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The Spectrum of MgF

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Measurements of the band heads and of the partially resolved rotational structure of the MgF absorption bands are used to evaluate the following constants for the $^2\Sigma$, $^2\Sigma$ system: $\nu_{00}=37{,}187.4$ cm^{-1}, $B_0'=0.537$, $B_0''=0.518\pm0.010$, $r_0''=1.75\times10^{-8}$ cm and for the $^2\Pi$, $^2\Sigma$ system: $\nu_{00}=27{,}846.5$, $B_0'=0.529$, $B_0''=0.518$, $A=-34.3$ (or $+38.3$). The isotope effect of Mg is observed in the $+1$ sequence of $^2\Sigma$, $^2\Sigma$ bands. The BeF bands do not appear in absorption under similar conditions.

WE have reported[1] qualitative observations on the absorption bands of MgF by using a 21-foot grating. The spectrum described by Walters and Barratt[2] was shown not to belong to this molecule. In absorption, we observe only the $^2\Sigma$, $^2\Sigma$ and $^2\Pi$, $^2\Sigma$ systems known in emission[3, 4] and a new system near λ2275. The latter apparently consists of a single sequence ($v'-v''=0$) of a doublet system, and may be analogous to the system designated[5] as $b^2\Pi$, $a^2\Sigma$ in CaF, SrF and BaF. Fig. 1e is a microphotometer curve of this group. It shows, besides the short sequence of band heads for which wave-lengths have been given,[1] an underlying continuous band with maximum absorption at λ2277.09. As a whole, it closely resembles the $+1$ sequence in the $a\,^2\Pi$, $^2\Sigma$ CaF bands,[6] and is probably to be interpreted similarly. The vibrational constants cannot be determined, because only one sequence is observed.

Measurements of our absorption plates have been made for the longer wave-length systems in order to find (1) approximate rotational constants, (2) the electronic doublet separation in the $^2\Pi$ state, and (3) definite evidence for the isotope effect of Mg. Much greater resolution than that afforded by a 21-foot grating is required to apply the combination principle to individual band lines. Enough of the rotational structure is resolved, however, to obtain some information on points (1) and (2).

$^2\Sigma$, $^2\Sigma$ SYSTEM

Figs. 1c and d shows the 0 sequence as it appears in absorption, and a microphotometer curve of this group. On the absorption spectrogram, measurements were made of 29 resolved lines, which obviously belong to the R branch of the strong 0,0 band. These could be accurately represented by the parabolic equation

$$\nu=37{,}259.49+2.5539\,M+0.01875\,M^2, \quad (1)$$

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[1] F. A. Jenkins and Rafael Grinfeld, Phys. Rev. **43**, 943 (1933).

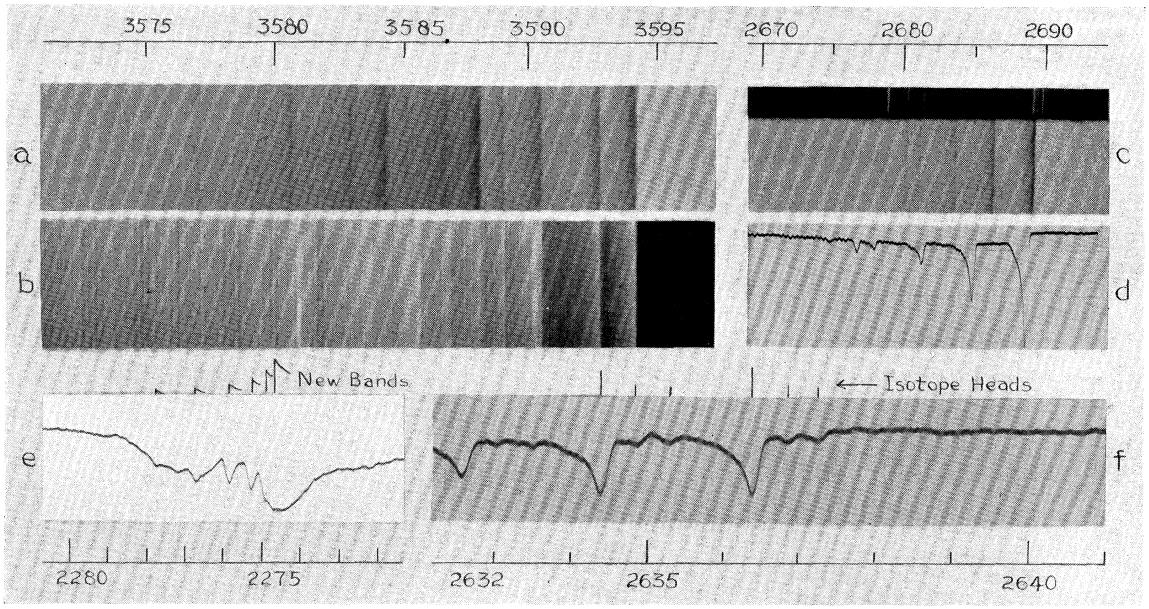
[2] O. H. Walters and S. Barratt, Proc. Roy. Soc. **A118**, 134 (1928).

