THE COMPLEX BAND SPECTRUM OF DIATOMIC MANGANESE CHLORIDE IN THE VISIBLE REGION.

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INTRODUCTION.

Characteristic bands due to diatomic molecule manganese chloride are known to occur in four spectral regions (1) around λ 2500, (2) between λ 3500 and λ 4000, (3) λ 4300–λ 4600, and (4) between λ 4800 and λ 5100. Following Bacher (1948), these four systems may be designated as α, β, γ' and γ respectively. A complete analysis of the β system showed that the transition is a $^7\Pi$–$^7\Sigma$, while the α system with a simpler structure is suggested by Bacher to arise in a $^7\Sigma$–$^7\Sigma$ transition, with $^7\Sigma$ as the ground state common to both the systems. Mention was also made by him of the existence of another system γ in MnCl, MnBr and MnF, which was suggested as an intercombination system due to the transition $^5\Pi$–$^7\Sigma$ involving the lower state as the ground state $^7\Sigma$. For both γ and γ' systems, only measurements of a few diffuse bands as reported by Mesnage are just available in the literature. The present paper deals with the results obtained by the author in a detailed study of these two systems.

EXPERIMENTAL.

The spectrum was excited in a heavy current discharge from a 2,000-volt D.C. generator using a fused silica discharge tube of special design, which was described previously by the author (1949). This source was found suitable for the excitation of the spectra of the halides of such refractory elements as manganese, chromium, iron, cobalt and nickel. For photographing the spectrum, a Fuess glass spectrograph of high light gathering power was employed as the band systems γ and γ' are comparatively weaker than the others. The dispersion of the instrument is about 25–30A° per mm. in the region under investigation. A higher dispersion instrument is found unsuitable for a good reproduction of the two systems. Exposures varying from half a minute to 2 minutes' duration were given employing Ilford Selo-chrome plates.

STRUCTURE AND ANALYSIS OF THE γ SYSTEM.

Plate XIV$_{(a)}$ is a reproduction of the γ system in the region between λ 4800 and λ 5100. The bands are apparently arranged in four groups which may be designated as groups I, II, III and IV respectively starting from the red end. It was found that the wavenumber intervals between certain prominent bands in the neighbourhood of λ 4977·8 in group III and those of group I around λ 5075 are approximately equal to the vibrational frequency 384·7 of the ground state of MnCl. This at once suggested that groups II and III, which stand out prominently and are well developed, may form the $\Delta v = 0$ sequence and groups I and IV the $\Delta v = -1$ and $+1$ sequences respectively. A closer examination of the plates revealed that there are some line-like bands between groups II and III which lent further support to the view that the members of the two groups form the $\Delta v = 0$ sequence. Some of the bands in the various groups are red-degraded while others are line-like.

Bacher also reported that the $\Delta G(v'')$ intervals in the γ system of MnCl, MnBr and MnF suggest that the ground state is the lower state of the system. From a comparison of the electronic transitions in Mn atom with those of MnH, MnF, MnCl, MnBr and MnI, he suggested that the γ system which occurs only in emission and with comparatively less intensity than the other systems, may be an intercombination system arising in the transition $^5\Pi$–$^7\Sigma$. It is shown in the present paper that it is possible to interpret the structure of the $\Delta v = 0$ sequence of the γ system of MnCl on the basis of a $^5\Pi$–$^7\Sigma$ transition.

The possible rotational heads for the transition $^5\Pi$–$^7\Sigma$ may be formulated as follows. The ground state $^7\Sigma$ corresponds to Hund's coupling case (b). In a Σ state ($\Lambda = 0$), there is a spin splitting of each rotational level, i.e. for each value of K there will be 7 component levels with $J = K+S$ to $J = K-S$, which following Mulliken, may be designated as F_1, $F_2 \ldots F_7$ respectively. The separations of these levels are not ordinarily resolvable. The upper $^5\pi$ state may belong to case (a) or (b) or an intermediate state between the two. In fact, it approaches case (a) for low values of K and case (b) for higher values of K. For case (a) we get by combining Λ with Σ, five levels $^5\pi_{-1}$, $^5\pi_0$, $^5\pi_1$, $^5\pi_2$ and $^5\pi_3$ which in case (b) on account of the spin splitting will become F_5, F_4, F_3, F_2 and F_1 levels respectively. For each value of K there will be five values of J and the selection rules are that $\Delta J = 0$ or ± 1 and ΔK can be either 0 or ± 1 or ± 2 or ± 3.

