EMISSION SPECTRA OF THE MANGANESE HALIDES

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Plates XXVA and B

ABSTRACT. Bacher's analysis of the MnCl bands in the region λ 3900–λ 3500, as arising from the electronic transition $^7\Pi-^7\Sigma$, is extended to the higher sequences $\Delta v=\pm 1$, ± 2, ± 3. A similar analysis is worked out for the $\Delta v=+1$ sequence of MnBr bands.

INTRODUCTION

In a short note, the author (Rao, 1948) reported characteristic bands in the region λ3900-λ3500 attributed to the diatomic molecule MnCl in a heavy current discharge. An analysis of these bands was communicated in a previous paper (1948 and 1949). Considering the previously published work of Rochester and Olsson (1939) on the band spectrum of MnF, the bands due to the MnCl molecule were attributed to the transition $^1\Pi-^1\Sigma$ and the vibrational constants $\omega'_e=413.3$ and $\omega''_e=385.6$ were estimated. It was, however, pointed out that there was the main difficulty in the above interpretation, namely, the very abnormal intensity peculiarity, chiefly, in the band heads forming the $\Delta v=0$ sequence. Mulier's (1943) suggestion of an electronic transition $^7\Pi-^7\Pi$ was also considered; but in view of the greater probability of a Σ-state as the ground state of the molecule, it was suggested that the observed complexity of the bands may be due to a high mulitiplicity Π term for the upper state only, the probable transition thus being $^7\Pi-^7\Sigma$. While a more detailed study of the bands, on this basis, of complex molecular terms was in progress, an interesting and comprehensive paper was published by Bacher (1948). This system of manganese chloride, designated by him, as system β, was obtained only in absorption. Besides this, the corresponding system in MnBr and MnI were also obtained in absorption. Emission bands were recorded only for manganese fluoride. In all these molecules the β system was attributed to the transition $^7\Pi-^7\Sigma$ similar to the one suggested by Pearse and Gaydon (1935) and established by Nevin (1948) in MnH. Bacher published an analysis completely for all the groups $\Delta v=0$, ± 1, ± 2, for the MnF molecule. In MnCl and MnBr, he gave the classification only for the $\Delta v=0$ sequence. Perhaps in the latter two molecules, since the absorption spectra alone were recorded, the groups with $\Delta v\neq 0$ might have been poorly developed. The emission spectra of these two molecules were obtained by the author in the present investigation with sufficient intensity as to justify an extension of the scheme to the higher sequences as well. This extended analysis is presented in the following sections.

The experimental arrangement was described in detail previously. It will be seen that a discharge tube of quite a simple design without either external heating of the substance or water cooling of the discharge tube and circulation of the helium gas, as used by Bacher, is found sufficient for the excitation of all the halide bands. The heavy current discharge itself produces enough local heating to vaporise the substance. In the case of MnF, the spectrum is obtained free from any trace of SiF bands. At a flash voltage of 1500 volts from a D. C. generator and with currents of 0.6, 0.5, and 0.3 amperes for MnF, MnCl and MnBr repectively, exposures of just 3 minutes' duration gave good spectra with a Hilger quartz Littrow spectrograph on Ilford S. R. plates. All the bands recorded by Bacher for the three molecules MnF, MnCl and MnBr have been obtained. But for the iodide, this experimental set-up was not suitable.

RESULTS

MnCl. Tables I to VI contain the observational data obtained with manganese chloride in the present work. They relate to the sequences $\Delta v = \pm 1, \pm 2, \pm 3$. The data on the $\Delta v = 0$ sequence is omitted as it was already completely reported by Bacher. The last two columns in these tables give the vibrational and the rotational assignments of the different heads. The classification is closely analogous to that determined for the $\Delta v = 0$ sequence by Bacher. The structure corresponds to the transition $^7\Pi - ^7\Sigma$. For a full discussion of the multiplet analysis, reference may be made to Bacher's

TABLE I

MnCl bands $\Delta v = +1$ sequence.

λ	ν	I	v′, v″	ΔJ		
				−1	0	+1
3663.17	27291.0	2	1,0	P_7		
62.36	27297.1	2			—	
61.55	27303.1	2	1,0	$^QP_{76}$	Q_7	
60.61	27310.1	3				
59.44	27318.8	•2	1,0	$^OP_{67}$		
58.32	27327.2	3	2,1	$^QP_{76}$	Q_7	
57.45	27333.7	1	1,0	P_6	$^PQ_{67}$	

TABLE I (*contd.*)

MnCl bands $\Delta v = +1$ sequence.

