Rotational line strengths in $^4\Sigma - ^4\Pi$ transition of diatomic molecules

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Abstract. A theoretical derivation of closed form expressions for the intensities of all the rotational branches arising out of $^4\Sigma - ^4\Pi$ electronic transition in a diatomic molecule is described. In the present theory the tradition of treating the coupling in the $^4\Sigma$ state as belonging to Hund's case (b) is discarded; instead a full-fledged intermediate coupling treatment which rigorously takes into account the spin-spin and second order spin-orbit effects is presented. Since accurate intermediate coupling treatment of $^4\Pi$, in analytically closed form, is not possible, the $^4\Pi$ is first restricted to the extreme coupling scheme Hund's case (a) (or case (b)); the effect of spin uncoupling (or spin-orbit and spin-spin interactions) is then incorporated through a first order perturbation calculation.

Keywords. Diatomic molecule; rotational Hamiltonian; rotational line strengths.

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1. Introduction

The intensity distribution in the rotational structure of the band spectrum of a molecule is governed, among other things, by the rotational line strengths. The rotational fine structure that accompanies a multiplet electronic transition of a diatomic molecule, in general, presents a complex appearance and a knowledge of the theoretical line strengths would be of immense help in the correct identification of the various rotational branches.

Expressions for line strengths for many electronic transitions of diatomic molecules have been documented (Kovács 1969). It is to be appreciated that the line strengths are profoundly influenced by the scheme of coupling to which the upper and lower electronic states conform. For multiplicities higher than three ($S > 1$), the secular equation for the rotational terms which arise in the context of diagonalising the rotational Hamiltonian does not admit of closed form expressions for the general case in which the coupling in the multiplet state is intermediate between Hund's case (a) and case (b). For this reason the line strength expressions of Kovács for multiplicities four and above are valid for either Hund's case (a) or case (b). While these idealised coupling schemes are seldom exactly realised, what one encounters more frequently are electronic states wherein the coupling is close to Hund's case (a) or to case (b). In such situations the deviation from Hund's case (a) due to spin uncoupling and from Hund's case (b) occasioned by spin-orbit and spin-spin interactions may not always be
negligible. It is then necessary to tackle such situations by standard perturbation
technique. Details of this approach for a $^4\Sigma$-$^4\Pi$ transition form the theme of the present
paper. This perpendicular type of transition occurs in many eleven valence electron
molecules like NO and O$_2^+$ which await quantitative elucidation of their intensity
distribution. This has provided a strong motivation for pursuing this problem. A
further impetus to this motivation is provided by the fortunate circumstance that closed
form intermediate coupling treatment of $^4\Sigma$ state is rigorously possible.

2. Theoretical details

2.1 Hamiltonian

In order to develop expressions for the rotational line strengths one should start with
the rotational eigenfunctions of the $^4\Sigma$ and $^4\Pi$ states. These are obtained by
diagonalising the rotational Hamiltonian (Hougen 1970).

$$H = BR^2 + \gamma R \cdot S + A L \cdot S + (2/3)(3S^2 - S^2),$$

with \( R = (J - L - S) \).

The angular momenta \( J, L \) and \( S \) (expressed in units of \( \hbar \)) have their customary
meaning (Hougen 1970). \( B \) is the rotational constant and \( \gamma \) represents the spin-rotation
interaction parameter. The constant \( \lambda \) includes both spin-spin and second order spin-
orbit contributions (Balasubramanian and Narasimham 1979). The term in \( A \) which
allows for first order spin-orbit effect is non-zero only for states other than \( \Sigma \). All the
parameters in Hamiltonian (1) are in wavenumber units. In arriving at the eigenfunc-
tions of (1) we prefer to work in case (a) basis. In what follows, a typical basis
function will be described as \( |2s + \lambda J_n \rangle \). We recall that in case (a) description the
components \( \Lambda, \Sigma \) and \( \Omega \) are along the internuclear axis which is the \( z \)
axis of the molecule-fixed \((x, y, z)\) frame. \( M = J_z \) represents the component of \( J \) along
the \( Z \) axis of a laboratory-fixed frame \((X, Y, Z)\). The relation between the two frames
has been elaborated by Kovács (1969).

