MOLECULAR ASYMMETRIC-TOP VIBRATION-ROTATION HAMILTONIANS

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I. INTRODUCTION

Generally, the infrared absorption spectra of molecules originate when a molecule is raised from one vibration-rotation state to another state with higher energy accompanied by the absorption of light. Therefore one of the principal problems of molecular spectroscopists has been the interpretation of the vibration-rotation energy level structure of the molecule under study.

Just as in the diatomic molecule case, in which the study of the infrared spectra gives precise information about the vibration-rotation energies and these energies lead to the accurate determination of the structure of the diatomic molecule, we may obtain information about bond distances, bond angles, vibrational frequencies, force constants, dissociation energies, anharmonic constants, centrifugal distortion constants, etc., by the analysis of the infrared spectra of polyatomic molecules. An understanding of these quantities leads to the determination of the detailed structure of the molecule and should ultimately help us to better understand the physico-chemical properties of matter in the aggregate.

In the case of polyatomic molecules the situation is often very complicated, since we are considering many-body problems. There are several internuclear distances, several force constants, several vibrational frequencies, etc. Therefore it has been found convenient to formulate the general theoretical expression for the energies of polyatomic molecules and then to apply it in the specific case instead of trying to deduce formulas for each specific case separately.

However, in the case of polyatomic molecules it is impossible to find exact general expressions for the energy levels. For this reason some assumptions are made which are valid in practice, and one treats the general formulation by an expansion formalism in successive orders of approximation. For instance, it is possible in the study of infrared spectra of polyatomic molecules to assume the validity of the Born-Oppenheimer approximation to separate the vibration-rotation motion of the nuclei from the electronic motion, and also one can safely ignore the energy contribution of the nuclear spins until a certain high order of approximation.

The general quantum mechanical Hamiltonian for the polyatomic molecule was first formulated and studied by Wilson and Howard.[1] Then Darling and Dennison[2] gave their general Hamiltonian for the polyatomic molecule which is of slightly different but equivalent form to that of Wilson and Howard. The formulation by Darling and Dennison proves somewhat more convenient for development. By use of the above-mentioned Hamiltonians the vibration-rotation energy levels of polyatomic molecules were calculated to the second order of approximation and it was found that the energy relations calculated explained certain anomalies of the infrared spectra of polyatomic molecules and gave the relations between the energies and the parameters which characterize the molecule and its dynamic behavior. This success established calculation of vibration-rotation energies from theoretical formulations.

In recent years improved experimental accuracy and resolution in the infrared work in many cases necessitated the taking into account of terms in the Hamiltonian higher than the second order of approximation in order to arrive at a satisfactory interpretation of experiment. Vibrational effects, rotational effects and vibration-rotation interaction effects higher than in the second order had been observed in various experiments.

Recognizing this situation, Nielsen, Amat, and Goldsmith[3-6] extended the expansion of the Hamiltonian to fourth order, and extensively regrouped the resulting terms to obtain the expansion of the vibration-rotation Hamiltonian in orders of approximation more closely corresponding to experimenal evidence. This newly formulated Hamiltonian gave satisfactory interpretations of the more recent experiments. However, this general Hamiltonian to fourth order contains a very large number of terms, many of them depending on the molecular parameters in a very complicated manner. Therefore it becomes important to review the expressions in the general Hamiltonian and simplify them for solution of particular eigenvalue problems. Such studies have been carried out for symmetric and spherical rotators, principally by Amat and his coworkers.[7]

Another large and important class of molecules is of the asymmetric rotator type. In asymmetric molecules the energy eigenvalue problem is more complicated than in symmetric or spherical rotators in the zeroth order of approximation; on the other hand, the Hamiltonian of the asymmetric rotator is considerably simpler in the vibrational and vibration-rotation interaction terms since in the asymmetric molecule there are no essential vibrational degeneracies such as occur in symmetric and spherical rotators.

Since the symmetry properties of a given polyatomic molecule qualitatively characterize its spectrum, it should be feasible to distinguish the Hamiltonians for each of the different symmetry groups of molecules. We have found that the symmetry properties of a particular point group or point groups of molecules greatly simplify the general Hamiltonian.

In this work we have studied the general vibration-rotation Hamiltonian of asymmetric rotator molecules in the Nielsen-Amat Goldsmith formulation by subjecting this Hamiltonian to the symmetry restrictions of the asymmetric rotator point groups. Particularly the second and fourth order centrifugal distortion constants, which will be defined later, and those terms of the Hamiltonian which can be interpreted as vibrational corrections to the rotational structure were of interest.

We shall first present a discussion of the general vibration-rotation Hamiltonian, and we will subsequently impose the symmetry restrictions of the asymmetric rotator point groups. Finally, we will discuss some properties of the symmetry restricted Hamiltonians.

II. THE GENERAL VIBRATION-ROTATION HAMILTONIAN

For the theoretical calculation of the energies of a molecule it is necessary to formulate a suitable quantum mechanical Hamiltonian. We shall reproduce the derivation of such a general quantum mechanical Hamiltonian for the vibrating-rotating molecule.

The total Hamiltonian of a molecule would have to include a portion which represents the electronic contribution to the total energy. This electronic energy is not of interest here, since we wish to consider vibration-rotation transition during which the molecule remains in its electronic ground state configuration. For such a case, Born and Oppenheimer[8] have shown that it is allowable to separate the electronic motion from the nuclear motion to a very good degree of approximation. Since the electrons are moving much faster than the nuclei and consequently the wave function of the electronic state is almost independent of the change in internuclear distances, the Born-Oppenheimer approximation is valid in most cases. Nielsen[9] has pointed out that one could calculate the vibration-rotation energy accurate to one part in 10^6 despite the Born-Oppenheimer approximation. We will adopt the Born-Oppenheimer approximation for the formulation of the general vibration-rotation Hamiltonian, and hereby will not consider directly the electronic motion any further. The potential energy of nuclear vibration will, of course, recognize indirectly the molecular electron configuration in the time average over the rapid electronic motions.

The classical kinetic energy of a molecular framework of N nuclei is

$$T = \frac{1}{2}\sum_{i=1}^{N} m_i V_i^2 \qquad \text{(II-1)}$$

where m_i is the mass of the i-th nucleus and V_i represents the velocity of the i-th nucleus in a space-fixed coordinate system. Using the position vector $\overline{R}$ to the origin of a moving coordinate system (whose manner of motion will be specified later), the angular velocity of the moving system, $\overline{\omega}$, and the position vector of the particle in the moving system, $\overline{r}_i(x_i, y_i, z_i)$, the velocity $\overline{V}_i$ can be expressed as[10]

$$\overline{V}_i = \overline{R} + \overline{r}_i + \overline{\omega}\times\overline{r}_i. \qquad \text{(II-2)}$$

Substituting $\overline{V}_i$ of (II-2) into (II-1) and utilizing the rules of vector algebra, the kinetic energy is found to be

$$T = \frac{1}{2}M\overline{R}^2 + \frac{1}{2}\sum_i m_i\left[r_i^2\omega^2 - (\overline{r}_i\cdot\overline{\omega})^2\right] + \frac{1}{2}\sum_i m_i v_i^2$$

$$+ \overline{R}\cdot\sum_i m_i\overline{v}_i + \overline{R}\cdot\overline{\omega}\times\sum_i m_i\overline{r}_i + \overline{\omega}\cdot\sum_i m_i\overline{r}_i\times\overline{v}_i, \qquad \text{(II-3)}$$

where M is the total mass $\sum_i m_i$, and $\bar{v}_i = \dot{\bar{r}}_i$.
The position vector $\bar{r}_i$ is the vector sum of the constant equilibrium position vector, $\bar{a}_i(x_i^o, y_i^o, z_i^o)$, and the displacement vector from the equilibrium position, $\bar{\rho}_i(x_i', y_i', z_i')$,

$$\bar{r}_i = \bar{a}_i + \bar{\rho}_i \qquad \text{(II-4)}$$

and

$$\bar{v}_i = \dot{\bar{\rho}}_i . \qquad \text{(II-5)}$$

We now take the origin of the moving system at the center of mass of the N-nuclei molecule. This is expressed by the so-called first Eckart condition,[11]

$$\sum_i m_i \bar{r}_i = 0 \ , \qquad \text{(II-6)}$$

which also implies, because of (II-4), that

$$\sum_i m_i \bar{\rho}_i = 0 \quad \text{and} \quad \sum_i m_i \bar{v}_i = 0 \ . \qquad \text{(II-7)}$$

Since the molecule is semi-rigid and the nuclei remain very close to their respective equilibrium positions, it is meaningful to require the second Eckart condition,

$$\sum_i m_i \bar{a}_i \times \bar{r}_i = 0 \qquad \text{(II-8)}$$

i.e., the moving system shall be "attached" to the nuclear equilibrium configuration.
Eq. (II-8) also implies, again through (II-4), that

$$\sum_i m_i \bar{a}_i \times \bar{v}_i = 0 \quad \text{and} \sum_i m_i \bar{a}_i \times \bar{\rho}_i = 0 \,. \qquad \text{(II-9)}$$

The second Eckart condition means that there is no rotation of the system as a whole relative to the body-fixed axes, since eq. (II-9) implies that the internal vibratory motions do not produce any rotational angular momentum of the molecule as a whole relative to the moving system. However, the particles may still rotate on infinitesimal orbits about their equilibrium positions. The Eckart conditions are six linear constraints on the moving system and the displacement vectors $\bar{\rho}_i$, and yield useful simplifications of the kinetic energy expression (II-3).

The first term of (II-3) is the translational kinetic energy, which is non-periodic and is related to the temperature of the molecular ensemble and the Doppler broadening effect in the spectrum. The translational energy is thus not of immediate interest in the vibration-rotation problem and can be omitted from the kinetic energy expression.

The second term of (II-3) is the rotational energy and can be expressed as

$$\tfrac{1}{2}\Big(\sum_{\alpha} I_{\alpha\alpha}\,\omega_\alpha^2 + \sum_{\substack{\alpha\beta \\ \alpha\neq\beta}} I_{\alpha\beta}\,\omega_\alpha\,\omega_\beta\Big), \qquad \text{(II-10)}$$

by defining the moments of inertia $I_{\alpha\alpha}$ and products of inertia $I_{\alpha\beta}$ $(\alpha\neq\beta)$ as follows:

$$I_{\alpha\alpha} = \sum_i m_i(\beta_i^2 + \gamma_i^2), \qquad \text{(II-11)}$$

$$I_{\alpha\beta} = -\sum_i m_i\alpha_i\beta_i \quad (\alpha\neq\beta) . \qquad \text{(II-12)}$$

The indices α, β, and γ are cyclic and each ranges over x, y, and z of the "body-fixed" coordinates, i.e. over x, y, and z of the moving system above.

Employing (II-4), we can express the moments and products of inertia as

$$I_{\alpha\alpha} = I^0_{\alpha\alpha} +2\sum_i m_i(\beta_i^0\beta_i' + \gamma_i^0\gamma_i') +\sum_i m_i(\beta_i'^2+\gamma_i'^2) \qquad \text{(II-13)}$$

$$I_{\alpha\beta} = I^0_{\alpha\beta} - \sum_i m_i(\alpha_i^0\beta_i' + \beta_i^0\alpha_i') -\sum_i m_i\alpha_i'\beta_i' , \qquad \text{(II-14)}$$

where $I^0_{\alpha\alpha}$ and $I^0_{\alpha\beta}$ are the equilibrium moments and products of inertia, respectively.

The third term of (II-3) is the vibrational energy and is equivalent to

$$\tfrac{1}{2}\sum_i m_i(\dot{x}_i'^2+\dot{y}_i'^2+\dot{z}_i'^2). \qquad \text{(II-15)}$$

It is convenient to assume a mass adjustment transformation on the displacement vector $\bar{\rho}_i$ and to express the vibration energy by mass-adjusted coordinates, s_i, as

$$\tfrac{1}{2}\sum_{i=1}^{3N} \dot{s}_i^2 , \qquad \text{(II-16)}$$

where

$$s_1 = \sqrt{m_1}x_1', \quad s_2 = \sqrt{m_1}y_1', \quad s_3 = \sqrt{m_1}z_1',$$

$$s_4 = \sqrt{m_2}\, x_2' , \qquad \ldots\ldots , \qquad s_{3N} = \sqrt{m_N}\, z_N' . \tag{II-17}$$

The fourth and fifth terms of (II-3) can be shown to vanish by the first Eckart condition.

The last term of (II-3) is the Coriolis term and represents the vibration-rotation interaction. By the second Eckart condition the Coriolis term can be written as

$$\bar{\omega} \cdot \left(\sum_i m_i \bar{r}_i \times \dot{\bar{r}}_i \right) . \tag{II-18}$$

Thus the kinetic energy will be

$$T = \tfrac{1}{2} \sum_\alpha I_{\alpha\alpha} \omega_\alpha^2 + \tfrac{1}{2} \sum_{\substack{\alpha\beta \\ \alpha \neq \beta}} I_{\alpha\beta}\, \omega_\alpha \omega_\beta + \tfrac{1}{2} \sum_{i=1}^{3N} \dot{s}_i^2 + \bar{\omega} \cdot \left(\sum_i m_i \bar{r}_i \times \dot{\bar{r}}_i \right) . \tag{II-19}$$

The general potential energy is composed of an "internal" potential energy due to the time-averaged electronic force field and an "external" potential energy. Assuming the overall molecular motion to proceed in force-free inertial space, the potential energy, V, is a function of the internal coordinates s_i only. Since the s_i's are generally small, one can expand the potential energy in a Taylor series about the nuclear equilibrium positions,

$$V = V_0 + \sum_{i=1}^{3N} \left(\frac{\partial V}{\partial s_i} \right)_0 s_i + \tfrac{1}{2} \sum_{ij} \left(\frac{\partial^2 V}{\partial s_i \partial s_j} \right)_0 s_i s_j + \tfrac{1}{6} \sum_{ijk} \left(\frac{\partial^3 V}{\partial s_i \partial s_j \partial s_k} \right)_0 s_i s_j s_k + \ldots . \tag{II-20}$$

However, the force at the equilibrium positions, $\left(\frac{\partial V}{\partial s_i} \right)_0$, must be zero, and the constant term V_0 is of no significance here, and can be set equal to zero. Therefore we write the potential energy as the sum of the quadratic simple harmonic terms, and higher anharmonic correction terms,

$$V = \tfrac{1}{2}\sum_{ij} f_{ij} s_i s_j + \tfrac{1}{6}\sum_{ijk} f_{ijk} s_i s_j s_k + \dots , \qquad \text{(II-21)}$$

where the force constants f are defined as

$$f_{ij} = \left(\frac{\partial^2 V}{\partial s_i \partial s_j}\right)_0 \qquad \text{(II-22)}$$

$$f_{ijk} = \left(\frac{\partial^3 V}{\partial s_i \partial s_j \partial s_k}\right)_0 , \quad \text{etc.} \qquad \text{(II-23)}$$

Let us introduce coefficients l_{is}^{α} which transform the coordinates s_i into linear combinations of the normal coordinates of vibration Q_s. Then in the asymmetric molecule in which essential degenerate modes of vibration are prevented due to insufficient symmetry[12] the mass-adjusted cartesian displacements will transform as

$$\sqrt{m_i}\,\alpha_i' = \sum_{s}^{n} l_{is}^{\alpha} Q_s , \qquad i=1, 2, \dots, N \quad \alpha = x, y \text{ or } z , \qquad \text{(II-24)}$$

or also

$$\dot{\alpha}_i' = \frac{1}{\sqrt{m_i}} \sum_{s}^{n} l_{is}^{\alpha}\, \dot{Q}_s . \qquad \text{(II-25)}$$

The index n is equal to the total number of vibrational modes of the molecule. Since the matrix of the coefficients l_{is}^{α} has the normalization property, we have

$$\sum_{i}\sum_{\alpha} l_{is}^{\alpha} l_{is'}^{\alpha} = \delta_{ss'} . \qquad \text{(II-26)}$$

The Eckart conditions constrain the l-matrix by the following relations;[13]

$$\sum_i \sqrt{m_i}\, l^{\alpha}_{is} = 0 \qquad \text{(II-27)}$$

$$\sum_i \sqrt{m_i}\,(\alpha_i l^{\beta}_{is} - \beta_i l^{\alpha}_{is}) = 0 \quad . \qquad \text{(II-28)}$$

Taking the body-fixed cartesian coordinate axes as the principal axes of the equilibrium inertia ellipsoid and substituting (II-24) into (II-13) and (II-14), we obtain expressions for the instantaneous moments and products of inertia in terms of the normal coordinates:

$$I_{\alpha\alpha} = I^{0}_{\alpha\alpha} + \sum_s a^{\alpha\alpha}_s Q_s + \sum_{ss'} A^{\alpha\alpha}_{ss'} Q_s Q_{s'} \;, \qquad \text{(II-29)}$$

$$I_{\alpha\beta} = \sum_s a^{\alpha\beta}_s Q_s + \sum_{ss'} A^{\alpha\beta}_{ss'} Q_s Q_{s'} \quad (\alpha \neq \beta), \qquad \text{(II-30)}$$

where $I^{0}_{\alpha\alpha}$ represents the principal equilibrium moments of inertia, and the constants $a^{\alpha\alpha}_s$, $a^{\alpha\beta}_s$, $A^{\alpha\alpha}_{ss'}$, and $A^{\alpha\beta}_{ss'}$ are defined by

$$\begin{aligned}
a^{\alpha\alpha}_s &= 2\sum_i \sqrt{m_i}\,(\beta^{0}_i l^{\beta}_{is} + \gamma^{0}_i l^{\gamma}_{is}) \;, \\
a^{\alpha\beta}_s &= -\sum_i \sqrt{m_i}\,(\alpha^{0}_i l^{\beta}_{is} + \beta^{0}_i l^{\alpha}_{is}) \;, \\
A^{\alpha\alpha}_{ss'} &= \sum_i (l^{\beta}_{is} l^{\beta}_{is'} + l^{\gamma}_{is} l^{\gamma}_{is'}) \;, \\
A^{\alpha\beta}_{ss'} &= -\sum_i l^{\alpha}_{is} l^{\beta}_{is'} \;.
\end{aligned} \qquad \text{(II-31)}$$

Substituting (II-24) into (II-16) and utilizing (II-26), the kinetic vibrational energy will be in normal coordinates,

$$\frac{1}{2}\sum_{s=1}^{n}\dot{Q}_s^{\,2} \quad . \tag{II-32}$$

The Coriolis term may be written by (II-24) and (II-25) as

$$\bar{\omega}\cdot\sum_i m_i\bar{\rho}_i\times\dot{\bar{\rho}}_i = \sum_\alpha\sum_{ss'}\zeta^\alpha_{ss'}Q_s\dot{Q}_{s'}\omega_\alpha \tag{II-33}$$

where the Coriolis coupling coefficients $\zeta^\alpha_{ss'}$ are defined as

$$\zeta^\alpha_{ss'} = \sum_i(l^\beta_{is}l^\gamma_{is'} - l^\beta_{is'}l^\gamma_{is}). \tag{II-34}$$

Thus we can write the kinetic energy of (II-19) as

$$T = \frac{1}{2}\sum_\alpha I_{\alpha\alpha}\omega_\alpha^{\,2} + \frac{1}{2}\sum_{\substack{\alpha\beta \\ \alpha\neq\beta}} I_{\alpha\beta}\omega_\alpha\omega_\beta + \frac{1}{2}\sum_s\dot{Q}_s^{\,2} + \sum_\alpha\sum_{ss'}\zeta^\alpha_{ss'}Q_s\dot{Q}_{s'}\omega_\alpha \,. \tag{II-35}$$

The potential energy of (II-21) becomes in terms of the normal coordinates

$$V = \frac{1}{2}\sum_s\lambda_s Q_s^{\,2} + \sum_{ss's''}k_{ss's''}Q_sQ_{s'}Q_{s''} + \dots \,, \tag{II-36}$$

where λ_s is the square of the s-th normal frequency and where the k's are the transformed force constants. These are now functions of the f's, m_i's and l^α_{is}'s.

From (II-35) and (II-36) one finds the conjugate angular momenta, P_α, for each ω_α and the linear momenta, p_s^*, conjugate to Q_s as

$$P_\alpha \equiv \frac{\partial T}{\partial\omega_\alpha} = I_{\alpha\alpha}\omega_\alpha + I_{\alpha\beta}\omega_\beta + I_{\alpha\gamma}\omega_\gamma + \sum_{ss'}\zeta^\alpha_{ss'}Q_s\dot{Q}_{s'}, \tag{II-37}$$

$$p_s^* \equiv \frac{\partial T}{\partial\dot{Q}_s} = \dot{Q}_s + \sum_\alpha\sum_{s'}\zeta^\alpha_{s's}Q_{s'}\omega_\alpha \,. \tag{II-38}$$

Summing (II-37) multiplied by ω_α over α and adding (II-38) multiplied by $\dot{Q}_s$ and summed over s, we obtain twice the kinetic energy,

$$2T = \sum_\alpha P_\alpha \omega_\alpha + \sum_s p_s{*}\dot{Q}_s \; . \qquad \text{(II-39)}$$

Substituting $\dot{Q}_s$ from (II-38) into (II-39), we have

$$T = \tfrac{1}{2}\sum_\alpha (P_\alpha - p_\alpha)\omega_\alpha + \tfrac{1}{2}\sum_s p_s{*}^2 \qquad \text{(II-40)}$$

where p_α is an internal angular momentum arising from the vibrational motions whithin the "body-fixed" system, and is equal to $(\sum_{ss'} \zeta^\alpha_{ss'} Q_s p^*_{s'})$.