λ	ν	I	v′, v″	ΔJ −1	ΔJ 0	ΔJ +1
56·12	27341·1	2	1,0	${}^{Q}P_{65}$	Q_6	${}^{Q}R_{67}$
55·49	27348·6	5				
54·59	27355·1	5	2,1	P_6	${}^{P}Q_{67}$	
53·55	27362·0	2	1,0	${}^{O}P_{56}$	${}^{O}Q_{57}$	
52·43	27371·3	3	2,1	${}^{Q}P_{65}$	Q_6	${}^{Q}R_{67}$
51·41	27378·9	5	1,0	P_5	${}^{P}Q_{56}$	${}^{P}R_{57}$
50·51	27385·4	1	1,0	${}^{Q}P_{54}$	Q_5	${}^{Q}R_{56}$
49·52	27393·1	3				
48·38	27401·7	5	2,1	P_5	${}^{P}Q_{56}$	${}^{P}R_{57}$
47·53	27408·0	5	1,0	${}^{O}P_{45}$	${}^{O}Q_{46}$	${}^{O}R_{47}$
46·53	27415·6	3	2,1	${}^{Q}P_{54}$	Q_5	${}^{Q}R_{56}$
45·33	27424·6	6	1,0	P_4	${}^{P}Q_{45}$	${}^{P}R_{46}$
44·53	27430·6	2	1,0	${}^{Q}P_{43}$	Q_4	${}^{Q}R_{45}$
43·99	27434·7	5	1,0	${}^{N}P_{35}$	${}^{N}Q_{36}$	${}^{N}R_{37}$
42·28	27447·5	6	2,1	P_4	${}^{P}Q_{45}$	${}^{P}R_{46}$
41·07	27456·7	6	1,0	${}^{O}P_{34}$	${}^{O}Q_{35}$	${}^{O}R_{36}$
39·82	27466·1	4				
39·15	27471·1	4	1,0	P_3	${}^{P}Q_{34}$	${}^{P}R_{35}$
38·09	27479·1	6	2,1	${}^{O}P_{34}$	${}^{O}Q_{35}$	${}^{O}R_{36}$
37·21	27485·8	3	1,0	${}^{N}P_{24}$	${}^{N}Q_{25}$	${}^{N}R_{26}$
36·23	27493·2	4	2,1	P_3	${}^{P}Q_{34}$	${}^{P}R_{35}$
35·07	27502·0	6	1,0	${}^{O}P_{23}$	${}^{O}Q_{24}$	${}^{O}R_{25}$
34·17	27508·8	3				
33·15	27516·5	4	1,0	P_2	${}^{P}Q_{23}$	${}^{P}R_{24}$
32·06	27524·8	5	2,1	${}^{O}P_{23}$	${}^{O}Q_{24}$	${}^{O}R_{25}$
29·82	27541·8	6				
28·87	27549·0	4	1,0	${}^{O}P_{12}$	${}^{O}Q_{13}$	${}^{O}R_{14}$
28·05	27555·2	3				
27·21	27561·6	3	1,0	P_1	${}^{P}Q_{12}$	${}^{P}R_{13}$

TABLE II

MnCl bands $\Delta v = +2$ sequence.