2.2 Eigenfunctions of $^4\Sigma$ state

For a $^4\Sigma$ state the diagonalization of the Hamiltonian is straightforward (see
Balasubramanian and Narasimham 1979). By a suitable choice of Wang sums of pairs
of basis functions formed out of the four basis functions \( |2s + \lambda J_n \rangle \) with \( \lambda = -3/2,
-1/2, 1/2 \) and \( 3/2 \), the \( 4 \times 4 \) secular determinant of the problem may be reduced to two
\( 2 \times 2 \) diagonal blocks which admit of closed form solutions. The resulting eigenfunc-
tions are given in table 1a. The coefficients \( a_j, b_j \) etc. appearing in the table are given by

$$a_j = \left[ 1 + \left( 1 + u(J) + v(J)^2 \right)^{1/2} \right]^{-1/2},$$
$$b_j = \left[ 1 + \left( 1 + u(J) + v(J)^2 \right)^{1/2} \right] \cdot a_j,$$
$$c_j = \left[ 1 + \left( 1 + u(J) + v(J)^2 \right)^{1/2} \right] \cdot c_j,$$
$$d_j = \left[ 1 + \left( 1 + u(J) + v(J)^2 \right)^{1/2} \right] \cdot d_j,$$

with

$$u(J) = 2\lambda/(B - \gamma/2) + (J - 3/2)/[3(J - 1/2)(J + 3/2)]^{1/2},$$
$$v(J) = 2\lambda/(B - \gamma/2) - (J + 5/2)/[3(J - 1/2)(J + 3/2)]^{1/2}.$$
Rotational line strengths in quartet transitions

To illustrate how table 1a may be used to obtain the rotational wave functions of \( ^4\Sigma \) we give below the example of \( |F_2(J)\rangle \). Referring to table 1a we readily write

\[
|F_2(J)\rangle = (c_+^J / \sqrt{2})|\Sigma_{-3/2}\rangle + (b_+^J / \sqrt{2})|\Sigma_{-1/2}\rangle - (d_+^J / \sqrt{2})|\Sigma_{1/2}\rangle
\]

2.3 Eigenfunctions of \( ^4\Pi \) state close to Hund's case (a)

The eigenfunctions of \( ^4\Pi \) state belonging to Hund’s case (a) can be designated as \( |\Pi_\Omega_0; \Omega M; p\rangle \) for short, with \( \Omega = -1/2, 1/2, 3/2 \) and \( 5/2 \) (parenthetically we remark that the function \( |\Pi_\Omega_0; \Omega M; p\rangle \) actually stands for either of the linear combinations \( \{ |\Pi_\Omega_0; \Omega M; p\rangle + (p)|\Pi_{-\Omega_0}; -\Omega M\rangle \} \) with \( p = + \) or \( - \). The choice of \( p \) is dictated by the particular \( \Lambda \)-component to which the transition occurs. In this idealised situation each base state is characterised by well-defined projection \( \Sigma \) of \( S \) along the molecular axis. In the rotating molecule, however, rotation tends to mix states with different \( \Sigma \) (and hence \( \Omega \)). This phenomenon is known as spin uncoupling (Herzberg 1950). In real situations the molecule starts out as case (a) for slow rotations but at faster rotations the spin uncoupling can introduce a considerable deviation from case (a). As has been pointed out right at the beginning, intermediate coupling calculation, in an analytically closed form, is not possible for the \( ^4\Pi \) state without serious approximations. Therefore, we are content to consider the spin uncoupling by a first order perturbation approach.