A schematic diagram for the transition $^5\Pi$–$^7\Sigma$ representing the various expected branches is represented in Fig. 1. The form of the branches is indicated in the usual notation $T\ S\ R\ O\ P\ Q\ N$ corresponding to ΔK values of $+3$, $+2$, $+1$, 0, -1, -2, and -3 respectively. The rotational lines can be represented by the formula

$$\begin{aligned} \nu &= \nu_0 + F'(K) - F''(K) \\ &= \nu_0 + B'K'(K'+1) - B''K''(K''+1) \end{aligned}$$

where ν_0 represents the frequency of the null line of the band. The formulae for the individual forms are

Form	ΔK	
T	$+3$	$\nu = \nu_0 + F'(K+3) - F''(K)$
		$= \nu_0 + 12B' + (7B' - B'')K + (B' - B'')K^2$
S	$+2$	$\nu = \nu_0 + F'(K+2) - F''(K)$
		$= \nu_0 + 6B' + (5B' - B'')K + (B' - B'')K^2$
R	$+1$	$\nu = \nu_0 + F'(K+1) - F''(K)$
		$= \nu_0 + 2B' + (3B' - B'')K + (B' - B'')K^2$
Q	0	$\nu = \nu_0 + F'(K) - F''(K)$
		$= \nu_0 + (B' - B'')K + (B' - B'')K^2$
P	-1	$\nu = \nu_0 + F'(K-1) - F''(K)$
		$= \nu_0 - (B' + B'')K + (B' - B'')K^2$
O	-2	$\nu = \nu_0 + F'(K-2) - F''(K)$
		$= \nu_0 + 2B' - (3B' + B'')K + (B' - B'')K^2$
N	-3	$\nu = \nu_0 + F'(K-3) - F''(K)$
		$= \nu_0 + 6B' - (5B' + B'')K + (B' - B'')K^2$

Differentiating the above expressions with respect to K and equating to zero (the condition for head formation) we get K_h, the value of K at which the head is formed. For the case in which $B'' > B'$ (red-degraded bands) K_h is positive for R, S, T forms and negative for the others if as usually the case $3B' > B''$. The K_h values for the latter are shown below.

ΔK	0	$+1$	$+2$
Form	Q	R	S
K_h	0	$\dfrac{3B' - B''}{2(B'' - B')}$	$\dfrac{5B' - B''}{2(B'' - B')}$

Hence in the present system of MnCl we expect only the Q, R, S forms only as head-forming. These transitions are shown in Fig. 1.

TABLE I.

MnCl bands. γ System.

