Fine Structure Analysis of the Red Bands of Magnesium Oxide and Isotope Effect.

By

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Abstract.

Measurements of the structure lines in the (0,1), (0,0), (1,0) and (2,0) bands of the red bands of magnesium oxide, MgO, are reported. Each band has two strong P and R branches associated with the main molecule, $Mg^{24}O$, and in most cases they are accompanied by fainter components which are definitely attributed to the two isotopic molecules, $Mg^{25}O$ and $Mg^{26}O$. The two main P and R branches are strictly single and their continuity in the vicinity of the band origin is interrupted by the absence of one line. This structure characterises the system as due to a $^1\Sigma \longrightarrow {}^1\Sigma$ transition.

The principal molecular constants evaluated from rotational term differences are as follows :—

Upper $^1\Sigma$ state.

$B_e' = 0.7625$ cm.$^{-1}$

$B_0' = 0.7594$

$B_1' = 0.7538$

$B_2' = 0.7470$

$a' = 0.0062$

$D_e' = -2.62 \times 10^{-6}$

$r_e' = 1.510 \times 10^{-8}$ cm.

$I_e' = 36.27 \times 10^{-40}$ gm. cm.^{2}

Lower $^1\Sigma$ state.

$B_e'' = 0.6852$ cm.$^{-1}$

$B_0'' = 0.6815$

$B_1'' = 0.6740$

$a'' = 0.0075$

$D_e'' = -2.57 \times 10^{-6}$

$r_e'' = 1.543 \times 10^{-8}$ cm.

$I_e'' = 40.36 \times 10^{-40}$ gm. cm.^{2}

Introduction.

Two band systems [1] are known for magnesium oxide. Both of them lie in the visible region, one in the green and the other in the red, extending however in the shorter wave-length region as far as λ4700. The distinctive feature about them is that while the band systems so far known for the other alkaline earth oxides are all degraded to the red, they are shaded towards the violet. Of the two systems the green bands are easily excited while the red bands are not of perceptible intensity in the usual flame surrounding the magnesium arc in air, but become fairly intense in processes where higher temperature is available for excitation. From this observation it would appear that although they lie on the longer wave-length side of the green bands, the energy of excitation of the red bands is much higher than those of the green. This would indicate that the levels involved in the emission of the former are different from those necessary for the appearance of the latter.

In the case of the oxides of beryllium,[2] calcium,[3] strontium,[4] and barium,[5] the rotational structure analysis for at least one of their band systems has been worked out thus enabling one to evaluate their more important molecular constants and to ascertain the nature of electronic states involved in the emission of the band systems. It is, therefore, of interest to study the fine structure of the bands of magnesium oxide with a view to complete our knowledge of the oxides of the alkaline earths and also to investigate the nature of isotope effect of magnesium, which is known to consist of three isotopes of masses 24, 25 and 26 and of relative abundance [6] of about 8 : 1 : 1.

The green system is of the familiar type in which the vibrational frequency and the moment of inertia are only slightly changed by the electron transition. The vibrational intensity distribution is also characteristic of this type resembling that of the green bands of beryllium oxide. It consists of only three

sequences, *viz.*, $\Delta v = v' - v'' = 0, \pm 1$.   Of these the zero-sequence is the most intense, while the two others are very weakly developed.   In each sequence the successive members are very closely spaced but the interval between their heads increases with increasing v', v'' values since while $\omega_e' > \omega_e''$, $\omega_e' x_e' < \omega_e'' x_e''$.   Even under the highest dispersion available, the (0,0) band is but partially resolved.   Moreover owing to the low intensity of (1,0) and (0,1) bands, it did not seem encouraging to take up the rotational structure analysis of the system under question as one would not get sufficient data for a verification of the combination principle and to arrive at the correct assignment of the rotational quantum numbers to the lines of the (0,0) band.

On the other hand the red system consists of a large number of sequences and the intense bands lie on a wider Condon parabola.   They are more open in structure than those of the green system and are thus more suitable for an investigation of their rotational structure.   The object of the present investigation is to present the results of such a study.   The bands (0,1), (0,0), (1,0) and (2,0) have been chosen for the purpose.

Measurements.

For the purpose of measurement, photographs of the selected bands were taken in the first orders of a 15 ft. and a 21 ft. concave grating set up on Paschen mounting and having dispersions of about 3·55A/mm. and 1·25 A/mm. respectively.   To secure the best definition of the structure lines, fine grained panchromatic plates were employed.   Several plates were taken for each of the four bands under investigation, the best ones being selected for the final measurement.   For each band at least four sets of independent measurements were carried out and in no case the individual measurements differed from one another by more than $\pm 0·01$ A. Neon lines and iron arc lines recommended as standards were used for comparison.   Reduction

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to wave-numbers in vacuo were made with the aid of Kayser's
" Tabelle der Schwingungzahlen."

The Structure of the Bands.

In each band the resolution is complete except for a few
lines at the head. The bands consist in main of two strong
series of lines which are pretty long due to the high temperature
of the source. Each of these series is in most cases accom-
panied by two comparatively fainter series of lines until the
next band of the sequence is encountered and is superposed by
the branches of the latter. Even then the two main series can
be followed very far with certainty as the succeeding bands are
very weak in intensity. The analysis given in the next section
reveals that while the two strong series are but the P and R
branch lines associated with the main molecule, $Mg^{24}O$, the
fainter series are due to the isotopic molecules $Mg^{25}O$ and $Mg^{26}O$.

Analysis of Band Structure.