The term in Hamiltonian (1) describing spin uncoupling may be shown to be

\[
H_\alpha' = -(B - \gamma/2)(J_+ S_- + J_- S_+),
\]

where

\[
J_+ = J_x + i J_y, \quad J_- = J_x - i J_y, \quad \text{etc.}
\]

In the light of this, (1) can be rewritten as:

\[
H = H_0^n + H_\alpha',
\]

where

\[
H_0^n = B\{ (J^2 - J_z^2) + (L_z^2 - L_z^2) \} + (B - \gamma)(S_z^2 - S_z^2)
+ AL_z S_z + (2\lambda/3)(3S_z^2 - S^2)
\]

(Hougen 1970). In (6) we have ignored certain terms which do not have matrix elements within the limited base states we are considering here. In this form \( H_0^n \) generates the eigenfunctions \( |\Pi_\Omega_0; \Omega M; p\rangle \) appropriate for pure case (a) which would serve as the zeroth order wave functions for the perturbation calculations. Our aim is to find the first order correction to the eigenfunctions due to the perturbation \( H_\alpha' \). The modified eigenfunction to first order is given by:

\[
|\psi_n\rangle = |\psi_n^0\rangle + \sum_{i \neq n} (H_\alpha')_{in} |\psi_i^0\rangle/(E_i^0 - E_n^0).
\]

(see Pauling and Wilson 1935). In (7) it is sufficient to restrict the summation to the four multiplet components of the \( ^4\Pi \) state. The zeroth order energies \( E_n^0[=T_0(J)] \) are as
Table 1. Rotational wave functions in case (a) basis for $^4 \Sigma$ and $^4 \Pi$ states. The coefficients as functions of $J$ are given under each base state.

| Rotational state | Base sub-state | $|^4 \Sigma_{-3/2}\rangle$ | $|^4 \Sigma_{-1/2}\rangle$ | $|^4 \Sigma_{1/2}\rangle$ | $|^4 \Sigma_{3/2}\rangle$ |
|------------------|----------------|----------------|----------------|----------------|----------------|
| $|F_1(J)\rangle$  | $a_J^\pm /\sqrt{2}$ | $b_J^+/\sqrt{2}$ | $b_J^-/\sqrt{2}$ | $a_J^+ /\sqrt{2}$ |
| $|F_2(J)\rangle$  | $c_J^+/\sqrt{2}$ | $d_J^-/\sqrt{2}$ | $-d_J^+/\sqrt{2}$ | $-c_J^+ /\sqrt{2}$ |
| $|F_3(J)\rangle$  | $a_J^-/\sqrt{2}$ | $b_J^-/\sqrt{2}$ | $b_J^+ /\sqrt{2}$ | $a_J^- /\sqrt{2}$ |
| $|F_4(J)\rangle$  | $c_J^-/\sqrt{2}$ | $d_J^+/\sqrt{2}$ | $-d_J^-/\sqrt{2}$ | $-c_J^- /\sqrt{2}$ |

I(b): $^4 \Pi$ close to Hund's case (a)

| Rotational state | Base sub-state | $|^4 \Pi_{-1/2}\rangle$ | $|^4 \Pi_{1/2}\rangle$ | $|^4 \Pi_{3/2}\rangle$ | $|^4 \Pi_{5/2}\rangle$ |
|------------------|----------------|----------------|----------------|----------------|----------------|
| $|\Psi_1(J)\rangle$ | 1 | $\sqrt{3} B(J+1/2)/({\bar{\alpha}}-4\lambda)$ | 0 | 0 | 0 |
| $|\Psi_2(J)\rangle$ | $-\sqrt{3} B(J+1/2)/({\bar{\alpha}}-4\lambda)$ | 1 | $2B[(J-1/2)(J+3/2)]^{1/2}/\bar{\alpha}$ | 0 | 0 |
| $|\Psi_3(J)\rangle$ | 0 | $-2B[(J-1/2)(J+3/2)]^{1/2}/\bar{\alpha}$ | 1 | $\sqrt{3} B[(J-3/2)(J+5/2)]^{1/2}/({\bar{\alpha}}+4\lambda)$ | 0 |
| $|\Psi_4(J)\rangle$ | 0 | 0 | $-\sqrt{3} B[(J+5/2)(J-3/2)]^{1/2}/({\bar{\alpha}}+4\lambda)$ | 1 |
I(c): $^4\Pi$ close to Hund's case (b) (All the coefficients should be multiplied by the factor $1/8\sqrt{2} J$)

