# INTENSITY FORMULAE FOR $^{\eta}\mathcal{I} \leftrightarrow ^{\eta}\mathcal{E}$ BAND

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Explicit expressions are given concerning the intensity distribution occurring in the branches of bands  ${}^{7}\Pi(a) \leftrightarrow {}^{7}\Sigma$ ,  ${}^{7}\Pi(b) \leftrightarrow {}^{7}\Sigma$ . The intensity distribution calculated on the basis of the established formulae is compared with measurements carried out on the  ${}^{7}\Pi \rightarrow {}^{7}\Sigma$  bands of MnH and relatively good agreement is found.

## 1. §.

The problem of intensity distribution occurring in the rotational spectra of multiplet bands has already been dealt with by many researchers, from the theoretical [1] as well as from the experimental point of view [2]. In general the theoretical investigations relate to a wider field than the experimental data, providing hereby the experimental researcher with some guidance in case of an analysis of a new kind [3]. The reverse rarely occurs, when namely the analysis of the band and the intensity distribution are known from the experimental side, but the appropriate theoretical formulae are missing. An example for such a case is NEVIN's work [4], which contains the analysis of a  $^7\Pi \rightarrow ^7\Sigma$  band in the spectrum of MnH as well as the estimation of the intensity of the observed spectrum lines. The purpose of the present paper is to give the lacking theoretical intensity formulae and to compare these with the experiment.

#### 2. §.

As is known, in case of the thermal equilibrium the intensity of the lines of emission bands can be given by the following expression :

$$I = g' \, \nu^4 \, i e^{-\frac{E_r}{kT}}, \qquad (1)$$

where g' is constant inside each band, whereas the other symbols have the usual meaning. The task of the theory is the calculation of the *i* factors for all branches occurring in the rotational transitions. For this the corresponding expressions for the amplitudes

$$\mathbf{z}_{a}(^{7}\Pi_{\Omega}\,^{7}\Sigma_{\Omega'}) = \int \Psi_{a}^{*}(^{7}\Pi_{\Omega}) \, \mathbf{z} \, \Psi_{a}(^{7}\Sigma_{\Omega'}) \, d\tau \tag{2}$$

are used, the absolute values of which may be found in a paper by KRONIG [5]. It is, however, known, that the  $\Sigma$  terms exist only in HUND's case b), therefore

concerning the  ${}^7\Sigma$  term the eigenfunctions of case b) of the following form are introduced :

$$\Psi_{b}({}^{7}\Sigma_{K'}) = \sum_{\Omega=+3}^{-3} S_{\Omega,K'}(\Sigma) \Psi_{a}({}^{7}\Sigma_{\Omega}); \qquad (3)$$

hereby the amplitudes become

$$\boldsymbol{z}(^{\boldsymbol{\gamma}}\boldsymbol{\Pi}_{\Omega}{}^{\boldsymbol{\gamma}}\boldsymbol{\Sigma}_{\boldsymbol{K}'}) = \int \boldsymbol{\Psi}_{a}^{*}(^{\boldsymbol{\gamma}}\boldsymbol{\Pi}_{\Omega}) \, \boldsymbol{z} \, \boldsymbol{\Psi}_{b}(^{\boldsymbol{\gamma}}\boldsymbol{\Sigma}_{\boldsymbol{K}'}) \, d\boldsymbol{\tau} \, ; \qquad (4)$$

the threefold square of which summed over the magnetic quantum numbers give the *i* factors referring to the transitions  ${}^{7}\Pi(a) \leftrightarrow {}^{7}\Sigma(b)$ . The transformation matrix elements  $S_{\Omega,K}(\Sigma)$  occurring in (3) for the  ${}^{7}\Sigma$  terms were already earlier published by us [6]. Part of the *i* factors which can be obtained on the basis of (4) occur in the third column of Table I. According to detailed calculations in the above case 147 branches can exist, from among which the

*i* factors of the branches  ${}^{R}P_{64}$ ,  ${}^{N}P_{24}$ ,  ${}^{S}Q_{64}$ ,  ${}^{O}Q_{24}$ ,  ${}^{T}R_{64}$ ,  ${}^{P}R_{24}$  are proportional to  $\frac{1}{J}$ , the intensity of the branches  ${}^{N}P_{46}$ ,  $P_4$ ,  ${}^{R}P_{42}$ ,  ${}^{O}Q_{46}$ ,  $Q_4$ ,  ${}^{S}Q_{42}$ ,  ${}^{P}R_{46}$ ,  $R_4$ ,  ${}^{T}R_{42}$ is zero, whereas the *i* factors of the other not enumerated branches are directly proportional to *J*. As regards branches with an intensity differing from zero, the rule holds that the intensity of the *Q* branches to good approximation is twice the intensity of the corresponding *P* resp. *R* branches. So as to save space, however, from among the 147 branches the *i* factors of those 55 branches only are given the intensity of which in case of a transition  ${}^{7}\Pi(b) \leftrightarrow {}^{7}\Sigma(b)$ does not differ from zero.

