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HÖNL–LONDON FACTORS FOR DOUBLET TRANSITIONS IN DIATOMIC MOLECULES

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SUMMARY

Hönl–London factors are given for the general doublet transition in a diatomic molecule between two states both of which are intermediate between Hund's coupling case (a) and case (b). As a necessary preliminary the energy levels for the intermediate case are derived.

1. INTRODUCTION

The appearance of a band system depends on two things: the disposition of the lines that constitute it, and the intensities of these lines. The intensities of the lines depend on the populations of molecules in the various rotational levels and on the probabilities of transitions between the upper and lower levels. The transition probabilities can be written as the product of two factors: one gives the band transition probability and is called the band strength; the second gives the relative distribution among the rotational branches within a band.

The relative intensity distribution factors were originally calculated by Hönl & London (1925) for singlet transitions. Now, however, these factors for any multiplicity bear their names.

Hill & Van Vleck (1928) gave the Hönl–London factors for transitions between two case (a) states* or two case (b) states, for any multiplicity. Since for singlet states the distinction between Hund's coupling cases (a) and (b) disappears, these two tables of factors include the original formulae of Hönl and London as a special case.

Hönl–London factors have been obtained for various particular triplet transitions; in some cases both states are in a coupling condition intermediate between cases (a) and (b) (Budó 1937; Kovács 1960, 1963, 1966; Kovács & Budó 1949; Kovács & Tőrös 1965; Tatum 1966, 1968). These have covered the important triplet transitions fairly completely.

The Hönl–London factors for doublet transitions which have been obtained are for the general doublet transition between two states both of which are case (a) or both of which are case (b) (Hill & Van Vleck 1928; Mulliken 1931) and for the $^2\Pi - {}^2\Sigma$ and $^2\Sigma - {}^2\Pi$ transitions, where the $^2\Pi$ state is in a coupling condition intermediate between cases (a) and (b) (Earls 1935). In addition, Hönl–London factors for the $^2\Delta - {}^2\Pi$ transition have been calculated by Kovacs but are unpublished. (Cited by Tatum (1967) as a personal communication to Tatum and Schadee.)

The present paper describes the calculation of the Hönl–London factors for the

* For a discussion of Hund's coupling cases see Herzberg (1950, p. 219).

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1970MNRAS.147...35B

general doublet transition in a diatomic molecule between two states both of which are intermediate between cases (a) and (b). All doublet transitions are now covered by these formulae, in particular the $^2\Pi - {}^2\Pi$ transition which is of some interest (Tatum 1967).

2. THEORY

Hund's coupling cases represent idealized limiting situations and although they often represent the observed states to a good approximation, multiplet states with $\Lambda > 0$ often belong to a case intermediate between (a) and (b). The amount of intermediate character depends on the relative strengths of the coupling of the spin to the molecular axis and the coupling between the spin and the molecular rotation. Thus case (a) can be a good approximation for small rotation, but, if the multiplet splitting is not too great, as the rotation increases and tends to uncouple the spin from the axis, the coupling approaches case (b).

In the mathematical derivation for the intermediate coupling case we may either start from case (b) and work back to case (a), that is, neglect at first the coupling of the spin to the axis and then take this as a perturbation; or start with case (a) and work back to case (b), that is, neglect at first the spin-rotation interaction and then take this as a perturbation. The latter approach is used here.

The theory will not be developed in detail here; only the essential points will be given. A full account will be given elsewhere (Bennett 1970).

The energy levels in case (a) may be written

$$E_{\alpha\Omega} = E_{n\Omega}{}^e(R_e) - \gamma_v[S(S+1) - \Sigma^2] + G(v) + F_v(J\Omega S\Sigma), \quad (1)$$

where $\alpha \equiv (nvJ)$ and $n \equiv (qS\Lambda)$, and where q provides information necessary to distinguish, for example, between $A\ ^2\Pi$ and $B\ ^2\Pi$. $E_{n\Omega}{}^e(R_e)$ is the electronic energy evaluated at the equilibrium internuclear separation R_e. Taking into account the relativistic electron spin-orbit interaction we may write to first order (Herzberg 1950, p. 214)

$$E_{n\Omega}{}^e(R_e) = E_n{}^e(R_e) + A(R_e)\Lambda\Sigma, \quad (2)$$

where $A(R_e)$ is the equilibrium multiplet splitting. The term $\gamma_v[S(S+1) - \Sigma^2]$ is the contribution to the energy from the relativistic spin-rotation interaction. The terms $G(v)$ and $F_v(J\Omega S\Sigma)$ are the vibrational and rotational energies respectively and may be represented according to Dunham (1932) but with the generalization to $S \neq 0$, $\Lambda \neq 0$ by

$$G(v) = \sum_{l=0}^{\infty} Y_{l0}(v+\tfrac{1}{2})^l \quad (3)$$

$$F_v(J\Omega S\Sigma) = B_v[J(J+1) - \Omega^2 + S(S+1) - \Sigma^2] - D_v[J(J+1) - \Omega^2 + S(S+1) - \Sigma^2]^2 + \ldots . \quad (4)$$

The total internal wave function for the molecule is

$$|\alpha\Omega M) = (\mathbf{r}_1 \ldots \mathbf{r}_N, \sigma_1 \ldots \sigma_N; R|n\Omega)\frac{1}{R}(R|n\Omega vJ) \times \left[\frac{2J+1}{8\pi^2}\right]^{1/2} D_{M\Omega}{}^{J*}(\alpha\beta\gamma), \quad (5)$$

where $(\mathbf{r}_1 \ldots \mathbf{r}_N, \sigma_1 \ldots \sigma_N; R|n\Omega)$ is the electronic wave function*, $(R|n\Omega vJ)$ is

* We take as electronic wave functions the zero-order wave functions with respect to the spin-orbit interaction.