One can show by manipulating (II-37) and (II-38) that

$$P_\alpha - p_\alpha = I'_{\alpha\alpha}\omega_\alpha - I'_{\alpha\beta}\omega_\beta - I'_{\alpha\gamma}\omega_\gamma \; , \qquad \text{(II-41)}$$

where

$$I'_{\alpha\alpha} = I_{\alpha\alpha} - \sum_s (\sum_{s'} \zeta^\alpha_{s's} Q_{s'})^2 \qquad \text{(II-42)}$$

$$I'_{\alpha\beta} = -I_{\alpha\beta} + \sum_s (\sum_{s'} \zeta^\alpha_{s's} Q_{s'})(\sum_{s'} \zeta^\beta_{s's} Q_{s'}) \; . \qquad \text{(II-43)}$$

Eq. (II-41) can be written in vector form,

$$\bar{P} - \bar{p} = [\mu_{\alpha\beta}]^{-1}\,\bar{\omega} \qquad \text{(II-44)}$$

where

$$[\mu_{\alpha\beta}]^{-1} = \begin{bmatrix} I'_{xx} & -I'_{xy} & -I'_{xz} \\ -I'_{yx} & I'_{yy} & -I'_{yz} \\ -I'_{zx} & -I'_{zy} & I'_{zz} \end{bmatrix} . \qquad \text{(II-45)}$$

The inverse equation to (II-44) is,

$$\overline{\pi} = [\mu_{\alpha\beta}](\overline{P} - \overline{p}) \qquad \text{(II-46)}$$

where the elements of $[\mu_{\alpha\beta}]$ are

$$\mu_{\alpha\beta} = \mu(I'_{\alpha\gamma}I'_{\gamma\beta} + I'_{\alpha\beta}I'_{\gamma\gamma}), \ (\alpha \neq \beta \neq \gamma) \qquad \text{(II-47)}$$

$$\mu_{\alpha\alpha} = \mu(I'_{\beta\beta}I'_{\gamma\gamma} - I'^{2}_{\beta\gamma}) \qquad \text{(II-48)}$$

with

$$\mu = \det[\mu_{\alpha\beta}] . \qquad \text{(II-49)}$$

Combining equations (II-36), (II-40), and (II-46) we have an expression for the total energy in the classical Hamiltonian form,

$$H = \tfrac{1}{2}\sum_{\alpha\beta}\mu_{\alpha\beta}(P_\alpha - p_\alpha)(P_\beta - p_\beta) + \tfrac{1}{2}\sum_s p_s^{*2} + \tfrac{1}{2}\sum_s \lambda_s Q_s^{2}$$
$$+ \sum_{ss's''} k_{ss's''} Q_s Q_{s'} Q_{s''} + \ldots \qquad \text{(II-50)}$$

Podolsky[14] considered the problem of obtaining the quantum mechanical Hamiltonian corresponding to the classical kinetic energy expressed in terms of momenta, p_i, conjugate to a set of generalized coordinates q_i. If the classical kinetic energy has the general form.

$$T = \tfrac{1}{2}\sum_{ij} g^{ij} p_i p_j \ , \qquad \text{(II-51)}$$

he showed that the proper quantum mechanical Hamiltonian should be

$$H = \tfrac{1}{2} g^{\frac{1}{4}} \sum_{ij} p_i g^{ij} g^{-\frac{1}{2}} p_j g^{\frac{1}{4}} + V \ , \qquad \text{(II-52)}$$

where $g = \det[g^{ij}]$. Eq. (II-52) is subject to the requirement that its eigenfunctions should be normalized in the configuration space q_i's,

$$\int \Psi^* \Psi \, dq_1 dq_2 \ldots dq_n = 1. \qquad \text{(II-53)}$$

From (II-50) the kinetic energy may be written in the form

$$T = \frac{1}{2}\sum_{ij} G^{ij} P_i P_j \,, \qquad \text{(II-54)}$$

by denoting

$$P_1 = P_x - p_x \,, \quad P_2 = P_y - p_y, \quad P_3 = P_z - p_z$$

$$P_4 = p_1^* \,, \quad P_5 = p_2^* \,, \ldots , \quad P_{n+3} = p_n^*, \qquad \text{(II-55)}$$

and

$$[G^{ij}] = \begin{bmatrix} [\mu_{\alpha\beta}] & 0 \\ 0 & [I] \end{bmatrix} , \text{ with } G = \det[G^{ij}] = \mu, \qquad \text{(II-56)}$$

where $[I]$ is the n x n identity matrix.

Then according to Podolsky the proper quantum mechanical Hamiltonian would be

$$H = \frac{1}{2}\, G^{\frac{1}{4}} \sum_{ij} P_i G^{ij} G^{-\frac{1}{2}} P_j G^{\frac{1}{4}} + V. \qquad \text{(II-57)}$$

However the conjugate coordinates to the momenta P_i do not meet the requirement (II-53). Thus we should transform P_i into the proper form to satisfy (II-53).

After this unitary transfomation is performed, the Hamiltonian (II-57) will become[9]

$$H = \frac{1}{2} G^{\frac{1}{4}} \sum_{ij} [(S^{-\frac{1}{2}} P_i S^{\frac{1}{2}}) G^{ij} G^{-\frac{1}{2}} (S^{-\frac{1}{2}} P_j S^{\frac{1}{2}})] G^{\frac{1}{4}} + V, \qquad \text{(II-58)}$$

with $S = (\sin\theta)^{-1}$.

Remembering that P_3 is independent of the Eulerian angle θ, which is the angle between the z-axis of the body-fixed system and the Z-axis of the space-fixed system, we finally obtain the proper quantum mechanical

Hamiltonian as

$$H = \tfrac{1}{2}\mu^{\frac{1}{4}}\sum_{\alpha\beta}(P_\alpha - p_\alpha)\mu_{\alpha\beta}\,\mu^{-\frac{1}{2}}(P_\beta - p_\beta)\mu^{\frac{1}{4}} + \tfrac{1}{2}\mu^{\frac{1}{4}}\sum_s p_s{}^*\mu^{-\frac{1}{2}}p_s{}^*\mu^{\frac{1}{4}}$$

$$+ \tfrac{1}{2}\sum_s \lambda_s Q_s{}^2 + \sum_{ss's''} k_{ss's''}Q_sQ_{s'}Q_{s''} + \dots, \qquad \text{(II-59)}$$

where P_x and P_y here represent the modified angular momenta $(\sin\theta)^{\frac{1}{2}}P_x(\sin\theta)^{-\frac{1}{2}}$ and $(\sin\theta)^{\frac{1}{2}}P_y(\sin\theta)^{-\frac{1}{2}}$, respectively.

In order to calculate the vibration-rotation energies of a molecule we should solve the Schroedinger equation for the Hamiltonian operator (II-59). However this Hamiltonian does by no means lend itself to an exact solution of the Schroedinger equation. Hence to make further progress, the Hamiltonian (II-59) has to be developed in orders of approximation. Since the desplacements α_i' are small relative to the equilibrium coordinates α_i^0, the Hamiltonian (II-59) can be expanded such that the zeroth order Hamiltonian will be the equilibrium Hamiltonian. In the following chapter we will perform this expansion.

III. DEVELOPMENT OF THE HAMILTONIAN

When we expand the Hamiltonian (II-59) we get the following operator expression,

$$H = \tfrac{1}{2}\sum_{\alpha\beta} \mu_{\alpha\beta} P_\alpha P_\beta - \tfrac{1}{2}\sum_{\alpha\beta} (p_\alpha \mu_{\alpha\beta} + \mu_{\alpha\beta} p_\alpha) P_\beta + \tfrac{1}{2}\sum_{\alpha\beta} p_\alpha \mu_{\alpha\beta} p_\beta$$
$$+ \tfrac{1}{2}\sum_s p_s^{*2} + \tfrac{1}{2}\Lambda + V \qquad \text{(III-1)}$$

where

$$\Lambda = \mu^{\frac{1}{4}} \sum_{\alpha\beta} (p_\alpha \mu_{\alpha\beta} \mu^{-\frac{1}{2}} (p_\beta \mu^{\frac{1}{4}})) + \mu^{\frac{1}{4}} \sum_s (p_s^* \mu^{-\frac{1}{2}} (p_s^* \mu^{\frac{1}{4}})).$$

The terms of (III-1) represent the pure rotational energy, the Coriolis coupling energy, the first correction to the Coriolis energy, the vibrational energy, the second correction to the Coriolis energy and the potential energy, in this order.

Since $\mu_{\alpha\beta}$ and μ are functions of the normal coordinates which, in turn, are functions of the displacement vectors from the equilibrium positions, it is possible to develop $\mu_{\alpha\beta}$ and μ in power series of the normal coordinates for the development of the Hamiltonian in the way mentioned at the end of Chapter II.

Let us write then,

$$\mu_{\alpha\beta} = \frac{1}{I^0_{\alpha\alpha} I^0_{\beta\beta}} (\mathcal{I}^{\alpha\beta} + \sum_s a_s^{\alpha\beta} Q_s + \sum_{ss'} A_{ss'}^{\alpha\beta} Q_s Q_{s'} + \ldots), \qquad \text{(III-2)}$$

$$\mu = \frac{1}{I^0_{\alpha\alpha} I^0_{\beta\beta} I^0_{\gamma\gamma}} (\rho + \sum_s \rho'_s Q_s + \ldots), \qquad \text{(III-3)}$$

where

$$\mathcal{I}^{\alpha\beta} = I^0_{\alpha\beta} \qquad \text{(III-4)}$$

$$\mu_s^{\alpha\beta} = -a_s^{\alpha\beta} \qquad \text{(III-4b)}$$

$$\mu_{ss'}^{\alpha\beta} = -A_{ss'}^{\alpha\beta} + \sum_{s''} \zeta_{ss''}^{\alpha} \zeta_{s's''}^{\beta} + \sum_{\delta} \frac{a_s^{\alpha\delta} a_{s'}^{\beta\delta}}{I^0_{\delta\delta}} . \qquad \text{(III-4c)}$$

We also have that

$$\varphi^{\alpha\alpha} = 1 \qquad \text{(III-5a)}$$

$$\rho = -\sum_{\delta} \frac{a_s^{\delta\delta}}{I^0_{\delta\delta}} \qquad \text{(III-5b)}$$

The index δ ranges over x, y, and z, and $I^0_{\alpha\beta}$ will vanish for $\alpha \neq \beta$ if we take the axes of the body-fixed system as the principal axes of the equilibrium moment of inertia ellipsoid. Substituting the expansions (III-2) and (III-3) into the terms of (III-1) each of these terms will have a series expansion in the normal coordinates. For example,

$$\Lambda = \Lambda^0 + \sum_s \Lambda_s Q_s + \sum_{ss'} \Lambda_{ss'} Q_s Q_{s'} + \ldots \qquad \text{(III-6)}$$

Now regrouping terms by estimated orders of magnitude, one gets the Hamiltonian in the series form

$$H = H_0 + \lambda H_1 + \lambda^2 H_2 + \lambda^3 H_3 + \ldots \qquad \text{(III-7)}$$

where λ is a numerical parameter of smallness.

We expanded (III-1) such that the zeroth order Hamiltonian H_0 would represent the "rigid-harmonic" Hamiltonian of the molecule, i.e., it represents the energies of a rigid rotator with the nuclear framework of the molecule in its equilibrium position plus the energies of vibration from a potential which is a quadratic form in the normal coordinates.

Replacing $\Omega^{\alpha\beta}$ by its value $I^0_{\alpha\beta}$, and Q_s and p^*_s by $(\hbar^2/\lambda_s)^{\frac{1}{4}}q_s$ and $(\lambda_s/\hbar^2)^{\frac{1}{4}}$ respectively, we obtain the first order terms, H_1, the second order term H_2, etc.,

$$H_0 = \frac{1}{2}\sum_{\alpha}\frac{P_\alpha{}^2}{I^0_{\alpha\alpha}} + (\hbar/2)\sum_s \lambda_s^{\frac{1}{2}}(p_s^2/\hbar^2 + q_s^2) \qquad \text{(III-8a)}$$

$$H_1 = \frac{1}{2}\sum_{\alpha\beta}\sum_s \frac{\Omega^{(1)\alpha\beta}_s}{I^0_{\alpha\alpha}\,I^0_{\beta\beta}}\left(\frac{\hbar^2}{\lambda_s}\right)^{\frac{1}{4}} q_s P_\alpha P_\beta - \sum_\alpha \frac{p_\alpha P_\alpha}{I^0_{\alpha\alpha}}$$

$$+hc\sum_{ss's''}K_{ss's''}q_s q_{s'} q_{s''} \qquad \text{(III-8b)}$$

$$H_2 = \frac{1}{2}\sum_{ss'}\sum_{\alpha\beta}\frac{\Omega^{(2)\alpha\beta}_{ss'}}{I^0_{\alpha\alpha}\,I^0_{\beta\beta}}\left(\frac{\hbar^4}{\lambda_s\lambda_{s'}}\right)^{\frac{1}{4}} q_s q_{s'} P_\alpha P_\beta + \frac{1}{2}\sum_\alpha \frac{p_\alpha{}^2}{I^0_{\alpha\alpha}}$$

$$-\frac{1}{2}\sum_{\alpha\beta}\sum_s \frac{\Omega^{(1)\alpha\beta}_s}{I^0_{\alpha\alpha}\,I^0_{\beta\beta}}\left(\frac{\hbar^2}{\lambda_s}\right)^{\frac{1}{4}}(p_\alpha q_s + q_s p_\alpha)$$

$$+ hc\sum_{ss's''s'''}K_{ss's''s'''}q_s q_{s'} q_{s''} q_{s'''} \qquad \text{(III-8c)}$$

where

$$hcK_{ss's''} = k_{ss's''}\left(\frac{\hbar^6}{\lambda_s\lambda_{s'}\lambda_{s''}}\right)^{\frac{1}{3}} \qquad \text{(III-9a)}$$

$$hcK_{ss's''s'''} = k_{ss's''s'''}\left(\frac{\hbar^8}{\lambda_s\lambda_{s'}\lambda_{s''}\lambda_{s'''}}\right)^{\frac{1}{4}} \qquad \text{(III-9b)}$$

and the internal angular momenta may be expressed as

$$p_\alpha = \sum_{ss'}\tilde{\zeta}_{ss'}(\lambda_{s'}/\lambda_s)^{\frac{1}{4}}q_s p_{s'} \qquad \text{(III-10)}$$

Higher order terms of the Hamiltonian are given in the reference.[3]

The energies of the system represented by the

Hamiltonian (III-7) can in principle be calculated in successive orders of approximation by the perturbation method. The zeroth order energy would be calculated only from the zeroth order term H_0. The first order correction energies, $E_n^{(1)}$, are computed only from the diagonal matrix elements of H_1. In the absence of degeneracies, the off-diagonal elements of H_1 will contribute to the second order rather than to the first order correction energies. This means that the off-diagonal matrix elements of H_1 complicate the computation only of the second order correction energies, $E_n^{(2)}$. To calculate the energies to the second order it is desirable to transform the Hamiltonian to a form more convenient for the perturbation calculation. Van Vleck suggested the so-called contact transformation.[15] By a suitable unitary transformation T, one attempts to find a Hamiltonian H',

$$H' = THT^{-1} = H_0' + \lambda H_1' + \lambda^2 H_2' + \dots \qquad \text{(III-11)}$$

such that the zeroth order term and the diagonal matrix elements of the first order term of the Hamiltonian remain unchanged while the off-diagonal elements of the first order term of the transformed Hamiltonian would vanish completely. This unitary transformation would leave the wave functions unchanged, and hence under this transformation the eigenfunctions of H_0 would become eigenfunctions of H_0+H_1', which is now "equivalent" to a zeroth order term. Since there are no off-diagonal matrix elements of H_1', we can treat H_2' as the first perturbation term and get the second order correction energy by taking the expectation values of H_2'.

Thus, except in the case of accidental degeneracies, it is advantageous to consider the partial diagonalization of the Hamiltonian in the vibrational quantum numbers by use of the contact transformation.
This is done by choosing a suitable operator T which leaves H_0 of (III-8a) unchanged and gives an H_1' independent of the vibrational operators.[16]
The simplest method of obtaining the suitable form of T is to set $T = e^{i\lambda S}$, where S is called the Herman-Shaffer operator. Then,

$$H' = THT^{-1} = (1+i\lambda S-\tfrac{1}{2}\lambda^2S^2+\ldots)\cdot(H_0+\lambda H_1+\lambda^2H_2+\ldots)\cdot(1-i\lambda S-\tfrac{1}{2}\lambda^2S^2+\ldots), \qquad \text{(III-12)}$$

or

$$H_0' = H_0 \qquad \text{(III-13a)}$$

$$H_1' = H_1 - i(H_0S-SH_0) \qquad \text{(III-13b)}$$

$$H_2' = H_2 + \tfrac{1}{2}i[S, (H_1+H_1')] \text{ and so on.} \qquad \text{(III-13c)}$$

The requirements for a suitable contact transformation are thus that we have for all v_s:

$$(\ldots v_s\ldots|i(H_0S-SH_0)|\ldots v_s\ldots)=0 \qquad \text{(III-14a)}$$

$$(\ldots v_s\ldots|i(H_0S-SH_0)|\ldots v_s'\ldots)= (\ldots v_s\ldots|H_1|\ldots v_s'\ldots) \quad \text{for } v_s\neq v_s' . \qquad \text{(III-14b)}$$

The proper operators S were found by Herman and Shaffer.[17] However, if we perform the contact transformation, a part of the Hamiltonian formally belonging to H_m' becomes of the order of magnitude of H_{m+1}'. Hence we need to regroup the terms in true orders of magnitude after the contact transformation. This transformed and regrouped Hamiltonian is

$$H' = h_0' + h_1' + h_2' + h_3' + \dots \qquad \text{(III-15)}$$

where

$$h_0' = H_0 \qquad \text{(III-16a)}$$

$$h_1' = -\sum_{\alpha} \frac{p_\alpha^* P_\alpha}{I_{\alpha\alpha}^0} \qquad \text{(III-16b)}$$

$$\begin{aligned} h_2' = {} & \sum_{\alpha\le\beta\le\gamma\le\delta} {}^{\alpha\beta\gamma\delta}_{(2)}Y P_\alpha P_\beta P_\gamma P_\delta + \sum_{\substack{abcd \\ a\le b\le c\le d}} {}_{(2)}Y_{abcd}\, q_a q_b q_c q_d \\ & + \sum_{\alpha\beta} \sum_{\substack{ab \\ a\le b}} \left({}^{\alpha\beta}_{(2)}Y^{ab} p_a p_b + {}^{\alpha\beta}_{(2)}Y_{ab} q_a q_b \right) P_\alpha P_\beta \\ & + \sum_{\substack{abcd \\ a\le b,\, c\le d}} {}_{(2)}Y_{ab}^{cd} \tfrac{1}{2}(q_a q_b p_c p_d + p_c p_d q_a q_b) + H_2'^* \end{aligned}$$

(III-16c)

where $H_2'^*$ includes all terms of H_2' non-diagonal in one or more vibrational quantum numbers,

$$\begin{aligned} H_2'^* = {} & \sum_{\alpha\beta\gamma} \sum_{a} \left({}^{\alpha\beta\gamma}_{(2)}Y^{a} \right) p_a P_\alpha P_\beta P_\gamma + \sum_{\alpha} \sum_{\substack{abc \\ a\le b\le c}} {}^{\alpha}_{(2)}Y^{abc} p_a p_b p_c P_\alpha \\ & + \sum_{\alpha} \sum_{\substack{abc \\ a\le b}} \left({}^{\alpha}_{(2)}Y^{c}_{ab} \right) \tfrac{1}{2}(q_a q_b p_c + p_c q_a q_b) P_\alpha . \end{aligned} \qquad \text{(III-17)}$$

p_α^* of h_1', which is $\sum\sum_{s\sigma<\sigma'} \zeta^{\alpha}_{s\sigma,s\sigma'}(q_{s\sigma} p_{s\sigma'} - q_{s\sigma'} p_{s\sigma})$ in the general case, vanishes for asymmetric molecules due to the absence of degenerate modes of vibration, because $\zeta^{\alpha}_{s\sigma,s\sigma'} = 0$ in asymmetric molecules since the index σ which enumerates degenerate modes of vibration for given s, $\sigma = \sigma' = 1$. The coefficients Y are complicated functions of the molecular constants and detailed expressions for them are given in the literature.[4-6]

In order to calculate the vibration-rotation energy to the fourth order, it is necessary to apply yet a second contact transformation $\mathcal{T}$ to the Hamiltonian H',

$$H^{+} = \mathcal{T} H' \mathcal{T}^{-1} = e^{i\lambda^2 \mathcal{S}} H' e^{-i\lambda^2 \mathcal{S}}$$

$$= H_0^{+} + \lambda H_1^{+} + \lambda^2 H_2^{+} + \lambda^3 H_3^{+} + \ldots \quad \text{(III-18)}$$

in such a manner that $H_0^{+} + \lambda H_1^{+} + \lambda^2 H_2^{+}$ will now be diagonal with respect to the vibrational quantum numbers in the representation for which H_0 is diagonal in the vibrational quantum numbers. Again one observes that the transformation will have the effect that certain terms of H^{+} which formally arise from the operator H_m^{+} contribute only to the order of magnitude of H_{m+1}^{+}. Hence it is also necessary to regroup the terms of the twice transformed Hamiltonian by true orders of magnitude. After this regrouping the Hamiltonian is of the form

$$H^{+} = \mathcal{T} H' \mathcal{T}^{-1} = h_0^{+} + h_1^{+} + h_2^{+} + h_3^{+} + \ldots \quad \text{(III-19)}$$

By the requirements for the contact transformation, h_0^+ is the zeroth order term H_0 unchanged and h_1^+ vanishes for asymmetric molecules. The detailed expressions for h_2^+, h_3^+, and h_4^+ are given by Amat and Nielsen[5,6] who have found the required transformation.

The Hamiltonian (III-19) can be used to calculate vibration-rotation energies to the fourth order of approximation by utilizing only those matrix elements of (III-19) which are diagonal in all vibrational quantum numbers v_s, because h_0^+, h_1^+, and h_2^+ are already diagonal in all v_s and off-diagonal matrix elements in any v_s of h_3^+ and h_4^+ will contribute to the energies only in orders of approximation higher than the fourth. The Hamiltonian (III-19) is diagonal to all orders in the rotational quantum numbers J(total angular momentum quantum number) and M(magnetic quantum number) but it is not diagonal in the quantum number K in a symmetric rotator representation. In particular, for asymmetric molecules h_0^+ is not diagonal in K, and no closed form general transformation is known which would bring the zero-order rigid asymmetric top Hamiltonian to the diagonal form. This is, of course, the essential fact which prevents one from obtaining an analytical expression for the rotation-vibration energies of asymmetric molecules in the general case despite the perturbation formalism.