The  $^{7}\Pi$  terms can in general be rendered well by the formulae of HUND's case a) only in the range of the lower rotational quantum numbers. With increasing rotational quantum numbers namely starts the transition towards the case b) and the difficulty in describing the conditions consists in that no expression is known concerning the  $^{7}\Pi$  energies valid with a satisfactory accuracy for any value of the binding constant Y = A/B. Thus we have to content ourselves with the knowledge of the energies of the relatively simple case b), respectively with the amplitudes produced by the use of the transformation matrix elements calculated with their aid

$$\boldsymbol{z}\left({}^{\boldsymbol{\gamma}}\boldsymbol{\Pi}_{K}{}^{\boldsymbol{\gamma}}\boldsymbol{\Sigma}_{K'}\right) = \int \boldsymbol{\Psi}_{b}^{*}\left({}^{\boldsymbol{\gamma}}\boldsymbol{\Pi}_{K}\right) \boldsymbol{z} \boldsymbol{\Psi}_{b}\left({}^{\boldsymbol{\gamma}}\boldsymbol{\Sigma}_{K'}\right) d\tau , \qquad (5)$$

where

$$\Psi_b(\Pi_K) = \sum_{\Omega=+3}^{-3} S_{\Omega,K}(\Pi) \Psi_a(\Pi_\Omega)$$
(6)

and the elements of the transformation of  $7\Pi$  state are the following

$$\begin{split} S_{4,J+3} &= + \sqrt{\frac{(J-3)(J-2)(J-1)J}{8(J+3)(2J+1)(2J+3)(2J+5)}};\\ S_{3,J+3} &= + \sqrt{\frac{3(J-2)(J-1)(J+4)}{4(J+3)(2J+1)(2J+3)(2J+5)}};\\ S_{2,J+3} &= + \sqrt{\frac{15(J-1)J(J+4)}{8(2J+1)(2J+3)(2J+5)}};\\ S_{1,J+3} &= + \sqrt{\frac{5J(J+2)(J+4)}{2(2J+1)(2J+3)(2J+5)}};\\ S_{0,J+3} &= + \sqrt{\frac{15(J+1)(J+2)(J+4)}{8(2J+1)(2J+3)(2J+5)}};\\ S_{-1,J+3} &= + \sqrt{\frac{3J(J+2)(J+4)}{4(2J+1)(2J+3)(2J+5)}};\\ S_{-2,J+3} &= + \sqrt{\frac{(J-1)J(J+4)}{8(2J+1)(2J+3)(2J+5)}};\\ \end{split}$$

$$\begin{split} S_{4,J+2} &= - \sqrt{\frac{3(J-3)(J-2)(J-1)(J+4)}{8(J+2)(J+3)(2J+1)(2J+3)}};\\ S_{3,J+2} &= - \sqrt{\frac{(J-2)(J-1)(2J+9)^2}{4(J+2)(J+3)(2J+1)(2J+3)}};\\ S_{2,J+2} &= - \sqrt{\frac{5(J-1)(J+6)^2}{8(J+2)(2J+1)(2J+3)}};\\ S_{1,J+2} &= - \sqrt{\frac{15}{2(2J+1)(2J+3)}};\\ S_{0,J+2} &= + \sqrt{\frac{5J(J+1)}{8(2J+1)(2J+3)}};\\ S_{-1,J+2} &= + \sqrt{\frac{2J+3}{4(2J+1)}};\\ S_{-2,J+2} &= + \sqrt{\frac{3(J-1)(J+2)}{8(2J+1)(2J+3)}}; \end{split}$$

$$\begin{split} S_{4,J+1} &= + \sqrt{\frac{15(J-3)(J-2)(J-1)(J+3)(J+4)}{8(J+1)(J+2)(2J-1)(2J+1)(2J+5)}};\\ S_{3,J+1} &= + \sqrt{\frac{5(J-2)(J-1)(J+3)(J+7)^2}{4(J+1)(J+2)(2J-1)(2J+1)(2J+5)}};\\ S_{2,J+1} &= - \sqrt{\frac{(J-1)(J^2-13J-50)^2}{8(J+1)(J+2)(2J-1)(2J+1)(2J+5)}};\\ S_{1,J+1} &= - \sqrt{\frac{3(J^2+2J-5)^2}{2(J+1)(2J-1)(2J+1)(2J+5)}};\\ S_{0,J+1} &= - \sqrt{\frac{J(J+7)^2}{8(2J-1)(2J+1)(2J+5)}};\\ S_{-1,J+1} &= + \sqrt{\frac{5(J+1)^3}{4(2J-1)(2J+1)(2J+5)}};\\ S_{-2,J+1} &= + \sqrt{\frac{15(J-1)(J+1)(J+2)}{8(2J-1)(2J+1)(2J+5)}}; \end{split}$$

