STUDIES IN THE CENTRIFUGAL DISTORTION THEORY OF TRIANGULAR TRIATOMIC MOLECULES

By

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ABSTRACT

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In this dissertation the molecular vibration-rotation Hamiltonian of Darling and Dennison is used in the expanded form of Nielsen, Amat, and Goldsmith. Expressions for four linearly independent linear combinations of the ten sextic centrifugal distortion coefficients of triangular triatomic molecules are presented. These combinations are formed in such a way that the resulting expressions depend only on the equilibrium geometry and the harmonic force field of the molecule. These expressions appear to be potentially useful as a set of planarity-constraints on the ten sextic coefficients obtained in the expansion of the Darling-Dennison Hamiltonian and can be utilized to effect a Watson-type reduction of the sextic portion of the Hamiltonian. Also in this dissertation, the quartic and sextic centrifugal distortion coefficients of ozone have been calculated and the results compared with experiment. The agreement is found to be quite satisfactory.

Dedicated to

Gholamhossein Gharehgozloo Hamedani, my husband

and

Mahmoud Niroomand-Rad, my father

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1. INTRODUCTION

One of the principal tasks of the molecular spectroscopist is to determine and to interpret the vibration-rotation energy level structure of the molecule under study. The analysis of the infrared spectra of molecules in the gas phase gives precise information about the vibration-rotation energies, and knowledge of these energies can lead to the accurate determination of molecular constants such as bond distances, bond angles, vibrational frequencies, force contants, centrifugal distortion constants, etc. An understanding of these quantities is relevant in the determination of the detailed structure and properties of the molecule and helps to better interpret the physical and chemical properties of bulk matter.

The vibration-rotation Hamiltonian of diatomic molecules has been treated to fourth and even higher orders of approximation many years ago, and also the case of linear triatomic molecules (CO_2-type molecules) has been studied extensively. It appears generally to be quite impossible to find exact analytic expressions for the energy levels of polyatomic molecules. For this reason, assumptions must be made which one hopes are valid in practice, and the general theoretical expression for the energies of polyatomic molecules must be treated by an expansion formalism in successive orders of approximation. For instance, assuming the validity of the Born-Oppenheimer approximation allows separation of the vibration-rotation motion of the nuclei from the electronic motion to a high degree of accuracy. Similarly, it has been found that one can often safely ignore the energy contribution of the nuclear spins to a high order of approximation.

During the last decade, the field of high resolution molecular spectroscopy has experienced many impressive developments in instrumentation, resulting in particular from the availability of on-line computing facilities, sensitive detectors, the progress of interferometric methods, and the use of laser sources and detection methods. For many polyatomic molecules, high quality rotation and rotation-vibration spectra are being obtained both in the infrared and the microwave regions. The complete interpretation of such spectra requires the use of very accurate formulas for the frequencies of the spectral lines expressed in terms of quantum numbers and molecular parameters. To this end, it is necessary to compute rotation-vibration energies to a high order of accuracy which means that fourth, and even higher, orders of perturbation theory need to be considered. In cases such as the triangular XYX-type (H_2O-type) molecule, fourth-order centrifugal distortion coefficients are required in order to account for the observed results to the experimental accuracy attainable, in some cases even for the low values of the angular momentum quantum number J[1]. Therefore, one needs to consider a fourth-order Hamiltonian to get a satisfactory and theoretically meaningful fit to the spectral data.

The general vibration-rotation Hamiltonian for asymmetric rotator molecules has been developed by Chung and Parker in the Nielsen-Amat Goldsmith[2] expansion of the Darling-Dennison vibration-rotation Hamiltonian through the consideration of symmetry restrictions imposed by the applicable asymmetric rotator point group. Later on, Watson[3] succeeded in developing a form of the Darling-Dennison Hamiltonian which greatly simplified subsequent calculations. However, even with this simplification, the general formulation of Amat-Nielsen-Goldsmith[4,5] is unnecessarily complicated when applied to the case of the asymmetric rotator, principally because of its inclusion of degenerate normal modes of vibration which are absent in asymmetric rotator molecules. Therefore, instead of working with the general formulation, Chan and Parker[6] started with the Darling-Dennison vibration-rotation Hamiltonian in Watson's simplified form for the XYZ-type molecule. Then the Hamiltonian was expanded and subjected to two successive contact transformations of the Van Vleck type. The resulting Hamiltonian for a given vibrational state has the form of a power series in the angular momentum components. By using an extended version of Watson's theory[3], this Hamiltonian can be related to experimental results in such a manner that meaningful fits to high-resolution experimental data are possible, at least in principle. Calculation of a complete set of fourth-order centrifugal distortion coefficients for XYZ and XYX-type triangular molecules was carried out by Sumberg and Parker[7] in a form which exhibits extensive cyclic and algebraic regularities and which could readily be used in the present work to determine a number of constraints on the sextic coefficients due to the planarity of the nuclear framework configuration of the molecule.

For the general case of asymmetric rotator molecules, Watson has shown that the number of independent sextic coefficients (or independent linear combination of these) is seven. The constraint due to planarity reduces this number by one, to a total of six. The principal aim of this thesis work was to find and to calculate, for triangular triatomic molecules, four linearly independent linear combinations of the ten sextic centrifugal distortion coefficients which would represent the complete specification of the constraint that reduces the ten original coefficients to six independent ones. This attempt was successful, since the linear combinations that were determined depend only on the equilibrium geometry and the harmonic force field parameters of the molecule, quantities which are ordinarily known to much better precision than either the calculated or the empirical values of the sextic coefficients.

The triangular XYX-type molecule is considered explicitly as a special case which leads to simplified expressions due to the higher symmetry. Finally, the complete set of centrifugal distortion coefficients of ozone has been calculated and the results were compared with the available experimental data. The agreement was found to be quite satisfactory.

2. MOLECULAR VIBRATION-ROTATION HAMILTONIAN

2.1 The Darling-Dennison Hamiltonian

For any theoretical calculation of the energies of a molecule, it is necessary to formulate a suitable quantum mechanical Hamiltonian. The total Hamiltonian of a molecule would have to include an electronic part as well as a vibration-rotation part. The electronic energy is not of interest here, since we wish to consider vibration-rotation transitions 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 wavefunction of the electronic state is almost independent of the change in the internuclear distances, the Born-Oppenheimer approximation is valid in many cases, especially when the electronic state is one of zero total electronic angular momentum. To the accuracy of the approximation, the total wavefunction can be written as the product of an electronic and a vibration-rotational wavefunction. For the present work, only the vibration-rotation Hamiltonian is of direct interest.

The Schrödinger equation

$$(H - E)\Psi = 0 \tag{2-1}$$

of a rotating and vibrating polyatomic molecule was first discussed by Wilson and Howard,[9] and somewhat later by Darling and Dennison.[10] The second formulation is now known to be equivalent to that of the former authors and proves more convenient for the present discussion. Essentially, the derivation is based on a classical development of the vibrational and rotational energies, subsequently transcribed into the proper quantum mechanical operator form. We therefore begin with the Darling-Dennison Hamiltonian for a polyatomic molecule which reads:

$$H = \tfrac{1}{2}\mu^{\frac{1}{4}}\Sigma_{\alpha,\beta}(P_\alpha - p_\alpha)\mu_{\alpha\beta}\mu^{-\frac{1}{2}}(P_\beta - p_\beta)\mu^{\frac{1}{4}}$$

$$+ \tfrac{1}{2}\mu^{\frac{1}{4}}\Sigma_s\, p_s^{*}\mu^{-\frac{1}{2}}p_s^{*}\mu^{\frac{1}{4}} + V\ . \qquad (2\text{-}2)$$

The lower-case Greek indices α and β (and lower-case Greek indices in general) range over x, y, and z, the principal axes directions of the equilibrium inertia tensor of the molecule. The (x,y,z) coordinate system is fixed with respect to the equilibrium configuration of the molecule ("body-fixed") and its origin is taken to coincide with the instantaneous center of mass. Let the equilibrium and instantaneous positions of the i-th nuclei in (x,y,z) be denoted by α_{o_i} and α_i, respectively. Then the displacement of the i-th nucleus from its position of equilibrium is:

$$\vec{\alpha}_i' = \vec{\alpha}_i - \vec{\alpha}_{0_i}\ . \qquad (2\text{-}3)$$

In Eq. (2-2), P_α is the α-th component of the total angular momentum referred to the body-fixed axes and can be expressed solely in terms of the Euler angles and the time derivatives with respect to these angles. Thus the Euler angles can be taken as the rotational coordinates of the problem. The vibrational coordinates to be used in connection with Eq. (2-2) are the normal coordinates Q_s. To transform to the normal coordinates, a set of transformation coefficients ℓ^{α}_{is} is introduced which transforms mass-weighted cartesian to normal coordinates as follows:

$$\sqrt{m_i}\alpha'_i = \Sigma_s \ell^{\alpha}_{is} Q_s \ . \tag{2-4}$$

Here m_i is the mass of the i-th nucleus. For asymmetric rotor molecules, no index enumerating essential degenerate modes of vibration is required as these do not occur.[11] The vibrational momentum p^*_s conjugate to the normal coordinate Q_s is defined as:

$$p^*_s = -i\hbar\frac{\partial}{\partial Q_s} \ . \tag{2-5}$$

The internal angular momentum p_α occurring in Eq. (2-2) can then be defined as:

$$p_\alpha = \Sigma_s A^{\alpha}_s p^*_s = \Sigma_s \Sigma_{s'} \zeta_{s's} Q_{s'} p^*_s \ , \tag{2-6}$$

where

$$\zeta^{\alpha}_{s's} = \Sigma_i(\ell^{\beta}_{is'}\ell^{\gamma}_{is} - \ell^{\beta}_{is}\ell^{\gamma}_{is'}), \qquad \alpha,\beta,\gamma \ \text{cyclic} \tag{2-7}$$

$$A^{\alpha}_s = \Sigma_{s'}\Sigma_i(\ell^{\beta}_{is'}\ell^{\gamma}_{is} - \ell^{\beta}_{is}\ell^{\gamma}_{is'})Q_{s'}$$

$$= \Sigma_{s'}\zeta^{\alpha}_{s's}Q_{s'} \ , \qquad \alpha,\beta,\gamma \ \text{cyclic.} \tag{2-8}$$

The $\zeta^{\alpha}_{s's}$ are the Coriolis coupling coefficients. It is clear from their definition that $\zeta^{\alpha}_{s's} = -\zeta^{\alpha}_{ss'}$ and $\zeta^{\alpha}_{ss} = 0$.

The effective moments and products of inertia, $I'_{\alpha\alpha}$ and $I'_{\alpha\beta}$ are defined, respectively, by:

$$I'_{\alpha\alpha} = I_{\alpha\alpha} - \Sigma_s (A_s^{\alpha})^2, \qquad (2\text{-}9)$$

$$I'_{\alpha\beta} = -I_{\alpha\beta} + \Sigma_s A_s^{\alpha} A_s^{\beta} , \qquad \alpha \neq \beta \qquad (2\text{-}10)$$

where

$$I_{\alpha\alpha} = \Sigma_i m_i (\beta_i^2 + \gamma_i^2), \qquad \alpha \neq \beta \neq \gamma \qquad (2\text{-}11)$$

$$I_{\alpha\beta} = -\Sigma_i m_i \alpha_i \beta_i, \qquad \alpha \neq \beta \qquad (2\text{-}12)$$

are the instantaneous moments and products of inertia. The effective inertia tensor and its determinant are defined by:

$$[\mu]^{-1} = \begin{bmatrix} I'_{xx} & -I'_{xy} & -I'_{xz} \\ -I'_{yx} & I'_{yy} & -I'_{yz} \\ -I'_{zx} & -I'_{zy} & I'_{zz} \end{bmatrix} = [I'] , \qquad (2\text{-}13)$$

$$[\mu] = [I']^{-1} , \qquad (2\text{-}14)$$

$$\mu = \det[\mu] = \frac{1}{\det[I']} , \qquad (2\text{-}15)$$

$$\mu_{\alpha\beta} = \mu(I'_{\gamma\gamma} I'_{\alpha\beta} + I'_{\alpha\gamma} I'_{\beta\gamma}), \quad \alpha \neq \beta \neq \gamma \qquad (2\text{-}16)$$

$$\mu_{\alpha\alpha} = \mu(I'_{\beta\beta} I'_{\gamma\gamma} - I'^{2}_{\beta\gamma}), \qquad \alpha \neq \beta \neq \gamma . \qquad (2\text{-}17)$$

The components of the effective rotational angular momentum, $P_\alpha - p_\alpha$, and the components of the angular velocity ω_α are related by

$$[P - p] = [I'][\omega] . \qquad (2\text{-}18)$$

Finally, V is the effective vibrational potential energy which is usually written as a positive definite power series in the normal coordinate Q_s, with the harmonic portion, quadratic in the Q_s, the leading and lowest power terms. All quantities occurring in the Hamiltonian (2-2) have now been defined.

2.2 Watson's Simplification of the Darling-Dennison Hamiltonian

If one commutes out μ from the first two terms of Eq. (2-2), the Darling-Dennison Hamiltonian becomes:

$$H = \tfrac{1}{2}\Sigma_{\alpha,\beta}(P_\alpha - p_\alpha)\mu_{\alpha\beta}(P_\beta - p_\beta) + \tfrac{1}{2}\Sigma_s p_s^{*2} + U + V \qquad (2\text{-}19)$$

where

$$U = -\tfrac{1}{2}\Sigma_{\alpha,\beta}\mu^{\frac{1}{4}}(P_\alpha - p_\alpha)\mu_{\alpha\beta}\mu^{-\frac{1}{2}}[p_\beta,\mu^{\frac{1}{4}}] - \tfrac{1}{2}\Sigma_{\alpha,\beta}\mu^{\frac{1}{4}}[p_\alpha,\mu^{-\frac{1}{2}}]$$
$$\times\ \mu_{\alpha\beta}(P_\beta - p_\beta) + \tfrac{1}{2}\Sigma_s\mu^{\frac{1}{4}}p_s^{*}\mu^{-\frac{1}{2}}[p_s^{*},\mu^{\frac{1}{4}}]$$
$$+\ \tfrac{1}{2}\Sigma_s\mu^{\frac{1}{4}}[p_s^{*},\mu^{-\frac{1}{2}}]p_s^{*}\ . \qquad (2\text{-}20)$$

To obtain this result, one uses the fact that P_α operates only on the Euler angles and thus commutes with all quantities in H except P_β and P_γ.

In applications of Eq. (2-19), it has been customary to start by introducing the power series expansion of $\mu_{\alpha\beta}$ and μ in terms of the normal coordinates, and to evaluate U from these expansions to the desired degree of approximation. However, Watson[3] has been able to show that it is much simpler to use the commutation relations and the properties of the $\mu_{\alpha\beta}$ tensor to evaluate U directly, without first expanding it. After lengthy calculation, Watson finds that:

$$U = -\frac{1}{8}\hbar^2 \Sigma_\alpha \mu_{\alpha\alpha}. \tag{2-21}$$

This amazingly simple result constitutes Watson's simplification of the Darling-Dennison vibration-rotation Hamiltonian which can thus be written as:

$$H = \tfrac{1}{2}\Sigma_{\alpha,\beta}(P_\alpha - p_\alpha)\mu_{\alpha\beta}(P_\beta - p_\beta) + \tfrac{1}{2}\Sigma_s p_s^{2*} - \frac{1}{8}\hbar^2\Sigma_\alpha\mu_{\alpha\alpha} + V . \tag{2-22}$$

This form of the Hamiltonian will be taken as the starting point for the expansion in the normal coordinates in the next section.

2.3 Expansion of the Hamiltonian

In this section, a review of the expansion of the Watson form of the fourth-order of approximation in the energy is given, and terms standing in the various orders of approximation are identified and written out explicitly in Amat-Nielsen-Tarrago[12] and also in Watson[13] notation. We start with Eq. (2-22) and write it as:

$$H = \tfrac{1}{2}\Sigma_{\alpha,\beta}\mu_{\alpha\beta}P_\alpha P_\beta - \tfrac{1}{2}\Sigma_{\alpha,\beta}(p_\alpha\mu_{\alpha\beta} + \mu_{\alpha\beta}p_\alpha)P_\beta + \tfrac{1}{2}\Sigma_{\alpha\beta}p_\alpha\mu_{\alpha\beta}p_\beta$$
$$- \frac{1}{8}\hbar^2\Sigma_\alpha\mu_{\alpha\alpha} + \tfrac{1}{2}\Sigma_s p_s^{*2} + V . \tag{2-23}$$

The terms represent, in succession, the pure rotational energy, the Coriolis coupling energy, a correction to the Coriolis energy, another correction to the Coriolis energy, the vibrational kinetic energy, and the potential energy of vibration.

It is not possible to find directly the eigenvalues of the Hamiltonian (2-23). We therefore seek an expansion in orders of magnitude of the general form:

$$H = H_0 + \lambda H_1 + \lambda^2 H_2 + \lambda^3 H_3 + \lambda^4 H_4 + \ldots \qquad (2\text{-}24)$$

where λ is the expansion parameter. This form will allow us to apply perturbation theory. We begin the expansion by writing the effective moments and products of inertia in terms of the normal coordinates. Substituting the appropriate form of Eq. (2-3) for α_i, β_i and γ_i into Eqs. (2-11) and (2-12), and using Eq. (2-4) to introduce the normal coordinates gives:

$$I_{\alpha\beta} = I^\circ_{\alpha\alpha}\delta_{\alpha\beta} + \Sigma_s\, a_s^{\alpha\beta} Q_s + \Sigma_{s,s'}\, A_{ss'}^{\alpha\beta} Q_s Q_{s'} \qquad \alpha,\ \beta = x,y,z \qquad (2\text{-}25)$$

where

$$I^\circ_{\alpha\alpha} = \Sigma_i\, m_i(\beta_{0_i}^2 + \gamma_{0_i}^2), \qquad \alpha \neq \beta \neq \gamma \qquad (2\text{-}26)$$

$$I^\circ_{\alpha\beta} = -\Sigma_i\, m_i \alpha_{0_i} \beta_{0_i}\ , \qquad (2\text{-}27)$$

$$a_s^{\alpha\alpha} = 2\Sigma_i \sqrt{m_i}\ (\beta_{0_i} \ell_{is}^{\beta} + \gamma_{0_i} \ell_{is}^{\gamma}), \quad \alpha \neq \beta \neq \gamma \qquad (2\text{-}28)$$

$$a_s^{\alpha\beta} = -\Sigma_i \sqrt{m_i}\ (\alpha_{0_i} \ell_{is}^{\beta} + \beta_{0_i} \ell_{is}^{\alpha}), \quad \alpha \neq \beta \neq \gamma \qquad (2\text{-}29)$$

$$A_{ss'}^{\alpha\alpha} = \Sigma_i (\ell_{is}^{\beta} \ell_{is'}^{\beta} + \ell_{is}^{\gamma} \ell_{is'}^{\gamma})\ , \quad \alpha \neq \beta \neq \gamma \qquad (2\text{-}30)$$

$$A_{ss'}^{\alpha\beta} = -\Sigma_i\, \ell_{is}^{\alpha} \ell_{is'}^{\beta}\ , \qquad \alpha \neq \beta\ . \qquad (2\text{-}31)$$

Substitution of Eqs. (2-25) and (2-8) into Eqs. (2-9) and (2-10) gives:

$$I'_{\alpha\beta} = I^\circ_{\alpha\alpha}\delta_{\alpha\beta} + \Sigma_s\, a_s^{\alpha\beta} Q_s + \Sigma_{s,s'} (A_{ss'}^{\alpha\beta})' Q_s Q_{s'} \qquad (2\text{-}32)$$

where

$$(A_{ss'}^{\alpha\beta})' = A_{ss'}^{\alpha\beta} - \Sigma_{s''}\, \zeta_{ss''}^{\alpha} \zeta_{s's''}^{\beta}\ . \qquad (2\text{-}33)$$

The equilibrium products of inertia $I^\circ_{\alpha\beta}$, $\alpha \neq \beta$, are zero in the principal axes system (x,y,z).

Let us now continue with the expansion of the kinetic energy part, H - V, of the Hamiltonian (2-23). To accomplish this, $\mu_{\alpha\beta}$ and $\mu_{\alpha\alpha}$ as defined by Eqs. (2-16) and (2-17) are written as a power series in the normal coordinates. This is permissible, because $\mu_{\alpha\beta}$ and $\mu_{\alpha\alpha}$ are functions of the components of the instantaneous inertia tensor, and therefore functions of the normal coordinates only. The normal coordinates, in turn, are linear combinations of the instantaneous cartesian displacement coordinates, assumed to be small compared to the equilibrium separations. The $\mu_{\alpha\beta}$ take the following general form:

$$\mu_{\alpha\beta} = \mu_{\beta\alpha} = (1/I^\circ_{\alpha\alpha} I^\circ_{\beta\beta})[\Omega(0)^{\alpha\beta} + \Sigma_s\ \Omega(1)^{\alpha\beta}_s Q_s$$
$$+ \Sigma_{s,s'}\ \Omega(2)^{\alpha\beta}_{ss'} Q_s Q_{s'} + \Sigma_{s,s',s''}\ \Omega(3)^{\alpha\beta}_{ss's''} Q_s Q_{s'} Q_{s''}$$
$$+ \Sigma_{s,s',s'',s'''}\ \Omega(4)^{\alpha\beta}_{ss's''s'''} Q_s Q_{s'} Q_{s''} Q_{s'''} + \ldots] \qquad (2\text{-}34)$$

where the various Ω are the coefficients obtained in the expansion. The most compact and convenient form of these coefficients appears to be the one given by Rothman and Clough[14] which is the following:

$$\Omega(0)^{\alpha\beta} = I^\circ_{\alpha\beta}\delta_{\alpha\beta}, \qquad (2\text{-}35)$$

$$\Omega(1)^{\alpha\beta}_s = 2I^\circ_{\alpha\alpha} I^\circ_{\beta\beta} \left(\frac{\lambda_s}{\hbar^2}\right)^{\frac{1}{4}}\ {}^1R^{\alpha\beta}_s \ , \qquad (2\text{-}36)$$

$$\Omega(2)^{\alpha\beta}_{ss'} = 2I^\circ_{\alpha\alpha} I^\circ_{\beta\beta} \left(\frac{\lambda_s\lambda_{s'}}{\hbar^4}\right)^{\frac{1}{4}}\ {}^2R^{\alpha\beta}_{ss'}, \qquad (2\text{-}37)$$

$$\Omega(3)^{\alpha\beta}_{ss's''} = 2I^\circ_{\alpha\alpha} I^\circ_{\beta\beta} \left(\frac{\lambda_s\lambda_{s'}\lambda_{s''}}{\hbar^6}\right)^{\frac{1}{4}}\ {}^3R^{\alpha\beta}_{ss's''}, \qquad (2\text{-}38)$$

$$\Omega(4)^{\alpha\beta}_{ss's''s'''} = 2I^{\circ}_{\alpha\alpha} I^{\circ}_{\beta\beta} \left(\frac{\lambda_s \lambda_{s'} \lambda_{s''} \lambda_{s'''}}{\hbar^8}\right)^{\frac{1}{2}} \, {}^4R^{\alpha\beta}_{ss's''s'''} , \tag{2-39}$$

with

$$ {}^1R^{\alpha\beta}_s = -\frac{A^{\alpha\beta}_s}{2I^{\circ}_{\alpha\alpha}} , \tag{2-40}$$

$$ {}^2R^{\alpha\beta}_{ss'} = -\frac{3}{8} \sum_\gamma \left({}^1R^{\alpha\gamma}_s A^{\gamma\beta}_{s'} + {}^1R^{\alpha\gamma}_{s'} A^{\gamma\beta}_s\right) , \tag{2-41}$$

$$ {}^3R^{\alpha\beta}_{ss's''} = -\frac{2}{9} \sum_\gamma \left({}^2R^{\alpha\gamma}_{ss'} A^{\gamma\beta}_{s''} + {}^2R^{\alpha\gamma}_{ss''} A^{\gamma\beta}_{s'} + {}^2R^{\alpha\gamma}_{s's''} A^{\gamma\beta}_{s}\right), \tag{2.42}$$

$$ {}^4R^{\alpha\beta}_{ss's''s'''} = -\frac{5}{32} \sum_\gamma \left({}^3R^{\alpha\gamma}_{ss's''} A^{\gamma\beta}_{s'''} + {}^3R^{\alpha\gamma}_{ss's'''} A^{\gamma\beta}_{s''} + {}^3R^{\alpha\gamma}_{ss''s'''} A^{\gamma\beta}_{s'} + {}^3R^{\alpha\gamma}_{s's''s'''} A^{\gamma\beta}_{s}\right), \tag{2-43}$$

and

$$A^{\alpha\beta}_s = \frac{a^{\alpha\beta}_s}{I^{\circ}_{\beta\beta}} \left(\frac{\hbar^2}{\lambda_s}\right)^{\frac{1}{2}} . \tag{2-44}$$

In these equations, the λ_s appear in the harmonic potential function as:

$$V_0 = \frac{1}{2} \sum_s \lambda_s Q_s^2 , \tag{2-45}$$

i.e., they are proportional to the squares of the corresponding normal frequencies. The potential energy function can be expanded as the Taylor series:

$$\begin{aligned} V = {} & V_0 + \Sigma_s \left(\frac{\partial V}{\partial \alpha'_s}\right)_0 \alpha'_s + \frac{1}{2!} \Sigma_{s,s'} \left(\frac{\partial^2 V}{\partial \alpha'_s \partial \alpha'_{s'}}\right)_0 \alpha'_s \alpha'_{s'} \\ & + \frac{1}{3!} \Sigma_{s,s',s''} \left(\frac{\partial^3 V}{\partial \alpha'_s \partial \alpha'_{s'} \partial \alpha'_{s''}}\right)_0 \alpha'_s \alpha'_{s'} \alpha'_{s''} + \dots \\ = {} & \tfrac{1}{2} \Sigma_s \lambda_s Q_s^2 + \Sigma_{s \le s' \le s''} K_{ss's''} Q_s Q_{s'} Q_{s''} \\ & + \Sigma_{s \le s' \le s'' \le s'''} K_{ss's''s'''} Q_s Q_{s'} Q_{s''} Q_{s'''} + \dots \end{aligned} \tag{2-46}$$

Since this Taylor series expansion of V is taken about the equilibrium positions of the nuclei, the total force at equilibrium in the s-th normal mode must be equal to zero, hence $\left(\frac{\partial V}{\partial Q_s}\right)_0 = 0$. The constant V_0 has no physical significance and may be set equal to zero, and V then can be rewritten as a function of the normal coordinates, as shown above, with

$$\lambda_s^{\frac{1}{2}} = 2\pi c\, \omega_s, \qquad (2\text{-}47)$$

where ω_s is the s-th normal frequency. The various sets of coefficients K are the force constants of the molecular force field in the various orders of the expansion.