The band heads are single, indicating that the band system
is due to a transition between two similar electronic states.
There is no sign of splitting into finer components even for the
last lines of the two strong series, evidently the P and R branch
lines, found in each band. This indicates that the levels involved
are singlets. It also excludes levels with $\Lambda = 1$ as in this case
one would expect each line of the series to be a narrow doublet
on account of the Λ-type doubling of each rotational energy level
in both electronic states. Further no lines, which could be
associated even with a short Q branch, are observed in any of
the bands investigated, thus showing that only the levels with
$\Lambda = 0$ are responsible for the emission of the band system. It
may here be pointed out that the theoretical intensities to
be expected in transition between two singlet electronic levels

both of which have the same value of Λ are given by the equations.

$$i_{Q(K)} = \frac{a(2K+1)\Lambda^2}{K(K+1)} \qquad \dots \quad (1)$$

$$i_{P(K)} = \frac{a(K^2-\Lambda^2)}{K} \qquad \dots \quad (2)$$

$$i_{R(K)} = \frac{a(K+1)^2 - \Lambda^2}{K+1} \qquad \dots \quad (3)$$

In these equations the Boltzmann factor has been assumed to be unity. It is readily seen that if $\Lambda=1$, *i.e.*, in a $^1\pi \rightarrow {}^1\pi$ transition, the bands should have a weak Q branch and the intensity of the first Q line is three times as great as that of the first R line, while the intensities of the other Q lines decrease rapidly for higher values of K. Similarly for $\Lambda=2$, *i.e.*, in a $^1\triangle \rightarrow {}^1\triangle$ transition the first Q line is very much stronger, and the intensities of the other lines decrease less rapidly. These considerations lead one to associate the band system under question to a $^1\Sigma \rightarrow {}^1\Sigma$ transition. Further evidence is secured from the criterion of missing lines, *viz.*, the first line of the R branch in the (0, 0) band begins definitely from $K=0$.

After sorting out the two main series of lines in each band, the next step was the identification of each series and the assignment of quantum numbers to the lines belonging to it. As the bands are degraded towards the shorter wave-length side, the series of lines starting from their heads evidently belong to the P branch in each case. Proceeding away from the head, one can unerringly identify the neighbouring lines as belonging either to P or R branch merely from a visual inspection of their relative intensities except in the regions where the lines of the two series coalesce into one. In many cases lines from the P and R branches dispose themselves in a manner as to appear like close

doublets, the doublets becoming single lines as they approach the head. It should, however, be noted that from the relative intensities of these apparent doublets, one can easily distinguish them from what would occur either when the electronic levels are doublets or when the rotational levels possess Λ-type doubling. Thus after identifying the two main R and P branches of the bands, it was only a matter of trial to find out the proper combination relationship between them and thereby to arrive at the unique assignment of quantum numbers to the lines of the two series. The correctness of their K-numbering was further confirmed from the close agreement between the calculated and observed magnitudes of the isotopic displacements of the rotational lines wherever available.

It is well known that the lines of the R and P branches are given theoretically by,

$$R(K) = T'(K+1) - T''(K) \qquad \ldots \quad (4)$$

$$P(K) = T'(K-1) - T''(K) \qquad \ldots \quad (5)$$

So that,

$$\triangle_2 T'(K) = R(K) - P(K) \qquad \ldots \quad (6)$$

$$\triangle_2 T''(K) = R(K-1) - P(K+1) \qquad \ldots \quad (7)$$

According to the combination principle all bands having the same upper vibrational state should yield sets of values of $\triangle_2 T'(K)$, which are numerically identical ; and similarly all bands having the same lower vibrational state should give identical sets of values of $\triangle_2 T''(K)$.

The wave-lengths and wave-numbers of the lines of P and R branches of each analysed band due to the main molecule, $Mg^{24}O$, together with their K-numbering are given in Tables I-IV.

TABLE I.

Structure of the (0, 0) band at λ6060·31.

	R		P	
K	λ(I.A.)	ν(cm.⁻¹)	λ(I.A.)	ν(cm.⁻¹)
0	6057·70	16503·36		
1	57·06	05·10		
2	56·35	07·04		
3	55·58	09·14		
4	54·75	11·40		
5	53·85	13·85		
6	52·89	16·47		
7	51·85	19·31		
8	50·79	22·21		
9	49·73	25·10		
10	48·62	28·13	6060·31	16496 25
11	47·46	31·30	60·25	96·41
12	46·30	34·47	60·20	96·55
13	45·12	37·70	60·13	96·64
14	43·87	41·12	59·98	97·15
15	42·55	44·74	59·77	96·72
16	41·16	48·54	59·48	98·51
17	89·71	52·51	59·13	99·46
18	88·20	56·65	58·72	16500·58
19	86·63	60·96	58·24	01·89
20	84·09	65·46	57·70	03·36
21	83·28	70·16	57·06	05·10
22	81·51	75·02	56·39	06·93
23	29·68	80·04	55·65	08 94
24	27·80	85·22	54 86	11·10
25	25·85	90·58	54·00	13·44

TABLE I (contd.).

K	R		P	
	λ (I.A.)	ν (cm.⁻¹)	λ (I.A.)	ν (cm.⁻¹)
26	6023·84	16596·12	6053·06	16516·01
27	21·77	16601·82	52·06	18·74
28	19·64	07·70	51·00	21·63
29	17·46	13·71	49·89	24·66
30	15·23	19·87	48·73	27·83
31	12·96	26·15	47·52	31·14
32	10·64	32·57	46·26	34·58
33	08·28	39·10	44·96	38·14
34	05·86	45·80	43·59	41·89
35	03·39	52·65	42·17	45·78
36	00·88	59·62	40·71	49·77
37	5998·33	66·70	39·20	53·91
38	95·73	73·93	37·64	58·19
39	93·08	81·30	36·02	62·63
40	90·37	88·85	34·36	67·19
41	87·63	96·51	32·64	71·91
42	84·82	16704·32	30·85	76·83
43	81·96	12·31	28·99	81·94
44	79·02	20·53	27·07	87·22
45	76·05	28·84	25·10	92·65
46	73·03	37·30	23·08	98·21
47	69·96	45·90	21·02	16603·89
48	66·84	54·66	18·90	09·74
49	63·67	63·57	16·72	15·76
50	60·45	72·62	14·47	21·97
51	57·18	81·83	12·18	28·30
52	53·85	91·21	09·87	34·79
53	50·46	16800·78	07·41	41·51

TABLE I (*contd.*).