$$\begin{split} S_{4,J} &= - \sqrt{\frac{5(J-3)(J-2)(J+3)(J+4)}{4J(J+1)(2J-1)(2J+3)}};\\ S_{3,J} &= - \sqrt{\frac{30(J-2)(J+3)}{J(J+1)(2J-1)(2J+3)}};\\ S_{2,J} &= + \sqrt{\frac{3(J-3)^2(J+4)^2}{4J(J+1)(2J-1)(2J+3)}};\\ S_{1,J} &= + \sqrt{\frac{9(J-1)(J+2)}{J(J+1)(2J-1)(2J+3)}};\\ S_{0,J} &= - \sqrt{\frac{3(J-1)(J+2)}{4(2J-1)(2J+3)}};\\ S_{-1,J} &= 0\\ S_{-2,J} &= + \sqrt{\frac{5J(J+1)}{4(2J-1)(2J+3)}}; \end{split}$$

$$\begin{split} S_{4,J-1} &= + \left| \sqrt{\frac{15(J-3)(J-2)(J+2)(J+3)(J+4)}{8(J-1)J(2J-3)(2J+1)(2J+3)}} \right|; \\ S_{3,J-1} &= - \left| \frac{\overline{5(J-6)^2(J-2)(J+2)(J+3)}}{4(J-1)J(2J-3)(2J+1)(2J+3)} \right|; \\ S_{2,J-1} &= - \left| \sqrt{\frac{(J+2)(J^2+15J-36)^2}{8(J-1)J(2J-3)(2J+1)(2J+3)}} \right|; \\ S_{1,J-1} &= + \left| \sqrt{\frac{3(J^2-6)^2}{2J(2J-3)(2J+1)(2J+3)}} \right|; \\ S_{0,J-1} &= - \left| \sqrt{\frac{(J-6)^2(J+1)}{8(2J-3)(2J+1)(2J+3)}} \right|; \\ S_{-1,J-1} &= - \left| \sqrt{\frac{5J^3}{4(2J-3)(2J+1)(2J+3)}} \right|; \\ S_{-2,J-1} &= + \left| \sqrt{\frac{15(J-1)J(J+2)}{8(2J-3)(2J+1)(2J+3)}} \right|; \end{split}$$

$$\begin{split} S_{4,J-2} &= - \left| \sqrt{\frac{3(J-3)(J+2)(J+3)(J+4)}{8(J-2)(J-1)(2J-1)(2J+1)}} \right|; \\ S_{3,J-2} &= + \left| \sqrt{\frac{(J+2)(J+3)(2J-7)^2}{4(J-2)(J-1)(2J-1)(2J+1)}} \right|; \\ S_{2,J-2} &= - \left| \sqrt{\frac{5(J-5)^2(J+2)}{8(J-1)(2J-1)(2J+1)}} \right|; \\ S_{1,J-2} &= - \left| \sqrt{\frac{15}{2(2J-1)(2J+1)}} \right|; \\ S_{0,J-2} &= + \left| \sqrt{\frac{5J(J+1)}{8(2J-1)(2J+1)}} \right|; \\ S_{-1,J-2} &= - \left| \sqrt{\frac{2J-1}{4(2J+1)}} \right|; \\ S_{-2,J-2} &= + \left| \sqrt{\frac{3(J-1)(J+2)}{8(2J-1)(2J+1)}} \right|; \end{split}$$

$$\begin{split} S_{4,J-3} &= + \sqrt{\frac{(J+1)(J+2)(J+3)(J+4)}{8(J-2)(2J-3)(2J-1)(2J+1)}};\\ S_{3,J-3} &= - \sqrt{\frac{3(J-3)(J+1)(J+2)(J+3)}{4(J-2)(2J-3)(2J-1)(2J+1)}};\\ S_{2,J-3} &= + \sqrt{\frac{15(J-3)(J+1)(J+2)}{8(2J-3)(2J-1)(2J+1)}};\\ S_{1,J-3} &= - \sqrt{\frac{5(J-3)(J-1)(J+1)}{2(2J-3)(2J-1)(2J+1)}};\\ S_{0,J-3} &= + \sqrt{\frac{15(J-3)(J-1)J}{8(2J-3)(2J-1)(2J+1)}};\\ S_{-1,J-3} &= - \sqrt{\frac{3(J-3)(J-1)(J+1)}{4(2J-3)(2J-1)(2J+1)}};\\ S_{-2,J-3} &= + \sqrt{\frac{(J-3)(J+1)(J+2)}{8(2J-3)(2J-1)(2J+1)}}. \end{split}$$

