Chapter VII

ASYMMETRIC-TOP MOLECULES

1 QUALITATIVE DESCRIPTION

2 ENERGIES OF THE RIGID ASYMMETRIC ROTOR
   Factorization of the Energy Matrix from Symmetry Properties
   Symmetry Classification of the Energy Levels
   Evaluation of the Energy Levels, Wave Functions, and Average Values

3 SLIGHTLY ASYMMETRIC ROTORS

4 SELECTION RULES AND INTENSITIES

5 IDENTIFICATION AND ANALYSIS OF ROTATIONAL SPECTRA
   Common Aids for Identification of Observed Transitions
   Computer Assignment and Analysis
   Double Resonance as an Aid to Spectral Assignment

6 EFFECTS OF VIBRATION
   Rotation–Vibration Hamiltonian
   Coriolis Perturbations

7 ASYMMETRIC ROTOR STRUCTURES

1 QUALITATIVE DESCRIPTION

When none of the three principal moments of inertia of a molecule is zero and if no two are equal, considerable complexity is encountered in its pure rotational spectrum. The rotational frequencies can no longer be expressed in convenient equations, as can be done for linear or symmetric-top molecules. Only for certain low \( J \) values can the energy levels of the asymmetric rotor be expressed in closed form, even if centrifugal distortion effects are neglected. The increased complexity of the pure rotational spectrum over that of the symmetric-top rotor is illustrated in Fig. 7.1. The various methods that have been used to give the energy levels and wave functions for the asymmetric rotor are considerably more involved than are those for symmetric rotors. The general procedure is to assume that the wave functions can be expanded in terms of an orthogonal set of functions (a natural basis would be the symmetric-top functions) and to set up the secular equations for the unknown coefficients and energies. The resulting secular determinant can be broken down into a number...
Fig. 7.1 (a) A condensed-scale scan of the spectrum of 1,3-cycloheptadiene ($\kappa \approx 0.85$) which has "$b$"-type transitions. Frequency markers are spaced 100 MHz apart and the sweep rate was about 5 MHz/sec. The zero field lines are down, Stark lobes are up. The separation between the $^2Q_{1/2}$ band heads is approximately 3110 MHz. $A=3419.424$, $B=3297.290$, and $C=1799.961$ MHz. From Avirah et al. [48]. (b) Condensed-scale, $R$-band spectrum of 2-cyanothiophene. The sample pressure was about 30 $\mu$m and the scan was about 3 MHz/sec. The Stark lobes are up and the zero field lines are down. Groups of closely spaced absorption lines ($J\rightarrow J+1$, $K_{1/2}\rightarrow K_{3/2}$) are observed separated by approximately 3175 MHz ($\approx B+C$). From T. K. Avirah, T. B. Malloy Jr., and R. L. Cook, *J. Mol. Struct.*, 29, 47 (1975).

of subdeterminants, the order of which increases with $J$. The solution of these subdeterminants yields the required energy levels and expansion coefficients. Details of these energy level calculations will be discussed in the next section.

Despite this complexity, much information useful to the chemist can be obtained from the microwave spectrum of an asymmetric-top molecule, in many instances without long labor or advanced mathematical skill. This is a fortunate circumstance since most molecules are of the asymmetric-top class. In the first place, both qualitative and quantitative spectrochemical analysis can be accomplished by measurements of microwave rotational spectra without an interpretation of their patterns. Second, somewhere in the wide span of the now workable microwave region there are usually low $J$ transitions whose
frequency can be expressed with closed algebraic equations, from which the principal moments of inertia can be immediately evaluated. Furthermore, except for a few very light molecules such as $\text{H}_2\text{O}$, the centrifugal distortion effects on very low $J$ transitions can usually be neglected. These lines cannot be identified from the simple pattern of the rotational spectrum as they can for the symmetric-top rotor, but the low $J$ transitions can be readily identified by their Stark patterns from which the electric dipole moment can also be obtained (see Chapter X). In some cases, the transition can be identified by nuclear quadrupole hyperfine structure. Third, extensive tables are available from which energy levels for various degrees of asymmetry can be obtained to a useful degree of approximation for high $J$ values.

To apply the equations and selection rules developed in the following sections, one must first become familiar with the notation used to designate the levels. Here we shall outline briefly the qualitative characteristics of the asymmetric rotor energy levels. In an asymmetric rotor there is no internal component of the angular momentum that is a constant of the motion; that is $P_\theta$ no longer commutes with $\mathscr{H}$ and only $J$ and $M$ are “good” quantum numbers. As for the symmetric rotor, we can write $P^2 = (\hbar/2\pi)^2 J(J+1)$ and $P_z = \hbar M/2\pi$, where $J$ and $M$ are integers as previously defined. Pseudo-quantum numbers, customarily designated by subscripts on $J$, are employed in the designation of the levels. The double subscript system of King et al. [1] is perhaps the most descriptive and useful; it will be employed extensively. Their system is best understood by a comparison of the limiting prolate and oblate symmetric tops. In the conventional order, $I_a < I_b < I_c$. Thus, when $I_b \to I_c$, the prolate symmetric top is approached; and when $I_b \to I_a$, the oblate symmetric top is approached. We can describe the behavior of the asymmetric rotor in terms of the parameter:

$$\kappa = \frac{2B - A - C}{A - C}$$

(7.1)

which is a measure of its asymmetry, with $A$, $B$, $C$, the rotational constants with respect to the $a$, $b$, $c$ axes. The limiting values for $\kappa$, $-1$ and $+1$, correspond to the prolate and oblate symmetric tops, respectively. The most asymmetric top has $\kappa = 0$. The energy levels of asymmetric rotors ($\kappa \approx -1$ or $\approx +1$) differ from the limiting symmetric-top ones essentially in that the levels corresponding to $-K$ and $+K$, which are always degenerate in the symmetric rotor, are separated in the asymmetric rotor. Thus, an asymmetric rotor has $(2J + 1)$ distinct rotational sublevels for each value of $J$, whereas the symmetric rotor has only $(J + 1)$ distinct sublevels for each value of $J$. With an increase in asymmetry, the “$K$ splitting” increases until there is no longer any close correspondence between the two levels and the degenerate $K$ levels of the symmetric top. Nevertheless, by connecting the $K$ levels for a given $J$ of the limiting prolate symmetric top with those of the limiting oblate symmetric top in the ordered sequence—highest to highest, next highest to next highest, and so on, as indicated in Fig. 1.2—one may obtain a qualitative indication of the levels of the asymmetric rotor. This chart also reveals the significance of the King-Hainer-Cross notation,
Fig. 7.2 Relation of the asymmetric rotor energy levels to those of the limiting prolate and oblate symmetric top. Note there is no crossing of sublevels of a given \( J \) although those of different \( J \) may cross. Also, the straight-line representation of the variation of the energy levels with \( k \) is only approximate.

\( J_{K_{-1}K_{1}} \). The first subscript, \( K_{-1} \), represents the \( K \) value of the limiting prolate top (left side in Fig. 7.2) with which the asymmetric-top level connects as \( \kappa \) approaches \(-1\). The second subscript, \( K_{1} \), represents the \( K \) value of the limiting oblate top with which the particular level connects as \( \kappa \) approaches \( 1 \). Note that the highest sublevels of the prolate symmetric top have the highest \( K \) values, whereas the highest sublevels for the oblate symmetric top have the lowest \( K \) values. Another important point evident from Fig. 7.2 is that the asymmetry
Table 7.1 Effective Rigid-Rotor Constants for the Ground Vibrational State of Some Asymmetric-top Molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$A_0$ (MHz)</th>
<th>$B_0$ (MHz)</th>
<th>$C_0$ (MHz)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OCl</td>
<td>42,064.35</td>
<td>6,296.88</td>
<td>5,670.62</td>
<td>b</td>
</tr>
<tr>
<td>CH$_2$F$_2$</td>
<td>49,138.4</td>
<td>10,603.89</td>
<td>9,249.20</td>
<td>c</td>
</tr>
<tr>
<td>CH$_2$(CN)$_2$</td>
<td>20,882.137</td>
<td>2,942.477</td>
<td>2,616.774</td>
<td>d</td>
</tr>
<tr>
<td>CH$_3$CH$_2$F</td>
<td>36,070.30</td>
<td>9,364.54</td>
<td>8,199.74</td>
<td>e</td>
</tr>
<tr>
<td>CH$_3$CHO$^a$</td>
<td>56,920.5</td>
<td>10,165.1</td>
<td>9,100.0</td>
<td>f</td>
</tr>
<tr>
<td>CH$_3$COF</td>
<td>11,039.28</td>
<td>9,685.65</td>
<td>5,322.05</td>
<td>g</td>
</tr>
<tr>
<td>CH$_2$═CHF</td>
<td>64,582.7</td>
<td>10,636.83</td>
<td>9,118.18</td>
<td>h</td>
</tr>
<tr>
<td>CH$_3$N═CH$_2$$^a$</td>
<td>52,523.75</td>
<td>10,666.13</td>
<td>9,377.19</td>
<td>i</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CH$_3$</td>
<td>29,207.36</td>
<td>8,446.07</td>
<td>7,458.98</td>
<td>j</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CH$_2$Cl (gauche)</td>
<td>11,829.22</td>
<td>3,322.58</td>
<td>2,853.06</td>
<td>k</td>
</tr>
<tr>
<td>CH$_3$CH═CHF (cis)</td>
<td>17,826.09</td>
<td>5,656.57</td>
<td>4,406.91</td>
<td>l</td>
</tr>
<tr>
<td>CH$_3$CH═C═O</td>
<td>38,920</td>
<td>4,507.349</td>
<td>4,136.983</td>
<td>m</td>
</tr>
<tr>
<td>(CH$_3$)$_2$O</td>
<td>38,788.5</td>
<td>10,056.6</td>
<td>8,886.9</td>
<td>n</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CO</td>
<td>10,165.60</td>
<td>8,514.95</td>
<td>4,910.17</td>
<td>o</td>
</tr>
<tr>
<td>C$_6$H$_4$O (furan)</td>
<td>9,446.96</td>
<td>9,246.61</td>
<td>4,670.88</td>
<td>p</td>
</tr>
<tr>
<td>C$_6$H$_5$F</td>
<td>5,663.54</td>
<td>2,570.64</td>
<td>1,767.94</td>
<td>q</td>
</tr>
<tr>
<td>C$_6$H$_5$OH</td>
<td>5,650.46</td>
<td>2,619.20</td>
<td>1,789.84</td>
<td>r</td>
</tr>
<tr>
<td>p-CH$_3$C$_6$H$_4$F</td>
<td>5,702.722</td>
<td>1,430.322</td>
<td>1,143.551</td>
<td>s</td>
</tr>
</tbody>
</table>

$^a$Rotational constants of the $A$ lines which have not been corrected for internal rotation effects.

splitting of the \( K \) levels decreases as \( K \) increases, and for a given \( K \), increases as \( J \) increases. The double subscript notation also gives the symmetry of the wave functions of the level, which is useful information for the application of the symmetry selection rules to be given later.

In the older notation still used widely in the literature, a single subscript on \( J \), designated \( \tau \), is employed. For the highest sublevels of a given \( J \), the subscript \( \tau \) is given the value \( J \); for the next highest, \( J - 1 \), and so on to the lowest level for which the subscript \( \tau \) is assigned the value of \(-J\). Since there are \((2J+1)\) discrete rotational sublevels for a given value of \( J \), there are \((2J+1)\) values of \( \tau \) ranging from \( \tau = J \) for the highest, to \( \tau = -J \) for the lowest level. From Fig. 7.2 it is clear that

\[
\tau = K -1 - K_1 \quad (7.2)
\]

It should be emphasized that \( \tau \) is not a quantum number (nor is \( K -1 \) or \( K_1 \)); it is simply a number used to designate the sequence of the sublevels. It is often called a pseudo-quantum number.

Characteristic rotational energies of the rigid asymmetric rotor for \( J \) values up to 15 have been obtained [2] in the form of algebraic equations which, in general, increase in power as \( J \) increases. For very low \( J \) values, only linear and quadratic equations are involved, and these can be readily solved to give the desired energies. Expressions for the energies for such cases have been given in terms of the rotational constants [3] \( A \), \( B \), and \( C \), and in terms of the asymmetry parameter [1] \( \kappa \). These are collected in Tables 7.6 and 7.7. The values of \( A \), \( B \), and \( C \) for some selected molecules are listed in Table 7.1. One can obtain the microwave rotational frequencies, as before, by finding the difference in the energies of the two levels between which a transition occurs. Various expansions can be employed for finding the energies of special classes of asymmetric rotors, such as those near the prolate or near the oblate limits. These methods will be discussed in Section 3 after a more complete description of the asymmetric rotor energy levels is given.

2 ENERGIES OF THE RIGID ASYMMETRIC ROTOR

The qualitative behavior of the energy levels of an asymmetric rotor has been described; however, quantitative calculations of the rotational energies require a discussion of the quantum mechanics of the system.