When Eq. (2-34) is substituted into Eq. (2-23), the expanded form of H, Eq. (2-24) is obtained, with:

$$H_0 = \frac{1}{2}\sum_s \sum_\alpha \left\{\frac{P_\alpha^2}{I^\circ_{\alpha\alpha}} + \hbar\lambda_s^{\frac{1}{2}}\left(\frac{p_s^2}{\hbar^2} + q_s^2\right)\right\} \qquad (2\text{-}48)$$

$$H_1 = \frac{1}{2}\sum_s \sum_{\alpha\beta}\left\{\frac{\Omega(1)_s^{\alpha\beta}}{I^\circ_{\alpha\alpha} I^\circ_{\beta\beta}}\left(\frac{\hbar^2}{\lambda_s}\right)^{\frac{1}{2}} q_s P_\alpha P_\beta - \frac{2p_\alpha P_\alpha}{I^\circ_{\alpha\alpha}}\right\} + V_1 \qquad (2\text{-}49)$$

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

$$\left. - \frac{\Omega(1)_s^{\alpha\beta}}{I^\circ_{\alpha\alpha} I^\circ_{\beta\beta}}\left(\frac{\hbar^2}{\lambda_s}\right)^{\frac{1}{2}}(p_\alpha q_s + q_{s'} p_\alpha)P_\beta + \frac{p_\alpha^2}{I^\circ_{\alpha\alpha}}\right\} + V_2 \qquad (2\text{-}50)$$

$$H_3 = \frac{1}{2}\sum_{ss's''} \sum_{\alpha\beta}\left\{\frac{\Omega(3)_{ss's''}^{\alpha\beta}}{I^\circ_{\alpha\alpha} I^\circ_{\beta\beta}}\left(\frac{\hbar^6}{\lambda_s\lambda_{s'}\lambda_{s''}}\right)^{\frac{1}{2}} q_s q_{s'} q_{s''} P_\alpha P_\beta\right.$$

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

$$\left. + \frac{\Omega(1)_s^{\alpha\beta}}{I^\circ_{\alpha\alpha} I^\circ_{\beta\beta}}\left(\frac{\hbar^2}{\lambda_s}\right)^{\frac{1}{2}} p_\alpha q_s p_\beta + \Lambda(3)_s\left(\frac{\hbar^2}{\lambda_s}\right)^{\frac{1}{2}} q_s\right\} + V_3 \qquad (2\text{-}51)$$

$$H_4 = \frac{1}{2} \sum_{ss's''s'''} \sum_{\alpha\beta} \{ \frac{\Omega(4)^{\alpha\beta}_{ss's''s'''}}{I^\circ_{\alpha\alpha} I^\circ_{\beta\beta}} (\frac{\hbar^8}{\lambda_s \lambda_{s'} \lambda_{s''} \lambda_{s'''}})^{\frac{1}{4}} q_s q_{s'} q_{s''} q_{s'''} p_\alpha p_\beta$$

$$- \frac{\Omega(3)^{\alpha\beta}_{ss's''}}{I^\circ_{\alpha\alpha} I^\circ_{\beta\beta}} (\frac{\hbar^6}{\lambda_s \lambda_{s''} \lambda_{s''}})^{\frac{1}{4}} (p_\alpha q_s q_{s'} q_{s''} + q_s q_{s'} q_{s''} p_\alpha) p_\beta$$

$$+ \frac{\Omega(2)^{\alpha\beta}_{ss'}}{I^\circ_{\alpha\alpha} I^\circ_{\beta\beta}} (\frac{\hbar^4}{\lambda_s \lambda_{s'}})^{\frac{1}{4}} p_\alpha q_s q_{s'} p_\beta + \Lambda(4)_{ss'} (\frac{\hbar^4}{\lambda_s \lambda_{s'}})^{\frac{1}{4}} q_s q_{s'} \} + V_4. \quad (2\text{-}52)$$

In these equations, q_s is a dimensionless normal coordinate and p_s is its conjugate momentum defined by:

$$q_s = (\lambda_s / \hbar^2)^{\frac{1}{4}} Q_s, \quad (2\text{-}53)$$

$$p_s = (\hbar^2/\lambda_s)^{\frac{1}{4}} P^*_s \, . \quad (2\text{-}54)$$

The symbols V_1, V_2, V_3 and V_4 denote, respectively, the cubic, quartic, quintic, and sextic portions of the anharmonic potential and are defined through:

$$V_1 = hc \sum_{s \le s' \le s''} k_{ss's''} q_s q_{s'} q_{s''} \, , \quad (2\text{-}55)$$

$$V_2 = hc \sum_{s \le s' \le s''} k_{ss's''s'''} \, q_s q_{s'} q_{s''} q_{s'''} \, , \quad (2\text{-}56)$$

$$V_3 = hc \sum_{\substack{s \le s' \le s'' \\ \le s''' \le s''''}} k_{ss's''s'''s''''} \, q_s q_{s'} q_{s''} q_{s'''} q_{s''''}, \quad (2\text{-}57)$$

$$V_4 = hc \sum_{\substack{s \le s' \le s'' \\ \le s''' \le s'''' \le s'''''}} k_{ss's''s'''s''''s'''''} q_s q_{s'} q_{s''} q_{s'''} q_{s''''} q_{s'''''} \, . \quad (2\text{-}58)$$

The quantities $\Lambda(3)_s$ and $\Lambda(4)_{ss'}$, which appear in H_3 and H_4 originate from the term U and are given by

$$\Lambda(3)_s = -\frac{\hbar^2}{4}\sum_\alpha \frac{\Omega(1)_s^{\alpha\alpha}}{(I^\circ_{\alpha\alpha})^2}\,, \tag{2-59}$$

$$\Lambda(4)_{ss'} = -\frac{\hbar^2}{4}\sum_\alpha \frac{\Omega(2)_{ss'}^{\alpha\alpha}}{(I^\circ_{\alpha\alpha})^2}\,. \tag{2-60}$$

The internal angular momenta p_α may be expressed as:

$$p_\alpha = \sum_{s,s'} (\lambda_{s'}/\lambda_s)^{\frac{1}{4}}\, \zeta^\alpha_{ss'} q_s q_{s'}\,. \tag{2-61}$$

It is convenient to denote the various terms in the expansion of the vibration-rotation Hamiltonian in a systematic manner by adopting Watson's[13] notational scheme in which the various terms are designated by H_{mn}, where the first subscript is the degree in the vibrational operators (coordinates and momenta) and the second subscript is the degree in the components of the total angular momentum vector J. To conform completely to Watson's notation, the following modifications must be introduced:

q_k, p_k: dimensionless normal coordinates and dimensionless momenta which correspond to Amat-Nielsen q_k, $\hbar\, p_k$,

ω_k: harmonic vibrational frequencies,

J_α: dimensionless angular momentum components which correspond to Amat-Nielsen $(P_\alpha/\hbar)$.

The terms H_{mn}, expressed in wavenumber units, can be related to H_0, H_1, H_2, H_3, and H_4 as follows:

$$H_0 = H_{02} + H_{20}, \tag{2-62}$$

$$H_1 = H_{12} + H_{21} + H_{30}, \tag{2-63}$$

$$H_2 = H_{22} + H_{31} + H_{40}^{*} + H_{00}^{**} + H_{40'} \tag{2-64}$$

$$H_3 = H_{32} + H_{41} + H_{50}^{*} + H_{10}^{**} + H_{50'} \tag{2-65}$$

$$H_4 = H_{42} + H_{51} + H_{60}^{*} + H_{20}^{**} + H_{60} \; . \tag{2-66}$$

To give the various H_{mn} explicitly and in a convenient form, one can define a set of rotational operators as listed in Table (2-1). These definitions constitute an extension of Watson's definitions. It will be seen that if an R operator has an upper index, it is linear in J_α, and if it has no upper index it is quadratic in J_α. Lower indices not separated by commas may be permuted, and interchanging an upper index with the corresponding lower index introduces a factor: - (ω upper/ω lower).

It is also helpful to define the set of coefficients B listed in Table (2-2). With the definitions just introduced, the terms of the vibration-rotation Hamiltonian can be written as given in Table (2-3).

It can be seen that in Table (2-3) all summations over vibrational indices are unrestricted. As a consequence, the anharmonic potential constants k' in the present scheme are not, in general, equal to the anharmonic potential constants k used in the Nielsen-Amat Scheme, Eqs. (2-55)-(2-58). Rather one has:

$$k'_{\ell\ell\ell} = 6k_{\ell\ell\ell}, \qquad k'_{\ell\ell m} = 2k_{\ell\ell m}, \qquad k'_{\ell mn} = k_{\ell mn} \tag{2-67}$$

$$k'_{\ell\ell\ell\ell} = 12k_{\ell\ell\ell\ell} \qquad\qquad k'_{\ell\ell\ell m} = 3k_{\ell\ell\ell m} \tag{2-68}$$

$$k'_{\ell\ell mm} = 2k_{\ell\ell mm}, \qquad\qquad k'_{\ell\ell mn} = k_{\ell\ell mn}, \tag{2-69}$$

Table (2-1). Rotational Operators R of the Expanded Hamiltonian Terms

$$R_k = \sum_{\alpha,\beta} B_k^{\alpha\beta} J_\alpha J_\beta$$

$$R_k^\ell = -(\omega_\ell/\omega_k)R_\ell^k = -2(\omega_\ell/\omega_k)^{\frac{1}{2}} \sum_\alpha B_\alpha \zeta_{k\ell}^\alpha J_\alpha$$

$$R_{k\ell} = R_{\ell k} = \frac{3}{8} \sum_{\alpha,\beta,\gamma} (B_k^{\gamma\alpha}B_\ell^{\gamma\beta} + B_k^{\gamma\beta}B_\ell^{\gamma\alpha})(J_\alpha J_\beta/B_\gamma)$$

$$R_{k,m}^\ell = -(\omega_\ell/\omega_k)R_{\ell,m}^k = -(\omega_\ell/\omega_k)^{\frac{1}{2}} \sum_{\alpha,\beta} B_m^{\alpha\beta} \zeta_{k\ell}^\beta J_\alpha$$

$$R_{\ell m,n} = R_{m\ell,n} = \frac{1}{4} \sum_{\substack{\alpha,\beta \\ \gamma,\varepsilon}} (B_\ell^{\delta\alpha}B_m^{\delta\gamma} + B_m^{\delta\alpha}B_\ell^{\delta\gamma})B_n^{\gamma\beta}(J_\alpha J_\beta/B_\delta B_\gamma)$$

$$R_{k,mn}^\ell = R_{k,nm}^\ell = -(\omega_\ell/\omega_k)R_{\ell,mn}^k$$

$$= -\frac{3}{8}(\omega_\ell/\omega_k)^{\frac{1}{2}} \sum_{\alpha,\beta,\gamma} (B_m^{\alpha\gamma}B_n^{\gamma\beta} + B_n^{\alpha\gamma}B_m^{\gamma\beta})\zeta_{k\ell}^\alpha(J_\beta/B_\gamma)$$

$$R_{k\ell,m,n} = R_{\ell k,m,n}$$

$$= \frac{5}{32} \sum_{\substack{\alpha,\beta,\gamma \\ \varepsilon,\eta}} (B_k^{\varepsilon\alpha}B_\ell^{\varepsilon\eta} + B_\ell^{\varepsilon\alpha}B_k^{\varepsilon\eta})B_m^{\eta\gamma}B_n^{\gamma\beta}(J_\alpha J_\beta/B_\gamma B_\varepsilon B_\eta)$$

$$R_{k,mn,j}^\ell = R_{k,nm,j}^\ell = -(\omega_\ell/\omega_k)R_{\ell,mn,j}^k$$

$$= -\frac{1}{4}(\omega_\ell/\omega_k)^{\frac{1}{2}} \sum_{\substack{\alpha,\beta,\gamma \\ \delta}} (B_m^{\delta\alpha}B_n^{\delta\gamma} + B_n^{\delta\alpha}B_m^{\delta\gamma})B_j^{\gamma\beta} \zeta_{k\ell}^\alpha(J_\beta/B_\gamma B_\delta)$$

Table (2-2). The B Coefficients of the Expanded Hamiltonian Terms

$$B_\alpha = \frac{1}{2}\,[\hbar/(2\pi c)I^\circ_{\alpha\alpha}]$$

$$B_k^{\alpha\beta} = -\frac{1}{2}\,[\hbar^{3/2}/(2\pi c)^{3/2}\omega_k^{1/2}](a_k^{\alpha\beta}/I^\circ_{\alpha\alpha}I^\circ_{\beta\beta})$$

$$B_{k,m}^{\ell,n} = B_{m,k}^{n,\ell} = -(\omega_\ell/\omega_k)B_{\ell,m}^{k,n} = -(\omega_n/\omega_m)B_{k,n}^{\ell,m}$$

$$= (\omega_\ell/\omega_k)^{1/2}(\omega_n/\omega_m)^{1/2}\sum_\alpha B_\alpha\,\zeta_{k\ell}^\alpha\zeta_{mn}^\alpha$$

$$B_{k,m,j}^{\ell,n} = B_{m,k,j}^{n,\ell} = -(\omega_\ell/\omega_k)B_{\ell,m,j}^{k,n} = -(\omega_n/\omega_m)B_{k,n,j}^{\ell,m}$$

$$= (\omega_\ell/\omega_k)^{1/2}(\omega_n/\omega_m)^{1/2}\sum_{\alpha,\beta} B_j^{\alpha\beta}\,\zeta_{k\ell}^\alpha\zeta_{mn}^\beta$$

$$B_k = -\frac{1}{4}\sum_\alpha B_k^{\alpha\alpha}$$

$$B_{k,m,jg}^{\ell,n} = B_{k,m,gj}^{\ell,n} = B_{m,k,jg}^{n,\ell} = -(\omega_\ell/\omega_k)B_{\ell,m,jg}^{k,n}$$

$$= -(\omega_n/\omega_m)B_{k,n,jg}^{\ell,m}$$

$$= \frac{3}{8}\,(\omega_\ell/\omega_k)^{1/2}(\omega_n/\omega_m)^{1/2}\sum_{\alpha,\beta,\gamma}(B_j^{\alpha\gamma}B_g^{\gamma\beta} + B_g^{\alpha\gamma}B_j^{\gamma\beta})(\zeta_{k\ell}^\alpha\zeta_{mn}^\alpha/B_\gamma)$$

$$B_{k\ell} = B_{\ell k} = -\frac{3}{16}\sum_{\alpha,\beta}(B_k^{\alpha\beta}B_\ell^{\alpha\beta}/B_\beta)$$

Table (2-3). Terms of the Expanded Vibration-Rotation Hamiltonian

$$H_{02} = R_0 = \sum_{\alpha} B_{\alpha} J_{\alpha}^2$$

$$H_{20} = \frac{1}{2} \sum_{k} \omega_k (p_k^2 + q_k^2)$$

$$H_{12} = \sum_{k} R_k q_k$$

$$H_{21} = \sum_{k,\ell} R_k^{\ell} q_k p_{\ell}$$

$$H_{30} = \frac{1}{6} \sum_{k,\ell,m} k'_{k\ell m} q_k q_{\ell} q_m$$

$$H_{22} = \sum_{k,\ell} R_{k\ell} q_k q_{\ell}$$

$$H_{31} = \sum_{k,\ell,m} R_{k,m}^{\ell} (q_k p_{\ell} q_m + q_m q_k p_{\ell})$$

$$H_{40}^{*} = \sum_{\substack{k,\ell,\\ m,n}} B_{k,m}^{\ell,n} q_k p_{\ell} q_m p_n$$

$$H_{00}^{**} = -\frac{1}{2} \sum_{\alpha} B_{\alpha}$$

$$H_{40} = \frac{1}{12} \sum_{k,\ell,m,n} k'_{k\ell mn} q_k q_{\ell} q_m q_n$$

$$H_{32} = \sum_{k,\ell,m} R_{k\ell,m} q_k q_{\ell} q_m$$

$$H_{41} = \sum_{k,\ell,m,n} R_{k,mn}^{\ell} (q_k p_{\ell} q_m q_n + q_m q_n q_k p_{\ell})$$

$$H_{50}^{*} = \sum_{k,\ell,m,n,j} B_{k,m,j}^{\ell,n} q_k p_{\ell} q_j q_m p_n$$

$$H_{10}^{**} = \sum_{k} B_k q_k$$

$$H_{50} = \frac{1}{60} \sum_{k,\ell,m,n,j} k'_{k\ell mnj} q_k q_{\ell} q_m q_n q_j$$

$$H_{42} = \sum_{\substack{k\ell\\ mn}} R_{k\ell,m,n} q_k q_{\ell} q_m q_n$$

Table (2-3) (continued)

$$H_{51} = \sum_{k,\ell,m,n,j} R^{\ell}_{k,mn,j} \; (q_k p_\ell q_m q_j + q_m q_n q_j q_k p_\ell)$$

$$H^{*}_{60} = \sum_{\substack{k,\ell,m,\\ n,j,g}} B^{\ell,n}_{k,m,jg} \; q_k p_\ell q_j q_g q_m p_n$$

$$H^{**}_{20} = \sum_{k\ell} B_k q_k q_\ell$$

$$H_{60} = \frac{1}{180} \sum_{\substack{k,\ell,m,\\ n,j,g}} k'_{k\ell mnjg} q_k q_\ell q_m q_n q_j q_g$$

$$k'_{\ell\ell\ell\ell\ell} = 60k_{\ell\ell\ell\ell\ell}, \qquad k'_{\ell\ell\ell\ell m} = 12k_{\ell\ell\ell\ell m}, \tag{2-70}$$

$$k'_{\ell\ell\ell mm} = 6k_{\ell\ell\ell mm}, \qquad k'_{\ell\ell\ell mn} = 3k_{\ell\ell\ell mn}, \tag{2-71}$$

$$k'_{\ell\ell mmn} = 2k_{\ell\ell mmn}, \tag{2-72}$$

$$k'_{\ell\ell\ell\ell\ell\ell} = 180k_{\ell\ell\ell\ell\ell\ell}, \qquad k'_{\ell\ell\ell\ell\ell m} = 30k_{\ell\ell\ell\ell\ell m}, \tag{2-73}$$

$$k'_{\ell\ell\ell\ell mm} = 12k_{\ell\ell\ell\ell mm}, \qquad k'_{\ell\ell\ell\ell mn} = 6k_{\ell\ell\ell\ell mn}, \tag{2-74}$$

$$k'_{\ell\ell\ell mmm} = 9k_{\ell\ell\ell mmm}, \qquad k'_{\ell\ell\ell mmn} = 3k_{\ell\ell\ell mmn}, \tag{2-75}$$

$$k'_{\ell\ell mmnn} = 2k_{\ell\ell mmnn}. \tag{2-76}$$

3. THE SUCCESSIVE VIBRATIONAL CONTACT TRANSFORMATION TECHNIQUE

3.1 First Contact Transformation

The energies of the system represented by the Hamiltonian (2-24) 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 part of the Hamiltonian, H_0. The first-order correction to the energy, E_1, is computed exclusively from the diagonal matrix elements of H_1. In the absence of degeneracies, the off-diagonal elements of H_1 will contribute only to the second and higher-order corrections. The perturbation calculation is thus principally complicated by the myriad of off-diagonal contributions, especially those from H_3 and H_4, and it is therefore highly desirable to transform the Hamiltonian to a more convenient form. To attain such a form, Van Vleck suggested the so-called contact transformation technique. By a suitable unitary operator T, one subjects the Hamiltonian H to a transformation and attempts to find a Hamiltonian H',

$$H' = THT^{-1} = H_0 + \lambda H_1' + \lambda^2 H_2' + \ldots , \qquad (3\text{-}1)$$

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 H_1, would vanish completely. The eigenfunctions of H_0

become eigenfunctions of $H_0 + H_1'$ which is thus effectively a zeroth-order term, if the zeroth-order energy is non-degenerate. Since now there are no off-diagonal matrix elements in H_1', the Hamiltonian H_2' can be treated as a first-order perturbation term, and the second-order corrections to the energy are obtained by taking the expectation values of H_2'.

Thus, except in the case of accidental degeneracies, it is advantageous to consider a partial diagonalization of the vibration-rotation Hamiltonian in the vibrational quantum numbers by use of the contact transformation. This can be done by determining the operator T which leave H_0 of Eq. (2-48) unchanged and gives an H_1' diagonal in the vibrational operators.[16] The simplest method of obtaining the suitable form of T is to set $T = \exp(i\lambda S^{(1)})$ where the Hamiltonian operator $S^{(1)}$ is called the Herman-Shaffer operator, and is chosen such that the operator $H_0 + \lambda H_1'$ has only diagonal matrix elements with respect to the vibrational quantum numbers v_s in the representation which diagonalizes H_0.

To carry out the first contact transformation, we let

$$H' = THT^{-1} = e^{i\lambda S^{(1)}} H \, e^{-i\lambda S^{(1)}} = H_0 + \lambda H_1' + \lambda^2 H_2' + \ldots \quad (3\text{-}2)$$

To obtain the general expressions for the operators H_n', Eq. (3-2) is expanded as

$$\begin{aligned} H' &= H_0' + \lambda H_1' + \lambda^2 H_2' + \lambda^3 H_3' + \ldots \\ &= (1 + i\lambda S^{(1)} - \tfrac{1}{2}\lambda^2 S^{(1)2} - \tfrac{1}{6} i\lambda^3 S^{(1)3} + \ldots)(H_0 + \lambda H_1 + \lambda^2 H_2 + \ldots) \\ &\quad (1 - i\lambda S^{(1)} - \tfrac{1}{2}\lambda^2 S^{(1)2} + \tfrac{1}{6} i\lambda^3 S^{(1)3} + \ldots). \end{aligned} \quad (3\text{-}3)$$

Equating the coefficients of like powers of λ, one obtains in general that

$$H'_n = H_n + i[S^{(1)}, H^{(2)}_{n-1}], \qquad (3\text{-}4)$$

where

$$H^{(2)}_{n-1} = H_{n-1} + \frac{i}{2}[S^{(1)}, H^{(3)}_{n-2}], \qquad (3\text{-}5)$$

and so on, to

$$H^{(m)}_n = H_n + \frac{i}{m}[S^{(1)}, H^{(m+1)}_{n-1}], \qquad (3\text{-}6)$$

with $H^{(m)}_0 = H_0$ for all values of m. Writing out the first few terms of H'_n explicitly, one obtains

$$H'_0 = H_0 \qquad (3\text{-}7)$$

$$H'_1 = H_1 + i[S^{(1)}, H_0] \qquad (3\text{-}8)$$

$$H'_2 = H_2 + i[S^{(1)},H_1] - \frac{1}{2}[S^{(1)},[S^{(1)},H_0]] \qquad (3\text{-}9)$$

$$H'_3 = H_3 + i[S^{(1)},H_2] - \frac{1}{2}[S^{(1)},[S^{(1)},H_1]]$$
$$- \frac{i}{6}[S^{(1)},[S^{(1)},[S^{(1)},H_0]]] \qquad (3\text{-}10)$$

$$H'_4 = H_4 + i[S^{(1)},H_3] - \frac{1}{2}[S^{(1)},[S^{(1)},H_2]]$$
$$- \frac{i}{6}[S^{(1)},[S^{(1)}[S^{(1)},H_1]]]$$
$$+ \frac{1}{24}[S^{(1)},[S^{(1)},[S^{(1)},[S^{(1)},H_0]]]] \qquad (3\text{-}11)$$

$$\vdots$$

In general,

$$H'_n = \sum_{k=0}^{n} \frac{(i)^{n-k}}{(n-k)!} \{S^{(1)n-k}, H_k\} \tag{3-12}$$

where

$$\{S^{(1)(0)}, H_n\} \equiv H_n \tag{3-13}$$

$$\{S^{(1)(1)}, H_n\} \equiv [S^{(1)}, H_n] \tag{3-14}$$

$$\{S^{(1)(2)}, H_n\} \equiv [S^{(1)},[S^{(1)}, H_n]] \tag{3-15}$$

$$\vdots$$

$$\{S^{(1)(k)}, H_n\} \equiv [S^{(1)},[S^{(1)},\ldots[S^{(1)},H_n\underbrace{]]\ldots]}_{\text{k brackets}} \tag{3-16}$$

According to Eq. (3-8), the required transformed first-order Hamiltonian H'_1 is obtained if $S^{(1)}$ is chosen such that

$$i[S^{(1)}, H_0] = -H_1 + H'_1 \tag{3-17}$$

where H'_1 is the portion of H_1 which is diagonal in the vibrational quantum numbers. This choice of $S^{(1)}$ removes all but the so-called first-order essential Coriolis term from the first order Hamiltonian. For the case of asymmetric rotator molecules, it can be shown that $H'_1 = 0$, because there is no symmetry-conditioned, essential Coriolis interaction for this type of rotator. Eq. (3-17) thus becomes

$$i[S^{(1)}, H_0] = -H_1, \tag{3-18}$$

and constitutes the defining equation for the $S^{(1)}$ function for the case of the asymmetric rotator molecule.

Now the Hermitian operator $S^{(1)}$, and the partial Hamiltonian $H_{n-1}^{(m+1)}$ whose commutator appears in Eq. (3-6), are each made up of combinations of the vibrational operators p_s and q_s and the rotational operators P_α. The two types of operator can be expressed symbolically as $S^{(1)} = \Sigma_k\, {}^kS$, and $H_{n-1}^{m+1} = \Sigma_k\, {}^{k'}H$ with ${}^kS = ({}^kS)_V({}^kS)_R$, and ${}^{k'}H = ({}^{k'}H)_V({}^{k'}H)_R$ where the subscripts V and R denote the vibrational and rotational parts. For any ${}^kS$ and ${}^{k'}H$, and suppressing the k-indices, one has that

$$[S^{(1)}, H] = [S^{(1)}, H]_v + [S^{(1)},H]_R \qquad (3\text{-}19)$$

where

$$[S^{(1)}, H]_v = [S_v^{(1)},H_v](S_R^{(1)}H_R + H_R S_R^{(1)})/2 \qquad (3\text{-}20)$$

$$[S^{(1)},H]_R = (S_v^{(1)}H_v + H_v S_v^{(1)})[S_R^{(1)},H_R]/2 \qquad (3\text{-}21)$$

It can be shown that if H_n is of order n, then $[S^{(1)},H]_v$ is of order n+1, whereas $[S^{(1)},H]_R$ is of order n+2. This comes about since the commutators $[P_\alpha, P_\beta]$ occurring in $[S_R^{(1)}, H_R]$ are equivalent to $-i\hbar P_\gamma$ and are therefore of one order of magnitude smaller than $P_\alpha P_\beta$, whereas the $[p,q]$ occurring in $[S_v^{(1)}, H_v]$ are equivalent to $-i\hbar$ and are therefore of the same order of magnitude as pq. For these reasons it is useful to allow for the possibility of regrouping terms into orders of magnitude in accordance with the above remarks, and the once-transformed Hamiltonian is therefore rewritten in the general form

$$H' = h_0' + h_1' + h_2' + h_3' + h_4' +\ldots \qquad (3\text{-}22)$$

From Eq. (3-4), the transformed Hamiltonian has the form

$$h_n' = H_n + i[S^{(1)}, h_{n-1}^{(2)}]_v + i[S^{(1)}, h_{n-2}^{(2)}]_R \tag{3-23}$$

where one has, in analogy with Eqs. (3-5) and (3-6),

$$h_n^{(2)} = H_n + \frac{i}{2}[S^{(1)}, h_{n-1}^{(3)}]_v + \frac{i}{2}[S^{(1)}, h_{n-2}^{(3)}]_R \tag{3-24}$$

$$\vdots$$

and in general

$$h_n^{(m)} = H_n + \frac{i}{m}[S^{(1)}, h_{n-1}^{(m+1)}]_v + \frac{i}{m}[S^{(1)}, h_{n-2}^{(m+1)}]_R\ . \tag{3-25}$$

For the asymmetric-rotator case, the above equations give explicitly that

$$h_0' = H_0 \tag{3-26}$$

$$h_1' = H_1 + i[S^{(1)}, H_0]_v = 0 \tag{3-27}$$

$$h_2' = H_2 + i[S^{(1)}, H_0]_R + \frac{1}{2} i[S^{(1)}, H_1]_v \tag{3-28}$$

$$h_3' = H_3 + \frac{1}{2} i[S^{(1)}, H_1]_R + \frac{1}{6}[S^{(1)},[S^{(1)},H_0]_R]_v$$

$$+ \frac{1}{3} i[S^{(1)}, 2h_2' + H_2]_v \tag{3-29}$$

$$h_4' = H_4 + i[S^{(1)}, H_3]_v - \frac{1}{4}[S^{(1)},[S^{(1)},h_2' + H_2]_v]_v$$

$$+ \frac{1}{12} i[S^{(1)},[S^{(1)},[S^{(1)},H_0]_R]_v]_v - \frac{1}{3}[S^{(1)},[S^{(1)},H_1]_R]_v$$

$$+ \frac{1}{3} i[S^{(1)},2h_2' + H_2]_R + \frac{1}{6}[S^{(1)},[S^{(1)},H_0]_R]_R. \tag{3-30}$$

Using Eqs. (3-20) and (3-21), and the commutation relations as stated by Herman and Shaffer,[17] it is possible to find the $S^{(1)}$ function defined by Eq. (3-27). It can be shown to have the general form

$$S^{(1)} = \Sigma_{\alpha,\beta}\Sigma_s\ {}^{\alpha\beta}S^s p_s P_\alpha P_\beta + \Sigma_\alpha \Sigma_{s<s'}({}^{\alpha}S_{ss'}\ q_s q_{s'}$$

$$+ {}^{\alpha}S^{ss'}\ p_s p_{s'})P_\alpha + \Sigma_{s\underline{<}s';s''}\ S^{s''}_{ss'}\ \frac{1}{2}(q_s q_{s'} p_{s''} + p_{s''} q_s q_{s'})$$

$$+ \Sigma_{s<s'<s''}\ S^{ss's''}\ p_s p_{s'} p_{s''}\ , \tag{3-31}$$

where

$${}^{\alpha\beta}S^s = \frac{a_s^{\alpha\beta}}{2(\hbar^2\lambda_s)^{3/4}\ I^\circ_{\alpha\alpha} I^\circ_{\beta\beta}}\ , \tag{3-32}$$

$${}^{\alpha}S_{ss'} = \left(\frac{1}{\lambda_s\lambda_{s'}}\right)^{\frac{1}{4}} \cdot \frac{\lambda_s + \lambda_{s'}}{\lambda_s - \lambda_{s'}} \cdot \frac{\zeta^\alpha_{ss'}}{I^\circ_{\alpha\alpha}}\ , \quad s \neq s' \tag{3-33}$$

$${}^{\alpha}S^{ss'} = \frac{2}{\hbar^2} \frac{(\lambda_s\lambda_{s'})^{\frac{1}{4}}}{\lambda_s - \lambda_{s'}} \frac{\zeta^\alpha_{ss'}}{I^\circ_{\alpha\alpha}}\ , \quad s \neq s' \tag{3-34}$$

$$S^{s''}_{ss'} = -\frac{2\pi c}{\hbar}(1 + \delta_{ss''} + \delta_{s's''}) \frac{\lambda^{\frac{1}{2}}_{s''}(\lambda_{s''} - \lambda_s - \lambda_{s'})}{G_{ss's''}}\ k_{ss's''}, \tag{3-35}$$

$$S^{ss's''} = \frac{4\pi c}{\hbar^3} \frac{(\lambda_s\lambda_{s'}\lambda_{s''})^{\frac{1}{2}}}{G_{ss's''}}\ k_{ss's''}\ , \tag{3-36}$$

with

$$G_{ss's''} = (\lambda_s^{\frac{1}{2}} + \lambda_{s'}^{\frac{1}{2}} + \lambda_{s''}^{\frac{1}{2}})(\lambda_s^{\frac{1}{2}} + \lambda_{s'}^{\frac{1}{2}} - \lambda_{s''}^{\frac{1}{2}})$$

$$(\lambda_s^{\frac{1}{2}} - \lambda_{s'}^{\frac{1}{2}} - \lambda_{s''}^{\frac{1}{2}})(\lambda_s^{\frac{1}{2}} - \lambda_{s'}^{\frac{1}{2}} + \lambda_{s''}^{\frac{1}{2}})\ . \tag{3-37}$$

It may be verified that $G_{ss's''}$ is invariant under all six possible permutations of the indices s, s', s''.