K	R		P	
	λ (I.A.)	ν (cm.⁻¹)	λ (I.A.)	ν (cm.⁻¹)
54	5947·01	16810·53	6004·93	16648·38
55	43·52	20·40	02·40	55·40
56	39·98	30·42	5999·81	62·59
57	36·39	40·60	97·17	69·92
58	32·75	50·93	94·47	77·43
59	5929·05	61·45	91·70	85·14
60	25·29	72·15	88·87	93·03
61	21·48	83·00	85·99	16701·06
62	17·64	93·96	83·05	09·27
63	13·76	16905·04	80·06	17·63
64	09·83	16·28	77·05	26·04
65	05·88	27·60	74·00	34·58
66	01·88	39·07	70·90	43·27
67	5897·82	50·73	67·72	52·19
68	93·69	62·61	64·52	61·18
69	89·49	74·70	61·19	70·54
70	85·24	86·96	57·84	79·97
71	80·95	99·35		
72	76·62	17011·88		
73	72·25	24·54		
74	67·84	87·34		
75	63·39	50·27		
76	58·90	63·33		

TABLE II.

Structure of the (0,1) band at λ 6311·65.

K	R		P	
	λ (I.A.)	ν (cm.⁻¹)	λ (I.A.)	ν (cm.⁻¹)
5	...	...	6311·65	15839·35
6	...	...	11·88	40·03
7	...	...	11·10	40·73
8	...	...	10·78	41·53
9	...	...	10·42	42·43
10	...	...	10·04	43·39
11	...	...	09·68	44·42
12	...	...	09·18	45·55
13	...	...	08·70	46·75
14	...	...	08·17	48·09
15	6288·95	15896·62	07·60	49·52
16	87·14	15901·10	06·98	51·08
17	85·28	05·80	06·31	52·76
18	83·36	10·66	05·58	54·60
19	81·38	15·68	04·78	56·61
20	79·35	20·82	03·93	58·74
21	77·27	26·10	03·03	61·01
22	75·14	31·50	02·08	63·40
23	72 95	37·07	01·06	65·97
24	70·70	42·78	6299·98	68·69
25	68·40	48·63	98·85	71·53
26	66·04	54·64	97·56	74·53
27	63·62	60·80	96·40	77·71
28	61·12	67·15	95·07	81·07
29	58·57	73·69	93·66	84·62
30	55·98	80·42	92·18	88·36

TABLE II (*contd.*).

K	R		P	
	λ (I·A.)	ν (cm.⁻¹)	λ (I·A.)	ν (cm.⁻¹)
31	6253·23	15987·32	6290·62	15892·30
32	50·46	94·41	88·99	96·42
33	47·63	16001·65	87·30	15900·69
34	44·75	09·03	85·55	05·12
35	41·81	16·57	83·74	09·70
36	38·80	24·30	81·86	14·46
37	35·73	32·19	79·92	19·38
38	32·62	40·19	77·92	24·45
39	29·46	48·32	75·87	29·65
40	26·25	56·60	73·76	35·01
41	22·97	65·06	71·59	40·52
42	19·63	73·69	69·35	46·22
43	16·24	82·45	67·05	52·07
44	12·78	91·41	64·69	58·08
45	09·27	16100·51	62·26	64·27
46	06·70	09·77	59·76	70·64
47	02·07	19·20	57·20	77·18
48	6198·39	28·77	54·58	83·87
49	94·65	38·51	51·90	90·72
50	90·84	48·44	49·15	97·76
51	86·97	58·54	46·33	16004·98
52	83·04	68·81	43·44	12·39
53	79·06	79·23	40·50	19·94
54	75·02	89·81	37·49	27·66
55	70·93	16200·54	43·04	35·53
56	66·79	11·42	31·30	43·59
57	62·59	22·47	28·11	51·90
58	58·34	33·66	24·87	60·16

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TABLE II (contd.).

K	R		P	
	λ (I. A.)	ν (cm.⁻¹)	λ (I. A.)	ν(cm.⁻¹)
59	6154·04	16245·00	6221·57	16068·68
60	49·69	56·50	18·21	77·36
61	45·29	68·14	14·79	86·21
62	40·86	79·87	11·30	95·25
63	36·40	91·70	07·78	16104·37
64	31·85	16303·70	04·23	13·59
65	27·30	15·90	00·64	22·92
66	22·67	28·23	6196·95	32·52
67	17·98	40·75	93·23	42·21
68	13·26	53·37	89·46	52·14
69	08·47	66·19	85·57	62·20
70	03·60	79·25	81·64	72·47
71	6098·70	92·41	77·64	82·94
72	93·72	16405·81	73·57	93·61
73	88·70	19·33	69·47	16204·38
74	83·62	33·04	65·30	15·33
75	78·50	46·88	61·07	26·47
76	73·29	60·99	56·74	37·88
77	68·08	75·13	52·40	49·33
78	62·80	89·47	47·98	61·02
79	57·48	16503·96	43·52	72·82
80	52·11	18·00	...	...

TABLE III.

Structure of the (1, 0) band at λ 5775·25.

K	R		P	
	λ (I. A.)	ν (cm.⁻¹)	λ (I. A.)	ν (cm.⁻¹)
10	...	...	5775·25	17310·48
11	...	...	75·00	11·23
12	...	...	74·72	12·07
13	...	...	74·41	13·08
14	5759·41	17358·09	74·08	13·99
15	58·09	62·06	73·73	15·04
16	56·73	66·17	73·35	16·18
17	55·39	70·21	72·94	17·41
18	54·00	74·41	72·49	18·76
19	52·60	78·64	72·05	20·08
20	51·17	82·96	71·57	21·52
21	49·70	87·40	71·06	23·05
22	48·19	91·97	70·54	24·61
23	46·64	96·66	69·97	26·32
24	45·07	17401·42	69·35	28·18
25	43·45	06·32	68·65	30·28
26	41·77	11·42	67·94	32·42
27	40·04	16·66	67·21	34·61
28	38·26	22·07	66·42	36·99
29	36·43	27·62	65·57	39·54
30	34·55	33·34	64·67	42·25
31	32·61	39·24	63·73	45·08
32	30·62	45·29	62·78	48·09
33	28·59	51·47	61·68	51·25
34	26·48	57·90	60·56	54·62
35	24·35	64·40	59·41	58·09

TABLE III (*contd.*).

