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VIBRATIONAL LEVELS AND HEAT OF DISSOCIATION OF NA_2

By F. W. Loomis

Abstract

According to Kemble's theory of the Zeeman effect in band spectra, there should be a magnetic rotation line at the head of each Na_2 absorption band. It is found that most of Wood's magnetic rotation lines in the blue-green region can be arranged into a band system, and integral vibrational quantum numbers, n' and n'', assigned, in terms of which their frequencies are given by the following polynomial:

$$\nu=20301.7+(124.13n'-0.84n'^2)-(158.5n''-0.73n''^2-0.0027n''^3)$$

The heat of dissociation is then calculated to be 1.0 ± 0.1 volt. The energies needed to dissociate the molecules which correspond to the upper levels of the blue-green and red systems are shown to be 0.6 volt and 1.25 volt, respectively, within about 0.1 volt. The lower level molecule, in both systems, dissociates by vibration into two normal (3^2S) atoms, while the upper level molecule, in both systems, dissociates into one atom in the normal state and one in a 3^2P state.

When the intensities of the magnetic rotation lines corresponding to the heads are tabulated, in the usual square array, according to n' and n'', a wide open parabola-like figure appears, of a type which Condon has accounted for in terms of an hypothesis of Franck. This affords an explanation of a puzzling phenomenon, reported by Wood, in the spectral distribution of the fluorescent light when excited by light of various frequencies.

THIS paper is based on R. W. Wood's investigations,[1] by means of fluorescence and "magnetic rotation," of the blue-green band system of sodium vapor. This spectrum is now generally attributed[2] to the diatomic molecule, Na_2. Much of the material presented here was included in a paper[3] read before the February 1927 meeting of the American Physical Society.

The absorption spectrum of sodium vapor consists of two distinctly separated band systems, one in the blue-green, the other in the red. These same systems appear, however, in a more extended manner, i.e., developed to higher values of the vibrational quantum numbers n' and n'', in the magnetic rotation and fluorescence spectra, and hence these, especially the magnetic rotation spectrum, afford a better basis for a vibrational energy formula and for the determination of the heat of dissociation.

Wood's magnetic rotation spectrum was obtained by sending the light from the crater of a carbon arc through two Nicols, between which was a tube of sodium vapor within the core of a powerful electromagnet. If the Nicols were set for extinction and the magnetic field then turned on, a spectrum flashed out which was very much simpler than the absorption spectrum. It consisted, in fact, of about 130 sharp lines in the blue-green and 340 in the red. Each of these lines was caused by light whose plane of

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[1] R. W. Wood, Proc. Am. Acad. **42**, 235 (1906), Astrophys. J. **30**, 339 (1909).

[2] Pringsheim, Handbuch der Physik, XXIII, pages 504–505.

[3] Loomis, Phys. Rev. **29**, 607A (1927).

polarization had been rotated by the magnetized sodium vapor; and the direction of rotation could be found, in the case of the stronger lines, by determining in which direction the second Nicol had to be rotated to re-extinguish the line.

The classical explanation[4] of magnetic rotation of the plane of polarization is that it occurs in the neighborhood of absorption lines, which are split into Zeeman patterns by a magnetic field. A line which exhibits the normal Zeeman effect, will, when viewed along the lines of force, be split into a right-handed circularly polarized component whose frequency is slightly increased by the field and a left-handed circularly polarized component whose frequency is slightly decreased. Each of these components will exhibit an anomalous dispersion curve of the usual sort, symmetrical about the displaced position of the component. The result will be that the velocity of the right-hand component will exceed that of the left-hand component everywhere except between them; and the region between them, if the magnetic separation is small, will be one of high absorption. Consequently, if plane polarized light enters the vapor, one of the two circularly polarized beams into which it is resolvable will be retarded with respect to the other; that is, the plane of polarization will be rotated. Moreover, the sign of the rotation will be the same for all frequencies near the absorbing line, except between the two magnetically separated components, where the light is largely absorbed. Hence the light which actually gets through will be almost wholly rotated like a right handed screw. A line having a complex Zeeman pattern may rotate in the opposite direction, depending on the relative intensities and separations of the Zeeman components.