[3] R. C. Johnson, Proc. Roy. Soc. **A122**, 199 (1929).

[4] W. Jevons, Proc. Roy. Soc. **A122**, 223 (1929).

[5] F. A. Jenkins and A. Harvey, Phys. Rev. **39**, 929 (1932).

[6] A. Harvey, Proc. Roy. Soc. **A133**, 336 (1931).



FIGS. 1. a and b. Absorption and emission, respectively, of the sequence $v'-v''=0$ in the $^2\Pi$, $^2\Sigma$ bands of MgF. Second order of the 21-foot grating. c. Absorption of the 0 sequence of $^2\Sigma$, $^2\Sigma$ bands, first order. d. Microphotometer curve of c on a slightly enlarged scale. e. Microphotometer curve of the new MgF bands on a first order plate. Positions of sharp heads are marked above. f. Microphotometer curve of the +1 sequence of $^2\Sigma$, $^2\Sigma$ bands, first order. The two subsidiary heads for each band are due to Mg ^{25}F and Mg ^{26}F, in the order of increasing wave-length.

TABLE I. *Lines of the R branch of the* $^2\Sigma$, $^2\Sigma$ *0,0 band.*

M	(obs.)	(calc.)	$o-c$	M	(obs.)	(calc.)	$o-c$
−14	37,227.38	37,227.41	−0.03	1	37,262.25	37,262.06	0.19
−13	229.34	229.45	−0.11	2	264.60	264.67	−0.07
−12	231.49	231.54	−0.09	3	267.32	267.32	0.00
−11	233.78	233.66	0.12	4	270.09	270.00	0.09
−10	235.86	235.82	0.04	5	272.57	272.72	−0.15
−9	238.03	238.02	0.01	6	275.29	275.49	−0.20
−8	240.24	240.26	−0.02	7	278.40	278.28	0.12
−7	242.73	242.53	0.20	8	281.24	281.12	0.12
−6	244.75	244.84	−0.09	9	283.69	283.99	−0.30
−5	246.97	247.19	−0.22	10	286.56	286.90	−0.34
−4	249.57	249.19	−0.38	11	289.89	289.85	0.04
−3	252.12	251.99	0.13	12	292.91	292.83	0.08
−2	254.44	254.45	−0.01	13	295.99	295.86	0.13
−1	257.02	256.95	0.07	14	299.06	298.92	0.14
0	259.63	259.49	0.14	—	—	—	—

which was found by least squares. The observed frequencies are compared with their calculated values in Table I. If the band has the structure assumed, this series should converge at the observed frequency of the 0,0 head. We find, from Eq. (1)

$$\nu_h \text{ (calc.)} = 37{,}172.52, \quad \nu_h \text{ (obs.)} = 37{,}172.69,$$

a very satisfactory agreement.

The 0,0 band shows, in absorption, a distinct minimum of intensity not far from the head. This we take to represent the band origin. We have measured its position both visually and on microphotometer curves, and find as a mean value $\nu_0 = 37{,}187.4 \pm 0.4$. This corresponds in Eq. (1) to the practically integral value $M = -39.96$, indicating that the true rotational quantum number for the R branch $K'' = M + 40$.