Neglecting components which are off-diagonal in the vibrational quantum numbers, we have the following types of term to the fourth order of approximation in the vibration-rotation Hamiltonian for the asymmetric molecule:

$$\begin{aligned}
&(a)\ {}_{(0)}Zr^2,\ {}_{(2)}Zr^4,\ {}_{(4)}Zr^6 + {}_{(4)}Zr^2 \\
&(b)\ {}_{(0)}ZP^2,\ {}_{(2)}ZP^4,\ {}_{(4)}ZP^2,\ {}_{(4)}ZP^6 \qquad\qquad \text{(III-20)} \\
&(c)\ {}_{(1)}Zr^2P,\ {}_{(2)}Zr^2P^2,\ {}_{(3)}Zr^4P,\ {}_{(3)}Zr^2P^3,\ {}_{(4)}Zr^2P^4,\ {}_{(4)}Zr^4P^2
\end{aligned}$$

where we have used the following notation: r^2 stands for products of any two vibrational operators $q_a q_b$, $p_a p_b$, $q_a p_b$, $p_a q_b$; r^4 for any product of four vibrational operators, etc.; P^n for any product of P_x, P_y, and P_z; and ${}_{(n)}Z$ stands for ${}^{\alpha\beta\cdots\cdots}_{(n)}Z^{a',b',\ldots}_{a,b,\ldots}$, which appear in H^+ as the coefficients to the various operators. The subscript (n) of ${}_{(n)}Z$ represents the order of approximation of the corresponding term. We also have omitted the summation sign over the rotational and vibrational indices. Detailed expressions of ${}_{(n)}Z$ are given in the references,[5,6] and we will write down explicitly only those ${}_{(n)}Z$ which will be needed in the present work and as the need arises.

Terms (a) constitute pure vibrational operators including anharmonicity corrections, terms (b) constitute pure rotational operators including centrifugal distortion corrections, and terms (c) may be interpreted as vibration-rotation interaction terms and comprise such contributions as the vibrational corrections to the rotational and centrifugal distortion constants. Generally the vibrational frequencies are 100 to 1000 times larger than the pure rotational frequencies. Therefore, as discussed by Amat and Nielsen,[18] the subscript (n) of ${}_{(n)}Z$ indicates the order of magnitude of the contribution by the term correctly for $J \approx 10$ to $J \approx 30$. If $J \approx 1$, then such terms as ${}_{(4)}Zr^2P^4$ and ${}_{(4)}ZP^6$ should more properly be regarded as contributions to the eighth and tenth orders of magnitude respectively rather than to the fourth order indicated by the subscripts. In any case, inclusion of all of the above types of term will be sufficient to fourth order for all reasonable J, and terms such as ${}_{(4)}ZP^6$ need be considered in the fourth order only for large values of J. The relative importance of the various types of terms for given J can be ascertained from Table I of the reference 18.

In cases of resonances, in which two or more energy levels are either closely spaced or actually degenerate, our preceeding arguments must be modified, since the contribution from the relevant operators h_n^+ will more pronounced than in the non-degenerate case. If two energy levels are very close, the off-diagonal matrix elements of h_n^+ will contribute to the energy in a much lower order than the 2n-th. In the general molecule there can occur two kinds of resonance. One is the accidental resonance which is due to the proximity of two interacting levels with different vibrational quantum numbers yet having nearly the same energies. Coriolis resonance and Fermi resonance are typical accidental resonances. The other kind of resonance is the essential resonance between levels which have the same vibrational quantum numbers but different internal angular momentum quantum numbers, e.g. l, or different K quantum numbers. In the asymmetric molecule essential degeneracies are absent because of the low symmetry of the molecule. Therefore in this work we need to consider only the accidental resonances. In fact, since it is very complicated to account for all possible accidental degeneracies, we will assume that our molecule is free of accidental resonances, or that, if they occur, the energy levels involved in such resonances may be excluded from consideration. Then the Hamiltonian (III-19) is quite appropriate for the calculation of energies to the fourth order.

Terms (a) of (III-20) are associated with the pure vibrational energies. We shall denote their total diagonal contribution to the Hamiltonian by h_V^{+*}. This h_V^{+*} gives the vibrational energies E_V to fourth order and will not concern us further, since we are principally interested in the rotational level structure built upon particular vibrational states rather than in the detailed calculation of the pure vibrational structure. From the general vibration-rotation Hamiltonian we find for asymmetric molecules that the ${}_{(1)}Zr^2P$-type terms have zero coefficients ${}_{(1)}Z$, and that the ${}_{(3)}Zr^4P$ and ${}_{(3)}Zr^2P^3$-type terms have no non-zero matrix elements diagonal in all v_s. Thus the odd order terms which are a source of considerable difficulties in symmetric and spherical rotators may be excluded from consideration in the asymmetric rotator case. Thus, to fourth order, we have:

$$H^+ = h_v^{+*} + h_o^+ + h_2^{+*} + h_4^{+*}, \qquad \text{(III-21)}$$

where

$$h_o^+ = {}_{(o)}ZP^2 = AP_x^2 + BP_y^2 + CP_z^2 , \qquad \text{(III-22)}$$

$$h_2^{+*} = {}_{(2)}Zr^2P^2 + {}_{(2)}ZP^4 , \qquad \text{(III-23)}$$

$$h_4^{+*} = {}_{(4)}ZP^2 + {}_{(4)}Zr^4P^2 + {}_{(4)}Zr^2P^4 + {}_{(4)}ZP^6 . \qquad \text{(III-24)}$$

The asterisks denote that terms of h_v^{+*} are to be omitted in h_2^{+*} and h_4^{+*} and also that terms of h_4^+ not diagonal in all v_s are to be omitted in h_4^{+*}.

IV. ZERO ORDER ASYMMETRIC ROTATOR HAMILTONIAN

We return to the part of Hamiltonian (III-8a), which remained unchanged under the two successive contact transformation. The first summation term of (III-8a) is the rigid rotator Hamiltonian and the second term is the Hamiltonian of n uncoupled simple harmonic oscillators.

The vibrational portion of (III-8a) was

$$H_{ov} = \tfrac{1}{2}\hbar\sum_s \lambda_s^{\frac{1}{2}}(p_s^2/\hbar^2 + q_s^2). \qquad \text{(IV-1)}$$

With the aid of the vibrational matrix elements

$$(v_s|q_s^2|v_s) = (v_s + \tfrac{1}{2}) \qquad \text{(IV-2a)}$$

$$(v_s|p_s^2|v_s) = \hbar^2(v_s + \tfrac{1}{2}), \qquad \text{(IV-2b)}$$

we obtain the vibrational energy of the molecule to zero order of approximation from (IV-1) as

$$E_{ov} = \hbar\sum_s \lambda_s^{\frac{1}{2}}(v_s + \tfrac{1}{2}). \qquad \text{(IV-3)}$$

We can write (IV-3) as

$$E_{ov} = hc\sum_s \omega_s(v_s + \tfrac{1}{2}), \qquad \text{(IV-4)}$$

where ω_s are the normal frequencies of oscillation expressed in cm^{-1}.

The zero order rotational Hamiltonian H_{or} can be written as

$$H_{or} = \tfrac{1}{2}\left(\frac{1}{I^0_{xx}}P_x^2 + \frac{1}{I^0_{yy}}P_y^2 + \frac{1}{I^0_{zz}}P_z^2\right) \qquad \text{(IV-5)}$$

where x, y, and z represent the directions of the principal axis of the inertia ellipsoid in the body fixed coordinate system. With the appreviations,

$$A = \frac{1}{2I^{o}_{xx}} , \quad B = \frac{1}{2I^{o}_{yy}} , \quad C = \frac{1}{2I^{o}_{zz}} \qquad \text{(IV-6)}$$

H_{or} will be

$$H_{or} = AP_x^{\,2} + BP_y^{\,2} + CP_z^{\,2} , \qquad \text{(IV-7)}$$

and the definition of the asymmetric top molecule implies

$$A \neq B \neq C .$$

We will assume A>B>C in this study. This ordering is not always the conventional one, but this work can be brought into agreement with any of the customary conventions by proper interchanges of A, B, and C.

The total angular momentum can be expressed as

$$P^2 = P_x^{\,2} + P_y^{\,2} + P_z^{\,2} = P_X^{\,2} + P_Y^{\,2} + P_Z^{\,2} \qquad \text{(IV-8)}$$

where X, Y, and Z are the axes of the space-fixed Cartesian coordinate system. Each component P_x, P_y, and P_z commutes with each of P_X, P_Y, and P_Z, and

$$[P_\alpha , P_\beta] = -i\hbar P_\gamma , \quad \alpha, \beta, \text{ and } \gamma \text{ cyclic}, \qquad \text{(IV-9)}$$

$$[P_a , P_b] = +i\hbar P_c , \quad a, b, \text{ and } c \text{ cyclic}, \qquad \text{(IV-10)}$$

in which α, β, and γ represent the body-fixed system coordinates and a, b, and c represent space-fixed system coordinates. The total angular momentum P^2 and

P_Z commute with H_{or}, but P_z does not commute with H_{or} for the asymmetric molecule. Hence the eigenfunctions of the asymmetric rotator will be designated by ψ_{JM} and a set of (2J+1) eigenfunctions ψ_{JM} will be associated with every possible pair of quantum numbers J and M ($M \leq J$);

$$P^2 \psi_{JM} = \hbar^2 J(J+1)\, \psi_{JM} \,, \tag{IV-11}$$

$$P_Z \psi_{JM} = \hbar\, M\, \psi_{JM} \,. \tag{IV-12}$$

The (2J+1) eigenfunctions associated with a given pair of values J and M would have been identified by the quantum number K in the symmetric rotator case, since for the symmetric rotator we have that $P_z \phi_{JKM} = hK\phi_{JKM}$, i.e., K is a "good" quantum number.

Wang[16] wrote ψ_{JM} as a linear combination of the eigenfunctions of the symmetric rotator, $_{JKM}$,

$$\psi_{JM} = \sum_K C_K \phi_{JKM} \,. \tag{IV-13}$$

Substituting (IV-13) into the Schroedinger equation of the asymmetric rotator we obtain

$$H_{or} \sum_K C_K \phi_{JKM} = E_{or} \sum_K C_K \phi_{JKM} \tag{IV-14}$$

and from the condition for the existence of non-trivial solutions of (IV-14) we obtain the secular equation for each pair of J and M as

$$\mathrm{Det}\,\left| H_{KK'} - E_{or}\,\delta_{KK'} \right| = 0 \qquad \text{(IV-15)}$$

where

$$H_{KK'} = \int \phi^{*}_{JKM}\, H_{or}\, \phi_{JK'M}\, d\tau \,. \qquad \text{(IV-16)}$$

In principle we can now calculate the energy levels of the asymmetric rotator from eq. (IV-15).

In the symmetric rotator case we have

$$P^2 \phi_{JKM} = \hbar^2 J(J+1)\, \phi_{JKM} \qquad \text{(IV-16a)}$$

$$P_Z \phi_{JKM} = \hbar M\, \phi_{JKM} \qquad \text{(IV-16b)}$$

$$P_z \phi_{JKM} = \hbar K\, \phi_{JKM} \quad . \qquad \text{(IV-16c)}$$

Taking the phase angle for the angular momentum components such that

$$(K|P_x|K+1) = (K+1|P_x|K) = \tfrac{1}{2}\hbar\left[(J-K)(J+K+1)\right]^{\frac{1}{2}} \qquad \text{(IV-17a)}$$

$$(K|P_y|K+1) = -(K+1|P_y|K) = -\frac{1}{2}\hbar\left[(J-K)(J+K+1)\right]^{\frac{1}{2}}, \qquad \text{(IV-17b)}$$

the non-vanishing matrix elements of P_x^2, P_y^2, and P_z^2 are given by

$$(K|P_x^2|K) = (K|P_y^2|K) = \tfrac{1}{2}\hbar^2\left[J(J+1)-K^2\right] \qquad \text{(IV-18a)}$$

$$\begin{aligned}(K|P_x^2|K\pm2) &= -(K|P_y^2|K\pm2) \qquad \text{(IV-18b)}\\ &= \tfrac{1}{4}\hbar^2\left[(J\mp K)(J\mp K+1)(J\pm K+1)(J\pm K+2)\right]^{\frac{1}{2}}\end{aligned}$$

$$(K|P_z^2|K) = \hbar^2 K^2 \qquad \text{(IV-18c)}$$

From these matrix elements we obtain the non-vanishing matrix elements of $[H_{KK'}]$ for given J and M as

$$(K|H_{or}|K)=\tfrac{1}{2}(A+B)[J(J+1)-K^2]\hbar^2+CK^2\hbar^2 \qquad \text{(IV-19a)}$$

$$(K|H_{or}|K+2)=(K+2|H_{or}|K) \qquad \text{(IV-19b)}$$

$$=-\tfrac{1}{4}\hbar^2(A-B)[(J-K-1)(J-K)(J+K+1)(J+K+2)]^{\frac{1}{2}}.$$

Eq. (IV-15) can be simplified by taking advantage of the symmetry properties of the wave functions of the system. Since the inertia ellipsoid must be invariant under rotation through an angle π around any principal axis, there exist symmetrized symmetric rotator wave functions invariant under these symmetry operations. According to Mulliken[17] the symmetrized wave functions belong to one of four symmetry species, designated by A, B_x, B_y, B_z, which are associated with three rotations C_2, and the identity operation I. The relation between the symmetry species and the rotational operations is as follow:

		Symmetry operators				
		C_2^x	C_2^y	C_2^z	I	
	A	+	+	+	+	
Symmetry species	B_x	+	-	-	+	(IV-20)
	B_y	-	+	-	+	
	B_z	-	-	+	+	

where + and - designate whether the wave function is symmetric or antisymmetric under a given operation. The symmetrized wave functions ϕ^S_{Kp} of the symmetric rotator are formed by

$$\phi^s_{Kp} = \frac{1}{\sqrt{2}}\left[\phi^x_K + (-1)^p \phi^x_{-K}\right] \qquad \text{for } K=1,2,\dots,J \quad p=0 \text{ or } 1 \qquad \text{(IV-21a)}$$

$$\phi^s_{00} = \phi^x_0 \qquad \text{for } K=0 \qquad \text{(IV-21b)}$$

where $\phi^x_K = \phi^x_{JKM} = (-1)^q \phi_{JKM}$ and $q=K$ when $K>M$ or $q=M$ when $K<M$.

From (IV-13) we construct the symmetrized wave functions of the asymmetric rotator using the symmetrized wave functions of the symmetric rotator of (IV-21), and get the corresponding secular equation to (IV-15) expressed by matrix elements in the symmetrized symmetric rotator representation,

$$\psi^s_{JM} = \sum_K C^s_K \phi^s_{JKM} \qquad \text{(IV-22)}$$

$$\text{Det}\,\left| H^s_{KK'p} - E_{or}\,\delta_{KK'} \right| = 0\ . \qquad \text{(IV-23)}$$

We find easily that the matrix $[H^s_{KK'p}]$ will split into two submatrices $[H^s_{KK'0}]$ and $[H^s_{KK'1}]$. Designating $[H^s_{KK'0}]$ and $[H^s_{KK'1}]$ by $[+]$ and $[-]$ respectively according to the sign of $(-1)^p$, the matrix $[H^s_{KK'}]$ will be of the form

$$\begin{array}{c|c|c|} & \phi^s_{K'0} & \phi^s_{K'1} \\ \hline \phi^s_{K0} & \overset{[+]}{(J+1)\times(J+1)} & 0 \\ \hline \phi^s_{K1} & 0 & \overset{[-]}{J \times J} \\ \hline \end{array} \qquad \text{(IV-24)}$$

Wang[20] has shown that $[+]$ and $[-]$ can be factorized into two submatrices each, by collecting elements with even K values and with odd K values. By performing this we can transform $[H_{KK'}]$ into a four-step matrix

$$\begin{bmatrix} E^{+} & & & \\ & E^{-} & & 0 \\ & & O^{+} & \\ 0 & & & O^{-} \end{bmatrix} \qquad \text{(IV-25)}$$

where E and O indicate even K or odd K respectively, whereas + and - signs indicate p=0 or p=1. According to (IV-25), the secular equation now factors into four equations of lower orders and all eigenfunctions $\psi^{s}_{JM,p}$ associated with a given "step" belong to only one of the four symmetry species. We give the form and the ranks of E^+, E^-, O^+, O^- in Table 1, and the symmetry species of their eigenfunctions in Table 2.

Although the orders of the factored secular equations are lower, closed form solutions of the energy eigenvalues are possible only for a few small J values. In most cases the calculation of the energy eigenvalues can only be made by numerical methods except in cases of small asymmetry for which case various approximation methods are available.

Table I E^+, E^-, O^+, O^- of asymmetric rigid rotator.

$$E^+=\begin{bmatrix} H_{00} & \sqrt{2}H_{02} & 0 & 0 & \cdot \\ \sqrt{2}H_{20} & H_{22} & H_{24} & 0 & \cdot \\ 0 & H_{42} & H_{44} & H_{46} & \cdot \\ 0 & 0 & H_{64} & H_{66} & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \qquad E^-=\begin{bmatrix} H_{22} & H_{24} & 0 & 0 & \cdot \\ H_{42} & H_{44} & H_{46} & 0 & \cdot \\ 0 & H_{64} & H_{66} & H_{68} & \cdot \\ 0 & 0 & H_{86} & H_{88} & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix}$$

$$O^+=\begin{bmatrix} (H_{11}+H_{-11}) & H_{13} & 0 & \cdot \\ H_{31} & H_{33} & H_{35} & \cdot \\ 0 & H_{53} & H_{55} & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{bmatrix} \qquad O^-=\begin{bmatrix} (H_{11}-H_{-11}) & H_{13} & 0 & \cdot \\ H_{31} & H_{33} & H_{35} & \cdot \\ 0 & H_{53} & H_{55} & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{bmatrix}$$

Table II Ranks and symmetry species of E^+, E^-, O^+, O^-.

step	K	p	rank		symmetry species	
			even J	odd J	even J	odd J
E^+	even	0	$\frac{1}{2}J+1$	$\frac{1}{2}(J+1)$	A	B_z
E^-	even	1	$\frac{1}{2}J$	$\frac{1}{2}(J-1)$	B_z	A
O^+	odd	0	$\frac{1}{2}J$	$\frac{1}{2}(J+1)$	B_y	B_x
O^-	odd	1	$\frac{1}{2}J$	$\frac{1}{2}(J+1)$	B_x	B_y

According to Ray[21] the numerical evaluation of rigid asymmetric rotator energies can be simplified by introducing an asymmetry parameter κ,

$$\kappa = \frac{(2B-A-C)}{(A-C)} , \quad -1 \leq \kappa \leq +1. \tag{IV-26}$$

If $\kappa=-1$ we have the case of the prolate symmetric rotator and if $\kappa=1$ we have the oblate symmetric rotator. For $\kappa=0$ we have the "most asymmetric" rotator. Denoting H_{or} by its associated energies E(A,B,C), we find from (IV-5) that

$$\begin{aligned} E(aA+b,aB+b,aC+b) &= a(AP_x{}^2+BP_y{}^2+CP_z{}^2) + bP^2 \\ &= aE(A,B,C) + b\hbar^2 J(J+1). \end{aligned} \tag{IV-27}$$

If we substitute

$$a = \frac{2}{A-C} , \quad b = -\frac{A+C}{A-C} , \quad \kappa = aB+b \tag{IV-28}$$

and rearrange (IV-27), we have E(A,B,C) as

$$E(A,B,C) = \frac{A-C}{2}E(\kappa) + \frac{A+C}{2}J(J+1)h^2 \tag{IV-29}$$

where $E(\kappa)$ is $E(1,\kappa,-1)$.

E(A,B,C) for fixed J can have (2J+1) values, and the (2J+1) values of $E(\kappa)$ as functions of κ associated with the given J can be proved not to "intersect" when κ is varied in the interval $-1<\kappa<1$. Therefore we can designate an index $\tau(=-J, -J+1, \ldots, J)$ to identify the (2J+1) energy levels associated with given J,

$$E^J_\tau = \frac{A-C}{2}E^J_\tau(\kappa) + \frac{A+C}{2}J(J+1)\hbar^2, \tag{IV-30}$$

in such a way that

$$E^J_{-J}(\kappa) < E^J_{-J+1}(\kappa) < \dots < E^J_J(\kappa). \qquad \text{(IV-31)}$$

It can be shown that

$$E^J_{\tau}(\kappa) = -E^J_{-\tau}(\kappa). \qquad \text{(IV-32)}$$

Remembering that one can assign in the limiting cases $\kappa=+1$ and $\kappa=-1$ to every E(A,B,C) absolute values K_{-1} and K_1 (which are the limiting symmetric top quantum numbers K) we can identify the energy levels by K_{-1} and K_1, and τ will be found to be equal to $K_{-1}-K_1$. Since we can relate the symmetry species of the rotational wave function in the two limiting cases to the K quantum numbers, we can also identify the symmetry species of an energy level by its τ value in the following way:

τ		J	J-1	J-2	J-3	J-4	...
Symmetry species	even J	A	B_x	B_y	B_z	A	...
	odd J	B_z	B_y	B_x	A	B_z	...

(IV-33)

In combination with Table 2 and (IV-33), we should be able to find the eigenvalues E^J_J, E^J_{J-1}, E^J_{J-2}, ... from the step matrices E^+, O^-, O^+, E^-, E^+, ... in this order.

Eq. (IV-29) is convenient for numerical calculations of the energies of the asymmetric rotator, since we could easily calculate the energies by obtaining $E(\kappa)$. However, the evaluation of $E(\kappa)$ is by no means simple. Hainer, Cross, and King[22] give a review of the methods of obtaining $E(\kappa)$, and calculated[23] $E(\kappa)$ for $J \leq 12$ for κ from 0 to 1 by steps of .1. Their evaluation of $E(\kappa)$ was done by solving the secular equation of (IV-23) in a continued fraction form. Later workers [24] have enlarged and extended the Hainer-Cross-King eigenvalue tables. Also, there exist methods which use Mathieu functions, harmonic oscillator functions, or power series expansions in the treatments of the secular determinants. Such methods have been discussed by Hainer, Cross, and King.[22] It should also be remarked that if one considers higher order approximations, the compilation of eigenvalue tables is no longer practical nor even feasible since entirely too many parameters are involved.