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1970MNRAS.147...35B

the wave function for the nuclear vibration, and $D_{M\Omega}^{J*}(\alpha\beta\gamma)$ is the rotation matrix as defined by Rose (1957, p. 52) describing the nuclear rotation, where $\alpha\beta\gamma$ are the Euler angles relating the coordinate system fixed on the molecule to the coordinate system fixed in space.

The spin-rotation perturbation is

$$H' = -2B[J_xS_x+J_yS_y]+\gamma[\mathbf{S}.\mathbf{R}-(n\Omega|\mathbf{S}.\mathbf{R}|n\Omega)] \tag{6}$$

$$= -2\left(B-\frac{\gamma}{2}\right)[J_xS_x+J_yS_y]-\gamma(n\Omega|\mathbf{S}.\mathbf{R}|n\Omega)-\gamma[\mathbf{S}^2-\mathbf{S}_z^2], \tag{7}$$

where $B(R) = \hbar^2/2\mu R^2$ and $\gamma(R)$ is the coupling constant of the relativistic interaction of the magnetic moment due to electron spin $\mathbf{S}$ and the magnetic field developed by the molecular rotation $\mathbf{R}$.

The perturbation connects the different multiplet components of the given electronic state. Since these are not degenerate we cannot use degenerate perturbation theory and because the coupling between them may become large compared to the energy separations between them (case (b)) we cannot use non-degenerate perturbation theory. A new perturbation theory must therefore be constructed and is described by Dalgarno (1961, p. 203). The perturbation is split into two parts H_1' and H_2' in such a way that if we take as the Hamiltonian of the unperturbed system the sum of the original unperturbed Hamiltonian H_0 and one of the parts H_1' the problem reduces to a degenerate one. We may then use degenerate perturbation theory taking as the perturbation $H_2' = H'-H_1'$.

In the intermediate case we write the energy as

$$E_{\alpha N} = E_{\alpha N}^{(0)}+E_{\alpha N}^{(1)}+\ldots, \quad N = |J-S|,\ldots J+S, \tag{8}$$

and wave function as

$$|\alpha NM) = |\alpha NM)^0+\ldots, \tag{9}$$

where

$$|\alpha NM)^0 = \sum_{\Omega=\Lambda-S}^{\Lambda+S}(\alpha N|\alpha\Omega)|\alpha\Omega M). \tag{10}$$

The transformation coefficients are chosen to make the $|\alpha NM)^0$ orthonormal so that

$$\sum_{\Omega=\Lambda-S}^{\Lambda+S}(\alpha\Omega|\alpha N')(\alpha N''|\alpha\Omega) = \delta(N', N''). \tag{11}$$

According to the modified perturbation theory if we take

$$E_{\alpha N}^{(0)} = E_{\alpha\Lambda-S}$$

we obtain the set of equations

$$\sum_{\Omega''=\Lambda-S}^{\Lambda+S}(\alpha N|\alpha\Omega'')[(\alpha\Omega'M|H'|\alpha\Omega''M)+(\Delta_{\Omega''}-E_{\alpha N}^{(1)})\delta(\Omega', \Omega'')] = 0,$$

$$\Omega' = \Lambda-S,\ldots\Lambda+S, \tag{12}$$

with

$$\Delta_{\Omega''} = E_{\alpha\Omega''}-E_{\alpha\Lambda-S}. \tag{13}$$

For a non-trivial solution we must have

$$det|(\alpha\Omega'M|H'|\alpha\Omega''M)+(\Delta_{\Omega''}-E_{\alpha N}^{(1)})\delta(\Omega', \Omega'')| = 0. \tag{14}$$

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The matrix elements of H' are easily shown to be (Van Vleck 1929)

$$(\alpha\Omega M\,|H'|\,\alpha\Omega M) = 0 \tag{15}$$

$$(\alpha\Omega \pm 1 M\,|H'|\,\alpha\Omega M) = \left(n\Omega \pm 1 v J\left|B-\frac{\gamma}{2}\right|n\Omega v J\right) \times [J(J+1)-\Omega(\Omega\pm 1)]^{1/2}[S(S+1)-\Sigma(\Sigma\pm 1)]^{1/2}, \tag{16}$$

with (James 1964)

$$\left(n\Omega \pm 1 v J\left|B-\frac{\gamma}{2}\right|n\Omega v J\right) \simeq B_v - 2D_v[J(J+1)-\Omega^2+S(S+1)-\Sigma^2-1\mp(\Omega+\Sigma)] - \frac{\gamma_v}{2}, \tag{17}$$

taking terms up to second-order in $B(R)$ and first-order in $\gamma(R)$.

