Band Spectra of MgCl, MgBr and MgI in Absorption

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The band spectra of MgCl, MgBr and MgI have been studied in absorption. Single systems of four-headed bands, lying between 3600 and 3950A for MgCl and between 3800 and 4000A for MgBr, have been observed. All of the bands degrade toward the violet. A vibrational analysis has been made for each of these systems. These vibrational analyses are consistent with the respective isotope shifts. The analysis of the system for MgCl is not in agreement with that proposed by Parker. A band system, lying between 4040 and 4200A and degrading toward the violet, was also observed for MgI. This system is insufficiently developed for a vibrational analysis.

O LMSTED[1] photographed the flame spectrum of MgCl, MgBr and MgI, but the bands were weak and overlapped by the magnesium oxide bands. Walters and Barratt[2] obtained the bands in absorption with a prism instrument but did not make a vibrational analysis. Parker[3] reported a vibrational analysis for the well-developed system of MgCl bands lying between 3600 and 3950A and also analyzed a weaker system lying in the same region and consisting of three bands, on the assumption that both systems have a common lower state.

EXPERIMENTAL

To obtain the band spectra of MgCl, MgBr and MgI in absorption, gaseous chlorine, bromine or iodine, respectively, was passed over magnesium metal that was heated in an open graphite tube about 30 cm in length in a carbon resistor furnace to a temperature of approximately 1600°C. Nitrogen gas was passed into the furnace to prevent, as far as possible, the oxidation of the magnesium and the burning of the graphite combustion tube. Light from a 500-watt incandescent lamp was passed through the graphite tube containing the vapor under investigation.

Preliminary observations were made on a Hilger E-1 quartz spectrograph, but all measurements were made on spectrograms taken on a 10-ft. concave grating which has a dispersion of approximately 2.7A per mm in the second order. Photographs were taken in the first, second and fourth orders, but most of the measurements were made on second-order plates.

MgCl BANDS

In MgCl only one system of bands was found in absorption. The bands degrade to the violet and apparently have four heads, but the heads are not of equal intensities. Table I shows the Deslandres arrangement of the heads of the bands due to $Mg^{24}Cl^{35}$ and Table II gives the vibrational quantum numbers, the observed wave numbers and the difference between the observed and calculated wave numbers for the Q_2 heads. Within the error of observation these Q_2 heads are represented by the equation:

$$\nu = 26,521.0 + 491.6u' - 2.54u'^2 \\ - 0.025u'^3 - 466.0u'' + 2.10u''^2,$$

where $u' = v' + \frac{1}{2}$ and $u'' = v'' + \frac{1}{2}$.

These tables contain the data on three strong sequences, $\Delta v = \pm 1$ and 0, and on two weak ones, $\Delta v = \pm 2$. In the $\Delta v = 0$ sequence the P_1 heads are considerably weaker than the P_2 heads and the P_2 heads are somewhat weaker than the heads due to the Q branches. In the -1 sequence the P_1 heads are stronger while in the $+1$ sequence they are weaker with respect to the Q heads than was the case in the $\Delta v = 0$ sequence. In both the $+1$ and -1 sequences an overlapping of the P heads occurs.

Each strong band due to $Mg^{24}Cl^{35}$ in the $+1$ or -1 sequence is accompanied by a weaker band due to $Mg^{24}Cl^{37}$ and $Mg^{25}Cl^{35}$. In favorable cases a still weaker band due to $Mg^{26}Cl^{35}$ and $Mg^{25}Cl^{37}$ was observed and in one case a band

[1] C. M. Olmsted, Zeits. f. wiss. Phot. **4**, 293 (1906).
[2] O. H. Walters and S. Barratt, Proc. Roy. Soc. **A118**, 120 (1928).
[3] A. E. Parker, Phys. Rev. **47**, 349 (1935).