K	R		P	
	λ(I.A.)	ν(cm.$^{-1}$)	λ(I.A.)	ν(cm.$^{-1}$)
36	5722·16	17471·08	5758·18	17361·80
37	19·94	77·86	56·89	65·69
38	17·67	84·80	55·57	69·67
39	15·35	91·90	54·20	73·80
40	12·99	99·12	52·78	78·09
41	10·59	17506·48	51·30	82·56
42	08·14	13·99	49·78	87·16
43	05·63	21·70	48·19	91·97
44	03·05	29·62	46·54	96·96
45	00·45	37·62	44·82	17402·17
46	5697·83	45·68	43·07	07·48
47	95·18	53·85	41·29	12·87
48	92·47	62·20	39·48	18·36
49	89·70	70·76	37·62	24·01
50	86·89	79·44	35·70	29·84
51	84·04	88·25	33·74	35·80
52	81·16	97·17	31·74	41·88
53	78·25	17606·19	29·72	48·03
54	75·27	15·43	27·63	54·40
55	72·25	24·81	25·48	60·95
56	69·18	34·35	23·25	67·75
57	66·08	44·00	20·99	74·65
58	62·95	53·76	18·72	81·59
59	59·77	68·67	16·40	86·69
60	56·57	78·67	14·02	95·97
61	53·32	83·83	11·61	17503·35
62	50·01	94·19	00·15	10·89

TABLE III (*contd.*).

K	R		P	
	λ(I.A.)	ν(cm.⁻¹)	λ(I.A.)	ν(cm.⁻¹)
63	5546·66	17704·68	5606·66	1718·53
64	43·27	15·32	04·12	26·34
65	89·83	26·12	01·52	34·33
66	86·35	737·07	98·87	542·48
67	82·83	48·15	96·16	50·83
68	29·26	59·40	93·39	59·37
69	25·65	70·80	90·58	68·04
70	22·00	82 34	87·72	76·87
71	18·30	94·05	84·84	85·78
72	14·57	17805·87	...	...
73	10·80	17·84	...	...
74	06·98	29·97	...	...
75	03·12	42·26	...	...
76	5599·24	54·62	...	...
77	95·32	67·13	...	...
78	91·38	79·72	...	...
79	87·40	92·46	...	...
80	83·39	17905·31	...	...
81	79·32	18·37	...	...
82	75·20	81·61	...	...

TABLE IV.

Structure of the (2, 0) band at λ 5518.70.

K	R		P	
	λ (I.A.)	$\nu(cm.^{-1})$	λ(I.A.)	$\nu(cm.^{-1})$.
14	5505·86	18157·44		
15	04·95	60·44		
16	03·93	63·80	5518·70	18115·19
17	02·88	67·27	18·61	15·49
18	01·78	70·90	18·41	16·14
19	00·63	74·70	18·17	16·93
20	5499·45	78·60	17·88	17·88
21	98·23	82·63	17·55	18·97
22	96·96	86·83	17·19	20·15
23	95·64	91·20	16·78	21·49
24	94·28	95·71	16·32	23·01
25	92·89	18200·31	15·81	24·68
26	91·47	05·02	15·26	26·49
27	90·02	09·82	14·67	28·43
28	88·54	14·73	14·05	30·47
29	87·03	19·75	13·39	32·64
30	85·47	24·93	12·69	34·94
31	83·86	30·28	11·95	37·37
32	82·21	35·77	11·18	39·91
33	80·52	41·39	10·37	42·57
34	78·79	47·15	09·51	45·41
35	77·02	53·05	08·61	48·37
36	75·21	59·08	07·67	51·47
37	73·35	65·29	06·69	54·70
38	71·45	71·63	05·67	58·06

TABLE IV (contd.).

K	R		P	
	λ(I.A.)	ν(cm.$^{-1}$)	λ(I.A.)	ν(cm.$^{-1}$)
39	5469·53	18278·04	5504·61	18161·56
40	67·58	81·56	03·52	65·16
41	65·59	291·21	02·40	168·8
42	63·56	98·01	01·23	72·72
43	61·48	18304·98	00·02	76·72
44	59·34	12·16	5498·75	80·91
45	57·14	19·54	97·43	85·28
46	54·90	27·06		
47	52·63	34·69		
48	50·32	42·46		
49	47·97	50·37		
50	45·59	58·39		

Calculation of Molecular Constants.

The next step was to calculate the rotational constants of the molecule from the combination differences, which are given in Tables V-VIII for the different vibrational states. The mean value of the combination differences, $\triangle_2 T(K)$, has been taken in cases where there was more than one datum available for a particular pair of rotational levels. Since the rotational energy of a molecule in a $^1\Sigma$ state is $T(K)$, where,

$$T(K) = B_v(K+1) + D_v K^2(K+1)^2 + \quad \cdots \quad \cdots \quad (8)$$

the combination differences can be expressed thus :

$$\triangle_2 T(K) = T(K+1) - T(K-1)$$
$$= 4B_v(K+\tfrac{1}{2}) + 8D_v(K+\tfrac{1}{2})^3 + \qquad \dots \text{ (9)}$$

where terms small in comparison with $8D_v (K+\tfrac{1}{2})^3$ are dropped. Both B_v and D_v depend upon v according to the relations

$$B_v = B_e - a(v+\tfrac{1}{2})$$
$$= B_o - av \qquad \dots \qquad \dots \qquad \dots \qquad \dots \text{ (10)}$$

and

$$D_v^3 = D_e + \beta(v+\tfrac{1}{2})$$
$$= D_o + \beta v \qquad \dots \qquad \dots \qquad \dots \qquad \dots \text{ (11)}$$

Here B_e and D_e are the extrapolated values of B_v and D_v corresponding to the non-vibrating molecule.