In general, the rotational problem is treated in terms of a Cartesian axis system \((x, y, z)\) tied, so to speak to the molecule so that it rotates with the molecule and has its origin located at the center of mass of the system. Furthermore, the molecule-fixed axis system is usually oriented so that its axes coincide with the principal axes of inertia, designated as \( a \), \( b \), and \( c \). The quantum mechanical Hamiltonian describing the rotation of a rigid asymmetric body is then

\[
\mathbf{H} = AP_a^2 + BP_b^2 + CP_c^2
\]  

\quad (7.3)
where \( A = \frac{\hbar^2}{8\pi^2 I_a} \), \( B = \frac{\hbar^2}{8\pi^2 I_b} \), and \( C = \frac{\hbar^2}{8\pi^2 I_c} \). This Hamiltonian is analogous to the classical Hamiltonian except that the components of the angular momentum of rotation \( P_a, P_b, P_c \) are replaced in quantum mechanics by their corresponding operators. For convenience, the \( \hbar \) factor has been included in the definition of the rotational constants so that the angular momenta are now expressed in units of \( \hbar \). The calculation of the energy levels is facilitated by rearrangement of (7.3) as proposed by Ray [4]:

\[
\mathcal{H} = \frac{1}{2}(A+C)P^2 + \frac{1}{2}(A-C)\mathcal{H}(\kappa)
\]

(7.4)

\[
\mathcal{H}(\kappa) = P_a^2 + \kappa P_b^2 - P_c^2 \quad \text{(Reduced Hamiltonian)}
\]

(7.5)

with \( P^2 = P_a^2 + P_b^2 + P_c^2 \) and \( \kappa \) a dimensionless number measuring the degree of asymmetry. That this expression is equivalent to (7.3) is readily seen by substitution of the definition of Ray's asymmetry parameter, (7.1) and collection of terms. The advantage of this formulation is that the reduced energies, which are the eigenvalues of \( \mathcal{H}(\kappa) \), depend only on the inertial asymmetry parameter \( \kappa \) and not on the individual rotational constants, and are hence easily tabulated. It may be noted that the reduced energies are simply eigenvalues of (7.3) for a hypothetical rotor with \( A = +1, B = \kappa, C = -1 \).

Unlike the symmetric rotor Hamiltonian, this Hamiltonian is such that the Schrödinger wave equation cannot be solved directly; thus, a closed general expression for the asymmetric rotor wave functions is not possible. However, they may be represented by a linear combination of symmetric rotor functions, that is,

\[
\psi_{j,m} = \sum_{j,k,m} a_{jkm} \psi_{jkm}
\]

(7.6)

where the \( a_{jkm} \)'s are numerical constants and where \( \psi_{jkm} \) is given by (2.103). The symmetric rotor wave functions are orthonormal:

\[
(J', K', M'|J, K, M) = \begin{cases} 
0 & \text{if } J'K'M' \neq JKM \\
1 & \text{if } J'K'M' = JKM 
\end{cases}
\]

(7.7)

and characterize a representation in which \( P_a^2, P_b^2, \) and \( P_c^2 \) are simultaneously diagonal. Since \( \mathcal{H} \) is a function of \( P_a^2, P_b^2, \) and \( P_c^2 \), the matrix elements of these operators will be required. In Table 7.2 we summarize the angular momenta matrix elements, with angular momentum measured in units of \( \hbar \). These have been discussed in Chapter II, Section 2.

Following the procedure outlined in Chapter II, Section 4, and noting that the Hamiltonian matrix elements vanish unless \( J', M' = J, M \) (see Table 7.2), we obtain the following set of homogeneous linear equations in the coefficients \( a_{jkm} \):

\[
\sum_{k=-j}^{+j} (\mathcal{H}_{kJ} - \delta_{kk} \lambda)a_{jkm} = 0 \quad K' = -J, \ldots, +J
\]

(7.8)

where \( \mathcal{H}_{kJ} = (J, K', M|\mathcal{H}|J, K, M) \). The square array \([\mathcal{H}_{kJ}]\) is in particular
Table 7.2  Angular Momentum Matrix Elements in a Symmetric Rotor Representation

Molecule-fixed Axis System

\( (J, K, M|P_{02}|J, K, M) = K \)
\( (J, K, M|P_{02}|J, K \pm 1, M) = \mp \sqrt{(J, K, M|P_{02}|J, K \pm 1, M)} = \frac{1}{2} \left[ J(J + 1) - K(K \pm 1) \right]^{1/2} \)
\( (J, K, M|P_{02}|J, K, M) = J(J + 1) \)
\( (J, K, M|P_{02}^2|J, K, M) = K^2 \)
\( (J, K, M|P_{02}^2|J, K, M) = (J, K, M|P_{02}^2|J, K, M) = \frac{1}{2} \left[ J(J + 1) - K^2 \right] \)
\( (J, K, M|P_{02}^2|J, K \pm 2, M) = -(J, K, M|P_{02}^2|J, K \pm 2, M) = \frac{1}{2} \left[ J(J + 1) - K(K \pm 1) \right] \left[ J(J + 1) - (K \pm 1)(K \pm 2) \right]^{1/2} \)

*Phase choice is that of King et al. [1] and the angular momentum is measured in units of \( \hbar \). Note the matrices are Hermitian, i.e., the elements are related by \( (R|P_{02}|R^*) = (R'|P_{02}|R)^* \) where \( R \) stands for the totality of quantum numbers \( JKM \) and the asterisk stands for the complex conjugate. The \( P_{02}^2 \) matrix elements are obtained by the ordinary matrix multiplication rule: \( (R|P_{02}^2|R') = \sum_{R''} (R|P_{02}|R'') \times (R''|P_{02}|R') \).*
a matrix representation of the Hamiltonian operator (energy matrix) with respect to the symmetric rotor basis functions. The foregoing set of equations has nontrivial solutions for the expansion coefficients only for certain values of $\lambda$. The special values of $\lambda$ (the allowed energy levels for an asymmetric rotor) are those for which the secular determinant vanishes $|\mathcal{H} - \mathbf{L}| = 0$ where $\mathbf{L}$ is a unit matrix. Because there are no off-diagonal matrix elements in $J$, the matrices for each value of $J$ are independent and may be treated separately (see Fig. 7.3). The fact that the energy matrix is diagonal in $J$ is to be expected since we noted previously that the total angular momentum is a constant of motion. Moreover, the matrix elements are independent of the value of $M$ (the energy independent of the spacial orientation of $\mathbf{P}$) so that its value need not concern us further. Consequently, we will have a secular determinant to solve for each value of $J$; and since $K$ takes on all integral values from $-J$ to $+J$, each determinant will have $2J + 1$ rows and columns. The energy eigenvalues or characteristic values are obtained by solution of the secular determinant.

To set up the energy matrix explicitly for a given $J$, it is necessary to know the nonvanishing matrix elements of the Hamiltonian, (7.4). These may be obtained from Table 7.2. Since $\frac{1}{2}(A + C)P^2$ contributes only a constant diagonal term, being independent of $K$, and since the factor $\frac{1}{2}(A - C)$ multiplies each matrix element of $\mathcal{H}(\kappa)$, a reduced energy matrix $\mathbf{E}(\kappa)$ may be defined, involving only the operator $\mathcal{H}(\kappa)$, with the secular determinant

$$|\mathbf{E}(\kappa) - \mathbf{L}| = 0$$  \hspace{1cm} (7.9)

The total rotational energy for a particular level is given by

$$E = \frac{1}{2}(A + C)J(J + 1) + \frac{1}{2}(A - C)E_{J\tau}(\kappa)$$  \hspace{1cm} (7.10)

Here the $2J + 1$ solutions of (7.9) are labeled by $E_{J\tau}(\kappa)$ where the magnitude of the subscript $\tau$ increases as the magnitude of the reduced energy increases. The nonvanishing matrix elements of $\mathbf{E}(\kappa)$ are

$$E_{K,K'} = (J, K, M|\mathcal{H}(\kappa)J, K, M) = \mathcal{F} \left[ J(J + 1) - K^2 \right] + GK^2$$  \hspace{1cm} (7.11)

![Fig. 7.3](image-url)  

Fig. 7.3 Factoring of the infinite order energy matrix into $J$-blocks.
Therefore for an asymmetric oblate type top with $\kappa$ close to +1 type III is the most useful form to employ.

The explicit form of the secular determinant, (7.9), for $J=3$ is

$$
\begin{array}{ccccccc}
K'K & -3 & -2 & -1 & 0 & 1 & 2 & 3 \\
-3 & E_{-3,-3} - \lambda & 0 & E_{-3,-1} & 0 & 0 & 0 & 0 \\
-2 & 0 & E_{-2,-2} - \lambda & 0 & E_{-2,0} & 0 & 0 & 0 \\
-1 & E_{-1,-1} - \lambda & 0 & E_{-1,-1} - \lambda & 0 & E_{-1,1} & 0 & 0 \\
0 & 0 & E_{0,-2} & 0 & E_{00} - \lambda & 0 & E_{02} & 0 \\
1 & 0 & 0 & E_{1,-1} & 0 & E_{11} - \lambda & 0 & E_{13} \\
2 & 0 & 0 & 0 & E_{20} & 0 & E_{22} - \lambda & 0 \\
3 & 0 & 0 & 0 & 0 & E_{31} & 0 & E_{33} - \lambda \\
\end{array}
$$

(7.17)

where, for clarity, the rows and columns are labeled in terms of the possible values of $K$. The numerical values of the matrix elements $E_{K'K}$ are obtained directly from (7.11) and (7.12) once a value of $\kappa$ is specified. It may be pointed out that this determinant can be factored into two subdeterminants made up, respectively, of even and odd $K$ indices, because there are no matrix elements connecting even and odd $K$. However, a further factoring is possible, which is suggested by the additional symmetry of the energy matrix about the secondary diagonal, and this will be discussed in the next section.

Factorization of the Energy Matrix from Symmetry Properties

Although the energy levels can be found from a solution of (7.9) and thus, in principle, the energy level calculation for an asymmetric rotor has been solved, a further simplification can be obtained by consideration of the symmetry properties of the Hamiltonian. The symmetry properties of the rotational problem may be deduced from its ellipsoid of inertia. The ellipsoid of inertia is symmetric not only to an identity operation $E$ but also to a rotation of $180^\circ$, $C_2$, about any one of its principal axes of inertia. This set of symmetry operations form a group which in the language of group theory is known as the Four-group designated by $V(a, b, c)$. These symmetry operations cause the angular momentum to transform in the following manner:

- $E$: $P_a \rightarrow P_a, P_b \rightarrow P_b, P_c \rightarrow P_c$
- $C_{2}^1$: $P_a \rightarrow P_a, P_b \rightarrow -P_b, P_c \rightarrow - P_c$
- $C_{2}^2$: $P_a \rightarrow -P_a, P_b \rightarrow P_b, P_c \rightarrow - P_c$
- $C_{2}^3$: $P_a \rightarrow -P_a, P_b \rightarrow -P_b, P_c \rightarrow P_c$

The Hamiltonian of a rigid asymmetric rotor is invariant under these operations and, therefore, has the symmetry of the Four-group. The symmetry group of the Hamiltonian is extremely important in quantum mechanics because a knowledge of it allows the classification of quantum states, simplification thereby of the energy matrix, and the determination of selection rules with
relative ease. In the present case, each asymmetric rotor wave function may be classified according to its behavior under \( V(a, b, c) \), the symmetry group of the asymmetric rotor Hamiltonian. The character table for the Four-group is given in Table 7.4. The notation for the symmetry species of \( V \) indicates the axis about which the rotation has a character of +1. A wave function which is, for example, symmetric (multiplied by +1) for a twofold rotation about axis \( a \) and antisymmetric (multiplied by −1) for a twofold rotation about the other two axes may be classified as belonging to species \( B_a \) of the group. A function that is invariant with respect to all symmetry operations of the group obviously belongs to species \( A \).

It would be advantageous to use a set of basis functions in the calculations of the rotational energies which also belong to this group. Each wave function could then be classified according to one of the symmetry species \( A, B_a, B_b, B_c \) of \( V \), and hence the matrix elements of the Hamiltonian \( \langle \psi_i | \mathcal{H} | \psi_j \rangle \) would be nonzero only between states of the same symmetry. This follows since the matrix elements are just numerical quantities and hence must be invariant under a transformation of coordinates such as the group symmetry operations that carry the system into an equivalent configuration, that is, one which is indistinguishable from the original. Therefore, since \( \mathcal{H} \) belongs to the species \( A \) being unchanged by any symmetry operations of the group, the wave functions must both have the same symmetry; otherwise, the matrix elements will change sign for two of the symmetry operations and must then vanish. (See also the discussion at the end of Appendix A.) As a consequence, the secular determinant for any value of \( J \) will factor into four independent subdeterminants, one for each of the symmetry species of the Four-group (see Fig. 7.4). This, of course, considerably simplifies the diagonalization problem and has the further advantage that pairs of degenerate or nearly degenerate \( K \) levels are separated into different submatrices. Without this separation of near degeneracies, the numerical evaluation of the roots by continued fraction techniques become more difficult.