Sequence.	Wavelength. A°	Wavenumber cm.$^{-1}$	I	v', v''	ΔJ. -1	ΔJ. 0	ΔJ. $+1$
$\Delta v = -1$	5086·5	19654·4	4				
,,	5078·4	19685·8	9	0,1	$^{Q}P_{5}$	Q_{56}	$^{Q}R_{57}$
,,	*5075·0	19699·0	5	0,1	$^{R}P_{54}$	$^{R}Q_{5}$	R_{56}
,,	5066·9	19730·5	2				
$\Delta v = 0$	5041·7	19829·1	6				
,,	5037·2	19846·8	7	0,0	$^{Q}P_{1}$	Q_{12}	$^{Q}R_{13}$
,,	5033·6	19861·0	5	0,0		$^{R}Q_{1}$	R_{12}
,,	*5029·8	19876·0	6	0,0			$^{S}R_{1}$
,,	5025·4	19893·4	7	1,1	$^{Q}P_{2}$	Q_{23}	$^{Q}R_{24}$
,,	5021·2	19910·0	4	0,0	$^{Q}P_{2}$	Q_{23}	$^{Q}R_{24}$
,,	5018·8	19919·5	6	0,0	$^{R}P_{21}$	$^{R}Q_{2}$	R_{23}
,,	5015·2	19933·8	4	0,0		$^{S}Q_{21}$	$^{S}R_{2}$
,,	5013·2	19941·8	6				
,,	5007·3	19965·3	4	0,0	$^{Q}P_{3}$	Q_{34}	$^{Q}R_{35}$
,,	*5004·8	19975·3	4	0,0	$^{R}P_{32}$	$^{R}Q_{3}$	R_{34}
,,	4998·3	20001·2	4				
,,	4991·0	20030·5	7	0,0	$^{R}P_{43}$	$^{R}Q_{4}$	R_{45}
,,	4981·5	20068·7	8	0,0	$^{Q}P_{5}$	Q_{56}	$^{Q}R_{57}$
,,	4977·8	20083·6	10	0,0	$^{R}P_{54}$	$^{R}Q_{5}$	R_{56}
$\Delta v = +1$	4900·8	20399·2	3	1,0	$^{R}P_{43}$	$^{R}Q_{4}$	R_{45}
,,	4891·3	20438·8	5	1,0	$^{Q}P_{5}$	Q_{56}	$^{Q}R_{57}$

* Bands superposed by Mn lines.

With the aid of the scheme of expected transitions in a $^{5}\Pi$–$^{7}\Sigma$ as shown in Fig. 1, the vibrational and rotational assignments of band heads were made as shown in Table I. The subscripts given in the last column relate to the numbering of F levels in the upper and lower states. For each of the spin rotational levels, the P, Q, R branches of the same form are not ordinarily resolvable even under high dispersion and therefore the same band is assigned for the three branches.

Plate XIV$_{(a)}$ shows the main head-forming R branches ($\Delta K = \Delta J = +1$) R_{56}, R_{45}, R_{34}, R_{23}, R_{12} of the $\Delta v = 0$ sequence. The interval separations between these heads as shown in Table II indicates that the coupling constant A is of the order of 56 cm.$^{-1}$.

TABLE II.

v', v''	R_{56}		R_{45}		R_{34}		R_{23}		R_{12}
0, 0	20083·6	53·1	20030·5	53·2	19975·3	55·8	19919·5	58·5	19861·0