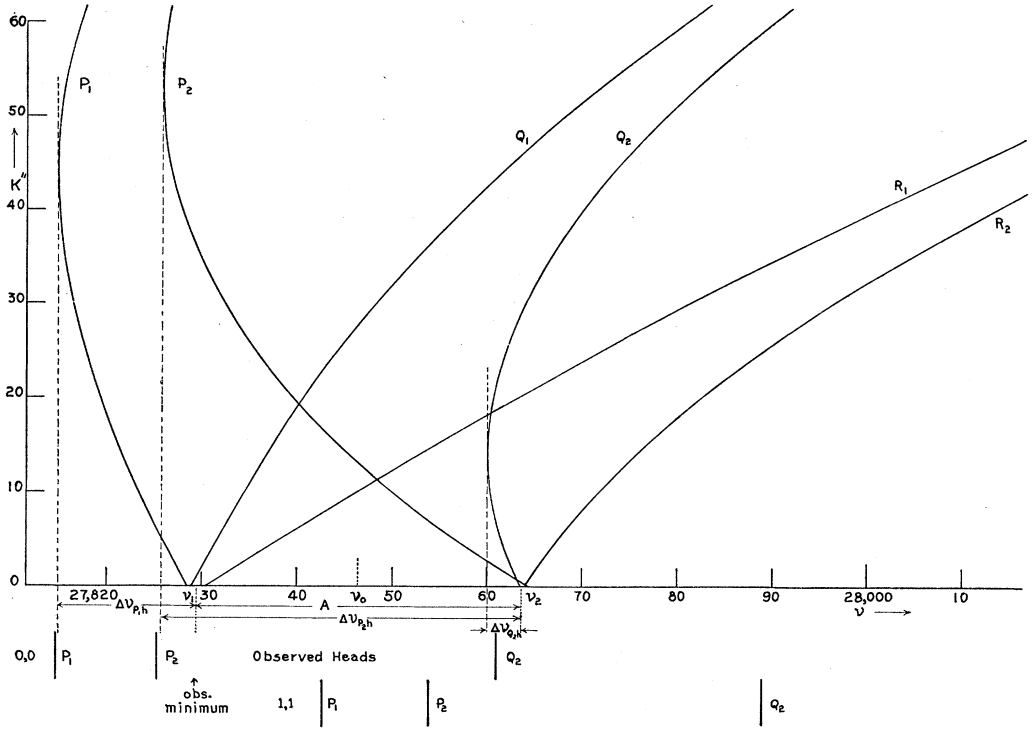


FIG. 2. Fortrat diagram of the 0,0 band of the $^2\Pi$, $^2\Sigma$ system, calculated by Eqs. (4), with the constants of Table II. The measured positions of the heads of the 0,0 and 1,1 bands are indicated below, as well as the position of minimum absorption, corresponding to one of the origins.

In $^2\Sigma$, $^2\Sigma$ bands the spacing of adjacent lines at the origin is[7] $B_0'+B_0''$, and from Eq. (1) we obtain $B_0'+B_0''=1.055\pm0.014$. The coefficient of M^2 in Eq. (1) gives $B_0'-B_0''=0.01875$ fairly accurately. Hence we have

$$B_0'=0.537\ \text{cm}^{-1}, \qquad I_0''=53.4\times10^{-40}\ \text{g cm}^2,$$
$$B_0''=0.518\pm0.010, \qquad r_0''=1.75\times10^{-8}\ \text{cm}.$$

This value of r_0'' fits well with the known values 1.36×10^{-8} for BeF[8] and 2.0×10^{-8} for CaF.[6]

$^2\Pi$, $^2\Sigma$ SYSTEM

Here the structure of the bands is more complex, as is evident in Figs. 1a and b. Hence measurements of the resolved lines cannot be as easily interpreted as in the simple $^2\Sigma$, $^2\Sigma$ bands. However, microphotometer curves of the absorption spectrum show two features which are of use. First, there is a distinct minimum at $\nu=27{,}829.4$, slightly on the long wave-length side of the second head of the 0,0 band. We interpret the three heads in each band as due to P_1, P_2 and Q_2 branches,[7] in the order of increasing frequency, and this minimum as the origin ν_1 of the low frequency sub-band, as indicated in Fig. 2. This sub-band is the $^2\Pi_{3/2}$, $^2\Sigma$ component, if the $^2\Pi$ state is inverted, as in BeF.[9] Second, a fairly regular series of lines appears in the tail of the sequence, which probably represents the Q branches of the 0,0 band. The two branches Q_1 and Q_2 must draw rapidly together, and become practically fused into one for high J values.

The position of the origin ν_2 of the $^2\Pi_{1/2}$, $^2\Sigma$ sub-band should lie very close to the Q_2 head, since the head of this branch occurs at a low quantum number. The measured frequency of this head is $\nu_{Q_2h}=27{,}861.02\sim\nu_2$. The mean of this and of the value of ν_1 found above gives the preliminary value $\nu_0=27{,}845.2$ as the origin of the whole 0,0 band. The lines of the assumed Q branch (mean of Q_1 and Q_2) should be given by $\nu=\nu_0+CM^2$, and their spacing by $\Delta\nu=2CM$.