With the explicit knowledge of the $S^{(1)}$-function, the first contact transformation can be carried out according to the procedures described by evaluating the required commutators. This has been done by Amat, Nielsen and co-workers. The lengthy results are collected in a reference book by Amat, Nielsen and Tarrago.[12] The explicit forms of h_0', h_1', and h_2' are

$$h_0' = H_0 \tag{3-38}$$

$$h_1' = 0 \tag{3-39}$$

$$\begin{aligned}
h_2' = {} & \sum_{\alpha\beta\gamma\delta} \left({}^{\alpha\beta\gamma\delta}_{(2)}Y\right) P_\alpha P_\beta P_\gamma P_\delta + \sum_{\alpha\beta\gamma} \sum_{s} \left({}^{\alpha\beta\gamma}_{(2)}Y^{s}\right) p_s P_\alpha P_\beta P_\gamma \\
& + \sum_{\alpha\beta} \sum_{\substack{s,s' \\ s\leq s'}} \left({}^{\alpha\beta}_{(2)}Y^{ss'} p_s p_{s'} + {}^{\alpha\beta}_{(2)}Y_{ss'} q_s q_{s'}\right) P_\alpha P_\beta \\
& + \sum_{\alpha} \sum_{\substack{s,s',s'' \\ s\leq s'\leq s''}} \left({}^{\alpha}_{(2)}Y^{ss's''}\right) p_s p_{s'} p_{s''} P_\alpha \\
& + \sum_{\alpha} \sum_{\substack{s,s',s'' \\ s\leq s''}} \left({}^{\alpha}_{(2)}Y^{s''}_{ss'}\right) \frac{1}{2}\left(q_s q_{s'} p_{s''} + p_{s''} q_s q_{s'}\right) P_\alpha \\
& + \sum_{\substack{s,s',s'',s''' \\ s\leq s';\, s''\leq s'''}} \left({}_{(2)}Y^{s''s'''}_{ss'}\right) \frac{1}{2}\left(q_s q_{s'} p_{s''} p_{s'''} + p_{s''} p_{s'''} q_s q_{s'}\right) \\
& + \sum_{\substack{s,s',s'',s''' \\ s\leq s'\leq s''\leq s'''}} \left({}_{(2)}Y_{ss's''s'''}\right) q_s q_{s'} q_{s''} q_{s'''} .
\end{aligned} \tag{3-40}$$

The expressions for h_3' and h_4' are also cited in entirety in the Amat-Nielson-Tarrago book, as are the detailed forms of the above coefficients ${}_{(2)}Y$ in terms of fundamental molecular parameters.

3.2 Second Contact Transformation

In order to cast the Hamiltonian into a form suitable for the calculation of the vibration-rotation energies to the fourth-order of approximation, it is necessary to perform a second contact transformation on the once-transformed Hamiltonian H', such that the twice-transformed Hamiltonian will be diagonal to second order in all vibrational quantum numbers. We therefore let

$$H'' = \tau H' \tau^{-1} = e^{i\lambda^2 S^{(2)}} H' e^{-i\lambda^2 S^{(2)}}$$

$$= H''_0 + \lambda H''_1 + \lambda^2 H''_2 + \lambda^3 H''_3 + \ldots \qquad (3\text{-}41)$$

where $H''_0 + \lambda H''_1 + \lambda^2 H''_2$ is required to be diagonal with respect to the vibrational quantum numbers v_s. On expansion of the exponentials and equating like powers of λ one obtains

$$H''_0 = h'_0 \qquad (3\text{-}42)$$

$$H''_1 = h'_1 \qquad (3\text{-}43)$$

$$H''_2 = h'_2 + i[S^{(2)}, h'_0] \qquad (3\text{-}44)$$

$$H''_3 = h'_3 + i[S^{(2)}, h'_1] \qquad (3\text{-}45)$$

$$H''_4 = h'_4 + i[S^{(2)}, h'_2] - \tfrac{1}{2}[S^{(2)}, [S^{(2)}, h_0]] \qquad (3\text{-}46)$$

$$H''_5 = h'_5 + i[S^{(2)}, h'_3] - \tfrac{1}{2}[S^{(2)}, [S^{(2)}, h'_1]] \qquad (3\text{-}47)$$

$$H''_6 = h'_6 + i[S^{(2)}, h'_4] - \tfrac{1}{2}[S^{(2)}, [S^{(2)}, h'_2]]$$

$$- \tfrac{i}{6}[S^{(2)}, [S^{(2)}, [S^{(2)}, h'_0]]] \quad \text{etc.} \qquad (3\text{-}48)$$

Again allowing for the possibility of regrouping the terms of the twice-transformed Hamiltonian by true orders of magnitude, it is expedient to write H'' as

$$H'' = h''_0 + h''_1 + h''_2 + h''_3 + \ldots \qquad (3\text{-}49)$$

The above Hamiltonian can be used to calculate the vibration-rotation energies to the fourth-order of approximation by including only those matrix elements which are diagonal in all vibrational quantum numbers v_s, because h''_0, h''_1 and h''_2 are diagonal in all v_s by virtue of the contact transformations, and those matrix elements of h''_3 and h''_4 which are off-diagonal in one or more vibrational quantum numbers can contribute to the energies only in orders of approximation higher than the fourth. The Hamiltonian H'' is diagonal to all orders in the rotational quantum numbers J (total angular momentum quantum number) and M (magnetic quantum number). However, it has matrix elements which are nondiagonal in the angular momentum projection quantum number k in a symmetric rotator representation whose basis functions are rigid-symmetric-top eigenfunctions Ψ_{JkM}.

It was found[4,5,18] that through the fourth-order of approximation, the general Hamiltonian has terms which can be classified into the following three categories:

(a) $_{(0)}Z\ r^2$, $_{(2)}Z\ r^4$, $_{(4)}Z\ r^6$;

(b) $_{(0)}Z\ P^2$, $_{(2)}Z\ P^4$, $_{(4)}Z\ P^2$, $_{(4)}Z\ P^6$;

(c) $_{(1)}Z\ r^2P$, $_{(2)}Z\ r^2P^2$, $_{(3)}Z\ r^4P$, $_{(3)}Z\ r^2P^3$, $_{(4)}Z\ r^2P^4$, $_{(4)}Z\ r^4P^2$,

where r^2 denotes any possible product of two vibrational operators i.e., $q_sq_{s'}$, $p_sp_{s'}$, $q_sp_{s'}$, or $p_sq_{s'}$; r^4 denotes any possible product of four vibrational operators, etc. The symbols P^n stands for any possible product of P_x, P_y and P_z of total power n, and

and ${}_{(m)}Z$ stands, in general, for the coefficient of an operator appearing in the m-th order of approximation.

The terms in (a) constitute pure vibrational operators including anharmonicity corrections, the terms in (b) constitute pure rotational operators including centrifugal distortion corrections, and the terms in (c) represent vibration-rotation interaction contributions.

The pure vibrational energies will not concern us here since we are interested principally in the rotational level structure built upon a particular vibrational state rather than in the detailed calculation of the pure vibrational level structure. In the absence of vibrational degeneracy, it is found that the ${}_{(1)}Z\ r^2\ P$-type terms have zero coefficients ${}_{(1)}Z$. Also, the ${}_{(3)}Z\ r^4 P$ and ${}_{(3)}Z\ r^2 P^3$-type terms have no non-zero matrix elements diagonal in all v_s to the fourth-order approximation. Thus the odd order terms may be excluded from consideration unless accidental resonances occur which would partially invalidate the order of approximation arrangement of the Hamiltonian. The Hamiltonian of interest has then the general schematic form:

$$H'' = h_0''^* + h_2''^* + h_4''^* \qquad (3\text{-}49)$$

where

$$h_0''^* = {}_{(0)}Z\ P^2 \qquad (3\text{-}50)$$

$$h_2''^* = {}_{(2)}Z\ r^2 P^2 + {}_{(2)}Z\ P^4 \qquad (3\text{-}51)$$

$$h_4''^* = {}_{(4)}Z\ P^2 + {}_{(4)}Z\ r^4 P^2 + {}_{(4)}Z\ r^2 P^4 + {}_{(4)}Z\ P^6\ . \qquad (3\text{-}52)$$

The asterisks indicate that terms of h''_2 and h''_4 which are of the pure-vibrational type are to be omitted in h''^*_2 and h''^*_4. Also terms of h''_4 not diagonal in all v_s are to be omitted in h''^*_4.

Regrouping terms in Eqs. (3-42)-(3-46) according to true orders of magnitude, the twice-transformed Hamiltonian takes the following general form:

$$h''_0 = h'_0 = H_0, \tag{3-53}$$

$$h''_1 = h'_1 = 0, \tag{3-54}$$

$$h''_2 = h'_2 + i[S^{(2)}, H_0]_v, \tag{3-55}$$

$$h''_3 = h'_3 + i[S^{(2)}, H_0]_R + i[S^{(2)}, h'_1]_v, \tag{3-56}$$

$$h''_4 = h'_4 + i[S^{(2)}, h'_1]_R + \frac{i}{2}[S^{(2)}, h'_2 + h''_2]_v. \tag{3-57}$$

The operator $S^{(2)}$ is determined through Eq. (3-55) by requiring the commutator $-i[S^{(2)}, H_0]_v$ to be of a form such that if offsets the vibrationally off-diagonal matrix elements of h'_2. This $S^{(2)}$ function is found to take the following form:

$$\begin{aligned} S^{(2)} = {} & \Sigma_{\alpha,\beta,\gamma}\Sigma_s\ {}^{\alpha\beta\gamma}S_s\ q_s\ P_\alpha P_\beta P_\gamma \\ & + \Sigma_{\alpha,\beta}\Sigma_{s,s'}\ {}^{\alpha\beta}S_s^{s'}\ \frac{1}{2}(q_s p_{s'} + p_{s'} q_s) P_\alpha P_\beta \\ & + \Sigma_\alpha \Sigma_{s\le s'\le s''}\ {}^{\alpha}S_{ss's''}\ q_s q_{s'} q_{s''}\ P_\alpha \\ & + \Sigma_\alpha \Sigma_{s;s'\le s''}\ {}^{\alpha}S_s^{s's''}\ \frac{1}{2}(q_s p_{s'} p_{s''} + p_{s'} p_{s''} q_s) P_\alpha \\ & + \Sigma_{s;s'\le s''\le s'''}\ S_s^{s's''s'''}\ \frac{1}{2}(q_s p_{s'} p_{s''} p_{s'''} + p_{s'} p_{s''} p_{s'''} q_s) \\ & + \Sigma_{s\le s'\le s'';s'''}\ S_{ss's''}^{s'''}\ \frac{1}{2}(q_s q_{s'} q_{s''} p_{s'''} + p_{s'''} q_s q_{s'} q_{s''}), \end{aligned} \tag{3-58}$$

where the coefficients $S^{(2)}$ are listed in the Amat-Nielsen-Tarrago[12] book. It may be allowable to omit the ${}_{(4)}Z\,P^2$ and ${}_{(4)}Z\,r^4P^2$ terms from Eq. (3-58), since they constitute fourth-order corrections to the second-order corrected rotational constants and as such their effects are probably undetectably small. Upon substitution of $S^{(2)}$ into Eq. (3-56), it is found that the diagonal matrix elements of h_3'' vanish; the off-diagonal matrix elements of h_3'' and h_4'' contribute to orders of approximation higher than the fourth. Extensive computation yields a twice-transformed Hamiltonian of the following form:

$$h_0'' = H_0 \tag{3-59}$$

$$h_1'' = 0 \tag{3-60}$$

$$\begin{aligned} h_2'' = & \sum_{\alpha\beta\gamma\delta} {}^{\alpha\beta\gamma\delta}_{(2)}Y\, P_\alpha P_\beta P_\gamma P_\delta \\ & + \sum_{\alpha\beta} \sum_{\substack{ss' \\ s=s'}} \left(\hbar^2\, {}^{\alpha\beta}_{(2)}Y^{ss'} + {}^{\alpha\beta}_{(2)}Y_{ss'}\right)\frac{1}{2}\left(q_s q_{s'} + \frac{p_s p_{s'}}{\hbar^2}\right)P_\alpha P_\beta \\ & + \text{pure-vibration terms.} \end{aligned} \tag{3-61}$$

The very complicated explicit results for h_2'', h_3'' and h_4'' will be found in the Amat-Nielsen-Tarrago book[12].

3.3 Third (and Higher) Contact Transformations

It is sometimes necessary to perform a third (or even higher) contact transformation such that the three-times-transformed Hamiltonian will be diagonal in all vibrational quantum numbers. One then takes:

$$H''' = \theta H'' \theta^{-1} = e^{i\lambda^3 S^{(3)}} H'' e^{-i\lambda^3 S^{(3)}}$$

$$= H_0''' + \lambda H_1''' + \lambda^2 H_2''' + \lambda^3 H_3''' + \lambda^4 H_4''' + \ldots, \qquad (3\text{-}62)$$

where $H_0''' + \lambda H_1''' + \lambda^4 H_4''' + \lambda^3 H_3'''$ are diagonal with respect to the vibrational quantum numbers v_s. In terms of the like powers of the parameter λ, Eq. (3-62) is equivalent to

$$H_0''' = h_0'' \qquad (3\text{-}63)$$

$$H_1''' = h_1'' \qquad (3\text{-}64)$$

$$H_2''' = h_2'' \qquad (3\text{-}65)$$

$$H_3''' = h_3'' + i[S^{(3)}, h_0''] \qquad (3\text{-}66)$$

$$H_4''' = h_4'' + i[S^{(3)}, h_1''] \qquad (3\text{-}67)$$

$$H_5''' = h_5'' + i[S^{(3)}, h_2''] \qquad (3\text{-}68)$$

$$H_6''' = h_6'' + i[S^{(3)}, h_3''] - \tfrac{1}{2}[S^{(3)},[S^{(3)}, h_0'']] \quad \text{etc.} \qquad (3\text{-}69)$$

Eq. (3-66) is the defining equation for the operator $S^{(3)}$. The function $S^{(3)}$ is constructed such that

$$i[S^{(3)}, h_0''] = -h_3''{}_{\text{off diag.}} \qquad (3\text{-}70)$$

Again allowing for the possibility of regrouping the terms of the three-times-transformed Hamiltonian into a "true" order of magnitude arrangement, one has

$$H''' = h_0''' + h_1''' + h_2''' + h_3''' + h_4''' + \ldots \qquad (3\text{-}71)$$

Recently Aliev and Watson[13] have calculated the sextic centrifugal distortion constants of polyatomic molecules by a so-called "reordered perturbation treatment", for which they had to consider the three-times transformed Hamiltonian. We will discuss this calculation in some detail in chapter 7.

The procedure of successive contact transformations could be applied as many times as required. The general theory of n-times-transformed molecular Hamiltonians has been explored in some detail by Aliev and Aleksanyan.[19]

4. THE NORMAL MODES PROBLEM FOR TRIANGULAR TRIATOMIC MOLECULES

In order to present and explore the details of the theory of centrifugal distortion in triangular triatomic molecules, it is necessary to review the normal-coordinate problem for this class of molecules. The XYX-type molecule was first considered by Shaffer and Nielsen,[20] and discussions have since appeared in numerous publications, e.g., those of Nielsen,[21] or Chung and Parker.[22] The XYZ-type molecule was first studied by Shaffer and Schuman,[23] and further details have been presented by others, including Chan and Parker.[6]

4.1 Equilibrium Geometry of the XYZ-type Molecule

Let the XYZ molecule lie in the $\bar{x}\bar{y}$ plane, as shown in Figure (4-1), with the origin of coordinates at the center of mass. The X and Z atoms are located at the base vertices of the

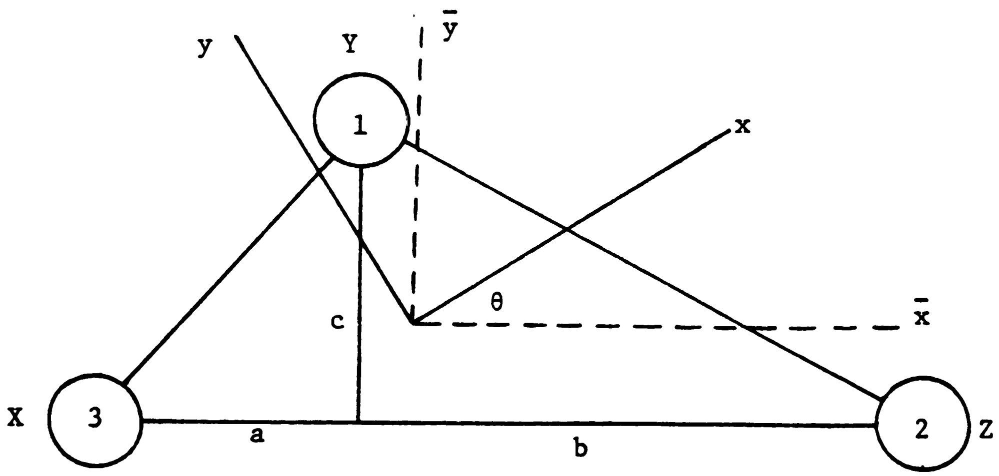


Figure (4-1). Equilibrium configuration of the triangular triatomic molecule.

triangle and the Y atom is at the top vertex. They are numbered 3, 2 and 1, respectively, and XZ is chosen parallel to the $\bar{x}$ axis. In the barred equilibrium coordinates $\bar{x}_{\circ i}$, $\bar{y}_{\circ i}$ and $\bar{z}_{\circ i}$, $i = 1,2,3$, one has that

$$a = \bar{x}_{\circ 1} - \bar{x}_{\circ 3}, \tag{4-1}$$

$$b = \bar{x}_{\circ 2} - \bar{x}_{\circ 1}, \tag{4-2}$$

$$c = \bar{y}_{\circ 1} - \bar{y}_{\circ 3}. \tag{4-3}$$

The principal axes of the molecule, designated as x, y, and z have the same origin as the $\bar{x}$, $\bar{y}$ and $\bar{z}$ coordinates. The z-axis coincides with the $\bar{z}$-axis and the x,y axes are in the plane of the molecule and make an angle θ with the $\bar{x}$, $\bar{y}$ axis. The equilibrium coordinates are found to be

$$\bar{x}_{\circ 1} = (m_3 a - m_2 b)/M, \tag{4-4}$$

$$\bar{x}_{\circ 2} = [m_3 a + (m_1 + m_2)b]/M, \tag{4-5}$$

$$\bar{x}_{\circ 3} = -[(m_1 + m_2)a + m_2 b]/M, \tag{4-6}$$

$$\bar{y}_{\circ 1} = (m_2 + m_3)c/M, \tag{4-7}$$

$$\bar{y}_{\circ 2} = -m_1 c/M, \tag{4-8}$$

$$\bar{y}_{\circ 3} = -m_1 c/M, \tag{4-9}$$

$$\bar{z}_{\circ 1} = \bar{z}_{\circ 2} = \bar{z}_{\circ 3} = 0, \tag{4-10}$$

with M being the total mass of the molecule, viz.,

$$M = m_1 + m_2 + m_3 . \tag{4-11}$$

Transformation to the principal axes system of the equilibrium inertia tensor is accomplished by taking

$$x_{o_i} = \bar{x}_{o_i}\cos\theta + \bar{y}_{o_i}\sin\theta, \tag{4-12}$$

$$y_{o_i} = -\bar{x}_{o_i}\sin\theta + \bar{y}_{o_i}\cos\theta, \tag{4-13}$$

$$z_{o_i} = \bar{z}_{o_i} = 0, \tag{4-14}$$

where the angle θ is given by

$$\tan 2\theta = T/\Omega, \tag{4-15}$$

with

$$T = 2m_1c(m_3a - m_2b), \tag{4-16}$$

$$\Omega = m_3(m_1 + m_2)a^2 + m_2(m_1 + m_3)b^2 - m_1(m_2 + m_3)c^2 + 2m_2m_3ab\ . \tag{4-17}$$

For the equilibrium coordinates in the principal axes system the transformation gives

$$x_{o_1} = \{(m_3a - m_2b)\cos\theta + (m_2 + m_3)c\cdot\sin\theta\}/M, \tag{4-18}$$

$$x_{o_2} = \{[m_3a + (m_1 + m_3)b]\cos\theta - m_3c\cdot\sin\theta\}/M, \tag{4-19}$$

$$x_{o_3} = -\{[(m_1 + m_2)a + m_2b]\cos\theta + m_1c\cdot\sin\theta\}/M, \tag{4-20}$$

$$y_{o_1} = -\{(m_3a - m_2b)\sin\theta - (m_2 + m_3)c\cdot\cos\theta\}/M, \tag{4-21}$$

$$y_{o_2} = -\{[m_3a + (m_1 + m_3)b]\sin\theta + m_1c\cdot\cos\theta\}/M, \tag{4-22}$$

$$y_{o_3} = \{[(m_1 + m_2)a + m_2b]\sin\theta - m_1c\cdot\cos\theta\}/M, \tag{4-23}$$

$$z_{o_1} = z_{o_2} = z_{o_3} = 0\ . \tag{4-24}$$

For the equilibrium principal moments of inertia one has

$$I^{\circ}_{xx} = \frac{1}{2}(I^{\circ}_{zz} - I'), \tag{4-25}$$

$$I^{\circ}_{yy} = \frac{1}{2}(I^{\circ}_{zz} + I'), \tag{4-26}$$

$$I^{\circ}_{zz} = I^{\circ}_{xx} + I^{\circ}_{yy} = [\Omega + 2m_1(m_2 + m_3)c^2]/M, \tag{4-27}$$

with

$$I' = [(T^2 + \Omega^2)/M^2]^{\frac{1}{2}}. \tag{4-28}$$

The equilibrium coordinates and the equilibrium principal moments of inertia of the HDO-type molecule can be obtained from the above more general expressions by setting $a = b$.

4.2 Normal Coordinates of the XYZ-type Molecule

Denoting instantaneous position coordinates by x_i, y_i and z_i, we have that $z_1 = z_2 = z_3 = 0$ because of the absence of out-of-plane vibrations. The Eckart conditions[24] can be written as

$$\sum_i m_i \bar{\alpha}_i = 0 \tag{4-29}$$

$$\sum_i m_i(\bar{\alpha}_{o_i} \times \bar{\alpha}_i) = 0 . \tag{4-30}$$

The first condition keeps the origin at the center of mass at all times while the second condition keeps the xyz coordinate system attached to the nuclear equilibrium configuration. We now introduce intermediate symmetry coordinates u,v,w as follows:

$$u = x_2 - x_3, \tag{4-31}$$

$$v = y_1 - (m_2y_2 + m_3y_3)/(m_2 + m_3), \tag{4-32}$$

$$w = x_1 - (m_2x_2 + m_3x_3)/(m_2 + m_3). \tag{4-33}$$

Eqs. (4-31)-(4-33) along with the Eckart conditions give for the instantaneous cartesian position coordinates:

$$x_1 = (\mu/m_1)w, \tag{4-34}$$

$$x_2 = (\mu'/m_2)u - [\mu/(m_2 + m_3)]w, \tag{4-35}$$

$$x_3 = -(\mu'/m_3)u - [\mu/(m_2 + m_3)]w, \tag{4-36}$$

$$y_1 = (\mu/m_1)v \tag{4-37}$$

$$y_2 = (\mu'\gamma/m_2)u + (\mu\alpha/m_2)v + (\mu''/m_2)w, \tag{4-38}$$

$$y_3 = -(\mu'\gamma/m_3)u - (\mu\beta/m_3)v - (\mu''/m_3)w, \tag{4-39}$$

with

$$\mu = [m_1(m_2 + m_3)]/M\ , \tag{4-40}$$

$$\mu' = m_2m_3/(m_2 + m_3), \tag{4-41}$$

$$\mu'' = m_1y_{\circ 1}/x_{23}, \tag{4-42}$$

$$\alpha = -x_{13}/x_{23}, \tag{4-43}$$

$$\beta = -x_{12}/x_{23}, \tag{4-44}$$

$$\gamma = y_{23}/x_{23} = -\tan\theta, \tag{4-45}$$

where

$$x_{12} = x_{\circ 1} - x_{\circ 2} = -b\cos\theta + c\sin\theta, \tag{4-46}$$

$$x_{13} = x_{\circ 1} - x_{\circ 3} = a\cos\theta + c\sin\theta, \tag{4-47}$$

$$x_{23} = x_{\circ 2} - x_{\circ 3} = (a + b)\cos\theta, \tag{4-48}$$

$$y_{23} = y_{\circ 2} - y_{\circ 3} = -(a + b)\sin\theta. \tag{4-49}$$

The vibrational kinetic energy is

$$T = \frac{1}{2} \sum_i m_i(\dot{x}_i^{\,2} + \dot{y}_i^{\,2} + \dot{z}_i^{\,2})$$

$$= \frac{1}{2} (\mu_{11}\dot{u}^{\,2} + \mu_{22}\dot{v}^{\,2} + \mu_{33}\dot{w}^{\,2} + 2\mu_{12}\dot{u}\dot{v}$$

$$+ 2\mu_{13}\dot{u}\dot{w} + 2\mu_{23}\dot{v}\dot{w}), \tag{4-50}$$

which can be expressed in terms of the intermediate coordinates as

$$T = \frac{1}{2} (\dot{w})(\mu)(\dot{w})^t , \tag{4-51}$$

where

$$\dot{w} = (\dot{u}\ \dot{v}\ \dot{w}), \tag{4-52}$$

and t denotes the transpose; (μ) is the 3×3 symmetric matrix with elements

$$\mu_{11} = \mu'(1 + \gamma^2), \tag{4-53}$$

$$\mu_{22} = \mu^2[(1/m_1) + (\alpha^2/m_2) + (\beta^2/m_3)], \tag{4-54}$$

$$\mu_{33} = \mu + (\mu''^2/\mu'), \tag{4-55}$$

$$\mu_{12} = \mu_{21} = \mu'''\gamma, \tag{4-56}$$

$$\mu_{13} = \mu_{31} = \mu''\gamma, \tag{4-57}$$

$$\mu_{23} = \mu_{32} = \mu''\mu'''/\mu', \tag{4-58}$$

where

$$\mu''' = -m_1x_{\circ 1}/x_{23} = \mu\mu'[(\alpha/m_2) + (\beta/m_3)]. \tag{4-59}$$

Now, the most general form for the harmonic potential energy can be expressed in the intermediate coordinates as

$$V = \frac{1}{2}(\omega)(k)(\omega)^t, \tag{4-60}$$

where $(\omega) = (u\ v\ w)$ and (k) is the 3×3 symmetric matrix of potential constants with elements k_{11}, k_{22}, k_{33}, $k_{12} = k_{21}$, $k_{13} = k_{31}$, $k_{23} = k_{32}$. The potential is invariant under the group symmetry of the molecule C_{1h} and can be written explicitly as

$$V = \frac{1}{2}\,(k_{11}u^2 + k_{22}v^2 + k_{33}w^2 + 2k_{12}uv$$
$$+ 2k_{13}uw + 2k_{23}vw)\ . \tag{4-61}$$

The symmetry coordinates u,v,w are related to the normal coordinates Q_s $(s = 1,2,3)$ through a set of transformation coefficients $n_{s's}$,

$$u = \Sigma_s\ n_{1s}Q_s, \qquad s = 1,2,3, \tag{4-62}$$

$$v = \Sigma_s\ n_{2s}Q_s, \qquad s = 1,2,3, \tag{4-63}$$

$$w = \Sigma_s\ n_{3s}Q_s, \qquad s = 1,2,3, \tag{4-64}$$

where these coefficients can be obtained in general only by solving the cubic secular equation

$$|\lambda(\mu) - (k)| = 0\ . \tag{4-65}$$

Each $n_{s's}$ can be expressed as

$$n_{s's} = \frac{N_{s's}}{N_s}\ , \tag{4-66}$$

where $N_{s's}$ is the cofactor of the s'-th element of any row of the determinant, Eq. (4-65), and where $\lambda = \lambda_s$ is the s-th root of Eq. (4-65). The quantity N_s is determined such that

$$T = \frac{1}{2} (\dot{Q}_1^2 + \dot{Q}_2^2 + \dot{Q}_3^2) , \tag{4-67}$$

which requires that

$$N_s^2 = \Sigma_{s'=1,3} [\mu_{s's'} N_{s's}^2 + \Sigma_{s''\neq s'} \mu_{s's''} N_{s's} N_{s''s}] . \tag{4-68}$$

Expressed in the normal coordinates, the harmonic portion of the potential energy becomes

$$V = \frac{1}{2} (\lambda_1 Q_1^2 + \lambda_2 Q_2^2 + \lambda_3 Q_3^2), \tag{4-69}$$

where the associated normal frequencies, in radians per second, are $\lambda_s^{\frac{1}{2}}$ (s = 1,2,3). The normal frequencies $\lambda_s^{\frac{1}{2}}$ could be specified in closed form as the roots of the general cubic equation. These expressions are of limited practical use, as ordinarily it is the three roots λ_s for which numerical values are known and the potential constants k_{ij} for which numerical values are sought. As there are three λ_s and six distinct potential constants k_{ij}, the problem is underdetermined and additional relations must be obtained through intercomparison of isotopically substituted species and through information derived via the second-order parameters of the Hamiltonian.