| Rotational sub-state | Base state $\rightarrow |^4\Pi_{-1/2} \rangle$ | $|^4\Pi_{1/2} \rangle$ | $|^4\Pi_{3/2} \rangle$ | $|^4\Pi_{5/2} \rangle$ |
|----------------------|---------------------------------|-----------------|-----------------|-----------------|
| $|F_1(J)\rangle$     | $[8J(2J-3)]^{1/2} + 3Y$        | $[24J(2J-3)]^{1/2} + \sqrt{3}Y + \mu$ | $\frac{24J(2J-3)(2J+3)}{(2J-1)} - \sqrt{3}Y + \mu$ | $\frac{8J(2J+3)(2J+5)}{(2J+1)} - 3Y - \sqrt{3}\mu$ |
|                      | $- \sqrt{3}\mu$                |                 |                 |                 |
| $|F_2(J)\rangle$     | $2J\frac{6(2J+1)}{(J+1)}^{1/2}$ | $\frac{\sqrt{8J(2J+5)}}{(J+1)(2J+1)}^{1/2}$ | $-2J(2J-7)\frac{2(2J+3)}{(J+1)(2J-1)(2J+1)}^{1/2}$ | $-2J\frac{6(2J-3)(2J+3)(2J+5)}{(J+1)(2J-1)(2J+1)}^{1/2}$ |
|                      | $+ \sqrt{3}Y - \mu$            |                 |                 |                 |
|                      | $-5Y + \sqrt{3}\mu$            | $-5Y - \sqrt{3}\mu$ | $+ \sqrt{3}Y + \mu$ |                 |
| $|F_3(J)\rangle$     | $[24J(2J+1)]^{1/2}$             | $-\sqrt{8J(2J-3)}$ | $-(2J+9)\frac{8J(2J-1)}{(2J+1)(2J+3)}^{1/2}$ | $\frac{24J(2J-3)(2J+3)(2J+5)}{(2J+1)(2J+3)}^{1/2}$ |
|                      | $\frac{(2J+1)}{2J+1}^{1/2}$    | $-\sqrt{3}Y + \mu$ | $-5Y + \sqrt{3}\mu$ | $+ 5Y + \sqrt{3}\mu$ |
|                      | $+ \sqrt{3}Y + \mu$            |                 |                 | $\sqrt{3}Y + \mu$ |
| $|F_4(J)\rangle$     | $2J\frac{2(2J+5)}{(J+1)}^{1/2}$ | $-2J\frac{6(2J+5)}{(J+1)}^{1/2}$ | $2J\frac{6(2J-1)(2J+5)}{(J+1)(2J+3)}^{1/2}$ | $-2J\frac{2(2J-3)(2J-1)}{(J+1)(2J+3)}^{1/2}$ |
|                      | $-3Y + \sqrt{3}\mu$            | $+ \sqrt{3}Y + \mu$ | $+ \sqrt{3}Y - \mu$ | $-3Y - \sqrt{3}\mu$ |

*The correlation between $|\Psi_i\rangle$ and $|F_i\rangle$ are as follows: For $A > 0$, $|\Psi_i\rangle \rightarrow |F_i\rangle$ and for $A < 0$, $|\Psi_i\rangle \rightarrow |F_{i-1}\rangle$. 
follows:

\[ E_1^0(\Omega = -1/2) = T - 3(A - 3\lambda - 3\gamma/2)/2 + B\{(J + 1/2)^2 + 1\}, \]
\[ E_2^0(\Omega = 1/2) = T - (A - \lambda - \gamma/2)/2 + B\{(J + 1/2)^2 + 3\}, \]
\[ E_3^0(\Omega = 3/2) = T + (A + \lambda + \gamma/2)/2 + B\{(J + 1/2)^2 + 1\}, \]
\[ E_4^0(\Omega = 5/2) = T + 3(A + 3\lambda + 3\gamma/2)/2 + B\{(J + 1/2)^2 - 5\}, \]