Despite the discouraging aspect of the complexity of the calculation of the zero order energy eigenvalues of the asymmetric rotator, we found that one could proceed to the consideration of higher order terms without producing an undue amount of additional complexity. In fact, as we shall show, some closed form solutions of the energies including the centrifugal distortion effects and vibration-rotation interactions can be given up to the fourth order of approximation.

Presently obtainable resolution in the infrared and microwave spectra of molecules requires that these higher order approximations be considered if a satisfactory interpretation of the spectra is to be obtained. We will undertake the consideration of higher order terms in the following chapters. Since the general symmetry properties of the Hamiltonian are important for the further development, we shall discuss these in the next chapter.

V. GENERAL SYMMETRY CONSIDERATIONS

The terms of the general Hamiltonian may either remain unchanged or change sign under any of the relevant symmetry operations which are coordinate transformations (reflections or rotations) which will produce an equilibrium configuration of the nuclei that is indistinguishable from the original one. Recognizing the axial vector nature of the angular momentum components and that the vibrational operators q_s and p_s must be symmetric or antisymmetric under the point group operations, it is found that for asymmetric molecule all terms of the Hamiltonian are either symmetric or antisymmetric under any symmetry operation. Of course, for higher symmetries more complicated situations arise; it is true only for the asymmetric rotator point groups that all irreducible representations of these groups are one-dimensional irreducible representations.

The Hamiltonian of a vibrating rotator must be invariant under all symmetry operations of the point group to which the rotator belongs. Hence all terms of the Hamiltonian which are antisymmetric under one or more symmetry operations of the relevant point group must be absent from the Hamiltonian for that group. All asymmetric molecules must belong to one of eight point groups. These eight point groups are contained within the set of thirty-two possible crystallographic point groups, and hence asymmetric rotator point groups can be referred to in the crystallographic language, if one so desires. These asymmetric rotator point groups and their nomenclature are summarized in Table III, where we give the symmetry operations for the various point groups in customary notation. The orthorhombic point groups have the highest symmetry, and hence one could foresee that the vibration-rotation Hamiltonian will have its simplest form for these point groups. The monoclinic point groups have lower symmetry than the orthorhombic point groups, but higher symmetry than the triclinic point groups. As one would expect we will see that the order of symmetry is closely related to the degree of complexity of the Hamiltonian. Therefore it is reasonable to discuss the vibration-rotation Hamiltonian for each point group separately and we will do this in the following chapters.

In the asymmetric molecule every vibrational mode is non-degenerate. For a given non-degenerate normal vibration a symmetry operation can at most bring about a simultaneous change of sign of all displacement coordinates belonging to a given non-degenerate vibration. Therefore a given symmetry operation will change the sign of all the normal coordinates or it will leave them all unchanged. Since a non-degenerate vibration can only be symmetric or antisymmetric with respect to any symmetry

Table III Asymmetric rotator point groups.

Crystallographic nomenclature	Group symbol	Group operations other than identity operation
Triclinic	C_1	none
	$C_i=S_2$	i
Monoclinic	$C_s=C_{1h}$	σ, Case(a) $\sigma(xy)$
		Case(b) $\sigma(yz)$
		Case(c) $\sigma(zx)$
	C_2	C_2, Case(a) $C_2(z)$
		Case(b) $C_2(x)$
		Case(c) $C_2(y)$
	C_{2h}	C_2,σ_h,i Case(a) $C_2(z),\sigma(xy)$
		Case(b) $C_2(x),\sigma(yz)$
		Case(c) $C_2(y),\sigma(zx)$
Orthorhombic	C_{2v}	C_2, two σ_v
	$V=D_2$	three mutually ⊥ C_2
	$V_h=D_{2h}$	three mutually ⊥ C_2, i,
		three mutually ⊥ σ

operation which is permitted by the symmetry of the molecule, our statement about the symmetry of the vibrational operators in the first paragraph of this chapter is valid. Now, from (III-20) we see that all vibrational operators are present in our Hamiltonian as even powers only. Since the vibrational operators q_s and p_s are either symmetric or antisymmetric under any symmetry operation for the asymmetric molecule, the vibrational portion of any operator term will always transform into itself. This means that all terms of our Hamiltonian will be symmetric or antisymmetric depending only upon the symmetry property of the rotational portion of the operators.

To find the symmetry properties of the rotational operators we have to consider the behavior of each component of the angular momentum under the possible symmetry operations for the asymmetric molecule. The symmetry properties of the coordinates and the angular momentum components are given in Table IV, where + sign stands for "symmetric" and - sign stands for "antisymmetric" behavior. Thus we can determine the symmetry property of any rotational operator by using Table IV. For example, the operator $P_xP_yP_xP_z$ is antisymmetric under the symmetry operation $\sigma(xy)$, but is symmetric under the symmetry operation $C_2(x)$. It is interesting to notice the symmetry operators $\sigma(xy)$, $\sigma(xz)$, and $\sigma(yz)$

behave equivalently to $C_2(z)$, $C_2(y)$, and $C_2(x)$, respectively for the angular momentum components.

The time-reversal symmetry has not been considered in this study, since we do not expect it to produce further simplification in our problem.

Table IV Symmetry properties of the coordinates and angular momentum components.

Symmetry operation	Coordinates			Angular momentum components		
	x	y	z	P_x	P_y	P_z
I	+	+	+	+	+	+
i	-	-	-	+	+	+
$\sigma(xy)$	+	+	-	-	-	+
$\sigma(xz)$	+	-	+	-	+	-
$\sigma(yz)$	-	+	+	+	-	-
$C_2(z)$	-	-	+	-	-	+
$C_2(x)$	+	-	-	+	-	-
$C_2(y)$	-	+	-	-	+	-

VI. ASYMMETRIC ROTATOR HAMILTONIAN TO THE FOURTH ORDER OF APPROXIMATION

The Hamiltonian appropriate for a vibrating-rotating asymmetric molecule was given to the fourth order of approximation by (III-21) in an abbreviation form. In greater detail (III-21) may be written as

$$H^{+} = (h_{v}{}^{+*}+h_{o}{}^{+}) + h_{2}{}^{+*} + h_{4}{}^{+*}, \qquad \text{(VI-1)}$$

with

$$h_{2}{}^{+*} = \sum_{\alpha\beta}\sum_{a}\left({}^{\alpha\beta}_{(2)}Y^{aa}p_{a}{}^{2} + {}^{\alpha\beta}_{(2)}Y_{aa}q_{a}{}^{2}\right)P_{\alpha}P_{\beta}$$

$$+\sum_{\alpha\beta\gamma\delta}{}^{\alpha\beta\gamma\delta}_{(2)}YP_{\alpha}P_{\beta}P_{\gamma}P_{\delta} \qquad \text{(VI-2)}$$

$$h_{4}{}^{+*} = \sum_{\alpha\beta}{}^{\alpha\beta}_{(4)}ZP_{\alpha}P_{\beta} + \sum_{\alpha\beta}\sum_{a,b}{}^{\alpha\beta}_{(4)}Z^{bb}_{aa}q_{a}{}^{2}p_{b}{}^{2}P_{\alpha}P_{\beta}$$

$$+\sum_{\alpha\beta}\sum_{a,b;a\leq b}\left({}^{\alpha\beta}_{(4)}Z_{aabb}q_{a}{}^{2}q_{b}{}^{2} + {}^{\alpha\beta}_{(4)}Z^{aabb}p_{a}{}^{2}p_{b}{}^{2}\right)P_{\alpha}P_{\beta}$$

$$+\sum_{\alpha\beta\gamma\delta}\sum_{a}\left({}^{\alpha\beta\gamma\delta}_{(4)}Z_{aa}q_{a}{}^{2} + {}^{\alpha\beta\gamma\delta}_{(4)}Z^{aa}p_{a}{}^{2}\right)P_{\alpha}P_{\beta}P_{\gamma}P_{\delta}$$

$$+\sum_{\alpha\beta\gamma\delta\epsilon\zeta}{}^{\alpha\beta\gamma\delta\epsilon\zeta}_{(4)}ZP_{\alpha}P_{\beta}P_{\gamma}P_{\delta}P_{\epsilon}P_{\zeta}\,. \qquad \text{(VI-3)}$$

As mentioned at the end of Chapter III the pure vibrational energy E_{v} from $h_{v}{}^{+*}$ is not of immediate interest in this study. The zero order rotational Hamiltonian $h_{o}{}^{+}(=H_{or})$ was discussed in Chapter IV. Therefore we will focus our discussion in this chapter on $h_{2}{}^{+*}$ and $h_{4}{}^{+*}$.

The second term of h_{2}^{+*} which is the second order

centrifugal distortion term, and the last term of h_4^{+*} which is the fourth order centrifugal distortion term, are important for the analysis of the rotational structure. In most molecules the fourth order centrifugal distortion term is very small except at very high J values. But in some rare cases, notably for H_2O, the effect of this fourth order centrifugal distortion terms is prominent for the lower J values too. This feature was shown by Benedict,[25] and by Parker and Brown.[26] Since in most cases these terms give unobservably small contributions, and since we want to discuss these terms in Chapter VIII, we will exclude these fourth order centrifugal terms in this chapter.

The second order centrifugal distortion terms can be written as

$$\frac{1}{4}\sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} P_\alpha P_\beta P_\gamma P_\delta \qquad \text{(VI-4)}$$

where thesecond order centrifugal distortion coefficients $\tau_{\alpha\beta\gamma\delta}$ are

$$\frac{1}{4}\tau_{\alpha\beta\gamma\delta} = {}^{\alpha\beta\gamma\delta}_{(2)}Y \ , \qquad \text{(VI-5)}$$

and where the factor $\frac{1}{4}$ is introduced in the definition (VI-5) to bring the $\tau_{\alpha\beta\gamma\delta}$ into agreement with the conventional definition of the second order centrifugal distortion constants. The coefficients $\tau_{\alpha\beta\gamma\delta}$ are proportional to

$$\sum_s \frac{a_s^{\alpha\beta}\; a_s^{\gamma\delta}}{I^o_{\alpha\alpha}\, I^o_{\beta\beta}\, I^o_{\gamma\gamma}\, I^o_{\delta\delta}} \qquad \text{(VI-6)}$$

where the molecular constants $a_s^{\alpha\beta}$ were defined by (II-31). We shall use for $\tau_{\alpha\beta\gamma\delta}$ the alternative notation $(\alpha\beta\gamma\delta)$ where convenient. Because of the non-commutativity of the angular momentum components P_α, (VI-4) shows that there could be a total of eighty-one $(\alpha\beta\gamma\delta)$. Because of (VI-6) many of these are equal to each other, and one has in fact that

$$\begin{aligned}(\alpha\beta\gamma\delta)&=(\gamma\delta\alpha\beta)=(\beta\alpha\gamma\delta)=(\alpha\beta\delta\gamma)\\ &=(\beta\alpha\delta\gamma)=(\delta\gamma\alpha\beta)=(\gamma\delta\beta\alpha)=(\delta\gamma\beta\alpha).\end{aligned} \qquad \text{(VI-7)}$$

Application of this condition to (VI-4) shows that many of the summation terms have common coefficients, and one arrives, as is well known, at twenty-one distinct $(\alpha\beta\gamma\delta)$. These are summarized in Table V and are further classified into four sets.

Symmetry properties of the operators associated with these coefficients are given in Table VI. It will be noticed that we have grouped the $(\alpha\beta\gamma\delta)$ on the basis of their symmetry behavior. A further advantage of this classification appears if one considers the position of the matrix elements of the second order centrifugal distortion terms in the total Hamiltonian matrix. In the symmetric rotator P^2, P_z diagonal representation, which was employed for the zero order problem in Chapter IV, the angular momentum operators whose $(\alpha\beta\gamma\delta)$ belong

Table V Tabulation of distinct second order centrifugal distortion constants. $\tau_n = 1, 2, 3, \ldots, 21$.

n	$(\alpha\beta\gamma\delta)$	Set
1	(xxxx)	I_1
2	(yyyy)	
3	(zzzz)	
4	(yyzz)=(zzyy)	
5	(zzxx)=(xxzz)	
6	(xxyy)=(yyxx)	
7	(yzyz)=(zyzy)=(yzzy)=(zyyz)	
8	(zxzx)=(xzxz)=(zxxz)=(xzzx)	
9	(xyxy)=(yxyx)=(xyyx)=(yxxy)	
10	(xxxy)=(xxyx)=(xyxx)=(yxxx)	I_2
11	(yyyx)=(yyxy)=(yxyy)=(xyyy)	
12	(xyzz)=(yxzz)=(zzxy)=(zzyx)	
13	(xzzy)=(yzzx)=(zxyz)=(zyxz) =(zxzy)=(zyzx)=(xzyz)=(yzxz)	
14	(yyyz)=(yyzy)=(yzyy)=(zyyy)	II_1
15	(zzzy)=(zzyz)=(zyzz)=(yzzz)	
16	(yzxx)=(zyxx)=(xxyz)=(xxzy)	
17	(yxxz)=(zxxy)=(xyzx)=(xzyx) =(xyxz)=(xzxy)=(yxzx)=(zxyx)	
18	(xxxz)=(xxzx)=(xzxx)=(zxxx)	II_2
19	(zzzx)=(zzxz)=(zxzz)=(xzzz)	
20	(zxyy)=(xzyy)=(yyzx)=(yyxz)	
21	(zyyx)=(xyyz)=(yzxy)=(yxzy) =(yzyx)=(yxyz)=(zyxy)=(xyzy)	

Table VI Symmetry properties of $P_{\alpha} P_{\beta} P_{\gamma} P_{\delta}$
associated with n.

Operator	I	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	$C_2(z)$	$C_2(x)$	$C_2(y)$
n = 1	+	+	+	+	+	+	+	+
2	+	+	+	+	+	+	+	+
3	+	+	+	+	+	+	+	+
4	+	+	+	+	+	+	+	+
5	+	+	+	+	+	+	+	+
6	+	+	+	+	+	+	+	+
7	+	+	+	+	+	+	+	+
8	+	+	+	+	+	+	+	+
9	+	+	+	+	+	+	+	+
10	+	+	+	-	-	+	-	-
11	+	+	+	-	-	+	-	-
12	+	+	+	-	-	+	-	-
13	+	+	+	-	-	+	-	-
14	+	+	-	-	+	-	+	-
15	+	+	-	-	+	-	+	-
16	+	+	-	-	+	-	+	-
17	+	+	-	-	+	-	+	-
18	+	+	-	+	-	-	-	+
19	+	+	-	+	-	-	-	+
20	+	+	-	+	-	-	-	+
21	+	+	-	+	-	-	-	+

to sets I_1 or I_2 may have nonvanishing matrix elements of types $(K|K)$, $(K|K\pm2)$, $(K|K\pm4)$ only, whereas sets II_1 or II_2 operators may have nonvanishing matrix elements of types $(K|K\pm1)$, $(K|K\pm3)$ only. Also, sets I_1 and II_2 matrix elements are real whereas sets I_2 and II_1 matrix elements are pure imaginary. If we write the matrix elements of (VI-4) in the symmetrized symmetric rotator representation (which was discussed previously for the zero order problem) we obtain a matrix which is Hermitian and, in addition, symmetric about the "nonprincipal" diagonal. After performing the Wang transformation, matrix elements of the four sets of terms will stand in the following positions in the transformed matrix for given J:

I_1	I_2	II_2	II_1
I_2	I_1	II_1	II_2
II_2	II_1	I_1	I_2
II_1	II_2	I_2	I_1

(VI-8)

If we add the transformed matrix of h_0^+ of (IV-25), we have the matrix representation of the Hamiltonian of the asymmetric rotator to the second order. To the four submatrices in the diagonal positions of (VI-8) will now be added E^+, E^-, O^+, O^-, respectively, of the Wang transformed matrix of the zero order Hamiltonian. In other words, the matrix of the second order Hamiltonian would be of the form (VI-9), where E^+, E^-, O^+, O^- now stands for the sum of E^+, E^-, O^+, O^- of the rigid rotator Hamiltonian, and the corresponding I_1's of (VI-8):

$$\begin{array}{|c|c|c|c|}\hline E^+ & I_2 & II_2 & II_1 \\ \hline I_2 & E^- & II_1 & II_2 \\ \hline II_2 & II_1 & O^+ & I_2 \\ \hline II_1 & II_2 & I_2 & O^- \\ \hline \end{array} \qquad (VI\text{-}9)$$

.

If we consider a properly partitioned four step matrix T which transforms (VI-9) to a basis in which only the blocks on the diagonal of (VI-9) are completely diagonal, we find that none of the I_2 or II elements will fall within the diagonal blocks because of the transformation. Thus only τ_1 through τ_9 (set I_1) are true second order constants, whereas τ_{10} through τ_{21} will contribute only to the fourth order of approximation of the energies. This argument is very important, since we shall use it to good advantage for the fourth order terms.

Because of the invariance requirement of the

Hamiltonian, if any P^4-type term of (VI-4) changes sign under one or more operations of a given point group, the corresponding $(\alpha\beta\gamma\delta)$ must be zero for that point group. Using the symmetry properties of the angular momentum components of Table IV, one finds that twenty-one distinct $(\alpha\beta\gamma\delta)$ will in general be nonvanishing for the triclinic point groups, whereas only thirteen distinct $(\alpha\beta\gamma\delta)$ will be nonvanishing for the monoclinic point groups, and only nine distinct $(\alpha\beta\gamma\delta)$ will be nonvanishing for the orthorhombic point groups. Thus Kivelson and Wilson's [27] second order centrifugal distortion treatment of (VI-4) will be applicable to second order to any asymmetric top molecule except the planar molecules, where we have linear dependences between nonvanishing $(\alpha\beta\gamma\delta)$. The planar asymmetric top molecule will be discussed later.

The remainder of h_2^{+*} and h_4^{+*} comprise vibration-rotation interaction terms and additional corrections due to the rotational motion of the molecule. These terms are not, in general, negligible and will be considered now.

The set I_1 of $(\alpha\beta\gamma\delta)$ was nonvanishing for all asymmetric point groups, whereas the sets I_2, II_1, II_2 vanished completely for the orthorhombic point groups and one of them was nonvanishing for the monoclinic point groups. The distinction between I_2, II_1, II_2

elements is not very significant and depends on the choice of which particular component P_α is taken diagonal, or also on the particular way in which the principal axes system is attached to the molecular equilibrium configuration. The three situation which can arise are shown in Table III as cases (a), (b), and (c). The contributions of I_1, I_2, II_1 and II_2 of the P^4-type terms to the energy and their direct correlation with the point groups give very useful hints for the development of the general fourth order Hamiltonian of (VI-1).

We rearrange (VI-1) into the form

$$H^+ = H^{+\prime} + h_a^+ + h_b^+ + h_c^+ \ , \qquad \text{(VI-10)}$$

where $H^{+\prime}$ includes all terms which are symmetric under the symmetry operations for the orthorhombic point groups C_{2v}, $V=D_2$ and $V_h=D_{2h}$, and $(h_a^+ + h_b^+ + h_c^+)$ represents the remainder of H^+, which is antisymmetric under the symmetry operations of the orthorhombic point groups. Thus $H^{+\prime}$ is the Hamiltonian to the fourth order of approximation of a molecule which belongs to the orthorhombic point groups. For monoclinic point groups, $C_s=C_{1h}$, C_2, and C_{2h}, additional terms beyond $H^{+\prime}$ appear in the Hamiltonian because of the lower symmetry. Which extra terms have to be added to $H^{+\prime}$ depends on the manner in which the body-fixe principal axes system is attached to the molecule, and one can distinguish three cases as in the case of $(\alpha\beta\gamma\delta)$ in the way pointed out in Table III. In eq. (VI-10) we denoted the additional terms for the case (a) of monoclinic point groups by h_a^+, the additional terms for the case (b) of monoclinic point groups by h_b^+ and the additional terms for the case (c) by h_c^+.

In the symmetrized basis, the entire orthorhombic Hamiltonian $H^{+'}$ will have nonvanishing matrix elements only within the four Wang blocks E^+, E^-, O^+, O^- and all additional terms allowed by the lower symmetries have non-zero matrix elements located only outside the diagonal blocks E^+, E^-, O^+, O^-. This is ascertained either by computing the matrix elements involved directly, or by examining the even-or-odd character of the matrix element integrands under the symmetry operations of the rotational inertia ellipsoid, $C_2(x)$, $C_2(y)$, $C_2(z)$, using the symmetrized basis wave functions. In this manner the following arrangement of non-zero matrix elements in the Wang matrix is found:

$$\left\{\begin{array}{cccc}
\begin{array}{c}E^+\\ \text{Orthorhombic}\end{array} & \begin{array}{c}\text{Monoclinic}\\ \text{case(a)}\end{array} & \begin{array}{c}\text{Monoclinic}\\ \text{case(c)}\end{array} & \begin{array}{c}\text{Monoclinic}\\ \text{case(b)}\end{array} \\
\begin{array}{c}\text{Monoclinic}\\ \text{case(a)}\end{array} & \begin{array}{c}E^-\\ \text{Orthorhombic}\end{array} & \begin{array}{c}\text{Monoclinic}\\ \text{case(b)}\end{array} & \begin{array}{c}\text{Monoclinic}\\ \text{case(c)}\end{array} \\
\begin{array}{c}\text{Monoclinic}\\ \text{case(c)}\end{array} & \begin{array}{c}\text{Monoclinic}\\ \text{case(b)}\end{array} & \begin{array}{c}O^+\\ \text{Orthorhombic}\end{array} & \begin{array}{c}\text{Monoclinic}\\ \text{case(a)}\end{array} \\
\begin{array}{c}\text{Monoclinic}\\ \text{case(b)}\end{array} & \begin{array}{c}\text{Monoclinic}\\ \text{case(c)}\end{array} & \begin{array}{c}\text{Monoclinic}\\ \text{case(a)}\end{array} & \begin{array}{c}O^-\\ \text{Orthorhombic}\end{array}
\end{array}\right\}$$

Now, as in the case of the P^4-type terms, if we consider a properly partitioned four-step matrix T which transforms the Hamiltonian to a basis in which only the Wang blocks E^+, E^-, O^+, and O^- are diagonal, then we find that none of the matrix elements located outside the Wang blocks will fall within the Wang blocks because of the transformation. This means that monoclinic matrix elements of h_2^{+*} will contribute to the fourth order of approximation, whereas elements of h_4^{+*} will contribute only to the eighth order. Therefore, to the fourth order we need consider only the monoclinic matrix elements of h_2^{+*}, but not those of h_4^{+*}. From eq.(VI-2) the terms of h_2^{+*} to be considered are $_{(2)}ZP^4$ and $_{(2)}Zr^2P^2$. The additional contributions of $_{(2)}Zr^2P^2$ will be combined with those of the P^4-type terms. As a result one obtains the additional terms for the monoclinic point groups to the fourth order of approximation, and we will give these simplified h_a^+, h_b^+, and h_c^+ later.