TABLE I. *MgCl bands.*

v'		v'' 0	1	2	3	4	5	6	7	8
0	P_1	26455.5	25998.9							
	Q_1	26478.6	26016.9							
	P_2	26516.6	26057.3							
	Q_2	26533.9	26071.5							
1	P_1	26939.0	26480.7	26028.0	25577.7					
	Q_1	26964.1	26503.6	26046.1	25592.2					
	P_2	26998.1*	26541.3	26086.0						
	Q_2	27019.2	26558.0	26100.5	25646.7					
2	P_1				26057.3	25611.9				
	Q_1	27447.8	26985.1	26528.0	26074.8	25625.6				
	P_2	27473.8	27017.5	26565.3	26115.3	25666.9				
	Q_2	27502.5	27039.5	26581.4	26129.0	25678.8				
3	P_1						25643.3			
	Q_1		27459.5	27004.8	26551.8	26103.2	25657.7			
	P_2			27036.1	26587.7	26142.2	25697.2			
	Q_2		27514.6	27057.7	26604.7	26155.5	25710.0			
4	P_1									
	Q_1			27476.8	27024.2	26575.3	26131.1	25688.5		
	P_2					26609.7	26167.1	25727.3		
	Q_2			27529.3	27076.2	26626.7	26180.2	25739.6		
5	P_1									
	Q_1				27487.0	27041.4	26597.1	26155.5	25718.2	
	P_2								25756.0	
	Q_2				27539.8	27092.5	26646.2	26205.0	25767.8	
6	P_1									
	Q_1					27497.0	27057.7	26617.5	26180.2	25746.5
	P_2									
	Q_2					27550.1	27104.6	26663.3	26226.6	
7	P_1									
	Q_1							27069.6	26634.7	
	P_2									
	Q_2							27113.7	26676.5	26242.2

* Overlapped by (3,2) $Mg^{24}Cl^{37}$ band.

was found which should probably be attributed to $Mg^{26}Cl^{37}$. The bands due to $Mg^{24}Cl^{37}$ and $Mg^{25}Cl^{35}$ appeared as one because the values of $(1-\rho)$ are 0.011 and 0.012, respectively, where ρ is the square root of the ratio of the reduced masses of $Mg^{24}Cl^{35}$ and $Mg^{24}Cl^{37}$ or $Mg^{24}Cl^{35}$ and $Mg^{25}Cl^{35}$, and consequently the heads should be separated by only about 0.5 cm^{-1} in either the $+1$ or -1 sequence. Only the heads of the bands due to the molecule $Mg^{24}Cl^{35}$ were strong enough to be measured in the $+2$ or -2 sequence. The average measured isotope shift for the $Mg^{24}Cl^{35}$ and $Mg^{24}Cl^{37}$ or $Mg^{25}Cl^{35}$ molecules for the -1 sequence is 5.0 cm^{-1}, while for the $+1$ sequence it is 6.3 cm^{-1}. The corresponding values, calculated from theory for the vibrational isotope shift, are 4.7 cm^{-1} for $Mg^{24}Cl^{37}$ for the -1 sequence and 5.8 cm^{-1} for $Mg^{24}Cl^{37}$ or 6.3 cm^{-1}

for $Mg^{25}Cl^{35}$ for the $+1$ sequence. In the -1 sequence the $Mg^{25}Cl^{35}$ heads should not be observed because of overlapping by the stronger $Mg^{24}Cl^{37}$ bands. This overlapping should not occur in the $+1$ sequence. The agreement of the observed with the calculated isotope shift is very good.

In order to fix the notation appropriate for the head forming branches, the method of Jevons[4] was followed. He showed that for bands that degrade toward the violet, the separation between the P and Q heads increases as v'' decreases and also as v' increases. The separation of the first and second heads and that of the second and fourth heads of each band in $Mg^{24}Cl^{35}$ have been recorded in Table III for the different

[4] Jevons, *Report on Band Spectra of Diatomic Molecules,* p. 55.

vibrational quantum numbers. From this table it is evident that separation of the first and second heads increases as v'' is decreased and as v' is increased, indicating that the first is a P head and the second is a Q head. Also it is seen from the table that the separation of the second and fourth heads do not systematically increase or decrease with an increase or decrease of v' or v''. Hence the second head cannot be a P head and has accordingly been designated as a Q_1 head.