The most complete theory, to date, of the Zeeman effect in bands has been published by Kemble.[5] He finds the magnitude of the Zeeman pattern should ordinarily be approximately inversely proportional to j; that is, it should decrease rapidly as one goes away from the origin, and should be very much smaller than in line spectra, except for the band lines nearest the origin. The magnetic rotation should therefore be largest near the origin and not observable at any considerable distance from it. Magnetic rotation should be particularly prominent just on the *violet* side[6] of the heads, since the region is influenced by the strong magnetic rotation due to several neighboring lines of low quantum number, and yet does not coincide with any absorption line.

Many of the strong magnetic rotation lines do actually correspond to heads in this way; and Wood has arranged some of the green ones into five series, whose spacing is approximately that of the fluorescence series and which undoubtedly are n'' progressions. The writer has extended this

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[4] Lorentz, Theory of Electrons, page 163.

[5] Kemble, National Research Council Report on "Molecular Spectra in Gases" pp. 337 ff.; Phys. Rev. **27**, 799A (1926); Kemble, Mulliken and Crawford, Phys. Rev. **30**, 438 (1927).

[6] The Na_2 bands are degraded [to the red, and] the heads are within a few lines of the origins. Cf. Smith, Proc. Roy. Soc. A**106**, 400 (1924).

arrangement by converting wave-lengths to frequencies and applying the usual combination principle methods, and finds that about 90 of the lines, including all the strong lines which rotate normally and none which rotate abnormally, can be assigned to such series. By comparison with the fluorescence series it is possible to assign vibration quantum numbers with certainty. The frequencies of these lines are represented by the following polynomial expression of the usual type:

$$\begin{aligned}\nu &= 20301.7+(124.13n'-0.84n'^2)-(158.5n''-0.73n''^2-0.0027n''^3)\\ &=\nu_0+T'(n')-T''(n'') \qquad n' \text{ and } n'' \text{ integral} \qquad (1)\end{aligned}$$

Table I exhibits the assignment of vibrational quantum numbers to these lines and the agreement between Eq. (1) and the observed frequencies.

TABLE I

Assignment of vibrational quantum numbers to magnetic rotation lines.

n'	n''	Intensity	Direction of rotation[7]	λ[8]	ν obs.	ν calc. by (1)	observed – calc. by (1)
0	0	10		4924.32	20301.7	20301.7	0.0
0	1	10	–	4962.85	20144.1	20144.0	+0.1
0	2	10	–	5001.57	19988.2	19987.8	+0.4
0	3	9	–	5040.65	19833.2	19833.1	+0.1
*0	4	8	–	5079.78	19680.4	19679.9	+0.5
0	5	8	–	5119.34	19528.3	19528.2	+0.1
0	6	6		5159.1	19377.8	19378.0	–0.2
*0	8	4		5238.9	19082.7	19082.1	+0.6
1	0	6	–	4894.58	20425.1	20425.0	+0.1
1	1	10	–	4932.64	20267.5	20267.3	+0.2
1	2	8		4970.85	20111.7	20111.1	+0.6
1	3	4		5009.4	19956.9	19956.4	+0.5
1	4	8		5048.49	19802.4	19803.2	–0.8
*1	5	8	–	5087.31	19651.3	19651.5	–0.2
1	6	8	–	5126.54	19500.9	19501.3	–0.4
1	7	8	–	5165.85	19352.5	19352.6	–0.1
*2	0	4		4865.59	20546.8	20546.6	+0.2
2	1	3		4903.38	20388.4	20388.9	–0.5
2	2	2		4941.6	20230.7	20232.7	–2.0
2	3	10	–	4979.34	20077.4	20078.0	–0.6
2	4	4		5017.5	19924.7	19924.8	–0.1
2	6	8		5094.78	19622.5	19622.9	–0.4
2	7	8	–	5133.73	19473.6	19474.2	–0.6
2	8	8	–	5172.82	19326.4	19327.0	–0.6
2	9	8		5211.71	19182.2	19181.3	+0.9
3	0	10		4837.49	20666.1	20666.5	–0.4
*3	1	2		4875.1	20506.7	20508.8	–2.1
3	2	6	–	4912.10	20352.2	20352.6	–0.4
3	5	5		5025.66	19892.4	19893.0	–0.6
3	7	4		5102.3	19593.6	19594.1	–0.5
3	8	8		5140.71	19447.2	19446.9	+0.3
3	9	8		5179.71	19300.7	19301.2	–0.5
3	10	8		5219.00	19155.4	19157.0	–1.6
4	0	10		4810.16	20783.5	20784.8	–1.3
4	1	4	–	4846.8	20626.4	20627.1	–0.7