From (5) the *i* factors relative to the transitions  ${}^{7}\Pi(b) \leftrightarrow {}^{7}\Sigma(b)$  can be calculated. Those differing from zero are to be found in the fourth column of Table I. Apart from the selection rule  $\Delta J = 0, \pm 1$  valid for case *a*) also the condition  $\Delta K = 0, \pm 1$  is characteristic for the latter. It can be stated in general that if the  ${}^{7}\Pi$  term is belonging to the case *b*), then the *i* factors of the main branches  $(\Delta J - \Delta K = 0)$  are proportional to *J*, among the satellite branches those, for which  $\Delta J - \Delta K = \pm 1$ , are proportional to 1/J, whereas those, for which  $\Delta J - \Delta K = \pm 2$ , are proportional to  $1/J^{3}$ . In the main branches the intensity of the *Q* branches is here also approximately twice that of the corresponding *P* respectively *R* branches, but in the satellite branches, if there exist corresponding branches, the situation is just the opposite.

### Table I

Intensity factors for  ${}^{7}\Pi \leftrightarrow {}^{7}\Sigma$  bands

Branches		2-factors		
$^{7}\Pi \rightarrow ^{7}\Sigma$	$^7\Sigma \rightarrow ^7\Pi$	°П(a)	<sup>7</sup> II(b)	
$P_1(J)$	R <sub>1</sub> (J1)	$\frac{(J+1)(J+2)^2(J+3)^2}{8J(2J-3)(2J-1)(2J+1)}$	$\frac{(J-4)(2J+1)}{2J-5}$	
$Q_1(J)$	$Q_1(J)$	$\frac{(J-2)(J+2)(J+3)^2}{8J(2J-3)(2J-1)}$	$\frac{(J-3)(J+1)(2J+1)}{(J-2)J}$	
$R_1(J)$	$P_1(J+1)$	$\frac{(J-2)(J-1)(J+2)(J+3)}{8(2J-3)(2J-1)(2J+1)}$	$\frac{(J-1)(2J+3)}{2J-3}$	
${}^{q}P_{21}(J)$	$^{QR_{12}}(J-1)$	$\frac{3(J-2)(J+1)^2(J+2)^2}{4J(2J-3)(2J-1)(2J+1)}$	$\frac{3(2J+1)}{(J-2)J}$	
${}^{R}Q_{21}(J)$	${}^{P}Q_{12}(J)$	$\frac{3(J-2)(J-1)(J+2)^2}{4J(2J-3)(2J-1)}$	$\frac{3(J-1)(2J+1)}{(J-2)J(2J-3)}$	
${}^{R}P_{31}(J)$	${}^{P}R_{13}(J-1)$	$\frac{15(J-2)(J-1)J(J+1)^2}{8J(2J-3)(2J-1)(2J+1)}$	$\frac{15(J-1)}{(J-2)J(2J-5)(2J-3)}$	
${}^{P}Q_{12}(J)$	$^{R}Q_{21}(J)$	$\frac{3(J-2)(J+2)(J+3)^2}{8J(J+1)(2J-1)}$	$\frac{3(J-3)(2J+1)}{(J-2)J(2J-3)}$	
${}^{q}\!R_{12}(J)$	${}^{\varrho}P_{21}(J+1)$	$\frac{3(J-2)(J-1)(J+2)(J+3)}{8(J+1)(2J-1)(2J+1)}$	$\frac{3(2J+3)}{(J-1)(J+2)}$	
$P_2(J)$	$R_2(J-1)$	$\frac{(J-2)(J+1)(J+2)^2}{J(2J-1)(2J+1)}$	$\frac{(J-3)^2(J+1)(2J+1)}{(J-2)J(2J-3)}$	
$Q_2(J)$	$Q_2(J)$	$\frac{(J-2)(J-1)(J+2)^2}{J(J+1)(2J-1)}$	$\frac{(J^2 - J - 5)^2(2J + 1)}{(J - 2)(J - 1)J(J + 1)}$	
$R_2(J)$	$P_2(J+1)$	$\frac{(J-2)(J-1)J(J+2)}{(J+1)(2J-1)(2J+1)}$	$\frac{(J-2)J(J+2)(2J+3)}{(J-1)(J+1)(2J-1)}$	
$P_{32}(J)$	<i>QR</i> <sub>23</sub> ( <i>J</i> −−1)	$\frac{5(J-2)(J-1)(J+1)}{8(2J-1)(2J+1)}$	$\frac{-5(J+1)(2J-5)}{(J-2)(J-1)J}$	
${}^{R}Q_{32}(J)$	${}^{P}Q_{23}(J)$	$\frac{5(J-2)(J-1)}{8(2J-1)}$	$\frac{5(J-2)(2J+1)(2J+3)}{(J-1)(J+1)(2J-3)(2J-1)}$	
${}^{_{R}}P_{42}(J)$	${}^{P}R_{24}(J-1)$	0	30 - (J-1)(2J-3)(2J-1)	