This factoring of the secular determinant is a typical example of the simplification that can result if basis functions are chosen which may be classified according to the symmetry species of the group which reflects the symmetry

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>( E )</th>
<th>( C_2^a )</th>
<th>( C_2^b )</th>
<th>( C_2^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( B_a )</td>
<td>1</td>
<td>1</td>
<td>−1</td>
<td>−1</td>
</tr>
<tr>
<td>( B_b )</td>
<td>1</td>
<td>−1</td>
<td>1</td>
<td>−1</td>
</tr>
<tr>
<td>( B_c )</td>
<td>1</td>
<td>−1</td>
<td>−1</td>
<td>1</td>
</tr>
</tbody>
</table>
ENERGIES OF THE RIGID ASYMMETRIC ROTOR  239

Fig. 7.4 Schematic illustration of the maximum factoring of the energy matrix by proper choice of basis functions. \( \psi(A) \), for example, signifies a set of basis functions with symmetry \( A \). Nonzero matrix elements of the Hamiltonian are present only in the shaded blocks. Each of the smaller submatrices may be solved separately since there are no connecting elements present.

of the problem. Molecular orbital calculations, which are of particular interest to the chemist, are greatly aided by exploitation of the symmetry of the molecule.

The symmetric rotor wave functions which have been used as the basis functions do not belong to \( V \) but to the continuous two-dimensional rotation group \( D_\infty \), which is comprised of \( C_\infty^z \), indicating full rotational symmetry about the \( z \) axis and an infinite number of twofold axes of symmetry, \( C_2 \)'s, at right angles to the principal symmetry axis \( z \). This group has an infinite number of symmetry species. However, as pointed out by Mulliken [5], the Wang [6] linear combinations of symmetric rotor functions do belong to the Four-group. The appropriate linear combinations are constructed from functions of the doubly degenerate \( K \)-states which differ in the sign of \( K \) and are defined for a given \( J \) and \( M \) as follows

\[
S_{JKM} = \frac{1}{\sqrt{2}} \left[ \psi_{JKM} + (-1)^\gamma \psi_{J,-KM} \right], \quad \text{for } K \neq 0
\]

\[
S_{J0M0} = \psi_{J0M}, \quad \text{for } K = 0
\]

(7.18)

where \( \gamma \) is 0 or 1 and \( K \) now takes on only positive values. The \( \gamma = 0 \) functions are the symmetric Wang functions whereas those with \( \gamma = 1 \) are the antisymmetric Wang functions. Here \( \psi_{JKM} = (-1)^\beta \psi_{JKM} \) with \( \beta = K \) if \( K \geq M \) or \( \beta = M \) if \( K \leq M \). This latter modification was suggested by Van Vleck [7] in discussing the phase of the wave functions. The phases of the symmetric rotor wave functions, of course, have no effect on the energies. However, they are important when the symmetry classification of Wang's functions are considered [5].

The foregoing equations relate the old basis (the symmetric rotor functions) to the new basis (the Wang functions or symmetrized functions) and may be written in matrix form, \( S = \hat{X} \psi^x \), in terms of the Wang symmetrizing transformation matrix, \( \hat{X} \), which defines the change of basis. For a given \( J \) we have explicitly:
\[
\begin{pmatrix}
\vdots \\
S_{21} \\
S_{11} \\
S_{00} = \frac{1}{\sqrt{2}} \\
S_{10} \\
S_{20} \\
\vdots
\end{pmatrix}
= \begin{pmatrix}
-1 & 0 & 0 & 0 & 1 \\
0 & -1 & 0 & 1 & 0 \\
0 & 0 & \sqrt{2} & 0 & 0 \\
0 & 1 & 0 & 0 & 1 \\
1 & 0 & 0 & 0 & 1 \\
\vdots & \vdots & \vdots & \vdots & \vdots
\end{pmatrix}
\begin{pmatrix}
\psi_x^1 \\
\psi_x^2 \\
\psi_x^3 \\
\psi_x^3 \\
\psi_x^3 \\
\vdots
\end{pmatrix}
\]

(7.19)

where all the subscripts except \( K \) and \( \gamma \) are suppressed and where the square matrix \( \tilde{X} = X^{-1} \) = \( X \) (the tilde indicates the transpose).

Each asymmetric rotor wave function may now be expressed as a linear combination of the symmetrized wave functions

\[
A_{J,M} = \sum_K a_K^M S_{JKM,\gamma}
\]  

(7.20)

Alternately, we might use the notation \( A_{JK,-K,M} \) to designate the asymmetric rotor wave function. The index \( M \) is not necessary since, as we have seen, the energy does not depend on the spatial orientation, at least in the absence of external fields, and is included only for completeness. Since the symmetrized functions can be classified to particular symmetry species of the asymmetric rotor group, the sum over \( K \) is to be carried out only over these \( S_{JKM,\gamma} \)'s that belong to the same symmetry species of \( V \) as does \( A_{J,M} \). Thus, the number of terms in (7.20) is much less than in (7.6). The change from an expansion in terms of the \( \psi_{JKM} \) to an expansion in terms of the \( S_{JKM,\gamma} \) will affect the form of the energy matrix. The new energy matrix \( E'(\kappa) \) may be readily obtained by the following transformation on the original energy matrix \( E(\kappa) \) (see Appendix A):

\[
E'(\kappa) = \tilde{X} E(\kappa) X = E^+(\kappa) + O^+(\kappa) + E^-(\kappa) + O^- (\kappa)
\]

(7.21)

This is the usual rule for relating the matrix representation of an operator (here the Hamiltonian) in an old basis to that in a new basis. The result of the matrix multiplication [use being made of (7.14)] is that \( E(\kappa) \) splits into two submatrices corresponding to \( \gamma = 0 \) and \( \gamma = 1 \). Each of these can be further factored as noted previously by arrangement of rows and columns so that even values of \( K \) are grouped together and odd values of \( K \) are grouped together. Thus in the notation used in (7.21) \( E \) and \( O \) refer to the evenness or oddness of the \( K \) values involved in the matrix elements and \( + \) and \( - \) to the evenness or oddness of \( \gamma \). Portions of the four submatrices are:

\[
E^+(\kappa) = \begin{bmatrix}
E_{00} & \sqrt{2}E_{02} & 0 & \cdots \\
\sqrt{2}E_{02} & E_{22} & E_{24} & 0 & \cdots \\
0 & E_{24} & E_{44} & E_{46} & \cdots \\
& & \cdots & \cdots & \cdots
\end{bmatrix}
\]
$E^-(\kappa) = \begin{bmatrix}
E_{22} & E_{24} & 0 & \cdots \\
E_{24} & E_{44} & E_{46} & 0 \\
0 & E_{46} & E_{66} & E_{68} \\
\vdots & 0 & E_{68} & E_{88} \\
\vdots & \vdots & \vdots & \ddots
\end{bmatrix}$

$O^+(\kappa) = \begin{bmatrix}
E_{11} + E_{-11} & E_{13} & 0 & \cdots \\
E_{13} & E_{33} & E_{35} & 0 \\
0 & E_{35} & E_{55} & E_{57} \\
\vdots & 0 & E_{57} & E_{77} \\
\vdots & \vdots & \vdots & \ddots
\end{bmatrix}$

$O^-(\kappa) = \begin{bmatrix}
E_{11} - E_{-11} & E_{13} & 0 & \cdots \\
E_{13} & E_{33} & E_{35} & 0 \\
0 & E_{35} & E_{55} & E_{57} \\
\vdots & 0 & E_{57} & E_{77} \\
\vdots & \vdots & \vdots & \ddots
\end{bmatrix}$

(7.22)

where the elements are calculable from (7.11)–(7.14). Each of these submatrices may now be diagonalized independently to give the reduced energies, $E_J(\kappa)$. Therefore, by symmetry considerations, the size of the secular determinant has been reduced; the order of the submatrices being approximately $J/2$.

Symmetry Classification of the Energy Levels

We have seen that the energy levels are conveniently labeled in terms of the limiting prolate and oblate $K$ values, that is, $J_{K_{-1}, K_1}$. This particular notation has the added advantage that the symmetry classification of a level to the species of $V(a, b, c)$ is given uniquely in terms of the parities of these limiting $K$ indices. Consider the limiting case of a symmetric prolate rotor. If $K_{-1}$ is an even integer ($0, \pm 2, \ldots$), the rotational wave function $\psi_{JKM}$ is symmetric with respect to a rotation of $\pi$ degrees about $a$; that is, it is an even function, not changing in sign with the rotation. The even characteristic is indicated by $e$. This is easily seen because such a rotation about the molecule-fixed symmetry axis (the $a$ axis) changes the angle $\phi$ into $\phi + \pi$, while leaving the other angles unaffected (see Chapter II, Section 5, Fig. 2.3). Since the angle $\phi$ enters $\psi_{JKM}$ through the factor $e^{ik\phi}$, we obtain

$$C^2: \psi_{JKM} \rightarrow e^{ik\phi} \psi_{JKM} = (-1)^k \psi_{JKM}$$

If $K_{-1} = \pm 1, \pm 3, \ldots$ (odd integer), $\psi_{JKM}$ is antisymmetric [changes sign, odd ($o$) function] with respect to this operation. Similarly, for an oblate rotor, if $K_1$ is an even integer, $\psi_{JKM}$ is symmetric ($e$ function) with respect to a rotation of $\pi$ degrees about the symmetry axis, that is, the $c$ axis; and if $K_1$ is an odd
integer, \( \psi_{JKM} \) is antisymmetric with respect to this operation. Now the symmetry of an asymmetric-top level must be invariant to changes in the moments of inertia, that is, \( \kappa \). It must then possess the behavior of the two limiting cases with which it correlates. Therefore, if \( K = -e \) and \( K = 0 \), then the asymmetric wave function is symmetric with respect to a rotation about \( a \) and antisymmetric with respect to a rotation about \( c \). Since a rotation about any two of the axes in succession is equivalent to a rotation about the third, a rotation about the \( b \) axis in the present case must yield an antisymmetric result. From Table 7.4 this implies that the function belongs to species \( B_a \). Similarly, if \( K = -ee, oo, \) or \( oe \), the wave function must belong to \( A, B_b \), and \( B_c \), respectively. Thus a knowledge of the evenness or oddness of \( K = -1 \), \( K \) gives us the symmetry classification of the level directly.

Another important point is the symmetry classification of each submatrix which has been discussed by King et al. [1]. The symmetrized functions \( S_{JKM_y} \) that occur in any particular submatrix must all belong to the same symmetry species of the Four-group. This fact may be used for classification of the submatrices. However, the symmetrized functions are constructed relative to the axes \( x, y, z \) and not relative to the axes \( a, b, c \); that is, the \( z \) axis is always taken as the symmetry axis which may coincide with \( a \) if the rotor is a prolate top or with \( c \) if it is an oblate top. Therefore, the functions are characterized by the representation \( A, B_x, B_y, B_z \) of the Four-group \( V(x, y, z) \) (here as before the species notation shows directly the axis of rotation for which the character is \( +1 \)). To classify the symmetrized functions one must find their behavior with respect to the group operations \( E, C_2^x, C_2^y, C_2^z \), of \( V(x, y, z) \), as Mulliken [5] has done, with the result

\[
E: S_{JKM_y} \rightarrow S_{JKM_y} \\
C_2^x: S_{JKM_y} \rightarrow (-1)^{J} S_{JKM_y} \\
C_2^y: S_{JKM_y} \rightarrow (-1)^{J+\gamma} S_{JKM_y} \\
C_2^z: S_{JKM_y} \rightarrow (-1)^{K} S_{JKM_y} \\
\tag{7.23}
\]

The parities are seen to depend only on the even or odd character of \( J + \gamma \) and \( K \), and this character is readily determined from the designation of each submatrix. Consider, for example, the \( E^+ \) submatrix where \( K \) and \( \gamma \) are even; therefore, for \( J_{even} \), all of the \( S_{JKM_y} \)'s of \( E^+ \) are symmetric with respect to all operations of the group and must belong to symmetric species \( A \). The symmetry classification of the various submatrices in \( V(x, y, z) \) are collected in Table 7.5.