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[7] Minus sign indicates "normal" direction of rotation; absence of any sign indicates direction of rotation not reported. No lines in this table show abnormal rotation (i.e. +).

[8] Wave-lengths given to 0.01A are taken from Wood, Proc. Am. Acad., 42, 259 (1906). The others are from Wood, Astrophys. J., 30, 360 (1909).

* Indicates a line which can be assigned quantum numbers in two ways.

TABLE I (continued)

n'	n''	Intensity	Direction of rotation[7]	λ[8]	ν obs.	ν calc. by (1)	observed — calc. by (1)
4	2	4		4883.81	20470.1	20470.9	−0.8
4	4	4		4958.62	20161.3	20163.0	−1.7
4	6	5		5033.54	19861.2	19861.1	+0.1
4	7	8		5071.50	19712.6	19712.4	+0.2
4	9	8		5147.50	19421.5	19419.5	+2.0
4	10	8		5186.70	19274.7	19275.3	−0.6
4	11	8		5225.34	19132.2	19132.6	−0.4
4	12	6		5263.8	18992.4	18991.4	+1.0
5	0	10	−	4782.89	20902.0	20901.4	+0.6
5	1	10		4819.43	20743.6	20743.6	0.0
5	3	6		4892.9	20432.1	20432.8	−0.7
5	5	4		4967.10	20126.9	20127.8	−0.9
*5	8	8	−	5079.78	19680.4	19681.8	−1.4
5	11	8		5192.3	19253.9	19249.2	+4.7
5	12	1		5232.2	19107.1	19108.0	−0.9
5	13	6		5270.3	18969.0	18968.2	+0.8
6	0	10		4756.6	21017.6	21016.2	+1.4
6	1	10	−	4792.4	20860.6	20858.5	+2.1
*6	3	4		4865.59	20546.8	20547.6	−0.8
6	7	4		5012.7	19943.8	19943.8	0.0
6	8	4		5049.56	19798.2	19796.6	+1.6
*6	9	8	−	5087.31	19651.3	19650.9	+0.4
*6	13	4		5238.9	19082.7	19083.1	−0.4
6	14	6		5276.6	18946.3	18944.9	−1.4
7	0	10		4731.4	21129.5	21129.5	0.0
7	1	10		4766.7	20973.0	20971.8	+1.2
7	2	10	−	4802.2	20818.0	20815.6	+2.4
7	3	4	−	4839.	20659.7	20660.8	−1.1
*7	4	2		4875.1	20506.7	20507.6	−0.9
7	9	4		5058.4	19763.6	19764.2	−0.6
7	15	6		5282.6	18924.8	18921.4	+3.4
8	0	10		4706.5	21241.3	21241.0	+0.3
8	1	10	−	4741.8	21083.2	21083.3	−0.1
8	2	4		4777.1	20927.4	20927.1	+0.3
8	3	4	−	4812.2	20774.7	20772.4	+2.3
8	4	4		4848.4	20619.6	20619.2	+0.4
8	16	6		5288.6	18903.4	18897.8	+5.6
*9	0	2		4682.6	21349.7	21350.8	−1.1
9	1	10		4716.9	21194.5	21193.1	+1.4
9	2	10		4752.04	21037.7	21036.9	+0.8
9	3	2		4787.5	20881.9	20882.2	−0.3
9	5	4		4858.3	20577.6	20577.3	+0.3
10	0	2		4658.6	21459.7	21459.0	+0.7
10	2	10	−	4727.52	21146.8	21145.1	+1.7
10	3	10		4762.7	20990.6	20990.4	+0.2
10	16	1		5228.3	19121.4	19115.8	+5.6
10	18	6		5298.9	18866.6	18849.9	+16.7
*11	2	10	−	4703.9	21253.0	21251.6	+1.4
11	3	10	−	4738.5	21097.8	21096.9	+0.9
12	2	2		4681.2	21356.1	21356.4	−0.3
*12	3	10		4715.63	21200.2	21201.7	−1.5
12	4	10	−	4749.3	21049.9	21048.5	+1.4
13	3			4692.54	21304.5	21304.8	−0.3
14	2	2		4636.7	21561.0	21561.0	0.0
14	3	2		4670.4	21405.5	21406.3	−0.8
*14	4	10	−	4703.9	21253.0	21253.1	−0.1
15	2	2		4615.8	21658.7	21660.8	−2.1
15	3	8		4648.9	21504.5	21506.0	−1.5
*15	4	2		4682.6	21349.7	21352.8	−3.1
*15	5	10		4715.63	21200.2	21201.2	−1.0
16	3	2		4628	21601.6	21604.1	−2.5
16	4	2		4661.2	21447.7	21450.9	−3.2