λ	ν	I	v', v''	ΔJ		
				-1	0	$+1$
3606.67	27718.5	1	2,0	${}^{O}P_{67}$		
05.51	27727.5	3	3,1	${}^{O}P_{76}$	Q_{7}	
03.81	27740.5	2	2,0	P_{6}	${}^{P}Q_{67}$	
02.18	27753.1	3	3,1	P_{6}	${}^{P}Q_{67}$	
00.31	27767.5	2	2,0	${}^{O}P_{56}$	${}^{O}Q_{57}$	
3598.17	27784.0	2	2,0	P_{5}	${}^{P}Q_{56}$	${}^{P}R_{57}$
96.37	27797.0	2	3,1	P_{5}	${}^{P}Q_{56}$	${}^{P}R_{57}$
92.90	27824.8	1				
91.87	27839.7	2	2,0	P_{4}	${}^{P}Q_{45}$	${}^{P}R_{46}$
89.46	27851.4	2	3,1	P_{4}	${}^{P}Q_{45}$	${}^{P}R_{46}$
87.76	27864.0	1	2,0	${}^{O}P_{34}$	${}^{O}Q_{35}$	${}^{O}R_{36}$
85.32	27883.0	2	3,1	${}^{O}P_{34}$	${}^{O}Q_{35}$	${}^{O}R_{36}$
83.40	27897.8	2	3,1	P_{3}	${}^{P}Q_{34}$	${}^{P}R_{35}$
81.70	27911.1	2	2,0	${}^{O}P_{23}$	${}^{O}Q_{24}$	${}^{O}R_{25}$
80.84	27918.5	2	2,0	P_{2}	${}^{P}Q_{23}$	${}^{P}R_{24}$
79.56	27928.5	2	3,1	${}^{O}P_{23}$	${}^{O}Q_{24}$	${}^{O}R_{25}$
76.86	27949.5	1				
75.73	27958.1	1	2,0	${}^{O}P_{12}$	${}^{O}Q_{13}$	${}^{O}R_{14}$

TABLE III

MnCl bands $\Delta v = +3$ sequence.

λ	ν	I	v', v''	ΔJ		
				-1	0	$+1$
3545.99	28192.9	1	3,0	P_{5}	${}^{P}Q_{56}$	${}^{P}R_{57}$
44.37	28205.7	1	4,1	P_{5}	${}^{P}Q_{56}$	${}^{P}R_{57}$
42.80	28218.2	1	3,0	${}^{O}P_{45}$	${}^{O}Q_{46}$	${}^{O}R_{47}$
40.69	28235.0	1	3,0	P_{4}	${}^{P}Q_{45}$	${}^{P}R_{46}$
38.59	28251.8	1	1,1	P_{4}	${}^{P}Q_{45}$	${}^{P}R_{46}$
37.05	28264.1	1	3,0	${}^{O}P_{34}$	${}^{O}Q_{35}$	${}^{O}R_{36}$
35.11	28279.6	1	4,1	${}^{O}P_{34}$	${}^{O}Q_{35}$	${}^{O}R_{36}$
32.98	28296.7	1	1,1	P_{3}	${}^{P}Q_{34}$	${}^{P}R_{35}$
30.40	28316.9	0	3,0	P_{2}	${}^{P}Q_{23}$	${}^{P}R_{24}$
28.9	28329.4	1	4,1	${}^{O}P_{23}$	${}^{O}Q_{24}$	${}^{O}R_{25}$
27.63	28339.6	2				
25.83	28354.0	1	3,0	${}^{O}P_{12}$	${}^{O}Q_{13}$	${}^{O}R_{14}$