The symmetry classification of the submatrices with respect to \( V(a, b, c) \) will depend on the correlation of \( x, y, z \) with \( a, b, c \); in particular, \( A \) corresponds to \( A \), and \( B_a, B_b, B_c \) correspond to \( B_x, B_y, B_z \) in the same way as \( a, b, c \) are related to \( x, y, z \). The symmetry classification in \( V(a, b, c) \) is also given in Table 7.5 along with the parities of \( K = -1, K \) which are included in parenthesis for the assignments considered. Thus a knowledge of the symmetry of a particular level also tells us in which of the four submatrices the level may be found.
Table 7.5  Symmetry Classification of the Submatrices in \( V(x, y, z) \) and \( V(a, b, c) \)

<table>
<thead>
<tr>
<th>Submatrix</th>
<th>( K )</th>
<th>( \gamma )</th>
<th>( J_{\text{even}} )</th>
<th>( J_{\text{odd}} )</th>
<th>( J_{\text{even}} )</th>
<th>( J_{\text{odd}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E^+ )</td>
<td>( e )</td>
<td>( e )</td>
<td>( e )</td>
<td>( e )</td>
<td>( A )</td>
<td>( B_z )</td>
</tr>
<tr>
<td>( E^- )</td>
<td>( e )</td>
<td>( o )</td>
<td>( e )</td>
<td>( e )</td>
<td>( B_z )</td>
<td>( A )</td>
</tr>
<tr>
<td>( O^+ )</td>
<td>( o )</td>
<td>( e )</td>
<td>( e )</td>
<td>( o )</td>
<td>( B_y )</td>
<td>( B_x )</td>
</tr>
<tr>
<td>( O^- )</td>
<td>( o )</td>
<td>( o )</td>
<td>( o )</td>
<td>( e )</td>
<td>( B_x )</td>
<td>( B_y )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type:</th>
<th>I'</th>
<th>II'</th>
<th>III'</th>
<th>I'</th>
<th>II'</th>
<th>III'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Submatrix</td>
<td>( J_{\text{even}} )</td>
<td>( J_{\text{odd}} )</td>
<td>( J_{\text{even}} )</td>
<td>( J_{\text{odd}} )</td>
<td>( J_{\text{even}} )</td>
<td>( J_{\text{odd}} )</td>
</tr>
<tr>
<td>( E^+ )</td>
<td>( A(ee) )</td>
<td>( B_4(oe) )</td>
<td>( A(ee) )</td>
<td>( B_4(oe) )</td>
<td>( A(ee) )</td>
<td>( B_4(oe) )</td>
</tr>
<tr>
<td>( E^- )</td>
<td>( B_4(oe) )</td>
<td>( A(oe) )</td>
<td>( B_4(oe) )</td>
<td>( A(oe) )</td>
<td>( B_4(oe) )</td>
<td>( A(oe) )</td>
</tr>
<tr>
<td>( O^+ )</td>
<td>( B_3(oe) )</td>
<td>( B_8(oo) )</td>
<td>( B_3(oo) )</td>
<td>( B_8(oo) )</td>
<td>( B_3(oe) )</td>
<td>( B_8(oe) )</td>
</tr>
<tr>
<td>( O^- )</td>
<td>( B_3(oe) )</td>
<td>( B_3(oe) )</td>
<td>( B_3(oe) )</td>
<td>( B_3(oe) )</td>
<td>( B_3(oe) )</td>
<td>( B_3(oe) )</td>
</tr>
</tbody>
</table>

*Symmetry classification of the levels are indicated with the parities of \( K_{-1}, K_1 \), indicated in parenthesis for various representations.*
Evaluation of the Energy Levels, Wave Functions, and Average Values

For relatively low values of $J$ one can find the energy levels by expanding the determinant of each submatrix of (7.22) and finding the roots of the resulting polynomial. Explicit expressions for $E(\kappa)$, for certain low $J$ values, are given in Table 7.6. Explicit expressions for the total rotational energy in terms of the rotational constants are given in Table 7.7. From a knowledge of the energy eigenvalues, the eigenvectors of the energy matrix can then be obtained by solution of a set of simultaneous equations, similar to (7.8), for each submatrix.

<table>
<thead>
<tr>
<th>$J_{K-1\kappa_1}$</th>
<th>$E(\kappa)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0_0</td>
<td>0</td>
</tr>
<tr>
<td>1_1</td>
<td>$\kappa + 1$</td>
</tr>
<tr>
<td>1_1</td>
<td>0</td>
</tr>
<tr>
<td>1_0</td>
<td>$\kappa - 1$</td>
</tr>
<tr>
<td>2_2</td>
<td>$2[\kappa + (\kappa^2 + 3)^{1/2}]$</td>
</tr>
<tr>
<td>2_2</td>
<td>$\kappa + 3$</td>
</tr>
<tr>
<td>2_2</td>
<td>$4\kappa$</td>
</tr>
<tr>
<td>2_2</td>
<td>$\kappa - 3$</td>
</tr>
<tr>
<td>2_0</td>
<td>$2[\kappa - (\kappa^2 + 3)^{1/2}]$</td>
</tr>
<tr>
<td>3_0</td>
<td>$5\kappa + 3 + 2(4\kappa^2 - 6\kappa + 6)^{1/2}$</td>
</tr>
<tr>
<td>3_1</td>
<td>$2[\kappa + (\kappa^2 + 15)^{1/2}]$</td>
</tr>
<tr>
<td>3_1</td>
<td>$5\kappa - 3 + 2(4\kappa^2 + 6\kappa + 6)^{1/2}$</td>
</tr>
<tr>
<td>3_2</td>
<td>$4\kappa$</td>
</tr>
<tr>
<td>3_2</td>
<td>$5\kappa - 3 - 2(4\kappa^2 - 6\kappa + 6)^{1/2}$</td>
</tr>
<tr>
<td>3_2</td>
<td>$2[\kappa - (\kappa^2 + 15)^{1/2}]$</td>
</tr>
<tr>
<td>3_2</td>
<td>$5\kappa - 3 - 2(4\kappa^2 + 6\kappa + 6)^{1/2}$</td>
</tr>
<tr>
<td>4_0</td>
<td>—</td>
</tr>
<tr>
<td>4_1</td>
<td>$5\kappa + 5 + 2(4\kappa^2 - 10\kappa + 22)^{1/2}$</td>
</tr>
<tr>
<td>4_1</td>
<td>$10\kappa + 2(9\kappa^2 + 7)^{1/2}$</td>
</tr>
<tr>
<td>4_2</td>
<td>$5\kappa - 5 + 2(4\kappa^2 + 10\kappa + 22)^{1/2}$</td>
</tr>
<tr>
<td>4_2</td>
<td>—</td>
</tr>
<tr>
<td>4_3</td>
<td>$5\kappa + 5 - 2(4\kappa^2 - 10\kappa + 22)^{1/2}$</td>
</tr>
<tr>
<td>4_3</td>
<td>$10\kappa - 2(9\kappa^2 + 7)^{1/2}$</td>
</tr>
<tr>
<td>4_4</td>
<td>$5\kappa - 5 - 2(4\kappa^2 + 10\kappa + 22)^{1/2}$</td>
</tr>
<tr>
<td>4_4</td>
<td>—</td>
</tr>
<tr>
<td>5_2</td>
<td>$10\kappa + 6(\kappa^2 + 3)^{1/2}$</td>
</tr>
<tr>
<td>5_2</td>
<td>$10\kappa + 6(\kappa^2 + 3)^{1/2}$</td>
</tr>
</tbody>
</table>

*In general, the sum rule for the reduced energy levels of a given $J$ is $\sum E_J(\kappa) = \frac{1}{2} J(J+1)(2J+1)\kappa$. *
Table 7.7  Explicit Expressions for the Total Rotational Energy in Terms of the Rotational Constants

<table>
<thead>
<tr>
<th>$J_{K-K_1}$</th>
<th>$E(A, B, C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>00</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>$A + B$</td>
</tr>
<tr>
<td>11</td>
<td>$A + C$</td>
</tr>
<tr>
<td>01</td>
<td>$B + C$</td>
</tr>
<tr>
<td>20</td>
<td>$2A + 2B + 2C + 2[(B - C)^2 + (A - C)(A - B)]^{1/2}$</td>
</tr>
<tr>
<td>21</td>
<td>$4A + B + C$</td>
</tr>
<tr>
<td>21</td>
<td>$A + 4B + C$</td>
</tr>
<tr>
<td>22</td>
<td>$A + B + 4C$</td>
</tr>
<tr>
<td>20</td>
<td>$2A + 2B + 2C - 2[(B - C)^2 + (A - C)(A - B)]^{1/2}$</td>
</tr>
<tr>
<td>30</td>
<td>$5A + 5B + 2C + 2[4(A - B)^2 + (A - C)(A - B)]^{1/2}$</td>
</tr>
<tr>
<td>31</td>
<td>$5A + 2B + 5C + 2[4(A - C)^2 - (A - B)(B - C)]^{1/2}$</td>
</tr>
<tr>
<td>31</td>
<td>$2A + 5B + 5C + 2[4(B - C)^2 + (A - B)(A - C)]^{1/2}$</td>
</tr>
<tr>
<td>32</td>
<td>$4A + 4B + 4C$</td>
</tr>
<tr>
<td>32</td>
<td>$5A + 5B + 2C - 2[4(A - B)^2 + (A - C)(B - C)]^{1/2}$</td>
</tr>
<tr>
<td>33</td>
<td>$5A + 2B + 5C - 2[4(A - C)^2 - (A - B)(B - C)]^{1/2}$</td>
</tr>
<tr>
<td>33</td>
<td>$2A + 5B + 5C - 2[4(B - C)^2 + (A - B)(A - C)]^{1/2}$</td>
</tr>
<tr>
<td>40</td>
<td>$10A + 5B + 5C + 2[4(B - C)^2 + 9(A - C)(A - B)]^{1/2}$</td>
</tr>
<tr>
<td>41</td>
<td>$5A + 10B + 5C + 2[4(A - C)^2 - 9(A - B)(B - C)]^{1/2}$</td>
</tr>
<tr>
<td>42</td>
<td>$5A + 5B + 10C + 2[4(A - B)^2 + 9(A - C)(B - C)]^{1/2}$</td>
</tr>
<tr>
<td>42</td>
<td>$10A + 5B + 5C - 2[4(B - C)^2 + 9(A - C)(A - B)]^{1/2}$</td>
</tr>
<tr>
<td>43</td>
<td>$5A + 10B + 5C - 2[4(A - C)^2 - 9(A - B)(B - C)]^{1/2}$</td>
</tr>
<tr>
<td>43</td>
<td>$5A + 5B + 10C - 2[4(A - B)^2 + 9(A - C)(B - C)]^{1/2}$</td>
</tr>
<tr>
<td>44</td>
<td>$10A + 10B + 10C + 6[(B - C)^2 + (A - B)(A - C)]^{1/2}$</td>
</tr>
<tr>
<td>50</td>
<td>$10A + 10B + 10C - 6[(B - C)^2 + (A - B)(A - C)]^{1/2}$</td>
</tr>
</tbody>
</table>

*In general, the sum rule for the energy levels of a given $J$ is $\sum_j E_j(A, B, C) = \frac{1}{2} J(J+1)(2J+1)(A + B + C)$.\

As pointed out in Appendix A, the matrix formed from the normalized eigenvectors (each column corresponding to an eigenvector associated with a particular energy level) constitutes a transformation matrix $T$ which diagonalizes the reduced energy matrix, that is,

$$\tilde{T}ET = \Lambda$$  \hspace{1cm} (7.24)

where $\Lambda$ is a diagonal matrix formed by the eigenvalues of $E$. A knowledge of $T$ is required whenever matrix elements of operators in the asymmetric rotor basis are needed.

Obviously, this technique of direct expansion becomes impractical for all but small $J$ values, and iterative matrix diagonalization procedures must be
used. The rapid development of high-speed digital computers has, however, made possible the relatively easy solution of such mathematical problems by the use of iterative procedures. A very useful diagonalization procedure due to Jacobi [8] determines the eigenvalues and eigenvectors simultaneously. This method is applicable to symmetric matrices and is unaffected by the presence of degenerate eigenvalues. The method consists in the application of a series of plane rotations (in a space of \( n \)-dimensions) which are chosen to reduce the size of the off-diagonal elements, the process being continued until the off-diagonal elements are small enough for the matrix to be considered diagonal. The product of the rotation matrices thus constitutes a transformation matrix which diagonalizes the energy matrix and hence is the matrix of eigenvectors.

Alternately, since the four submatrices are of tridiagonal form, that is, with nonzero elements along the diagonal and immediately above and below the principal diagonal, the secular determinant may be cast into a continued fraction form. The continued fraction expansion is particularly efficient for numerical evaluation of the eigenvalues and allows the roots to be determined very accurately. Both first- [1, 9] and second-order [10] iterative techniques for the continued fraction method have been described, as well as efficient procedures for evaluation of eigenvectors. This method is discussed in Appendix B.