It will be noted that none of the lines to which it has been possible to assign quantum numbers n' and n'', i.e., none of the magnetic rotation lines coinciding with band heads, were found by Wood to show positive magnetic rotation. That is, all the assigned lines either definitely show negative (i.e., normal) rotation, or rotation too slight to permit determination of its sign. The fact that some of the fluorescence series are doublets indicates the presence of R and P branches; while the fact that the bands degrade to the red shows that the heads are on R branches. One is therefore justified in concluding, empirically, that, for the kind of magnetic rotation which occurs near the origins of the Na_2 bands, the lines on the R branch rotate normally $(-)$; and, undoubtedly, those on the P branch rotate abnormally $(+)$. This is the opposite of the rule found by the writer[9] in the iodine bands. Kemble's theory[10] indicates that the rule for Na_2 is what one should ordinarily expect, while that for I_2 is unusual, both in direction and in that the rotation is strong for lines far from the origin.

The cause of the magnetic rotation lines which do not correspond to heads is puzzling. It is natural to suspect that they correspond to perturbations, since perturbed lines are known to show abnormally large Zeeman patterns; but if so they should form n', or possibly n'', progressions, which they do not appear to do. Nor do they, according to Fredrickson and Watson's[11] analysis of fine structure, occur, when on P and R branches, as pairs of lines with the same m'; nor recur in the same locations in bands of a progression.

Before using Eq. (1) to calculate the heat of dissociation of Na_2, it is necessary to decide whether or not it is more suitable for the purpose than the more recent and somewhat different equations which Fredrickson and Watson[12] have published for both the blue-green and the red systems. Their equations are as follows:

$$\text{Green}\quad \nu=20301.62+(123.84n'-0.79n'^2)-(157.57n''-0.57n''^2) \qquad (2)$$

$$\text{Red}\quad \nu=15006.68+(115.69n'-0.427n'^2)-(157.81n''-0.538n''^2) \qquad (3)$$

Frequencies calculated by (2) differ systematically from those of the magnetic rotation lines in Table I. The difference amounts to as much as 50 cm^{-1} for lines with large n''. Hence it is evident that (2) is quite inadequate to represent the magnetic rotation lines, particularly those with high quantum numbers; whereas column 8 shows that (1) is about as accurate as the data warrant.

