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THE VIBRATIONAL QUANTUM ANALYSIS OF THE BLUE-GREEN BANDS OF MAGNESIUM OXIDE

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Abstract

The paper deals with the assignment of the vibration quantum numbers of the violet degrading system of the magnesium oxide bands. The frequencies of vibration for infinitesimal amplitude are found to be 716 cm^{-1} and 751 cm^{-1} for the upper (initial) and lower (final) states respectively. The heat of dissociation as calculated from the extrapolation of the $\omega^n:n$ curve is nearly 5.8 volts.

Introduction

A REVIEW of the studies of the band spectrum of magnesium oxide has been given by Kayser[1] till the year 1910. Since then there has been no further investigation of the bands which are found to lie in the red, green and ultraviolet regions.

Lecoq[2] was the first to observe the bands of MgO in the green region. The bands lying in this as well as in the two other regions have been measured by Eder,[3] Brooks,[4] Olmstedt[5] and others. They excited these bands either by sparking through a solution of magnesium chloride, or by burning magnesium ribbon in air, or by burning the salts in an oxy-hydrogen flame or by arcing or sparking between magnesium electrodes in oxygen at reduced pressure.

The necessity of the presence of oxygen in the production of these bands has been shown by Dewar[6] and also by Brooks.[4] These bands were found to come out in the presence of air and CO_2 but would completely disappear when nitrogen or hydrogen was substituted. Even when the sparking between the magnesium electrodes was continued for a long time in the atmosphere of CO_2, these bands would gradually become fainter and finally disappear.

By using a new method of excitation, we have obtained the bands lying in the blue and green regions but the bands in the ultraviolet region observed by Olmstedt did not come out.

So far no relations, either empirical or theoretical, have been found among the various heads of the magnesium oxide bands. The object of the present paper is to obtain the vibrational quantum analysis of the bands com-

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[1] Kayser, Handbuch der Spectroscopie, **5,** 717 (1920).

[2] Lecoq, Spectres Lumineu, Paris, 1874.

[3] Eder, Beitrage zur Photochemie und Spectral Analysis, 1904, pp. 410.

[4] Brooks, Proc. Roy. Soc. **A80,** 218 (1908); Nat. Acad. **78,** 198 (1908).

[5] Olmstedt, Zeits. f. Wiss. Photogr. **4,** 255 (1906).

[6] Dewar, Proc. Roy. Inst. **9,** 204 (1882).

posing the blue-green system. The rotational structure of these bands shall be treated in a later communication.

EXPERIMENTAL

A quartz spectrograph (Model E 1 of Adam Hilger) of the Littrow type has been used in the investigation. The burning of magnesium ribbon in air or in an atmosphere of oxygen is certainly the most natural way of exciting the oxide bands for they come out only during the combination of magnesium with oxygen. But the magnesium ribbon while so burning forms a flocculent white oxide which glows in the light and becomes a source of continuous radiation. To avoid this, a mixture of powdered magnesium metal and nitrate of magnesium in suitable proportions was used. This mixture, on being ignited, produces an explosive flash and quickly disperses away the flocculent oxide. In this case it was found that the spectrum showed a larger number of bands than when magnesium ribbon was simply burned in air or in the atmosphere of oxygen. The heat generated during the flash was enough to melt a platinum wire (about a millimeter in thickness) which was used as the sparking arrangement. The flash so produced was focussed by a quartz lens on the slit of the spectrograph and the number of flashes required for an exposure depended on the sensitiveness of the photographic plate in the region in which the bands were photographed. From a preliminary observation, these bands were found to lie between the regions λ5210 and λ4700. Ilford Special Process Panchromatic Plates were used which gave the best results in these regions.

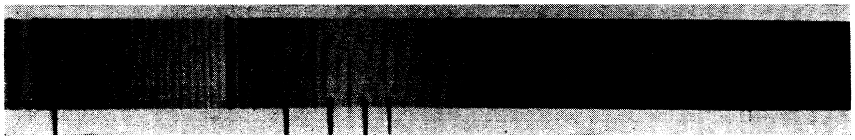

Fig. 1.

The comparison lines for calculating the wave-lengths were obtained from a Pfund iron arc. They were photographed on either side of the bands. The standard wave-lengths used were those of Meggers, Kiess and Burns. Actual measurements of the band-heads were done on a Hilger comparator. On account of a general diffuse character of some of the bands and high magnifying power of the comparator used, difficulties were encountered in the correct location and measurement of the weak bands. It is, however, very well known that it is the identification and location of the "null" or "zero" line in an individual band, which is of more importance than that of its head or edge, in arranging the bands into various n' and n'' progressions. Unless the line structure of a band be studied under sufficient dispersion, the "null" line can hardly be located. Thus the frequency of the head may be taken to fit the various progressions. This, however, will produce some error. R. S. Mulliken[7] is in favour of setting the cross-wire of the comparator on the point

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[7] R. S. Mulliken, Phys. Rev. **26**, 2 (1925).

of maximum blackening for each band as it reduces the uncertainty in locating a band-head. This procedure has been adopted by us in the measurements of the bands where possible. No where within the range of our measurements could we find a band in which the head could be distinguished from the "null" line either by a gap in the shading or even by a mere lightening—so the method of indirectly calculating the null lines from the observed bands could not be applied.