We have attributed this four-headed band system to a $^2\Pi\leftarrow{}^2\Sigma$ transition. This identification is not in agreement with that of Parker[3] who attributes it to a $^2\Sigma\rightarrow{}^2\Sigma$ or a $^2\Pi\rightarrow{}^2\Pi$ transition. His identification is based primarily on the fact that he observed only two heads for each band. We prefer our assignment for the following reasons:

1. This system resembles the $^2\Pi\rightleftarrows{}^2\Sigma$ system of MgF for which Jenkins and Grinfeld[5] have given a rotational analysis.

2. There is also a marked similarity between it and the $^2\Pi\rightarrow{}^2\Sigma$ system of BeCl which has been analyzed by Fredrickson and Hogan.[6]

3. The electronic structures of MgF, MgCl and MgBr are similar and this fact suggests that the same ground state might be expected in each case. In the MgBr system each band has four heads, suggesting that the transition should be $^2\Pi\leftarrow{}^2\Sigma$ or $^2\Sigma\leftarrow{}^2\Pi$. On a frequency scale the band system of MgCl lies between the band system of MgF and the band system of MgBr. This fact suggests

TABLE II. *Analysis of MgCl bands.*

v'	v''	ν(observed)	ν(obs.)-ν(calc.)	v'	v''	ν(observed)	ν(obs.)-ν(calc.)
1	3	25646.7	0.4	4	4	26626.7	1.7
2	4	678.8	−0.4	5	5	646.2	1.9
3	5	710.0	0.1	6	6	663.3	1.4
4	6	739.6	0.4	7	7	676.5	−1.2
5	7	767.8	0.9	8	8	688.3	−3.1
0	1	26071.5	−0.4	1	0	27019.2	−0.9
1	2	100.5	−0.2	2	1	039.5	0.1
2	3	129.0	0.5	3	2	057.7	0.3
3	4	155.5	0.6	4	3	076.2	2.0
4	5	180.2	0.2	5	4	092.5	3.2
5	6	205.0	1.5	6	5	104.6	1.9
6	7	226.6	1.3	7	6	113.7	−0.6
7	8	242.2	−3.2	2	0	502.5	1.3
0	0	533.9	0.2	3	1	514.6	−0.5
1	1	558.0	−0.3	4	2	529.3	1.7
2	2	581.4	−0.4	5	3	539.8	1.3
3	3	604.7	0.6	6	4	550.1	2.4

[5] F. A. Jenkins and R. Grinfeld, Phys. Rev. **45**, 229 (1934).

[6] W. R. Fredrickson and M. E. Hogan, Phys. Rev. **46**, 454 (1934).

that the three systems should have the same upper and lower states. If the transition for MgF is $^2\Pi\rightleftarrows{}^2\Sigma$, as suggested by Jenkins and Grinfeld, it seems highly probable that the band system of MgBr and that for MgCl should be attributed to a $^2\Pi\leftarrow{}^2\Sigma$ transition.

4. The correctness of this assignment is further indicated by the fact that all of the observed heads of the MgCl system are included in this analysis without assuming large perturbations and that the intensities of the bands vary in a regular manner.

MgBr BANDS

In MgBr a single band system, lying somewhat farther toward the red than the system for MgCl, was found. These bands also degrade toward the violet, but in this case each sequence is separated into two parts. Four sequences, the ±1, 0 and -2 were observed. Table IV shows the Deslandres arrangement of the observed bands and Table V gives the vibrational analysis, the observed wave numbers and the difference between the observed and calculated wave numbers of the Q_1 heads. Within the error of observation, the following formula represents the wave numbers of the Q_1 heads.

$$\nu = 25{,}765.2 + 393.8u' - 2.05u'^2$$
$$- 0.040u'^3 - 373.2u'' + 1.34u''^2,$$

where $u' = v' + \frac{1}{2}$ and $u'' = v'' + \frac{1}{2}$.