Branches		i-factors	
$^{7}\Pi \rightarrow ^{7}\Sigma$	$^7\Sigma \rightarrow ^7\Pi$	<sup>7</sup> 11(a)	² II(b)
${}^{P}R_{13}(J)$	$^{R}P_{31}(J+1)$	$\frac{15(J-2)^2(J-1)(J+2)(J+3)}{8(J+1)(2J-3)(2J+1)(2J+3)}$	$\frac{15(J-2)}{(J-1)(J+1)(2J-3)(2J-1)}$
${}^{P}Q_{23}(J)$	$^{R}Q_{32}(J)$	$\frac{5(J-3)^2(J-1)(J+2)^2}{4J(J+1)(2J-3)(2J+3)}$	$\frac{5(J-2)^2(2J+1)(2J+3)}{(J-1)J(J+1)(2J-3)(2J-1)}$
${}^{q}R_{23}(J)$	°P <sub>32</sub> (J+1)	$\frac{5(J-3)^2(J-1)J(J+2)}{4(J+1)(2J-3)(2J+1)(2J+3)}$	$\frac{5(J+2)(2J-3)}{(J-1)J(J+1)}$
$P_3(J)$	$R_3(J-1)$	$\frac{(J-1)(J+1)(J+6)^2}{8(2J-3)(2J+1)(2J+3)}$	$\frac{(J-2)^2(J+1)(2J-5)(2J+3)}{(J-1)J(2J-3)(2J-1)}$
$Q_{\mathfrak{s}}(J)$	$Q_3(J)$	$\frac{(J-1)(J+6)^2}{8(2J-3)(2J+3)}$	$rac{(J^2-6)^2(2J+1)}{(J-1)J^2(J+1)}$
$R_{\mathfrak{z}}(J)$	$P_{3}(J+1)$	$\frac{(J-1)J(J+6)^2}{8(2J-3)(2J+1)(2J+3)}$	$\frac{(J-1)(J+2)(2J-3)(2J+5)}{J(2J-1)(2J+1)}$
${}^{Q}P_{43}(J)$	${}^{\varrho}R_{34}(J-1)$	$\frac{3(J-1)^2 J(J+1)}{2(2J-3)(2J+1)(2J+3)}$	$rac{6(J-2)(2J+3)}{(J-1)J^2}$
${}^{\scriptscriptstyle B}Q_{43}(J)$	${}^{P}Q_{34}(J)$	$\frac{3(J-1)J(J+1)}{2(2J-3)(2J+3)}$	$\frac{6(J+2)(2J-3)}{J^2(2J-1)}$
${}^{R}P_{53}(J)$	${}^{P}R_{35}(J-1)$	$\left  \begin{array}{c} (J-2)(J-1)^2(J+6)^2 \\ \overline{8J(2J-3)(2J+1)(2J+3)} \end{array} \right $	$\frac{36(J+1)}{J^2(2J-1)(2J+1)}$
${}^{P}R_{24}(J)$	$^{R}P_{42}(J+1)$	$\frac{15(J-1)J}{2(J+1)(2J-1)(2J+3)}$	$\frac{30(J-1)}{J(J+1)(2J-1)(2J+1)}$
${}^{P}Q_{34}(J)$	$^{R}Q_{43}(J)$	$\frac{3(J-1)(J+2)(2J+1)}{4(2J-1)(2J+3)}$	$\frac{6(J-1)(J+2)(2J-3)}{J^2(J+1)(2J-1)}$
${}^{q}R_{34}(J)$	${}^{q}P_{43}(J+1)$	$\frac{3(J-1)J(J+2)}{4(2J-1)(2J+3)}$	$\frac{6(J-1)(2J+5)}{J(J+1)^2}$
$P_4(J)$	$R_4(J-1)$	0	$\frac{(J-2)(J-1)(J+2)(2J-3)(2J+3)}{J^2(2J-1)(2J+1)}$
$Q_4(J)$	$Q_4(J)$	0	$\frac{(J-2)^2(J+3)^2(2J+1)}{J^2(J+1)^2}$
$R_4(J)$	$P_4(J+1)$	0	$\frac{(J-1)(J+2)(J+3)(2J-1)(2J+5)}{(J+1)^2(2J+1)(2J+3)}$
${}^{\varrho}P_{54}(J)$	$^{\it Q}R_{45}(J-1)$	$\frac{3(J-2)(J-1)^2(J+2)}{4J(2J-1)(2J+3)}$	$\frac{-6(J+2)(2J-3)}{J^2(J+1)}$
