面上看來，似乎比前人的工作進了一步，但他工作的內容還有些地方可以討論的。第一有好些光帶他量的很不準確。第二他所羅列出來的光帶是否都屬於鈉分子的，是一個疑問，例如在 $\lambda\lambda$ 3072·5 — 3058·4 之間，他加入了四條，而且強度也比較的大；在 $\lambda\lambda$ 3180 — 3100 之間他列出二十多條來；由前人工作的總結中及現在實驗的結果看來，這些似不應認為是由於鈉分子產生的，應認為由於其他雜質而來的。因為除了辛哈外，別人都沒有觀察到，如果說這種極顯明的區別，是由於片子感光性的不同或是由於吸收管的溫度的差異，是很難解釋得通的。第三在分類上也仍然有些不妥當處，$\lambda\lambda$ 3500 — 3180 之間的光帶與 $\lambda\lambda$ 3100 — 2900 之間的光帶，是屬於兩個不同的系的，而辛哈把這給混起來了。

本文所討論的僅限於 $\lambda\lambda$ 3100 — 2750 之間，因此仍是不完全的。在這範圍內，把所觀察到的光帶，分為兩個系別，每一系都起源於基能層，第一系包括着在 λ 3100 到 λ 2940 之間的各光帶，這一系在威米和庫爾普的工作中被分為兩個不同的系的；這一系與辛哈的第三系也有不同，就是包括了 $v'=0$ 的一序列而除去了那些被認為是起於雜質的光帶。這種觀點的正確性，可由 $G(v'')$ 式子來證明：$G(v'')$ 是基於這種分類法算出來的，它與魯米和那斯鮑的式子很接近，而後者被認為是極準確的。本文的第二系包括了在 λ 2889 到 λ 2750 之間的光帶，這一系的 $G(v'')$ 式子是與上邊那系的完全相合的。

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SODIUM BANDS IN THE ULTRA-VIOLET λλ 3100-2750

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In absorption by sodium vapour, Walter and Barratt[1] observed, in 1929, numerous bands of sodium in the ultra-violet λλ 3530-2740. Those bands were analysed by Weizel and Kulp[2] into five different systems, systems 1, 2, and 3 covering λλ 3530-3180 and systems 4 and 5 covering λλ 3100-2960. Some of those systems appear to be rather incomplete. Recently, in 1947, Sinha[3] published his investigations in the same region, that is, the ultra-violet λλ 3530-2740, giving as many as seven systems. His first three systems are, according to his own words, complete, while the others are merely tentative. Sinha's system 1 includes all the intense bands in the region λλ 3530-3180 formerly arranged, by Weizel and Kulp, into three systems. Sinha's systems 3 corresponds to the systems 4 and 5 of Weizel and Kulp, his system 2 being scattered between his system 1 and system 3. Though Sinha lists a larger number of bands in his vibrational schemes than Weizel and Kulp, there seem to be several points which might be criticized. His measurements are not accurate; the errors of measurements are as large as several Ångstroms. Again, it is doubtful whether all of his measurements are actually representing the bands of sodium. For instance, between bands λ 3072·5 and λ3058·4 (his measurements being 3072·6 and 3057·7) he inserted four bands: 3071·6, 3069·6, 3067·6 and 3060·1. The intensities of those six bands given in order of decrease of wave length are 1, 2, 1, 3, 4 and 2 respectively, that is, the strongest band, according to Sinha, is 3060·1. In the present inspection the four intermediate bands are not observed and the intensities

1. Walter, J. M. and Barratt, S. *Proc. Roy. Soc.* **A119** (1928), 265.
2. Weizel, W. and Kulp, K. *Ann. Phys., Lpz.*, **4** (1930), 971.
3. Sinha, S. P. *Proc. Phys. Soc.* **59** (1947), 610.

of the other two are comparatively strong. In the range $\lambda\lambda$ 3180-3100, no trace of bands was observed by Walter and Barratt, nor by the present writer, while in Sinha's paper about twenty are given. These discrepancies suggest that some of his bands might be due to impurities, for it seems difficult to account for such variations in intensity on the basis of any plausible differencies in temperature or in plate-sensitivity. Finally, bands in the region $\lambda\lambda$ 3100-2900 seem to have little connection in classification with those lying in the region $\lambda\lambda$ 3500-3180, while his system 2 covers both of the two regions. For these reasons, the bands in the region $\lambda\lambda$ 3100-2750 are remeasured and a new analysis is attempted.