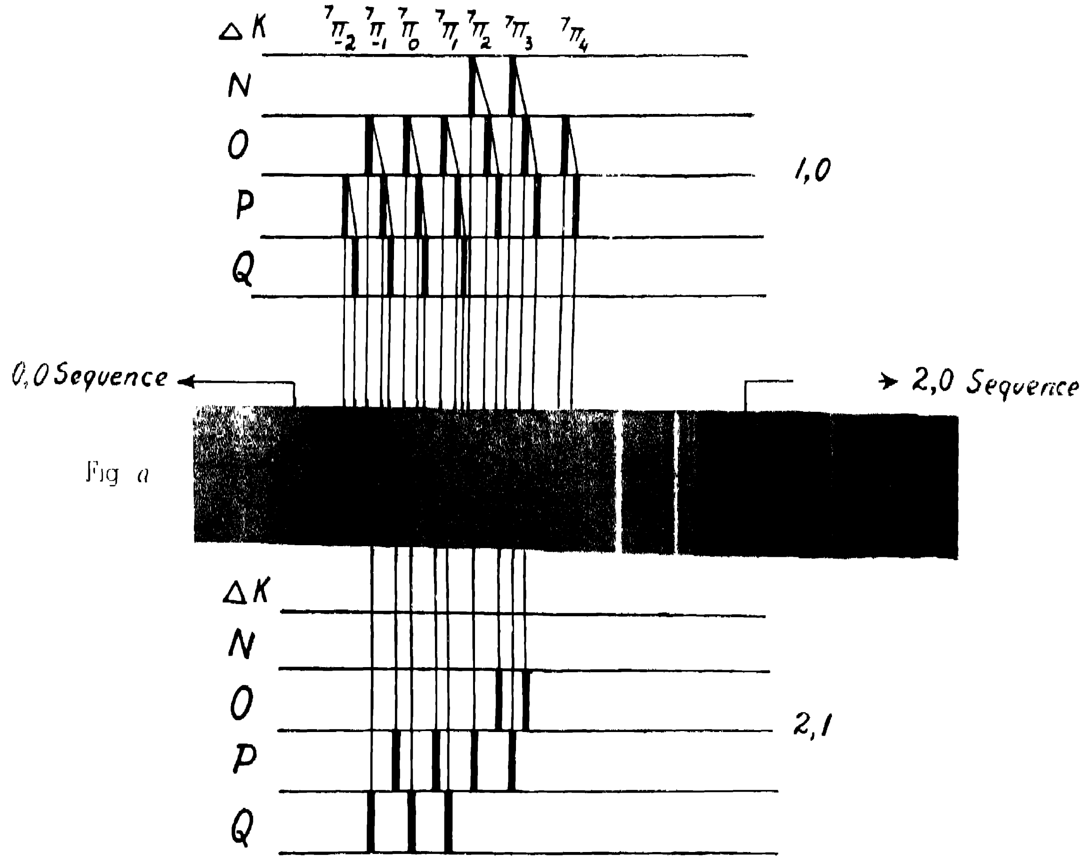


Fig *a*

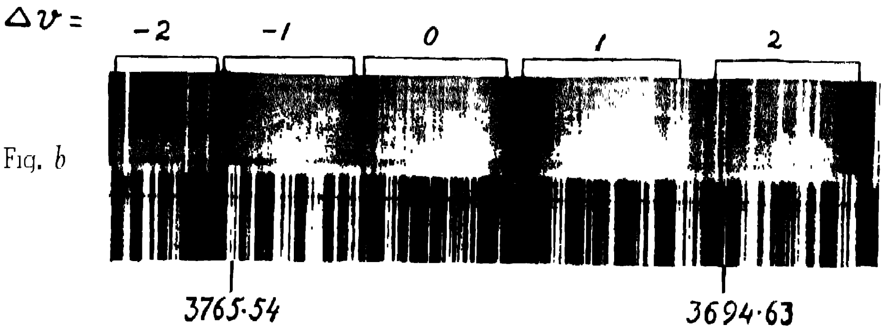
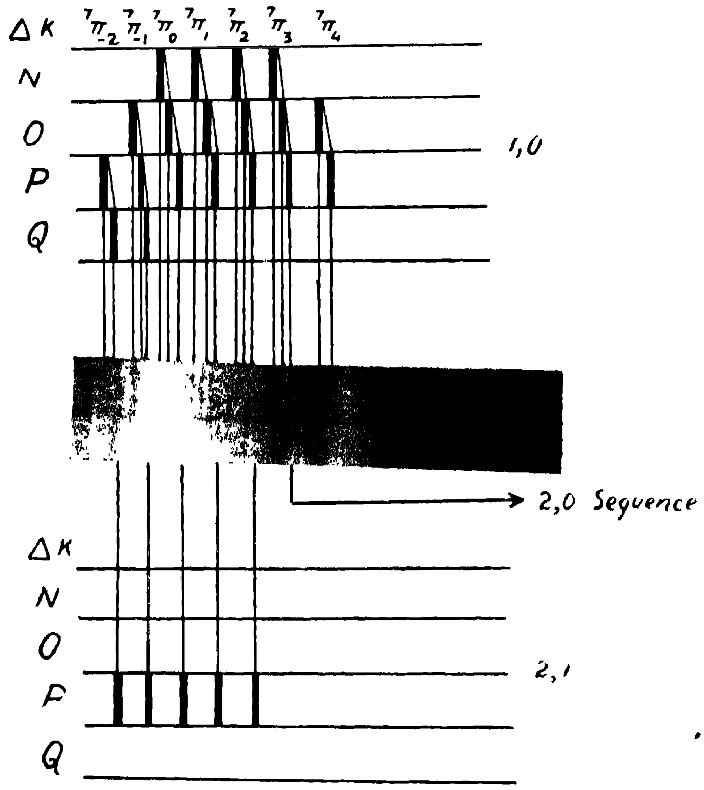


Fig. *b*

MnCl bands. Fig. *a*—(1,0) sequence, Fig. *b*—Overall picture.