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Branches		i-factors	
$\overline{\gamma}_{\Pi} \rightarrow \overline{\gamma}_{\Sigma}$	$^{7}\Sigma \rightarrow ^{7}\Pi$	<sup>7</sup> Π(a)	7П(b)
<sup>R</sup> Q <sub>64</sub> (J)	${}^{P}Q_{45}(J)$	$\frac{3(J-1)^2(J+2)^2(2J+1)}{4J(J+1)(2J-1)(2J+3)}$	$\frac{6(J-1)(J+2)(2J+5)}{J(J+1)^2(2J+3)}$
${}^{\mu}P_{6i}(J)$	${}^{PR_{45}}(J-1)$	$\frac{15(J-3)(J-2)}{2J(2J-1)(2J+3)}$	$\frac{30(J+2)}{J(J+1)(2J+1)(2J+3)}$
$^{\mathbb{P}R}_{35}(J)$	$^{BP_{53}}(J+1)$	$\boxed{\frac{(J-5)^2 J (J+2)}{8(2J-1)(2J+1)(2J+5)}}$	$\frac{36J}{(J+1)^2(2J+1)(2J+3)}$
${}^{P}Q_{45}(J)$	$^{R}Q_{54}(J)$	$\frac{3J(J+1)(J+2)}{2(2J-1)(2J+5)}$	$rac{6(J-1)(2J+5)}{(J+1)^2(2J+3)}$
$QR_{45}(J)$	$^{9}P_{54}(J+1)$	$\frac{3J(J+1)(J+2)^2}{2(2J-1)(2J+1)(2J+5)}$	$\frac{6(J+3)(2J+1)}{(J+1)^2(J+2)}$
$P_{s}(J)$	$R_{5}(J-1)$	$\frac{(J-5)^2(J-2)(J-1)(J+2)}{8J(2J-1)(2J+1)(2J+5)}$	$\frac{(J-1)(J+2)(2J-3)(2J+5)}{(J+1)(2J+1)(2J+3)}$
$Q_5(J)$	$Q_5(J)$	$\frac{(J-5)^2(J-1)(J+2)^2}{8J(J+1)(2J-1)(2J+5)}$	$\frac{(J^2+2J-5)^2(2J+1)}{J(J+1)^2(J+2)}$
$R_{\mathfrak{s}}(J)$	$P_{5}(J+1)$	$\frac{(J-5)^2(J+2)^2(J+3)}{8(J+1)(2J-1)(2J+1)(2J+5)}$	$\frac{J(J+3)^2(2J-1)(2J+7)}{(J+1)(J+2)(2J+3)(2J+5)}$
$^{q}P_{65}(J)$	${}^{q}R_{56}(J-1)$	$\frac{5(J-3)(J-2)(J-1)(J+4)^2}{4J(2J-1)(2J+1)(2J+5)}$	$\frac{5(J-1)(2J+5)}{J(J+1)(J+2)}$
$^{\varrho}Q_{\mathfrak{s}5}(J)$	${}^{P}Q_{56}(J)$	$\frac{5(J-2)(J-1)(J+3)(J+4)^2}{4J(J+1)(2J-1)(2J+5)}$	$\frac{5(J+3)^2(2J-1)(2J+1)}{J(J+1)(J+2)(2J+3)(2J+5)}$
${}^{R}P_{75}(J)$	${}^{P}R_{57}(J-1)$	$\frac{15(J-4)(J-3)(J-2)(J-1)(J+3)}{8J(2J-1)(2J+1)(2J+5)}$	$\frac{15(J+3)}{J(J+2)(2J+3)(2J+5)}$
$PR_{46}(J)$	$^{R}P_{64}(J+1)$	0	$\frac{30}{(J+2)(2J+3)(2J+5)}$
$PQ_{58}(J)$	${}^{R}Q_{65}(J)$	$\frac{5(J-1)(J+2)^2(J+3)}{8J(J+1)(2J+3)}$	$\frac{5(J+3)(2J-1)(2J+1)}{J(J+2)(2J+3)(2J+5)}$
${}^{\varrho}R_{56}(J)$	${}^{q}P_{65}(J+1)$	$\frac{5(J+2)^2(J+3)^2}{8(J+1)(2J+1)(2J+3)}$	$\frac{5J(2J+7)}{(J+1)(J+2)(J+3)}$
$P_{\epsilon}(J)$	$R_{6}(J-1)$	$\frac{(J-3)(J-2)(J-1)(J+3)}{J(2J+1)(2J+3)}$	$\frac{(J-1)(J+1)(J+3)(2J-1)}{J(J+2)(2J+3)}$