[7] R. S. Mulliken, Rev. Mod. Phys. **3**, 89 (1931).
[8] F. A. Jenkins, Phys. Rev. **35**, 315 (1930).
[9] R. S. Mulliken, Phys. Rev. **38**, 836 (1931).

The spacing of the regular lines observed near the tail is 2.09 at $\nu=27{,}952$. Using the above expressions for ν and $\Delta\nu$, we obtain as a preliminary value $C=0.0103$. From this, $B'=(B_1+B_2)/2=B''+C=0.518+C=0.528$, since the value of B'' must be the same for this system as that found above for the $^2\Sigma$, $^2\Sigma$ system. A better value for ν_2 may now be obtained by correcting for the distance from the head to the origin $\Delta\nu_{Q_2h}=B_2^2/4C_2$. C_2 may be found from the relation[7] $C_2=C-2B'^2/A$, where A is the preliminary value of the electronic separation, -31.6 cm^{-1}. This yields $C_2=0.028$, and $\Delta\nu_{Q_2h}=2.7$ cm^{-1}. We therefore have, for the origins of the 0,0 band:

$$\nu_1=27{,}829.4, \qquad \nu_2=27{,}863.7, \qquad A=-34.3.$$

A more reliable value of C may now be obtained by applying the known formulas[7] for the separation of the P heads from the origins in this type of band, namely

$$\Delta\nu_{P_1h}=B_1^2/4C_1, \tag{2}$$

$$\Delta\nu_{P_2h}=(B_2+2B'')^2/4C_2. \tag{3}$$

Using the measured values of P_{1h} and P_{2h} given in Table II, we obtain from Eq. (2) $C_1=0.0044$ and from Eq. (3) $C_2=0.0170$. The former is somewhat too large, because of the rotational distortion, and the latter too small for the same reason. But the mean value, $C=0.0107$ should be accurate, and agrees well with the above preliminary value, 0.0103.

As a check on the value of the constants we have obtained, we have used them in the general Hill and Van Vleck term-formula for $^2\Pi$ states, and computed the frequencies of the band heads. With the equations

$$\begin{aligned} &\nu=\nu_0+F'-F'' \\ &F'_{2,\,1}=B'[(J+\tfrac{1}{2})^2-\Lambda^2 \\ &\qquad\pm\{(J+\tfrac{1}{2})^2-(A/B)(1-A/4B)\}^{\frac{1}{2}}] \\ &F''=B''K(K+1), \end{aligned} \tag{4}$$

with the constants given in Table II, the minimum values of ν for the P_1, P_2 and Q_2 branches can be found. The agreement with the measured values, shown in Table II, could probably be improved by further adjustment of the constants.

It is of interest that the modifications in relative intensity of the heads in passing from emission (arc, $T\sim4500$°C) to absorption (furnace, $T=1200$°C) are in exact accord with what we should expect due to the difference in temperature. In particular, the Q_2 heads, which occur at low J values, are greatly enhanced in absorption.

TABLE II. *Adopted constants and computed positions of the heads of the 0,0 $^2\Pi$, $^2\Sigma$ band.*

$A=-34.3$, $B''=0.5180$, $B'=0.5287$, $\nu_0=27{,}846.5$.

	ν_h(calc.)	ν_h(obs.)	J_h(calc.)
P_{1h}	27,814.7	27,814.4	$14\frac{1}{2}$
P_{2h}	27,825.7	27,825.2	$43\frac{1}{2}$
Q_{2h}	27,860.0	27,861.0	$52\frac{1}{2}$

Our value of the electronic separation in the $^2\Pi$ state, $A=-34.3$, differs from the previous estimates of 22 and 18.6 given by Mecke[10] and by Johnson,[3] respectively. However, these authors used the separations of certain *heads*, which do not even approximately represent the separations of the band origins where the rotational distortion is as great as in the present case ($A/B=-66.2$). In our work we have assumed a negative sign for A (inverted $^2\Pi$ state) merely by analogy with the corresponding bands in BeF.[9] If the analogy does not hold, and the doublet is normal, an equally good fit could be obtained by using $A=+38.3$ in the Hill and Van Vleck formula.