The normal vibrations problem has been presented above in such a way that specializing the results of this and the following section to the XYX-type molecule will reduce these directly to the results of Chung and Parker,[22] Yallabandi and Parker,[25] and Chan, Wilardjo, and Parker.[26]

The normal mode $s = 1$ specifies the X-Y bond stretching mode, $s = 2$ specifies the bending mode, and $s = 3$ the Y-Z bond stretching mode. The three normal modes are sketched in Figure (4-2).

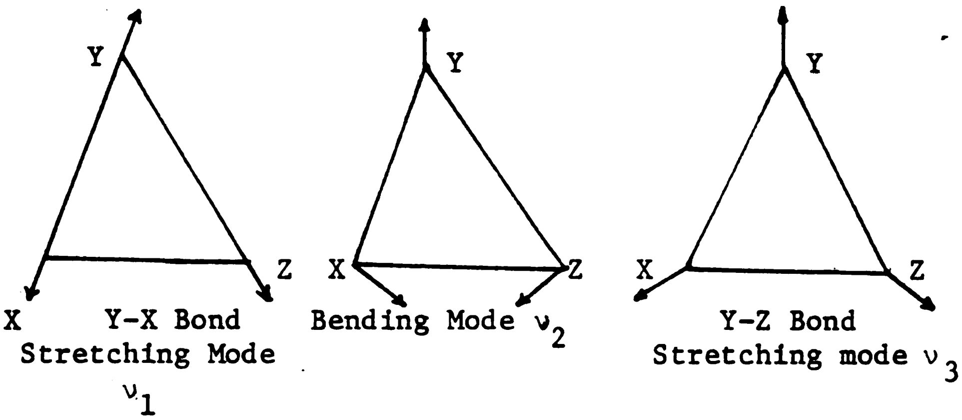


Figure (4-2). Normal Modes of the XYZ Molecule.

4.3 Molecular Parameters of the XYZ-type Molecule

The coefficients ℓ^{α}_{is}, $\alpha = x,y,z$ of the transformation from instantaneous position coordinates to normal coordinates are defined by Eq. (2-4) and can be constructed for the XYZ-type molecule with the aid of Eqs. (4-34)-(4-39) and (4-62)-(4-64). In this manner one determines that

$$\ell^{x}_{1s} = (\mu/m_1^{1/2})n_{3s}, \tag{4-70}$$

$$\ell^{x}_{2s} = (\mu'/m_2^{1/2})n_{1s} - [\mu m_2^{1/2}/(m_2 + m_3)]n_{3s} \tag{4-71}$$

$$\ell^{x}_{3s} = -(\mu'/m_3^{1/2})n_{1s} - [\mu m_3^{1/2}/(m_2 + m_3)]n_{3s}, \tag{4-72}$$

$$\ell^{y}_{1s} = (\mu/m_1^{1/2})n_{2s}, \tag{4-73}$$

$$\ell^{y}_{2s} = (\mu'\gamma/m_2^{1/2})n_{1s} + (\mu\alpha/m_2^{1/2})n_{2s} + (\mu''/m_2^{1/2})n_{3s}, \tag{4-74}$$

$$\ell^{y}_{3s} = -(\mu'\gamma/m_3^{1/2})n_{1s} - (\mu\beta/m_3^{1/2})n_{2s} - (\mu''/m_3^{1/2})n_{3s}, \tag{4-75}$$

$$\ell^z_{1s} = \ell^z_{2s} = \ell^z_{3s} = 0 \qquad s = 1,2,3. \tag{4-76}$$

Knowing the set of coefficients ℓ^α_{is}, one can construct the Coriolis constants, $\zeta^\alpha_{ss'}$ from Eq. (2-7) as

$$\zeta^\alpha_{ss'} = \sum_{i=1}^{3} (\ell^\beta_{is}\ell^\gamma_{is'} - \ell^\gamma_{is}\ell^\beta_{is'}), \tag{4-77}$$

where α,β, and γ denote x,y, and z, respectively, or one of their two cyclic permutations. One finds that

$$\zeta^x_{ss'} = \zeta^y_{ss'} = \zeta^z_{ss} = 0, \tag{4-78}$$

for any s and s'. The only non-vanishing Coriolis constants are the following:

$$\zeta^z_{ss'} = -\zeta^z_{s's} = -\mu(n_{2s}n_{3s'} - n_{2s'}n_{3s}) + \mu'''(n_{1s}n_{2s'} - n_{1s'}n_{2s})$$
$$+ \mu''(n_{1s}n_{3s'} - n_{1s'}n_{3s}),\ s \neq s'. \tag{4-79}$$

It is customary to suppress the upper index for $\zeta^z_{ss'}$. There are then three distinct non-vanishing Coriolis constants, viz.,

$$\zeta_{12} = -\zeta_{21} \qquad \zeta_{13} = -\zeta_{31} \qquad \zeta_{23} = -\zeta_{32}, \tag{4-80}$$

and these constants obey the sum rule[4,28]

$$\zeta^2_{12} + \zeta^2_{13} + \zeta^2_{23} = 1. \tag{4-81}$$

The coefficients of expansion of the instantaneous moments and products of inertia introduced in Eqs. (2-28) and (2-29) take the following form for the XYZ-type molecule:

$$a^{xx}_s = t^{xx}_1 n_{1s} + t^{xx}_2 n_{2s} + t^{xx}_3 n_{3s}, \tag{4-82}$$

$$a_s^{yy} = t_1^{yy}n_{1s} + t_2^{yy}n_{2s} + t_3^{yy}n_{3s}, \tag{4-83}$$

$$a_s^{zz} = t_1^{zz}n_{1s} + t_2^{zz}n_{2s} + t_3^{zz}n_{3s} = a_s^{xx} + a_s^{yy}, \tag{4-84}$$

$$a_s^{xy} = t_1^{xy}n_{1s} + t_2^{xy}n_{2s} + t_3^{xy}n_{3s} = a_s^{yx}, \tag{4-85}$$

where the coefficients $t_i^{\alpha\beta}$ are summarized in Table (4-1). All other $a_s^{\alpha\beta}$ vanish. The non-vanishing $(A_{ss'}^{\alpha\alpha})'$ and $(A_{ss'}^{\alpha\beta})'$ are given by

$$(A_{ss'}^{yy})' = (A_{s's}^{yy})' = A_{ss'}^{yy} = A_{s's}^{yy}$$

$$= \mu' n_{1s}n_{1s'} + \mu n_{3s}n_{3s'}, \tag{4-86}$$

$$(A_{11}^{zz})' = (\zeta_{23})^2,\ (A_{22}^{zz})' = (\zeta_{13})^2,\ (A_{33}^{zz})' = (\zeta_{12})^2, \tag{4-87}$$

$$(A_{12}^{zz})' = -\zeta_{13}\zeta_{23},\ (A_{13}^{zz})' = \zeta_{12}\zeta_{23},\ (A_{23}^{zz})' = -\zeta_{12}\zeta_{13}, \tag{4-88}$$

$$(A_{ss'}^{xy})' = (A_{s's}^{yx}) = A_{ss'}^{xy} = A_{s's}^{yx}$$

$$= -(\mu'\gamma\, n_{1s}n_{1s'} + \mu''' n_{1s}n_{2s'} + \mu'' n_{1s}n_{3s'}$$

$$+ \mu\, n_{3s}n_{2s'}). \tag{4-89}$$

In Eqs. (4-87) and (4-88), we have used that $A_{ss'}^{zz} = \delta_{ss'}$.

Direct computation of $(A_{ss'}^{xx})'$ yields the rather complicated expression

$$(A_{ss'}^{xx})' = (A_{s's}^{xx})' = A_{ss'}^{xx} = A_{s's}^{xx} = \mu'\gamma^2 n_{1s}n_{1s'} + \mu^2\left(\frac{1}{m_1} + \frac{\alpha^2}{m_2} + \frac{\beta^2}{m_3}\right)n_{2s}n_{2s'}$$

$$+ \frac{\mu''^2}{\mu'} n_{3s}n_{3s'} + \mu'''\gamma(n_{1s}n_{2s'} + n_{1s'}n_{2s})$$

$$+ \mu''\gamma(n_{1s}n_{3s'} + n_{1s'}n_{3s}) + \frac{\mu''\mu'''}{\mu'}(n_{2s}n_{3s'} + n_{2s'}n_{3s}). \tag{4-90}$$

Table (4-1). The Coefficients $t_i^{\alpha\beta}$ Introduced in Eqs. (4-82)-(4-85)

$$t_1^{xx} = \frac{2m_2m_3(a + b)\sin^2\theta}{(m_2 + m_3)\cos\theta} \qquad t_1^{yy} = \frac{2m_2m_3(a + b)\ \cos\theta}{(m_2 + m_3)}$$

$$t_2^{xx} = \frac{2m_1(m_2 + m_3)c}{M\ \cos\theta} \qquad t_2^{yy} = 0$$

$$t_3^{xx} = -2m_1y_{\circ 1}\ \tan\theta \qquad t_3^{yy} = 2m_1x_{\circ 1}$$

$$t_1^{zz} = \frac{2m_2m_3(a + b)}{(m_2 + m_3)\ \cos\theta} = t_1^{xx} + t_1^{yy} \qquad t_1^{xy} = \frac{2m_2m_3(a + b)\ \sin\theta}{(m_2 + m_3)}$$

$$t_2^{zz} = t_2^{xx} \qquad t_2^{xy} = 0$$

$$t_3^{zz} = \frac{2m_1(m_3a - m_2b)}{M\ \cos\theta} = t_3^{xx} + t_3^{yy} \qquad t_3^{xy} = -2m_1y_{\circ 1}$$

$x_{\circ 1}$ and $y_{\circ 1}$ are as given by Eqs. (4-18) and (4-21)

Using the sum rule of Oka and Morino[28] given for $s = s'$, namely $\sum_\alpha A_{ss}^{\alpha\beta} = 2$, one can avoid the above result and write $(A_{ss}^{xx})'$ for the XYZ-type molecule simply as

$$(A_{ss}^{xx})' = 1 - (A_{ss}^{yy})', \qquad s = 1,2,3, \tag{4-91}$$

with $(A_{ss}^{yy})'$ given by Eq. (4-86). For $s \neq s'$, Amat and Henry[12] have shown that

$$(A_{ss'}^{xx})' = -(A_{ss'}^{yy})' \ . \tag{4-92}$$

Combining Eqs. (4-91) and (4-92), we have

$$(A_{ss'}^{xx})' + (A_{ss'}^{yy})' = \delta_{ss'} \ . \tag{4-93}$$

Amat and Henry have also shown that the following simple relations exist between the $a_s^{\alpha\beta}$ and the $A_{ss'}^{\alpha\beta}$:

$$(A_{ss'}^{\alpha\alpha})' = \frac{1}{4} \Sigma_\gamma \ a_s^{\alpha\gamma} a_{s'}^{\alpha\gamma}/I_{\gamma\gamma}^\circ , \tag{4-94}$$

$$(A_{ss'}^{\alpha\beta})' + (A_{ss'}^{\beta\alpha})' = \frac{1}{4} \Sigma_\gamma (a_s^{\alpha\gamma} a_{s'}^{\beta\gamma} + a_{s'}^{\alpha\gamma} a_s^{\beta\gamma})/I_{\gamma\gamma}^\circ \ . \tag{4-95}$$

Another useful sum rule is given for $\sum_s A_{ss}^{\alpha\alpha}$ which for XYZ yields

$$(A_{11}^{xx})' + (A_{22}^{xx})' + (A_{33}^{xx})' = \frac{3}{2} + (I_{xx}^\circ - I_{yy}^\circ)/2I_{zz}^\circ \tag{4-96}$$

$$(A_{11}^{yy})' + (A_{22}^{yy})' + (A_{33}^{yy})' = \frac{3}{2} + (I_{yy}^\circ - I_{xx}^\circ)/2I_{zz}^\circ \ . \tag{4-97}$$

The equations, coefficients and sum rules given in this section can be specialized to XYX-type molecules. This case will be discussed in the following section.

4.4 Molecular Parameters of the XYX-type Molecule

The normal modes problem for the XYX-type molecule has been discussed by Chung and Parker.[22] The problem can be considered as a special case of the XYZ development just presented above. Let the molecule be in the xy plane as shown in Figure (4-3) with the origin at the center of mass. The X atoms are located at the base vertices

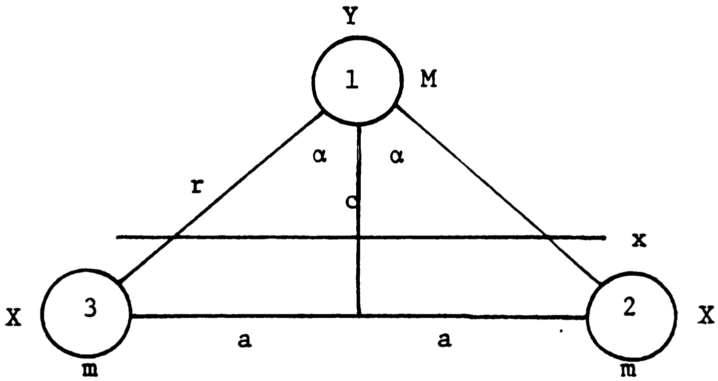


Figure (4-3). Equilibrium configuration of the non-linear XYX molecule.

while the Y atom is at the top vertex of the triangle, and XX is chosen parallel to the x axis. The equilibrium coordinates x_{oi}, y_{oi}, $i = 1,2,3$ are:

$$x_{01} = 0, \tag{4-98}$$

$$x_{02} = r \sin\alpha, \tag{4-99}$$

$$x_{03} = -r \sin\alpha, \tag{4-100}$$

$$y_{01} = \frac{\mu}{M} r \cos\alpha, \tag{4-101}$$

$$y_{02} = -\frac{\mu}{2m} r \cos\alpha, \tag{4-102}$$

$$y_{03} = -\frac{\mu}{2m} r \cos\alpha, \tag{4-103}$$

where

$$\mu = \frac{2m\ M}{2m + M}\ . \tag{4-104}$$

The equilibrium principal moments of inertia are

$$I^\circ_{xx} = \mu r^2 \cos^2\alpha, \tag{4-105}$$

$$I^\circ_{yy} = 2m\ r^2 \sin^2\alpha, \tag{4-106}$$

$$I^\circ_{zz} = I^\circ_{xx} + I^\circ_{yy} = 2m(\frac{\mu_3}{\mu}) r^2 \sin^2\alpha, \tag{4-107}$$

where

$$\mu_3 = \mu[1 + (\mu/2m)\cot^2\alpha]. \tag{4-108}$$

Denoting instantaneous position coordinates by x_i and y_i, we have for the Eckart conditions

$$m(x_2 + x_3) + Mx_1 = 0, \tag{4-109}$$

$$m(y_2 + y_3) + My_1 = 0, \tag{4-110}$$

$$m\ r\ \sin\ (y_2 - y_3) = \frac{1}{2}\ \mu\ r\ \cos\alpha(2x_1 - x_2 - x_3). \tag{4-111}$$

If we now introduce mass-adjusted symmetry coordinates u, v, w as follows:

$$u = (m/2)^{\frac{1}{2}}(x_2 - x_3), \tag{4-112}$$

$$v = \mu^{\frac{1}{2}}[y_1 - \frac{1}{2}(y_2 + y_3)\ , \tag{4-113}$$

$$w = \mu_3^{\frac{1}{2}}[x_1 - \frac{1}{2}(x_2 + x_3)], \tag{4-114}$$

then the vibrational kinetic energy becomes

$$T = \frac{1}{2}(\dot{u}^2 + \dot{v}^2 + \dot{w}^2), \tag{4-115}$$

and the harmonic potential energy is

$$V = \frac{1}{2}(k_{11}u^2 + k_{22}v^2 + k_{33}w^2 + 2k_{12}uv). \tag{4-116}$$

It is important to note that when the comparison is made between a molecule of the XYX-type and one of the XYZ-type, the conventional definition of the intermediate coordinates of XYX, Eqs. (4-112)-(4-114), is inconsistent with the corresponding definition for XYZ, Eqs. (4-31)-(4-33). Hence there arises an inconsistency in the definition of the harmonic potential constants. This discrepancy must be taken into account whenever expressions applying to XYZ are specialized to XYX according to the replacement scheme:

$$k_{11}(XYX') \rightarrow \frac{1}{2}\, m_2 k_{11}(XYX), \tag{4-117}$$

$$k_{22}(XYX') \rightarrow \mu k_{22}(XYX), \tag{4-118}$$

$$k_{33}(XYX') \rightarrow \mu_3 k_{33}(XYX), \tag{4-119}$$

$$k_{12}(XYX') \rightarrow (\frac{1}{2}\, \mu m_2)^{\frac{1}{2}} k_{12}(XYX), \tag{4-120}$$

$$k_{13}(XYX') \rightarrow 0, \tag{4-121}$$

$$k_{23}(XYX') \rightarrow 0. \tag{4-122}$$

Also, specializing to XYX, the angle θ defined by Eqs. (4-15)-(4-17) is equal to zero. The transformation from symmetry coordinates u,v,w to normal coordinates Q_1,Q_2,Q_3 can be taken as

$$u = Q_1\cos\gamma - Q_2\sin\gamma, \tag{4-123}$$

$$v = Q_1\sin\gamma + Q_2\cos\gamma, \tag{4-124}$$

$$w = Q_3, \tag{4-125}$$

with

$$\sin\gamma = +(1/\sqrt{2})(1 - \{\Delta k/[(\Delta k)^2 + 4k_{12}{}^2]^{\frac{1}{2}}\})^{\frac{1}{2}}, \tag{4-126}$$

$$\cos\gamma = +(1 - \sin^2\gamma)^{\frac{1}{2}}, \tag{4-127}$$

and with

$$\Delta k = (k_{11} - k_{22}). \tag{4-128}$$

The normal coordinate transformation is such that Q_1 is the coordinate of the symmetric bond stretching or "breathing mode", Q_2 is the coordinate of the bending mode, and Q_3 is the coordinate of the asymmetric bond stretching mode. The normal frequencies $\lambda_1^{\frac{1}{2}}$, $\lambda_2^{\frac{1}{2}}$, $\lambda_3^{\frac{1}{2}}$ (in radians per second) are given by

$$\lambda_1 = \frac{1}{2}(k_{11} + k_{22}) + \frac{1}{2}[(\Delta k)^2 + 4k_{12}{}^2]^{\frac{1}{2}}, \tag{4-129}$$

$$\lambda_2 = \frac{1}{2}(k_{11} + k_{22}) - \frac{1}{2}[(\Delta k)^2 + 4k_{12}{}^2]^{\frac{1}{2}}, \tag{4-130}$$

$$\lambda_3 = k_{33} . \tag{4-131}$$

The transformation between displacement coordinates and normal coordinates, of the form

$$m_i^{\frac{1}{2}}\alpha_i = \sum_n \ell_{is}^{\alpha} Q_s \qquad \alpha = x,y,z, \tag{4-132}$$

can be developed and the transformation coefficients ℓ_{is}^{α} are found to be the following ones.

$$\ell_{11}{}^{x} = 0 \qquad \ell_{11}{}^{y} = (\mu/M)^{\frac{1}{2}}\sin\gamma \tag{4-133}$$

$$\ell_{21}{}^{x} = \cos\gamma/\sqrt{2} \qquad \ell_{21}{}^{y} = -\tfrac{1}{2}(\mu/m)^{\frac{1}{2}}\sin\gamma \tag{4-134}$$

$$\ell_{31}{}^{x} = -\cos\gamma/\sqrt{2} \qquad \ell_{31}{}^{y} = -\tfrac{1}{2}(\mu/m)^{\frac{1}{2}}\sin\gamma \tag{4-135}$$

and

$$\ell_{12}^{x} = 0 \qquad \ell_{12}^{y} = (\mu/M)^{\frac{1}{2}}\cos\gamma \tag{4-136}$$

$$\ell_{22}^{x} = -\sin\gamma/\sqrt{2} \qquad \ell_{22}^{y} = -\tfrac{1}{2}(\mu/m)^{\frac{1}{2}}\cos\gamma \tag{4-137}$$

$$\ell_{32}^{x} = \sin\gamma/\sqrt{2} \qquad \ell_{32}^{y} = -\tfrac{1}{2}(\mu/m)^{\frac{1}{2}}\cos\gamma \tag{4-138}$$

and

$$\ell_{13}^{x} = (\mu/M)(M/\mu_3)^{\frac{1}{2}} \qquad \ell_{13}^{y} = 0 \tag{4-139}$$

$$\ell_{23}^{x} = -(\mu/2m)(m/\mu_3)^{\frac{1}{2}} \qquad \ell_{23}^{y} = (\mu/2m)(m/\mu_3)^{\frac{1}{2}}\cot\alpha_0 \tag{4-140}$$

$$\ell_{33}^{x} = -(\mu/2m)(m/\mu_3)^{\frac{1}{2}} \qquad \ell_{33}^{y} = -(\mu/2m)(m/\mu_3)^{\frac{1}{2}}\cot\alpha_0 \tag{4-141}$$

and

$$\ell_{in}^{z} = 0, \; i = 1,2,3; \; n = 1,2,3. \tag{4-142}$$

Knowing the ℓ_{is}^{α} coefficients, we can construct the Coriolis constants ζ_{mn}^{α} from Eq. (4-77),

$$\zeta_{mn}^{\alpha} = \sum_{i} (\ell_{im}^{\beta}\ell_{in}^{\gamma} - \ell_{in}^{\beta}\ell_{im}^{\gamma}), \tag{4-143}$$

with α,β,γ denoting a cyclic permutation of x,y,z. This gives

$$\zeta_{mn}^{x} = \zeta_{mn}^{y} = 0, \qquad m = 1,2,3; \; n = 1,2,3; \tag{4-144}$$

$$\zeta_{12}^{z} = \zeta_{21}^{z} = 0; \tag{4-145}$$

$$\zeta_{13}^{z} = -\zeta_{31}^{z} = (I_x/I_z)^{\frac{1}{2}}\cos\gamma - (I_y/I_z)^{\frac{1}{2}}\sin\gamma, \tag{4-146}$$

$$\zeta_{23}^{z} = -\zeta_{32}^{z} = -(I_x/I_z)^{\frac{1}{2}}\sin\gamma - (I_y/I_z)^{\frac{1}{2}}\cos\gamma, \tag{4-147}$$

$$(\zeta_{13}^{z})^2 + (\zeta_{23}^{z})^2 = 1. \tag{4-148}$$

Again the superscript z can be omitted since the only non-zero Coriolis constants are those with superscript z.

We also will need the coefficients of expansion $a_s^{\alpha\beta}$ and $(A_{ss'}^{\alpha\beta})'$ of the instantaneous moments and products of inertia introduced in Eqs. (2-28) and (2-29). The non-vanishing coefficients $a_n^{\alpha\beta}$ are

$$a_1^{xx} = 2I_x^{\frac{1}{2}}\sin\gamma \qquad a_2^{xx} = 2I_x^{\frac{1}{2}}\cos\gamma \tag{4-149}$$

$$a_1^{yy} = 2I_y^{\frac{1}{2}}\cos\gamma \qquad a_2^{yy} = -2I_y^{\frac{1}{2}}\sin\gamma \tag{4-150}$$

$$a_1^{zz} = a_1^{xx} + a_1^{yy} = -2I_z^{\frac{1}{2}}\zeta_{23} \qquad a_2^{zz} = a_2^{xx} + a_2^{yy} = -2I_z^{\frac{1}{2}}\zeta_{31} \tag{4-151}$$

and

$$a_3^{xy} = -2(I_xI_y/I_z)^{\frac{1}{2}} \tag{4-152}$$

The non-vanishing $(A_{ss'}^{\alpha\alpha})'$ and $(A_{ss'}^{\alpha\beta})'$ are given as

$$(A_{11}^{xx})' = (A_{22}^{yy})' = \sin^2\gamma \tag{4-153}$$

$$(A_{22}^{xx})' = (A_{11}^{yy})' = \cos^2\gamma \tag{4-154}$$

$$(A_{33}^{xx})' = I_x/I_z \tag{4-155}$$

$$(A_{33}^{yy})' = I_y/I_z \tag{4-156}$$

$$(A_{12}^{xx})' = (A_{21}^{xx})' = -(A_{12}^{yy})' = -(A_{21}^{yy})' = \sin\gamma\cos\gamma \tag{4-157}$$

and

$$(A_{13}^{xy})' = (A_{31}^{yx})' = -(I_x/I_z)^{\frac{1}{2}}\cos\gamma \tag{4-158}$$

$$(A_{31}^{xy})' = (A_{13}^{yx})' = -(I_y/I_z)^{\frac{1}{2}}\sin\gamma \tag{4-159}$$

$$(A_{23}^{xy})' = (A_{32}^{yx})' = +(I_x/I_z)^{\frac{1}{2}}\sin\gamma \tag{4-160}$$

$$(A_{32}^{xy})' = (A_{23}^{yx})' = -(I_y/I_z)^{\frac{1}{2}}\cos\gamma \tag{4-161}$$

These coefficients will be used in Chapter 9 for calculating the centrifugal distortion coefficients of ozone.

5. CENTRIGUFAL DISTORTION COEFFICIENTS FOR TRIANGULAR TRIATOMIC MOLECULES

In this chapter there will be described a number of schemes of development and rearrangement of the Hamiltonian into a form in which the effects of centrifugal distortion on the rotational energies are explicitly apparent.

5.1 Development of the Hamiltonian

It was shown by Kneizys, Freedman, and Clough[29] that the vibration-rotation Hamiltonian for the XYZ-type molecule in general, and for XYX in particular, could be given in a simplified form through extensive rearrangement based on the angular momentum commutation relations

$$[P_\alpha, P_\beta] = -i \hbar P_\gamma, \qquad \alpha,\beta,\gamma \text{ cyclic.} \tag{5-1}$$

The form of the resulting Hamiltonian is, for a given vibrational state, a power series in the angular momentum components which needs for its specification, to fourth order of approximation, three coefficients A, B, and C, of terms of the second power in the body-fixed angular momentum components; six coefficients T_i of fourth-power angular momentum terms; and ten coefficients of sixth-power angular momentum terms. For XYX-type molecules, the Hamiltonian of a given vibrational state can eventually be written as[29]

$$H = H_2 + H_4 + H_6 \ , \tag{5-2}$$

where

$$H_2 = A\,P_x^2 + B\,P_y^2 + C\,P_z^2, \tag{5-3}$$

$$H_4 = T_1P_x^4 + T_2P_y^4 + T_3P_z^4 + T_4(P_y^2P_z^2 + P_z^2P_y^2) + T_5(P_z^2P_x^2 + P_x^2P_z^2) + T_6(P_x^2P_y^2 + P_y^2P_x^2), \tag{5-4}$$

$$H_6 = \Phi_1P_x^6 + \Phi_2P_y^6 + \Phi_3P_z^6 + \Phi_4(P_x^2P_y^4 + P_y^4P_x^2) + \Phi_5(P_y^2P_x^4 + P_x^4P_y^2) + \Phi_6(P_y^2P_z^4 + P_z^4P_y^2) + \Phi_7(P_z^2P_y^4 + P_y^4P_z^2) + \Phi_8(P_z^2P_x^4 + P_x^4P_z^2) + \Phi_9(P_x^2P_z^4 + P_z^4P_x^2) + \Phi_{10}(P_x^2P_z^2P_y^2 + P_y^2P_z^2P_x^2) \ , \tag{5-5}$$

For the XYZ-type molecule, an additional contribution must be added to (5-2), viz.,

$$H_{6a} = D(P_xP_y + P_yP_x) + \frac{1}{4}\,\tau_{10}(P_x^3P_y + P_yP_x^3) + \frac{1}{4}\,\tau_{11}(P_y^3P_x + P_xP_y^3) + \frac{1}{4}\,\tau_{12}(P_xP_z^2P_y + P_yP_z^2P_x). \tag{5-6}$$

This contribution was originally developed by Chung and Parker.[18] The coefficients τ appear here with numerical subscripts. These take the place of the more elaborate notation $\tau_{\alpha\beta\gamma\delta}$.[18] The coefficients of the terms quadratic in P_α are the effective rotational constants, equal to the equilibrium rotational constants $(1/2I^\circ_{\alpha\alpha})$ of O(0) [order zero], plus second-order centrifugal distortion corrections to the equilibrium τ_i, plus second-order vibrational corrections, α_s^α. There are also terms of O(4). More explicitly:

$$A = 1/(2I^{\circ}_{xx}) + \Sigma_{s=1}^{3} \alpha_s^x (v_s + \tfrac{1}{2}) - \tfrac{1}{2} \hbar^2 \tau_9 + O(4), \tag{5-7}$$

$$B = 1/(2I^{\circ}_{yy}) + \Sigma_{s=1}^{3} \alpha_s^y (v_s + \tfrac{1}{2}) - \tfrac{1}{2} \hbar^2 \tau_9 + O(4), \tag{5-8}$$

$$C = 1/(2I^{\circ}_{zz}) + \Sigma_{s=1}^{3} \alpha_s^z (v + \tfrac{1}{2}) + \tfrac{3}{4} \hbar^2 \tau_9 + O(4), \tag{5-9}$$

where

$$\alpha_s^{\alpha} = {}^{\alpha\alpha}_{(2)}X_{ss} + {}^{\alpha\alpha}\gamma_s + \hbar^2({}^{\alpha\alpha}\gamma^{ss}). \tag{5-10}$$

The coefficients ${}^{\alpha\alpha}_{(2)}X_{ss}$, ${}^{\alpha\alpha}\gamma_s$, and ${}^{\alpha\alpha}\gamma^{ss}$ are given by Amat, Nielsen and Tarrago.[12] The other coefficients in Eqs. (5-3)-(5-6) are given by:

$$D = \Sigma_{s=1}^{3}[{}^{xy}_{(2)}X_{ss} + {}^{xy}\gamma_{ss} + \hbar^2({}^{xy}\gamma^{ss})](v_s + \tfrac{1}{2})$$

$$- \tfrac{1}{4} \hbar^2(\tau_{10} + \tau_{11} - 2\,\tau_{12}), \tag{5-11}$$

$$T_1 = \tfrac{1}{4} (\tau_1 + \rho_1) + \hbar^2 \Phi_{11}, \tag{5-12}$$

$$T_2 = \tfrac{1}{4} (\tau_2 + \rho_2) + \hbar^2 \Phi_{12}, \tag{5-13}$$

$$T_3 = \tfrac{1}{4} (\tau_3 + \rho_3) + \hbar^2 \Phi_{13}, \tag{5-14}$$

$$T_4 = \tfrac{1}{4} (\tau_4 + \rho_4^*) + \hbar^2 \Phi_{14}, \tag{5-15}$$

$$T_5 = \tfrac{1}{4} (\tau_5 + \rho_5^*) + \hbar^2 \Phi_{15}, \tag{5-16}$$

$$T_6 = \tfrac{1}{4} (\tau_6^* + \rho_6^*) + \hbar^2 \Phi_{16}, \tag{5-17}$$

where the τ_i are the centrifugal distortion coefficients of $O(2)$, ρ_1 to ρ_3, ρ_4^* to ρ_6^*, of $O(4)$, are the vibrational corrections to the τ_i, and Φ_{11} to Φ_{16} are rotational corrections to τ of $O(4)$. The terms Φ_{11} to Φ_{16} and the ρ-coefficients are not the subject of the present investigation, and their extremely complicated forms will be omitted. The quantity τ_6^* is defined as

$$\tau_6^* = \tau_6 + 2\tau_9 \; . \tag{5-18}$$

Finally, the coefficients of the P^6 terms are the fourth-order centrifugal distortion coefficients, Φ_1 to Φ_{10} in which we are interested in this dissertation. These coefficients have been discussed extensively by Sumberg and Parker,[7] and have been given in a form which exhibits extensive cyclic and algebraic regularities.