The doublet case is the only one for which equation (14) is soluble analytically. Neglecting higher terms in equation (4) and solving for $E_{\alpha N}^{(1)}$ and adding to $E_{\alpha N}^{(0)}$ we obtain to first-order

$$E_{\alpha N} = E_n^e(R_e) - \frac{\gamma_v}{2} - D_v\Lambda^2 + G(v) + B_v[(J+\tfrac{1}{2})^2-\Lambda^2] - D_v[(J+\tfrac{1}{2})^2-\Lambda^2]^2 \pm B_v W, \tag{18}$$

where

$$W = +\tfrac{1}{2}\left[4\left(1-2\tilde{D}_v X-\frac{\tilde{\gamma}_v}{2}\right)^2(J+\tfrac{1}{2})^2+(Y-\tilde{\gamma}_v)(Y-4+8\tilde{D}_v X+\tilde{\gamma}_v)\Lambda^2\right]^{1/2}, \tag{19}$$

$$Y = \frac{A}{B_v}, \quad X = (J+\tfrac{1}{2})^2-\Lambda^2, \tag{20}$$

and where $\sim$ implies that the quantity is divided by B_v.

Substituting in equations (12) and using equations (11) we obtain

$$(\alpha J+\tfrac{1}{2}\,|\,\alpha\Lambda+\tfrac{1}{2}) = (\alpha J-\tfrac{1}{2}\,|\,\alpha\Lambda-\tfrac{1}{2}) = \left[\frac{1+\Lambda ZU}{2}\right]^{1/2}$$

$$(\alpha J+\tfrac{1}{2}\,|\,\alpha\Lambda-\tfrac{1}{2}) = -(\alpha J-\tfrac{1}{2}\,|\,\alpha\Lambda+\tfrac{1}{2}) = \left[\frac{1-\Lambda ZU}{2}\right]^{1/2} \tag{21}$$

where

$$U = \frac{1}{2W}, \quad Z = Y-2+4\tilde{D}_v X. \tag{22}$$

The $(\alpha N\,|\,\alpha\Omega)$ may in general have arbitrary phase factors but it was shown by Hill & Van Vleck (1928) that for the calculation of intensity formulae they can be disregarded so that the $(\alpha N\,|\,\alpha\Omega)$ may be taken as real.

Both γ_v and D_v are usually small compared with B_v and if they are neglected equation (18) reduces to that given by Hill & Van Vleck (1928) and Van Vleck (1929). The parameter Y is a measure of the relative strengths of the spin-axis and spin-rotation couplings, thus, $Y\to\infty$ corresponds to pure case (a) (regular), $Y=\tilde{\gamma}_v$ (or $4-8\tilde{D}_v X-\tilde{\gamma}_v$) corresponds to pure case (b) and $Y\to-\infty$ corresponds to pure case (a) (inverted).

Fig. 1 shows the energy level diagram for a $^2\Pi$ state. On the left the state belongs to case (a) (regular); on the right to case (a) (inverted); and in the centre to case (b). We know that as the spin becomes uncoupled from the axis the levels in case (a) must eventually go over to those in case (b), and must do so in such a way that J remains unchanged and levels with equal J do not cross. In this way we obtain the

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1970MNRAS.147...35B

connecting lines, which represent only schematically the behaviour of the levels for intermediate coupling conditions. In an actual molecule the coupling changes from one level to the next, approaching case (b) for the higher levels.

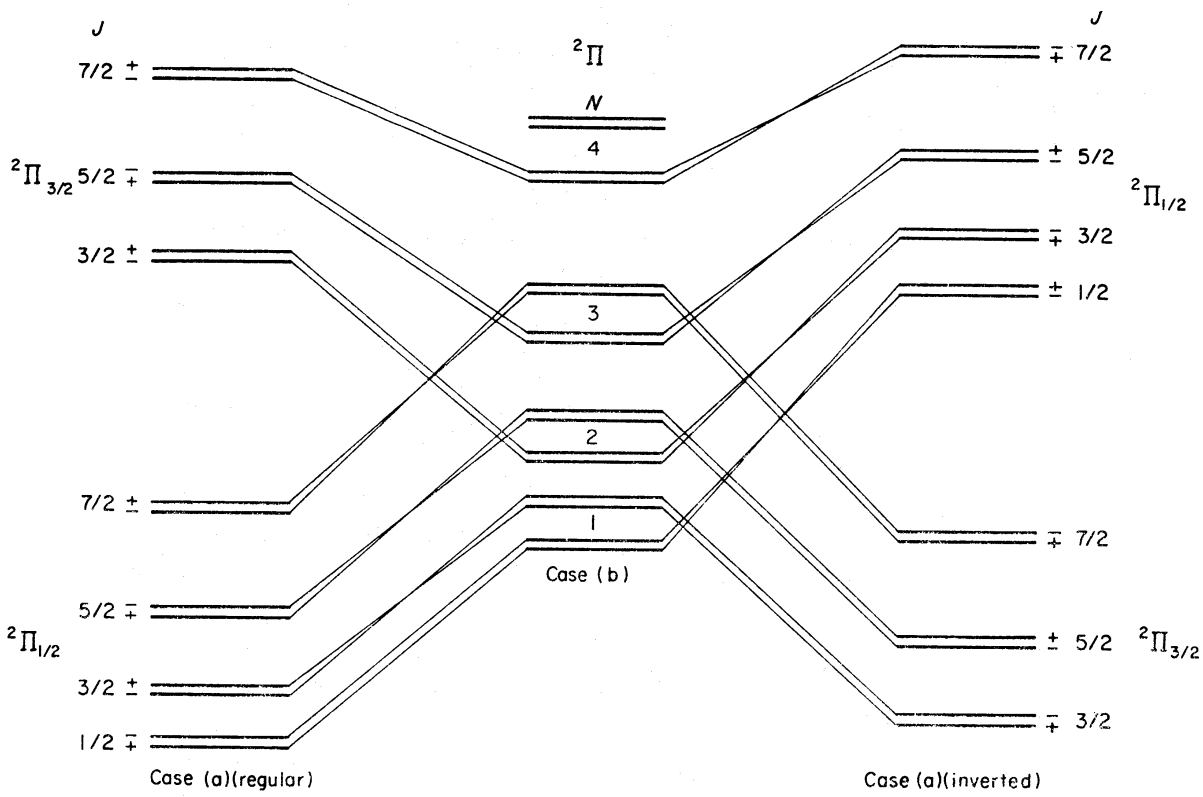

FIG. 1. *Correlation of the energy levels in case (a) and case (b) for a* $^2\Pi$ *state.*