Fig. 1 shows to what extent the three formulas for the term in n'' represent the absorption data of Fredrickson and Watson. The abscissa is n''. The circles represent the terms in n'', obtained, by subtraction, from their data on the green system, according to the equation

$$T''(n'')=\nu(n',\ 0)-\nu(n',\ n'') \qquad (4)$$

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[9] Loomis, Phys. Rev. **29**, 112 (1927).

[10] L.c. page 344.

[11] Fredrickson and Watson, Phys. Rev. **30**, 429 (1927).

[12] L.c., page 430.

The crosses represent $T''(n'')$ obtained, in the same way, from their data on the red system. The magnetic rotation data are omitted to avoid confusing the figure. The continuous curve represents $T''(n'')$ according to (2); the broken curve according to (3). In each case $T''(n'')$ according to (1), i.e.,

$$T''(n'') = 158.5n'' - 0.73n''^2 - 0.0027n''^3 \tag{5}$$

has been subtracted, for convenience in plotting. Hence the axis of abscissas represents $T''(n'')$ according to (1).

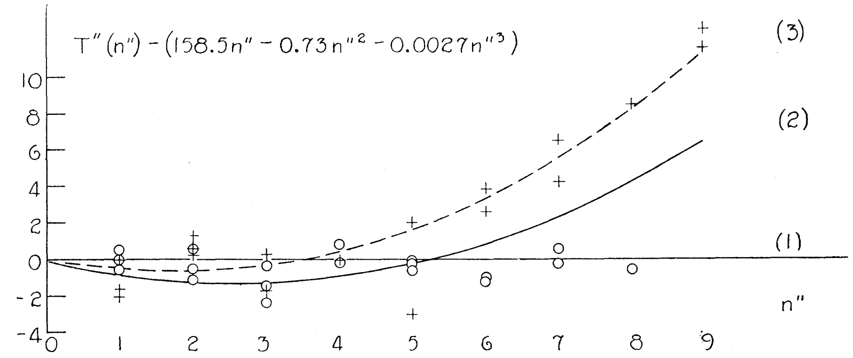

Fig. 1. Comparison of lower level terms, $T''(n'')$ from Fredrickson and Watson's absorption data for green and red systems with those from Eqs. (1), (2) and (3). Circles represent the green system, crosses the red system.

It will be seen that the Eq. (1) represents even Fredrickson and Watson's data on the green system rather better than their own Eq. (2); while it has been shown that Eq. (2) fails badly when extrapolated to cover the magnetic rotation lines of high quantum numbers. It is therefore certain that Eq. (1) is to be preferred as a basis for calculating the heat of dissociation.

It is a little surprising, however, to find that (1) does not represent their data for the red system; and, in fact, that it is impossible to represent $T''(n'')$ for both the green and red systems by the same formula within what appears to be the probable error of their measurements. One is forced to conclude, either that the two systems do not have a common lower level, or that ther is some systematic error in the frequencies of the bands, amounting to as much as 12 cm^{-1} in the extreme red.

The difference is in the wrong direction, and much too large, to be accounted for as due to the use of heads in place of origins. The writer inclines, however, to the belief that the lower levels in the two systems are really identical. Certainly, as is shown below, they both dissociate by vibration into unexcited atoms; and they have sensibly identical values of ω_0''. It is also shown below that Eq. (3) leads to seriously inconsistent estimates of the energies of dissociation. Moreover, the questionable red bands seem to lie anomalously on the intensity diagram.[13] Unfortunately

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[13] Fredrickson and Watson, l.c., Table III.

no evidence is available from the red magnetic rotation spectrum, since it is so rich, and contains so many of the anomalous lines discussed above, that the writer has not yet been able to assign quantum numbers to it.