Branches		i-factors	
$^{\eta}\Pi \rightarrow {}^{\eta}\Sigma$	$^{7}\Sigma \rightarrow ^{7}\Pi$	<sup>7</sup> Π (a)	<sup>7</sup> П (b)
$Q_6(J)$	$Q_6(J)$	$\frac{(J-2)(J-1)(J+3)^2}{J(J+1)(2J+3)}$	$\frac{(J^2+3J-3)^2(2J+1)}{J(J+1)(J+2)(J+3)}$
$R_{\rm s}(J)$	$P_{6}(J+1)$	$\frac{(J-1)(J+3)^2(J+4)}{(J+1)(2J+1)(2J+3)}$	$\frac{J(J+4)^2(2J+1)}{(J+1)(J+3)(2J+5)}$
${}^{\varrho}P_{76}(J)$	${}^{\varrho}R_{67}(J-1)$	$\frac{3(J-4)(J-3)(J-2)(J-1)}{8J(2J+1)(2J+3)}$	$\frac{3(2 J - 1)}{J(J + 1)}$
<sup>B</sup> Q <sub>76</sub> (J)	$PQ_{67}(J)$	$\frac{3(J-3)(J-2)(J-1)(J+4)}{8J(J+1)(2J+3)}$	$\frac{3(J+4)(2J+1)}{(J+1)(J+3)(2J+5)}$
${}^{P}R_{57}(J)$	$^{R}P_{75}(J+1)$	$\frac{15J(J+2)^2(J+3)^2}{8(J+1)(2J+1)(2J+3)(2J+5)}$	$\frac{15(J+2)}{(J+1)(J+3)(2J+5)(2J+7)}$
${}^{P}Q_{67}(J)$	<sup>E</sup> Q <sub>76</sub> (J)	$\frac{3(J-3)(J-2)(J-1)(J+4)}{4(J+1)(2J+3)(2J+5)}$	$\frac{3(J+2)(2J+1)}{(J+1)(J+3)(2J+5)}$
${}^{q}\!R_{67}(J)$	<sup>Q</sup> P <sub>76</sub> (J+1)	$\frac{3(J-2)(J-1)J(J+4)(J+5)}{4(J+1)(2J+1)(2J+3)(2J+5)}$	$\frac{3(2J+1)}{(J+1)(2J+3)}$
$P_{7}(J)$	$R_7(J-1)$	$\frac{(J-4)(J-3)(J-2)(J-1)}{8(2J+1)(2J+3)(2J+5)}$	$\frac{(J+2)(2J-1)}{2J+5}$
$Q_7(J)$	$Q_7(J)$	$\frac{(J-3)(J-2)(J-1)(J+4)}{8(J+1)(2J+3)(2J+5)}$	$\frac{J(J+4)(2J+1)}{(J+1)(J+3)}$
$R_7(J)$	$P_{7}(J+1)$	(J-2)(J-1)J(J+4)(J+5)8(J+1)(2J+1)(2J+3)(2J+5)	$\frac{(J+5)(2J+1)}{2J+7}$