\((T\) is an additive constant). The non-vanishing matrix elements of \(H'_b\) are given by

\[ (H'_{bb})_{12} = (H'_{bb})_{21} = -(B - \gamma/2)\sqrt{3}(J + 1/2), \]
\[ (H'_{bb})_{23} = (H'_{bb})_{32} = -2(B - \gamma/2)[(J - 1/2)(J + 3/2)]^{1/2}, \]
\[ (H'_{bb})_{34} = (H'_{bb})_{43} = -(B - \gamma/2)[3(J + 5/2)(J - 3/2)]^{1/2}. \]

Other elements like \((H'_{bb})_{13}, (H'_{bb})_{14}\) and \((H'_{bb})_{24}\) etc vanish. Substituting the various parameters in \((7)\) we obtain the eigenfunctions for the four-rotational term series, correct to first order. Table 1b sums up the results. The quantities \(\tilde{A}, \tilde{B}\) and \(\tilde{\lambda}\) appearing in the table are defined as

\[ \tilde{A} = A - 2B, \quad \tilde{B} = B - \gamma/2 \quad \text{and} \quad \tilde{\lambda} = \lambda - \tilde{B}. \]

The correlation between \(|\psi_i(J)\rangle\) and the more familiar \(|F_r(J)\rangle\) is given by

\[ |\psi_i(J)\rangle \leftrightarrow |F_r(J)\rangle \quad \text{for regular} \ (A > 0) \ \text{multiplet}, \]
\[ |\psi_i(J)\rangle \leftrightarrow |F_{5-i}(J)\rangle \quad \text{for inverted} \ (A < 0) \ \text{multiplet}. \]

2.4 Eigenfunctions of \(^4\Pi\) close to Hund's case (b)

The zeroth order eigenfunctions and energies which form the basis for our perturbation calculations are obtained by diagonalizing Hamiltonian \((1)\) in which we set \(A = 0\) and \(\lambda = 0\). With this substitution Hamiltonian \((1)\), which we now call \(H'_b\), describes the ideal case (b). The first order spin-orbit term \(AL_zS_z\) together with the term in \(\lambda\) in \((1)\) now provides the perturbation \(H'_b\) which causes a deviation from case (b). As before we rewrite \((1)\) as \(H = H'_b + H''_b\) with

\[ H'_b = AL_zS_z + (2\lambda/3)(3S_z^2 - S^2) \]
\[ H''_b = B(J - L - S)^2, \]

where we have neglected the small term in \(\gamma\). The zeroth order wave functions for pure case (b) are expressed as linear combinations of case (a) basis functions. The appropriate coefficient may be obtained from table 1c by setting \(Y(= A/B) = \mu\) \((= \lambda/B) = 0\)

For carrying out perturbation calculation, we need the matrix elements of \(H'_b\) between pairs of the four zeroth order wave functions. While the evaluation of these matrix elements poses no particular difficulty, the final expressions are unduly cumbersome. In order to effect further simplification we observe that while a \(^4\Pi\) state always starts out as case (a) for small rotations, the case (b) character is fully realised only in the asymptotic limit \(J \to \infty\). From this observation, we readily realise that in evaluating the matrix elements of \(H'_b\), it is just sufficient to make use of the asymptotic form for the case (b) coefficients. This will not entail a serious error because we are using the asymptotic form merely to evaluate the perturbation matrix elements. In this limit,
the non-diagonal matrix elements are given by
\begin{align*}
(H_b)_{12} &= (H_b)_{21} = (H_b)_{34} = (H_b)_{43} = -\sqrt{3} Y/2, \\
(H_b)_{13} &= (H_b)_{31} = (H_b)_{24} = (H_b)_{42} = \mu, \\
(H_b)_{23} &= (H_b)_{32} = -Y \quad \text{and} \quad (H_b)_{14} = (H_b)_{41} = 0.
\end{align*}