The heat of dissociation can now be calculated from Eq. (1) by the method of Birge and Sponer.[14] By differentiation one finds that the maximum of T'' occurs when $n''=76.3$. The corresponding value of T'' is: $T_{\text{max}}''=6644$ cm$^{-1}=0.82$ volt. The writer originally reported this as the heat of dissociation of the normal Na_2 molecule, but Professor Birge has kindly pointed out to him that a more accurate value is usually obtained by disregarding the cubic term in $T''(n'')$, since its effect is to some extent compensated by higher power terms of opposite sign. Moreover, it is likely that the true value lies somewhere between those obtained with and without the use of the cubic term. If the cubic term were disregarded, the calculated heat of dissociation would be $T_{\text{max}}''=8604$ cm$^{-1}=1.06$ volt. It is probably safe to conclude that the true heat of dissociation of the unexcited molecule is 1.0 ± 0.1 volt.

Proceeding in the same way with the upper level, for which only a quadratic formula is available, one finds that $T_{\text{max}}'=4586$ cm$^{-1}=0.57$ volt.

Since $\nu_0=20302$ cm$^{-1}=2.50$ volt is accurately known, it follows that the excess of energy of the pair of atoms into which the upper level molecule dissociates, over those into which the lower level molecule dissociates, is given by $\nu_0+T_{\text{max}}'-T_{\text{max}}''=2.50+0.57-1.0=2.07$ volt. Now the lowest excited levels of the sodium atom are the 3^2P, which are the initial states for the emission of the D lines and lie 16973 cm^{-1} and 16956 cm^{-1} or 2.10 volts above the normal level, 3^2S. The next level above 3^2P is 4^2S at 25743 cm$^{-1}=3.18$ volts. Since it has just been shown that the heat of dissociation of the lower level molecule is 1.0 ± 0.1 volt, it is clear, from considerations of stability, that it dissociates into two normal (3^2S) atoms. Inasmuch as an error of over one volt in the above estimate of $\nu_0+T_{\text{max}}'-T_{\text{max}}''$ is out of the question, there is no other possibility than that the upper level molecule dissociates into one normal (3^2S) atom and one atom in a 3^2P state. Having settled this point, it is possible to set $\nu_0+T_{\text{max}}'-T_{\text{max}}''=2.10$ volt, the accurately known energy of excitation of the D lines, and to combine it with the above values, $\nu_0=2.50$ volt, $T_{\text{max}}'=0.57$ volt, to obtain an independent estimate of the heat of dissociation, $T_{\text{max}}''=0.97$ volt. The closeness with which this agrees with the above estimate is probably partly accidental.

It remains to consider the red system. According to Fredrickson and Watson's Eq. (3), $\nu_0=15007$ cm$^{-1}=1.85$ volt; $T_{\text{max}}'=7838$ cm$^{-1}=0.97$ volt,[15] $T_{\text{max}}''=11570$ cm$^{-1}=1.43$ volt; $\nu_0+T_{\text{max}}'-T_{\text{max}}''=1.4$ volt. If, however, it is assumed that the lower levels of both red and green systems are identical,

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[14] Birge and Sponer, Phys. Rev. **28**, 259 (1926).

[15] The writer finds that $T'(n')=114.94n'-0.353n'^2$ corresponds to most of Fredrickson and Watson's absorption data rather more closely than does Eq. (3). The resulting value of T'_{max} is 9360cm$^{-1}=1.16$ volt, which agrees well with the indirectly and independently calculated value, 1.25 volt.