For each vibrational level, the values of $\triangle_2 T(K)$ were plotted against K. It was found that for low values of K the points lay approximately on a straight line, whose slope gave a good approximation to the value of $4B_v$ in each case. The approximate value of D_v was calculated from the theoretical relation,

$$D = 4B^3/\omega^2 \qquad \dots \qquad \dots \qquad \dots \text{ (12)}$$

Then by successive approximation and repeated trials, values are finally assigned to B_v and D_v. The variation of D_v with v was of negligible magnitude, so that D_e was taken equal to D_v. The final values of the different constants thus evaluated are collected in Table IX.

To ensure the correct valuation of B_v and D_v values, $\triangle_2 T(K)$ values were calculated from equation (2) for each vibrational state. To illustrate their agreements with the observed $\triangle_2 T(K)$ values, they have been included in Tables V and VII only for the vibrational states $v'=0$ and $v''=0$.

TABLE V.

Combination differences, $\triangle_2 T'(K)$, *in the upper state,*
$v = 0.$

K	$\triangle_2 T'(K)$ (Obs.)			$\triangle_2 T'(K)$ (Calc.)	$O-C.$
	(0, 0)	(0, 1)	Mean		
10	31·88		31·88	31·87	+0·01
11	34·89		34·89	34·90	−0·01
12	37·92		37·92	37·93	−0·01
13	40·96		40·96	40·96	0·00
14	43·97		43·97	43·99	−0·02
15	47·02	47·00	47·01	47·00	+0.01
16	50·03	50·02	50·03	50·03	0·00
17	53 05	53·04	53·05	53·05	0·00
18	56·07	56·06	56·07	56·07	0·00
19	59·07	59·07	59·07	59·08	−0·01
20	62·10	62.08	62·09	62·09	0-00
21	65·06	65·09	65·08	65·10	−0·02
22	68·09	68·10	68·10	68·11	−0·01
23	71·10	71·10	71·10	71·11	−0·01
24	74·12	74·09	74·11	74·11	0·00
25	77·14	77·10	77·12	77·11	+0·01
26	80·11	80·11	80·11	80·11	0·00
27	83·08	83·09	83·09	83·09	0·00
28	96·07	86·08	86·08	86·08	0·00
29	89·05	89·07	89·06	89·07	−0·01
30	92·04	92·06	92·05	92 06	−0·01
31	95·01	95·02	95·02	95·02	0·00
32	97·99	97·99	97·99	98·00	−0·01
33	100·96	100·96	100·96	100·97	−0·01
34	103·91	103·91	103·91	103·94	−0·03
35	106.87	106·87	106·87	106·89	−0·02

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TABLE V (*contd.*).

K	$\triangle_2 T'(K)$ (Obs.)			$\triangle_2 T'(K)$ (Calc.)	$O-C.$
	(0, 0)	(0, 1)	Mean		
36	109·85	109·84	109·85	109·85	0·00
37	112·79	112·81	112·80	112·80	0·00
38	115·74	115·74	115·74	115·75	−0·01
39	118·67	118·67	118·67	118·69	−0·02
40	121·66	121·59	121·63	121·63	0·00
41	124·60	124·54	124·57	124·56	+0·01
42	127·49	127·47	127·48	127·49	−0·01
43	130·37	130·38	130·38	130·40	−0·02
44	133·31	133·33	133·32	133·32	0·00
45	136·19	136·24	136·22	136·24	−0·02
46	139·09	139 13	139·11	139·14	−0·03
47	142·01	142·02	142·02	142·04	−0·02
48	144·92	144·90	144·91	144·93	−0·02
49	147·81	147·79	147·80	147·82	−0·02
50	150·65	150·68	150 67	150·69	−0·02
51	153·53	153·56	153·55	153·57	−0·02
52	156·42	156·42	156·42	156·43	−0·01
53	159·27	159·29	159·28	159·80	−0·02
54	162·15	162·15	162·15	162·16	−0·01
55	165·00	165·01	165·01	165·01	0·00
56	167·83	167·83	167·83	167·84	−0·01
57	170·68	170·67	170·68	170·67	+0·01
58	173·50	173·50	173·50	173·50	0·00
59	176·31	176·32	176·32	176·32	0·00
60	179·12	179·14	179·13	179·13	0·00
61	181·94	181·93	181·94	181·93	+0·01
62	184·69	184·62	184·66	184·73	−0·07

TABLE V. (contd.).

K	$\Delta_2 T'(K)$ (obs.)			$\Delta_2 T'(K)$ (calc.)	O−C
	(0, 0)	(0, 1)	Mean		
63	187·42	187·33	187·38	187·52	−0·14
64	190·24	190·20	190·22	190·30	−0·08
65	193·02	192·98	193·00	193·07	−0·07
66	195·80	195·71	195·76	195·84	−0·08
67	198·54	198·54	198·54	198·59	−0·05
68	201·43	201·23	201·33	201·34	−0·01
69	204·16	203·09	204·08	204·07	+0·01
70	206·99	206·78	206·89	206·80	+0·09
71		209·47	209·47	209·53	−0·06
72		212·20	212·20	212·24	−0·04
73		214·95	214·95	214·94	+0·01
74		217·71	217·71	217·63	+0·08
75		220·41	220·41	220·32	+0·09
76		223·11	293·11	223·00	+0·11
77		225·80	125·80	225·65	+0·15
78		228·45	228·45	228·31	+0·14
79		231·14	231·14	230·96	+0·18

TABLE VI.

Combination difference, $\Delta_2 T'(K)$, in the upper state,
$v' = 1$ and $v' = 2$

K	$\Delta_2 T'(K)$ $v'=1$ (1, 0)	$\Delta_2 T'(K)$ $v'=2$ (2, 0)	K	$\Delta_2 T'(K)$ $v'=1$ (1, 0)	$\Delta_2 T'(K)$ $v'=2$ (2, 0)
14	44·10		17	52·80	51·78
15	47·02		18	55·65	54·76
16	49·99	48·61	19	58·56	57·77

TABLE VI (contd.).