MnBr bands, structure of the (1,0) sequence

TABLE IV

MnCl bands: $\Delta v = -1$ sequence.

λ	ν	I	v′, v″	ΔJ: −1	ΔJ: 0	ΔJ: +1
3772.83	26497.8	2	0,1	P_7		
70.84	26511.8	3	0,1	${}^{Q}P_{76}$	Q_7	
69.71	26519.7	3				
66.38	26543.2	4	0,1	P_6	${}^{Q}P_{67}$	
64.64	26555.6	3	0,1	${}^{Q}P_{65}$	Q_6	${}^{Q}R_{67}$
63.72	26561.9					
62.11	26573.3	4	0,1	${}^{O}P_{66}$	${}^{O}Q_{57}$	
60.70	26582.9	2	1,2	${}^{O}P_{65}$	Q_6	${}^{Q}R_{67}$
59.95	26588.0	4	0,1	P_5	${}^{P}Q_{56}$	${}^{P}R_{57}$
58.17	26601.2	6	0,1	${}^{O}P_{54}$	Q_5	${}^{Q}R_{56}$
56.79	26610.9	2				
55.85	26617.6	7	0,1	${}^{O}P_{45}$	${}^{O}Q_{46}$	${}^{O}R_{47}$
53.69	26632.9	7	0,1	P_4	${}^{P}Q_{45}$	${}^{P}R_{46}$
52.33	26642.6	2	0,1	${}^{Q}P_{43}$	Q_4	${}^{Q}R_{45}$
51.67	26647.3	7	0,1	${}^{N}P_{35}$	${}^{N}Q_{36}$	${}^{N}R_{37}$
50.34	26656.7	3	1,2	P_1	${}^{P}Q_{45}$	${}^{P}R_{46}$
49.14	26665.2	6	0,1	${}^{O}P_{31}$	${}^{O}Q_{35}$	${}^{O}R_{36}$
47.31	26678.3	7	0,1	P_3	${}^{P}Q_{34}$	${}^{P}R_{35}$
46.23	26686.0	3	0,1	${}^{Q}P_{32}$	Q_3	${}^{Q}R_{34}$
44.91	26695.4	6	0,1	${}^{N}P_{24}$	${}^{N}Q_{25}$	${}^{N}R_{26}$
43.43	26706.0	3	1,2	P_3	${}^{P}Q_{34}$	${}^{P}R_{35}$
42.35	26713.6	1	0,1	${}^{O}P_{23}$	${}^{O}Q_{24}$	${}^{O}R_{25}$
40.66	26725.7	4	0,1	P_2	${}^{P}Q_{23}$	${}^{P}R_{24}$
39.46	26734.3	4	0,1	${}^{Q}P_{21}$	Q_2	${}^{Q}R_{23}$
38.25	26742.9	4	1,2	${}^{O}P_{23}$	${}^{O}Q_{24}$	${}^{O}R_{25}$
35.56	26762.5	3	0,1	${}^{O}P_{12}$	${}^{O}Q_{13}$	${}^{O}R_{11}$
33.89	26774.1	2	0,1	P_1	${}^{P}Q_{12}$	${}^{P}R_{13}$
32.79	26782.0	1	0,1		Q_1	${}^{Q}R_{12}$

TABLE V

MnCl bands $\Delta v = -2$ sequence.