the much more accurate value of $T_{\text{max}}'' = 1.0 \pm 0.1$ volt is available. Combining this with $\nu_0 + T_{\text{max}}'$ from Eq. (3) one obtains $\nu_0 + T_{\text{max}}' - T_{\text{max}}'' = 1.8$ volt. In either case the arguments applied to the green system hold here with even greater force, and show that, in the red system also, the lower level molecule dissociates into normal 3^2S atoms and the upper level molecule into one normal 3^2S and one in a 3^2P state. Hence $\nu_0 + T_{\text{max}}' - T_{\text{max}}'' = 2.10$ volt, accurately as in the green system. Assuming the lower levels of the two systems to be identical and hence that $T_{\text{max}}'' = 1.0$ volt, one obtains $T_{\text{max}}' = 1.25 \pm 0.1$ volt. That is, the molecules in the upper state of the red system, although they have a smaller ω_0', and are therefore to be thought of as less tightly bound, than those in the upper state of the green system, nevertheless require much more energy to effect dissociation. No conceivable revision of the above figures could affect this conclusion. The assumption that the two lower levels are different and that T_{max}'' is to be taken from (3) as 1.43 volt, would make the T_{max}' for the red system even greater. The above results are summarized in Fig. 2.

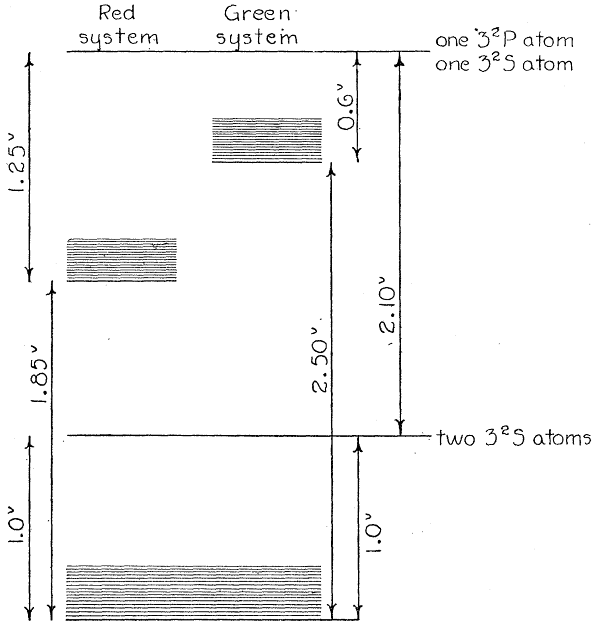

Fig. 2. Vibrational energy levels in the red and green systems.

In Fig. 3 the intensities of all the magnetic rotation lines in Table I are indicated in the circles opposite the appropriate values of n' and n''. It will be seen that the lines arrange themselves into a well developed parabola-like figure, of a type which Condon[16] has recently explained in terms of an hypothesis of Franck. Indeed, the likeness of Fig. 3 to that given by Condon

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[16] Condon, Phys. Rev. **28**, 1182 (1926).

for CO is very striking. Both are of the wide open type which, on Condon's theory, corresponds to an electronic transition which results in a rather large change of moment of inertia. This signifies that the band heads are near the origins and helps to justify the assumptions on which the present analysis is based.

Fig. 3 also affords as explanation of an interesting phenomenon which Wood has reported. When light from a monochromator is used to excite fluorescence, the effect of varying the frequency of the exciting light is shown