The correct zeroth order energy values needed in the perturbation calculation are given by
\begin{align}
F^0_0(J) &= B\{(J - 3/2)(J - 1/2) - 1\}, \\
F^0_2(J) &= B\{(J - 1/2)(J + 1/2) - 1\}, \\
F^0_3(J) &= B\{(J + 1/2)(J + 3/2) - 1\}, \\
F^0_4(J) &= B\{(J + 3/2)(J + 5/2) - 1\},
\end{align}

(13)

The superscript 0 in (13) is to remind us that these are the zeroth order energies. Using (7) along with (12) and (13), we finally arrive at the wave functions correct to first order. Again, the corrected wave functions are expressed in case (a) basis and are given in table 1c.

2.5 Calculation of rotational line strengths

The general problem of calculating line strengths is laborious. For a detailed account we refer the reader to earlier works (Kovács 1969; Hougen 1970). In the present discussion we shall give only a bare outline of the procedure followed in our calculation.

We first recall that the line strength is given by:
\begin{equation}
S_{ij}(J', J'') = \sum_{M, M'} |\langle F_i' (J') | \mu_R | F_j'' (J'') \rangle|^2,
\end{equation}

(14)

where
\begin{align*}
i, j &= 1, 2, 3, 4 \quad \text{and} \quad R = X, Y, Z.
\end{align*}

Here \(\mu_R\) represents the \(R\)th component of the electric dipole moment in the space-fixed frame \(X, Y, Z\). \(|F_i(J)\rangle\) is, of course, the rotational wave function for the \(i\)th multiplet component discussed in detail in previous sections. (Note that the wave functions have an \(M\)-labelling which is not explicit in our notation). As we have chosen to express the rotational eigenfunctions in case (a) basis which exploits the molecular \(z\) axis as the quantization axis, it is necessary that we express \(\mu_R\) in terms of the molecule fixed components \(\mu_r\) through the direction cosines \(\alpha_{rr}\). The relation is
\begin{equation}
\mu_R = \sum_r \alpha_{rr}\mu_r.
\end{equation}

(15)

In order to proceed further we first note that for molecules in gas phase and field-free environment all directions in space are equivalent. It is sufficient, therefore, to compute \(S_{ij}\) for one particular component \(\mu_R\) without loss of generality. We shall then specialize for the \(Z\)th component \(\mu_R\) in our calculations. This choice is the simplest because it gives the especially simple \(M\) selection rule, \(\Delta M = 0\). By using (15), we can show that
\begin{equation}
\mu_L = (\mu_x - i\mu_y)(\alpha_{zx} + i\alpha_{zy})/2 + (\mu_x + i\mu_y)(\alpha_{zx} - i\alpha_{zy})/2 + \mu_z \alpha_{zz}.
\end{equation}

(16)

The various non-vanishing matrix elements of (16) between case (a) base states are tabulated by Hougen (1970). In our problem, we are treating an orbitally-allowed, spin-
allowed electric dipole transition. So, we have the obvious selection rule $\Delta \Sigma = 0$ for the spin projection $\Sigma$. Application of this to the general transition

$$|F'_i(J')\rangle \rightarrow |F''_j(J'')\rangle,$$

reduces the problem to one of evaluating the transition amplitudes for the four case (a) sub-transitions:

$$|4\Sigma_{-3/2}\rangle \rightarrow |4\Pi_{-1/2}\rangle, |4\Sigma_{-1/2}\rangle \rightarrow |4\Pi_{1/2}\rangle,$$

$$|4\Sigma_{1/2}\rangle \rightarrow |4\Pi_{3/2}\rangle \quad \text{and} \quad |4\Sigma_{3/2}\rangle \rightarrow |4\Pi_{5/2}\rangle.$$

Each of these sub-transitions obey the $J$ selection rule $\Delta J = 0, \pm 1$, leading to the familiar $Q, R$ and $P$ branches. We have evaluated the effective transition amplitudes for all the above sub-transitions and for each of the branches. These are summarized in table 2.