3. INTENSITIES

The line strength in case (a) for electric dipole radiation is defined as (Condon & Shortley 1963, p. 98)

$$S(\alpha'\Omega', \alpha\Omega) = \sum_{M'=-J'}^{J'} \sum_{M=-J}^{J} \sum_{i} |(\alpha'\Omega'M'|P_i|\alpha\Omega M)|^2 \qquad (23)$$

where P_i $(i = X, Y, Z)$ are the components of the electric dipole moment referred to space-fixed axes. This can be written (Rose 1957, p. 64)

$$S(\alpha'\Omega', \alpha\Omega) = \sum_{M'M} \sum_{q} |(\alpha'\Omega'M'|P_q^{(1)}|\alpha\Omega M)|^2 \qquad (24)$$

where

$$P_{\pm 1}^{(1)} = \mp(\tfrac{1}{2})^{1/2}(P_x \pm iP_y)$$

and

$$P_0^{(1)} = P_z \qquad (25)$$

are the components of the irreducible tensor operator of rank 1 representing the electric dipole moment, referred to molecular-fixed axes. Following Rasmussen & Brodersen (1968) we have

$$(\alpha'\Omega'M'|P_q^{(1)}|\alpha\Omega M) = \left[\frac{2J+1}{2J'+1}\right]^{1/2} C(J1J'; M\Delta MM')\delta(\Delta M, q) \times C(J1J'; \Omega\Delta\Omega\Omega')(\alpha'\Omega'|P_{\Delta\Omega}^{(1)}|\alpha\Omega), \qquad (26)$$

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1970MNRAS.147...35B

which becomes on integrating over spin coordinates

$$(\alpha'\Omega'M'|P_q^{(1)}|\alpha\Omega M) = \left[\frac{2J+1}{2J'+1}\right]^{1/2} C(J1J';M\Delta MM')\delta(\Delta M,q) \times C(J1J';\Omega\Delta\Lambda\Omega')(\alpha'\Omega'|P_{\Delta\Lambda}^{(1)}|\alpha\Omega)\delta(S',S)\delta(\Sigma',\Sigma) \quad (27)$$

where $C(J1J';M\,\Delta M\,M')$ and $C(J1J';\Omega\ \Delta\Lambda\ \Omega')$ are Clebsch–Gordan coefficients as defined by Rose (1957, p. 33). Substituting in equation (24) and using the orthogonality properties of the Clebsch–Gordan coefficients (Rose 1957, p. 34) we have

$$S(\alpha'\Omega',\alpha\Omega) = (2J+1)C(J1J';\Omega\Delta\Lambda\Omega')^2(\alpha'\Omega'|P_{\Delta\Lambda}^{(1)}|\alpha\Omega)^2\delta(S',S)\delta(\Sigma',\Sigma) \quad (28)$$

$$= (\alpha'\Omega'|P_{\Lambda\Delta}^{(1)}|\alpha\Omega)^2\,\mathscr{S}(\Omega'J',\Omega J)\delta(S',S)\delta(\Sigma',\Sigma), \quad (29)$$

where

$$\mathscr{S}(\Lambda'+\Sigma J',\Lambda+\Sigma J) = (2J+1)C(J1J';\Lambda+\Sigma\ \Delta\Lambda\ \Lambda'+\Sigma)^2 \quad (30)$$

is the Hönl–London factor.

Although it is not necessary in case (a), in order to separate off the Hönl–London factor in the intermediate case it is necessary to assume

$$(\alpha'\Lambda'-\tfrac{1}{2}|P_{\Delta\Lambda}^{(1)}|\alpha\Lambda-\tfrac{1}{2})^2 = (\alpha'\Lambda'+\tfrac{1}{2}|P_{\Delta\Lambda}^{(1)}|\alpha\Lambda+\tfrac{1}{2})^2.$$

The integral over R is virtually independent of the spin orientation as the potential curves for the two multiplet components usually run very nearly parallel. Thus we may approximate equation (29) as

$$S(\alpha'\Omega',\alpha\Omega) = S(\alpha',\alpha)\,\mathscr{S}(\Omega'J',\Omega J)\delta(S',S)\delta(\Sigma',\Sigma), \quad (31)$$

and $S(\alpha',\alpha)$ is called the band strength.