The basic form of the transformed Hamiltonian given by Eqs. (5-2)-(5-6) is referred to as the "Φ-form".[25] An alternate form of the Hamiltonian which considerably reduces the computation of matrix elements is expressed in powers of P^2 and P_z (where $P^2 = P_x^2 + P_y^2 + P_z^2$). This is the so-called "H-form":[25,29]

$$H_2 = (A - D_6^*)P_x^2 + (B - D_6^*)P_y^2 + (C - \tfrac{3}{2} D_6^*)P_z^2, \tag{5-19}$$

$$\begin{aligned} H_4 = {} & D_1^* P^4 + D_2^* P^2P_z^2 + D_3^* P_z^4 + D_4^* P^2(P_x^2 - P_y^2) \\ & + D_5^* [P_z^2(P_x^2 - P_y^2) + (P_x^2 - P_y^2)P_z^2] + D_6^* [(P_x^2 - P_y^2)^2 \\ & - \tfrac{1}{2} (P^4 - 2P^2P_z^2 + P_z^4) + \hbar^2(P^2 - \tfrac{5}{2} P_z^2)], \end{aligned} \tag{5-20}$$

$$\begin{aligned} H_6 = {} & H_1 P^6 + H_2 P^4P_z^2 + H_3P^2P_z^4 + H_4P_z^6 + H_5 P^4(P_x^2 - P_y^2) \\ & + H_6[P^2(P_x^2 - P_y^2)^2 - \tfrac{1}{2} (P^6 - 2P^4P_z^2 + P^2P_z^4) \\ & + \hbar^2(P^4 - \tfrac{5}{2} P^2P_z^2)] + H_7\{P^2[P_z^2(P_x^2 - P_y^2) + (P_x^2 - P_y^2)P_z^2]\} \\ & + H_8[P_z^4(P_x^2 - P_y^2) + (P_x^2 - P_y^2)P_z^4] + H_9\{[P_z^2(P_x^2 - P_y^2)^2 \\ & + (P_x^2 - P_y^2)^2P_z^2] - (P^4P_z^2 - 2P^2P_z^4 + P_z^6) \\ & + 2 \hbar^2(P^2P_z^2 - \tfrac{5}{2} P_z^4)\} + H_{10}(P_x^2 - P_y^2)^3, \end{aligned} \tag{5-21}$$

where

$$D_1^* = M_1 + \kappa^2(-2H_1 - H_2 - H_6 + 3H_9), \tag{5-22}$$

$$D_2^* = M_2 + \kappa^2(12H_1 + 6H_2 + H_6 - 20H_9), \tag{5-23}$$

$$D_3^* = M_3 + \kappa^2(-10H_1 - 5H_2 + 20H_9), \tag{5-24}$$

$$D_4^* = M_4, \tag{5-25}$$

$$D_5^* = M_5 + \kappa^2(2H_5 + 4H_7 + 2H_{10}), \tag{5-26}$$

$$D_6^* = M_6 + \kappa^2(4H_1 + 2H_2 - 6H_9), \tag{5-27}$$

with

$$M_1 = \frac{3}{8}(T_1 + T_2) + \frac{1}{4}T_6, \tag{5-28}$$

$$M_2 = -\frac{3}{4}(T_1 + T_2) + (T_4 + T_5) - \frac{1}{2}T_6, \tag{5-29}$$

$$M_3 = \frac{3}{8}(T_1 + T_2) + T_3 - (T_4 + T_5) + \frac{1}{4}T_6, \tag{5-30}$$

$$M_4 = \frac{1}{2}(T_1 - T_2), \tag{5-31}$$

$$M_5 = -\frac{1}{4}(T_1 - T_2) - \frac{1}{2}(T_4 - T_5), \tag{5-32}$$

$$M_6 = \frac{1}{4}(T_1 + T_2) - \frac{1}{2}T_6, \tag{5-33}$$

and

$$H_1 = \frac{5}{16}(\Phi_1 + \Phi_2) + \frac{1}{8}(\Phi_4 + \Phi_5), \tag{5-34}$$

$$H_2 = -\frac{15}{16}(\Phi_1 + \Phi_2) - \frac{3}{8}(\Phi_4 + \Phi_5) + \frac{3}{4}(\Phi_7 + \Phi_8) + \frac{1}{4}\Phi_{10}, \tag{5-35}$$

$$H_3 = \frac{15}{16} (\Phi_1 + \Phi_2) + \frac{3}{8} (\Phi_4 + \Phi_5) + (\Phi_6 + \Phi_9)$$

$$- \frac{3}{2} (\Phi_7 + \Phi_8) - \frac{1}{2} \Phi_{10}, \tag{5-36}$$

$$H_4 = - \frac{5}{16} (\Phi_1 + \Phi_2) + \Phi_3 - \frac{1}{8} (\Phi_4 + \Phi_5) - (\Phi_6 + \Phi_9)$$

$$+ \frac{3}{4} (\Phi_7 + \Phi_8) + \frac{1}{4} \Phi_{10}, \tag{5-37}$$

$$H_5 = \frac{3}{8} (\Phi_1 - \Phi_2) - \frac{1}{4} (\Phi_4 - \Phi_5), \tag{5-38}$$

$$H_6 = \frac{3}{8} (\Phi_1 + \Phi_2) - \frac{1}{4} (\Phi_4 + \Phi_5), \tag{5-39}$$

$$H_7 = - \frac{3}{8} (\Phi_1 - \Phi_2) + \frac{1}{4} (\Phi_4 - \Phi_5) - \frac{1}{2} (\Phi_7 - \Phi_8), \tag{5-40}$$

$$H_8 = \frac{3}{16} (\Phi_1 - \Phi_2) - \frac{1}{8} (\Phi_4 - \Phi_5) - \frac{1}{2} (\Phi_6 - \Phi_9)$$

$$+ \frac{1}{2} (\Phi_7 - \Phi_8), \tag{5-41}$$

$$H_9 = - \frac{3}{16} (\Phi_1 + \Phi_2) + \frac{1}{8} (\Phi_4 + \Phi_5) + \frac{1}{4} (\Phi_7 + \Phi_8)$$

$$- \frac{1}{4} \Phi_{10}, \tag{5-42}$$

$$H_{10} = \frac{1}{8} (\Phi_1 - \Phi_2) + \frac{1}{4} (\Phi_4 - \Phi_5) \; . \tag{5-43}$$

The equivalence of the H-form to the Φ-form can be verified by substitution of Eqs. (5-22)-(5-43) into Eqs. (5-19)-(5-21) and by rearranging the resulting expressions to the form specified by Eqs. (5-3)-(5-5). Here the last term, viz., H_{6a}, has been omitted and can be set equal to zero since the theoretical expressions for the non-zero coefficients D, τ_{10}, τ_{11} and τ_{12} cannot be determined from experiment. This result has been obtained by Watson[30] who showed that the transformed Hamiltonian can be reduced to a form in which all indeterminacies inherent in fitting the complete Hamiltonian to observed energy levels can be avoided.

5.2 Second-order Centrifugal Distortion Constants

From the information of Sections 4.3 and 4.4, the second-order centrifugal distortion constants,

$$\tau_{\alpha\beta\gamma\delta} = -\frac{1}{2}\sum_s a_s^{\alpha\beta}\, a_s^{\gamma\delta}/I_\alpha I_\beta I_\gamma I_\delta \lambda_s, \tag{5-44}$$

can be constructed. These are the coefficients of the fourth-power angular momentum terms of the vibration-rotation Hamiltonian of triangular triatomic molecules. Taking account of the symmetry properties of the $a_s^{\alpha\beta}$ for the case of planar molecules (i.e. $a_s^{\alpha\beta} = a_s^{\beta\alpha}$ and $a_s^{xz} = a_s^{yz} = 0$), one obtains a total of thirteen distinct non-zero coefficients $\tau_{\alpha\beta\gamma\delta}$ according to Eq. (5-44). These coefficients are given in Table (5-1).

Shaffer and Nielsen[20] have originally calculated these constants. They obey the relations of Dowling,[33,34] and Oka and Morino[35] which hold in general for planar asymmetric-top molecules:

$$\tau_1 = (I^\circ_{zz}/I^\circ_{xx})^2\tau_5 - (I^\circ_{yy}/I^\circ_{xx})^2\tau_6 \tag{5-45}$$

$$\tau_2 = (I^\circ_{zz}/I^\circ_{yy})^2\tau_4 - (I^\circ_{xx}/I^\circ_{yy})^2\tau_6 \tag{5-46}$$

$$\tau_3 = (I^\circ_{yy}/I^\circ_{zz})^2\tau_4 + (I^\circ_{xx}/I^\circ_{zz})^2\tau_5 \tag{5-47}$$

$$\tau_7 = \tau_8 = 0\ . \tag{5-48}$$

Thus there are four independent distortion constants from among τ_1 to τ_9. For the XYZ-type molecule, Parker[32] finds that additionally

Table (5-1). Abbreviated Notation for $\tau_{\alpha\beta\gamma\delta}$ Coefficients

	$(\alpha\beta\gamma\delta)$
τ_1 :	(xxxx)
τ_2 :	(yyyy)
τ_3 :	(zzzz)
τ_4 :	(yyzz); (zzyy)
τ_5 :	(xxzz); (zzxx)
τ_6 :	(xxyy); (yyxx)
τ_7 :	(yzyz); (zyzy); (zyyz); (yzzy)
τ_8 :	(xzxz); (zxzx); (zxxz); (xzzx)
τ_9 :	(xyxy); (yxyx); (xyyx); (yxxy)
τ_{10}:	(xxxy); (yxxx)
τ_{11}:	(yyyx); (xyyy)
τ_{12}:	(xyzz); (zzyx)
τ_{13}:	(xzzy); (yzzx)

$$\tau_{12} = (I^{\circ}_{xx}/I^{\circ}_{zz})^2\tau_{10} + (I^{\circ}_{yy}/I^{\circ}_{zz})^2\tau_{11} \tag{5-49}$$

and

$$\tau_{13} = 0, \tag{5-50}$$

whereas for the XYX-type molecule $\tau_{10} = \tau_{11} = \tau_{12} = 0$.

The centrifugal distortion constants τ_1 through τ_6, and τ_9 with the molecule in the xy plane can be constructed with the help of the information introduced in Chapter 4 and this gives the following result:

$$\tau_1 = -(1/2I_x^4)[(t_1^{xx})^2\sigma_{11} + (t_2^{xx})^2\sigma_{22} + (t_3^{xx})^2\sigma_{33} + (2t_1^{xx}t_2^{xx})\sigma_{12} + (2t_2^{xx}t_3^{xx})\sigma_{23} + (2t_3^{xx}t_1^{xx})\sigma_{31}], \tag{5-51}$$

$$\tau_2 = -(1/2I_y^4)[(t_1^{yy})^2\sigma_{11} + (t_3^{yy})^2\sigma_{33} + (2t_3^{yy}t_1^{yy})\sigma_{31}], \tag{5-52}$$

$$\tau_3 = -(1/2I_z^4)[(t_1^{zz})^2\sigma_{11} + (t_2^{zz})^2\sigma_{22} + (t_3^{zz})^2\sigma_{33} + (2t_1^{zz}t_2^{zz})\sigma_{12} + (2t_2^{zz}t_3^{zz})\sigma_{23} + (2t_3^{zz}t_1^{zz})\sigma_{31}], \tag{5-53}$$

$$\tau_4 = -(1/2I_y^2I_z^2)[(t_1^{yy}t_1^{zz})\sigma_{11} + (t_3^{yy}t_3^{zz})\sigma_{33} + (t_1^{yy}t_2^{zz})\sigma_{12} + (t_2^{zz}t_3^{yy})\sigma_{23} + (t_3^{yy}t_1^{zz} + t_3^{zz}t_1^{yy})\sigma_{31}], \tag{5-54}$$

$$\tau_5 = -(1/2I_z^2I_x^2)[(t_1^{xx}I_1^{zz})\sigma_{11} + (t_2^{xx}t_2^{zz})\sigma_{22} + (t_3^{xx}t_3^{zz})\sigma_{33} + (t_1^{xx}t_2^{zz} + t_1^{zz}t_2^{xx})\sigma_{12} + (t_2^{xx}t_3^{zz} + t_2^{zz}t_3^{xx})\sigma_{23} + (t_3^{xx}t_1^{zz} + t_3^{zz}t_1^{xx})\sigma_{31}], \tag{5-55}$$

$$\tau_6 = -(1/2I_x^2I_y^2)[(t_1^{xx}t_1^{yy})\sigma_{11} + (t_3^{xx}t_3^{yy})\sigma_{33} + (t_1^{yy}t_2^{xx})\sigma_{12}$$

$$+ (t_2^{xx}t_3^{yy})\sigma_{23} + (t_3^{xx}t_1^{yy} + t_3^{yy}t_1^{xx})\sigma_{31}], \tag{5-56}$$

$$\tau_9 = -(1/2I_x^2I_y^2)[(t_1^{xy})^2\sigma_{11} + (t_3^{xy})^2\sigma_{33} + (2t_1^{xy}t_3^{xy})\sigma_{31}], \tag{5-57}$$

where the coefficients $t_i^{\alpha\beta}$ are given in Table (4-1),

$$\sigma_{ss'} = \sum_{i=1}^{3} \frac{n_{si}n_{s'i}}{\lambda_i}. \tag{5-58}$$

The symbols x_{12}, x_{13}, x_{23}, y_{23} are defined by Eqs. (4-46)-(4-49); and

$$y_{12} \equiv y_{\circ 1} - y_{\circ 2} = b \sin\theta + c \cos\theta, \tag{5-59}$$

$$y_{13} \equiv y_{\circ 1} - y_{\circ 3} = -a \sin\theta + c \cos\theta. \tag{5-60}$$

Furthermore for brevity we have written all $I^\circ_{\alpha\alpha}$ as I_α, and the latter designation will be used henceforth.

One can now write down the second-order centrifugal distortion constants for XYX-type molecules as a special case of the XYZ molecule and the following results are obtained.

$$\tau_1 = -(2/I_x^3)\sigma_1, \tag{5-61}$$

$$\tau_2 = -(2/I_y^3)\sigma_2, \tag{5-62}$$

$$\tau_3 = -(2/I_z^4)[I_x\sigma_1 + I_y\sigma_2 + 2(I_xI_y)^{\frac{1}{2}}\sigma_3]$$

$$= -(2/I_z^3)[(\zeta_{23}^2/\lambda_1) + (\zeta_{13}^2/\lambda_2)] \tag{5-63}$$

$$\tau_4 = -(2/I_y^2I_z^2)[I_y\sigma_2 + (I_yI_x)^{\frac{1}{2}}\sigma_3] \tag{5-64}$$

$$\tau_5 = -(2/I_z^2I_x^2)[I_x\sigma_1 + (I_xI_y)^{\frac{1}{2}}\sigma_3] \tag{5-65}$$

$$\tau_6 = -(2/I_x^2 I_y^2)(I_x I_y)^{½}\sigma_3 \tag{5-66}$$

$$\tau_9 = -(2/I_x I_y I_z \lambda_3) \tag{5-67}$$

with

$$\sigma_1 = \frac{\sin^2\gamma}{\lambda_1} + \frac{\cos^2\gamma}{\lambda_2} > 0 \tag{5-68}$$

$$\sigma_2 = \frac{\cos^2\gamma}{\lambda_1} + \frac{\sin^2\gamma}{\lambda_2} > 0 \tag{5-69}$$

$$\sigma_3 = \sin\gamma \cos\gamma \left[\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right] < 0 \,. \tag{5-70}$$

Since $\lambda_1 > \lambda_2$ from Eq. (4-129) and (4-130), always $\sigma_3 < 0$.

5.3 Fourth-order Centrifugal Distortion Constants

The principal information of interest obtainable from the fourth-order centrifugal distortion coefficients concerns the cubic potential constants $k_{ss's''}$, which are the coefficients appearing in the anharmonic portion V_3 of the Taylor series expansion of the potential energy in dimensionless normal coordinates. For XYZ-type molecules, the expansion takes the form:

$$\begin{aligned} V_3 = hc\,(&k_{111}\, q_1^3 + k_{222}\, q_2^3 + k_{333}\, q_3^3 + k_{112}\, q_1^2 q_2 \\ &+ k_{113}\, q_1^2 q_3 + k_{122}\, q_1 q_2^2 + k_{223}\, q_2^2 q_3 + k_{133}\, q_1 q_3^2 \\ &+ k_{233}\, q_2 q_3^2 + k_{123}\, q_1 q_2 q_3), \end{aligned} \tag{5-71}$$

with the dimensionless normal coordinates q_s defined by

$$q_s = (\lambda_s/\hbar^2)^{½} Q_s \,. \tag{5-72}$$

The potential constants $k_{ss's''}$ are in cm^{-1} when V_3 is in ergs. It should be noted from (5-71) that for XYZ there are ten distinct cubic potential constants. Yet, only seven Φ_i or combinations thereof are determinable experimentally. Thus, not enough information is available to determine the full set of cubic potential constants from the fourth-order centrifugal distortion constants alone. However, cubic potential constants also appear in the coefficients α_s^α which specify the second-order vibrational corrections to the equilibrium rotational constants. Full use of both the α_s^α and the Φ_i thus opens the possibility of obtaining a complete, consistent, and accurate set of cubic potential constants. Furthermore, it is observed[7] that the α_s^α do not contain those potential constants $k_{ss's''}$ for which $s \neq s' \neq s''$. Therefore, for XYZ the cubic potential constant k_{123} is obtainable only through a determination of the Φ_i. For XYX molecules, there are only six cubic potential constants, and in principle, the full set can be obtained either from the Φ_i alone, or from the α_s^α alone.

By extensive regrouping and redefining of terms, Sumberg and Parker[7] have been able to express the ten Φ_i coefficients in a relatively compact form. Let us introduce the following definitions:

$$b_s^{\alpha\beta} = a_s^{\alpha\beta}/\lambda_s^{3/4} , \tag{5-73}$$

$$B_s^{\alpha\beta} = a_s^{\alpha\beta}/\lambda_s , \tag{5-74}$$

$$(B\zeta)_{\alpha\beta} = B_1^{\alpha\beta}\,\zeta_{23} + B_2^{\alpha\beta}\,\zeta_{31} + B_3^{\alpha\beta}\,\zeta_{12} , \tag{5-75}$$

$$I^{\alpha\alpha} = (I_\gamma - I_\beta)/I_{\alpha\gamma} \quad \alpha \neq \beta \neq \gamma \text{ and cyclic.} \tag{5-76}$$

Thus,

$$I^{zz} = (I_y - I_x)/I_z \ , \tag{5-77}$$

and recognizing that $I_x + I_y = I_z$ one has that

$$I^{xx} = +1, \quad I^{yy} = -1. \tag{5-78}$$

Also let

$$N = \frac{\pi c}{\hbar^{1/2}} \ . \tag{5-79}$$

In terms of the above definitons, the Φ_i coefficients are listed in Table (5-2).

Each of the Φ_i has a set of terms linear in the cubic potential constants $k_{ss's''}$ with coefficients that are symmetrized products of the $b_s^{\alpha\beta}$. In addition, there occur terms independent of the $k_{ss's''}$. These terms depend only on the parameters of the harmonic vibration problem and on the equilibrium geometry. Thus, the fourth-order centrifugal distortion coefficients may be regarded as resulting from the sum of two contributions: cubic anharmonic and harmonic.

The equilibrium geometry of a particular molecule and the parameters of the normal-vibrations problem are usually known through the zeroth and second-order part of the analysis of the high-resolution data, and therefore one may regard the only unknown parameters occurring in the fourth-order centrifugal distortion constants to be the full set of cubic potential constants of the molecule.

Table (5-2). The Fourth-order Centrifugal Distortion Coefficients of XYZ as Calculated by Sumberg-Parker

$$I_x^6\Phi_1 = \frac{1}{4}N \sum\sum_{s\le s'\le s''}\sum (b_s^{xx}b_{s'}^{xx}b_{s''}^{xx})k_{ss's''} + \frac{3}{8}\sum_s\sum_{s'} B_s^{xx}B_{s'}^{xx}(A_{ss'}^{xx})'$$

$$I_y^6\Phi_2 = \frac{1}{4}N \sum\sum_{s\le s'\le s''}\sum (b_s^{yy}b_{s'}^{yy}b_{s''}^{yy})k_{ss's''} + \frac{3}{8}\sum_s\sum_{s'} B_s^{yy}B_{s'}^{yy}(A_{ss'}^{yy})'$$

$$I_z^6\Phi_3 = \frac{1}{4}N \sum\sum_{s\le s'\le s''}\sum (b_s^{zz}b_{s'}^{zz}b_{s''}^{zz})k_{ss's''} + \frac{1}{2}(B\zeta)_{zz}^2 - \frac{1}{8}\sum_s (B_s^{zz})^2$$

$$\begin{aligned} I_x^2I_y^4\Phi_4 = {} & \frac{1}{8}N \sum\sum_{s\le s'\le s''}\sum (b_s^{xx}b_{s'}^{yy}b_{s''}^{yy} + b_{s'}^{xx}b_s^{yy}b_{s''}^{yy} + b_{s''}^{xx}b_{s'}^{yy}b_s^{yy} \\ & + 4b_s^{yy}b_{s'}^{xy}b_{s''}^{xy} + 4b_{s'}^{yy}b_s^{xy}b_{s''}^{xy} + 4b_{s''}^{yy}b_{s'}^{xy}b_s^{xy})k_{ss's''} \\ & + \frac{3}{16}\sum_s\sum_{s'} \{B_s^{yy}B_{s'}^{yy}(A_{ss'}^{xx})' + 2(B_s^{xx}B_{s'}^{yy} + 2B_s^{xy}B_{s'}^{xy})(A_{ss'}^{yy})' \\ & + 4B_s^{xy}B_{s'}^{yy}[(A_{ss'}^{xy})' + (A_{s's}^{xy})']\} \\ & + \frac{1}{12} I^{zz} \sum\sum_{s<s'} \zeta_{ss'}[\frac{\lambda_s + \lambda_{s'}}{\lambda_s - \lambda_{s'}}](B_s^{xy}B_{s'}^{yy} + B_{s'}^{xy}B_s^{yy}) \end{aligned}$$

$I_x^4I_y^2\Phi_5$ same as $I_x^2I_y^4\Phi_4$ with yy interchanged with xx and with I^{zz} replaced by $-I^{zz}$

$$\begin{aligned} I_y^2I_z^4\Phi_6 = {} & \frac{1}{8}N \sum\sum_{s\le s'\le s''}\sum (b_s^{yy}b_{s'}^{zz}b_{s''}^{zz} + b_{s'}^{yy}b_s^{zz}b_{s''}^{zz} + b_{s''}^{yy}b_{s'}^{zz}b_s^{zz})k_{ss's''} \\ & + \frac{1}{2}(B\zeta)_{yy}(B\zeta)_{zz} - \frac{1}{8}\sum_s B_s^{yy}B_s^{zz} + \frac{3}{16}\sum_s\sum_{s'} B_s^{zz}B_{s'}^{zz}(A_{ss'}^{yy})' \\ & - \frac{1}{6}\sum\sum_{s<s'} [\frac{\zeta_{ss'}}{\lambda_s - \lambda_{s'}}][B_s^{zz}B_{s'}^{xy}(\lambda_{s'} - 2\lambda_s) + B_{s'}^{zz}B_s^{xy}(\lambda_s - 2\lambda_{s'})] \end{aligned}$$

Table (5-2) (continued)

$$I_y^4 I_z^2 \Phi_7 = \frac{1}{8}N \sum_{s\le s'\le s''}\sum\sum (b_s^{yy} b_{s'}^{yy} b_{s''}^{zz} + b_s^{yy} b_{s''}^{yy} b_{s'}^{zz} + b_{s'}^{yy} b_{s''}^{yy} b_s^{zz}) k_{ss's''}$$

$$+ \frac{1}{4}(B\zeta)^2_{yy} - \frac{1}{16}\sum_s (B_s^{yy})^2 - \frac{1}{4}\sum_s (B_s^{xy})^2 + \frac{3}{8}\sum_s\sum_{s'} B_s^{yy} B_{s'}^{zz} (A_{ss'}^{yy})'$$

$$- \frac{1}{6}\sum_{s<s'}\sum \left[\frac{\zeta_{ss'}}{\lambda_s - \lambda_{s'}}\right][B_s^{xy} B_{s'}^{yy}(\lambda_s - 2\lambda_{s'}) + B_{s'}^{xy} B_s^{yy}(\lambda_{s'} - 2\lambda_s)]$$

$I_x^4 I_z^2 \Phi_8$ same as $I_y^4 I_z^2 \Phi_7$ with yy replaced by xx throughout and change sign of last sum

$I_x^2 I_z^4 \Phi_9$ same as $I_y^2 I_z^4 \Phi_6$ with yy replaced by xx throughout and change sign of last sum

$$I_x^2 I_y^2 I_z^2 \Phi_{10} = \frac{1}{8}N \sum_{s\le s'\le s''}\sum\sum (b_s^{xx} b_{s'}^{yy} b_{s''}^{zz} + b_s^{xx} b_{s''}^{yy} b_{s'}^{zz} + b_{s''}^{xx} b_{s'}^{yy} b_s^{zz}$$

$$+ b_{s'}^{xx} b_s^{yy} b_{s''}^{zz} + b_{s''}^{xx} b_s^{yy} b_{s'}^{zz} + b_{s'}^{xx} b_{s''}^{yy} b_s^{zz} + 4b_s^{xy} b_{s'}^{xy} b_{s''}^{zz}$$

$$+ 4b_s^{xy} b_{s''}^{xy} b_{s'}^{zz} + 4b_{s''}^{xy} b_{s'}^{xy} b_s^{zz}) k_{ss's''} + \frac{1}{2}(B\zeta)_{xx}(B\zeta)_{yy} + (B\zeta)^2_{xy}$$

$$- \frac{1}{4}\sum_s [I^{xx} B_s^{xx} + I^{yy} B_s^{yy} + I^{zz} B_s^{zz}]^2 - \frac{1}{8}\sum_s B_s^{xx} B_s^{yy}$$

$$+ \frac{1}{4}\sum_s (B_s^{xy})^2 + \frac{3}{8}\sum_s\sum_{s'} B_{s'}^{zz}[B_s^{xx}(A_{ss'}^{yy})' + B_s^{yy}(A_{ss'}^{xx})']$$

$$+ \frac{3}{4}\sum_s\sum_{s'} B_{s'}^{zz} B_s^{xy}[(A_{ss'}^{xy})' + (A_{s's}^{xy})']$$

$$- \frac{1}{2}\sum_{s\ne s'}\sum \zeta_{ss'}\left[\frac{\lambda_{s'}}{\lambda_{s'} - \lambda_s}\right](B_s^{xx} - B_s^{yy}) B_{s'}^{xy}$$

$$- \frac{1}{4} I^{zz} \sum_{s\ne s'}\sum \zeta_{s's}\left[\frac{\lambda_{s'} - 3\lambda_s}{\lambda_{s'} - \lambda_s}\right] B_s^{xy} B_s^{zz} .$$

6. ROTATIONAL CONTACT TRANSFORMATION TECHNIQUE AND THE REDUCTION OF THE HAMILTONIAN

6.1 Reduced Hamiltonian and Determinable Combinations of Coefficients

We have discussed earlier that in the absence of resonances, the rotational energy levels of an asymmetric-top molecule in a given vibrational state are the eigenvalues of a rotational Hamiltonian which is obtained, in the form of a power series in the components of the total angular momentum, from a perturbation treatment of the vibration-rotation Hamiltonian. The coefficients of this power series are the rotational and centrifugal distortion constants of the vibrational state under consideration. Therefore, if the values of these constants are known initially, at least in principle, it is possible to compute the rotational energy levels from them. However, the situation that arises experimentally is the reverse of this: one wishes to determine the values of the rotational and centrifugal constants from the observed rotational structure of the spectrum. These coefficients can then, in conjunction with the theoretical formulation, provide information about the structure and force field of the molecule under study.