λ	ν	I	v′, v″	ΔJ: −1	ΔJ: 0	ΔJ: +1
3820.75	26165.5	2	0,2	P_6	${}^{P}Q_{67}$	
18.79	26178.9	2	0,2	${}^{Q}P_{65}$	Q_6	
16.57	26194.1	2	1,3	P_6	${}^{P}Q_{67}$	${}^{Q}R_{67}$
14.64	26207.1	2	0,2	P_5	${}^{P}Q_{56}$	
11.77	26227.1	2				${}^{P}R_{57}$
08.52	26249.5	2	0,2	P_4	${}^{P}Q_{45}$	
05.28	26271.9	3	0,2	${}^{N}P_{35}$	${}^{N}Q_{36}$	${}^{P}R_{46}$
03.19	26286.3	3	1,3	P_4	${}^{P}Q_{45}$	${}^{N}R_{37}$
00.82	26302.7	3	0,2	P_3	${}^{P}Q_{34}$	${}^{P}R_{46}$
3798.81	26316.6	3	0,2	${}^{N}P_{24}$	${}^{N}Q_{25}$	${}^{P}R_{35}$
96.59	26332.0	3	1,3	P_3	${}^{P}Q_{31}$	${}^{N}R_{26}$
94.26	26348.2	3	0,2	P_2	${}^{P}Q_{23}$	${}^{P}R_{35}$
91.97	26364.1	2	1,3	${}^{O}P_{23}$	${}^{O}Q_{21}$	${}^{P}R_{24}$
90.47	26374.5	3	1,3	P_2	${}^{P}Q_{23}$	${}^{O}R_{25}$
87.61	26394.4	2	0,2	P_1	${}^{P}Q_{12}$	${}^{P}R_{24}$
85.29	26410.6	1				${}^{P}R_{13}$

TABLE VI

MnCl bands $\Delta v = -3$ sequence.

λ	ν	I	v', v''	ΔJ: −1	ΔJ: 0	ΔJ: +1
3863.09	25874.7	1	0,3	P_4	$^PQ_{45}$	$^PR_{46}$
61.99	2588[illegible].1	1				
60.25	25897.7	1	0,3	$^NP_{35}$	$^NQ_{36}$	$^NR_{37}$
57.00	25919.6	2	0,3	P_3	$^PQ_{34}$	$^PR_{35}$
55.10	25932.3	2				
53.50	25943.1	1	0,3	$^NP_{21}$	$^NQ_{25}$	$^NR_{26}$
51.93	25953.7	2	1,4	P_3	$^PQ_{34}$	$^PR_{35}$
50.28	25964.8	2	0,3	P_2	$^PQ_{23}$	$^PR_{24}$
47.32	25984.8	2	1,4	$^OP_{23}$	$^OQ_{24}$	$^OR_{25}$
45.50	25996.7	1	1,4	P_2	$^PQ_{23}$	$^PR_{24}$

excellent paper. Table VII briefly gives the different forms of branches expected in this system consisting of violet-degraded bands with $B' > B''$, in conformity with the selection rules applicable to transitions between rotational energy levels ($\Delta J = 0$ or ± 1 excluding $0 \rightarrow 0$ and $\Delta K = 0, \pm 1, \pm 2$, etc.)

TABLE VII

ΔK	0	−1	−2	−3
"Form"	*Q*	*P*	*O*	*N*

As an illustration, a schematic diagram of the transitions is shown for the (1,0) sequence of MnCl in Plate XXV A Fig.(*a*). from which the classification of each band can be clearly understood.

Tables VIII and IX present the interval data between the component Π terms for the (0,1) and (1,0) bands respectively. The intervals *Q—P*, *P—O*, *O—N* show the expected increase. The $^7\Pi$ intervals show a very slight increase

TABLE VIII

MnCl Differences between wavenumbers of (0,1) bands.

	$^7\Pi_{-2}$		$^7\Pi_{-1}$		$^7\Pi_0$		$^7\Pi_1$		$^7\Pi_2$		$^7\Pi_3$		$^7\Pi_4$
Q		43.8		45.6		41.4		13.4		48.3		47.7	
	14.0		*12.4*		*12.0*		*9.7*		*7.7*		- *8.6*		*7.9*
P		45.1		45.4		44.3		15.4		17.4		48.4	
					15.3		*13.3*		*13.1*		*12.1*		*11.6*
O						44.3		47.5		48.4		48.9	
							17.9		*18.2*				
N										48.1			

TABLE IX

MnCl Differences between wavenumbers of (1,0) bands

	$^7\Pi_{-2}$		$^7\Pi_{-1}$		$^7\Pi_0$		$^7\Pi_1$		$^7\Pi_2$		$^7\Pi_3$		$^7\Pi_4$
Q		38.3		4.0									
	12.1		7.7		*6.5*		*6.0*						
P		42.7		45.2		45.7		46.5		45.4		45.1	
			14.9		*16.0*		*10.6*		*11.1*		*14.5*		*12.6*
O				41.1		45.1		48.7		45.3		47.0	
									22.0		*16.2*		
N								51.1					

MnBr. The experimental data on the MnBr bands belonging to the $\Delta v = +1$ sequence and the classification of the individual heads are given in Table X. The transitions are reproduced in Plate XXVB.