For a $^4\Sigma - ^4\Pi$ transition one expects, in general, 48 branches of various types (Herzberg 1950). While it is straightforward to obtain the line strengths for each such branch by adopting the procedure indicated above, it is not feasible to tabulate the formulae, in the interest of space. We shall, therefore, be content with giving two illustrative examples of how the contents of tables 1 and 2 may be used in arriving at the line strengths for any particular branch.

2.6 Illustrative examples

(i) $^4\Sigma$(int) $\rightarrow$ $^4\Pi_1(\sim a)$, line strength of $P_{31}(J)$ line:

For this case, explicitly, the rotational transition is $|F'_i(J-1)\rangle \rightarrow |F''_j(J)\rangle$. Referring to tables 1a, b and 2 (row 1 for $P$ branch) we find the transition amplitude to be

$$a_{J-1}/\sqrt{2} \times 1 \times -[(2J-1)(2J-3)/8J]^{1/2} + b_{J-1}/\sqrt{2} \times \sqrt{3B(J+1/2)/2A-4\lambda} \times -[(2J-1)(2J+1)/8J]^{1/2} + a_{J-1}/\sqrt{2} \times 0 \times -[(2J+1)(2J+3)/8J]^{1/2} + a_{J-1}/\sqrt{2} \times 0 \times -[(2J+5)(2J+3)/8J]^{1/2}.$$

The line strength for the $P_{31}(J)$ line is obtained by squaring this amplitude which, on simplification becomes

$$\{(2J-1)/8J\} \{a_{J-1}(2J-3)^{1/2} + \sqrt{3B} (2J+1)(2J+1)^{1/2}/2(2A-4\lambda)\}^2$$

the coefficients $a_j$, $b_j$ etc are given by (2) and (3).

In a similar fashion the line strengths for the other branches may be worked out.

(ii) $^4\Sigma$(int) $\rightarrow$ $^4\Pi_1(\sim b)$, line strength of $Q_{24}(J)$:

Explicitly, the rotational transition is

$$|F'_i(J)\rangle \rightarrow |F''_j(J)\rangle.$$

Since the $^4\Pi$ is close to case (b), we have to refer to table 1c for the wave functions. Referring now to tables 1a, c and 2 (row 2 for $Q$ branch), we obtain the transition amplitude to be
Table 2. Electric dipole transition amplitudes for $^4\Sigma \rightarrow ^4\Pi$ case (a) sub-transitions.