Performing the symmetry operations of the orthorhombic point groups upon (VI-1) but without the last term of h_4^{+*}, we get $H^{+'}$ as

$$H^{+'} = (h_v^{+*}+h_o^{+}) + h_2^{+*'} + h_4^{+*'}, \qquad \text{(VI-11)}$$

with

$$h_2^{+*'} = \sum_{\alpha}\sum_{a}\left({}^{\alpha\alpha}_{(2)}Y^{aa}p_a^{\,2} + {}^{\alpha\alpha}_{(2)}Y_{aa}q_a^{\,2}\right)P_{\alpha}^{\,2}$$

$$+ \sum_{\alpha\beta\gamma\delta}{}' \left({}^{\alpha\beta\gamma\delta}_{(2)}Y P_{\alpha}P_{\beta}P_{\gamma}P_{\delta}\right) \qquad \text{(VI-12)}$$

$$h_4^{+*'} = \sum_{\alpha}\left({}^{\alpha\alpha}_{(4)}Z P_{\alpha}^{\,2}\right)$$

$$+ \sum_{\alpha}\sum_{a,b}{}' \, {}^{\alpha\alpha}_{(4)}Z^{bb}_{aa}q_a^{\,2}q_b^{\,2}P_{\alpha}^{\,2}$$

$$+ \sum_{a,b;\,a\leq b}\left({}^{\alpha\alpha}_{(4)}Z_{aabb}q_a^{\,2}q_b^{\,2} + {}^{\alpha\alpha}_{(4)}Z^{aabb}p_a^{\,2}p_b^{\,2}\right) P_{\alpha}^2$$

$$+ \sum_{\alpha\beta\gamma\delta}{}'\sum_{a}\left({}^{\alpha\beta\gamma\delta}_{(4)}Z_{aa}q_a^{\,2} + {}^{\alpha\beta\gamma\delta}_{(4)}Z^{aa}p_a^{\,2}\right)P_{\alpha}P_{\beta}P_{\gamma}P_{\delta}\,, \qquad \text{(VI-13)}$$

where $\sum'$ means the summation over only those $P_{\alpha}P_{\beta}P_{\gamma}P_{\delta}$ which are symmetric under the symmetry operations.

With the aid of the vibrational matrix elements (IV-2) and the following additional vibrational matrix elements

$$(v_a,v_b|q_a^{\,2}p_b^{\,2}|v_a,v_b) = \hbar^2(v_a+\tfrac{1}{2})(v_b+\tfrac{1}{2})$$

$$(v_a,v_b|q_a^{\,2}q_b^{\,2}|v_a,v_b) = (v_a+\tfrac{1}{2})(v_b+\tfrac{1}{2}) \qquad \text{(VI-14)}$$

$$(v_a,v_b|p_a^{\,2}p_b^{\,2}|v_a,v_b) = \hbar^4(v_a+\tfrac{1}{2})(v_b+\tfrac{1}{2})$$

the vibration-rotation Hamiltonian $H^{+'}$ for the asymmetric molecules belonging to the orthorhombic point groups is

$$H^{+'} = h_v^{+*} + (A+A'+A''+A''')P_x^{\,2} + (B+B'+B''+B''')P_y^{\,2}$$

$$+(C+C'+C''+C''')P_z^{\,2} + \tfrac{1}{4}\sum_{\alpha\beta\gamma\delta}{}'\left(\tau_{\alpha\beta\gamma\delta} + \tau'_{\alpha\beta\gamma\delta}\right)P_{\alpha}P_{\beta}P_{\gamma}P_{\delta}\,. \qquad \text{(VI-15)}$$

In (VI-15) we have that

$$A' = \sum_{a}\left(\hbar^2\,{}^{xx}_{(2)}Y^{aa} + {}^{xx}_{(2)}Y_{aa}\right)(v_a+\tfrac{1}{2}) \equiv \sum_{a}\left({}_{(2)}\alpha'_a\right)(v_a+\tfrac{1}{2})$$

$$B' = \sum_{a}(\hbar^{2}\,{}^{yy}_{(2)}Y^{aa} + {}^{yy}_{(2)}Y_{aa})(v_a+\tfrac{1}{2}) \equiv \sum_{a}({}_{(2)}\beta_a{}')(v_a+\tfrac{1}{2})$$

$$C' = \sum_{a}(\hbar^{2}\,{}^{zz}_{(2)}Y^{aa} + {}^{zz}_{(2)}Y_{aa})(v_a+\tfrac{1}{2}) \equiv \sum_{a}({}_{(2)}\gamma_a{}')(v_a+\tfrac{1}{2}), \qquad \text{(VI-16)}$$

and that

$$A'' = {}^{xx}_{(4)}Z \equiv {}_{(4)}\alpha''$$

$$B'' = {}^{yy}_{(4)}Z \equiv {}_{(4)}\beta'' \qquad \text{(VI-17)}$$

$$C'' = {}^{zz}_{(4)}Z \equiv {}_{(4)}\gamma'' ,$$

$$A''' = \sum_{a,b} \hbar^{2}\,{}^{xx}_{(4)}Z^{bb}_{aa}(v_a+\tfrac{1}{2})(v_b+\tfrac{1}{2})$$

$$+ \sum_{a,b;a\leq b} ({}^{xx}_{(4)}Z_{aabb} + \hbar^{4}\,{}^{xx}_{(4)}Z^{aabb})(v_a+\tfrac{1}{2})(v_b+\tfrac{1}{2})$$

$$= \sum_{a,b}({}_{(4)}\alpha'''_{ab})(v_a+\tfrac{1}{2})(v_b+\tfrac{1}{2})$$

$$B''' = \sum_{a,b} \hbar^{2}\,{}^{yy}_{(4)}Z^{bb}_{aa}(v_a+\tfrac{1}{2})(v_b+\tfrac{1}{2})$$

$$+ \sum_{a,b;a\leq b} ({}^{yy}_{(4)}Z_{aabb} + \hbar^{4}\,{}^{yy}Z^{aabb})(v_a+\tfrac{1}{2})(v_b+\tfrac{1}{2})$$

$$\equiv \sum_{a,b}({}_{(4)}3'''_{ab})(v_a+\tfrac{1}{2})(v_b+\tfrac{1}{2})$$

$$C''' = \sum_{a,b} \hbar^{2}\,{}^{zz}_{(4)}Z^{bb}_{aa}(v_a+\tfrac{1}{2})(v_b+\tfrac{1}{2})$$

$$+ \sum_{a,b;a\ b} ({}^{zz}_{(4)}Z_{aabb} + \hbar^{4}\,{}^{zz}_{(4)}Z^{aabb})(v_a+\tfrac{1}{2})(v_b+\tfrac{1}{2})$$

$$\equiv \sum_{a,b}({}_{(4)}\gamma'''_{ab})(v_a+\tfrac{1}{2})(v_b+\tfrac{1}{2}) . \qquad \text{(VI-18)}$$

Thus the effective rotational constants $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{C}$ are to fourth order

$$\mathcal{A} = A+A'+A''+A'''$$

$$= A+\sum_a({}_{(2)}\alpha'_a)(v_a+\tfrac{1}{2})+{}_{(4)}\alpha''+\sum_{a,b}({}_{(4)}\alpha'''_{ab})(v_a+\tfrac{1}{2})(v_b+\tfrac{1}{2})$$

$$\mathcal{B} = B+B'+B''+B'''$$

$$= B+\sum_a({}_{(2)}\beta'_a)(v_a+\tfrac{1}{2})+{}_{(4)}\beta''+\sum_{a,b}({}_{(4)}\beta'''_{ab})(v_a+\tfrac{1}{2})(v_b+\tfrac{1}{2})$$

$$\mathcal{C} = C+C'+C''+C'''$$

$$= C+\sum_a({}_{(2)}\gamma'_a)(v_a+\tfrac{1}{2})+{}_{(4)}\gamma''+\sum_{a,b}({}_{(4)}\gamma'''_{ab})(v_a+\tfrac{1}{2})(v_b+\tfrac{1}{2}). \tag{VI-19}$$

The various coefficients α, β, and γ introduced here are related to the coefficients Y and Z of references 5 and 6 through (VI-16), (VI-17), and (VI-18), and depend on the molecular constans in a complicated manner. Also in (VI-15) we have that

$$\tfrac{1}{4}\,\tau'_{\alpha\beta\gamma\delta} = \sum_a({}^{\alpha\beta\gamma\delta}_{(4)}Z_{aa}+\hbar^2\,{}^{\alpha\beta\gamma\delta}_{(4)}Z^{aa})(v_a+\tfrac{1}{2})$$

$$\equiv \sum_a({}^{\alpha\beta\gamma\delta}_{(4)}r_a)(v_a+\tfrac{1}{2}) \equiv \tfrac{1}{4}\,\rho_{\alpha\beta\gamma\delta}\,. \tag{VI-20}$$

We have examined $\tau_{\alpha\beta\gamma\delta}$ of (VI-15) in the first part of this chapter, and the detailed expression for $\rho_{\alpha\beta\gamma\delta}$ reveals that $\rho_{\alpha\beta\gamma\delta} = \rho_{\delta\gamma\beta\alpha}$. We have reindexed $\rho_{\alpha\beta\gamma\delta}$ in Table VII. With the aid of Tables V and VII we can write the Hamiltonian for the orthorhombic point groups to fourth order of approximation,

$$\begin{aligned} H^{+'} = {}& h_v^{+*} + \mathcal{A}P_x^2 + \mathcal{B}P_y^2 + \mathcal{C}P_z^2 \\ & +\tfrac{1}{4}(\tau_1+\rho_1)P_x^4+\tfrac{1}{4}(\tau_2+\rho_2)P_y^4+(\tau_3+\rho_3)P_z^4 \\ & +\tfrac{1}{4}(\tau_4+\rho_4)(P_y^2P_z^2+P_z^2P_y^2)+\tfrac{1}{4}(\tau_5+\rho_5)(P_z^2P_x^2+P_x^2P_z^2) \end{aligned}$$

Table VII Nonvanishing $\rho_{\alpha\beta\gamma\delta}$.

$(\alpha\beta\gamma\delta)$	$\rho_n = \rho_{\alpha\beta\gamma\delta}$
(xxxx)	ρ_1
(yyyy)	ρ_2
(zzzz)	ρ_3
(yyzz), (zzyy)	ρ_4
(zzxx), (xxzz)	ρ_5
(xxyy), (yyxx)	ρ_6
(yzyz), (zyzy)	ρ_7
(xzxz), (zxzx)	ρ_8
(xyxy), (yxyx)	ρ_9
(zyyz)	ρ_{10}
(yzzy)	ρ_{11}
(zxxz)	ρ_{12}
(xzzx)	ρ_{13}
(xyyx)	ρ_{14}
(yxxy)	ρ_{15}

$$+\tfrac{1}{4}(\tau_6+\rho_6)(P_x^2P_y^2+P_y^2P_x^2)$$

$$+\tfrac{1}{4}\tau_7(P_yP_z+P_zP_y)^2+\tfrac{1}{4}\tau_8(P_zP_x+P_xP_z)^2+\tfrac{1}{4}\tau_9(P_xP_y+P_yP_x)^2$$

$$+\tfrac{1}{4}\rho_7(P_yP_zP_yP_z+P_zP_yP_zP_y)+\tfrac{1}{4}\rho_8(P_zP_xP_zP_x+P_xP_zP_xP_z)$$

$$+\tfrac{1}{4}\rho_9(P_xP_yP_xP_y+P_yP_xP_yP_x)$$

$$+\tfrac{1}{4}\rho_{10}(P_zP_y^2P_z)+\tfrac{1}{4}\rho_{11}(P_yP_z^2P_y)+\tfrac{1}{4}\rho_{12}(P_zP_x^2P_z)$$

$$+\tfrac{1}{4}\rho_{13}(P_xP_z^2P_x)+\tfrac{1}{4}\rho_{14}(P_xP_y^2P_x)+\tfrac{1}{4}\rho_{15}(P_yP_x^2P_y). \quad \text{(VI-21)}$$

From the angular momentum commutation relations Kivelson and Wilson[27] have established that

$$(P_\alpha P_\beta+P_\beta P_\alpha)^2=2(P_\alpha^2P_\beta^2+P_\beta^2P_\alpha^2)+\hbar^2(3P_\gamma^2-2P_\alpha^2-2P_\beta^2),$$
$$(\alpha\neq\beta\neq\gamma, \text{ and cyclic}). \quad \text{(VI-22)}$$

With the aid of these identities, (VI-21) can be simplified somewhat to:

$$H^{+\prime} = h_v^{+*} + \mathcal{A}P_x^2+\mathcal{B}P_y^2+\mathcal{C}P_z^2$$

$$+\tfrac{1}{4}(\tau_1+\rho_1)P_x^2+\tfrac{1}{4}(\tau_2+\rho_2)P_y^2+\tfrac{1}{4}(\tau_3+\rho_3)P_z^2$$

$$+\tfrac{1}{4}(\tau_4+2\tau_7+\rho_4)(P_y^2P_z^2+P_z^2P_y^2)$$

$$+\tfrac{1}{4}(\tau_5+2\tau_8+\rho_5)(P_z^2P_x^2+P_x^2P_z^2)$$

$$+\tfrac{1}{4}(\tau_6+2\tau_9+\rho_6)(P_x^2P_y^2+P_y^2P_x^2)$$

$$+\tfrac{1}{4}\rho_7(P_yP_zP_yP_z+P_zP_yP_zP_y)+\tfrac{1}{4}\rho_8(P_xP_zP_xP_z+P_zP_xP_zP_x)$$

$$+\tfrac{1}{4}\rho_9(P_xP_yP_xP_y+P_yP_xP_yP_x)$$

$$+\tfrac{1}{4}\rho_{10}(P_zP_y^2P_z)+\tfrac{1}{4}\rho_{11}(P_yP_z^2P_y)+\tfrac{1}{4}\rho_{12}(P_zP_x^2P_z)$$

$$+\tfrac{1}{4}\rho_{13}(P_xP_z^2P_x)+\tfrac{1}{4}\rho_{14}(P_xP_y^2P_x)+\tfrac{1}{4}\rho_{15}(P_yP_x^2P_y). \qquad \text{(VI-23)}$$

The relation (VI-22) has the effect of combining the coefficients τ_7, τ_8, and τ_9 of $(P_\alpha P_\beta+P_\beta P_\alpha)^2$ with τ_4, τ_5, and τ_6 of $(P_\alpha{}^2P_\beta{}^2+P_\beta{}^2P_\alpha{}^2)$. The grouping of τ_4 through τ_9 occurs as $(\tau_4+2\tau_7)$, $(\tau_5+2\tau_8)$ and $(\tau_6+2\tau_9)$. Thus, in general case only these combinations (in addition to τ_1, τ_2, and τ_3) can be obtained by fitting experimental frequencies. Hence for these cases only six independent distortion coefficients can be found and τ_4, τ_5, τ_6 cannot be separated from τ_7, τ_8, τ_9, unless enough additional information is available to compute some of the τ's involved directly from their definition. Also, the expressions for $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{C}$ acquire the additional terms $\tfrac{1}{4}\hbar^2(3\tau_9-2\tau_7-2\tau_8)$, $\tfrac{1}{4}\hbar^2(3\tau_8-2\tau_9-2\tau_7)$, and $\tfrac{1}{4}\hbar^2(3\tau_7-2\tau_8-2\tau_9)$ respectively, as a consequence of the application of (VI-22)

The nonvanishing matrix elements of the Hamiltonian (VI-23) in the symmetric rotator representation are given in Appendix I. For a particular choice of J, the diagonal blocks E^+, E^-, O^+, O^- can be constructed easily from these matrix elements of Appendix I. In Appendix II we give those eigenvalues of (VI-23) which can be established in closed form.

The additional contribution to the Hamiltonian for the monoclinic point groups will be:

Case (a).

$$h_a^+ = \tfrac{1}{4}\tau_{10}(P_x^3P_y+P_x^2P_yP_x+P_xP_yP_x^2+P_yP_x^3)$$
$$+\tfrac{1}{4}\tau_{11}(P_y^3P_x+P_y^2P_xP_y+P_yP_xP_y^2+P_xP_y^3)$$
$$+\tfrac{1}{4}\tau_{12}(P_xP_yP_z^2+P_yP_xP_z^2+P_z^2P_xP_y+P_z^2P_yP_x)$$
$$+\tfrac{1}{4}\tau_{13}(P_xP_z^2P_y+P_yP_z^2P_x+P_zP_xP_yP_z+P_zP_yP_xP_z$$
$$+P_zP_xP_zP_y+P_zP_yP_zP_x+P_xP_zP_yP_z+P_yP_zP_xP_z)$$
$$+d\mathcal{Y}(P_xP_y+P_yP_x), \qquad \text{(VI-24)}$$

where

$$d\mathcal{Y} = \sum_a ({}_{(2)}\delta_a')(v_a+\tfrac{1}{2}), \qquad \text{(VI-26)}$$

and

$${}_{(2)}\delta_a' = {}_{(2)}^{xy}Y^{aa}\hbar^2 + {}_{(2)}^{xy}Y_{aa} . \qquad \text{(VI-26)}$$

The nonvanishing matrix elements of h_a^+ in the symmetric rotator representation are given in Appendix III.

Case (b). The additional contributions h_b^+ can be found from (VI-24), (VI-25), and (VI-26) by making in these the replacements indicated in Table VIII. Nonvanishing matrix elements of h_b^+ in the symmetric rotator representation are given in Appendix III.

Case (c). The additional contribution h_c^+ can be found from (VI-24), (VI-25), and (VI-26) by making in these the replacements indicated in Table VIII. Nonvanishing

Table VIII Corresponding quantities for the monoclinic contributions to the Hamiltonian.

h_a^+	h_b^+	h_c^+
τ_{10}	τ_{14}	τ_{18}
τ_{11}	τ_{15}	τ_{19}
τ_{12}	τ_{16}	τ_{20}
τ_{13}	τ_{17}	τ_{21}
x	y	z
y	z	x
z	x	y
ϑ	ε	$\mathcal{J}'$
${}^{xy}_{(2)}Y_{aa}$	${}^{yz}_{(2)}Y_{aa}$	${}^{zx}_{(2)}Y_{aa}$
${}^{xy}_{(2)}Y^{aa}$	${}^{yz}_{(2)}Y^{aa}$	${}^{zx}_{(2)}Y^{aa}$
${}_{(2)}\delta_a'$	${}_{(2)}\varepsilon_a'$	${}_{(2)}\gamma_a'$

matrix elements of h_c^+ in the symmetric rotator representation are given in Appendix III.

For the triclinic point groups, C_1 and $C_i=S_2$, the Hamiltonian to the fourth order of approximation is given by

$$H^{+\prime} + h_a^+ + h_b^+ + h_c^+ \qquad \text{(VI-27)}$$

where $H^{+\prime}$ is given by (VI-23) and h_a^+, h_b^+, and h_c^+ are those of the monoclinic point groups.

VII. PLANAR ROTATORS

When the equilibrium configuration of the molecule is planar a number of "simplifying" features will apply. Planar molecules must have at least one reflection plane, viz., the reflection plane which lies in the plane of the molecule. Thus, four of the eight asymmetric rotator point groups from Table III need not be considered here. Furthermore, it can be shown by giving specific examples that all asymmetric rotator point groups which do have at least one reflection plane will admit the planar condition, and

$$\gamma_i^o = 0 \ , \qquad \text{(VII-1)}$$

where the γ-axis is perpendicular to the plane in which the molecule lies.

We refer to Table IX for the planar asymmetric rotator point groups. It is noted that the triclinic point groups do not admit of planar rotators. Hence, the most general planar rotator Hamiltonian can contain at most thirteen τ's, and to fourth order of approximation is composed of $H^{+\prime}$ and only one of $h_a{}^+$, $h_b{}^+$, or $h_c{}^+$, as explained in Chapter VI.

The condition for the planar molecule (VII-1) implies

$$I_{\alpha\alpha}^o + I_{\beta\beta}^o = I_{\gamma\gamma}^o \ , \qquad \text{(VII-2)}$$

Table IX Planar asymmetric rotator point groups.

Crystallographic nomenclature	Group symbol	Sets of $\tau_{\alpha\beta\gamma\delta}$ and form of Hamiltonian	Example
Monoclinic	$C_s=C_{1h}$	I_1 and one of I_2, II_1, II_2 $H^{+\prime}$ and one of h_a^+, h_b^+, h_c^+	non-linear XYZ
	C_{2h}	I_1 and one of I_2, II_1, II_2 $H^{+\prime}$ and one of h_a^+, h_b^+, h_c^+	Planar trans $C_2H_2Cl_2$
Orthorhombic	C_{2v}	I_1 $H^{+\prime}$	non-linear XYX
	$V_h=D_{2h}$	I_1 $H^{+\prime}$	Planar C_2H_4

by the definition of the principal moments of inertia. If we choose for convenience of discussion the x-y plane as the plane in which the molecule lies, we have from (VII-2) that

$$1/A + 1/B = 1/C \tag{VII-3}$$

from the definition of A, B, C in (IV-6). One should not confuse the equilibrium rotational constans A, B, C with $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$ of eq. (VI-19) which represent the instantaneous rotational constants of the molecule. Due to the inertia defect and non-rigidity one does not have the same kind of relation (VII-3) among $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$, and (VI-19) directly shows the relationship between the equilibrium rotational constants and the instantaneous rotational constants.