The difficulty which arises in this reverse calculation is that some constants or combinations of constants truly contribute to the observed energy levels while others can be arbitrarily assigned without changing the energy eigenvalues. Watson[36] has shown that this problem can be approached by making use of the fact that the eigenvalues of the Hamiltonian are unaltered when the Hamiltonian is similarity-transformed by an arbitrary unitary operator. If the unitary operator is a power series in the angular momentum components, then the transformed Hamiltonian will again be a power series in the angular momentum components with exactly the same eigenvalues as the original Hamiltonian. Therefore on the basis of the experimental results, the two Hamiltonians are indistinguishable. The transformed Hamiltonian is called the "reduced Hamiltonian", and the coefficients in this reduced Hamiltonian are, in general, functions of the coefficients in the original Hamiltonian. Unitary transformations whose effects are equivalent to merely changing the values of the coefficients in the Hamiltonian are found to lead to arbitrary contributions to some of the coefficients. Since the sets of coefficients before and after transformation are equally consistent with the given set of eigenvalues, the arbitrary contributions are not physically significant and can be removed through particular choices of the coefficients of the originally arbitrary unitary transformation operator. This "reduction" is not unique and depends on the particular way in which the removable terms are eliminated. However, certain combinations of coefficients are unique and these are referred to as "determinable combinations of coefficients." The only determinable combinations are those which are obtained through elimination of the coefficients of the unitary transformation. The number of determinable combinations is therefore equal to the number of coefficients which contribute independently to the Hamiltonian minus the number of parameters which contribute independently to the unitary transformation. Consideration of the orders of magnitude of the various coefficients involved allows one to associate particular degrees of freedom in the unitary transformation with particular terms in the Hamiltonian. It is then fairly easy to find the number of determinable combinations of the coefficients of the various types of term. The arbitrary parameters specifying the unitary operator are chosen such as to eliminate as many terms as possible from the transformed Hamiltonian. Then the coefficients of the remaining terms are of the maximum number that can be determined from experiment.

6.2 Rotational Contact Transformation

Let us suppose that the usual vibrational perturbation treatment has been performed for a general asymmetric-top molecule so that the calculation of the rotational levels of a particular vibrational level has been reduced to finding the eigenvalues of a rotational Hamiltonian whose coefficients are appropriate to the vibrational state in question. Now the only remaining dynamical variables are the components of the total angular momentum, and it is assumed that the Hamiltonian is expressed as a power series in them. These components, in units of $\hbar$, are denoted by J_x, J_y, J_z; they satisfy the commutation relations

$$[J_x, J_y] = -iJ_z, \text{ cyclic,} \tag{6-1}$$

appropriate to the components in moving or "molecule-fixed" axes. These commutation relations can obviously be used to alter any expression involving the angular mementa in a way which is equivalent to changing the coefficients of the various terms. To see this, let us consider the following general expression for the rotational Hamiltonian:

$$H = \sum_{p,q,r=0}^{\infty} h_{pqr}(J_x^p J_y^q J_z^r + J_z^r J_y^q J_x^p), \qquad (6\text{-}2)$$

which contains one independent term for each combination of powers of J_x, J_y, J_z. The expression in parentheses is chosen in the manner shown because it is convenient that each term be Hermitian. The h_{pqr} are constant coefficients. If we now have a quantum product of p factors J_x, q factors J_y, and r factors J_z, in any order, then because of commutation rules, it differs from $\frac{1}{2}(J_x^p J_y^q J_z^r + J_z^r J_y^q J_x^p)$ by terms only of lower degree in the components of J. These latter terms, in turn, differ from similar expressions of (6-2) by terms of yet lower degree in J, and so on. By carrying through this procedure, one can therefore express any term of the quantum-mechanical Hamiltonian in terms of the form (6-2). It follows that the rotational Hamiltonian may be assumed, without loss of generality, to be in the form (6-2) which is referred to as the "standard form".

The vibrational perturbation treatment can be performed so as to preserve the Hermitian property of the Hamiltonian. Since the expression in parentheses in (6-2) is Hermitian, it follows that the coefficients h_{pqr} in the standard form are all real. A second property of the Hamiltonian, which should also be preserved in the perturbation treatment, is its invariance under the operation of time reversal, i.e., reversal of all momenta accompanied by complex conjugation of all coefficients. When applied to the standard form (6-2), this means that the coefficients h_{pqr} are real for even values of $n = p + q + r$ and purely imaginary for odd values of $n = p + q + r$. It follows that the coefficients of terms with odd values of n must vanish, and that the coefficients of terms with even values of n are real. The number and species of terms in the standard form of the Hamiltonian (6-2) is given in Table (6-1).

When the Hamiltonian (6-2) is subjected to a general unitary transformation, all the coefficients in the Hamiltonian are changed to some extent. However, the change is not significant if it is of small magnitude relative to the coefficient itself, and in such cases the coefficient is regarded as "determinable". On the other hand, if the change is of the same order of magnitude as the coefficient itself, the coefficient is "indeterminable". When the

Table (6-1). The Number and Species of Terms in the Standard Form of the Hamiltonian (6-2)[a]

D_2 Species	p	q	r	number of terms
A	e	e	e	$\frac{1}{2}$ (m+1)(m+2)
Bx	e	o	o	$\frac{1}{2}$ m(m+1)
By	o	e	o	$\frac{1}{2}$ m(m+1)
Bz	o	o	e	$\frac{1}{2}$ m(m+1)
Total	-------------			(2m+1)(m+1)

[a] $p + q + r = 2m$, for fixed m; e is even, o is odd.

coefficient is indeterminable in this way, the parameters in the unitary transformation can be chosen to eliminate the corresponding term from the Hamiltonian. However, all terms whose coefficients are individually indeterminable cannot be eliminated simultaneously because certain coefficients of this type occur in determinable combinations. The reduced Hamiltonian is obtained by choosing the unitary transformation so as to leave only these determinable combinations of coefficients.

If U is some unitary operation $(U^+ = U^{-1})$, then the transformed Hamiltonian $\tilde{H}$ can be written as

$$\tilde{H} = U^{-1}HU \ . \qquad (6\text{-}3)$$

We suppose that a set of unitary transformations is applied successively, which is equivalent to expressing U as a product. Since we want $\tilde{H}$ to be purely a function of J_x, J_y, J_z, we choose U to be such a function. If U is also chosen to be invariant to time reversal, then $\tilde{H}$ will be invariant if H is invariant. The most convenient form for a unitary operator is

$$U = \exp(iS). \qquad (6\text{-}4)$$

The unitary condition requires S to be Hermitian. The invariance of U under time reversal requires that S change sign. Together these two requirements imply that, when S is expressed in a "standard form" analogous to (6-2), it has real coefficients and contains terms of odd n only.

On the basis of this result, we can introduce the factorized form of U:

$$U = \exp(iS_1)\exp(iS_3)\exp(iS_5)\ \ldots, \tag{6-5}$$

where S_n contains only terms with $n = p + q + r$:

$$S_n = \sum_{n=p+q+r} S_{pqr}(J_x^p J_y^q J_z^r + J_z^r J_y^q J_x^p), \tag{6-6}$$

with real coefficients S_{pqr}. The number and species of terms in the standard form (6-6) of S_{2m-1} is listed in Table (6-2).

Table (6-2). The Number and Species of Terms in the Standard Form (6-6) of S_{2m-1}.[a]

D_2 Species	p	q	r	number of terms
A	o	o	o	$\frac{1}{2}$ m(m+1)
Bx	o	e	e	$\frac{1}{2}$ m(m+1)
By	e	o	e	$\frac{1}{2}$ m(m+1)
Bz	e	e	o	$\frac{1}{2}$ m(m+1)
Total	-------------			m(2m+1)

[a] $p+q+r = 2m-1$, for fixed m; e is even, o is odd.

We now introduce the notation

$$H_{2m+2} = \exp(-iS_{2m+1})H_{2m}\exp(iS_{2m+1}), \tag{6-7}$$

where m takes the values 0,1,2,... and H_0 is the Hamiltonian H of (6-2). Then

$$H_2 = \exp(-iS_1)H_0 \exp(iS_1), \tag{6-8}$$

$$H_4 = \exp(-iS_3)H_2 \exp(iS_3), \tag{6-9}$$

$$\vdots$$

$$H_\infty = \tilde{H} . \tag{6-10}$$

When H_{2m} has been reduced to standard form, it can be written as:

$$H_{2m} = \sum_{\substack{p+q+r \\ \text{even}}}^{\infty} h_{pqr}^{(2m)} (J_x^p J_y^q J_z^r + J_z^r J_y^q J_x^p). \tag{6-11}$$

It is found that S_1 specifies that part of the complete transformation which brings the rigid rotor Hamiltonian to principal axes. Since this has already been anticipated in the expansion of the Darling-Dennison Hamiltonian, one may take $S_1 = 0$, $\exp(iS_1) = 1$, and proceed to H_4 of (6-9). This part of the Hamiltonian is associated with the determinability of the quartic coefficeints. From Table (6-1), there are fifteen independent quartic terms, $(2m = 4)$, in the Hamiltonian, while from Table (6-2), one sees that there are ten independent terms in S_3. Thus, if all these terms in S_3 would affect the Hamiltonian independently, then the number of determinable combinations of the quartic coefficients obtained is $15 - 10 = 5$.

The angular momentum commutation rules (6-1) are invariant under the operations of the point group D_2, and H_2 is, of course, totally symmetric. Therefore in the expansion of H_4,

$$H_4 = H_2 + i[H_2, S_3] + \ldots, \tag{6-12}$$

the terms in $i[H_2, S_3]$ are of the same symmetry species as the corresponding terms in S_3. One can therefore discuss the determinability of the coefficients of the quartic terms of the different symmetry species separately.

We first consider the Bx species which is typical of the three B species of D_2. Putting $m = 2$ in Tables (6-1) and (6-2), we find that there are three quartic terms in H of species Bx, and three terms in S_3 of species Bx. The corresponding coefficients are h_{031}, h_{013}, h_{211} and S_{120}, S_{102}, S_{300}. Development of (6-12) leads to the relations

$$h^{(4)}_{031} = h^{(2)}_{031} + 2(C-B)S_{120}, \tag{6-13}$$

$$h^{(4)}_{013} = h^{(2)}_{013} + 2(C-B)S_{102}, \tag{6-14}$$

$$h^{(4)}_{211} = h^{(2)}_{211} + 6(C-B)S_{300} + 4(A-C)S_{120} + 4(B-A)S_{102}. \tag{6-15}$$

The three coefficients $h^{(4)}_{031}$, $h^{(4)}_{013}$, $h^{(4)}_{211}$ are independent functions of S_{120}, S_{102}, S_{300} and by a suitable choice of the latter, they could be made to take any arbitrary values, subject only to order-of-magnitude restrictions. These coefficients are therefore indeterminable, and the transformation should be chosen to eliminate the corresponding terms from the reduced Hamiltonian, and thus

$$h^{(4)}_{031} = h^{(4)}_{013} = h^{(4)}_{211} = 0. \tag{6-16}$$

Similar results hold for the By and the Bz terms. It can therefore be concluded that the non-totally symmetric (non-orthorhombic) quartic terms should always be omitted from the reduced Hamiltonian, even when the particular point group symmetry of the molecule allows them to be present.

We now consider the A-species terms. We see from Tables (6-1) and (6-2) that there are six quartic terms in H and one corresponding term in S_3. The former have coefficients h_{400}, h_{040}, h_{004}, h_{022}, h_{202}, h_{220}, and the latter has coefficient S_{111}. It is found that $h^{(4)}_{400}$, $h^{(4)}_{040}$, $h^{(4)}_{004}$ differ insignificantly from $h^{(2)}_{400}$, $h^{(2)}_{040}$, $h^{(2)}_{004}$, respectively, whereas for the remaining coefficients we have

$$h^{(4)}_{022} = h^{(2)}_{022} + 2(C-B)S_{111}, \tag{6-17}$$

$$h^{(4)}_{202} = h^{(2)}_{202} + 2(A-C)S_{111}, \tag{6-18}$$

$$h^{(4)}_{220} = h^{(2)}_{220} + 2(B-A)S_{111}. \tag{6-19}$$

Since each of $h^{(4)}_{022}$, $h^{(4)}_{202}$, $h^{(4)}_{220}$ is affected by this degree of freedom in the unitary transformation, each of them is indeterminable individually. However, we can eliminate the parameter S_{111} from Eqs. (6-17)-(6-19) in two independent ways which yields two determinable combinations of these coefficients. The most symmetrical choice is

$$h^{(4)}_{022} + h^{(4)}_{202} + h^{(4)}_{220} = h^{(2)}_{022} + h^{(2)}_{202} + h^{(2)}_{220} \tag{6-20}$$

and

$$Ah^{(4)}_{022} + Bh^{(4)}_{202} + Ch^{(4)}_{220} = Ah^{(2)}_{022} + Bh^{(2)}_{202} + Ch^{(2)}_{220} \tag{6-21}$$

Therefore a set of five independent determinable combinations of the quartic coefficients is: $h^{(2)}_{400}$, $h^{(2)}_{040}$, $h^{(2)}_{004}$, $h^{(2)}_{022} + h^{(2)}_{202} + h^{(2)}_{220}$ and $Ah^{(2)}_{022} + Bh^{(2)}_{202} + Ch^{(2)}_{220}$, since none of these is affected significantly by the similarity transformation.

The parameter S_{111} is now chosen so that only five independent quartic terms are left in the reduced Hamiltonian. It is convenient to make a choice for S_{111} which simplifies the calculation of the eigenvalues of the reduced Hamiltonian. Once the choice has been made, all the coefficients of S_3 will have been chosen in a definite way.

6.3 Determination of Quartic and Sextic Determinable Combinations of Coefficients

For an orthorhombic molecule, the rotational Hamiltonian as obtained from the vibrational perturbation treatment contains only terms of species A in D_2 because of molecular symmetry. For molecules of lower symmetry there are, in general, also terms which are non-totally symmetric in D_2. In the latter case we assume that the non-totally symmetric terms in the operators S_1 and S_3 have been chosen such as to remove the non-totally symmetric quadratic and quartic terms from the Hamiltonian, as described in the previous section. Thus in either case, we are left with only the A-species terms in the standard form (6-2). Therefore we can concentrate on the one-parameter problem of the reduction of the A-species quartic terms.

In the form of the Hamiltonian (6-2) appropriate to an orthorhombic molecule, the only terms present have p, q and r all even. Thus for this case, Eq. (6-2) becomes, up to sextic terms,

$$H = H_2 + H_4 + H_6, \tag{6-22}$$

where H_2, H_4 and H_6 are defined by Eqs. (5-3)-(5-5). Here the h_{pqr} notation, which was useful for the general discussion, has been dropped in favor of our previous notation.

We now proceed to consider the transformation of the Hamiltonian (6-2) by the unitary operator

$$U = \exp(iS_3)\exp(iS_5), \tag{6-23}$$

where

$$S_3 = S_{111}(J_xJ_yJ_z + J_zJ_yJ_x), \tag{6-24}$$

and

$$S_5 = S_{311}(J_x^3J_yJ_z + J_zJ_yJ_x^3) + S_{131}(J_xJ_y^3J_z + J_zJ_y^3J_x) + S_{113}(J_xJ_yJ_z^3 + J_z^3J_yJ_x). \tag{6-25}$$

The four real coefficients S_{pqr} are the parameters of the unitary transformation (6-23).

Carrying out the transformation one obtains the transformed Hamiltonian

$$\tilde{H} = U^{-1}HU = \tilde{H}_2 + \tilde{H}_4 + \tilde{H}_6, \tag{6-26}$$

where

$$\tilde{H}_2 = H_2, \tag{6-27}$$

$$\tilde{H}_4 = H_4 + i[H_2, S_3], \tag{6-28}$$

$$\tilde{H}_6 = H_6 + i[H_4, S_3] + i[H_2, S_5] - \tfrac{1}{2}[[H_2, S_3], S_3]. \tag{6-29}$$

After evaluation of the above commutators, $\tilde{H}$ can be rearranged to the form of Eqs. (5-2)-(5-5), with new coefficients that will be distinguished by tildes, as follows:

$$\tilde{A} = A, \qquad \tilde{B} = B, \qquad \tilde{C} = C \tag{6-30}$$

$$\tilde{T}_1 = T_1, \qquad \tilde{T}_2 = T_2, \qquad \tilde{T}_3 = T_3 \tag{6-31}$$

$$\tilde{T}_4 = T_4 + 2(C-B)S_{111}, \tag{6-32}$$

$$\tilde{T}_5 = T_5 + 2(A-C)S_{111}, \tag{6-33}$$

$$\tilde{T}_6 = T_6 + 2(B-A)S_{111}, \tag{6-34}$$

$$\tilde{\Phi}_1 = \Phi_1, \qquad \tilde{\Phi}_2 = \Phi_2, \qquad \tilde{\Phi}_3 = \Phi_3, \tag{6-35}$$

$$\tilde{\Phi}_4 = \Phi_4 + 2(B-A)S_{131} + 4(T_2-T_6)S_{111} + 4(A-B)S_{111}^2, \tag{6-36}$$

$$\tilde{\Phi}_5 = \Phi_5 + 2(B-A)S_{311} - 4(T_1-T_6)S_{111} + 4(B-A)S_{111}^2, \tag{6-37}$$

$$\tilde{\Phi}_6 = \Phi_6 + 2(C-B)S_{113} + 4(T_3-T_4)S_{111} + 4(B-C)S_{111}^2, \tag{6-38}$$

$$\tilde{\Phi}_7 = \Phi_7 + 2(C-B)S_{131} - 4(T_2-T_4)S_{111} + 4(C-B)S_{111}^2, \tag{6-39}$$

$$\tilde{\Phi}_8 = \Phi_8 + 2(A-C)S_{311} + 4(T_1-T_5)S_{111} + 4(C-A)S_{111}^2, \tag{6-40}$$

$$\tilde{\Phi}_9 = \Phi_9 + 2(A-C)S_{113} - 4(T_3-T_5)S_{111} + 4(A-C)S_{111}^2, \tag{6-41}$$

$$\tilde{\Phi}_{10} = \Phi_{10} + 6[(C-B)S_{311} + (A-C)S_{131} + (B-A)S_{113}]. \tag{6-42}$$

It can be seen that the coefficients A, B, C, T_1, T_2, T_3, Φ_1, Φ_2, and Φ_3 are, by themselves, invariant and therefore determinable. The other determinable combinations must be obtained by elimination of the S-parameters. The most symmetrical choice of transformation-invariant functions appears to be:

$$T_4 + T_5 + T_6, \tag{6-43}$$

$$AT_4 + BT_5 + CT_6, \tag{6-44}$$

$$3(\Phi_5 + \Phi_8 + \Phi_7 + \Phi_4 + \Phi_9 + \Phi_6) + \Phi_{10}, \tag{6-45}$$

$$(A-C)\Phi_5 + (A-B)\Phi_8 - 2(T_1-T_6)(T_1-T_5), \tag{6-46}$$

$$(B-C)\Phi_4 + (B-A)\Phi_7 - 2(T_2-T_6)(T_2-T_4), \tag{6-47}$$

$$(C-B)\Phi_9 + (C-A)\Phi_6 - 2(T_3-T_5)(T_3-T_4). \tag{6-48}$$

Any other choice of a set of determinable combinations can be expressed in terms of those given above. It is convenient in practice to have all of the invariant quantities involving the Φ_i with the same dimensions. To this end, in place of (6-46)-(6-48), one may divide each of these by $(A-B)$ to obtain:

$$2\Phi_8 + (1-\sigma)\Phi_5 - 4(T_1-T_6)(T_1-T_5)/(A-B) \tag{6-49}$$

$$2\Phi_7 + (1+\sigma)\Phi_4 + 4(T_2-T_6)(T_2-T_4)/(A-B) \tag{6-50}$$

$$(\sigma+1)\Phi_9 + (\sigma-1)\Phi_6 - 4(T_3-T_5)(T_3-T_4)/(A-B) \tag{6-51}$$

where

$$\sigma = (2C - A - B)/(A-B). \tag{6-52}$$

7. CALCULATION OF ASYMMETRIC-ROTATOR CENTRIFUGAL DISTORTION COEFFICIENTS BY THE ALIEV-WATSON METHOD

In 1976, Aliev and Watson[13] presented a very direct and efficient method for the calculation of the fourth-order centrifugal distortion constants of asymmetric, as well as symmetric and spherical, rotator molecules. Their very compact results, when applied to triatomic molecules, are consistent (but not identical) with those of Sumberg and Parker[7]. It was deemed useful to give a more extended discussion of the Aliev-Watson method in this chapter, because the results are relevant to the present work, because the method appears potentially useful for the calculation of higher-order vibration-rotation interaction coefficients, and also because the original paper gives only a very brief presentation whose verification in detail required much effort. We also present in this chapter a detailed comparison between the Aliev-Watson and the Sumberg-Parker sextic centrifugal distortion coefficients and account for all discrepancies between the two sets of results.

7.1 Direct Perturbation Treatment for the Calculation of the Sextic Centrifugal Distortion Coefficients

Using Watson's notation as discussed in Section 2.3, we let $\tilde{H}_{mn}$ denote the various terms of the effective Hamiltonian resulting from the perturbation treatment. The perturbation calculation of the desired terms, viz., $\tilde{H}_{06}$, can be carried out in two stages. In the first stage, two successive vibrational contact transformations are performed to eliminate terms off-diagonal in the vibrational quantum numbers v_s. This can be done by the technique described in Chapter 3. We denote the result of this transformation by $\tilde{H}_{06}^{(v)}$. In the second stage the rotational Hamiltonian is subjected to a rotational contact transformation to produce a reduced rotational Hamiltonian containing only experimentally determinable coefficients. This can be done by the technique described in Chapter 6. We denote the result of this transformation by $\tilde{H}_{06}^{(R)}$. The final expression for $\tilde{H}_{06}$ can be written as

$$\tilde{H}_{06} = \tilde{H}_{06}^{(v)} + \tilde{H}_{06}^{(R)}. \qquad (7\text{-}1)$$

The vibrational contact transformations are carried out such that at each stage only those terms that contribute to the desired order of magnitude, $k^{10}\omega_{vib}$, and a degree of six or greater in J_α are retained. The power of k indicates the order of magnitude of the coefficients relative to the harmonic vibrational frequencies.[38] To express the two requirements together, we introduce the notation k^{m-n}, where m indicates the order of the magnitude of the coefficients and $m-n$ is equal to the total power of J_α of the associated operator. It is found that the terms required in the calculation of $\tilde{H}_{06}$ are:

$$H_{20}(k^{0-0}),\ H_{02}(k^{2-0}),\ H_{12}(k^{3-1}),\ H_{22}(k^{4-2}),\ H_{21}(k^{2-1}),\ H_{30}(k^{1-0}) \qquad (7\text{-}2)$$

where the explicit expressions for these terms are given in Table (2-3). The contributions of these terms can be conveniently grouped into the following three classes:

(a) Anharmonic: $H_{30}H_{12}H_{12}H_{12}$

(b) Harmonic: $H_{12}H_{12}H_{22}$

(c) Coriolis: $H_{12}H_{12}H_{21}H_{21}$, $H_{12}H_{12}H_{21}H_{02}$, $H_{12}H_{12}H_{02}H_{02}$.

In the contact-transformation formulation, each of the above terms denotes a product in which the individual factors can be either $S_{mn}^{(k)}$ functions or H_{mn} functions to be identified with the appropriate commutator brackets of the transformed Hamiltonians. No other combinations of terms from the Hamiltonian of Table (2-3) satisfy the specified requirements. If we now express our initial Hamiltonian in the form:

$$H = H_0 + \lambda H_1 + \lambda^2 H_2, \tag{7-6}$$

with

$$H_0 = H_{20}, \tag{7-7}$$

$$H_1 = H_{02} + H_{12} + H_{21} + H_{30}, \tag{7-8}$$

$$H_2 = H_{22}, \tag{7-9}$$

then the above contributions all appear in the fourth-order of perturbation theory.

Now the first vibrational contact transformation can be written as:

$$H_0' = H_0 \tag{7-10}$$

$$H_1' = H_1 + i[S^{(1)}, H_0] \tag{7-11}$$

$$H_2' = H_2 + i[S^{(1)}, H_1] - \frac{1}{2}[S^{(1)},[S^{(1)}, H_0]] \tag{7-12}$$

$$H_3' = \cancelto{=0}{H_3} + i[S^{(1)}, H_2] - \frac{1}{2}[S^{(1)},[S^{(1)}, H_1]]$$
$$- \frac{i}{6}[S^{(1)},[S^{(1)},[S^{(1)}, H_0]]] \tag{7-13}$$

$$H_4' = \cancelto{=0}{H_4} + i[S^{(1)}, \cancelto{0}{H_3}] - \frac{1}{2}[S^{(1)},[S^{(1)}, H_2]]$$
$$- \frac{i}{6}[S^{(1)},[S^{(1)},[S^{(1)}, H_1]]]$$
$$+ \frac{1}{24}[S^{(1)},[S^{(1)},[S^{(1)},[S^{(1)}, H_0]]]]. \tag{7-14}$$

Eq. (7-11) defines the operator $S^{(1)}$ which is constructed such that off-diagonal elements in the vibrational quantum numbers v_s are removed. Therefore Eq. (7-11) can be written as:

$$i[S^{(1)}, H_0] = -H_1(\text{off diag.}) \tag{7-15}$$

where

$$H_1 = H_{02}(k^{2-0}) + H_{12}(k^{3-1}) + H_{21}(k^{2-1}) + H_{30}(k^{1-0}) . \tag{7-16}$$

Considering vibrational commutators only, we can assign separate functions of $S^{(1)}$ to each term of H_1 with the exception of the H_{02} term , and these functions are respectively denoted by

$$S^{(1)} = S_{12}^{(1)}(k^{3-1}) + S_{21}^{(1)}(k^{2-1}) + S_{30}^{(1)}(k^{1-0}). \tag{7-17}$$

Now considering the second vibrational contact transformation, we can write:

$$H_0'' = H_0' \tag{7-18}$$

$$H_1'' = H_1' \tag{7-19}$$

$$H''_2 = H'_2 + i[S^{(2)}, H'_0] \qquad (7\text{-}20)$$

$$H''_3 = H'_3 + i[S^{(2)}, H'_1] \qquad (7\text{-}21)$$

$$H''_4 = H'_4 + i[S^{(2)}, H'_2] - \frac{1}{2}[S^{(2)},[S^{(2)}, H'_0]]. \qquad (7\text{-}22)$$

Using the fact that

$$[S^{(1)}, H_0] = -i(H'_1 - H_1), \qquad (7\text{-}23)$$

we can write Eq. (7-20) in the following way:

$$H''_2 = H_2 + \frac{i}{2}[S^{(1)}, (H_1 + H'_1)] + i[S^{(2)}, H_0] \ . \qquad (7\text{-}24)$$

This equation now serves as the defining equation for the operator $S^{(2)}$. From Eq. (7-22) it can be seen that the only $S^{(2)}_{mn}$ term contributing to $\tilde{H}_{06}$ is $S^{(2)}_{13}(k^{5-2})$. Therefore in Eq. (7-24), the operator $S^{(2)}_{13}$ has to be chosen such that it removes the off-diagonal elements, viz.,

$$[S^{(2)}, H_0] = -i\{-H_2 - \frac{i}{2}[S^{(1)}, (H_1 + H'_1)]\}_{\text{off-diag.}} \qquad (7\text{-}25)$$

where

$$H'_1 = H_{02} + \tilde{H}_{21} = \tilde{H}_1, \qquad (7\text{-}26)$$

and $\tilde{H}_{21}$ is the diagonal part of H_{21}. It is seen from Eq. (7-25) that the needed part $S^{(2)}_{13}$ of S_{13} must satisfy

$$[H_0, S^{(2)}_{13}] = \frac{1}{2}[S^{(1)}_{12}, (2H_{02} + H_{21} + \tilde{H}_{21})] + \frac{1}{2}[S^{(1)}_{21}, H_{12}]. \qquad (7\text{-}27)$$

The expressions for $S^{(1)}_{12}$, $S^{(1)}_{21}$, $S^{(1)}_{30}$, and $S^{(2)}_{13}$ are given in Table (7-1). On substitution of these into their respective defining

Table (7-1). S Operators for the Vibrational Contact Transformation[a,b]

$S_{12}^{(1)} = -\sum_k R_k p_k/\omega_k$
$S_{21}^{(1)} = \frac{1}{2}\{\sum_{k\ell} R_\ell^k (q_k q_\ell - p_k p_\ell)/(\omega_k + \omega_\ell) + \sum_{k\ell}^{*} R_\ell^k (q_k q_\ell + p_k p_\ell)/(\omega_k - \omega_\ell)\}$
$S_{30}^{(1)} = -\frac{1}{6}\sum_{\ell mn} k'_{\ell mn}\{2\omega_\ell\omega_m\omega_n\, p_\ell p_m p_n + 3\omega_m(\omega_\ell^2 - \omega_m^2 + \omega_n^2) q_\ell p_m q_n\}/\Omega_{\ell mn}$
$S_{13}^{(2)} = -\frac{1}{4}\{\sum_k q_k\ \{\sum_\ell (3\omega_k + 5\omega_\ell) R_\ell R_\ell^k/(\omega_k + \omega_\ell)\omega_k\omega_\ell$
$- \sum_\ell^{*} (\omega_k + \omega_\ell) R_\ell R_\ell^k/(\omega_k - \omega_\ell)\omega_k\omega_\ell + 4i[R_k, H_{02}]/\omega_k^2$

[a] $\Omega_{\ell mn} = (\omega_\ell + \omega_m + \omega_n)(-\omega_\ell + \omega_m + \omega_n)(\omega_\ell - \omega_m + \omega_n)(\omega_\ell + \omega_m - \omega_n)$. The other notations are described in Chapter 2.