A number of tables are available which give numerical values of \( E_{J\ell}(\kappa) \) for values of \( \kappa \) in steps of 0.1 [1, 11] and 0.01 [12] with values of \( J \) up to 12. Also available are tables for values of \( \kappa \) in steps of 0.1 [13] and 0.001 [14] up to \( J = 40 \) and \( J = 18 \), respectively. These tables provide a convenient means by which the energies of any asymmetric rotor may be approximated. To calculate the characteristic rotational energy for a particular level, one merely selects from the table the reduced energy, \( E_{J \ell}(\kappa) \), corresponding to the desired \( J \ell \) and \( \kappa \) values, and then makes use of (7.10). Interpolation between tabulated values of \( \kappa \) may be used, but in most tables the intervals in \( \kappa \) are not small enough to give the required accuracy for microwave work. However, the tabulation for intervals of 0.001 in \( \kappa \) are sufficiently close to allow accurate interpolation. Usually only positive or negative values are tabulated since the reduced energy matrix has a form such that

\[
E_{J\ell}(\kappa) = -E_{J -\ell}(-\kappa)
\]

or

\[
E_{JK -\ell K_1}(\kappa) = -E_{JK_1 -\ell K_1}(-\kappa)
\]

(7.25)

The quantities of interest in the calculation are, of course, the rotational transition frequencies, obtained by division of the energy difference by Planck’s constant. It is common practice to express the rotational spectroscopic constants in units of megahertz so that

\[
A = \frac{\hbar}{8\pi^2 I_a}, \text{ etc.}
\]
\[ A \text{ (MHz)} = \frac{5.05376 \times 10^5}{I_a \text{(amu} \cdot \text{Å}^2)}, \text{ etc.} \]  

This conversion factor is based on the $^{12}$C atomic mass scale and constants of Appendix D.

In (7.20) the asymmetric rotor wave functions were synthesized from the symmetrized symmetric rotor wave functions by means of the expansion coefficients $a^{J\kappa}_k$, which give the relative contributions of the various symmetric rotor states to the asymmetric rotor state with their squares giving the probability for rotation with a particular angular momentum $J$ and $\pm K$. For a very slightly asymmetric rotor, one of the $a^{J\kappa}_k$'s approaches unity while the others approach zero and each asymmetric rotor wave function $A_{J\kappa}$ will be closely approximated by one $S_{J\kappa}$. The different sets of coefficients, the eigenvectors of the energy matrix, are discriminated by means of the index $\kappa$. The eigenvectors are required for the calculation of line strengths of asymmetric rotors. They are also useful for calculation of the average values of $P^2_x$ and $P^4_x$, that is, the values of $P^2_x$ and $P^4_x$ averaged over the asymmetric rotor wave functions. Such quantities find frequent use particularly in the analysis of centrifugal distortion, quadrupole and internal rotation effects. Consider, for example, the average value of $P^2_x$, where $\tau$ represents the unique molecule-fixed axis of quantization, we have

\[ \langle P^2_x \rangle = (J, \tau | P^2_x | J, \tau) \]  

(7.27)

where $\langle P^2_x \rangle$ is the average value of $P^2_x$ associated with the level $J, \tau$. From (7.20) which gives $A_{J\kappa}$ in terms of $S_{J\kappa}$'s, recalling the definition of $S_{J\kappa}$ and the fact that $P^2_x$ is diagonal in the $\psi_{J\kappa}$ basis, we obtain

\[ \langle P^2_x \rangle = \sum_k (a^{J\kappa}_k)^2 K^2 \]  

(7.28)

The summation over $K$ will be only over those $K$'s that occur along the main diagonal of the submatrix to which the level $J, \tau$ belongs. A similar expression would result for $\langle P^2_x \rangle$ except that $K^2$ would be replaced by $K^4$. Usually only a limited number of terms in the sum are required to give results of sufficient accuracy. For a slightly asymmetric rotor, where one of the $a^{J\kappa}_k$'s approaches unity and the others approach zero, the $\langle P^2_x \rangle$ approaches the value of $K^2$ for the limiting symmetric rotor level. Tables of $\langle P^2_x \rangle$ and $\langle P^4_x \rangle$ tabulated in increments of 0.1 [15] and 0.002 [16] in $\kappa$ are available. Formulas for $\langle P^2_x \rangle$ and $\langle P^4_x \rangle$ based on continued fractions have been given [17], which are very convenient when the rigid rotor energy levels are calculated by the continued fraction method. It is also possible to express the $\langle P^2_x \rangle$ simply in terms of $P^2, E$, and $\langle P^2 \rangle$, $g = x, y, z$ (see Chapter VIII, Section 3).

The average values of $P^2_x, P^2_y$, and $P^2_z$ are also directly related to the derivatives of the rotational energy with respect to the rotational constants. Specifically,
it has been shown by Bragg and Golden \([18, 19]\) that

\[
\langle P^2_a \rangle = \frac{\partial E}{\partial A} \tag{7.29}
\]

\[
\langle P^2_b \rangle = \frac{\partial E}{\partial B} \tag{7.30}
\]

\[
\langle P^2_c \rangle = \frac{\partial E}{\partial C} \tag{7.31}
\]

Therefore, on differentiating (7.10) with respect to \(A\), \(B\), and \(C\), we find the following convenient expressions

\[
\langle P^2_a \rangle = \frac{\partial E}{\partial A} = \frac{1}{2} \left[ J(J+1) + E(\kappa) - (\kappa + 1) \frac{\partial E(\kappa)}{\partial \kappa} \right] \tag{7.32}
\]

\[
\langle P^2_b \rangle = \frac{\partial E}{\partial B} = \frac{\partial E(\kappa)}{\partial \kappa} \tag{7.33}
\]

\[
\langle P^2_c \rangle = \frac{\partial E}{\partial C} = \frac{1}{2} \left[ J(J+1) - E(\kappa) + (\kappa - 1) \frac{\partial E(\kappa)}{\partial \kappa} \right] \tag{7.34}
\]

The \(\langle P^2_a \rangle\), \(\langle P^2_b \rangle\), \(\langle P^2_c \rangle\) are identified with the \(\langle P^2_a \rangle\), \(\langle P^2_b \rangle\), \(\langle P^2_c \rangle\) according to the way \(a, b, c\) are related to \(x, y, z\). The values of \(\partial E/\partial \kappa\) may be obtained from Tables of \(E(\kappa)\) if differences of \(E(\kappa)\) between two appropriate values of \(\kappa\) are taken. Tables with small increments in \(\kappa\) should be employed.

To indicate the use of Table 7.5 and to illustrate some of the previous concepts, we look at a simple example. Consider the case of a prolate asymmetric rotor in a type \(I^*\) representation for \(J=2\). The allowed energy levels are \(2_{02}\), \(2_{12}\), \(2_{11}\), \(2_{21}\), and \(2_{20}\). We see from the Table 7.5 that the levels will be found in the following submatrices: \(2_{02}\), \(2_{20}\) in \(E^+\); \(2_{21}\) in \(E^-\); \(2_{12}\) in \(O^+\), and \(2_{11}\) in \(O^-\). \(E^+\) gives a \(2 \times 2\) secular determinant, and the others are all one-dimensional.

The wave functions associated with the levels in the various submatrices have the symmetry: \(E^+\leftrightarrow A, E^-\leftrightarrow B_a, O^+\leftrightarrow B_c,\) and \(O^-\leftrightarrow B_b\). The largest eigenvalue in \(E^+\) will be associated with \(2_{20}\) level and the other with the \(2_{02}\) level. The \(E^+\) matrix has the following secular equation:

\[
\begin{vmatrix}
E_{00} - \lambda & \sqrt{2}E_{02} \\
\sqrt{2}E_{02} & E_{22} - \lambda
\end{vmatrix} = \begin{vmatrix}
3(\kappa - 1) - \lambda & -\sqrt{3}(\kappa + 1) \\
-\sqrt{3}(\kappa + 1) & (\kappa + 3) - \lambda
\end{vmatrix} = 0
\]

Upon expansion, the determinant yields a quadratic equation in \(\lambda\) with the roots:

\[
E_{220} = E_{22} = 2[\kappa + (\kappa^2 + 3)^{1/2}]
\]

\[
E_{202} = E_{2_{20}} = \sqrt{\kappa - (\kappa^2 + 3)^{1/2}}
\]

The asymmetric rotor wave functions for the two states have the form:

\[
A_{22} = a^2_{2}S_{200} + a^2_{2}S_{220}
\]

\[
A_{2_{20}} = a^2_{2}S_{200} + a^2_{2}S_{220}
\]
where the $M$ index is suppressed. The coefficients $a_k^z$ in the above expressions are determined from the simultaneous equations:

$$(E_{00} - \lambda)a_0^z + \sqrt{2} E_{02} a_2^z = 0$$

$$\sqrt{2} E_{02} a_0^z + (E_{22} - \lambda)a_2^z = 0$$

A system of equations such as these do not determine the $a_k^z$'s uniquely, but give only their ratios. We can evaluate an arbitrary or relative set from either of the foregoing equations by setting one $a_k^z = 1$ and solving for the remaining one. Using the first of the foregoing equations and setting $\lambda = E_{22}$, we find the relative eigenvectors to be

$$a_0^z = 1 \quad \text{and} \quad a_2^z = \frac{(\kappa - 3) - 2(\kappa^2 + 3)^{1/2}}{\sqrt{3}(\kappa + 1)}$$

The values are fixed by means of the relation,

$$a_k^z = \frac{a_k^z \text{ (relative)}}{\Sigma_k \left[a_k^z \text{ (relative)}\right]^2}^{1/2}$$

which ensures the eigenvectors will be normalized, that is, $\Sigma_k (a_k^z)^2 = 1$. The normalized set of eigenvectors are:

$$a_0^z = \frac{(\sqrt{3}/2)(\kappa + 1)}{(\kappa^2 + 3)^{1/2} [2(\kappa^2 + 3)^{1/2} + (3 - \kappa)]^{1/2}}$$

$$a_2^z = -\frac{1}{2} \left[ 2 + \frac{(3 - \kappa)}{(\kappa^2 + 3)^{1/2}} \right]^{1/2}$$

Likewise, we find for the $2_{02}$ level that

$$a_2^{-2} = a_2^0 \quad \text{and} \quad a_0^{-2} = -a_2^2$$

If for example, $\kappa = -0.968$, we find that

$$E_{22} = 2.0324, \quad a_0^2 = 0.00698, \quad a_2^2 = -0.99998$$

$$E_{2^{-2}} = -5.9044, \quad a_0^{-2} = 0.99998, \quad a_2^{-2} = 0.00698$$

By means of the eigenvectors we calculate

$$\langle P_2^2 \rangle_{22} = 3.9998 \quad \text{and} \quad \langle P_2^2 \rangle_{2^{-2}} = 0.0002$$

As mentioned previously, the original energy matrix can be brought to diagonal form by a similarity transformation, (7.23), with the matrix of eigenvectors. In the present case, we have explicitly:

$$\hat{T} \quad E^+ \quad T$$

$$\begin{bmatrix}
0.99998 & 0.00698 \\
0.00698 & -0.99998
\end{bmatrix}
\begin{bmatrix}
-5.9040 & -0.0554 \\
-0.0554 & 2.0320
\end{bmatrix}
\begin{bmatrix}
0.99998 & 0.00698 \\
0.00698 & -0.99998
\end{bmatrix}$$

$$= \begin{bmatrix}
-5.9044 & 0.0000 \\
0.0000 & 2.0324
\end{bmatrix}$$

which provides a check of our calculations.
3 SLIGHTLY ASYMMETRIC ROTORS

It would be convenient to have expressions that give the explicit dependence of the energies on the rotational quantum numbers. This is not possible for molecules with large asymmetry; however, there are a large number of molecules that may be classified as slightly asymmetric tops, for example, HN$_3$, HNCO, CH$_2$DBr, NOBr, CH$_3$SH, H$_2$S$_2$, P$^{35}$Cl$_2$,$^{37}$Cl, etc. The spectrum of a slightly asymmetric rotor is illustrated in Fig. 7.5. For this type, the energies can be expressed with sufficient accuracy as a series expansion in powers of an asymmetry parameter. Various asymmetry parameters have been employed for finding the energies of this special class of asymmetric rotors. An asymmetry parameter introduced by Wang [6] is particularly useful for such expansions. The rotational Hamiltonian for a near-prolate rotor type I', in terms of Wang's asymmetry parameter is written in the form

\[ \mathcal{H} = AP_a^2 + BP_b^2 + CP_c^2 = \frac{1}{2}(B + C)P^2 + \left[A - \frac{1}{2}(B + C)\right]\mathcal{H}(b_p) \]  \hspace{1cm} (7.35)

with

\[ \mathcal{H}(b_p) = P_a^2 + b_p(P_c^2 - P_b^2) \]  \hspace{1cm} (7.36)

where the $a$ axis is the unique axis of quantization and the asymmetry parameter is defined as

\[ b_p = \frac{C - B}{2A - B - C} = \frac{\kappa + 1}{\kappa - 3} \]  \hspace{1cm} (7.37)

in which $-1 \leq b_p \leq 0$ with $b_p = -\frac{1}{3}$ corresponding to the maximum degree of asymmetry. In a symmetric rotor representation the nonvanishing matrix elements are:

\[ (J, K, M|P^2|J, K, M) = J(J + 1) \]  \hspace{1cm} (7.38)

\[ (J, K, M|\mathcal{H}(b_p)|J, K, M) = K^2 \]  \hspace{1cm} (7.39)

\[ (J, K, M|\mathcal{H}(b_p)|J, K \pm 2, M) = b_p[f(J, K \pm 1)]^{1/2} \]  \hspace{1cm} (7.40)