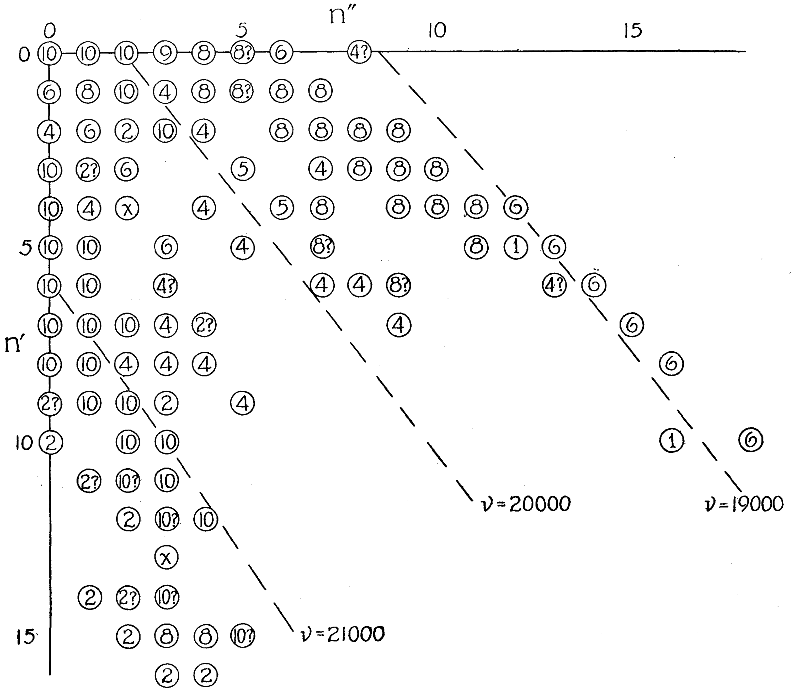


Fig. 3. Intensities in the blue-green magnetic rotation spectrum.

in Fig. 4.[17] It will be seen that when the exciting light, indicated by the double arrow, is in the blue, there are two patches of fluorescent light; one in the blue, the other in the yellow-green. As the wave-length of the exciting light is increased, the two patches move together, and finally fuse. The bluer region always includes the exciting light. By reference to Fig. 3, on which the spectral regions are indicated by the sloping lines, it will be seen that the blue light excites molecules having low n'' and lifts them to high values of n'. When these molecules emit the fluorescent light they may either return to their original n'', or one near it, corresponding to the left arm of the parabola, in which case the fluorescent light will be in the blue, near the exciting light; or they may fall back to a much higher value of n'',

[17] R. W. Wood, Proc. Am. Acad. **42**, Fig. 6c, 235 (1906).

corresponding to the same *n′* but on the right arm of the parabola, and then the fluorescent light will be in the yellow-green. As the patch of exciting light moves toward lower frequencies, successively lower values of *n′* will occur and the patches of fluorescent light corresponding to the arms of the parabola will move together and finally fuse at the vertex.

The knowledge of the vibrational energy levels in the lower electronic state makes it possible to plot the fluorescence series excited by various bright line sources, in a way very much like that used for iodine. In many cases the wave-lengths are not accurately enough known, and the possible exciting lines are too numerous, to make unambiguous arrangement into fluorescence series possible. There are, however, enough clear cases to make it evident that there are both singlet and doublet series, with the singlet series predominating. There seem to be no triplet series. Consequently the emission or absorption spectrum must consist of *P*, *Q* and *R* branches, but the initial state for emission of the *Q* branch must be different from that for the *P* and *R* branches.

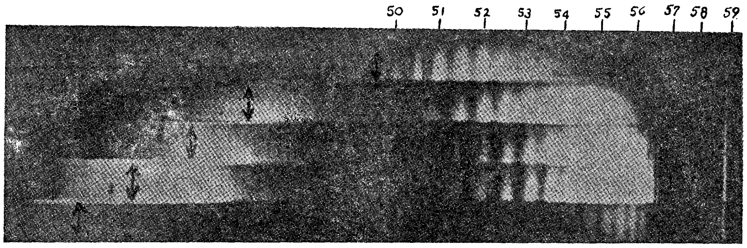
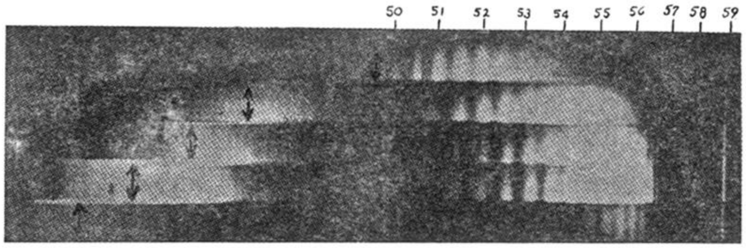


Fig. 4. Effect of varying frequency of exciting light, on intensity distribution of fluorescence. From Wood, Proc. Am. Acad. **40,** 235 (1906) Fig. 6c.

New York University,
December, 1927.



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