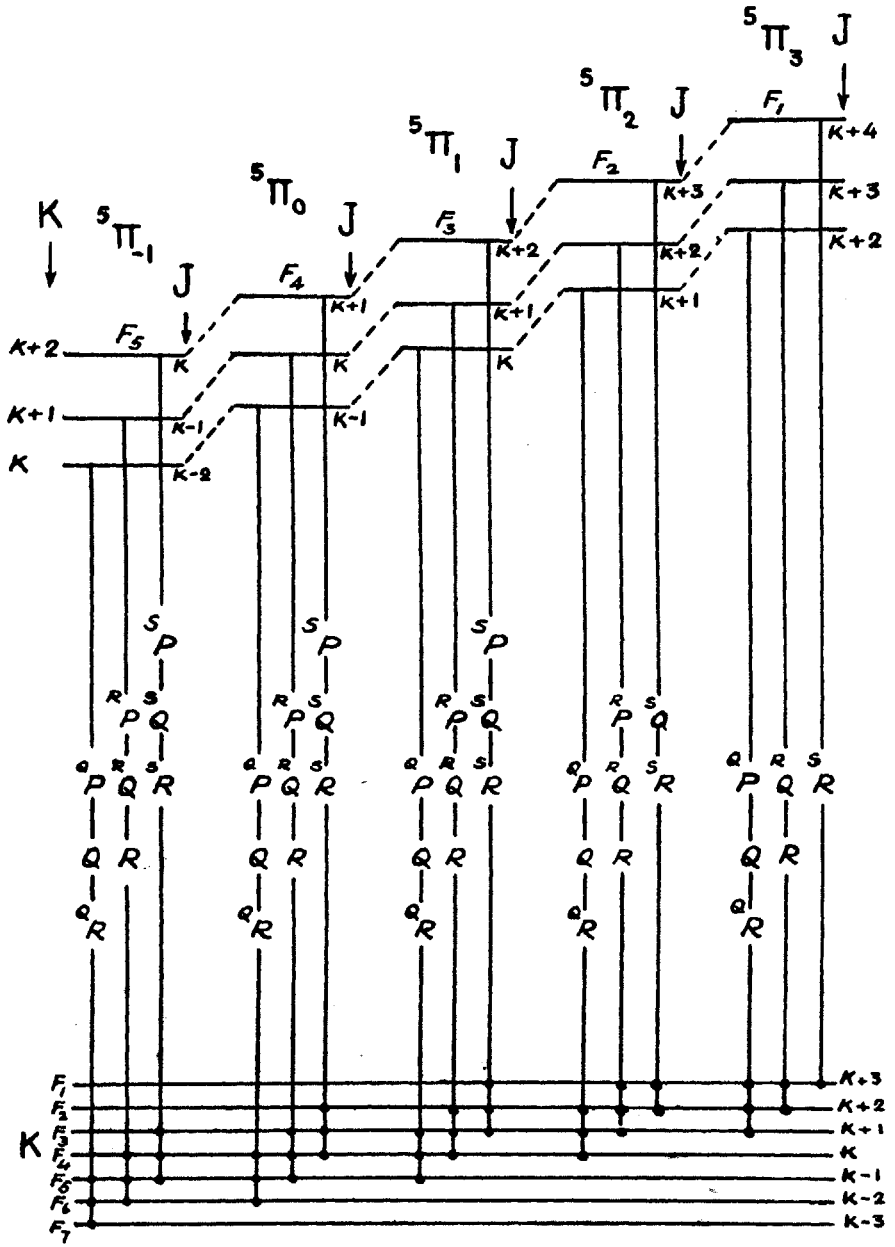
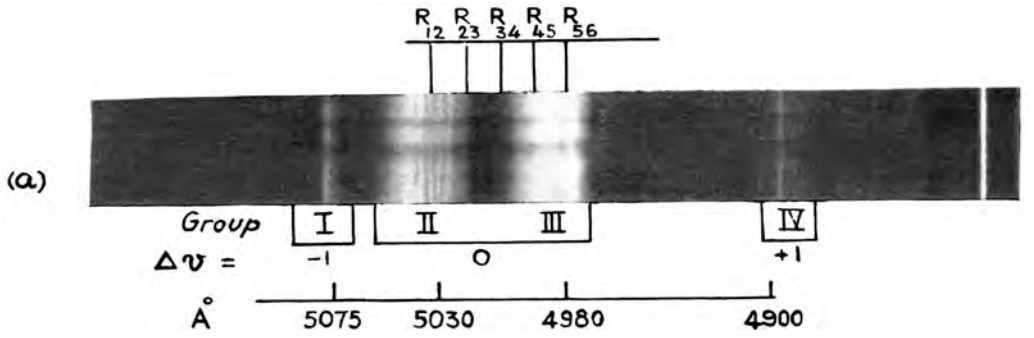
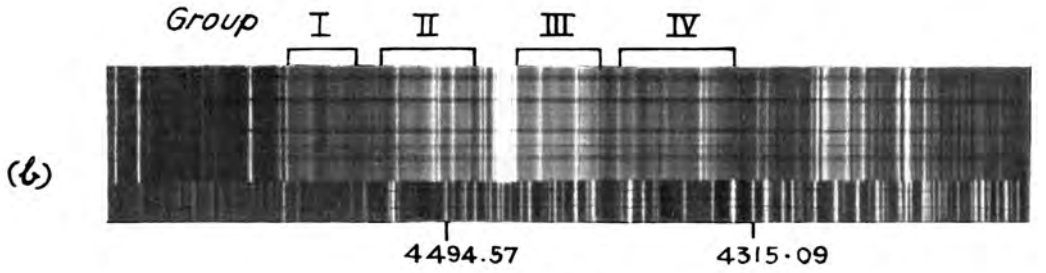


Fig. 1.