As with Ray's formulation, the determination of the eigenvalues of $\mathcal{H}$ is reduced to finding those of $\mathcal{H}(b_p)$. If the matrix of the Wang operator, (7.39) and (7.40),

![Fig. 7.5 Illustration of the rotational spectrum of the slightly asymmetric prolate rotor HN$_3$ ($b_p = -20.9 \times 10^{-3}$) observed in the millimeter region. The frequencies of the absorption lines increase from left to right. Separation of the lines for different values of $K$ is due to centrifugal distortion effects. The $K = 1$ and $K = 2$ lines are split (1263.1 and 1.5 MHz, respectively) because of the small asymmetry of the molecule. The $K = 3$ line shows quadrupole splitting which is unresolved in the other lines. After R. Kewley, K. V. L. N. Sastry, and M. Winnewisser, J. Mol. Spectrosc. 12, 387 (1964).](image)
is subjected to the Wang transformation, four matrices will result similarly to the $E^\pm$, $O^\pm$ matrices, discussed previously. The only difference is that now the matrix elements are given by (7.39) and (7.40). The roots of these secular determinants are the reduced energies $W_{J_s}(b_p)$ with the characteristic rotational energy being given by:

$$E = \frac{1}{4}(B + C)J(J + 1) + \left[A - \frac{3}{4}(B + C)\right]W_{J_s}(b_p)$$  \hspace{1cm} (7.41)

All of the symmetry properties given previously are still valid. For the prolate symmetric limit, $B = C$, we have $b_p = 0$ and $W_{J_s}(b_p) = K_{-1}^2$ so that the energy expression reduces to that given for a symmetric top. Alternately, near the symmetric rotor limit, that is, $b_p \approx 0$, the reduced energies may be expressed as:

$$W_{J_s}(b_p) = K_{-1}^2 + C_1 b_p^2 + C_2 b_p^4 + C_3 b_p^6 + \cdots$$  \hspace{1cm} (7.42)

where $K_{-1}$ is the limiting prolate index of the level. The coefficients $C_i$ for the powers of $b_p$ can be evaluated by standard perturbation techniques, with the term in $b_p$ of $\mathcal{H}(b_p)$ being treated as the perturbation operator. The Wang linear combinations of symmetric rotor wave functions are used as the basis functions, with the coefficient of $b_p^n$ being provided by $n$th order perturbation. The expressions for the coefficients [13, 20] up to $C_5$ are given in Table 7.8. They depend only on the rotational quantum numbers. Numerically tabulated coefficients for various energy levels have also been reported [12, 20].

We may, for example, by use of Table 7.8 immediately write down the asymmetry splitting between the two $K=1$ levels of a slightly asymmetric rotor. We find (retaining terms up to $b_p^2$)  

$$\Delta W(b_p) = b_p J(J + 1)$$

which indicates directly that the degenerate level splitting increases with $J$. An approximate general expression for the asymmetry splitting of the $K$ levels has been given by Wang [6]

$$\Delta W(b) = \frac{b^K(J + K)!}{8^{K-1}(J-K)![(K-1)!]^2}$$  \hspace{1cm} (7.43)

in which $\Delta W$ is the reduced energy difference with $b$ and $K$, respectively, $b_p$ and $K_{-1}$ for a near prolate top, or $b_o$ and $K_1$ for a near oblate top. Equation 7.43 reveals that the degenerate level splitting decreases with increasing $K$ (see Fig. 7.2). A more accurate expression, correct to $(K+2)$-power of $b$, is also available [21].

The energy expression for a near-oblate top, type III, is obtained by a simple interchange of $A$ and $C$ in the preceding relations. The total rotational energy for an asymmetric oblate top is then:

$$E = \frac{1}{2}(A + B)J(J + 1) + \left[C - \frac{3}{4}(A + B)\right]W_{J_s}(b_o)$$  \hspace{1cm} (7.44)

with

$$b_o = \frac{A - B}{2C - B - A} = \frac{\kappa - 1}{\kappa + 3}$$  \hspace{1cm} (7.45)
Table 7.8 General Expressions for the Coefficients $C_i$ for a Near Prolate Top

\[
C_1 = \pm \frac{J(J+1)}{2} \quad \text{for } K=1, O^\pm
\]

$C_1 = 0$ for all other $K$ values

\[
C_2 = \left[ \frac{f(J, K-1)}{4(K-1)} - \frac{f(J, K+1)}{4(K+1)} \right] \quad \text{for all } K \text{ values}
\]

$C_3 = \pm \frac{J(J+1)f(J, 2)}{128} \quad \text{for } K=1, O^\pm$

$C_3 = 0 \quad \text{for all other } K \text{ values}$

$C_4 = C_4 - \frac{J^2(J+1)^2f(J, 2)}{2048} \quad \text{for } K=1, C_4 \text{ given below}$

$C_4 = C_4 + \frac{J^2(J+1)^2f(J, 2)}{2048} \quad \text{for } K=3, C_4 \text{ given below}$

\[
C_4 = C_4 - \frac{f(J, K-1)}{128(K-1)^2} \left[ \frac{2f(J, K+1)}{(K+1)} - \frac{2f(J, K-1)}{(K-1)} + \frac{f(J, K-3)}{(K-2)} \right] \\
\quad - \frac{f(J, K+1)}{128(K+1)^2} \left[ \frac{2f(J, K-1)}{(K-1)} - \frac{2f(J, K+1)}{(K+1)} + \frac{f(J, K+3)}{(K+2)} \right] \quad \text{for all other } K \text{ values}
\]

$C_5 = \frac{\pm J(J+1)f(J, 2)}{294,912} \left[ 108f(J, 2) - 9J^2(J+1)^2 - 28f(J, 4) \right] \quad \text{for } K=1, O^\pm$

$C_5 = \frac{\pm J(J+1)f(J, 2)}{294,912} \left[ 108f(J, 2) - 9J^2(J+1)^2 - 27f(J, 4) \right] \quad \text{for } K=3, O^\pm$

$C_5 = \frac{\pm J(J+1)f(J, 2)f(J, 4)}{294,912} \quad \text{for } K=5, O^\pm$

$C_5 = 0 \quad \text{for all other } K \text{ values}$

*Here $K$ refers to the limiting prolate index of a level. The symbol $O^\pm$ identifies the submatrix to which a level belongs, see Table 7.5, and indicates which sign to use; for example, if level in $O^+$ for $K=1$, minus sign is to be used for calculation of $C_3$. The functions $f(J, K \pm 1)$ are given by (7.13) of text, except that $f(J, 1) = \frac{1}{2}J(J+1)(J+1/2)$. Furthermore, $f(J, 1)$ must be taken to be zero in computation of $C_2$ or $C_4$ for the $E^\pm$ levels. Also $f(J, 0)$ and $f(J, -1)$ must always be set equal to zero. After Allen and Cross [13].

The range is the same as $b_p$, that is, $-1 \leq b_o \leq 0$ and the most symmetric case is again represented by the value $-\frac{1}{2}$. For an oblate limit $A = B$, we have $b_0 = 0$, so that an expansion in terms of $b_o$ is the most appropriate for expressing the reduced energy of a slightly asymmetric oblate rotor

\[
W_{2s}(b_o) = K_1^2 + C_1 b_o + C_2 b_o^2 + C_3 b_o^3 + \cdots \quad (7.46)
\]

where $K_1$ is the appropriate limiting oblate index. The $C$'s for the oblate case may be obtained from Table 7.8 for the prolate case as follows: If the
oblate level of interest is \( J_{K_{-1,K}} \), then one computes the coefficients for the prolate rotor level \( J_{K,K} \). The use of such expansions for energy level calculations are, of course, dictated by the size of the asymmetry parameter \( b \) and the accuracy that is desired. If the asymmetry is too large, the series expansion, (7.42) or (7.46), will not converge rapidly enough. The expansions are, in general, most accurate for very small asymmetries and become progressively worse with increasing asymmetry.

For asymmetric rotors where the power series expansion is not appropriate, the Wang formulation suffers from the fact that extensive tables of reduced energies are available in terms of \( \kappa \) rather than Wang's asymmetry parameter. However, if necessary, Wang's reduced energy can be calculated from the tabulated values of Ray's reduced energy by means of the relation

\[
E_{J_{\kappa}}(\kappa) = F(J + 1) + (G - F)W_{J_{\kappa}}(b) \tag{7.47}
\]

where \( b \) is either \( b_p \) or \( b_z \), depending on whether one is considering a prolate or oblate asymmetric rotor. The values of \( F \) and \( G \) are given in Table 7.2 for the two possible cases. This relation can be obtained simply by equating the different expressions for the total energy.

In cases where the expansion can be used satisfactorily, we can write the average values of \( P_z^2 \) in an asymmetric rotor basis as an expansion in terms of the asymmetry parameter, thereby circumventing the more laborious calculations using the eigenvectors. As an example, consider the derivation of \( \langle P_z^2 \rangle \). For the \( a \) axis identified with the \( z \) axis, type \( I' \), we have from (7.41), on differentiating with respect to \( A \),

\[
\left( \frac{\partial E}{\partial A} \right) = W(b_p) + [A - \frac{1}{2}(B + C)] \left( \frac{\partial W(b_p)}{\partial A} \right) \tag{7.48}
\]

Now

\[
\left( \frac{\partial W(b_p)}{\partial A} \right) = \left( \frac{\partial W(b_p)}{\partial b_p} \right) \left( \frac{\partial b_p}{\partial A} \right) = \frac{-b_p}{A - \frac{1}{2}(B + C)} \left( \frac{\partial W(b_p)}{\partial b_p} \right)
\]

Therefore

\[
\langle P_z^2 \rangle = \frac{W(b_p)}{b_p} \left( \frac{\partial W(b_p)}{\partial b_p} \right) \tag{7.49}
\]

This is a general expression for \( \langle P_z^2 \rangle \). If, however, we assume \( W(b_p) \) is given by (7.42), we obtain the following expression

\[
\langle P_z^2 \rangle = K_{-1}^2 + \sum_{n=1}^{\infty} (1 - n) C_n b_p^2 \tag{7.50}
\]

From a knowledge of \( \langle P_z^2 \rangle \), we can calculate \( \langle P_x^2 \rangle \) and \( \langle P_y^2 \rangle \) from the relations

\[
\frac{\partial E}{\partial B} = \langle P_x^2 \rangle = \frac{1}{2} [J(J + 1) - (1 + \sigma)(P_z^2) + \sigma W(b_p)] \tag{7.51}
\]
\[
\frac{\delta E}{\delta C} = \langle P_r^2 \rangle = \frac{1}{2} \left[ J(J + 1) + (\sigma - 1) \langle P_r^2 \rangle - \sigma W(b_p) \right]
\]

(7.52)

with \( \sigma = -1/b_p \). The method of calculation of \( \langle P_r^2 \rangle \) and \( W(b_p) \) in the foregoing expressions is, of course, dictated by the size of the asymmetry. For slightly asymmetric rotors, the \( \langle P_r^2 \rangle \) can be roughly approximated by

\[
\langle P_r^2 \rangle \approx \langle P_r^2 \rangle^2
\]

(7.53)

A more accurate approximation has been given by Kivelson and Wilson [17] for slightly asymmetric rotors.

4 SELECTION RULES AND INTENSITIES

The allowed changes in \( J \) for dipole absorption of radiation are:

\[
\Delta J = 0, \pm 1
\]

(7.54)

As in previous instances, these “permitted” transitions result from the nonvanishing property of the dipole matrix elements, \( \int A_{J,}\mu A_{J',}\mu \, d\tau \), when \( J' = J \) or \( J' = J \pm 1 \). For other values of \( J' \), all matrix elements of the dipole components along fixed axes in space are found to be zero. This is to be expected since the asymmetric rotor wave functions are expressed as linear combinations of symmetric rotor functions, all having the same value of \( J \). Therefore, only those matrix elements will be nonvanishing for change of \( J \) which were nonvanishing for the symmetric rotor. In an asymmetric rotor, each of the three changes might give rise to an absorption line, whereas, for a symmetric rotor, the level with higher \( J \) always lies highest, and only \( \Delta J = +1 \) gives rise to rotational absorption. The \( \Delta J = -1 \) transitions are designated as \( P \)-branch; the \( \Delta J = 0 \), as \( Q \)-branch; and the \( \Delta J = +1 \), as \( R \)-branch transitions.