Since the molecule lies in the x-y plane we have the following for $a_s^{\alpha\beta}$ and $a_s^{\alpha\alpha}$ of (II-31) and by the condition $z_i^o = 0$;

$$\begin{aligned} a_s^{xz} &= 0 \\ a_s^{yz} &= 0 , \end{aligned} \tag{VII-4}$$

and

$$a_s^{xx} + a_s^{yy} = a_s^{zz} . \tag{VII-5}$$

Also, in planar molecules we have the following properties of the elements of the normal coordinate transformation matrix l:

$l_{is}^x \neq 0$, $l_{is}^y \neq 0$, $l_{is}^z = 0$ for in-plane vibrations,

$$l_{is}^x = 0,\ l_{is}^y = 0,\ l_{is}^z \neq 0 \quad \text{for out-of-plane vibrations.} \qquad \text{(VII-6)}$$

For the planar molecule Oka and Morino[12] found the relations,

$$a_s^{xx} = a_s^{yy} = a_s^{zz} = 0 \text{ for out-of-plane vibrations,} \qquad \text{(VII-7)}$$

and

$$A_{ss}^{xx} + A_{ss}^{yy} = A_{ss}^{zz} = 1 \text{ for in-plane vibrations,}$$

$$A_{ss}^{xx} = A_{ss}^{yy} = 1 \text{ and } A_{ss}^{zz} = 0 \quad \text{for out-of-plane vibrations.} \qquad \text{(VII-8)}$$

$a_s^{\alpha\alpha}$ and $A_{ss}^{\gamma\alpha}$ were defined by (II-31).

Similarly, one secures easily the following results for the Coriolis coupling coefficient ζ_{ab}^{α} of (II-34) of the planar molecule by the relation (VII-6):

If a and b are both in-plane vibrations,

$$\zeta_{ab}^x = 0, \qquad \zeta_{ab}^y = 0, \qquad \zeta_{ab}^z \neq 0. \qquad \text{(VII-9a)}$$

If a and b are both out-of-plane vibrations,

$$\zeta_{ab}^x = 0, \qquad \zeta_{ab}^y = 0, \qquad \zeta_{ab}^z = 0. \qquad \text{(VII-9b)}$$

If only one of a or b is an in-plane vibration,

$$\zeta_{ab}^x \neq 0, \qquad \zeta_{ab}^y \neq 0, \qquad \zeta_{ab}^z = 0. \qquad \text{(VII-9c)}$$

Triatomic molecules, which are a special case of general planar molecules, admit only in-plane vibrations. In cases in which the plane of the molecule is the y-z plane or the z-x plane, the appropriate equations corresponding to (VII-4) through (VII-9c) may be obtained by permuting x, y, z cyclically.

When we apply (VII-4) to the definition of $\tau_{\alpha\beta\gamma\delta}$,

$$\tau_{\alpha\beta\gamma\delta} = -\tfrac{1}{2}\sum_s \frac{a_s^{\alpha\beta}\ a_s^{\gamma\delta}}{I^0_{\alpha\alpha}\ I^0_{\beta\beta}\ I^0_{\gamma\gamma}\ I^0_{\delta\delta}} ,$$

we obtain after some rearrangement the Dowling[28] relationships among τ_1 through τ_9:

$$\begin{aligned} \tau_7 &= \tau_8 = 0 , \\ \tau_1 &= (A/C)^2\tau_5 - (A/B)^2\tau_6 , \\ \tau_2 &= (B/C)^2\tau_4 - (B/A)^2\tau_6 , \\ \tau_3 &= (C/A)^2\tau_5 + (C/B)^2\tau_4 , \end{aligned} \qquad \text{(VII-10)}$$

if the molecule lies in the x-y plane. Thus there are only four independent distortion constants among τ_1 through τ_9. Eq. (VII-7) reveals that the four independent τ's may be built up from contributions of the in-plane vibrations only, so that the summation over vibrational modes could be restricted to in-plane vibrations only. Hill and Edwards[29] gave the specific expressions for the second order centrifugal-distortion energy in planar asymmetric-top molecules in terms of the four independent distortion constants.

Multiplying (VII-5) by a_s^{xy}, it is easy to prove a relationship among the four additional τ's which appear in molecules belonging to one of the monoclinic point groups. For the x-y planar molecule we find in this way

$$(1/A)^2\tau_{10} + (1/B)^2\tau_{11} = (1/C)^2\tau_{12} , \qquad \text{(VII-11)}$$

and from (VII-4) we immediately secure that

$$\tau_{13} = 0 . \qquad \text{(VII-12)}$$

We summarize the conditions and relationships among the τ's in Table X, in which we give the appropriate equations for the y-z planar molecules and x-z planar molecules corresponding to (VII-10), (VII-11), and (VII-12).

The planar condition introduces also many simplifications into the detailed definitions of the ρ's, but no simple relationships similar to those holding for the τ's appear to hold among the ρ's.

Table X Relationships among planar rotator distortion constants.

Plane of molecule	Relationships
x-y	$\tau_7 = \tau_8 = \tau_{13} = 0$
	$\tau_1 = (A/C)^2\tau_5 - (A/B)^2\tau_6$
	$\tau_2 = (B/C)^2\tau_4 - (B/A)^2\tau_6$
	$\tau_3 = (C/A)^2\tau_5 + (C/B)^2\tau_4$
	$(1/A)^2\tau_{10}+(1/B)^2\tau_{11}=(1/C)^2\tau_{12}$ (monoclinic)
	$\tau_{10} = \tau_{11} = \tau_{12} = 0$ (orthorhombic)
y-z	$\tau_8 = \tau_9 = \tau_{17} = 0$
	$\tau_1 = (A/B)^2\tau_6 + (A/C)^2\tau_5$
	$\tau_2 = (B/A)^2\tau_6 - (B/C)^2\tau_4$
	$\tau_3 = (C/A)^2\tau_5 - (C/B)^2\tau_4$
	$(1/B)^2\tau_{14}+(1/C)^2\tau_{15}=(1/A)^2\tau_{16}$ (monoclinic)
	$\tau_{14} = \tau_{15} = \tau_{16} = 0$ (orthorhombic)
z-x	$\tau_7 = \tau_9 = \tau_{21} = 0$
	$\tau_1 = (A/B)^2\tau_6 - (A/C)^2\tau_5$
	$\tau_2 = (B/C)^2\tau_4 + (B/A)^2\tau_6$
	$\tau_3 = (C/B)^2\tau_4 - (C/A)^2\tau_5$
	$(1/A)^2\tau_{18}+(1/C)^2\tau_{19}=(1/B)^2\tau_{20}$ (monoclinic)
	$\tau_{18} = \tau_{19} = \tau_{20} = 0$ (orthorhombic)

VIII. FOURTH ORDER CENTRIFUGAL DISTORTION TERMS.

In the previous chapter we neglected the fourth order centrifugal distortion terms (P^6-type terms), since their contribution to the energy is only significant for $J \geq 30$ in general cases. However, as indicated in the previous chapter, experimental results[25] indicate that the second order centrifugal distortion terms (P^4-type terms) are inadequate to describe the stretching effects in some cases, such as for the planar triatomic molecule H_2O, even for the lower J values. In these cases it is necessary to consider the fourth order centrifugal distortion effects to get a satisfactory fit to the spectral data. For these reasons we present in this chapter a survey of the fourth order centrifugal distortion terms.

These fourth order centrifugal distortion terms were given by the last term of eq. (VI-3) as

$$H^* = \sum_{\alpha\beta\gamma\delta\epsilon\eta} {}^{\alpha\beta\gamma\delta\epsilon\eta}_{(4)}Z P_\alpha P_\beta P_\gamma P_\delta P_\epsilon P_\eta \,, \qquad \text{(VIII-1)}$$

where ${}^{\alpha\beta\gamma\delta\epsilon\eta}_{(4)}Z$ are the fourth order centrifugal distortion constants (coefficients) and the detailed and very lengthy expression of them in terms of molecular constants is given in Appendix IV. We shall use the alternative notation $[\alpha\beta\gamma\delta\epsilon\eta]$ for ${}^{\alpha\beta\gamma\delta\epsilon\eta}_{(4)}Z$ where convenient and further denote $[\alpha\beta\gamma\delta\epsilon\eta]$ by Θ_i, $i=1,2,3,\ldots$

where the numbering of the θ's will be established later.

Because of the noncommutativity of the angular momentum components P_α, (VIII-1) shows that there is a total of $3^6=729$ coefficients $[\alpha\beta\gamma\delta\epsilon\eta]$. However, if we apply the symmetry operations upon the P^6-type operators we find that only 183 terms are nonvanishing for orthorhombic point groups and 365 terms are nonvanishing for the monoclinic point groups. The P^6-type operators, whose $[\alpha\beta\gamma\delta\epsilon\eta]$'s do not vanish for the orthorhombic point groups are found to have real matrix elements of type $(K|K)$, $(K|K\pm2)$, $(K|K\pm4)$, $(K|K\pm6)$ only. Therefore, as in the case of the second order centrifugal distortion terms, the entire matrix elements of the 183 nonvanishing P^6-type terms for the orthorhombic point groups will lie only within the four Wang blocks E^+, E^-, O^+, O^- in the symmetrized symmetric rotator representation. Further, all <u>additional</u> terms allowed by the lower symmetries in the case of monoclinic or triclinic point groups have nonvanishing matrix elements located only outside the Wang blocks. This is ascertained in the same manner as for the P^4-type terms.

Now, as in the case of the P^4-type terms, if we consider a properly partitioned four step matrix T' which transforms H^* to a basis in which only the Wang blocks are diagonal, we find that none of the matrix elements located outside the Wang blocks will be brought into the Wang blocks due to the transformation. This means that we need to consider only the 183 P^6-type terms which are invariant under the symmetry operations of the orthorhombic point groups in the study of the fourth order centrifugal distortion effects not only for the orthorhombic point groups but also for the monoclinic and triclinic point groups, since the remaining nonvanishing matrix elements will contribute to the energies only in approximations higher than the fourth.

Close examination of the parameters in the expression of $[\alpha\beta\gamma\delta\epsilon\eta]$ in Appendix IV reveals the following relations:

$$ {}^{\alpha\beta}S^m = {}^{\beta\alpha}S^m \qquad \text{(VIII-2a)} $$

$$ {}^{\alpha\beta\gamma}_{(2)}U^n = {}^{\gamma\beta\alpha}_{(2)}U^n \qquad \text{(VIII-2b)} $$

$$ {}^{\alpha\beta\gamma}\alpha^n = {}^{\gamma\beta\alpha}\alpha^n \qquad \text{(VIII-2c)} $$

$$ {}^{\alpha\beta}_{(2)}U_{mn} = {}^{\beta\alpha}_{(2)}U_{mn} \qquad \text{(VIII-2d)} $$

for asymmetric molecules. From these we are able to obtain among the $[\alpha\beta\gamma\delta\epsilon\eta]$ the very useful relation

$$ [\alpha\beta\gamma\delta\epsilon\eta] = [\eta\epsilon\delta\gamma\beta\alpha] \, . \qquad \text{(VIII-3)} $$

Relation (VIII-3) reduces the 183 coefficients to 105 independent fourth order centrifugal distortion coefficients. The 105 independent coefficients may be classified as

Type $[\alpha\alpha\alpha\alpha\alpha\alpha]$	3	coefficients,
Type $[\alpha\alpha\alpha\alpha\beta\beta]$ and permutations thereof,	54	coefficients, $(\alpha \neq \beta)$
Type $[\alpha\alpha\beta\beta\gamma\gamma]$ and permutations thereof,	48	coefficients, $(\alpha \neq \beta \neq \gamma)$
Total	105	coefficients.

(VIII-4)

These 105 distinct coefficients are given in Table XI, where they are grouped in the manner of (VIII-4), and indexed by i of θ_i. The fourth order centrifugal distortion terms can now be expressed by the 105 θ_i's and their associated P^6-type operators with the aid of Table XI and (VIII-1). This expression would be accurate to the fourth order of approximation for the general asymmetric-top molecule.

Since H_2O, one of the molecules which show the effect of P^6-type stretching terms even for low J values, is triatomic, and further simplifications are feasible for triatomic molecules, we considered the fourth order centrifugal distortion effects in triatomic asymmetric-top molecules as a special case.

In triatomic molecules simplifications arise due to (a) planarity (any triatomic molecule is necessarily a planar molecule), and (b) the absence of out-of-plane vibrations in these molecules. The planarity condition

Table XI Coefficients of fourth-order centrifugal distortion operators $[\alpha\beta\gamma\delta\epsilon\eta] = \Theta_i$ and relationships among them.

i	$[\alpha\beta\gamma\delta\epsilon\eta]$	Relationships* for triatomic molecules		
		xy-plane	yz-plane	zx-plane
1	xxxxxx			
2	yyyyyy			
3	zzzzzz			
4	xxyyyy=yyyyxx	6=7=8	12=0	6=7=8=0
5	yyxxyy	9=10=11=12	10=7+9	11=12=0
6	yxyyxy			9=10
7	xyyyxy=yxyyyx			
8	xyyyyx			
9	xyxyyy=yyyxyx			
10	yxyxyy=yyxyxy			
11	xyyxyy=yyxyyx			
12	yxxyyy=yyyxxy			
13	yyxxxx=xxxxyy	15=16=17	15=16=17=0	21=0
14	xxyyxx	18=19=20=21	20=21=0	19=16+18
15	xyxxyx		18=19	
16	yxxxyx=xyxxxy			
17	yxxxxy			
18	yxyxxx=xxxyxy			
19	xyxyxx=xxyxyx			
20	yxxyxx=xxyxxy			
21	xyyxxx=xxxyyx			

(continued)

		xy-plane	yz-plane	zx-plane
22	yyzzzz=zzzzyy	24=25=26=0	24=25=26	30=0
23	zzyyzz	29=30=0	27=28=29=30	28=25+27
24	zyzzyz	27=28		
25	yzzzyz=zyzzzy			
26	yzzzzy			
27	yzyzzz=zzzyzy			
28	zyzyzz=zzyzyz			
29	yzzyzz=zzyzzy			
30	zyyzzz=zzzyyz			
31	zzyyyy=yyyyzz	39=0	33=34=35	33=34=35=0
32	yyzzyy	37=34+36	36=37=38=39	38=39=0
33	yzyyzy			36=37
34	zyyyzy=yzyyyz			
35	zyyyyz			
36	zyzyyy=yyyzyz			
37	yzyzyy=yyzyzy			
38	zyyzyy=yyzyyz			
39	yzzyyy=yyyzzy			
40	zzxxxx=xxxxzz	41=0	42=43=44=0	42=43=44
41	xxzzxx	46=43+45	47=48=0	45=46=47=48
42	xzxxzx		45=46	
43	zxxxzx=xzxxxz			
44	zxxxxz			
45	zxzxxx=xxxzxz			
46	xzxzxx=xxzxzx			

(continued)

		(xy-plane)	(yz-plane)	(xz-plane)
47	zxxzxx=xxzxxz			
48	xzzxxx=xxxzzx			
49	xxzzzz=zzzzxx	51=52=53=0	57=0	51=52=53
50	zzxxzz	56=57=0	55=52+54	54=55=56=57
51	zxzzxz	54=55		
52	xzzzxz=zxzzzx			
53	xzzzzx			
54	xzxzzz=zzzxzx			
55	zxzxzz=zzxzxz			
56	xzzxzz=zzxzzx			
57	zxxzzz=zzzxxz			
58	xxyyzz=zzyyxx			
59	yyzzxx=xxzzyy			
60	zzxxyy=yyxxzz			
61	xyyzzx=xzzyyx	61=62=0	62=63=0	63=61=0
62	yzzxxy=yxxzzy			
63	zxxyyz=zyyxxz			
64	yxxyzz=zzyxxy	64=65	66=67	68=69
65	xyxyzz=zzyxyx	68=0	64=0	66=0
66	zyyzxx=xxzyyz			
67	yzyzxx=xxzyzy			
68	xzzxyy=yyxzzx			
69	zxzxyy=yyxzxz			

(continued)

		xy-plane	yz-plane	zx-plane
70	xyyxzz=zzxyyx	70=71	72=73	74=75
71	yxyxzz=zzxyxy	72=0	74=0	70=0
72	yzzyxx=xxyzzy			
73	zyzyxx=xxyzyz			
74	zxxzyy=yyzxxz			
75	xzxzyy=yyzxzx			
76	yxyzzx=xzzyxy	76=77=0	78=79=0	80=81=0
77	xyxzzy=yzzxyx	78=81=82=83	77=80=83=84	76=79=84=82
78	zyzxxy=yxxzyz	80=75-69	76=71-65	78=73-67
79	yzyxxz=zxxyzy	79=67-73	81=69-75	77=65-71
80	xzxyyz=zyyxzx			
81	zxzyyx=xyyzxz			
82	yxyzxz=zxzyxy			
83	zyzxyx=xyxzyz			
84	xzxyzy=yzyxzx			
85	xzyxzy=yzxyzx	85=88=91	86=89=92	87=90=93
86	yxzyxz=zxyzxy	86=87+89-93	87=85+90-91	85=86+88-92
87	zyxzyx=xyzxyz			
88	yzxxzy			
89	zxyyxz			
90	xyzzyx			
91	xzyyzx			
92	yxzzxy			
93	zyxxyz			

(continued)

		xy-plane	yz-plane	xz-plane
94	xzyyxz=zxyyzx	95=92= 90+70-64 +105-93	96=93= 88+72-66 +103-91	94=91= 89+74-68 +104-92
95	yxzzyx=xyzzxy			
96	zyxxzy=yzxxyz			
97	xzyxyz=zyxyzx	97=96	98=94	99=95
98	yxzyzx=xzyzxy	100=94	101=95	102=96
99	zyxzxy=yxzxyz	99=101= 87+105-93	97=102= 85+103-91	98=100= 86+104-92
100	yzxyxz=zxyxzy			
101	zxyzyx=xyzyxz	102=103= 81+97	100=104= 77+98	101=105= 79+99
102	xyzxzy=yzxzyx	98=104= 81+100	99=105= 77+101	97=103= 79+102
103	xyzyzx=xzyzxy			
104	yzxzxy=yxzxzy			
105	zxyxyz=zyxyxz			

*For the entries in these columns, θ_i is replaced by i in the interest of clarity of reproduction.

gives us, as shown in Chapter VII, the following properties of $a_s^{\alpha\beta}$ of (II-31):

$$a_s^{\alpha\beta} \neq 0 \qquad\qquad (\alpha \neq \beta) \qquad\qquad \text{(VIII-5)}$$
$$a_s^{\alpha\gamma} = a_s^{\beta\gamma} = 0,$$

if the molecule lies in the $\alpha\beta$-plane. Also, from (VII-9a), which was proved in Chapter VII from the properties of the normal coordinate transformation matrix, we have the following properties of the Coriolis coupling constants due to the absence of out-of-plane vibrations:

$$\zeta_{ab}^{\alpha} = \zeta_{ab}^{\beta} = 0 \qquad (\alpha \neq \beta), \qquad\qquad \text{(VIII-6)}$$

if the molecule lies in the $\alpha\beta$-plane.

Applying (VIII-5) and (VIII-6) to the expressions of the parameters appearing in Appendix IV, we have found:

$${}^{\gamma\alpha}S^m = {}^{\alpha\gamma}S^m = {}^{\beta\gamma}S^m = {}^{\gamma\beta}S^m = 0 \qquad\qquad \text{(VIII-7)}$$

$${}^{\alpha}S_{mn} = {}^{\beta}S_{mn} = 0 \qquad\qquad \text{(VIII-8)}$$

$${}^{\gamma\alpha}_{(2)}U_{mn} = {}^{\alpha\gamma}_{(2)}U_{mn} = {}^{\beta\gamma}_{(2)}U_{mn} = {}^{\gamma\beta}_{(2)}U_{mn} = 0 \qquad\qquad \text{(VIII-9)}$$

$${}^{\alpha\alpha\alpha}_{(2)}U^n = {}^{\beta\beta\beta}_{(2)}U^n = 0 \qquad\qquad \text{(VIII-10a)}$$

$${}^{\alpha\beta\alpha}_{(2)}U^n = {}^{\beta\alpha\beta}_{(2)}U^n = {}^{\gamma\alpha\gamma}_{(2)}U^n = {}^{\gamma\beta\gamma}_{(2)}U^n = 0 \qquad\qquad \text{(VIII-10b)}$$

$${}^{\alpha\alpha\beta}_{(2)}U^n = {}^{\beta\alpha\alpha}_{(2)}U^n = {}^{\alpha\beta\beta}_{(2)}U^n = {}^{\beta\beta\alpha}_{(2)}U^n = 0 \qquad\qquad \text{(VIII-10c)}$$

$${}^{\alpha\gamma\gamma}_{(2)}U^n = {}^{\gamma\gamma\alpha}_{(2)}U^n = {}^{\beta\gamma\gamma}_{(2)}U^n = {}^{\gamma\gamma\beta}_{(2)}U^n = 0 \qquad\qquad \text{(VIII-10d)}$$

$${}^{\alpha\alpha\alpha}\alpha^n = {}^{\beta\beta\beta}\alpha^n = {}^{\gamma\gamma\gamma}\alpha^n = 0 \qquad\qquad \text{(VIII-11a)}$$

$$ {}^{\alpha\beta\alpha}{}_{\alpha}n = {}^{\beta\alpha\beta}{}_{\alpha}n = {}^{\gamma\alpha\gamma}{}_{\alpha}n = {}^{\gamma\beta\gamma}{}_{\alpha}n = 0 \qquad \text{(VIII-11b)} $$

$$ {}^{\alpha\alpha\beta}{}_{\alpha}n = {}^{\beta\alpha\alpha}{}_{\alpha}n = {}^{\alpha\beta\beta}{}_{\alpha}n = {}^{\beta\beta\alpha}{}_{\alpha}n = 0 \qquad \text{(VIII-11c)} $$

$$ {}^{\alpha\gamma\gamma}{}_{\alpha}n = {}^{\gamma\gamma\alpha}{}_{\alpha}n = {}^{\beta\gamma\gamma}{}_{\alpha}n = {}^{\gamma\gamma\beta}{}_{\alpha}n = 0 \qquad \text{(VIII-11d)} $$

The nonvanishing parameters are also further simplified by application of (VIII-5) and (VIII-6) for the triatomic case. Substituting (VIII-7) to (VIII-11d), one finds that 18 of the 105 distinct coefficients now vanish and that there exist 34 linear relationships among the nonvanishing θ_i's. Therefore, we now have only 53 independent distinct fourth order centrifugal distortion constants for triatomic molecules. We summarized these conditions in Table XI for xy-plane, xz-plane, and yz-plane planar triatomic molecules.