Isotope Effect

Some evidence for the Mg isotope effect in the $^2\Pi$, $^2\Sigma$ bands has been found by Johnson[3] in the measurements of the emission spectrum by Datta.[11] Magnesium has isotopes 24, 25 and 26 with an abundance ratio 7 : 1 : 1. Johnson identified 8 faint heads associated with the Q_2 heads of the 1,0 sequence, which he attributed to Mg ^{25}F. Since the observed shifts varied between 4.31 and 6.99 cm^{-1} (theoretical value ~6.4) and since no corresponding heads of Mg ^{26}F were found the evidence is not satisfactory.

The absorption spectrum is more suitable for the detection of faint isotopes. Since we first reported[1] two isotope heads associated with the 1,0 band of the $^2\Sigma$, $^2\Sigma$ system, plates showing stronger absorption have been taken, with the absorption tube at 1240°C. Fig. 1f shows a

[10] R. Mecke, Zeits. f. Physik **42**, 390 (1927).

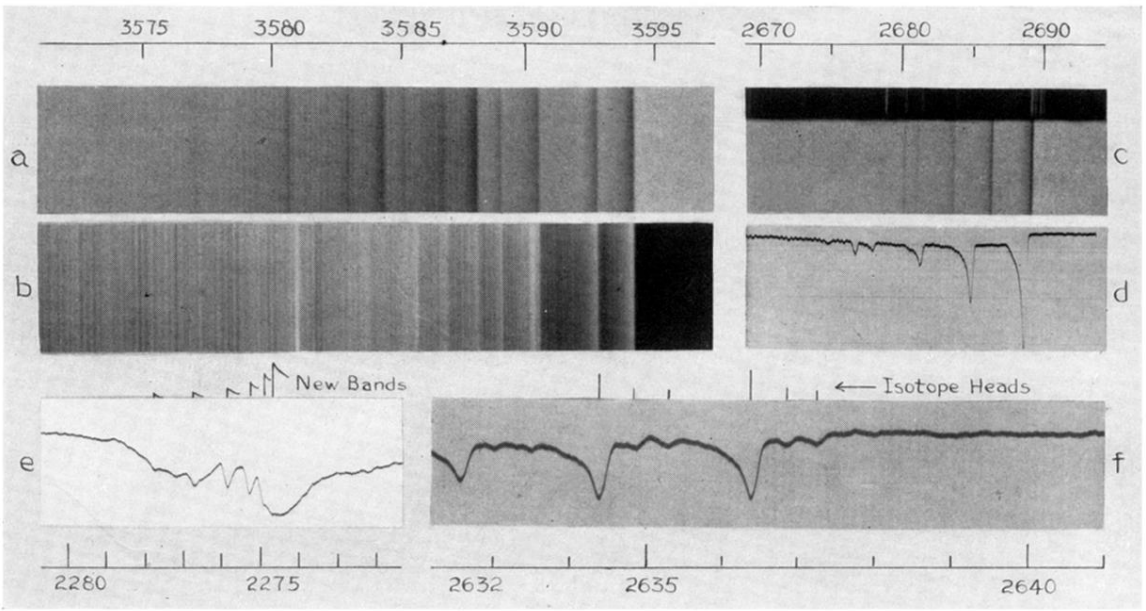
[11] S. Datta, Proc. Roy. Soc. **A99**, 436 (1921).

TABLE III. *Isotope shifts in the* $^2\Sigma$, $^2\Sigma$ *system.*

Band	Mg ^{24}F	Mg ^{25}F	Mg ^{26}F	$\Delta\nu$ (24,25) obs.	calc.	$\Delta\nu$ (24,26) obs.	calc.
1,0	37,918.9	37,912.5	37,906.8	6.4	6.92	12.1	13.35
2,1	947.8	940.8	934.9	7.0	7.18	12.9	13.85
3,2	973.9	(967.6)	960.5	(6.3)	7.41	13.4	14.30

microphotometer curve of the +1 sequence on these plates, and the isotopic bands due to Mg ^{25}F and Mg ^{26}F are apparent, not only for the 1,0 band, but also for 2,1 and 3,2. Measurements on these curves of the isotope shifts are given in Table III. The theoretical shifts were calculated by the approximate relation $\nu_v{}^i-\nu_v=(\rho-1)\nu_v$, with $\rho=1.00888$ for Mg ^{25}F and 1.01714 for Mg ^{26}F. The agreement is rather poor, because of the faintness of the heads and the neglect of the rotational shift.

In conclusion, it seems of value to report attempts to observe the BeF bands in absorption. This would be very desirable in order to verify the reported existence of the isotope Be^8. However, by using a procedure similar to that for MgF, that is, by heating pure BeF_2 with metallic Be and Mg, no absorption was obtained up to temperatures of 1200°C.



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