Scheme of transitions in $^5\Pi$–$^7\Sigma$ when $^5\pi$ is intermediate between case (*a*) and (*b*).





MnCl bands.

$I_{(a)}$. γ system.
$I_{(b)}$. γ' system.

With a multiplicity of 5 for the upper state, the overall width of the multiplet is $4\times56 = 224$ cm.$^{-1}$ Hence there should be no overlapping of band heads of the $\Delta v = 0$ sequence with those of the $\Delta v = -1$ sequence. This feature is also evident from the reproduction. The multiplet analysis was shown in detail in the case of band heads of the $\Delta v = 0$ sequence as the development of $\Delta v = -1$ and $+1$ sequences is poor. From the observed $\Delta G(v)$ intervals as shown in Table III, the following approximate vibrational constants were derived for the system :

$$\omega_e' = 370 \text{ cm.}^{-1}$$

$$\omega_e'' = 384 \text{ cm.}^{-1}$$

TABLE III.

$\Delta K = \Delta J$ Heads v', v''	R_{56}	Q_{56}
0, 0	20083·6	20068·7
	384·6	382·9
0, 1	19699·0	19685·8
$\Delta K = \Delta J$ Heads v', v''	Q_{56}	R_{45}
0, 0	20068·7	20030·5
	370·1	368·7
1, 0	20438·8	20399·2

The γ' system of MnCl.

Plate XIV$_{(b)}$ is a reproduction of the γ' system occurring in the region between λ 4300 and λ 4600. It consists of four groups which, starting from the red end, may be designated as groups I, II, III and IV respectively. Some of the bands seem to be degraded towards the red while some are headless and others are diffuse. It is not possible to interpret the structure of this system owing to the poor development of sufficient number of band heads in any group. However, a wavenumber interval of approximately 384 cm.$^{-1}$ is observed between certain prominent bands of groups I and II as shown in Table II. This suggests that the ground state $^7\Sigma$ may be the lower state of the system.

TABLE IV.

Group II.		Group I.
22302·3		21917·9
	384·4	
22184·5		21800·4
	384·1	
22166·3		21782·3
	384·0	

As the groups are not well developed, only a catalogue of the band heads is given in Table V.

TABLE V.

MnCl bands. γ' System.

Group.	Wavelength.	Intensity.	Wavenumber.
I	4595·0(*R*)	2	21756·7
,,	4589·6	2	21782·3
,,	4585·8	8	21800·4
,,	4569·3	3	21879·1
,,	4561·2	5	21917·9
,,	4556·8	3	21939·1
,,	4551·4	5	21965·1
II	4514·9(*R*)	6	22142·7
,,	4510·1	3	22166·3
,,	*4506·4	7	22184·5
,,	4482·6(*R*)	10	22302·3
III	4468·0(*R*)	4	22375·1
,,	4463·6	3	22397·2
,,	4427·4(*R*)	10	22580·3
,,	4423·8	3	22598·7
,,	4421·7	2	22609·4
,,	4405·7	5	22691·5
IV	4383·5(*D*)	5	22806·4
,,	4354·0(*V*)	4	22961·0
,,	4346·5	4	23000·6
,,	4329·8	4	23089·3
,,	4326·0	3	23109·6

* Band superposed by Mn line.
R—Red-degraded. *V*—Violet-degraded. *D*—Diffuse.

ABSTRACT.

The emission spectrum of diatomic manganese chloride is excited in a heavy current discharge through the vapour and photographed in the visible region using a Fuess glass spectrograph. Two systems designated here as γ and γ' were obtained more extensively than those reported by Mesnage. The γ system occurring in the region λ 4800–λ 5100 has been interpreted on the basis of a $^5\pi$–$^7\Sigma$ transition involving terms of high multiplicity. The vibrational constants ω_e' and ω_e'' were approximately obtained as 370 cm.$^{-1}$ and 384 cm.$^{-1}$ respectively.

Measurements of 22 bands occurring in four groups of the γ' system were given and a recurring wavenumber interval of 384 cm.$^{-1}$ between some bands is also indicated.

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