The contribution of the fourth order centrifugal distortion terms to the energy levels could be calculated, in principle, in terms of 105 θ's for the general case and in terms of 53 θ's for the triatomic case by evaluating the matrix elements of the relevant P^6-type operators. For those energy levels listed in Appendix II it would be possible to give closed form expressions for the energy contributed by the P^6-type terms. However, this has not been done because of the length of these expressions, and therefore we have not listed the matrix elements of these terms.

IX. CONCLUSION

By taking advantage of symmetry considerations, the vast number of terms appearing in the general vibration-rotation Hamiltonian for asymmetric molecules to the fourth order of approximation can be reduced considerably. In fact, by distinguishing three types of Hamiltonians, for orthorhombic point groups, monoclinic point groups, and triclinic point groups, we were able to rearrange the Hamiltonian into reasonably tractable form.

For the orthorhombic point groups the Hamiltonian takes the simplest form and closed form solutions for the energy levels for a few low J values were obtained. Although closed solutions for the energy levels are not available for most higher J levels, we expect that numerical analysis can now be invoked to higher accuracy with the aid of computers. Therefore it will now be possible to analyze centrifugal distortion effects and vibration-rotation interactions in higher orders from the deduced Hamiltonian.

For the monoclinic and triclinic point groups we face even greater difficulty in getting closed form solutions for the energy levels. However, as in higher J cases of the orthorhombic point groups, it would be possible to employ numerical analysis with the aid of

computer techniques, and thus our Hamiltonians should be of practical interest.

Further simplification of the Hamiltonians can be had in the case of molecules with planar equilibrium configurations, and for triatomic planar molecules, especially, the analysis of fourth order centrifugal distortion effects should become feasible.

Because fourth order effects are now in many cases within the limit of experimental accuracy, this work should be of value in obtaining still more satisfactory analysis of the infrared and microwave spectra of asymmetric molecules.

APPENDIX I

Herein are given the nonvanishing matrix elements of (VI-23). The phase angle chosen for the angular momentum components is such that

$$(K|P_x|K+1) = (K+1|P_x|K) = \tfrac{1}{2}\hbar[(J-K)(J+K+1)]^{\frac{1}{2}}$$

$$(K|P_y|K+1) = -(K+1|P_y|K) = -\tfrac{1}{2}i\hbar[(J-K)(J+K+1)]^{\frac{1}{2}}$$

$$(K|P_z|K) = \hbar K$$

and $f=J(J+1)$.

$$\begin{aligned}
(K|H^{+'}|K) = E_v &+ \tfrac{1}{2}\hbar^2(\alpha+\beta)(f-K^2) + \hbar^2\gamma K^2 \\
&+ \tfrac{1}{4}\hbar^4(\tau_3+\rho_3)K^4 \\
&+ \frac{1}{16}\hbar^4(\tau_1+\tau_2+2\tau_6+4\tau_9+\rho_1+\rho_2+2\rho_6)(f-K^2)^2 \\
&+ \tfrac{1}{4}\hbar^4(\tau_4+\tau_5+2\tau_7+2\tau_8+\rho_4+\rho_5+\rho_7+\rho_8 \\
&\qquad +\tfrac{1}{2}\rho_{10}+\tfrac{1}{2}\rho_{11}+\tfrac{1}{2}\rho_{12}+\tfrac{1}{2}\rho_{13})(f-K^2)K^2 \\
&+ \frac{1}{64}\hbar^4(\tau_1+\tau_2-2\tau_6-4\tau_9+\rho_1+\rho_2-2\rho_6+2\rho_9+\rho_{14}+\rho_{15}) \\
&\quad \times\{[f-K(K+1)][f-(K+1)(K+2)] \\
&\qquad\qquad +[f-K(K-1)][f-(K-1)(K-2)]\} \\
&+ \frac{1}{8}\hbar^4(\rho_{11}+\rho_{13})f \\
&+ \frac{1}{8}\hbar^4(-2\rho_7-2\rho_8-\rho_9-3\rho_{11}-3\rho_{13}+\tfrac{1}{2}\rho_{14}+\tfrac{1}{2}\rho_{15})K^4
\end{aligned}$$

$$
\begin{aligned}
(K|H^{+\prime}|K\pm 2) = \Big\{ & \hbar^2(\alpha-\beta) \\
& + \tfrac{1}{4}\hbar^4(\tau_1-\tau_2+\rho_1-\rho_2)\left[f-\tfrac{1}{2}K^2-\tfrac{1}{2}(K\pm 2)^2\right] \\
& + \tfrac{1}{4}\hbar^4(-\tau_4+\tau_5-2\tau_7+2\tau_8-\rho_4+\rho_5)\left[K^2+(K\pm 2)^2\right] \\
& + \tfrac{1}{4}\hbar^4(-2\rho_7+2\rho_8-\rho_{11}+\rho_{13})(K\pm 1)^2 \\
& + \tfrac{1}{4}\hbar^4(-\rho_{10}+\rho_{12})K(K\pm 2) \\
& + \tfrac{1}{4}h^4(\rho_{14}-\rho_{15})\Big\} \\
& x\ \tfrac{1}{4}\left[f-K(K\pm 1)\right]^{\frac{1}{2}}\left[f-(K\pm 1)(K\pm 2)\right]^{\frac{1}{2}}
\end{aligned}
$$

$$
\begin{aligned}
(K|H^{+\prime}|K\pm 4) = {} & \frac{\hbar^4}{64}(\tau_1+\tau_2-2\tau_6-4\tau_9+\rho_1+\rho_2-2\rho_6-2\rho_9-\rho_{14}-\rho_{[illegible]}) \\
& x\ \left[f-K(K\pm 1)\right]^{\frac{1}{2}}\left[f-(K\pm 1)(K\pm 2)\right]^{\frac{1}{2}} \\
& x\ \left[f-(K\pm 2)(K\pm 3)\right]^{\frac{1}{2}}\left[f-(K\pm 3)(K\pm 4)\right]^{\frac{1}{2}}
\end{aligned}
$$

APPENDIX II

Herein are given those eigenvalues of (VI-23) which can be established in closed form.*

$$E(0_{00}) = E_v$$

$$E(1_{01}) = E_v+\hbar^2(\mathcal{A}+\mathcal{C})+\tfrac{1}{4}\hbar^4(\tau_1+\tau_3+2\tau_5+4\tau_8+\rho_1+\rho_3+2\rho_5+\rho_{10}+\rho_{14})$$

$$E(1_{11}) = E_v+\hbar^2(\mathcal{B}+\mathcal{C})+\tfrac{1}{4}\hbar^4(\tau_2+\tau_3+2\tau_4+4\tau_7+\rho_2+\rho_3+2\rho_4+\rho_{12}+\rho_{15})$$

$$E(1_{10}) = E_v+\hbar^2(\mathcal{A}+\mathcal{B})+\tfrac{1}{4}\hbar^4(\tau_1+\tau_2+2\tau_6+4\tau_9+\rho_1+\rho_2+2\rho_6+\rho_{11}+\rho_{13})$$

$$E(2_{02}) = E_v+\tfrac{1}{2}[\alpha_1-(\beta_1{}^2+4\gamma_1{}^2)^{\frac{1}{2}}]$$

$$\begin{aligned}E(2_{12}) = {} & E_v+\hbar^2(\mathcal{A}+\mathcal{B}+4\mathcal{C})\\ & +\hbar^4(\tfrac{1}{4}\tau_1+\tfrac{1}{4}\tau_2+4\tau_3+2\tau_4+2\tau_5+\tfrac{1}{2}\tau_6+4\tau_7+4\tau_8+\tau_9\\ & \quad +\tfrac{1}{4}\rho_1+\tfrac{1}{4}\rho_2+4\rho_3+2\rho_4+2\rho_5+\tfrac{1}{2}\rho_6+\rho_7+\rho_8+\rho_9\\ & \quad +\rho_{10}+\tfrac{1}{4}\rho_{11}+\rho_{12}+\tfrac{1}{4}\rho_{13}+\rho_{14}+\rho_{15})\end{aligned}$$

$$\begin{aligned}E(2_{11}) = {} & E_v+\hbar^2(4\mathcal{A}+\mathcal{B}+\mathcal{C})\\ & +\hbar^4(4\tau_1+\tfrac{1}{4}\tau_2+\tfrac{1}{4}\tau_3+\tfrac{1}{2}\tau_4+2\tau_5+2\tau_6+\tau_7+4\tau_8+4\tau_9\\ & \quad +4\rho_1+\tfrac{1}{4}\rho_2+\tfrac{1}{4}\rho_3+\tfrac{1}{2}\rho_4+2\rho_5+2\rho_6+\rho_7+\rho_8+\rho_9\\ & \quad +\rho_{10}+\rho_{11}+\tfrac{1}{4}\rho_{12}+\rho_{13}+\rho_{14}+\tfrac{1}{4}\rho_{15})\end{aligned}$$

$$\begin{aligned}E(2_{21}) = {} & E_v+h^2(\mathcal{A}+4\mathcal{B}+\mathcal{C})\\ & +h^4(\tfrac{1}{4}\tau_1+4\tau_2+\tfrac{1}{4}\tau_3+2\tau_4+\tfrac{1}{2}\tau_5+2\tau_6+4\tau_7+\tau_8+4\tau_9\\ & \quad +\tfrac{1}{4}\rho_1+4\rho_2+\tfrac{1}{4}\rho_3+2\rho_4+\tfrac{1}{2}\rho_5+2\rho_6+\rho_7+\rho_8+\rho_9\\ & \quad +\tfrac{1}{4}\rho_{10}+\rho_{11}+\rho_{12}+\rho_{13}+\tfrac{1}{4}\rho_{14}+\rho_{15})\end{aligned}$$

$$E(2_{20}) = E_v+\tfrac{1}{2}[\alpha_1+(\beta_1{}^2+4\gamma_1{}^2)^{\frac{1}{2}}]$$

$$E(3_{03}) = E_v+\tfrac{1}{2}[\alpha_2-(\beta_2{}^2+4\gamma_2{}^2)^{\frac{1}{2}}]$$

$$E(3_{13}) = E_v+\tfrac{1}{2}[\alpha_3-(\beta_3{}^2+4\gamma_3{}^2)^{\frac{1}{2}}]$$

$$E(3_{12}) = E_v+\tfrac{1}{2}[\alpha_4-(\beta_4{}^2+4\gamma_4{}^2)^{\frac{1}{2}}]$$

$$E(3_{22}) = E_v + 4\hbar^2(\mathcal{A}+\mathcal{B}+\mathcal{C})$$
$$+\hbar^4(4\tau_1+4\tau_2+4\tau_3+8\tau_4+8\tau_5+8\tau_6+16\tau_7+16\tau_8+16\tau_9$$
$$+4\rho_1+4\rho_2+4\rho_3+8\rho_4+8\rho_5+8\rho_6+7\rho_7+7\rho_8+7\rho_9$$
$$+4\rho_{10}+4\rho_{11}+4\rho_{12}+4\rho_{13}+4\rho_{14}+4\rho_{15})$$
$$E(3_{21}) = E_v+\tfrac{1}{2}[\alpha_2+(\beta_2{}^2+4\gamma_2{}^2)^{\frac{1}{2}}]$$
$$E(3_{31}) = E_v+\tfrac{1}{2}[\alpha_3+(\beta_3{}^2+4\gamma_3{}^2)^{\frac{1}{2}}]$$
$$E(3_{30}) = E_v+\tfrac{1}{2}[\alpha_4+(\beta_4{}^2+4\gamma_4{}^2)^{\frac{1}{2}}]$$
$$E(4_{14}) = E_v+\tfrac{1}{2}[\alpha_5-(\beta_5{}^2+4\gamma_5{}^2)^{\frac{1}{2}}]$$
$$E(4_{13}) = E_v+\tfrac{1}{2}[\alpha_6-(\beta_6{}^2+4\gamma_6{}^2)^{\frac{1}{2}}]$$
$$E(4_{23}) = E_v+\tfrac{1}{2}[\alpha_7-(\beta_7{}^2+4\gamma_7{}^2)^{\frac{1}{2}}]$$
$$E(4_{32}) = E_v+\tfrac{1}{2}[\alpha_5+(\beta_5{}^2+4\gamma_5{}^2)^{\frac{1}{2}}]$$
$$E(4_{31}) = E_v+\tfrac{1}{2}[\alpha_6+(\beta_6{}^2+4\gamma_6{}^2)^{\frac{1}{2}}]$$
$$E(4_{41}) = E_v+\tfrac{1}{2}[\alpha_7+(\beta_7{}^2+4\gamma_7{}^2)^{\frac{1}{2}}]$$
$$E(5_{24}) = E_v+\tfrac{1}{2}[\alpha_8-(\beta_8{}^2+4\gamma_8{}^2)^{\frac{1}{2}}]$$
$$E(5_{42}) = E_v+\tfrac{1}{2}[\alpha_8+(\beta_8{}^2+4\gamma_8{}^2)^{\frac{1}{2}}]$$

where

$$\alpha_1 = 4\hbar^2(\mathcal{A}+\mathcal{B}+\mathcal{C})$$
$$+\hbar^4(4\tau_1+4\tau_2+4\tau_3+2\tau_4+2\tau_5+2\tau_6+4\tau_7+4\tau_8+4\tau_9$$
$$+4\rho_1+4\rho_2+4\rho_3+2\rho_4+2\rho_5+2\rho_6+\rho_7+\rho_8+\rho_9$$
$$+\rho_{10}+\rho_{11}+\rho_{12}+\rho_{13}+\rho_{14}+\rho_{15})$$
$$\beta_1 = 2\hbar^2(\mathcal{A}+\mathcal{B}-2\mathcal{C})$$
$$+\hbar^4(2\tau_1+2\tau_2-4\tau_3-2\tau_4-2\tau_5+4\tau_6-4\tau_7-4\tau_8+8\tau_9$$
$$+2\rho_1+2\rho_2-4\rho_3-2\rho_4-2\rho_5+4\rho_6-\rho_7-\rho_8+2\rho_9$$
$$-\rho_{10}+\tfrac{1}{2}\rho_{11}-\rho_{12}+\tfrac{1}{2}\rho_{13}+\tfrac{1}{2}\rho_{14}+\tfrac{1}{2}\rho_{15})$$

$$\gamma_1 = (3)^{\frac{1}{2}}\hbar^2(\mathcal{A}-\mathcal{B})$$
$$+(3)^{\frac{1}{2}}\hbar^4(\tau_1-\tau_2-\tau_4+\tau_5-2\tau_7+2\tau_8$$
$$+\rho_1-\rho_2-\rho_4+\rho_5-\tfrac{1}{2}\rho_7+\tfrac{1}{2}\rho_8-\tfrac{1}{4}\rho_{11}+\tfrac{1}{4}\rho_{13}+\tfrac{1}{4}\rho_{14}-\tfrac{1}{4}\rho_{15})$$

$$\alpha_2 = \hbar^2(10\mathcal{A}+4\mathcal{B}+10\mathcal{C})$$
$$+\hbar^4(\frac{41}{2}\tau_1+4\tau_2+\frac{41}{2}\tau_3+8\tau_4+11\tau_5+8\tau_6+16\tau_7+22\tau_8+16\tau_9$$
$$+\frac{41}{2}\rho_1+4\rho_2+\frac{41}{2}\rho_3+8\rho_4+11\rho_5+8\rho_6+7\rho_7+7\rho_8+7\rho_9$$
$$+\frac{11}{2}\rho_{10}+4\rho_{11}+4\rho_{12}+4\rho_{13}+\frac{11}{2}\rho_{14}+4\rho_{15})$$

$$\beta_2 = \hbar^2(7\mathcal{A}+\mathcal{B}-8\mathcal{C})$$
$$+\hbar^4(\frac{35}{2}\tau_1+\tau_2-20\tau_3-\frac{11}{2}\tau_4-\frac{5}{2}\tau_5+\frac{19}{2}\tau_6-11\tau_7-5\tau_8+19\tau_9$$
$$+\frac{35}{2}\rho_1+\rho_2-20\rho_3-\frac{11}{2}\rho_4-\frac{5}{2}\rho_5+\frac{19}{2}\rho_6-2\rho_7-2\rho_8+\frac{19}{2}\rho_9$$
$$-\frac{5}{4}\rho_{10}+\rho_{11}-\frac{11}{4}\rho_{12}+\rho_{13}+\frac{5}{2}\rho_{14}+\rho_{15})$$

$$\gamma_2 = \tfrac{1}{2}(15)^{\frac{1}{2}}\hbar^2(\mathcal{A}-\mathcal{B})$$
$$+\tfrac{1}{4}(15)^{\frac{1}{2}}\hbar^4(5\tau_1-2\tau_2-5\tau_4+5\tau_5-3\tau_6-10\tau_7+10\tau_8-6\tau_9$$
$$+5\rho_1-2\rho_2-5\rho_4+5\rho_5-3\rho_6-4\rho_7+4\rho_8-3\rho_9$$
$$-\frac{3}{2}\rho_{10}-2\rho_{11}+\frac{3}{2}\rho_{12}+2\rho_{13}-\rho_{14}-2\rho_{15})$$

$$\alpha_3 = \hbar^2(4\mathcal{A}+10\mathcal{B}+10\mathcal{C})$$
$$+\tfrac{1}{2}\hbar^4(8\tau_1+41\tau_2+41\tau_3+22\tau_4+16\tau_5+16\tau_6+44\tau_7+32\tau_8+32\tau_9$$
$$+8\rho_1+41\rho_2+41\rho_3+22\rho_4+16\rho_5+16\rho_6+14\rho_7+14\rho_8+14\rho_9$$
$$+8\rho_{10}+8\rho_{11}+11\rho_{12}+8\rho_{13}+8\rho_{14}+11\rho_{15})$$

$$\beta_3 = \hbar^2(\mathcal{A}+7\mathcal{B}-8\mathcal{C})$$
$$+\tfrac{1}{2}\hbar^4(2\tau_1+35\tau_2-40\tau_3-5\tau_4-11\tau_5+19\tau_6-10\tau_7-22\tau_8+38\tau_9$$
$$+2\rho_1+35\rho_2-40\rho_3-5\rho_4-11\rho_5+19\rho_6-4\rho_7-4\rho_8+11\rho_9$$
$$+2\rho_{11}-\frac{5}{2}\rho_{12}+2\rho_{13}+2\rho_{14}+5\rho_{15})$$

$$\begin{aligned}\gamma_3 = {} & \tfrac{1}{2}(15)^{\frac{1}{2}}\hbar^2(\mathcal{A}-\mathcal{B}) \\ & +\tfrac{1}{4}(15)^{\frac{1}{2}}\hbar^4(2\tau_1-5\tau_2-5\tau_4+5\tau_5+3\tau_6-10\tau_7+10\tau_8+6\tau_9 \\ & \qquad +2\rho_1-5\rho_2-5\rho_4-5\rho_5+3\rho_6-4\rho_7+4\rho_8+3\rho_9 \\ & \qquad -\tfrac{3}{2}\rho_{10}-2\rho_{11}+\tfrac{3}{2}\rho_{12}+2\rho_{13}+2\rho_{14}+\rho_{15})\end{aligned}$$

$$\begin{aligned}\alpha_4 = {} & \hbar^2(10\mathcal{A}+10\mathcal{B}+4\mathcal{C}) \\ & +\tfrac{1}{2}\hbar^4(41\tau_1+41\tau_2+8\tau_3+16\tau_4+16\tau_5+22\tau_6+32\tau_7+32\tau_8+44\tau_9 \\ & \qquad +41\rho_1+41\rho_2+8\rho_3+16\rho_4+16\rho_5+22\rho_6+14\rho_7+14\rho_8+14\rho_9 \\ & \qquad +8\rho_{10}+11\rho_{11}+8\rho_{12}+11\rho_{13}+8\rho_{14}+8\rho_{15})\end{aligned}$$

$$\begin{aligned}\beta_4 = {} & \hbar^2(2\mathcal{A}+2\mathcal{B}-4\mathcal{C}) \\ & +\hbar^4(5\tau_1+5\tau_2-4\tau_3-8\tau_4-8\tau_5+10\tau_6-16\tau_7-16\tau_8+20\tau_9 \\ & \qquad +5\rho_1+5\rho_2-4\rho_3-8\rho_4-8\rho_5+10\rho_6-7\rho_7-7\rho_8+8\rho_9 \\ & \qquad -4\rho_{10}-\tfrac{5}{2}\rho_{11}-4\rho_{12}-\tfrac{5}{2}\rho_{13}+\tfrac{7}{2}\rho_{14}+\tfrac{7}{2}\rho_{15})\end{aligned}$$

$$\begin{aligned}\gamma_4 = {} & (15)^{\frac{1}{2}}\hbar^2(\mathcal{A}-\mathcal{B}) \\ & +(15)^{\frac{1}{2}}\hbar^4(\tfrac{5}{2}\tau_1-\tfrac{5}{2}\tau_2-\tau_4+\tau_5-2\tau_7+2\tau_8 \\ & \qquad +\tfrac{5}{2}\rho_1-\tfrac{5}{2}\rho_2-\rho_4+\rho_5-\tfrac{1}{2}\rho_7+\tfrac{1}{2}\rho_8 \\ & \qquad -\tfrac{1}{4}\rho_{11}+\tfrac{1}{4}\rho_{13}+\tfrac{1}{4}\rho_{14}-\tfrac{1}{4}\rho_{15})\end{aligned}$$

$$\begin{aligned}\alpha_5 = {} & 10\hbar^2(\mathcal{A}+\mathcal{B}+2\mathcal{C}) \\ & +\hbar^4(\tfrac{41}{2}\tau_1+\tfrac{41}{2}\tau_2+68\tau_3+32\tau_4+32\tau_5+27\tau_6+64\tau_7+64\tau_8+54\tau_9 \\ & \qquad +\tfrac{41}{2}\rho_1+\tfrac{41}{2}\rho_2+68\rho_3+32\rho_4+32\rho_5+27\rho_6+27\rho_7+27\rho_8+27\rho_9 \\ & \qquad +16\rho_{10}+\tfrac{27}{2}\rho_{11}+16\rho_{12}+\tfrac{27}{2}\rho_{13}+16\rho_{14}+16\rho_{15})\end{aligned}$$