ANALYSIS OF MgO BANDS

A visual inspection of the plate indicates that the bands near about λ 5211 have been resolved inspite of the low dispersion of the quartz spectrograph in this region. They have, however, been identified to be the hydride bands of magnesium. Considerable difficulty was, therefore, met with in locating the oxide bands lying in this region. It is, however, found that the bands at λ 5007 come out very easily, even when magnesium ribbon is simply burned in air. This fact seems to be in agreement with the intensity measurements and with the excellent reproduction of Eder and Valenta ("Atlas typischer Spektren," Wien, 1928). Hence they were taken as the O-sequence.

WAVE-LENGTH DATA

The results of the present measurements together with the data of the previous investigators are given in the following table.

TABLE I.

		Authors			Previous investigators		
n'	n''	λ_{air}(I.A.)	ν (Vac)	O−C	Eder λ (R.S.)	Brooks λ (R.S.)	Morse λ (R.S.)
0	1	5190.91	19,259	−1.00	5190.60 (1)	5191.00	
1	2	5177.18	19,310	2.00	5177.23 (1)		
2	3	5162.99	19,363	1.00	5162.81 (½)	5162.00	
3	4	5148.50	19,418	−4.00	5145.87 (½)	5145.00	
4	5	5130.34	19,486	0.00	5130.34 (½)		
5	6	5113.47	19,551	3.00			
6	7	5097.95	19,610	1.00	5096.02 (1)		
7	8	5085.42	19,659	−4.00			5086.50
8	9	5072.64	19,708	1.00			5072.00
0	0	5007.13	19,966	−1.00	5007.44 (10)		
1	1	4996.84	20,007	4.00	4996.85 (8)		
2	2	4986.32	20,049	2.00	4986.23 (6)		
3	3	4975.51	20,093	−3.00	4974.81 (4)		
4	4	4962.40	20,146	−2.00	4962.45 (3)		
5	5	4949.19	20,200	−1.00	4949.30 (2)		
6	6	4935.20	20,257	5 00	4935.01 (1)		
7	7	4923.80	20,304	2.00	4923.65 (1)		
8	8	4913.40	20,347	−1.00	4913.37 (½)		
9	9	4903.35	20,388	−3.00	4903.36 (½)		
10	10	4892.82	20,432	2.00			
1	0	4826.12	20,715	0.00		4826.00	
2	1	4818.92	20,746	2.00		4820.00	
3	2	4810.96	20,780	0.00		4811.00	
4	3	4801.93	20,819	−2.00		4802.00	
5	4	4790.95	20,867	2.00		4791.00	
6	5	4780.72	20,911	1.00		4781.00	
7	6	4771.08	20,954	0.00		4771.00	
8	7	4761.78	20,994	0.00			

To start with, the band at λ 5007.13 was taken as the 0–0 band and the rest of the band system was then arranged into the Deslandre's progressions according to the criterion of Heurlinger and Kratzer for the assignment of the vibrational quantum numbers. The vibrational isotopic effect was looked for but no evidence of it was obtained.

The equation in terms of the parameters n' and n'' capable of representing the position of the measured heads is given below.

$$\nu_h = 19{,}967 + (751n' - 3.06n'^2) - (716n'' - 5.96n''^2).$$

CALCULATION OF THE HEAT OF DISSOCIATION

Having made the assignment of the vibration quantum numbers for the system of bands, the average values of each ΔG_n, i.e., ω^n for the two progressions were calculated and plotted as a function of n. The interval between successive vibrational levels in the lower electronic state is zero when $n' = 125$, i.e. when $751 - 6n' = 0$. The area on the $\omega^n : n$ diagram therefore gives 5.80 volts, which is the heat of dissociation of MgO(gas) into Mg(gas) and O(gas).

DISCUSSION

Mecke,[8] Mulliken,[9] Birge[10] and Hund[11] have shown that the band spectra of diatomic molecules bear a simple systematic relationship with the line spectra of atoms having similar outer electronic configuration. In the case of these it has been definitely proved by Dewar and by Brooks as well that the presence of oxygen is essential to produce these bands. Their emitter, may therefore be legitimately assumed as the oxide of magnesium. The band spectra of MgO will then resemble the line spectra of argon since they have the same outer electronic configuration. The ground state is therefore a singlet ^1S-state in both cases, and in the excited states, one would get singlets and triplets. Hence the MgO bands would be singlets and triplets in character.

There, however, remains the other possibility that the emitter of these bands may be MgO^+. If so, the band spectra would resemble the line spectra of ionized argon atom or of the normal chlorine atom. In either case, they would be doublet in structure.

But in the region in which these bands lie, the quartz spectrograph has a low dispersion and hence the separation of the bands into doublets or triplets could not be detected. We, therefore, reserve our opinion about the nature of the emitter till the line analysis of each individual band is made.

Our best thanks are due to Professor Birge for kindly sending us his monograph for the rapid calculation of the least squares solution of a polynomial, which has been of great use in our investigation.

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[8] Mecke, Phys. Zeits. **25**, 597 (1924); Zeits. f. Physik **28**, 261 (1924); **31**, 709, (1925).

[9] Mulliken, Nat. Acad. Proc. **12**, 144 (1926); Phys. Rev. **28**, 19 and 32 (1928).

[10] Birge, Nat. Acad. Proc. **12**, 146 (1926).

[11] Hund, Zeits. f. Physik **40**, 742 (1927); **42**, 93 (1927).

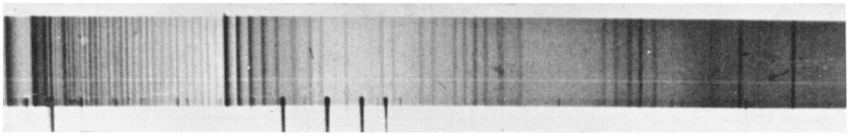

Fig. 1.