In addition to these selection rules for \( J \), there are also restrictions on the changes that can occur in the subscripts of \( J \), in the pseudo-quantum numbers. These restrictions result from the symmetry properties of the ellipsoid of inertia. To discuss these selection rules, we must again inquire into the nonvanishing property of the matrix elements of the dipole components along axes fixed in space. The component of the electric moment along a space-fixed axis \( F \), can be written as

\[
\mu_F = \sum_g \cos (Fg)\mu_g \quad F = X, Y, Z; \, g = a, b, c
\]

(7.55)

where \( \mu_g \) are the components of the permanent molecular dipole moment resolved along the principal axes of inertia. The \( \cos (Fg) \) are the cosines of the angles between the nonrotating \( F \) and rotating \( g \) axes. These quantities may be expressed as explicit functions of the Eulerian angles \( \theta, \phi, \chi \) which specify the orientation of the molecule-fixed axis system with respect to the space-fixed
axis system. The direction cosines are commonly indicated by the symbol \( \Phi_{FS} \). They find extensive use whenever it is desirable to refer a vector whose components are known in the rotating coordinate system to the nonrotating system, or vice versa. For the case where the electric moment lies only along one of the principal axes, say the \( a \) axis, since the direction cosines are functions of the rotational coordinates, the dipole matrix element is

\[
(J, K_{-1}, K_1 | \mu_F | J', K'_{-1}, K'_1) = \mu_a(J, K_{-1}, K_1) \cos(Fa) | J', K'_{-1}, K'_1 \)  \quad (7.56)
\]

If this integral is not to vanish, it must be unchanged (no change in sign) for any operation that carries the system into a configuration indistinguishable from the original. This is tantamount to saying that the integrand \( A_{JK_{-1}, K_1}^J \cos(Fa)A_{J'K'_{-1}, K'_1} \) transforms according to the totally symmetric representation \( A \). The symmetry in which we are interested is not the molecule symmetry but the symmetry of the inertia ellipsoid, which for the asymmetric rotor is characterized by the Four-group operations. If the integrand is to belong to species \( A \), then for each symmetry operation of \( V \) either each term of the integrand is even, or one term is even and the other two are odd. Under the Four-group operations, the direction cosines have \( B \) symmetries. For a rotation of 180° about \( a, C_2 \), the \( \cos(Fa) \) does not change, but it does change sign for a rotation about \( b \) or \( c \) since the angle changes from \( Fa \) to \( \pi - Fa \). It transforms, therefore, according to the \( B_a(\text{eo}) \) representation. Likewise, \( \cos(Fb) \), does not change sign for the \( C_b \) symmetry operation but does change sign for the \( C_2 \) and \( C_2' \) operations and thus transforms as the species \( B_b(oo) \). For similar reasons, \( \cos(Fc) \) has \( B_c(oe) \) symmetry. For the case under consideration (\( \mu_a \neq 0 \) with \( \mu_b = \mu_c = 0 \)) where the direction cosine transforms as \( B_a \), it is readily apparent from Table 7.3 that if the integrand is to have symmetry \( A \), the functions \( A_{JK_{-1}, K_1}^J \) must be of symmetry \( A \) and \( B_a \), or of symmetry \( B_b \) and \( B_c \). The allowed transitions are then \( A \leftrightarrow B_a \), and \( B_b \leftrightarrow B_c \). The other selection rules for electric dipole components along the \( b \) and \( c \) axes are similarly established. For \( \mu_b \neq 0 \) with \( \mu_a = \mu_c = 0 \), the allowed transitions are \( A \leftrightarrow B_b \) and \( B_a \leftrightarrow B_c \), whereas for \( \mu_c \neq 0 \) and \( \mu_a = \mu_b = 0 \) they are \( A \leftrightarrow B_c \) and \( B_a \leftrightarrow B_b \). Often, the symmetry selection rules are stated in terms of the evenness or oddness of the \( K_{-1}, K_1 \) subscripts. In this notation they are:

<table>
<thead>
<tr>
<th>Dipole Component</th>
<th>Permitted Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_a \neq 0 ) (along axis of least moment of inertia)</td>
<td>( ee \leftrightarrow eo )</td>
</tr>
<tr>
<td>( \mu_b \neq 0 ) (along axis of intermediate moment of inertia)</td>
<td>( oe \leftrightarrow oo )</td>
</tr>
<tr>
<td>( \mu_c \neq 0 ) (along axis of greatest moment of inertia)</td>
<td>( eo \leftrightarrow oe )</td>
</tr>
</tbody>
</table>
In terms of permitted changes in the $K_{-1}$ and $K_1$ subscripts, the selection rules are:

<table>
<thead>
<tr>
<th>Dipole Component</th>
<th>$\Delta K_{-1}$</th>
<th>$\Delta K_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_a \neq 0$ (along axis of least moment of inertia)</td>
<td>0, $\pm 2, \ldots$</td>
<td>$\pm 1, \pm 3, \ldots$</td>
</tr>
<tr>
<td>$\mu_b \neq 0$ (along axis of intermediate moment of inertia)</td>
<td>$\pm 1, \pm 3, \ldots$</td>
<td>$\pm 1, \pm 3, \ldots$</td>
</tr>
<tr>
<td>$\mu_c \neq 0$ (along axis of greatest moment of inertia)</td>
<td>$\pm 1, \pm 3, \ldots$</td>
<td>0, $\pm 2, \ldots$</td>
</tr>
</tbody>
</table>

If the dipole moment lies wholly along one of the principal inertial axes, only those changes in the subscript notation listed in the preceding tables for that component are allowed. If there are dipole components along each of the principal inertial axes, all changes listed in the tables are allowed. Any given transition will be due to only one component of the molecular dipole, for example, $\mu_a$, $\mu_b$, or $\mu_c$. The transitions due to the $\mu_a$ component are designated as "$a$"-type transitions, those due to $\mu_b$ as "$b$"-type, and those due to $\mu_c$ as "$c$"-type transitions.

The presence of different types of transitions for asymmetric rotors, although at times creating additional complexity, can also be an advantage. For instance, with moderately large organic molecules one or more rotational isomers may exist, and one conformation might, from preliminary information, be expected to exhibit "$a$"-type transitions whereas another both "$a$"- and "$b$"-type transitions. This information can be of great aid in distinguishing the isomers and in the assignment of the spectrum. The dependence of the type of transition on the structure in the asymmetric rotor [22] is illustrated with $H_2S_2$ in Fig. 7.6 (see also Fig. 12.19).

While any changes indicated in the previous stable are permitted by the selection rules, it is found that absorption lines corresponding to large changes in either subscript ($K_{-1}$ or $K_1$) are weak. Also, if the dipole along a particular principal axis is small, the transitions arising from this component will be weak. Furthermore, if the rotor is near the limiting prolate symmetric-top case ($\kappa \approx -1$), the changes in $K_{-1}$ which correspond to the symmetric-top selection rules, $\Delta K_{-1} = 0, \pm 1$, will be the only ones of significant strength, but those for larger changes in $\Delta K_1$ may have observable strength. Conversely, if the molecule approximates the oblate symmetric rotor ($\kappa \approx 1$), only the lines corresponding to $\Delta K_1 = 0, \pm 1$ will have significant strength, but relatively large changes in $K_{-1}$ can give rise to measurable lines. When neither symmetric-top case is approached ($\kappa \approx 0$, or asymmetry large), the strongest lines will correspond to 0 and $\pm 1$ change in both $K_{-1}$ and $K_1$, but lines of significant strength may occur which correspond to larger changes in either or both subscripts. It should also be pointed out that when the dipole moment lies wholly along the symmetry axis, the symmetric-top selection rule is simply $\Delta K = 0$ (commonly referred to
as parallel-type transitions), and that when it is entirely perpendicular to the symmetry axis, $\Delta K = \pm 1$ (perpendicular-type transitions). Hence, we can obtain further information about the probable intensity of a transition by noting the direction of the dipole moment with reference to that principal inertial axis which would in the limit become the symmetry axis.

It is often convenient in the analysis of spectra to group transitions into series or branches which are characterized by the changes in $J, K_{-1}$ and $K_1$. The notation used to specify each branch, which is frequently found in the literature, is

$$^gQ_{\Delta K = -1, \Delta K_1}, ^gR_{\Delta K = -1, \Delta K_1}, ^gP_{\Delta K = -1, \Delta K_1}$$
Here \( Q(\Delta J=0) \) and \( R(\Delta J=+1) \) indicate the changes in \( J(J\rightarrow J \) and \( J\rightarrow J+1) \) while the change in \( K_{-1} \) is indicated by the first subscript. The second subscript gives \( \Delta K \). The dipole component responsible for the transition is given as a superscript, \( g=a, b, \) and \( c \). A summary of the stronger asymmetric rotor transitions is provided in Table 7.9. These stronger branches can often provide more easily recognized spectral patterns which are useful in the assignment of rotational spectra.

The intensities of absorption lines are proportional to the squares of absolute values of direction cosine matrix elements. As shown in (2.108), the direction cosine matrix elements in a symmetric rotor basis may be written as a product of three factors. Each factor depends only on the rotational quantum numbers indicated. The various factors have been given in Table 2.1. They are also seen to depend on the internal axes \( g \) and the external axes \( F \). For the linear and symmetric-top molecules, the electric moment could be assumed to be along the axis \( z \) so that only the matrix elements of \( \Phi_{Fz} \) were required. In contrast, the asymmetric rotor often has components of its dipole moment along all three principal axes \( x, y, z \).

For an asymmetric rotor basis the direction cosine matrix elements may also be written in a form similar to (2.108). Each asymmetric rotor wave function is expressed as a linear combination of Wang symmetric rotor functions all

**Table 7.9 Stronger Asymmetric Rotor Transitions**

<table>
<thead>
<tr>
<th>Near-Oblate Rotor</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^aQ_{01}, ^aQ_{0-1}, ^aQ_{2-1}, ^aQ_{21} )</td>
</tr>
<tr>
<td>( ^aR_{01}, ^aR_{0-1}, ^bR_{2-1}, ^bP_{21} )</td>
</tr>
<tr>
<td>( ^bQ_{11}, ^bQ_{11} )</td>
</tr>
<tr>
<td>( ^bR_{11}, ^bR_{1-1}, ^bR_{3-1}, ^bP_{31} )</td>
</tr>
<tr>
<td>( ^cQ_{10}, ^cQ_{10}, ^cP_{10} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Near-Prolate Rotor</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^aQ_{01}, ^aQ_{0-1} )</td>
</tr>
<tr>
<td>( ^aR_{01}, ^aP_{0-1} )</td>
</tr>
<tr>
<td>( ^bQ_{11}, ^bQ_{11} )</td>
</tr>
<tr>
<td>( ^bR_{11}, ^bR_{1-1}, ^bR_{1-3}, ^bP_{1-3} )</td>
</tr>
<tr>
<td>( ^cQ_{10}, ^cQ_{10}, ^cP_{10}, ^cP_{1-2}, ^cR_{12} )</td>
</tr>
</tbody>
</table>

*The stronger branches are indicated. Here the "\( g"\)-type, \( \Delta J=0 \) and \( \Delta J=+1 \) branches are specified with the notation \( ^aQ_{\Delta K,-\Delta K}, \) and \( ^aR_{\Delta K,-\Delta K}, \) respectively.*

*Such reverse transitions are designated by \( P(\Delta J=-1) \).*
having the same value of $J$ and $M$ but different values of $K$. The $J$ and $M$ dependence of the matrix elements in an asymmetric rotor basis will thus be the same as that for a symmetric rotor basis, and we may write

$$ (J, \tau, M | \Phi_{Fg} | J', \tau', M') = (J | \Phi_{Fg} | J') (J, \tau | \Phi_{Fg} | J', \tau') (J, M | \Phi_{Fg} | J', M') $$  \hspace{1cm} (7.57) 

The calculation of the $(J, \tau | \Phi_{Fg} | J', \tau')$ factor requires a knowledge of the eigenvectors associated with the two states $J_\tau$ and $J_\tau'$. Evaluation of this direction cosine matrix has been discussed by Cross et al. [23] and by Schwendeman [24]. The latter author has given the matrix elements of the direction cosines in the Wang symmetric rotor basis and has discussed the properties of the matrices, symmetry, and so on. Also the forms chosen for the matrix elements are convenient for transformation to the asymmetric rotor basis by means of a digital computer. In the case of slightly asymmetric rotors, perturbation theory may be used to give the asymmetric rotor wave functions by use of the Wang functions as basis functions. Simple expressions may then be obtained for the direction cosine matrix elements in terms of the symmetric rotor matrix elements and correction terms dependent on the asymmetry. This has been carried out by Lide [25] to second-order, and the results applicable to molecules with $|\kappa| \geq 0.9$ are collected in Table 7.10.