K	$\Delta_2 T'(K)$ $v'=1$ (1, 0)	$\Delta_2 T'(K)$ $v'=2$ (2, 0)	K	$\Delta_2 T'(K)$ $v'=1$ (1, 0)	$\Delta_2 T'(K)$ $v'=2$ (2, 0)
20	61·44	60·72	46	138·20	
21	64·35	63·66	47	140·98	
22	67·36	66·68	48	143·84	
23	70·34	69·71	49	146·75	
24	73·24	72·70	50	149·60	
25	76·04	75·63	51	152·45	
26	79·00	78·53	52	155·29	
27	82·05	81·39	53	158·16	
28	85·08	84·26	54	161·03	
29	88·08	87·11	55	163·86	
30	91·09	89·99	56	166·60	
31	94·16	92·91	57	169 35	
32	97·20	95·86	58	172·17	
33	100·22	98·82	59	174·98	
34	103·28	100·74	60	177·70	
35	106·31	104·68	61	180·48	
36	109·28	107·61	62	183·30	
37	112·17	110·59	63	186·15	
38	115·13	113·57	64	188·98	
39	118·10	116·48	65	191·79	
40	121·03	119·04	66	194·59	
41	123·92	122·36	67	197·32	
42	126·83	125·29	68	200·08	
43	129·73	128·26	69	202·76	
44	132·66	131·25	70	205·47	
45	135·45	134·26	71	208·27	

TABLE VII.

Combination differences, $\triangle_2 T''(K)$, in the lower state, $v''=0$.

K	$\triangle_2 T''(K)$ (obs.)				$\triangle_2 T''(K)$ (calc.)	$O-C$
	(0,0)	(1,0)	(2,0)	Mean		
9	25·96			25·96	25·88	+ 0·08
10	28·69			28·69	28·60	+ 0·09
11	31·58			31·58	31·32	+ 0·26
12	34·56			34·56	34·04	+ 0·52
13	37·32			37·32	36·75	+ 0·57
14	39·98			39·98	39·47	+ 0·51
15	42·61	41·91	42·25	42·26	42·17	+ 0·09
16	45·28	44·65	44·95	44·96	44·89	+ 0·07
17	47·96	47·41	47·66	47·68	47·60	+ 0·08
18	50·62	50·13	50·34	50·36	50·30	+ 0·06
19	53·29	52·89	53·02	53·07	53·01	+ 0·06
20	55·86	55·59	55·73	55·73	55·70	+ 0·03
21	58·53	58·35	58·45	58·44	58·41	+ 0·03
22	61·22	61·08	61·14	61·15	61·11	+ 0·04
23	63·92	63·79	63·82	63·84	63·79	+ 0·05
24	66·60	66·38	66·52	66·50	66·49	+ 0·01
25	69·21	69·00	69·22	69·14	69·17	− 0·03
26	71·84	71·71	71·88	71·81	71·86	−0·05
27	74·49	74·43	74·55	74·49	74·54	− 0·05
28	77·16	77·12	77·18	77·15	77·21	− 0·06
29	79·87	79·82	79·79	79·83	79·89	− 0·06
30	82·57	82·54	82·38	82·50	82·56	− 0·06
31	85·29	85·25	85·02	85·19	85·23	− 0·04
32	88·01	87·99	87·71	87·90	87·89	+ 0·01
33	90·68	90·67	90·36	90·57	90·55	+ 0·02
34	93·32	93·38	93·02	93·24	93·21	+ 0·03
35	96·03	96·10	95·68	95·94	95·85	+ 0·09

TABLE VII (*contd.*).

K	$\triangle_2 T''$ (K) (obs.)				$\triangle_2 T''$ (K) (calc.)	O − C
	(0,0)	(1,0)	(2,0)	Mean		
36	98·74	98·71	98·35	98·60	98·50	+ 0·10
37	101·43	101·41	101·02	101·29	101·15	+ 0·14
38	104·07	104·06	103·73	103·95	103·78	+ 0·17
39	106·74	106·71	106·47	106·64	106·41	+ 0·23
40	109·39	109·34	109·19	109·31	109·03	+ 0·28
41	112·02	111·96	111·84	111·94	111·66	+ 0·28
42	114·57	114·51	114·49	114·52	114·28	+ 0·24
43	117·10	117 03	117·10	117·08	116·89	+ 0·19
44	119·66	119·53	119·70	119·63	119·50	+ 0·13
45	122·32	122·14		122·23	122·09	+ 0·14
46	124·95	124·75		124·85	124·69	+ 0·16
47	127·46	127·32		127·39	127·29	+ 0·10
48	130·14	129·84		129·99	129·86	+ 0·13
49	132·69	132·36		132·53	132·45	+ 0·08
50	135·27	134·96		135·12	135·01	+ 0·11
51	137·83	137·56		137·70	137·58	+ 0·12
52	140·32	140·22		140·27	140·14	+ 0·13
53	142·83	142·77		142·80	142·69	+ 0·11
54	145·38	145·24		145·31	145·24	+ 0·07
55	147·94	147·68		147·81	147·77	+ 0·04
56	150·48	150·16		150·32	150·31	+ 0·01
57	152·99	152·76		152·88	152·84	+ 0·04
58	155·46	155·31		155·39	155·35	+ 0·04
59	157·90	157·79		157·85	157·87	+ 0·02
60	160·39	160·32		160·36	160·37	− 0·01
61	162·88	162·78		162·83	162·87	− 0·04
62	165·88	165·80		165·84	165·86	− 0·02
63	167·92	167·85		167·89	167·83	+ 0·06

TABLE VII   (contd.).