<table>
<thead>
<tr>
<th>Branch</th>
<th>$^4\Sigma_{-3/2} \rightarrow ^4\Pi_{-1/2}$</th>
<th>$^4\Sigma_{-1/2} \rightarrow ^4\Pi_{1/2}$</th>
<th>$^4\Sigma_{1/2} \rightarrow ^4\Pi_{3/2}$</th>
<th>$^4\Sigma_{3/2} \rightarrow ^4\Pi_{5/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P )</td>
<td>(- \left[ \frac{(2J - 1)(2J - 3)}{8J} \right]^{1/2} )</td>
<td>(- \left[ \frac{(2J - 1)(2J + 1)}{8J} \right]^{1/2} )</td>
<td>(- \left[ \frac{(2J + 1)(2J + 3)}{8J} \right]^{1/2} )</td>
<td>(- \left[ \frac{(2J + 5)(2J + 3)}{8J} \right]^{1/2} )</td>
</tr>
<tr>
<td>( Q )</td>
<td>( + \left[ \frac{(2J - 1)(2J + 1)(2J + 3)}{8J(J + 1)} \right]^{1/2} )</td>
<td>( + (2J + 1) \left[ \frac{(2J + 1)}{8J(J + 1)} \right]^{1/2} )</td>
<td>( + \left[ \frac{(2J - 1)(2J + 1)(2J + 3)}{8J(J + 1)} \right]^{1/2} )</td>
<td>( + \left[ \frac{(2J + 5)(2J - 3)(2J + 1)}{8J(J + 1)} \right]^{1/2} )</td>
</tr>
<tr>
<td>( R )</td>
<td>( + \left[ \frac{(2J + 3)(2J + 5)}{8(J + 1)} \right]^{1/2} )</td>
<td>( + \left[ \frac{(2J + 1)(2J + 3)}{8(J + 1)} \right]^{1/2} )</td>
<td>( + \left[ \frac{(2J - 1)(2J + 1)}{8(J + 1)} \right]^{1/2} )</td>
<td>( + \left[ \frac{(2J - 1)(2J - 3)}{8(J + 1)} \right]^{1/2} )</td>
</tr>
</tbody>
</table>
\[
\begin{align*}
\left\{ c^+_J/\sqrt{2} \right\} \times (1/8\sqrt{2J}) & \times \left\{ 2J \left[ 2(2J + 5)/(J + 1) \right]^{1/2} - 3Y + \sqrt{3}\mu \right\} \\
\times \left\{ (2J - 1)(2J + 1)(2J + 3)/8J(J + 1) \right\}^{1/2} \\
+ \left\{ d^+_J/\sqrt{2} \right\} \times (1/8\sqrt{2J}) & \times \left\{ (-2J) \left[ 6(2J + 5)/(J + 1) \right]^{1/2} + \sqrt{3}\mu + \mu \right\} \\
\times \left\{ (2J + 1) \left[ (2J + 1)/8J(J + 1) \right]^{1/2} \right\} \\
+ \left\{ (-d_J^+)/\sqrt{2} \right\} \times (1/8\sqrt{2J}) & \times \left\{ 2J \left[ 6(2J - 1)(2J + 5)/(J + 1)(2J + 3) \right]^{1/2} \\
+ \sqrt{3}\mu\right\} \\
\times \left\{ (2J - 1)(2J + 1)(2J + 3)/8J(J + 1) \right\}^{1/2} \\
+ \left\{ (-c_J^+)/\sqrt{2} \right\} \times (1/8\sqrt{2J}) & \times \left\{ (-2J) \left[ 2(2J - 3)(2J - 1)/(J + 1) \right]^{1/2} \\
\times (2J + 3)^{1/2} - 3Y - \sqrt{3}\mu \right\} \times \left\{ (2J + 5)(2J - 3)(2J + 1)/8J(J + 1) \right\}^{1/2}.
\end{align*}
\]

As before, the line strength for \( Q_24(J) \) is given by squaring the above expression.

3. Discussion

In deriving the expressions for line strengths in this way, we have incorporated two useful generalizations: (i) the \( ^4\Sigma \) has been treated as belonging to intermediate case (\( \lambda \) finite) and (ii) the \( ^4\Pi \) is close to either case (a) or to case (b) including the pure cases (a) and (b) as special cases. In fact by setting \( \lambda = 0 \) for the \( ^4\Sigma \) state and \( |A| = \infty \) for \( ^4\Pi \), we have verified that our expressions indeed reduce to those given by Kovács (1969) for the particular case \( ^4\Sigma(b)-^4\Pi(a) \). Likewise setting \( \lambda = 0 \) for the \( ^4\Sigma \) state and \( Y = \mu = 0 \) for the \( ^4\Pi \) state, we could verify that the expressions of Kovács for \( ^4\Sigma(b)-^4\Pi(b) \) are reproduced. Note that in Kovács’s calculations the \( ^4\Sigma \) has always been treated as case (b) whereas here we have presented a rigorous intermediate coupling treatment. We have further verified that when we specialise our expressions for the transition \( ^4\Sigma(b)-^4\Pi(b) \), the intensities of all the rotational branches which violate the case (b) selection rule (\( \Delta N = 0, \pm 1 \)) vanish, vindicating a consistent choice of phases of our wave functions. For the transition \( ^4\Sigma(\text{int})-^4\Pi (\sim a) \) simplified line strength expressions for all the 48 branches are available with the authors which may be obtained on request.

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