[b] In the Σ^* sums, terms with zero denominators are omitted.

equations, it can be verified that these functions were chosen correctly. Now using Eq. (7-25) along with the commutators of the first vibrational contact transformation in Eq. (7-10)-(7-14), we can write the fourth-order Hamiltonian in the form

$$\tilde{H}^{(4)} = H_4'' = -\frac{i}{8}[S^{(1)},[S^{(1)},[S^{(1)}, (H_1 + \frac{1}{3}\tilde{H}_1)]]] - \frac{1}{2}[S^{(1)},[S^{(1)}, H_2]] + \frac{1}{2}[S^{(2)},[S^{(2)}, H_0]] \ . \tag{7-28}$$

From the various operators and commutators, the three classes of term in $\tilde{H}_{06}^{(v)}$ can be calculated by means of the equations

$$\tilde{H}_{06}^{(v)}(\text{anharmonic}) = -\frac{i}{8}[S_{12}^{(1)},[S_{12}^{(1)},[S_{12}^{(1)}, H_{30}] + [S_{30}^{(1)}, H_{12}]]] \tag{7-29}$$

$$\tilde{H}_{06}^{(v)}(\text{harmonic}) = -\frac{1}{2}[S_{12}^{(1)},[S_{12}^{(1)}, H_{22}]] \tag{7-30}$$

$$\tilde{H}_{06}^{(v)}(\text{Coriolis}) = -\frac{i}{24}\{[S_{12}^{(1)},[S_{12}^{(1)},[S_{21}^{(1)},(4H_{02} + 3H_{21} + \tilde{H}_{21})]]]$$

$$+ [S_{12}^{(1)},[S_{21}^{(1)},[S_{12}^{(1)},(4H_{02} + 3H_{21} + \tilde{H}_{21})]]]\}$$

$$- \frac{i}{8}[S_{12}^{(1)},[S_{21}^{(1)},[S_{21}^{(1)}, H_{12}]]] + \frac{1}{2}[S_{13}^{(2)},[S_{13}^{(2)}, H_0]]. \tag{7-31}$$

The commutators containing H_{02} in the above equations are evaluated as rotational commutators; all the other commutators are vibrational commutators. The diagonal Coriolis term $\tilde{H}_{21}$ is included for completeness in order to be able to apply the results to symmetric and spherical tops as well as asymmetric tops. For asymmetric rotators $\tilde{H}_{21} = 0$. After considerable algebraic manipulation, the very compact resulting expression for $\tilde{H}_{06}^{(v)}$ is obtained as listed in Table (7-2).

Table (7-2). Sextic Centrifugal Distortion Hamiltonian of an Arbitrary Molecule[a]

$$\tilde{H}_{06}^{(V)} = \tilde{H}_{06}^{(V)}(\text{harmonic}) + \tilde{H}_{06}^{(V)}(\text{Coriolis}) + \tilde{H}_{06}^{(V)}(\text{anharmonic})$$

$$\tilde{H}_{06}^{(V)}(\text{harmonic}) = \sum_{k\ell} R_k R_{k\ell} R_\ell / \omega_k \omega_\ell$$

$$\tilde{H}_{06}^{(V)}(\text{Coriolis}) = -\frac{1}{2}\sum_k \{\sum_\ell R_\ell R_\ell^k / \omega_\ell \omega_k^{1/2} + i[R_k, H_{02}]/\omega_k^{3/2}\}^2$$

$$\frac{i}{6}[\sum_{k\ell} \frac{R_k R_\ell R_\ell^k}{(\omega_k + \omega_\ell)\omega_k \omega_\ell} + \sum_{k\ell}^{*} \frac{R_k R_\ell R_\ell^k}{(\omega_k - \omega_\ell)\omega_k \omega_\ell}, H_{02}]$$

$$\tilde{H}_{06}^{(V)}(\text{anharmonic}) = -\frac{1}{6}\sum_{\ell mn} k'_{\ell mn} R_\ell R_m R_n / \omega_\ell \omega_m \omega_n$$

[a]Notation as in Table (7-1).

Next, we proceed to calculate $\tilde{H}_{06}^{(R)}$ by subjecting the rotational Hamiltonian

$$\tilde{H}^{(v)}_{rot} = \tilde{H}_{02} + \tilde{H}^{(v)}_{04} + \tilde{H}^{(v)}_{06} + \ldots, \tag{7-32}$$

to a rotational contact transformation by a purely rotational operator. This operator is taken in the form

$$U = \exp(i\ S_{05})\exp(i\ S_{03}). \tag{7-33}$$

Then the transformed Hamiltonian can be written as:

$$\begin{aligned}\tilde{H}_{rot} &= U^{-1}\tilde{H}^{(v)}_{rot}U \\ &= \tilde{H}_{02} + \tilde{H}_{04} + \tilde{H}_{06} + \ldots,\end{aligned} \tag{7-34}$$

with

$$\tilde{H}_{02} = H_{02}, \tag{7-35}$$

$$\tilde{H}_{04} = \tilde{H}^{(V)}_{04} + i[S_{03}, H_{02}] = \tilde{H}^{(V)}_{04} + \tilde{H}^{(R)}_{04}, \tag{7-36}$$

$$\begin{aligned}\tilde{H}_{06} &= \tilde{H}^{(V)}_{06} - \tfrac{1}{2}[S_{03},[S_{03}, H_{02}]] + i[S_{03},\tilde{H}^{(V)}_{04}] + i[S_{03},\tilde{H}_{02}] \\ &= \tilde{H}^{(V)}_{06} + \tilde{H}^{(R)}_{06},\end{aligned} \tag{7-37}$$

where the second-order fourth-power (in J_α) Hamiltonian $\tilde{H}^{(V)}_{04}$ is defined as:

$$\tilde{H}^{(V)}_{04} = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} J_\alpha J_\beta J_\gamma J_\delta. \tag{7-38}$$

For convenience of reference, all possible asymmetric rotator point groups[32] are listed in Table (7-3). The asymmetric-top rigid-rotor Hamiltonian H_{02} is invariant under the operation of the orthorhombic group D_2. Therefore the terms of $\tilde{H}^{(v)}_{04}$, $\tilde{H}^{(v)}_{06}$, S_{03}, and S_{05} can be classified according to the symmetry species of this group. As mentioned in Chapter 6, even for non-orthorhombic molecules, Table (7-3). 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
	C_2	C_2
	C_{2h}	C_2, σ_h, i
Orthorhombic	C_{2v} **	C_2, two σ_v,
	$V = D_2$	three mutually $\perp$ C_2
	$V_h = D_{2h}$	three mutually $\perp$ C_2, i, three mutually $\perp$ σ

* XYZ-type molecule has point group symmetry C_s.

** XYX-type molecule has point group symmetry C_{2v}.

the non-orthorhombic terms of S_{03} and S_{05} can be chosen to eliminate all the non-orthorhombic terms from $\tilde{H}_{04}$ and $\tilde{H}_{06}$ so that it is sufficient to consider $\tilde{H}_{04}$ and $\tilde{H}_{06}$ as orthorhombic operators. Such operators contain only even powers of the individual components J_α. The non-orthorhombic terms of $\tilde{H}_{04}^{(v)}$ and S_{03} in Eq. (7-36), however, do contribute to orthorhombic terms in fourth order.

It is found that the operator form of the last two sums of $\tilde{H}_{06}^{(v)}$ (Coriolis) as given in Table (7-2) is such that these terms can be completely removed by the choice of an appropriate term in S_{05}. Therefore this part of the Coriolis contribution can be omitted.

The remaining terms of S_{03} and S_{05} are associated with the reduction of the Hamiltonian to avoid indeterminacies in the fitting of experimental data, and since this reduction is not unique, there is no unique choice for the remaining S-parameters in S_{03} and S_{05}.

The final expressions for the various sextic distortion constants are obtained from $\tilde{H}_{06}^{(v)}$ by:

(a) adding the second-order contributions resulting from the elimination of the non-orthorhombic terms from $\tilde{H}_{04}$, and

(b) eliminating all the non-orthorhombic terms and the orthorhombic contribution from the last term of $\tilde{H}_{06}^{(v)}$ (Coriolis).

The resulting expressions are presented in Table (7-4). In order to effect a detailed comparison between the Aliev-Watson coefficients and the Sumberg-Parker coefficients, the former have been transcribed into Sumberg-Parker notation.

The contributions $\Phi_i^{(R)}$ to the complete coefficients Φ_i which result from the elimination of the non-orthorhombic terms in the second-order part of the Hamiltonian are listed in Table (7-5), again in Sumberg-Parker notation. For triangular molecules, these contributions arise only for the XYZ case. For XYX the $\Phi_i^{(R)}$ all vanish identically. The Sumberg-Parker calculation failed to include the non-orthorhombic terms for the XYZ case, and hence their results should be augmented by including the $\Phi_i^{(R)}$ as listed in Table (7-5). Table (7-6) presents the Sumberg-Parker coefficients augmented by the non-orthorhombic contributions of Table (7-5).

Table (7-4). The Fourth-Order Centrifugal Distortion Coefficients of XYZ as Calculated by Aliev-Watson

$$I_x^6\Phi_1' = \frac{1}{4}N \sum\sum_{s\leq s'\leq s''}\sum (b_s^{xx}b_{s'}^{xx}b_{s''}^{xx})k_{ss's''} + \frac{3}{8}\sum_s\sum_{s'} B_s^{xx}B_{s'}^{xx}(A_{ss'}^{xx})'$$
$$+ \frac{1}{8}[I_x/I_y(I_y - I_x)]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{xx}B_{s'}^{xx}$$

$$I_y^6\Phi_2' = \frac{1}{4}N \sum\sum_{s\leq s'\leq s''}\sum (b_s^{yy}b_{s'}^{yy}b_{s''}^{yy})k_{ss's''} + \frac{3}{8}\sum_s\sum_{s'} B_s^{yy}B_{s'}^{yy}(A_{ss'}^{yy})'$$
$$- \frac{1}{8}[I_y/I_x(I_y - I_x)]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{yy}B_{s'}^{yy}$$

$$I_z^6\Phi_3' = \frac{1}{4}N \sum\sum_{s\leq s'\leq s''}\sum (b_s^{zz}b_{s'}^{zz}b_{s''}^{zz})k_{ss's''} + \frac{1}{2}(B\zeta)_{zz}^2 - \frac{1}{8}\sum_s (B_s^{zz})^2$$

$$I_x^2I_y^4\Phi_4' = \frac{1}{8}N \sum\sum_{s\leq s'\leq s''}\sum (b_s^{xx}b_{s'}^{yy}b_{s''}^{yy} + b_{s'}^{xx}b_s^{yy}b_{s''}^{yy} + b_{s''}^{xx}b_{s'}^{yy}b_s^{yy} + 4b_s^{yy}b_{s'}^{xy}b_{s''}^{xy}$$
$$+ 4b_{s'}^{yy}b_s^{xy}b_{s''}^{xy} + 4b_{s''}^{yy}b_{s'}^{xy}b_s^{xy})k_{ss's''} + \frac{3}{16}\sum_s\sum_{s'} \{B_s^{yy}B_{s'}^{yy}(A_{ss'}^{xx})'$$
$$+ 2(B_s^{xx}B_{s'}^{yy} + 2B_s^{xy}B_{s'}^{xy})(A_{ss'}^{yy})' + 4B_s^{xy}B_{s'}^{xy}[(A_{ss'}^{xy})'$$
$$+ (A_{s's}^{xy})']\} - \frac{9}{8}[I_y/I_x(I_y - I_x)]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{yy}B_{s'}^{xx}$$
$$+ \frac{1}{8}[I_x/I_y(I_y - I_x)\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{yy}B_{s'}^{yy}$$

$I_x^4I_y^2\Phi_5'$ same as $I_x^2I_y^4\Phi_4$ with yy interchanged with xx

$$I_y^2I_z^4\Phi_6' = \frac{1}{8}N \sum\sum_{s\leq s'\leq s''}\sum (b_s^{yy}b_{s'}^{zz}b_{s''}^{zz} + b_{s'}^{yy}b_s^{zz}b_{s''}^{zz} + b_{s''}^{yy}b_{s'}^{zz}b_s^{zz})k_{ss's''}$$
$$+ \frac{1}{2}(B\zeta)_{yy}(B\zeta)_{zz} - \frac{1}{8}\sum_s B_s^{yy}B_s^{zz} + \frac{3}{16}\sum_s\sum_{s'} B_s^{zz}B_{s'}^{zz}(A_{ss'}^{yy})'$$
$$+ \frac{1}{4}\sum_{s<s'}\sum \zeta_{ss'}(B_s^{zz}B_{s'}^{xy} - B_{s'}^{zz}B_s^{xy})$$
$$- \frac{1}{16}[I_y/I_x(I_y - I_x)]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{zz}B_{s'}^{zz}$$
$$- \frac{1}{8}[I_z/(I_y - I_x)^2]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{zz}[(I_yB_{s'}^{yy}/I_x) - I_yB_{s'}^{xx}/I_x)]$$

Table (7-4) (continued)

$$I_y^4 I_z^2 \Phi_7' = \frac{1}{8}N \sum\sum_{s\le s'\le s''}\sum \left(b_s^{yy} b_{s'}^{yy} b_{s''}^{zz} + b_s^{yy} b_{s''}^{yy} b_{s'}^{zz} + b_{s'}^{yy} b_{s''}^{yy} b_s^{zz}\right) k_{ss's''}$$

$$+ \frac{1}{4}(B\zeta)^2_{yy} - \frac{1}{16}\sum_s (B_s^{yy})^2 - \frac{1}{4}\sum_s (B_s^{xy})^2 + \frac{3}{8}\sum_s\sum_{s'} B_s^{yy} B_{s'}^{zz} (A_{ss'}^{yy})'$$

$$- \frac{1}{4}\sum_{s<s'}\sum \zeta_{ss'}(B_s^{xy} B_{s'}^{yy} - B_{s'}^{yy} B_s^{yy})$$

$$- \frac{1}{8}[I_y/I_x(I_y - I_x)]\sum_{s,s'}\sum \lambda_s\lambda_{s'} B_s^{xy} B_{s'}^{xy} B_s^{yy} B_{s'}^{zz}$$

$$- \frac{1}{8}[I_z/(I_y-I_x)^2 \sum_{s,s'}\sum \lambda_s\lambda_{s'} B_s^{xy} B_{s'}^{xy} B_s^{yy}[(I_y B_{s'}^{xx})/I_x - (I_x B_{s'}^{yy})/I_y]$$

$I_x^4 I_z^2 \Phi_8'$ same as $I_y^4 I_z^2 \Phi_7$ with yy replaced by xx throughout

$I_x^2 I_z^4 \Phi_9'$ same as $I_y^2 I_z^4 \Phi_6$ with yy replaced by xx throughout

$$I_x^2 I_y^2 I_z^2 \Phi_{10}' = \frac{1}{8}N \sum\sum_{s\le s'\le s''}\sum \left(b_s^{xx} b_{s'}^{yy} b_{s''}^{zz} + b_s^{xx} b_{s''}^{yy} b_{s'}^{zz} + b_{s''}^{xx} b_{s'}^{yy} b_s^{zz}\right.$$

$$+ b_{s'}^{xx} b_s^{yy} b_{s''}^{zz} + b_{s''}^{xx} b_s^{yy} b_{s'}^{zz} + b_{s'}^{xx} b_{s''}^{yy} b_s^{zz} + 4b_s^{xy} b_{s'}^{xy} b_{s''}^{zz}$$

$$\left.+ 4b_s^{xy} b_{s''}^{xy} b_{s'}^{zz} + 4b_{s''}^{xy} b_{s'}^{xy} b_s^{zz}\right) k_{ss's''} + \frac{1}{2}(B\zeta)_{xx}(B\zeta)_{yy}$$

$$+ (B\zeta)^2_{xy} - \frac{1}{4}\sum_s [I^{xx}B_s^{xx} + I^{yy}B_s^{yy} + I^{zz}B_s^{zz}]^2$$

$$- \frac{1}{8}\sum_s B_s^{xx} B_s^{yy} + \frac{1}{4}\sum_s (B_s^{xy})^2 + \frac{3}{8}\sum_s\sum_{s'} B_{s'}^{zz}[B_s^{xx}(A_{ss'}^{yy})'$$

$$+ B_s^{yy}(A_{ss'}^{xx})'] + \frac{3}{4}\sum_s\sum_{s'} B_{s'}^{zz} B_s^{xy}[(A_{ss'}^{xy})' + (A_{s's}^{xy})']$$

$$- \frac{1}{4}\sum_{s\ne s'}\sum \zeta_{ss'} B_{s'}^{xy}[(B_s^{xx} - B_s^{yy}) + 2I^{zz}B_s^{zz}]$$

$$+ \frac{3}{8}[I_z/(I_y - I_x)^2]\sum_{s,s'}\sum \lambda_s\lambda_{s'} B_s^{xy} B_{s'}^{xy}[(I_y B_s^{xx} B_{s'}^{xx})/I_x$$

$$+ (I_x B_s^{yy} B_{s'}^{yy})/I_y - (I_y/I_x + I_x/I_y) B_s^{xx} B_{s'}^{yy}]$$

Table (7-5). Contribution to the Distortion Constants Resulting from the Elimination of the Non-Orthorhombic Terms

$$I_x^6\Phi_1^{(R)} = \frac{1}{8}[I_x/I_y(I_y - I_x)]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{xx}B_{s'}^{xx}$$

$I_y^6\Phi_2^{(R)}$ same as $I_x^6\Phi_1^{(R)}$ with xx and yy interchanged throughout

$$I_z^6\Phi_3^{(R)} = 0$$

$$I_x^2I_y^4\Phi_4^{(R)} = -\frac{9}{8}[I_y/I_x(I_y - I_x)]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{yy}B_{s'}^{xx}$$
$$+\frac{1}{8}[I_x/I_y(I_y - I_x)]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{yy}B_{s'}^{yy}$$

$I_y^2I_x^4\Phi_5^{(R)}$ same as $I_x^2I_y^4\Phi_4^{(R)}$ with xx and yy interchanged throughout

$$I_y^2I_z^4\Phi_6^{(R)} = -\frac{1}{16}[I_y/I_x(I_y - I_x)]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{zz}B_{s'}^{zz}$$
$$-\frac{1}{8}[I_z/(I_y - I_x)^2]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{zz}[I_xB_{s'}^{yy}/I_y - I_yB_{s'}^{xx}/I_x]$$

$$I_y^4I_z^2\Phi_7^{(R)} = -\frac{1}{8}[I_y/I_x(I_y - I_x)]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{yy}B_{s'}^{zz}$$
$$-\frac{1}{8}[I_z/(I_y - I_x)^2]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{yy}[I_yB_{s'}^{xx}/I_x - I_xB_{s'}^{yy}/I_y]$$

$I_x^4I_z^2\Phi_8^{(R)}$ same as $I_y^4I_z^2\Phi_7^{(R)}$ with xx and yy interchanged throughout

$I_x^2I_z^4\Phi_9^{(R)}$ same as $I_y^2I_z^4\Phi_6^{(R)}$ with xx and yy interchanged throughout

$$I_x^2I_y^2I_z^2\Phi_{10}^{(R)} = \frac{3}{8}[I_z/(I_y - I_x)^2]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}[(I_yB_s^{xx}B_{s'}^{xx})/I_x$$
$$+ (I_xB_s^{yy}B_{s'}^{yy})/I_y - (I_y/I_x + I_x/I_y)B_s^{xx}B_{s'}^{yy}$$

Table (7-6). The Complete Expressions for the Fourth-Order Centrifugal Distortion Coefficient of XYZ as Calculated by Sumberg-Parker

$$I_x^6\Phi_1 = \frac{1}{4}N \sum_{s\le s'\le s''}\sum\sum (b_s^{xx}b_{s'}^{xx}b_{s''}^{xx})k_{ss's''} + \frac{3}{8}\sum_s\sum_{s'} B_s^{xx}B_{s'}^{xx}(A_{ss'}^{xx})'$$

$$+ \frac{1}{8}[I_x/I_y(I_y - I_x)]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{xx}B_{s'}^{xx}$$

$$I_y^6\Phi_2 = \frac{1}{4}N \sum_{s\le s'\le s''}\sum\sum (b_s^{yy}b_{s'}^{yy}b_{s''}^{yy})k_{ss's''} + \frac{3}{8}\sum_s\sum_{s'} B_s^{yy}B_{s'}^{yy}(A_{ss'}^{yy})'$$

$$+ \frac{1}{8}[I_y/I_x(I_x - I_y)]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{yy}B_{s'}^{yy}$$

$$I_z^6\Phi_3 = \frac{1}{4}N \sum_{s\le s'\le s''}\sum\sum (b_s^{zz}b_{s'}^{zz}b_{s''}^{zz})k_{ss's''} + \frac{1}{2}(B\zeta)_{zz}^2 - \frac{1}{8}\sum_s(B_s^{zz})^2$$

$$I_x^2I_y^4\Phi_4 = \frac{1}{8}N \sum_{s\le s'\le s''}\sum\sum (b_s^{xx}b_{s'}^{yy}b_{s''}^{yy} + b_{s'}^{xx}b_s^{yy}b_{s''}^{yy}) + b_{s''}^{xx}b_{s'}^{yy}b_s^{yy}$$

$$+ 4b_s^{yy}b_{s'}^{xy}b_{s''}^{xy} + 4b_{s'}^{yy}b_s^{xy}b_{s''}^{xy} + 4b_{s''}^{yy}b_{s'}^{xy}b_s^{xy})k_{ss's''}$$

$$+ \frac{3}{16}\sum_s\sum_{s'}\{B_s^{yy}B_{s'}^{yy}(A_{ss'}^{xx})' + 2(B_s^{xx}B_{s'}^{yy} + 2B_s^{xy}B_{s'}^{xy})(A_{ss'}^{yy})'$$

$$+ 4B_s^{xy}B_{s'}^{yy}[(A_{ss'}^{xy})' + (A_{s's}^{xy})']\}$$

$$+ \frac{1}{12}I^{zz}\sum_{s<s'}\sum \zeta_{ss'}[\frac{\lambda_s + \lambda_{s'}}{\lambda_s - \lambda_{s'}}](B_s^{xy}B_{s'}^{yy} + B_{s'}^{xy}B_s^{xy})$$

$$- \frac{9}{8}[I_y/I_x(I_y - I_x)]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{yy}B_{s'}^{xx}$$

$$+ \frac{1}{8}[I_x/I_y(I_y - I_x)]\sum_{s,s'}\sum \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{yy}B_{s'}^{yy}$$

$I_x^4I_y^2\Phi_5$ same as $I_x^2I_y^4\Phi_4$ with yy interchanged with xx and with $\zeta_{ss'}$ replaced by $-\zeta_{ss'}$

Table (7-6) (continued)

$$I_y^2 I_z^4 \Phi_6 = \frac{1}{8}N \sum_{s\le s'\le s''}\sum\sum (b_s^{yy} b_{s'}^{zz} b_{s''}^{zz} + b_{s'}^{yy} b_s^{zz} b_{s''}^{zz} + b_{s''}^{yy} b_{s'}^{zz} b_s^{zz}) k_{ss's''}$$

$$+ \frac{1}{2}(B\zeta)_{yy}(B\zeta)_{zz} - \frac{1}{8}\sum_s B_s^{yy} B_s^{zz} + \frac{3}{16}\sum_s\sum_{s'} B_s^{zz} B_{s'}^{zz} (A_{ss'}^{yy})'$$

$$- \frac{1}{6}\sum_{s<s'}\sum \left[\frac{\zeta_{ss'}}{\lambda_s - \lambda_{s'}}\right][B_s^{zz} B_{s'}^{xy}(\lambda_{s'} - 2\lambda_s) + B_{s'}^{zz} B_s^{xy}(\lambda_s - 2\lambda_{s'})]$$

$$- \frac{1}{16}[I_y/I_x(I_y - I_x)]\sum_{s,s'}\sum \lambda_s\lambda_{s'} B_s^{xy} B_{s'}^{xy} B_s^{zz} B_{s'}^{zz}$$

$$- \frac{1}{8}[I_z/(I_y - I_x)^2]\sum_{s,s'}\sum \lambda_s\lambda_{s'} B_s^{xy} B_{s'}^{xy} B_s^{zz}[(I_x B_{s'}^{yy})/I_y - (I_y B_{s'}^{xx})/I_x]$$

$$I_y^4 I_z^2 \Phi_7 = \frac{1}{8}N \sum_{s\le s'\le s''}\sum\sum (b_s^{yy} b_{s'}^{yy} b_{s''}^{zz} + b_s^{yy} b_{s''}^{yy} b_{s'}^{zz} + b_{s'}^{yy} b_{s''}^{yy} b_s^{zz}) k_{ss's''}$$

$$+ \frac{1}{4}(B\xi)_{yy}^2 - \frac{1}{16}\sum_s (B_s^{yy})^2 - \frac{1}{4}\sum_s (B_s^{xy})^2 + \frac{3}{8}\sum_s\sum_{s'} B_s^{yy} B_{s'}^{zz} (A_{ss'}^{yy})'$$

$$- \frac{1}{6}\sum_{s<s'} \left[\frac{\zeta_{ss'}}{\lambda_s - \lambda_{s'}}\right][B_s^{xy} B_{s'}^{yy}(\lambda_s - 2\lambda_{s'}) + B_{s'}^{xy} B_s^{yy}(\lambda_{s'} - 2\lambda_s)]$$

$$- \frac{1}{8}[I_y/I_x(I_y - I_x)]\sum_{s,s'}\sum \lambda_s\lambda_{s'} B_s^{xy} B_{s'}^{xy} B_s^{yy} B_{s'}^{zz}$$

$$- \frac{1}{8}[I_z/(I_y - I_x)^2]\sum_{s,s'}\sum \lambda_s\lambda_{s'} B_s^{xy} B_{s'}^{xy} B_s^{yy}[(I_y B_{s'}^{xx})/I_x - (I_x B_{s'}^{yy})/I_y]$$

$I_x^4 I_z^2 \Phi_8$ same as $I_y^4 I_z^2 \Phi_7$ above with yy replaced by xx throughout and with $\zeta_{ss'}$ replaced by $-\zeta_{ss'}$

$I_x^2 I_z^4 \Phi_9$ same as $I_y^2 I_z^4 \Phi_6$ above with yy replaced by xx throughout and with $\zeta_{ss'}$ replaced by $-\zeta_{ss'}$

Table (7-6) (continued)

$$
\begin{aligned}
I_x^2 I_y^2 I_z^2 \Phi_{10} = {} & \frac{1}{8} N \sum_{s \le s' \le s''} \sum \sum (b_s^{xx} b_{s'}^{yy} b_{s''}^{zz} + b_s^{xx} b_{s''}^{yy} b_{s'}^{zz} + b_{s''}^{xx} b_{s'}^{yy} b_s^{zz} \\
& + b_{s'}^{xx} b_s^{yy} b_{s''}^{zz} + b_{s''}^{xx} b_s^{yy} b_{s'}^{zz} + b_{s'}^{xx} b_{s''}^{yy} b_s^{zz} + 4 b_s^{xy} b_{s'}^{xy} b_{s''}^{zz} \\
& + 4 b_s^{xy} b_{s''}^{xy} b_{s'}^{zz} + 4 b_{s''}^{xy} b_{s'}^{xy} b_s^{zz}) k_{ss's''} + \frac{1}{2} (B\zeta)_{xx} (B\zeta)_{yy} \\
& + (B\zeta)_{xy}^2 - \frac{1}{4} \sum_s [I^{xx} B_s^{xx} + I^{yy} B_s^{yy} + I^{zz} B_s^{zz}]^2 \\
& - \frac{1}{8} \sum_s B_s^{xx} B_s^{yy} + \frac{1}{4} \sum_s (B_s^{xy})^2 + \frac{3}{8} \sum_s \sum_{s'} B_{s'}^{zz} [B_s^{xx} (A_{ss'}^{yy})' \\
& + B_s^{yy} (A_{ss'}^{xx})'] + \frac{3}{4} \sum_s \sum_{s'} B_{s'}^{zz} B_s^{xy} [(A_{ss'}^{xy})' + (A_{s's}^{xy})'] \\
& - \frac{1}{2} \sum_{s \ne s'} \sum \zeta_{ss'} [\frac{\lambda_{s'}}{\lambda_{s'} - \lambda_s}] (B_s^{xx} - B_s^{yy}) B_{s'}^{xy} \\
& - \frac{1}{4} I^{zz} \sum_{s \ne s'} \sum \zeta_{s's} [\frac{\lambda_{s'} - 3\lambda_s}{\lambda_{s'} - \lambda_s}] B_s^{xy} B_{s'}^{zz} \\
& + \frac{3}{8} [I_z / (I_y - I_x)^2] \sum_{s,s'} \sum \lambda_s \lambda_{s'} B_s^{xy} B_{s'}^{xy} [(I_y B_s^{xx} B_{s'}^{xx}) / I_x \\
& + (I_x B_s^{yy} B_{s'}^{yy}) / I_y - (I_y / I_x + I_x / I_y) B_s^{xx} B_{s'}^{yy}]
\end{aligned}
$$

By comparing Tables (7-4) and (7-6), we can now trace the remaining differences between the sextic centrifugal distortion coefficients of Aliev-Watson and Sumberg-Parker. These differences are due exclusively to the Coriolis-type contributions which are handled differently in the two formalisms, viz., in the Aliev-Watson procedure, part of the Coriolis contribution is removed through the rotational contact transformation, as described previously. These differences, listed in Table (7-7), are defined as

$$\Delta\Phi_i = \Phi_i(\text{Sumberg-Parker}) - \Phi_i'(\text{Aliev-Watson}). \qquad (7\text{-}39)$$

We have now fully accounted for the differences between the Aliev-Watson results and the Sumberg-Parker results.