The Q_2 heads appear to converge and for the sequences, $\Delta v = 0$ and $\Delta v = 1$, the heads crowd together in such a way that they give the appearance of a broad absorption band. For the $\Delta v = 0$ sequence this absorption band extends from about 25,895 to 25,900 cm^{-1}. The heads designated as P heads are stronger in comparison to the Q heads than they were in the case of MgCl.

TABLE III. *Head-origin separations for MgCl bands.*

v'		v'' 0	1	2	3	4	5
0	Q_1-P_1	23.1	18.0				
	Q_2-Q_1	55.3	54.6				
1	Q_1-P_1	25.1	22.9	18.1	14.5		
	Q_2-Q_1	55.1	54.4	54.4	54.4		
2	Q_1-P_1				17.5	13.7	
	Q_2-Q_1	54.7	54.4	53.4	54.2	53.2	
3	Q_1-P_1						14.4
	Q_2-Q_1		55.1	52.9	52.9	52.3	52.3

TABLE IV. *MgBr bands.*

v''		0	1	2	3	4	5	6
v'								
	P_1	25762.5	25393.8					
0	Q_1	25775.3	25404.4					
	P_2	25872.1	25503.9					
	Q_2	25886.4	25514.8					
	P_1	26147.1	25780.9	25415.4	25052.0			
1	Q_1	26164.6	25794.5	25425.8	25060.1			
	P_2	26245.2	25880.7					
	Q_2	26263.6	25895.6	25527.6				
	P_1		26161.0	25798.1	25435.1	25074.7		
2	Q_1		26179.1	25811.8	25446.3	25083.9		
	P_2		26254.1	25887.7				
	Q_2		26265.3	25896.9	25531.9			
	P_1			26173.1		25453.5	25095.7	
3	Q_1			26191.5	25827.2	25464.8	25105.0	
	P_2			26258.8				
	Q_2				25898.1			
	P_1				26185.0		25469.3	25113.7
4	Q_1				26201.4	25840.6	25480.9	25123.9
	P_2							
	Q_2							
	P_1					26196.3		
5	Q_1					26206.4	25847.3	25490.7
	P_2							
	Q_2							

Since $(1-\rho)$ for the molecules $Mg^{24}Br^{79}$ and $Mg^{24}Br^{81}$ is only 0.003, the heads due to the different isotopes of bromine have not been resolved completely, although in the second order of the 10-ft grating the heads of the -2 sequence appear to be double and in the fourth order the heads of the $+1$ and -1 sequences also appear to be double. Band heads due to $Mg^{25}Br$ and $Mg^{26}Br$ have been observed under favorable conditions.

In the case of MgBr as in the case of MgCl, the method of Jevons was used to distinguish between the P and Q branches.

MgI BANDS

In MgI there appeared three regions of nearly continuous absorption, lying slightly to the red when compared to the bands found for MgBr. In these regions some band heads appear. In addition to these three regions of nearly continuous absorption there was, farther toward the red, a band system consisting of a few bands that degrade toward the violet. The observed wave numbers of three short sequences, probably $\Delta v = \pm 1$ and 0, of this system are recorded in

Table VI. The bands appear to be double headed, but since the heads lie so close together it has not been possible to classify them. If the first head of each sequence is a P head, ω'' should be approximately the difference between the first head of the 0 sequence and first head of the -1 sequence, while ω' should be approximately the difference between the first heads of the $+1$ and 0 sequences. Thus ω'' should be about 312 cm^{-1} and ω' about 318 cm^{-1}.