K	$\triangle_2 T''$ (K) (obs.)				$\triangle_2 T''$ (K) (Calc.)	$O-C.$
	(0, 0)	(1, 0)	(2, 0)	Mean.		
64	170·46	170·35		170·41	170·31	+ 0·10
65	173·01	172·84		172·98	172·77	+ 0·16
66	175·41	175·29		175·35	175·23	+ 0·12
67	177·89	177·70		177·80	177·69	+ 0·11
68	180·19	180·11		180·15	180·12	+ 0·03
69	182·64	182·53		182·59	182·56	+ 0·03
70		185·02		185·02	184·97	+ 0·05

TABLE VIII.

Combination differences, $\triangle_2 T''(K)$, in the lower state,
$$v'' = 1.$$

K	$\triangle_2 T''(K)$ (0, 1)	K	$\triangle_2 T''(K)$ (0, 1)	K	$\triangle_2 T''(K)$ (0, 1)
16	43·76	27	73·57	38	102·54
17	46·50	28	76·18	39	105·18
18	49·19	29	78·79	40	107·80
19	51·92	30	81·39	41	110·38
20	54·67	31	84·00	42	112·99
21	57·42	32	86·63	43	115·61
22	60·13	33	89·29	44	118·18
23	62·81	34	91·95	45	120·77
24	65·54	35	94·57	46	123·33
25	68·25	36	97·19	47	125·90
26	70·92	37	99·85	48	128·48

TABLE VIII (*contd.*).

K	$\triangle_2''(K)$ (0, 1)	K	$\triangle_2 T''(K)$ (0, 1)	K	$\triangle_2 T''(K)$ (0, 1)
49	131·01	59	156·30	69	180·90
50	135·53	60	158·79	70	183·25
51	136·05	61	161·25	71	185·64
52	138·60	62	163·77	72	188·03
53	141·15	63	166·28	73	190·48
54	143·70	64	168·78	74	192·86
55	146·22	65	171·27	75	195·16
56	148·74	66	173·69	76	197·55
57	151·26	67	176·09	77	199·97
58	153·79	68	178·55	78	202·31

TABLE IX.

Rotational Constants.

Upper $'\Sigma$ state.

$B_e' = 0·7625$ cm^{-1}.
$B_0' = 0·7694$
$B_1' = 0·7538$
$B_2' = 0·7470$
$a' = 0·0062$
$D_e' = -0·262 \times 10^{-6}$
$r_e' = 1·510 \times 10^{-8}$ cm.
$I_e' = 36·27 \times 10^{-40}$ gm. cm.^{2}

Lower $'\Sigma$ state.

$B_e'' = 0·6852$ cm^{-1}.
$B_0'' = 0·6815$
$B_1'' = 0·6740$
$a'' = 0·0075$
$D_e'' = -2·57 \times 10^{-6}$
$r_e'' = 1·593 \times 10^{-8}$ cm.
$I_e'' = 40·36 \times 10^{-40}$ gm. cm^2.

Isotope Effect.

The theory of the isotope separations in band spectra was developed for vibration-rotation bands by Loomis[7] and by Kratzer.[8] The first evidence of the isotope effect was found by them in Ime's data on the infra-red spectrum of HCl. Later

on, Mulliken[9] worked out in detail the theory of isotopic separations for electronic bands and obtained confirmation of the theoretically predicted effects in the band systems of several diatomic molecules. Further points in the theory have however been elucidated in recent years chiefly by Gibson,[10] Birge[11] and by Patkowski and Curtis.[12] It may be noted here that in addition to the isotopes whose existence had already been established by Aston by means of the mass spectrograph, rare isotopes notably of O, N, C and H have been discovered by the band-spectrum method.

For magnesium there are three isotopes of masses 24, 25 and 26 in order of abundance 8 : 1 : 1. Their effects in band spectra have been detected by Watson and Rudnick[13] in the green system of MgH and by Pearse[14] in the ultra-violet bands of MgH$^+$. Considering the relative masses of oxygen and magnesium atoms the band systems of magnesium oxide may reasonably be expected to bring out the effects of magnesium isotopes more favourably.

It is well known that in the spectrum of a mixture of two or more isotopic molecules the bands of the less abundant ones are similar to, but displaced from, the weaker than those of more abundant molecule. The lines of the latter are adopted as points of reference on account of their intensity and being more easily measurable. Using the notation suggested by Birge in which the corresponding quantities for two isotopic molecules are distinguished by affixing a superscript 'i' to all symbols for the less abundant molecule and keeping those for more abundant unaltered, we have the isotopic displacement of a line in an electronic band (v', v'') given by

$$\nu^i - \nu = (\nu_e^i - \nu_e) + (\nu_v^i - \nu_v) + (\nu_r^i - \nu_r) \qquad \ldots \qquad \ldots \quad (13)$$

For practical purposes, the electronic isotope displacement may be left out of account owing to its negligibly small magnitude. The exact expression for the vibrational isotope displacement is given approximately by

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$$\nu_v^i - \nu_v = (\rho - 1) \left\{ \omega_e'(v' + \tfrac{1}{2}) - \omega_e''(v'' + \tfrac{1}{2}) \right\}$$

$$- (\rho^2 - 1) \left\{ x_e'\omega_e'(v' + \tfrac{1}{2})^2 - x_e''\omega_e''(v'' + \tfrac{1}{2})^2 \right\} + \ \dots \ (14)$$

It is evident from the above equation that the vibrational isotopic displacement is constant for all lines of a given band. But it increases in magnitude from band to band of a system almost linearly with the interval, ν_v, from the system origin, ν_o, to the band origin and extrapolates to zero at the system origin. It would therefore be zero in any band whose origin happens to coincide with the system origin but it is not zero in the $(0,0)$ band.

The rotational isotope displacement is approximately given by

$\nu_r^i - \nu_r = (\rho^2 - 1) \times$ the wave-number interval between the line, whose isotope shift is to be calculated and the band origin, ν_o ...   .   (15)

It is also evident from equation (15) that the rotational displacement vanishes at the band origin.