The limited region $\lambda\lambda$ 3100-2750 implies that the work is far from being complete. Due to circumstances, we are not yet able to offer an adequate discussion of the upper states of all the systems in ultra-violet.

The spectra are photographed in a large quartz Littrow instrument on Eastman III-0 plates. The effective path-length is estimated at 30 cm. and the temperature at about 800°C. A few centimeters of inert gas are admitted into the absorption tube in order to facilitate the appearance of the absorption bands. Under these conditions bands in this region are well developed, and at the short-wave end the structure of the bands can be traced to about λ 2570. The strongest bands lie in the range $\lambda\lambda$ 3100-2750.

The present band-head measurements in this region are analysed into two systems, both of which involve the ground state. The first system covers the region from λ 3100 to λ 2940, which was formerly split by Weizel and Kulp into two systems—system 4 and system 5, the former corresponding to the right limb, and the latter corresponding to the left limb of the Condon parabola of the present system. The present arrangement also differs from Sinha's system 3 by including the progression with $v' = 0$ and by excluding those bands, most of which, as mentioned above, might be due to impurities. The correctness of the present vibrational scheme given in Table I is to some extent justified by $G(v'')$ expression derived therefrom, which seems to be very close to that calculated by Loomis and Nusbaum.[4] The second system of the present

4. Loomis, F. W. and Nusbaum, R. E. *Phys. Rev.* **40** (1932), 380.

classification includes all the strong bands in the region $\lambda\lambda$ 2889-2750. These bands were also observed by Walter and Barratt, though, so far as we know, no analysis has been given except Sinha's. More than twenty bands are measured for this system to make the vibrational analysis reasonably certain. There is little doubt about the values of v' and v'' as the system is bounded by an intense progression with $v''=0$. The concordance of the $G(v'')$ expression seems also to confirm the correctness of the analysis.

TABLE 1

v' \ v''	0		1		2		3		4		5		6		7
0					33147·9	155·3	32992·6	155·9	32838·7	151·4	32687·3	150	32537·3	148·6	32388·7
					110.3		110.3		110.4						
1			33413·8	155·6	33258·2	155·3	33102·9	153·8	32949·1						
			110·9		109·9		110·0								
2	33682·9	158·2	33524·7	156·6	33368·1	155·2	33212·9								
	107·0		107·2		107·2										
3	33789·9	158·0	33631·9	156·6	33475·3										
	111·1		110·1												
4	33901·0	159·0	33742·0												
	105·0		106·2												
5	34006·0	157·8	33848·2												
	105·5														
6	34111·5														
	103·9														
7	34215·4														
	102·2														
8	34317·6														

Table I is the Deslandres scheme of the present first system. The frequencies are represented by the following equation (1):

$$\nu = 33486{\cdot}8 + 111{\cdot}3\left(v' + \frac{1}{2}\right) - 0{\cdot}48\left(v' + \frac{1}{2}\right)^2 - 159{\cdot}5\left(v'' + \frac{1}{2}\right)$$

$$+ 0{\cdot}72\left(v'' + \frac{1}{2}\right)^2 \qquad (1)$$

which has been developed by the method of least squares. The $G(v'')$

expression derived by Loomis and Nusbaum based on a large number of band-heads (about two hundred) is of the form

$$G(v'') = 159{\cdot}23\left(v'' + \frac{1}{2}\right) - 0{\cdot}72\left(v'' + \frac{1}{2}\right)^2 - 0{\cdot}0027\left(v'' + \frac{1}{2}\right)^3,$$

which is known to be of high degree of accuracy. Comparing the present

$$G(v'') = 159{\cdot}5\left(v'' + \frac{1}{2}\right) - 0{\cdot}72\left(v'' + \frac{1}{2}\right)^2$$

with theirs we may suggest that the difference is very little and arises because bands of high values of v' and v'' are not observed in the present investigation. However, equation (1) is quite satisfactory to represent the observed bands for the present purpose. Table 3 gives the difference of wave numbers between the observed and calculated bands. It is observed that the agreement is fairly good.