For a transition $J, \tau \rightarrow J', \tau'$ caused by a component of the electric moment $\mu_\sigma$, a convenient quantity called the line strength is defined as

$$ \lambda_g(J, \tau; J', \tau') = \sum_{FMM'} |(J, \tau, M | \Phi_{Fg} | J', \tau', M')|^2 $$  \hspace{1cm} (7.58) 

where the sum extends over the three directions of the space-fixed system and over all values of $M$ and $M'$. The latter sum over $M$ and $M'$ takes into account all possible transitions which in the absence of external fields will be degenerate. The line strength depends only on the inertial asymmetry parameter $\kappa$ and not on the individual rotational constants; thus it is easily tabulated. Extensive tables of line strengths for various values of $\kappa$ are available [23, 26–28]. The summation over $F$ in the absence of external fields can be accomplished by multiplying the results for a given $F$ by 3, that is,

$$ \lambda_g(J, \tau; J', \tau') = 3 \sum_{M'M'} |(J, \tau, M | \Phi_{Fg} | J', \tau', M')|^2 $$  \hspace{1cm} (7.59) 

The dipole moment matrix element appearing in (3.24) may be expressed in terms of the line strength. We have for a field-free rotor

$$ |(J, \tau | \mu | J', \tau')|^2 = \sum_{M'M} |(J, \tau, M | \mu_F | J', \tau', M')|^2 $$

$$ = \sum_{M'M} |(J, \tau, M | \Phi_{Fg} | J', \tau', M')|^2 $$  \hspace{1cm} (7.60) 

since $\mu_F = \sum_g \mu_g \Phi_{Fg}$ and for a given transition only one term in the sum over $g$
<table>
<thead>
<tr>
<th>$K=0$</th>
<th>$\gamma=0$</th>
<th>$0$</th>
<th>$\frac{\sqrt{2}}{8} [f(J, 1)]^{1/2} \left{ \delta + \frac{\delta^2}{2} \right}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K=1$, $\gamma=0$</td>
<td>$0$</td>
<td>$\frac{1}{16} [f(J, 2)]^{1/2} \left{ \delta + \frac{[16 + J(J+1)]\delta^2}{32} \right}$</td>
<td></td>
</tr>
<tr>
<td>$K=1$, $\gamma=1$</td>
<td>$0$</td>
<td>$\frac{1}{16} [f(J, 2)]^{1/2} \left{ \delta + \frac{[16 - J(J+1)]\delta^2}{32} \right}$</td>
<td></td>
</tr>
<tr>
<td>$K=2$, $\gamma=0$</td>
<td>$-\frac{\sqrt{2}}{8} [f(J, 1)]^{1/2} \left{ \delta + \frac{\delta^2}{2} \right}$</td>
<td>$\frac{1}{24} [f(J, 3)]^{1/2} \left{ \delta + \frac{\delta^2}{2} \right}$</td>
<td></td>
</tr>
<tr>
<td>$K=2$, $\gamma=1$</td>
<td>$0$</td>
<td>$\frac{1}{24} [f(J, 3)]^{1/2} \left{ \delta + \frac{\delta^2}{2} \right}$</td>
<td></td>
</tr>
<tr>
<td>$K=3$, $\gamma=0$</td>
<td>$-\frac{1}{16} [f(J, 2)]^{1/2} \left{ \delta + \frac{[16 + J(J+1)]\delta^2}{32} \right}$</td>
<td>$\frac{1}{32} [f(J, 4)]^{1/2} \left{ \delta + \frac{\delta^2}{2} \right}$</td>
<td></td>
</tr>
<tr>
<td>$K=3$, $\gamma=1$</td>
<td>$-\frac{1}{16} [f(J, 2)]^{1/2} \left{ \delta + \frac{[16 - J(J+1)]\delta^2}{32} \right}$</td>
<td>$\frac{1}{32} [f(J, 4)]^{1/2} \left{ \delta + \frac{\delta^2}{2} \right}$</td>
<td></td>
</tr>
<tr>
<td>$K &gt; 3$</td>
<td>$-\frac{[f(J, K-1)]^{1/2} \left{ \delta + \frac{\delta^2}{2} \right}}{8(K-1)}$</td>
<td>$\frac{[f(J, K+1)]^{1/2} \left{ \delta + \frac{\delta^2}{2} \right}}{8(K+1)}$</td>
<td></td>
</tr>
</tbody>
</table>
From Lide [25].

Here \( K \) stands for \( K_{-1} \) and \( \gamma = 0 \) if \( J + K + K_1 \) is even and \( \gamma = 1 \) if \( J + K + K_1 \) is odd. The parameter \( \delta = (B - C)/ (A - C) \). The direction cosine matrix elements are evaluated from the relations:

\[
(j, k, k_1 | \Phi_{F_0} | j', k, k_1') = [1 - (\alpha^2 + \beta^2 + \alpha^2 + \beta^2)/2] (j, k | \Phi_{F_0} | j', k) + \beta \alpha (j, k - 2 | \Phi_{F_0} | j', k - 2) \\
+ \beta \alpha (j, k + 2 | \Phi_{F_0} | j', k + 2)
\]

and

\[
(j, k, k_1 | \Phi_{F_0} | j', k + 1, k_1') = [1 - (\alpha^2 + \beta^2 + \alpha^2 + \beta^2)/2] (j, k | \Phi_{F_0} | j', k + 1) + \beta \alpha (j, k - 2 | \Phi_{F_0} | j', k - 1) \\
+ \beta \alpha (j, k + 2 | \Phi_{F_0} | j', k + 3)
\]

The \( (j, k | \Phi_{F_0} | j', k') \) are the symmetric rotor direction cosine matrix elements and \( \alpha, \beta \), calculable from the above table, refer to the level \( J, K, K_1 \) and \( x', \beta' \) to the level \( J', K', K_1' \). For \((j, 0 | \Phi_{F_0} | j', 1)\) the expression given in Table 2.1 must, in this particular case, be multiplied by \( 2^{1/2} \).
remains from symmetry arguments. The results are

\[ \lambda_g(J, \tau; J', \tau') = (2J + 1) \sum_{F M} |\langle J, \tau, M|\Phi_{fg}|J', \tau', M' \rangle|^2 \]

\[ = (2J + 1) \langle J, \tau|\mu|J', \tau' \rangle^2 / \mu_g^2 \]  

\[ = (2J' + 1) \sum_{F M} |\langle J', \tau', M'|\Phi_{fg}|J, \tau, M \rangle|^2 \]

\[ = (2J' + 1) \langle J', \tau'|\mu|J, \tau \rangle^2 / \mu_g^2 \]  

(7.61)  

(7.62)

The direction cosine matrix elements can also be conveniently expressed in terms of the line strengths. For \( F = Z \) and any \( g \), the line strength can be expressed in terms of the matrix elements \( |\langle J, \tau|\Phi_{Zg}|J', \tau' \rangle|^2 \) by use of (7.57), Table 2.1, and carrying out the summation. Note that the sum over \( M' \) reduces to one term since \( \Phi_{Zg} \) is diagonal in \( M \) [see (10.71)–(10.73)]. We find

\[ \lambda_g(J, \tau; J', \tau') = \frac{1}{4} R |\langle J, \tau|\Phi_{Zg}|J', \tau' \rangle|^2 \]  

(7.63)

where \( R \) is defined as \( 1/J, (2J + 1)/J(J + 1), \) or \( 1/(J + 1) \) for \( J' = J - 1, J, \) or \( J + 1, \) respectively. Since from (7.57)

\[ |\langle J, \tau|\Phi_{Zg}|J', \tau' \rangle|^2 = \frac{|\langle J, \tau, M|\Phi_{Zg}|J', \tau', M \rangle|^2}{|\langle J|\Phi_{Zg}|J' \rangle|^2 \cdot |\langle J, M|\Phi_{Zg}|J', M \rangle|^2} \]  

(7.64)

one obtains from (7.63) and Table 2.1

\[ |\langle J, \tau, M|\Phi_{Zg}|J - 1, \tau', M \rangle|^2 = \frac{J^2 - M^2}{J(2J - 1)(2J + 1)} \lambda_g(J, \tau; J - 1, \tau') \]  

(7.65)

\[ |\langle J, \tau, M|\Phi_{Zg}|J, \tau', M \rangle|^2 = \frac{M^2}{J(J + 1)(2J + 1)} \lambda_g(J, \tau; J, \tau') \]  

(7.66)

\[ |\langle J, \tau, M|\Phi_{Zg}|J + 1, \tau', M \rangle|^2 = \frac{(J + 1)^2 - M^2}{(J + 1)(2J + 1)(2J + 3)} \lambda_g(J, \tau; J + 1, \tau') \]  

(7.67)

These expressions multiplied by \( \mu_g^2 \) represent the dipole matrix elements for particular Stark or Zeeman components with the field along \( Z \) analogous to (2.109) and (2.115) for a symmetric top

\[ |\langle J, \tau, M|\mu_2|J', \tau', M \rangle|^2 = \mu_g^2 |\langle J, \tau, M|\Phi_{Zg}|J', \tau', M \rangle|^2 \]  

(7.68)

It may also be readily shown that

\[ \sum_{M = -J}^{+J} |\langle J, \tau, M|\Phi_{Zg}|J', \tau', M \rangle|^2 = \frac{3}{2} \lambda_g(J, \tau; J', \tau') \]  

(7.69)

since \( \Sigma M^2 = \frac{1}{2} J(J + 1)(2J + 1) \). A number of useful sum rules exist because of the orthogonal properties of the direction cosine matrices [23]. Rudolph [29, 30]
has also derived a number of additional relations involving the line strengths, reduced energy, and average of $P_g^2$.

A knowledge of the line strength is important in accessing the intensity of a given line and how the intensity can be expected to change with $\kappa$ or variations in $J$ or $K$. The larger $|\Delta \tau|$ in the transition the smaller the value of the corresponding $\lambda$. The line strength is independent of the direction of the transition. For a given $\kappa$

$$\lambda_g(J, \tau; J', \tau') = \lambda_g(J', \tau'; J, \tau) \quad (7.70)$$

Also the line strength for an oblate asymmetric rotor transition $J_{K_{-1}K_1} \rightarrow J'_{K_{-1}K_1}$ can be obtained from the prolate asymmetric rotor transition $J_{K_1K_{-1}} \rightarrow J'_{K_1K_{-1}}$ with the subscripts reversed by the means of the relation

$$\lambda_g(J, \tau; J', \tau'; \kappa) = \lambda_g(J, -\tau; J', -\tau'; -\kappa) \quad (7.71)$$

Here the explicit dependence on $\kappa$ is indicated, and the axes change $g \rightarrow g'$ as follows: $a \rightarrow c$, $b \rightarrow b$, and $c \rightarrow a$.

For small asymmetry the direction cosine matrix elements may be evaluated with the aid of Table 7.10 and hence the line strengths [see (7.63)]. Explicit expressions for the line strengths of low $J$ rotational transitions have been given by Gora [31]. The line strengths for the symmetric top limit, which are useful simple approximations to the line strengths for near asymmetric tops, follow from (7.63) and Table 7.10 with $\delta = 0$ and Table 2.1.

The dipole matrix element factor appearing in (3.27) for the absorption coefficient is related to the line strength from (7.61) as follows:

$$|(J, \tau|\mu|J', \tau')|^2 = \frac{\mu_g^2 \lambda_g(J, \tau; J', \tau')}{(2J+1)} \quad (7.72)$$

If (7.72) and (3.25), (3.26), and (3.66) (the latter equation modified for an asymmetric rotor as indicated in Chapter III, Section 3) are inserted into (3.27), the peak absorption coefficient for the transition $J, \tau \rightarrow J', \tau'$ may be written as

$$\alpha_{\text{max}} = 3.85 \times 10^{-14} F_v \sigma(ABC)^{1/2} \mu_g^2 \lambda_g(J, \tau; J', \tau') \left( \frac{\nu_0^2}{(\Delta \nu); T^{5/2}} \right) g I e^{-\frac{E_J}{kT}} \quad (7.73)$$

where it is assumed that $h\nu_0 \ll kT$. The rotational constants $A, B, C$, the resonant frequency $\nu_0$, and the line breadth $(\Delta \nu)$, are in megahertz, with $\mu_g$ in debye units and $\alpha_{\text{max}}$ in cm$^{-1}$. If the lowest vibrational frequency is much greater than $kT$ (say 1000 cm$^{-1}$ for room temperature), the vibrational partition function is nearly equal to unity, and, for the ground vibrational state, $F_v$ may hence be taken to be unity. Other things being equal (such as the Boltzmann factor), the strongest lines of a spectrum will be those which have the largest line strength. For asymmetric rotors with no symmetry $\sigma$, $g_I = 1$. When equivalent nuclei may be exchanged, the rotational level populations are affected and hence the relative intensities. The effects of nuclear spin statistics and the evaluation of $g_I$ have been discussed in Chapter III, Section 4.