$$\begin{aligned}\beta_5 = {} & 6\hbar^2(\mathcal{A}+\mathcal{B}-2\mathcal{C}) \\ & +\hbar^4(15\tau_1+15\tau_2-60\tau_3+30\tau_6+60\tau_9 \\ & \qquad +15\rho_1+15\rho_2-60\rho_3+30\rho_6+3\rho_7+3\rho_8+24\rho_9 \\ & \qquad +\tfrac{9}{2}\rho_{11}+\tfrac{9}{2}\rho_{13}+\tfrac{21}{2}\rho_{14}+\tfrac{21}{2}\rho_{15})\end{aligned}$$

$$\begin{aligned}
\gamma_5 = {} & (7)^{\frac{1}{2}}\hbar^2(\mathcal{A}-\mathcal{B}) \\
& +\tfrac{1}{2}(7)^{\frac{1}{2}}\hbar^4(5\tau_1-5\tau_2-10\tau_4+10\tau_5-20\tau_7+20\tau_8 \\
& \quad +5\rho_1-5\rho_2-10\rho_4+10\rho_5-9\rho_7+9\rho_8 \\
& \quad -4\rho_{10}-\tfrac{9}{2}\rho_{11}+4\rho_{12}+\tfrac{9}{2}\rho_{13}+\tfrac{1}{2}\rho_{14}-\tfrac{1}{2}\rho_{15})
\end{aligned}$$

$$\begin{aligned}
\alpha_6 = {} & \hbar^2(20\mathcal{A}+10\mathcal{B}+10\mathcal{C}) \\
& +\hbar^4(68\tau_1+\tfrac{41}{2}\tau_2+\tfrac{41}{2}\tau_3+27\tau_4+32\tau_5+32\tau_6+54\tau_7+64\tau_8+64\tau_9 \\
& \quad +68\rho_1+\tfrac{41}{2}\rho_2+\tfrac{41}{2}\rho_3+27\rho_4+32\rho_5+32\rho_6+27\rho_7+27\rho_8+27\rho_9 \\
& \quad +16\rho_{10}+16\rho_{11}+\tfrac{27}{2}\rho_{12}+16\rho_{13}+16\rho_{14}+\tfrac{27}{2}\rho_{15})
\end{aligned}$$

$$\begin{aligned}
\beta_6 = {} & \hbar^2(9\mathcal{A}-\mathcal{B}-8\mathcal{C}) \\
& +\tfrac{1}{2}\hbar^4(90\tau_1-5\tau_2-40\tau_3-45\tau_4-35\tau_5+35\tau_6-90\tau_7-70\tau_8+70\tau_9 \\
& \quad +90\rho_1-5\rho_2-40\rho_3-45\rho_4-35\rho_5+35\rho_6-36\rho_7-36\rho_8+27\rho_9 \\
& \quad -\tfrac{35}{2}\rho_{10}-14\rho_{11}-\tfrac{45}{2}\rho_{12}-14\rho_{13}+13\rho_{14}+8\rho_{15})
\end{aligned}$$

$$\begin{aligned}
\gamma_6 = {} & (7)^{\frac{1}{2}}\tfrac{3}{2}\hbar^2(\mathcal{A}-\mathcal{B}) \\
& +(7)^{\frac{1}{2}}\tfrac{3}{4}\hbar^4(10\tau_1-5\tau_2-5\tau_4+5\tau_5-5\tau_6-10\tau_7+10\tau_8-10\tau_9 \\
& \quad +10\rho_1-5\rho_2-5\rho_4+5\rho_5-5\rho_6-4\rho_7+4\rho_8-5\rho_9 \\
& \quad -\tfrac{3}{2}\rho_{10}-2\rho_{11}+\tfrac{3}{2}\rho_{12}+2\rho_{13}-2\rho_{14}-3\rho_{15})
\end{aligned}$$

$$\begin{aligned}
\alpha_7 = {} & \hbar^2(10\mathcal{A}+20\mathcal{B}+10\mathcal{C}) \\
& +\hbar^4(\tfrac{41}{2}\tau_1+68\tau_2+\tfrac{41}{2}\tau_3+32\tau_4+27\tau_5+32\tau_6+64\tau_7+54\tau_8+64\tau_9 \\
& \quad +\tfrac{41}{2}\rho_1+68\rho_2+\tfrac{41}{2}\rho_3+32\rho_4+27\rho_5+32\rho_6+27\rho_7+27\rho_8+27\rho_9 \\
& \quad +\tfrac{27}{2}\rho_{10}+16\rho_{11}+16\rho_{12}+16\rho_{13}+\tfrac{27}{2}\rho_{14}+16\rho_{15})
\end{aligned}$$

$$\begin{aligned}
\beta_7 = {} & \hbar^2(-\mathcal{A}+9\mathcal{B}-8\mathcal{C}) \\
& +\tfrac{1}{2}\hbar^4(-5\tau_1+90\tau_2-40\tau_3-35\tau_4-45\tau_5+35\tau_6-70\tau_7-90\tau_8+70\tau_9 \\
& \quad -5\rho_1+90\rho_2-40\rho_3-35\rho_4-45\rho_5+35\rho_6-36\rho_7-36\rho_8+27\rho_9 \\
& \quad -45\rho_{10}-14\rho_{11}-\tfrac{35}{2}\rho_{12}-14\rho_{13}+8\rho_{14}+13\rho_{15})
\end{aligned}$$

$$\gamma_7 = \frac{3}{2}(7)^{\frac{1}{2}}\hbar^2(a-b)$$

$$+\frac{3}{4}(7)^{\frac{1}{2}}\hbar^4(5\tau_1-10\tau_2-5\tau_4+5\tau_5+5\tau_6-10\tau_7+10\tau_8+10\tau_9$$

$$+5\rho_1-10\rho_2-5\rho_4+5\rho_5+5\rho_6-4\rho_7+4\rho_8+5\rho_9$$

$$-\frac{3}{2}\rho_{10}-2\rho_{11}+\frac{3}{2}\rho_{12}+2\rho_{13}+3\rho_{14}+2\rho_{15})$$

$$\alpha_8 =20h^2(a+b+c)$$

$$+\hbar^4(68\tau_1+68\tau_2+68\tau_3+82\tau_4+82\tau_5+82\tau_6+164\tau_7+164\tau_8$$

$$+68\rho_1+68\rho_2+68\rho_3+82\rho_4+82\rho_5+82\rho_6+77\rho_7+77\rho_8+77\rho_9$$

$$+41\rho_{10}+41\rho_{11}+41\rho_{12}+41\rho_{13}+41\rho_{14}+41\rho_{15}+164\tau_9)$$

$$\beta_8 = 6h^2(a+b-2c)$$

$$+\hbar^4(30\tau_1+30\tau_2-60\tau_3-30\tau_4-30\tau_5+60\tau_6-60\tau_7-60\tau_8+120\tau_9$$

$$+30\rho_1+30\rho_2-60\rho_3-30\rho_4-30\rho_5+60\rho_6-27\rho_7-27\rho_8+54\rho_9$$

$$-15\rho_{10}-\frac{21}{2}\rho_{11}-15\rho_{12}-\frac{21}{2}\rho_{13}+\frac{51}{2}\rho_{14}+\frac{51}{2}\rho_{15})$$

$$\gamma_8 = 3(3)^{\frac{1}{2}}\hbar^2(a-b)$$

$$+\frac{3}{4}(3)^{\frac{1}{2}}\hbar^4(20\tau_1-20\tau_2-20\tau_4+20\tau_5-40\tau_7+40\tau_8$$

$$+20\rho_1-20\rho_2-20\rho_4+20\rho_5-18\rho_7+18\rho_8$$

$$-8\rho_{10}-9\rho_{11}+8\rho_{12}+9\rho_{13}+\rho_{14}-\rho_{15}).$$

*The rotational energy levels are designated by $E(J_{K_{-1}K_1})$.

APPENDIX III

Herein are given the nonvanishing matrix elements of h_a^+, h_b^+, and h_c^+ introduced in Chapter VI.

$$(K|h_a^+|K\pm 2) = \mp i\tfrac{1}{2}[\tfrac{1}{4}\hbar^4(\tau_{10}+\tau_{11})f+\tfrac{1}{4}\hbar^4\tau_{13}(2K\pm 1)(2K\pm 3)$$

$$-\tfrac{1}{4}\hbar^4(\tau_{10}+\tau_{11}+2\tau_{12})(K^2\pm 2K+2) + \hbar^2\varepsilon$$

$$\times [f-K(K\pm 1)]^{\frac{1}{2}}[f-(K\pm 1)(K\pm 2)]^{\frac{1}{2}}$$

$$(K|h_a^+|K\pm 4) = \mp i(1/16)\hbar^4(\tau_{10}-\tau_{11})$$

$$\times [f-K(K\pm 1)]^{\frac{1}{2}}[f-(K\pm 1)(K\pm 2)]^{\frac{1}{2}}$$

$$\times [f-(K\pm 2)(K\pm 3)]^{\frac{1}{2}}[f-(K\pm 3)(K\pm 4)]^{\frac{1}{2}}$$

$$(K|h_b^+|K\pm 1) = \mp i\tfrac{1}{2}(2K\pm 1)[f-K(K\pm 1)]^{\frac{1}{2}}$$

$$\times [(1/8)\hbar^4(3\tau_{14}+\tau_{16}+2\tau_{17})f$$

$$-(1/8)\hbar^4(3\tau_{14}+\tau_{16}+2\tau_{17})K^2$$

$$-\tfrac{1}{2}\hbar^4(\pm\tfrac{3}{4}\tau_{14}-\tau_{15}\pm\tfrac{1}{4}\tau_{16}\pm\tfrac{1}{2}\tau_{17})K$$

$$+\hbar^2\varepsilon(-\tfrac{1}{2}\hbar^4\tau_{14}+\tfrac{1}{4}\hbar^4\tau_{16}-\tfrac{3}{4}\hbar^4\tau_{17})]$$

$$(K|h_b^+|K\pm 3) = \pm i(1/16)\hbar^4(\tau_{14}-\tau_{16}-2\tau_{17})(2K\pm 3)$$

$$\times [f-K(K\pm 1)]^{\frac{1}{2}}[f-(K\pm 1)(K\pm 2)]^{\frac{1}{2}}[f-(K\pm 2)(K\pm 3)]^{\frac{1}{2}}$$

$$(K|h_c^+|K\pm 3) = (1/16)\hbar^4(\tau_{18}-\tau_{20}-2\tau_{21})(2K\pm 3)$$

$$\times [f-K(K\pm 1)]^{\frac{1}{2}}[f-(K\pm 1)(K\pm 2)]^{\frac{1}{2}}[f-(K\pm 2)(K\pm 3)]^{\frac{1}{2}}$$

$$
\begin{aligned}
(K|h_c{}^{+}|K\pm 1) = {} & \tfrac{1}{2}(2K\pm 1)\left[f-K(K\pm 1)\right]^{\frac{1}{2}} \\
& \times \Big[(1/8)\hbar^4(3\tau_{18}+\tau_{20}+2\tau_{21})f \\
& -(1/8)\hbar^4(3\tau_{18}+\tau_{20}+2\tau_{21})K^2 \\
& -\tfrac{1}{2}\hbar^4(\pm\tfrac{3}{4}\tau_{18}-\tau_{19}\pm\tfrac{1}{4}\tau_{20}\pm\tfrac{1}{2}\tau_{21})K \\
& +\hbar^2\mathcal{T}-\tfrac{1}{2}\hbar^4\tau_{18}+\tfrac{1}{4}\hbar^4\tau_{20}-\tfrac{3}{4}\hbar^4\tau_{21})\Big].
\end{aligned}
$$

APPENDIX IV

Here is the detailed expression of $[\alpha\beta\gamma\delta\epsilon\eta]$.

$$[\alpha\beta\gamma\delta\epsilon\eta] = -\frac{\hbar}{8}\sum_{\substack{mn\\ m\neq n}}\Big\{{}^{\alpha\beta}S^m\big({}^{\gamma}S_{mn}\,{}^{\delta\epsilon\eta}_{(2)}U^n + {}^{\eta}S_{mn}\,{}^{\gamma\delta\epsilon}_{(2)}U^n\big)$$

$$+\,{}^{\epsilon\eta}S^m\big({}^{\alpha}S_{mn}\,{}^{\beta\gamma\delta}_{(2)}U^n + {}^{\delta}S_{mn}\,{}^{\alpha\beta\gamma}_{(2)}U^n\big)\Big\}$$

$$+\frac{\hbar}{8}\sum_{mn}\Big\{{}^{\alpha\beta}S^m\big({}^{\gamma\delta}S^n\,{}^{\epsilon\eta}_{(2)}U_{mn} + {}^{\epsilon\eta}S^n\,{}^{\gamma\delta}_{(2)}U_{mn}\big)$$

$$+\,{}^{\epsilon\eta}S^m\big({}^{\alpha\beta}S^n\,{}^{\gamma\delta}_{(2)}U_{mn} + {}^{\gamma\delta}S^n\,{}^{\alpha\beta}_{(2)}U_{mn}\big)\Big\}(1+\delta_{mn})$$

$$-\frac{\hbar}{2}\sum_{n}\frac{1}{\lambda_n^{\frac{1}{2}}}\Big(2\,{}^{\alpha\beta\gamma}_{(2)}U^n+\frac{1}{3}\,{}^{\alpha\beta\gamma}\alpha^n\Big)\Big(2\,{}^{\delta\epsilon\eta}_{(2)}U^n+\frac{1}{3}\,{}^{\delta\epsilon\eta}\alpha^n\Big).$$

where

$${}^{\alpha\beta}S^m = \frac{a_m^{\alpha\beta}}{2I^0_{\alpha\alpha}\,I^0_{\beta\beta}\,\hbar^{3/2}\lambda_m^{3/4}}$$

$${}^{\alpha}S_{mn} = \frac{\zeta^{\alpha}_{mn}\,(\lambda_m+\lambda_n)}{(\lambda_m-\lambda_n)I^0_{\alpha\alpha}\lambda_m^{\frac{1}{4}}\lambda_n^{\frac{1}{4}}}$$

$${}^{\alpha\beta\gamma}_{(2)}U^n = \frac{\lambda_n^{\frac{1}{4}}}{16\hbar^{\frac{1}{2}}I^0_{\alpha\alpha}\,I^0_{\beta\beta}\,I^0_{\gamma\gamma}}\sum_{\substack{l\\ l\neq n}}\frac{(3\lambda_l-\lambda_n)}{\lambda_l(\lambda_n-\lambda_l)}\big(\zeta^{\alpha}_{ln}a_l^{\beta\gamma}+\zeta^{\gamma}_{ln}a_l^{\alpha\beta}\big)+\frac{1}{3}\,{}^{\alpha\beta\gamma}\alpha^n$$

$${}^{\alpha\beta\gamma}\alpha^n = \frac{1}{4\hbar^{\frac{1}{2}}\lambda_n^{3/4}}\Big\{\frac{a_n^{\alpha'\gamma}\delta_{\alpha'\beta}}{I^0_{\alpha\alpha}\,I^0_{\beta\beta}\,I^0_{\gamma\gamma}}+\frac{a_n^{\beta'\gamma}\delta_{\alpha\beta''}}{I^0_{\alpha\alpha}\,I^0_{\beta\beta}\,I^0_{\gamma\gamma}}+\frac{a_n^{\alpha\beta'}\delta_{\beta''\gamma}}{I^0_{\alpha\alpha}\,I^0_{\beta'\beta'}\,I^0_{\gamma\gamma}}$$

$$+\frac{a_n^{\alpha\gamma'}\delta_{\beta\gamma''}}{I^0_{\alpha\alpha}\,I^0_{\beta\beta}\,I^0_{\gamma'\gamma'}}-\frac{a_n^{\alpha''\gamma}\delta_{\alpha'\beta}}{I^0_{\alpha'\alpha'}\,I^0_{\beta\beta}\,I^0_{\gamma\gamma}}-\frac{a_n^{\beta''\gamma}\delta_{\alpha\beta'}}{I^0_{\alpha\alpha}\,I^0_{\beta'\beta'}\,I^0_{\gamma\gamma}}$$

$$-\frac{a_n^{\alpha\beta''}\delta_{\beta'\gamma}}{I^0_{\alpha\alpha}\,I^0_{\beta'\beta'}\,I^0_{\gamma\gamma}}-\frac{a_n^{\alpha\gamma'}\delta_{\beta\gamma}}{I^0_{\alpha\alpha}\,I^0_{\beta\beta}\,I^0_{\gamma\gamma}}\Big\}$$

$${}^{\alpha\beta}_{(2)}U_{mn} = \frac{3\hbar}{8I^0_{\alpha\alpha}\,I^0_{\beta\beta}\,(\lambda_m\lambda_n)^{\frac{1}{4}}(1+\delta_{mn})}\sum_{\xi}\frac{(a_m^{\alpha\xi}a_n^{\beta\xi}+a_n^{\alpha\xi}a_m^{\beta\xi})}{I^0_{\xi\xi}}$$

$$+\frac{\pi c\hbar^{\frac{1}{2}}}{4I^0_{\alpha\alpha}\,I^0_{\beta\beta}}\sum_{l}K_{mnl}\,a_l^{\alpha\beta}\,(1+\delta_{ml}+\delta_{nl})\Big(\frac{1}{\lambda_l^{3/4}}+\frac{C_{mn,l}}{\lambda_l^{\frac{1}{4}}}\Big)$$

$$+ \frac{\hbar}{8I^{0}_{\alpha\alpha} I^{0}_{\beta\beta} (\lambda_m \lambda_n)^{\frac{1}{4}} (1+\delta_{mn})}$$

$$\times \left\{ \sum_{\substack{l \\ l \neq n}} (\zeta^{\alpha}_{ml} \zeta^{\beta}_{nl} + \zeta^{\beta}_{ml} \zeta^{\alpha}_{nl}) \frac{\lambda_n + \lambda_l}{\lambda_n - \lambda_l} (1 + \frac{\delta_{ml}}{3}) \right.$$

$$+ \sum_{\substack{l \\ l \neq m}} (\zeta^{\alpha}_{ml} \zeta^{\beta}_{nl} + \zeta^{\beta}_{ml} \zeta^{\alpha}_{nl}) \frac{\lambda_m + \lambda_l}{\lambda_m - \lambda_l} (1 + \frac{\delta_{nl}}{3})$$

$$- \frac{\hbar (\lambda_m + \lambda_n) \zeta^{\gamma}_{mn}}{6(\lambda_m - \lambda_n)(\lambda_m \lambda_n)^{\frac{1}{4}} I^{0}} \left(\frac{1}{I^{0}_{\gamma\gamma}} - \frac{1}{I^{0}_{\gamma'\gamma'}} \right) \quad \begin{pmatrix} \alpha \neq \beta \\ m \neq n \end{pmatrix}$$

and

$$C_{mn,l} = \lambda_l^{\frac{1}{2}} (\lambda_l - \lambda_m - \lambda_n)(\lambda_m^{\frac{1}{2}} + \lambda_n^{\frac{1}{2}} + \lambda_l^{\frac{1}{2}})^{-1} (\lambda_m^{\frac{1}{2}} + \lambda_n^{\frac{1}{2}} - \lambda_l^{\frac{1}{2}})^{-1}$$
$$(\lambda_m^{\frac{1}{2}} - \lambda_n^{\frac{1}{2}} - \lambda_l^{\frac{1}{2}})^{-1} (\lambda_m^{\frac{1}{2}} - \lambda_n^{\frac{1}{2}} + \lambda_l^{\frac{1}{2}})^{-1}$$

The primed Greek superscripts and subscripts (e.g. α, α', and α'') are defined such that the order $\alpha, \alpha', \alpha''$ presents a cyclic permutation of x, y, z.

BIBLIOGRAPHY

1. E. B. Wilson, Jr. and J. B. Howard, J. Chem. Phys. 4, 262 (1936).
2. B. T. Darling and D. M. Dennison, Phys. Rev. 57, 128 (1940).
3. M. Goldsmith, G. Amat, and H. H. Nielsen, J. Chem. Phys. 24, 1178 (1956).
4. M. Goldsmith, G. Amat, and H. H. Nielsen, J. Chem. Phys. 27, 838 (1957).
5. G. Amat and H. H. Nielsen, J. Chem. Phys. 27, 845 (1957).
6. G. Amat and H. H. Nielsen, J. Chem. Phys. 29, 665 (1958).
7. For example, M. L. Grenier-Besson, J. Physique Rad. 21, 555 (1960)
8. M. Born and R. Oppenheimer, Ann. Physik 84, 457 (1927).
9. H. H. Nielsen, Handbuch der Physik Vol. XXXVII/1, 173 (1959).
10. H. Goldstein, Classical Mechanics (Addison-Wesley Publishing Company, 1950).
11. C. Eckart, Phys. Rev. 47, 552 (1932).
12. G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules (D. Van Nostrand Company, Inc., 1945).
13. T. Oka and Y. Morino, J. Phys. Soc. Japan 16, 1235 (1961).
14. B. Podolsky, Phys. Rev. 32, 812 (1928).
15. J. H. Van Vleck, Phys. Rev. 33, 467 (1929).
16. W. H. Shaffer, H. H. Nielsen, and L. H. Thomas, Phys. Rev. 56, 895 (1939)
17. R. C. Herman and W. H. Shaffer, J. Chem. Phys. 16, 453 (1948).

18. G. Amat and H. H. Nielsen, J. Chem. Phys. 36, 1859 (1962).

19. R. S. Mulliken, Phys. Rev. 59, 873 (1941).

20. S. C. Wang, Phys. Rev. 34, 243 (1929).

21. B. S. Ray, Z. Phys. 78, 74 (1932).

22. R. M. Hainer, P. C. Cross, and G. W. King, J. Chem. Phys. 17, 826 (1949).

23. G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. 11, 27 (1943).

24. For example, T. E. Turner, B. L. Hicks, and G. Reitwiesner, Ballistics Research Laboratories Report No. 878 (1953).

25. W. S. Benedict, Phys. Rev. 75, 1317A (1949).

26. P. M. Parker and L. C. Brown, J. Chem. Phys. 31, 1227 (1959).

27. D. Kivelson and E. B. Wilson, Jr., J. Chem. Phys. 20, 1575 (1952).

28. J. M. Dowling, J. Mol. Spectroscopy 6, 550 (1961).

29. R. A. Hill and T. H. Edwards, J. Mol. Spectroscopy 9, 494 (1962).