Thus for any line of a given band the observed isotopic displacement is the algebraic sum of the constant vibrational and the varying rotational displacement given respectively by equations (14) and (15). If there are more than two isotopes, we may expect as many components of the band lines as there are isotopes, whose relative masses determine the positions of the corresponding lines in the spectrum. It may here be noted that in the preceding expressions, ρ is given by

$$\rho = \sqrt{\mu/\mu^i} \qquad \dots \qquad \dots \qquad \dots \ (16)$$

where μ is the reduced or effective mass of the molecule so that if M_1 stands for the mass of the isotopic atom and M_2 for the non-isotopic atom, we have

$$\mu = \frac{M_1 M_2}{M_1 + M_2} \quad \text{and} \quad \mu' = \frac{M_1' M_2}{M_1' + M_2} \qquad \ldots \ (17)$$

For the bands under consideration, if we assume that the lines associated with the rare isotopes of oxygen would be too faint to be observed, we can treat the oxygen atom as non-isotopic, so that taking Mg^{24} as the main isotope of magnesium, we have

	$Mg^{25}O$	$Mg^{26}O$
$\rho - 1$	-0.00803	-0.01552
$\rho^2 - 1$	-0.01600	-0.03080

Using these values of $(\rho - 1)$ and $(\rho^2 - 1)$ together with the cal- culated origins of the bands analysed, the isotopic displacements for each stronger line are calculated by means of equations (14) and (15). Fainter series of lines due to the less abundant mole- cules $Mg^{25}O$ and $Mg^{26}O$ were found in most cases in their calcu- lated positions within the errors of measurement. Definite evidence of their presence was secured by accounting for the lines which lie in the region not superposed by the lines of the succeed- ing band and which are not included in the two main P and R branches. The data for the (0,0) band are given in Table I to illustrate the agreement between the calculated and observed positions of the lines of the less abundant molecules. This establishes further the correctness of the K-numbering of the lines of the different bands in addition to confirming the identity of their emitter.

TABLE X.

Isotope Effect in (0, 0) band.

R-branch lines.

K	Mg^{25}O			Mg^{26}O		
	R^i (K)	$\triangle\nu$ (obs.)	$\triangle\nu$ (calc.)	R^i_2 (K)	$\triangle\nu$ (obs.)	$\triangle\nu$ (calc.)
9	16524·66	0·44	0·35	16524·36	0·74	0·68
10	27·83	0·30	0·40	27·40	0·73	0·77
11	30·78	0·52	0·45	30·34	0·96	0·87
12	34·01	0·46	0·50	35·57	0·90	0·97
13	37·10	0·60	0.56	36·63	1·07	1·07
14	40·60	0·52	0·61	39·94	1·18	1·17
15	44·10	0·64	0·67	43·39	1·35	1·29
16	47·83	0·71	0·73	47·09	1·45	1·40
17	51·67	0·84	0·79	51·01	1·50	1·52
18	55·78	0·87	0·86	55·01	1·64	1·65
19	59·94	1·02	0·93	59·07	1·89	1·79
20	64·44	1·02	1·00	63·54	1·92	1·92
21	68·97	1·19	1·07	67·96	2·20	2·07
22	73·80	1·22	1·15	...	...	2·22
23	78·78	1·26	1·23	77·65	2·39	2·37
24	83·90	1·32	1·32	82·72	2·50	2·53
25	89·04	1·54	1·40	...	...	2·70
26	94·50	1·62	1·49	...	...	2·87
27	16600·17	1·65	1·58	98·91	2·91	3·04
28	06·07	1·63	1·68	16604·42	3·28	3·22
29	11·95	1·76	1·77	10·29	3·42	3·41
30	17·83	2·04	1·87	(arc line)	...	3·60
31	(arc line)	...	1·97	22·33	3·82	3·79
32	30·46	2·11	2·07	28·67	3·90	3·99
33	36·83	2·27	2·18	34·79	4·31	4·19

TABLE X (contd.).

K	Mg²⁵O			Mg²⁶O		
	R^i (K)	$\triangle\nu$ (obs.)	$\triangle\nu$ (calc.)	$R^i_{\perp}$ (K)	$\triangle\nu$ (obs.)	$\triangle\nu$ (calc.)
34	16643·53	2·27	2·28	16641·51	4·29	4·40
35	50·27	2·38	2·39	48·02	4·63	4·61
36	57·09	2·53	2·51	54·79	4·83	4·82
37	64·01	2·69	2·62	61·07	5·03	5·04
38	71·12	2·81	2·73			
89	78·52	2·78	2·85			
40	85·70	3·15	2·97			
41	93·39	3·12	3·10			
42	16701·06	3·26	3·22			
43	08·85	3·46	3·35			
44	17·06	3·47	8·48			
45	25·20	3·64	3·61			
46	33·40	3·90	3·75			
47	42·09	3·81	8·89			
48	50·59	4·07	4·03			
49	59·43	4·14	4·17			
50	68·23	4·39	4·31			
51	77·41	4·42	4·46			
52	86·59	4·52	4·61			
53	96·15	4·63	4·76			
54	16805·53	5·00	4·92			
55	15·14	5·26	5·08			

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TABLE X (contd.).
P-branch lines.

K	Mg^{25}O			Mg^{26}O		
	P' (K)	Δν (obs.)	Δν (calc.)	P' (K)	Δν (obs.)	Δν (calc.)
29	16524·36	0·30	0·35	16523·98	0·68	0·67
30	27·40	0·43	0·40	26·98	0·85	9·76
31	30·73	0·86	0·45	30·34	0·80	0·87
32	34·01	0·57	0·51	33·57	1·01	0·97
33	87·70	0·44	0·56	37·10	1·04	1·08
34	41·12	0·77	0·62	40·60	1·29	1·20
35	45·01	0·77	0·68	44·59	1·29	1·32
36	49·01	0·76	0·75	48·24	1·53	1·44
37	53·09	0·82	0·81	52·27	1·64	1·57
38	57·17	1·02	0·88	56·44	1·75	1·70
39	61·67	0·96	0·95	60·96	1·67	1·84
40	66·12	1·07	1·03	65·19	2·00	1·98
41	...	...	1·10	69·64	2·27	2·12

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