While the short wave-length sides of the regions of continuous absorption are not sharply defined, they are sharper than the long wave-

TABLE V. *Analysis of MgBr bands.*

v'	v''	ν(obs.)	ν(obs.)-ν(calc.)	v'	v''	ν(obs.)	ν(obs.)-ν(calc.)
1	3	25060.1	-0.3	0	0	25775.3	0.0
2	4	083.9	-0.1	1	1	794.5	0.1
3	5	105.0	0.4	2	2	811.8	0.1
4	6	123.9	0.9	3	3	827.2	0.3
5	7	136.2	-2.6	4	4	840.6	0.7
0	1	404.4	-0.4	5	5	847.3	-3.0
1	2	425.8	-0.8	1	0	26164.6	-0.3
2	3	446.3	-0.2	2	1	179.1	-0.4
3	4	464.8	0.4	3	2	191.5	-1.1
4	5	480.9	0.8	4	3	201.4	-1.0
5	6	490.7	-2.5	5	4	206.4	-3.7

length sides and are in the neighborhood of 24,980, 25,290, and 25,594 cm^{-1}. If the three regions correspond to the -1, 0, and $+1$ sequences, respectively, the difference between the first two numbers should give an approximate value of ω'', while the difference between the second and third numbers should correspond roughly to ω'. Thus ω'' for this system may be expected to be about 310 cm^{-1}, and ω' about 304 cm^{-1}. This value of ω'' is in good agreement with the value, 312 cm^{-1}, for the other system.

The author wishes to express his appreciation

TABLE VI. *MgI bands.*

$v'-v''$	-1	0	$+1$
	24010.6	24322.2	24640.2
	16.4	29.0	45.5
	19.2	36.3	50.7
	26.2		
	28.9		
	36.0		

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The Spectrum of Indium Oxide

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A rather complex spectrum of InO lying between the two In resonance lines at 4102A and 4511A is described. Most of the band heads are assigned to a $^2\Pi \rightarrow {}^2\Sigma$ system with the frequencies of the main $(R_2+Q_2?)$ heads given by the formula $\nu = 23{,}595.10 + 626.66(v'+\frac{1}{2}) - 3.40(v'+\frac{1}{2})^2 - 703.09(v''+\frac{1}{2}) + 3.71(v''+\frac{1}{2})^2 + 0.285(v''+\frac{1}{2})^3$. ν_e for the other spin component is at 23,033.10. The large cubic term causes rapid convergence of the few band sequences, giving rise to prominent "tail" bands.

IN a report of the analysis of a band system due to the GaO molecule, Marjorie L. Guernsey[1] discussed briefly a complex spectrum of indium oxide lying largely between the two In resonance lines at 4102A and 4511A. Although the experimental conditions indicated the InO molecule to be the emitter, no obvious regularities in the distribution of bands were noted. And since among the band heads degrading predominantly to the red there occur a number of violet degrading heads, it was suggested that there are two InO band systems overlapping in this region. A reproduction of this spectrum is given in Fig. 1.

Spectra are known[2] for the diatomic oxides of all the other elements of Group III of the periodic table excepting Tl and Ac. These band systems are all transitions between $^2\Pi$ and $^2\Sigma$ electronic states, with a $^2\Sigma$ state lying lowest in the level scheme for each molecule. Similarly we find that the vast majority of the InO band heads

constitute either a $^2\Pi \rightarrow {}^2\Sigma$ or a $^2\Sigma \rightarrow {}^2\Pi$ system, with the former designation preferred because of the energy level arrangement of the related molecules. The complexity of the spectrum arises from the near equality of the doublet interval in the $^2\Pi$ state with many of the $\Delta G(v)$ values in both states, producing interlacing of the band sequences, as well as the rapid convergence of these sequences to cause "tail" bands. We give the details below.

A Tl arc burning in air gives rise to no oxide band spectrum in the region of the resonance lines of Tl I. We conclude that one or both of the corresponding Tl O levels are unstable repulsion states, a situation harbingered by the fairly low stability of the lower state of the InO band system discussed in the present paper. This instability is to be contrasted with the apparently rather large dissociation energy of the ground state and the relative abundance of electronic levels in the intervening LaO molecule[3] in this group.

[1] M. L. Guernsey, Phys. Rev. **46**, 114 (1934).

[2] Cf. W. Jevons, *Report on Band Spectra of Diatomic Molecules*, or H. Sponer, *Molekülspektren*, for constants of the known energy levels and references to original papers.

[3] W. Jevons, Proc. Phys. Soc. **41**, 520 (1929).