TABLE 2

v' \ v''	0		1		2		3		4		5		6
0			35371·5	155·7	35215·8	155·6	(35060·2)	153·1	34907·1	151·6	34755·5	150·4	34605·1
			105·4		104·5		104·8				104·2		
1			35476·9	156·6	35320·3	155·3	35165·0				34859·7		
			103·6		103·9		104·2						
2	35738·2	157·7	35580·5	156·3	35424·2	155·0	35269·2	153·6	35115·6				
	107·6		106·7										
3	35845·8	158·6	35687·2										
	100·6		100·9										
4	35946·4	158·3	35788·1										
	98·5												
5	36044·9												
	100·3												
6	36145·2												
	97·0												
7	36242·2												

Table 2 is the Deslandres scheme for the present second system. The $G(v'')$ levels are concordant with those of the preceding system and the upper vibrational levels appear to be rather irregular. The $v' = 3$ level is abnormally large. It is possible that the abnormality is due to perturbations. The observed wave numbers are represented by equation (2):

$$\nu = 35557{\cdot}0 + 106{\cdot}2\left(v' + \frac{1}{2}\right) - 0{\cdot}65\left(v' + \frac{1}{2}\right)^2 - 159{\cdot}5\left(v'' + \frac{1}{2}\right) + 0{\cdot}72\left(v'' + \frac{1}{2}\right)^2, \qquad (2)$$

which has been derived on the assumption that the heads of the bands with $v' = 3$ are displaced so as to lie about 5 cm^{-1} too low. Equation (2) fits the values for the other band-heads satisfactorily. Table 3 gives the difference of wave numbers between the observed and calculated band-heads.

TABLE 3.

v'	v''	Intensity	Observed	Calculated
		System 1		
0	7	1	32388·7	32386·5
0	6	2	32537·3	32536·0
0	5	4	32687·3	32686·8
0	4	4	32838·7	32839·1
1	4	1	32949·1	32949·5
0	3	3	32992·6	32992·9
1	3	6	33102·9	33103·3
0	2	2	33147·9	33148·0
2	3	2	33212·9	33212·7
1	2	4	33258·2	33258·4
2	2	6	33368·1	33367·8
1	1	1	33413·8	33415·1
3	2	2	33475·3	33476·2
2	1	3	33524·7	33524·5
3	1	5	33631·9	33632·9
2	0	2	33682·9	33682·5
4	1	5	33742·0	33740·3
3	0	4	33789·9	33790·9
5	1	3	33848·2	33846·8
4	0	7	33901·0	33898·3
5	0	8	34006·0	34004·8
6	0	8	34111·5	34110·4
7	0	8	34215·4	34215·0
8	0	7	34317·6	34318·6

System 2

0	6	1	34605·1	34604·6
0	5	2	34755·5	34754·4
1	5	1	34859·7	34859·4
0	4	3	34907·1	34906·7
0	3		(35060·2)	35060·5
2	4	1	35115·6	35115·3
1	3	2	35165·0	35165·5
0	2	3	35215·8	35215·6
2	3	1	35269·2	35269·1
1	2	3	35320·3	35320·6
0	1	1	35371·5	35372·3
2	2	2	35424·2	35424·2
1	1	3	35476·9	35477·3
2	1	4	35580·5	35580·9
3	1	4	35687·2	35688·3
2	0	2	35738·2	35738·9
4	1	4	35788·1	35789·3
3	0	3	35845·8	35846·3
4	0	5	35946·4	35947·3
5	0	5	36044·9	36047·0
6	0	5	36145·2	36145·7
7	0	4	36242·2	36242·9

Bands below λ 2750 cannot be measured very accurately owing to the comparatively weak intensity in the present case. Reasonable analyses are therefore impossible. Further observations under more favourable conditions are in progress.

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