The line strength in the intermediate case is

$$S(\alpha'N',\alpha N) = \sum_{M'M}\sum_q |(\alpha'N'M'|P_q^{(1)}|\alpha NM)|^2. \quad (32)$$

Taking $|\alpha NM)$ to zero-order, equation (10), equation (32) becomes

$$S(\alpha'N',\alpha N) = \sum_{M'M}\sum_q \left|\sum_{\Omega'\Omega}(\alpha'N'|\alpha'\Omega')(\alpha'\Omega'M'|P_q^{(1)}|\alpha\Omega M)(\alpha N|\alpha\Omega)\right|^2, \quad (33)$$

and substituting from equation (27) and summing over M' and M this reduces to

$$S(\alpha'N',\alpha N) = \left[\sum_{\Omega'\Omega}(\alpha'N'|\alpha'\Omega')(2J+1)^{1/2}C(J1J';\Omega\ \Delta\Lambda\ \Omega')(\alpha'\Omega'|P_{\Delta\Lambda}^{(1)}|\alpha\Omega) \times\delta(S',S)\delta(\Sigma',\Sigma)(\alpha N|\alpha\Omega)\right]^2. \quad (34)$$

From equation (28) we may write

$$S(\alpha'N',\alpha N) = \left[\sum_{\Omega'\Omega}(\alpha'N'|\alpha'\Omega')S(\alpha'\Omega',\alpha\Omega)^{1/2}(\alpha N|\alpha\Omega)\right]^2, \quad (35)$$

which leaves an ambiguity in sign which may be resolved in the case (b) limit. Substituting from equation (31) we have

$$S(\alpha'N',\alpha N) = S(\alpha',\alpha)\,\mathscr{S}(N'J',NJ)\delta(S',S), \quad (36)$$

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TABLE I

Hönl–London factors for doublet transitions—both states case (a)

	$\Delta\Lambda = 0$	$\Delta\Lambda = +1$	$\Delta\Lambda = -1$
R_1	$\dfrac{(2J+1+2\Lambda)(2J+3-2\Lambda)}{4(J+1)}$	$\dfrac{(2J+1+2\Lambda)(2J+3+2\Lambda)}{8(J+1)}$	$\dfrac{(2J+3-2\Lambda)(2J+5-2\Lambda)}{8(J+1)}$
Q_1	$\dfrac{(2J+1)(2\Lambda-1)^2}{4J(J+1)}$	$\dfrac{(2J+1)(2J+1-2\Lambda)(2J+1+2\Lambda)}{8J(J+1)}$	$\dfrac{(2J+1)(2J-1+2\Lambda)(2J+3-2\Lambda)}{8J(J+1)}$
P_1	$\dfrac{(2J-1+2\Lambda)(2J+1-2\Lambda)}{4J}$	$\dfrac{(2J-1-2\Lambda)(2J+1-2\Lambda)}{8J}$	$\dfrac{(2J-3+2\Lambda)(2J-1+2\Lambda)}{8J}$
R_2	$\dfrac{(2J+1-2\Lambda)(2J+3+2\Lambda)}{4(J+1)}$	$\dfrac{(2J+3+2\Lambda)(2J+5+2\Lambda)}{8(J+1)}$	$\dfrac{(2J+1-2\Lambda)(2J+3-2\Lambda)}{8(J+1)}$
Q_2	$\dfrac{(2J+1)(2\Lambda+1)^2}{4J(J+1)}$	$\dfrac{(2J+1)(2J-1-2\Lambda)(2J+3+2\Lambda)}{8J(J+1)}$	$\dfrac{(2J+1)(2J+1-2\Lambda)(2J+1+2\Lambda)}{8J(J+1)}$
P_2	$\dfrac{(2J-1-2\Lambda)(2J+1+2\Lambda)}{4J}$	$\dfrac{(2J-3-2\Lambda)(2J-1-2\Lambda)}{8J}$	$\dfrac{(2J-1+2\Lambda)(2J+1+2\Lambda)}{8J}$

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where

$$\mathcal{S}(N'J', NJ) = \left[\sum_{\Sigma} (\alpha' N' | \alpha' \Lambda' + \Sigma)\, \mathcal{S}(\Lambda' + \Sigma J', \Lambda + \Sigma J)^{1/2} (\alpha N | \alpha \Lambda + \Sigma)\right]^2 \quad (37)$$

is the Hönl–London factor in the intermediate case.

4. RESULTS

The Clebsch–Gordan coefficients can be obtained from Rose (1957, p. 225) and the Hönl–London factors in case (a) are given in Table I. The Hönl–London factors in the intermediate case then follow and are given in Tables II, III, IV. In these tables the following abbreviations are used:

$$A(a) = [(2a+1)^2 - 4\Lambda^2][(2J+1)^2 - 4\Lambda^2]\left[1 - 2\tilde{D}_v' X' - \frac{\tilde{\gamma}_v'}{2}\right]\left[1 - 2\tilde{D}_v X - \frac{\tilde{\gamma}_v}{2}\right], \quad (38)$$

$$B(a) = [(2J+1)^2 - 4a^2][(2J+1)^2 - 4\Lambda^2]\left[1 - 2\tilde{D}_v' X' - \frac{\tilde{\gamma}_v'}{2}\right]\left[1 - 2\tilde{D}_v X - \frac{\tilde{\gamma}_v}{2}\right], \quad (39)$$

$$C_{\pm}(a, b) = [2a + 1 \pm 2b][(2J+1)^2 - 4\Lambda^2]\left[1 - 2\tilde{D}_v' X' - \frac{\tilde{\gamma}_v'}{2}\right]\left[1 - 2\tilde{D}_v X - \frac{\tilde{\gamma}_v}{2}\right], \quad (40)$$

$$D(a) = (2a+1)(2J+1) - 4\Lambda^2, \quad (41)$$

$$E(a) = (2J+1)^2 - 4a\Lambda - 2. \quad (42)$$

Expressions for U and Z are given in equation (22) and for Y in equation (20).

All unprimed quantities refer to the lower state and primed quantities to the upper state.