Table XI gives the differences in MnBr similar to those shown in Tables VIII and IX for MnCl. The tables are self-explanatory.

TABLE X

MnBr bands $\Delta v = +1$ sequence

λ	ν	I	v', v''	ΔJ −1	ΔJ 0	ΔJ +1
3779.50	26151.0	4	1,0	$^{Q}P_{76}$	Q_7	
77.76	26163.2	4	2,1	P_1		
76.44	26172.5	2	2,1	$^{Q}P_{76}$	Q_7	
74.03	26489.1	3	1,0	$^{O}P_{67}$		
72.55	26499.8	10	1,0	P_6	$^{P}Q_{67}$	
71.59	26506.5	9	1,0	$^{Q}P_{65}$	Q_6	$^{Q}R_{67}$
70.15	26516.0	9	2,1	P_6	$^{P}Q_{67}$	
69.27	26522.8	8	2,1	$^{Q}P_{65}$	Q_6	$^{Q}R_{67}$
67.89	26532.5	6	1,0	$^{N}P_{57}$		
65.98	26546.0	6	1,0	$^{O}P_{56}$	$^{O}Q_{57}$	
63.96	26560.2	7	1,0	P_5	$^{P}Q_{56}$	$^{P}R_{57}$
62.13	26572.3	7	2,1	P_5	$^{P}Q_{56}$	$^{P}R_{57}$
59.75	26590.0	6	1,0	$^{N}P_{46}$	$^{N}Q_{47}$	
57.56	26605.5	7	1,0	$^{O}P_{45}$	$^{O}Q_{46}$	$^{O}R_{47}$
55.42	26620.6	6	1,0	P_4	$^{P}Q_{45}$	$^{P}R_{46}$
53.65	26633.2	6	2,1	P_4	$^{P}Q_{46}$	$^{P}R_{47}$
52.23	26643.3	4	1,0			
50.84	26653.2	6	1,0	$^{N}P_{35}$	$^{N}Q_{36}$	$^{N}R_{37}$
49.10	26665.5	5	1,0	$^{O}P_{34}$	$^{O}Q_{35}$	$^{O}R_{36}$
46.98	26680.0	7	1,0	P_3	$^{P}Q_{34}$	$^{P}R_{35}$
45.47	26691.4	5	2,1	P_3	$^{P}Q_{34}$	$^{P}R_{35}$
41.88	26717.0	5	1,0	$^{N}P_{24}$	$^{N}Q_{25}$	$^{N}R_{26}$
40.16	26729.3	6	1,0	$^{O}P_{23}$	$^{O}Q_{21}$	$^{O}R_{25}$
38.47	26741.3	4	1,0	P_2	$^{P}Q_{23}$	$^{P}R_{24}$
31.02	26794.7	7	1,0	$^{O}P_{12}$	$^{O}Q_{13}$	$^{O}R_{14}$
28.97	26809.5	10	1,0	P_1	$^{P}Q_{12}$	$^{P}R_{13}$

TABLE XI

MnBr Differences between wavenumbers of (1,0) bands.

	$^7\Pi_{-2}$		$^7\Pi_{-1}$		$^7\Pi_0$		$^7\Pi_1$		$^7\Pi_2$		$^7\Pi_3$		$^7\Pi_4$
Q	55.5												
		6.7											
P			59.4		60.1		60.0		60.1		68.2		
		10.1		11.2		15.1		15.1		12.0			11.8
O			56.6		59.5		60.0		63.8		65.4		
				13.5		15.5		12.3		12.3			
N					67.5		63.2		63.8				

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REFERENCES

Bacher, 1948, *Helv. Phy. Acta.*, **21**, 379
Muller, 1913, ,, ,, ,, **16**, 1.
Nevin, 1945, *Proc. Irish. Acad.*, **50**, 123.
Pearse and Gaydon, 1938, *Proc. Phys. Soc.*, **50**, 201.
Rao, Tiruvengauna, 1948, *Curr. Sci.*, **17**, 209
,, 1949, *Ind. Jour. Phy.*, **23**, 301
Rochester and Olsson, 1939, *Zeit. f. Physik.*, **114** 495