In Table I the <sup>7</sup> $\Pi$  term was assumed to be normal. In case of inverted terms  $\Omega = 4$  corresponds not to the state K = J + 3, but to K = J - 3 and for the transition  ${}^{7}\Pi(a) \rightarrow {}^{7}\Sigma(b)$  the first indices 1, 2, ... 7 in the denotation of the branches should be replaced by the denotation 7, 6, ... 1. (For  ${}^{7}\Sigma(b) \rightarrow {}^{7}\Pi(a)$  the second.)

#### 3. §. Comparison with the experiment

Two  ${}^{7}\Pi \rightarrow {}^{7}\Sigma$  bands were analysed by NEVIN in the spectrum of MnH for wave lengths  $\lambda = 5677$  A and  $\lambda = 6237$  A, which arise from the transitions (0,0) and (0,1) [4]. For the comparison of the theoretical values with the ex-

periment the intensity values which were estimated with the eye and which are written up beside the spectrum lines of the (0,0) band were used. The total intensity distribution of the rotational spectrum lines is given by formula (1), the exponent of which contains the effective arc temperature. This has been determined from experimental data by means of the method published by NOLAN and JENKINS [2]. Computing the arc temperature from the branches belonging to the individual term components owing to the dispersion of the measuring data the following values are obtained :

$${}^{7}\Pi_{4}$$
: 3706 K°;  ${}^{7}\Pi_{3}$ : 3812 K°;  ${}^{7}\Pi_{2}$ : 3733 K°;  ${}^{7}\Pi_{1}$ : 3869 K°;  
 ${}^{7}\Pi_{0}$ : 3863 K°;  ${}^{7}\Pi_{-1}$ : 3863 K°;  ${}^{7}\Pi_{-2}$ : 3781 K°.

The exponential factor was computed with their arithmetic mean i. e. 3803 K°, and the intensity values belonging to the individual lines divided by it. The circles in the Figure give separately for every branch observed by NEVIN [4] the dependence of the experimental *i* factors on *K*. By the continuous line the values of the theoretical *i* factors computed from Table I are given in case  ${}^{7}\Pi(b) \leftrightarrow {}^{7}\Sigma$  against the rotational quantum numbers. The proportionality factor given here has been chosen so that the observed and the computed intensity values of the  $Q_{2}$  branch overlap as well as possible.

The dispersion of the experimental values is rather considerable which can be attributed to the fact that the employed experimental data do not arise from quantitative intensity measurements, but were estimated by NEVIN during the analysis with the naked eye only and characterized by whole numbers from 0-50.

It should be noted that there exist also rotational lines the wave length of which coincides with the wave length of the line of some other branch, moreover even three and fourfold coincidences might occur. The intensities of these of course add up and in the experimental data for each term of such coinciding line pair or group always the joint intensity occurs. If these lines had always been taken into account with the given intensity values, then in our Figures numerous line intensities protruding to a high extent would have appeared and finally would have led to the falsification of the real situation. In order to avoid this the experimental intensity values for such line ensembles were divided up between the terms of the group in the proportion of the intensities expected from the theoretical calculations. Hereby several projecting points could be eliminated (101 double, 13 triple, 2 quadruple groups).

Detailed investigation of the course of terms shows that the term  $^{7}\Pi$  can be considered from about K = 15—20 to a good approximation as case b), that means that in case of K > 20 the conditions are correctly described by the *i* factors of case b). In case of K > 20 the theoretical and experimental *i* factors of the main-branches are in good agreement and here — under the



















usually occurring conditions — the intensity of the satellite branches is according to the theory already below the limit of measurability and indeed in this region observations do not exist. In case of K < 20 two effects mix : the first is the transition towards case a), the consequence of which is the breaking



down of the selection rule  $\Delta K = 0, \pm 1$  and hereby the appearance of further satellite branches differing from those permitted in case b), whereas the other effect is the strong perturbation appearing in the  $^{7}\Pi$  term for low quantum numbers. The latter results in deviations from the theoretical intensity values of case a), which can be particularly well observed on the main branches  $P_1, R_1$  as well as on some satellite branches. The exact interpretation of these

deviations is possible only after detailed investigation of the occurring perturbations, if at the same time quantitative measurement of the intensity values are available. Considering what has been said above the agreement of the theoretical and experimental results can be considered as fairly good.

#### REFERENCES

- 1. E. L. HILL and J. H. VAN VLECK, Phys. Rev., 32, 250, 1928; A. BUDÓ, Zs. f. Phys., 105,
- E. WERHAGEN, Ark. f. Phys., 6, 399, 1953 ; I. Kovács and O. SCARI, Acta Phys. Hung., 8, 425, 1958.

4. T. E. NEVIN, Proc. Roy. Ir. Acad., 48A, 1, 1942; 50A, 123, 1945.

- 5. R. L. KRONIG, Zs. f. Phys., 45, 458, 1927.
- 6. I. Kovács, Proc. Roy. Ir. Acad., in press, 1959.

### ФОРМУЛЫ ИНТЕНСИВНОСТЕЙ СЕПТЕТНЫХ ПОЛОС

### И. КОВАЧ и О. СКАРИ

#### Резюме

Даны явные выражения для распределения интенсивностей в ветвях полос  ${}^{7}\Pi(a) \leftrightarrow {}^{7}\Sigma, {}^{7}\Pi(b) \leftrightarrow {}^{7}\Sigma$ . Распределения вычислены по формулам, сравнены с результатами измерений на полосах  ${}^{7}\Pi \rightarrow {}^{7}\Sigma$  в спектре MnH, и найдено удовлетворительное согласие.