From the properties of the Clebsch–Gordan coefficients (Rose 1957, p. 35), it can be shown that the sum of the Hönl–London factors in case (a) for all transitions

TABLE II

Hönl–London factors for doublet transitions with $\Delta\Lambda = 0$—both states intermediate

R_1	$\frac{1}{8(J+1)}[D(J+1) + 4\Lambda^2 Z'U' + 4\Lambda^2 ZU + [\Lambda^2 Z'ZD(J+1) + A(J+1)]U'U]$
Q_1	$\frac{2J+1}{8J(J+1)}[1 + 4\Lambda^2 - 4\Lambda^2 Z'U' - 4\Lambda^2 ZU + [\Lambda^2(4\Lambda^2+1)Z'Z - A(0)]U'U]$
P_1	$\frac{1}{8J}[D(J-1) + 4\Lambda^2 Z'U' + 4\Lambda^2 ZU + [\Lambda^2 Z'ZD(J-1) + A(J-1)]U'U]$
${}^{Q}R_{12}$	$\frac{1}{8(J+1)}[D(J+1) + 4\Lambda^2 Z'U' - 4\Lambda^2 ZU - [\Lambda^2 Z'ZD(J+1) + A(J+1)]U'U]$
${}^{P}Q_{12}$	$\frac{2J+1}{8J(J+1)}[1 + 4\Lambda^2 - 4\Lambda^2 Z'U' + 4\Lambda^2 ZU - [\Lambda^2(4\Lambda^2+1)Z'Z - A(0)]U'U]$
${}^{O}P_{12}$	$\frac{1}{8J}[D(J-1) + 4\Lambda^2 Z'U' - 4\Lambda^2 ZU - [\Lambda^2 Z'ZD(J-1) + A(J-1)]U'U]$
${}^{S}R_{21}$	$\frac{1}{8(J+1)}[D(J+1) - 4\Lambda^2 Z'U' + 4\Lambda^2 ZU - [\Lambda^2 Z'ZD(J+1) + A(J+1)]U'U]$
${}^{R}Q_{21}$	$\frac{2J+1}{8J(J+1)}[1 + 4\Lambda^2 + 4\Lambda^2 Z'U' - 4\Lambda^2 ZU - [\Lambda^2(4\Lambda^2+1)Z'Z - A(0)]U'U]$
${}^{Q}P_{21}$	$\frac{1}{8J}[D(J-1) - 4\Lambda^2 Z'U' + 4\Lambda^2 ZU - [\Lambda^2 Z'ZD(J-1) + A(J-1)]U'U]$
R_2	$\frac{1}{8(J+1)}[D(J+1) - 4\Lambda^2 Z'U' - 4\Lambda^2 ZU + [\Lambda^2 Z'ZD(J+1) + A(J+1)]U'U]$
Q_2	$\frac{2J+1}{8J(J+1)}[1 + 4\Lambda^2 + 4\Lambda^2 Z'U' + 4\Lambda^2 ZU + [\Lambda^2(4\Lambda^2+1)Z'Z - A(0)]U'U]$
P_2	$\frac{1}{8J}[D(J-1) - 4\Lambda^2 Z'U' - 4\Lambda^2 ZU + [\Lambda^2 Z'ZD(J-1) + A(J-1)]U'U]$

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TABLE III

Hönl–London factors for doublet transitions with $\Delta\Lambda = +1$—both states intermediate

R_1	$\frac{2J+3+2\Lambda}{16(J+1)}[(2J+3+2\Lambda)-2(\Lambda+1)Z'U'-2\Lambda ZU+[\Lambda(\Lambda+1)(2J+3+2\Lambda)Z'Z+C_+(J+1,\Lambda+1)]U'U]$
Q_1	$\frac{2J+1}{16J(J+1)}[E(\Lambda+1)+2(\Lambda+1)(2\Lambda+1)Z'U'+2\Lambda(2\Lambda+1)ZU+[\Lambda(\Lambda+1)Z'ZE(\Lambda+1)+B(\Lambda+1)]U'U]$
P_1	$\frac{2J-1-2\Lambda}{16J}[(2J-1-2\Lambda)+2(\Lambda+1)Z'U'+2\Lambda ZU+[\Lambda(\Lambda+1)(2J-1-2\Lambda)Z'Z+C_-(J-1,\Lambda+1)]U'U]$
${}^{Q}R_{12}$	$\frac{2J+3+2\Lambda}{16(J+1)}[(2J+3+2\Lambda)-2(\Lambda+1)Z'U'+2\Lambda ZU-[\Lambda(\Lambda+1)(2J+3+2\Lambda)Z'Z+C_+(J+1,\Lambda+1)]U'U]$
${}^{P}Q_{12}$	$\frac{2J+1}{16J(J+1)}[E(\Lambda+1)+2(\Lambda+1)(2\Lambda+1)Z'U'-2\Lambda(2\Lambda+1)ZU-[\Lambda(\Lambda+1)Z'ZE(\Lambda+1)+B(\Lambda+1)]U'U]$
${}^{O}P_{12}$	$\frac{2J-1-2\Lambda}{16J}[(2J-1-2\Lambda)+2(\Lambda+1)Z'U'-2\Lambda ZU-[\Lambda(\Lambda+1)(2J-1-2\Lambda)Z'Z+C_-(J-1,\Lambda+1)]U'U]$
${}^{S}R_{21}$	$\frac{2J+3+2\Lambda}{16(J+1)}[(2J+3+2\Lambda)+2(\Lambda+1)Z'U'-2\Lambda ZU-[\Lambda(\Lambda+1)(2J+3+2\Lambda)Z'Z+C_+(J+1,\Lambda+1)]U'U]$
${}^{R}Q_{21}$	$\frac{2J+1}{16J(J+1)}[E(\Lambda+1)-2(\Lambda+1)(2\Lambda+1)Z'U'+2\Lambda(2\Lambda+1)ZU-[\Lambda(\Lambda+1)Z'ZE(\Lambda+1)+B(\Lambda+1)]U'U]$
${}^{Q}P_{21}$	$\frac{2J-1-2\Lambda}{16J}[(2J-1-2\Lambda)-2(\Lambda+1)Z'U'+2\Lambda ZU-[\Lambda(\Lambda+1)(2J-1-2\Lambda)Z'Z+C_-(J-1,\Lambda+1)]U'U]$
R_2	$\frac{2J+3+2\Lambda}{16(J+1)}[(2J+3+2\Lambda)+2(\Lambda+1)Z'U'+2\Lambda ZU+[\Lambda(\Lambda+1)(2J+3+2\Lambda)Z'Z+C_+(J+1,\Lambda+1)]U'U]$
Q_2	$\frac{2J+1}{16J(J+1)}[E(\Lambda+1)-2(\Lambda+1)(2\Lambda+1)Z'U'-2\Lambda(2\Lambda+1)ZU+[\Lambda(\Lambda+1)Z'ZE(\Lambda+1)+B(\Lambda+1)]U'U]$
P_2	$\frac{2J-1-2\Lambda}{16J}[(2J-1-2\Lambda)-2(\Lambda+1)Z'U'-2\Lambda ZU+[\Lambda(\Lambda+1)(2J-1-2\Lambda)Z'Z+C_-(J-1,\Lambda+1)]U'U]$

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1970MNRAS.147...35B

TABLE IV

Hönl–London factors for doublet transitions with $\Delta\Lambda = -1$—both states intermediate

$$R_1 \quad \frac{2J+3-2\Lambda}{16(J+1)}[(2J+3-2\Lambda)+2(\Lambda-1)Z'U'+2\Lambda ZU+[\Lambda(\Lambda-1)(2J+3-2\Lambda)Z'Z+C_-(J+1,\Lambda-1)]U'U]$$

$$Q_1 \quad \frac{2J+1}{16J(J+1)}[E(\Lambda-1)+2(\Lambda-1)(2\Lambda-1)Z'U'+2\Lambda(2\Lambda-1)ZU+[\Lambda(\Lambda-1)Z'ZE(\Lambda-1)+B(\Lambda-1)]U'U]$$

$$P_1 \quad \frac{2J-1+2\Lambda}{16J}[(2J-1+2\Lambda)-2(\Lambda-1)Z'U'-2\Lambda ZU+[\Lambda(\Lambda-1)(2J-1+2\Lambda)Z'Z+C_+(J-1,\Lambda-1)]U'U]$$

$$^{Q}R_{12} \quad \frac{2J+3-2\Lambda}{16(J+1)}[(2J+3-2\Lambda)+2(\Lambda-1)Z'U'-2\Lambda ZU-[\Lambda(\Lambda-1)(2J+3-2\Lambda)Z'Z+C_-(J+1,\Lambda-1)]U'U]$$

$$^{P}Q_{12} \quad \frac{2J+1}{16J(J+1)}[E(\Lambda-1)+2(\Lambda-1)(2\Lambda-1)Z'U'-2\Lambda(2\Lambda-1)ZU-[\Lambda(\Lambda-1)Z'ZE(\Lambda-1)+B(\Lambda-1)]U'U]$$

$$^{O}P_{12} \quad \frac{2J-1+2\Lambda}{16J}[(2J-1+2\Lambda)-2(\Lambda-1)Z'U'+2\Lambda ZU-[\Lambda(\Lambda-1)(2J-1+2\Lambda)Z'Z+C_+(J-1,\Lambda-1)]U'U]$$

$$^{S}R_{21} \quad \frac{2J+3-2\Lambda}{16(J+1)}[(2J+3-2\Lambda)-2(\Lambda-1)Z'U'+2\Lambda ZU-[\Lambda(\Lambda-1)(2J+3-2\Lambda)Z'Z+C_-(J+1,\Lambda-1)]U'U]$$

$$^{R}Q_{21} \quad \frac{2J+1}{16J(J+1)}[E(\Lambda-1)-2(\Lambda-1)(2\Lambda-1)Z'U'+2\Lambda(2\Lambda-1)ZU-[\Lambda(\Lambda-1)Z'ZE(\Lambda-1)+B(\Lambda-1)]U'U]$$

$$^{Q}P_{21} \quad \frac{2J-1+2\Lambda}{16J}[(2J-1+2\Lambda)+2(\Lambda-1)Z'U'-2\Lambda ZU-[\Lambda(\Lambda-1)(2J-1+2\Lambda)Z'Z+C_+(J-1,\Lambda-1)]U'U]$$

$$R_2 \quad \frac{2J+3-2\Lambda}{16(J+1)}[(2J+3-2\Lambda)-2(\Lambda-1)Z'U'-2\Lambda ZU+[\Lambda(\Lambda-1)(2J+3-2\Lambda)Z'Z+C_-(J+1,\Lambda-1)]U'U]$$

$$Q_2 \quad \frac{2J+1}{16J(J+1)}[E(\Lambda-1)-2(\Lambda-1)(2\Lambda-1)Z'U'-2\Lambda(2\Lambda-1)ZU+[\Lambda(\Lambda-1)Z'ZE(\Lambda-1)+B(\Lambda-1)]U'U]$$

$$P_2 \quad \frac{2J-1+2\Lambda}{16J}[(2J-1+2\Lambda)+2(\Lambda-1)Z'U'+2\Lambda ZU+[\Lambda(\Lambda-1)(2J-1+2\Lambda)Z'Z+C_+(J-1,\Lambda-1)]U'U]$$

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1970MNRAS.147...35B

from a level with a given J is equal to the statistical weight $2J+1$ of that level, that is

$$\sum_{J'} \mathscr{S}(\Lambda'+\Sigma J', \Lambda+\Sigma J) = 2J+1. \tag{43}$$

It follows that the sum of the Hönl–London factors for all branches in a band is

$$\sum_{\Sigma=-S}^{S} \sum_{J'} \mathscr{S}(\Lambda'+\Sigma J', \Lambda+\Sigma J) = (2S+1)(2J+1). \tag{44}$$

From the properties of the Clebsch–Gordan coefficients and the transformation coefficients $(\alpha N|\alpha\Omega)$, equation (11), it can be shown that the Hönl–London factors in the intermediate case are normalized in the same way, as they should be, that is

$$\sum_{J'} \sum_{N'=|J'-S|}^{J'+S} \sum_{N=|J-S|}^{J+S} \mathscr{S}(N'J', NJ) = (2S+1)(2J+1). \tag{45}$$

As mentioned in the Introduction there are three published tabulations of Hönl–London factors for doublet transitions: these have been used to check the algebra by verifying that as (1) Y', $Y\to\infty$, (2) $Y' = \tilde{\gamma}_v'$, $Y = \tilde{\gamma}_v$, (3) $\Lambda' = 1$, $\Lambda = 0$, $Y = \tilde{\gamma}_v$; $\Lambda' = 0$, $Y' = \tilde{\gamma}_v'$, $\Lambda = 1$ the formulae here go over to the formulae there. It was found that all three checks were necessary as no one tabulation completely checked the formulae.

Fig. 2 shows the permitted transitions between two $^2\Pi$ states in a compact level scheme. For $J = \frac{5}{2}$, all the transitions shown occur in intermediate coupling. Only the broken lines apply if both states are pure case (a). The dotted lines are absent if both states are pure case (b).

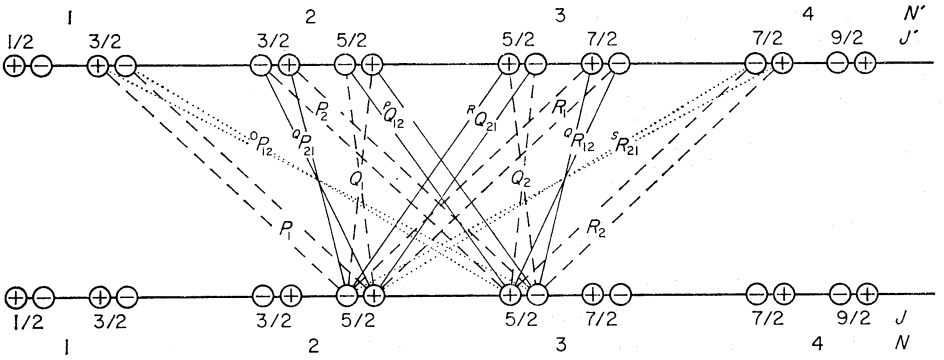

FIG. 2. *Transitions between two* $^2\Pi$ *states.*

5. DISCUSSION

The equation for the doublet energy levels in the intermediate case obtained by Hill and Van Vleck was extended to include rotational centrifugal distortion by Almy & Horsfall (1937) and later by James (1964) who also included the relativistic part of the spin-rotation interaction. Almy and Horsfall attempted to take account of the rotational centrifugal distortion by a procedure which as pointed out by James was incorrect. Neglecting other effects considered by James his equation agrees with the one given here.

Starting the perturbation treatment from case (b) Hill and Van Vleck obtained the coefficients for the doublet case (neglecting D_v and γ_v) relating the wave functions in the intermediate case with those in case (b). However, as it is more convenient to derive the Hönl–London factors in the intermediate case from case (a) these coefficients must be transformed to relate the wave functions in the intermediate

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case to those in case (a). These coefficients then agree with the ones given here, to the same approximation.

The method of calculation (Section 3) has apparently never been described in detail. Most discussions (see Hill & Van Vleck 1928; Budó 1937) give only the transition moment for the intermediate case from which equation (32) is derived. The derivation of equation (37) is not trivial and involves certain approximations which require justification. Probably the worst approximation is to assume that the vibrational wave functions are independent of the spin orientation, for in some cases the potential curves for the different multiplets are far from parallel. For the $A\ ^2\Pi$ state in HgH, $A(R_e) = 3684\ \text{cm}^{-1}$ compared with

$$A(\infty) = E(Hg, {}^3P_1) - E(Hg, {}^3P_0) = 1767\ \text{cm}^{-1}.$$

Unfortunately this approximation is necessary in order that the Hönl–London factor in the intermediate case can be defined.

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NOTE ADDED IN PROOF

Tables similar to Tables II–IV have been given by Kovács in *Rotational Structure in the Spectra of Diatomic Molecules*, Adam Hilger, London, shortly to be published (November, 1969). The formulae contained within them agree with the present ones, when D_v and γ_v are neglected.

The theory is given here in a fuller and more consistent way.

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