For fitting to experimental data, the contact transformation is, finally, fully specified and one may proceed to obtain a reduced rotational Hamiltonian in the manner described in Chapter 6. The result can be expressed as:

$$\begin{aligned}\tilde{H}_{06} = {} & \tilde{\Phi}_1 J_x^6 + \tilde{\Phi}_2 J_y^6 + \tilde{\Phi}_3 J_z^6 + \tilde{\Phi}_4(J_y^4 J_x^2 + J_x^2 J_y^4) + \tilde{\Phi}_5(J_x^4 J_y^2 + J_y^2 J_x^4) \\ & + \tilde{\Phi}_6(J_z^4 J_y^2 + J_y^2 J_z^4) + \tilde{\Phi}_7(J_y^4 J_z^2 + J_z^2 J_y^4) + \tilde{\Phi}_8(J_x^4 J_z^2 + J_z^2 J_x^4) \\ & + \tilde{\Phi}_9(J_z^4 J_x^2 + J_x^2 J_z^4) + \tilde{\Phi}_{10}(J_x^2 J_y^2 J_z^2 + J_z^2 J_x^2 J_y^2). \qquad (7\text{-}40)\end{aligned}$$

The relations between the coefficients $\tilde{\Phi}_i$ and $\tilde{\Phi}_i'$ are given in Eqs. (6-40)-(6-47) with Φ_i replaced by Φ_i'.

Table (7-7). The Differences Between Sumberg-Parker and Aliev-Watson Sextic Centrifugal Distortion Coefficients

$I_x^6 \Delta\Phi_1 = 0$

$I_y^6 \Delta\Phi_2 = 0$

$I_z^6 \Delta\Phi_3 = 0$

$$I_x^2 I_y^4 \Delta\Phi_4 = \frac{1}{12} I^{zz} \sum_{s<s'}\sum \zeta_{ss'} \left(\frac{\lambda_s + \lambda_{s'}}{\lambda_s - \lambda_{s'}}\right) (B_s^{xy} B_{s'}^{yy} + B_{s'}^{xy} B_s^{yy})$$

$I_y^2 I_x^4 \Delta\Phi_5$ same as $I_x^2 I_y^4 \Delta\Phi_4$ with xx replaced by yy throughout and with $\zeta_{ss'}$ replaced by $-\zeta_{ss'}$.

$$I_y^2 I_z^4 \Delta\Phi_6 = \frac{1}{12} \sum_{s<s'}\sum \zeta_{ss'} \left(\frac{\lambda_s + \lambda_{s'}}{\lambda_s - \lambda_{s'}}\right) (B_s^{zz} B_{s'}^{xy} + B_{s'}^{zz} B_s^{xy})$$

$$I_y^4 I_z^2 \Delta\Phi_7 = \frac{1}{12} \sum_{s<s'}\sum \zeta_{ss'} \left(\frac{\lambda_s + \lambda_{s'}}{\lambda_s - \lambda_{s'}}\right) (B_s^{xy} B_{s'}^{yy} + B_{s'}^{xy} B_s^{yy})$$

$I_x^4 I_z^2 \Delta\Phi_8$ same as $I_y^4 I_z^2 \Delta\Phi_7$ with yy replaced by xx throughout and with $\zeta_{ss'}$ replaced by $-\zeta_{ss'}$.

$I_x^2 I_z^4 \Delta\Phi_9$ same as $I_y^2 I_z^4 \Delta\Phi_6$ with yy replaced by xx throughout and with $\zeta_{ss'}$ replaced by $-\zeta_{ss'}$

$$I_x^2 I_y^2 I_z^2 \Delta\Phi_{10} = +\frac{1}{4} I^{zz} \sum_{s\neq s'}\sum \zeta_{ss'} \left(\frac{\lambda_s + \lambda_{s'}}{\lambda_s - \lambda_{s'}}\right) B_s^{xy} B_{s'}^{zz}$$
$$+ \frac{1}{4} \sum_{s<s'}\sum \zeta_{ss'} [B_s^{xy}(B_{s'}^{yy} - B_{s'}^{xx}) - B_{s'}^{xy}(B_s^{yy} - B_s^{xx})]$$
$$+ \frac{1}{2} \sum_{s\neq s'}\sum \zeta_{ss'} \left(\frac{\lambda_{s'}}{\lambda_s - \lambda_{s'}}\right) B_{s'}^{xy} (B_s^{yy} - B_s^{xx})$$

7.2 Reordered Perturbation Treatment for the Calculation of the Sextic Centrifugal Distortion Coefficients

In an appendix of their paper, Aliev and Watson[13] show that the calculation of $\tilde{H}_{06}^{(v)}$ may be simplified considerably by reassigning the orders of expansion of the terms in the perturbation treatment. The terms are ordered according to the degree in the vibrational operators, except that, as usual, H_{20} is taken as the zero-order Hamiltonian H_0, while H_{02} is placed in H_2. Furthermore, the initial Hamiltonian (7-6)-(7-9) can be broken up into three parts to suit the three different classes of term as expressed by Eqs. (7-3)-(7-5).

In case of $\tilde{H}_{06}^{(v)}$ (harmonic), the relevant terms from the initial Hamiltonian are:

$$H = H_0 + \lambda H_1 + \lambda^2 H_2 \tag{7-41}$$

with

$$H_0 = H_{20}(k^{0-0}) \tag{7-42}$$

$$H_1 = H_{12}(k^{3-1}) \tag{7-43}$$

$$H_2 = H_{22}(k^{4-2}) \tag{7-44}$$

Subjecting the Hamiltonian (7-41) to the first contact transformation, one obtains

$$H_0' = H_0 \tag{7-45}$$

$$H_1' = H_1 + i[S^{(1)}, H_0] \tag{7-46}$$

$$H_2' = H_2 + i[S^{(1)}, H_1] - \tfrac{1}{2}[S^{(1)},[S^{(1)}, H_0]] \tag{7-47}$$

$$H_3' = i[S^{(1)}, H_2] - \frac{1}{2}[S^{(1)},[S^{(1)}, H_1]]$$

$$- \frac{i}{6}[S^{(1)},[S^{(1)},[S^{(1)}, H_0]]] \tag{7-48}$$

$$H_4' = - \frac{1}{2}[S^{(1)},[S^{(1)}, H_2]] - \frac{i}{6}[S^{(1)},[S^{(1)},[S^{(1)}, H_1]]]$$

$$+ \frac{1}{24}[S^{(1)},S^{(1)},[S^{(1)},[S^{(1)}, H_0]]]]. \tag{7-49}$$

Eq. (7-46) now defines the $S^{(1)}$ operator such that

$$i[S^{(1)}, H_0] = -H_{1\text{ off-diagonal}} = -H_{12\text{ off-diagonal}}. \tag{7-50}$$

In this case we have only one type of function for the operator $S^{(1)}$, namely $S_{12}^{(1)}(k^{3-1})$. The harmonic contribution can then be obtained from H_4', and gives, as before,

$$H_4' = \tilde{H}_{06}^{(v)}(\text{harmonic}) = - \frac{1}{2}[S_{12}^{(1)},[S_{12}^{(1)}, H_{22}]] . \tag{7-51}$$

Next we consider the anharmonic part. The initial Hamiltonian can be written as:

$$H = H_0 + \lambda H_1 + \lambda^3 H_3 \tag{7-52}$$

with

$$H_0 = H_{20}(k^{0-0}) \tag{7-53}$$

$$H_1 = H_{12}(k^{3-1}) \tag{7-54}$$

$$H_3 = H_{30}(k^{1-0}) . \tag{7-55}$$

We now subject this Hamiltonian to the first contact transformation, giving

$$H_0' = H_0 \tag{7-56}$$

$$H_1' = H_1 + i[S^{(1)}, H_0] \tag{7-57}$$

$$H_2' = H_2 + i[S^{(1)}, H_1] - \frac{1}{2}[S^{(1)},[S^{(1)}, H_0]] \tag{7-58}$$

$$H_3' = H_3 + i[S^{(1)}, H_2] - \frac{1}{2}[S^{(1)},[S^{(1)}, H_1]] - \frac{i}{6}[S^{(1)},[S^{(1)},[S^{(1)}, H_0]]] \tag{7-59}$$

$$H_4' = i[S^{(1)}, H_3] - \frac{1}{2}[S^{(1)},[S^{(1)}, H_2]] - \frac{i}{6}[S^{(1)},[S^{(1)},[S^{(1)}, H_1]]] + \frac{1}{24}[S^{(1)},[S^{(1)},[S^{(1)},[S^{(1)}, H_0]]]] \tag{7-60}$$

$$H_5' = -\frac{1}{2}[S^{(1)},[S^{(1)}, H_3]] - \frac{i}{6}[S^{(1)},[S^{(1)},[S^{(1)}, H_2]]] + \frac{1}{24}[S^{(1)},[S^{(1)},[S^{(1)},[S^{(1)}, H_1]]]] + \frac{i}{120}[S^{(1)},[S^{(1)},[S^{(1)},[S^{(1)},[S^{(1)}, H_0]]]]] \tag{7-61}$$

$$H_6' = -\frac{i}{6}[S^{(1)},[S^{(1)},[S^{(1)}, H_3]]] + \frac{1}{24}[S^{(1)},[S^{(1)},[S^{(1)},[S^{(1)}, H_2]]]] + \frac{i}{120}[S^{(1)},[S^{(1)},[S^{(1)},[S^{(1)},[S^{(1)}, H_1]]]]] - \frac{1}{720}[S^{(1)},[S^{(1)},[S^{(1)},[S^{(1)},[S^{(1)},[S^{(1)}, H_0]]]]]]. \tag{7-62}$$

Again $S^{(1)}$ consists of the single contribution $S_{12}^{(1)}(k^{3-1})$. An examination of the terms shows that the anharmonic contribution to $\tilde{H}_{06}^{(v)}$ arises with H'_6 only, viz.,

$$\tilde{H}_{06}^{(v)}(\text{anharmonic}) = -\frac{i}{6}[S_{12}^{(1)},[S_{12}^{(1)},[S_{12}^{(1)}, H_{30}]]]. \tag{7-63}$$

For the calculation of $\tilde{H}_{06}^{(v)}$ (Coriolis) the appropriate terms are

$$H = H_0 + \lambda H_1 + \lambda^2 H_2 \tag{7-64}$$

with

$$H_0 = H_{20}(k^{0-0}) \tag{7-65}$$

$$H_1 = H_{12}(k^{3-1}) \tag{7-66}$$

$$H_2 = H_{21}(k^{2-1}) + H_{02}(k^{2-0}). \tag{7-67}$$

Subjecting this Hamiltonian to the first contact transformation, we have a set of equations identical to (7-56)-(7-62). However now H_2 is given by (7-67). Proceeding to the second contact transformation, we can write

$$H_0'' = H_0' \tag{7-68}$$

$$H_1'' = H_1' = 0 \tag{7-69}$$

$$H_2'' = H_2' + i[S^{(2)}, H_0] \tag{7-70}$$

$$H_3'' = H_3' + i[S^{(2)}, \cancelto{0}{H_1'}\,] = H_3' \tag{7-71}$$

$$H_4'' = H_4' + i[S^{(2)}, H_2'] - \tfrac{1}{2}[S^{(2)},[S^{(2)}, H_0]] \tag{7-72}$$

$$H_5'' = H_5' + i[S^{(2)}, H_3'] - \tfrac{1}{2}[S^{(2)}, [S^{(2)}, \cancelto{0}{H_1'}\,]] \tag{7-73}$$

$$H_6'' = H_6' + i[S^{(2)}, H_4'] - \tfrac{1}{2}[S^{(2)},[S^{(2)}, H_2']]$$
$$- \tfrac{i}{6}[S^{(2)},[S^{(2)},[S^{(2)}, H_0]]] \; . \tag{7-74}$$

Eq. (7-70) defines $S^{(2)}$ such that:

$$i[S^{(2)}, H_0] = -\{H_2 + i[S^{(1)}, H_1] - \tfrac{1}{2}[S^{(1)},[S^{(1)}, H_0]]\}_{\text{off-diag.}} \tag{7-75}$$

Now the third contact transformation can be written as:

$$H_0''' = H_0'' \tag{7-76}$$

$$H_1''' = H_1'' = 0 \tag{7-77}$$

$$H_2''' = H_2'' \tag{7-78}$$

$$H_3''' = H_3'' + i[S^{(3)}, H_0] \tag{7-79}$$

$$H_4''' = H_4'' + i[S^{(3)}, H_1''] \tag{7-80}$$

$$H_5''' = H_5'' + i[S^{(3)}, H_2''] \tag{7-81}$$

$$H_6''' = H_6'' + i[S^{(3)}, H_3''] - \frac{1}{2}[S^{(3)},[S^{(3)}, H_0]] \quad . \tag{7-82}$$

Eq. (7-79) defines $S^{(3)}$ such that

$$\begin{aligned} i[S^{(3)}, H_0] &= -H''_{3\text{off-diag.}} = -H'_{3\text{off-diag.}} \\ &= -\{i[S^{(1)}, H_2] - \frac{1}{2}[S^{(1)},[S^{(1)}, H_1]] \\ &\quad - \frac{i}{6}[S^{(1)},[S^{(1)},[S^{(1)}, H_0]]]\}_{\text{off-diag.}} \end{aligned} \tag{7-83}$$

Since $S^{(1)}$ is linear in the vibrational operators, the second and third commutator terms vanish and

$$[S^{(3)}, H_0] = -[S^{(1)}, H_2]_{\text{off-diag.}} \tag{7-84}$$

The required part of $S^{(3)}$ is $S^{(3)}_{13}$, and it is given by

$$S^{(3)}_{13} = -\sum_k q_k\{\sum_\ell R^k_\ell R_\ell(\omega_\ell\omega_k)^{-1} + i[R_k, H_{02}]\omega_k^{-2}\}. \tag{7-85}$$

Now Eq. (7-82) can be written as

$$H_6''' = -\frac{i}{2}[S^{(2)},[S^{(1)},[S^{(1)}, H_2]]] - \frac{1}{2}[S^{(2)},[S^{(2)}, H_2]]$$
$$- \frac{i}{2}[S^{(2)},[S^{(2)},[S^{(1)}, H_1]]] + \frac{1}{4}[S^{(2)},[S^{(2)},[S^{(1)},[S^{(1)},H_0]]]]$$
$$- \frac{i}{6}[S^{(2)},[S^{(2)},[S^{(2)}, H_0]]] - [S^{(3)},[S^{(1)},H_2]]$$
$$- \frac{i}{2}[S^{(3)},[S^{(1)},[S^{(1)}, H_1]]] + \frac{1}{6}[S^{(3)},[S^{(1)},[S^{(1)},[S^{(1)},H_0]]]]$$
$$- \frac{1}{2}[S^{(3)},[S^{(3)}, H_0]]. \qquad (7\text{-}86)$$

Using Eqs. (7-75) and (7-83), we have:

$$H_6''' = -\frac{i}{2}[S^{(2)},[S^{(1)},[S^{(1)}, H_2]]] + \frac{i}{3}[S^{(2)},[S^{(2)},[S^{(2)}, H_{20}]]]$$
$$+ \frac{1}{2}[S^{(3)},[S^{(3)}, H_{20}]]. \qquad (7\text{-}87)$$

An examination of the terms shows that the only contribution to $\tilde{H}_{06}^{(v)}$ (Coriolis) is

$$H_6''' = \tilde{H}_{06}^{(v)}(\text{Coriolis}) = \frac{1}{2}[S_{13}^{(3)},[S_{13}^{(3)}, H_{20}]] . \qquad (7\text{-}88)$$

Evaluation of Eq. (7-88) yields the result in Table (7-2) without the last two sums of $\tilde{H}_{06}^{(v)}$(Coriolis). These were the sums that were removed by a rotational contact transformation in the previous procedure. In the present procedure, these terms do not arise in the first place. Altogether, the result from Eq. (7-88) is the same as that finally obtained in Section 7.1, but clearly Eq. (7-88) is considerably simpler to employ than Eq. (7-31) because it is unnecessary to evaluate $S_{21}^{(1)}$, and the Coriolis contribution is obtained by a much more direct procedure.

From the three different initial Hamiltonians (7-41)-(7-44), (7-52)-(7-55), and (7-64)-(7-67), for the harmonic, anharmonic and Coriolis contributions, respectively, we can see that it is permissible to combine the harmonic and anharmonic Hamiltonians without any change in the result. We could also combine the anharmonic and Coriolis parts and get the same result. However, one cannot combine the harmonic and Coriolis Hamiltonians since the H_1 term has been defined differently for each case.

8. CENTRIFUGAL DISTORTION SUM RULES

8.1 Second-Order Centrifugal Distortion Sum Rules

As mentioned in Section 5.2, the second-order centrifugal distortion constants τ_i which are the coefficients of the fourth-power angular momentum operators of the rotational Hamiltonian can be constructed from Eq. (5-44). Considering the fact that the coefficients τ_i have to be totally symmetric with respect to the covering operations of the point group of the molecule under consideration, one obtains a total of nine distinct non-zero coefficients for orthorhombic molecules (such as the XYX-type molecule), and a total of thirteen distinct non-zero coefficients for monoclinic molecules (such as the XYZ-type molecule), and a total of twenty one distinct non-zero coefficients for triclinic molecules.

For planar asymmetric top molecules, Oka and Morino[34] and Dowling[32] have proved that among τ_1 to τ_9, the relationships (5-45)-(5-48) exist. To obtain these relationships one starts with the planarity condition:

$$a_s^{xx} + a_s^{yy} = a_s^{zz}, \text{ for all } s, \tag{8-1}$$

if the molecule lies in the xy plane. This condition follows immediately from the definition of the inertial derivatives $a_s^{\alpha\beta}$, Eqs. (4-82)-(4-85). Multiplying (8-1) by a_s^{xx} and dividing by

$I_x^2\lambda_s$, yields Eq. (5-45), viz.,

$$(a_s^{xx}a_s^{xx}/I_x^2\lambda_s) + (a_s^{xx}a_s^{yy}/I_x^2\lambda_s) = (a_s^{xx}a_s^{zz}/I_x^2\lambda_s) \tag{8-2}$$

or:

$$(I_x^2a_s^{xx}a_s^{xx}/I_x^4\lambda_s) + (I_y^2a_s^{xx}a_s^{yy}/I_x^2I_y^2\lambda_s) = (I_z^2a_s^{xx}a_s^{zz}/I_x^2I_z^2\lambda_s) \ . \tag{8-3}$$

Subsequent use of the definition (5-44) then leads to the relation

$$\tau_1 = (I_z/I_x)^2\tau_5 - (I_y/I_z)^2\tau_6 \ . \tag{8-4}$$

Similarly multiplying (8-1) by a_s^{yy} and dividing by $I_y^2\lambda_s$, gives Eq. (5-46), viz.,

$$(a_s^{yy}a_s^{xx}/I_y^2\lambda_s) + (a_s^{yy}a_s^{yy}/I_y^2\lambda_s) = (a_s^{yy}a_s^{zz}/I_y^2\lambda_s) \tag{8-5}$$

or:

$$(I_x^2a_s^{yy}a_s^{xx}/I_x^2I_y^2\lambda_s) + (I_y^2a_s^{yy}a_s^{yy}/I_y^4\lambda_s) = (I_z^2a_s^{yy}a_s^{zz}/I_z^2I_y^2\lambda_s), \tag{8-6}$$

from which

$$\tau_2 = (I_z/I_y)^2\tau_4 - (I_x/I_y)^2\tau_6 \ . \tag{8-7}$$

Also multiplying (8-1) by a_s^{zz} and dividing by $I_z^2\lambda_s$, gives Eq. (5-47), viz.,

$$(a_s^{zz}a_s^{xx}/I_z^2\lambda_s) + (a_s^{zz}a_s^{yy}/I_z^2\lambda_s) = (a_s^{zz}a_s^{zz}/I_z^2\lambda_s) \tag{8-8}$$

or:

$$(I_x^2a_s^{zz}a_s^{xx}/I_x^2I_z^2\lambda_s) + (I_y^2a_s^{zz}a_s^{yy}/I_z^2I_y^2\lambda_s) = (I_z^2a_s^{zz}a_s^{zz}/I_z^4\lambda_s), \tag{8-9}$$

from which

$$\tau_3 = (I_y/I_z)^2\tau_4 + (I_x/I_z)^2\tau_5 \ . \qquad (8\text{-}10)$$

Moreover, using the fact that $a_s^{xz} = a_s^{yz} = 0$, the definition (5-44) gives Eq. (5-48), viz.,

$$\tau_7 = \tau_{yzyz} = 0, \qquad (8\text{-}11)$$

$$\tau_8 = \tau_{xzxz} = 0. \qquad (8\text{-}12)$$

Therefore, in planar molecules, there are five constraints among τ_1 to τ_9. This means that there are only four independent τ's among τ_1 to τ_9 for orthorhombic molecules.

For the monoclinic space groups, it is easy to prove that in addition to the above five constraints, there are two more constraints among τ_{10} through τ_{13}. Again multiplying (8-1) by a_s^{xy} and dividing by $I_xI_y\lambda_s$ yields Eq. (5-49), viz.,

$$(a_s^{xy}a_s^{xx}/I_xI_y\lambda_s) + (a_s^{xy}a_s^{yy}/I_xI_y\lambda_s) = (a_s^{xy}a_s^{zz}/I_xI_y\lambda_s), \qquad (8\text{-}13)$$

or:

$$(I_x^2a_s^{xy}a_s^{xx}/I_x^3I_y\lambda_s) + (I_y^2a_s^{xy}a_s^{yy}/I_xI_y^3\lambda_s) = (I_z^2a_s^{xy}a_s^{zz}/I_xI_yI_z^2\lambda_s) \qquad (8\text{-}14)$$

from which

$$\tau_{12} = (I_x/I_z)^2\tau_{10} + (I_y/I_z)^2\tau_{11} \ . \qquad (8\text{-}15)$$

Therefore there are altogether seven constraints among τ_1 through τ_{13}. This gives us six independent τ's for monoclinic space groups.

However, as discussed in Chapter 6, Watson[30] has shown that the non-totally symmetric quartic terms, i.e., non-orthorhombic terms, can be omitted from the reduced second-order Hamiltonian. This can be done irrespective of the symmetry of the molecule. The non-totally symmetric terms do not contribute to the energy in second order, and they can be transformed completely into the terms of higher degree in the Hamiltonian. Therefore the effects of these terms in second or higher order are indistinguishable from the effects of higher degree terms in the Hamiltonian. Thus we can conclude that in general in the planar case there are three sum rules and two zero τ's, hence four independent determinable coefficients for the second-order centrifugal distortion coefficients τ_i.

8.2 Fourth-order Centrifugal Distortion Sum Rules

In the fitting of molecular rotational energies with a sixth-degree rotational Hamiltonian, some of the sextic distortion constants are frequently found to have large experimental uncertainties. This can limit the usefulness of these constants as sources of information on the cubic anharmonic potential of the molecule. In such circumstances, it is advantageous to apply as a constraint any theoretical relation existing between the sextic distortion constants. Such a constraint will normally reduce the uncertainity of the constants without interfering with the deduction of potential constants from them. While a relation of this type is unlikely to exist for a completely arbitrary molecule, Watson[39] has shown that there exists a general relation for planar molecules. This relation is analogous to a planarity condition for the quartic distortion constants, and like these is only strictly valid for the equilibrium constants.

For the general case of the asymmetric rotator, Watson[30] has shown that the number of independent sextic coefficients or independent linear combinations of these is seven. Since the planarity relation (8-1) introduces an additional constraint, planarity would be expected to reduce the number of independent sextic coefficients by one, to a total of six. Therefore, there should exist four linearly independent relations among the fourth-order centrifugal distortion constants. The construction and calculation of these four sextic equations of constraint forms a part of the original work of this dissertation. The manner in which these results might be useful in the analysis of high-resolution vibration-rotation data will also be discussed.

By inspection of the anharmonic portions of the theoretical expressions Φ_i, and by repeated use of the conditions of planarity (8-1), it is found that the following four linear combinations of the sextic constants Φ_i are independent of the cubic anharmonic potential constants:

$$F_1 = \frac{3}{2}I_z^6\Phi_3 - I_y^2I_z^4\Phi_6 - I_x^2I_z^4\Phi_9, \tag{8-16}$$

$$F_2 = I_x^2I_z^4\Phi_9 - I_y^2I_z^4\Phi_6 - I_x^4I_z^2\Phi_8 + I_y^4I_z^2\Phi_7, \tag{8-17}$$

$$F_3 = I_x^6\Phi_1 + I_y^6\Phi_2 + \frac{1}{2}I_z^6\Phi_3 - I_y^4I_z^2\Phi_7 - I_x^4I_z^2\Phi_8, \tag{8-18}$$

$$F_4 = I_x^6\Phi_1 + I_y^6\Phi_2 - I_z^6\Phi_3 - 2I_x^2I_y^4\Phi_4 - 2I_x^4I_y^2\Phi_5 + 2I_x^2I_y^2I_z^2\Phi_{10}. \tag{8-19}$$

These expressions depend thus only on the equilibrium geometry and the harmonic force field parameters of the molecule, quantities which are ordinarily known to considerably better precision than either the calculated or the empirical values of the sextic coefficients. These expressions therefore appear potentially useful as planarity-conditioned constraints on the ten sextic centrifugal distortion coefficients obtained in the expansion of the Darling-Dennison Hamiltonian.

The indexing of Φ_i corresponds to the sextic part of the Hamiltonian as follows:

$$\begin{aligned} H_6 = {} & \Phi_1 P_x^6 + \Phi_2 P_y^6 + \Phi_3 P_z^6 + \Phi_4 (P_x^2 P_y^4 + P_y^4 P_x^2) + \Phi_5 (P_y^2 P_x^4 + P_x^4 P_y^2) \\ & + \Phi_6 (P_y^2 P_z^4 + P_z^4 P_y^2) + \Phi_7 (P_z^2 P_y^4 + P_y^4 P_z^2) + \Phi_8 (P_z^2 P_x^4 + P_x^4 P_z^2) \\ & + \Phi_9 (P_x^2 P_z^4 + P_z^4 P_x^2) + \Phi_{10} (P_x^2 P_z^2 P_y^2 + P_y^2 P_z^2 P_x^2) . \end{aligned} \tag{8-20}$$

In our formulation, the molecular framework is located in the xy plane. If it is desired to have the molecule located in the yz or zx plane, the appropriate cyclic permutations of the cartesian coordinates can easily be carried out. It should be recalled from Chapter 7 that the theoretical expressions for the sextic coefficients Φ_i' given by Aliev and Watson[13] (Table 7-4)) differ in part from those given by Sumberg and Parker (Table (7-6)), in the manner described in Chapter 7. An independent calculation carried out by Georghiou[40] and using a different pertubation procedure gives the same results as the calculation of Aliev and Watson. Which of the two available sets of coefficients gives better agreement with experiment must ultimately be decided by experiment. At the present time, neither set has been tested extensively. Aliev and Watson[13] find reasonably good agreement with experiment for

SO_2, and Georghiou[40] for H_2S. Using both the Sumberg-Parker coefficients and the Aliev-Watson coefficients, we find reasonably good agreement for the ozone molecule with either set of coefficients. These results will be given in the next chapter.

The computation of the functions F_i given by Eqs. (8-16)-(8-19) is mostly straightforward, though somewhat tedious. Frequent use is made of the planarity condition, Eq. (8-1), in simplifying and consolidating the expressions as the calculation proceeds. Tables (8-1) and (8-2), respectively, list the results obtained on the basis of the Sumberg-Parker coefficients and on the basis of the Aliev-Watson coefficients for the XYX (C_2V) case. The more complicated results for the general triatomic XYZ (C_s) case are listed in Tables (8-3) and (8-4). In all these tables, ΔB_s denotes $B_s^{yy} - B_s^{xx}$. For ease of comparison, we have transcribed the Aliev-Watson based functions into the Sumberg-Parker notation and dimensions. As required by the respective formalisms, we verified that the Aliev-Watson based functions F_i^{AW} yield the corresponding Sumberg-Parker based functions F_i^{SP} except for the Coriolis-type contributions which are different in the two formalisms.

In the cgs system of units, the Φ_i are in $g^{-5}cm^{-10}s^4$ and can be changed to wavenumber units (cm^{-1}) by multiplying by $(\hbar^5/2\pi c)$. The dimensions of the functions F_i are $g\ cm^2 s^4$, and the coefficients $B_s^{\alpha\beta}$ are in $g^{\frac{1}{2}}cm\ s^2$.

Table (8-1). The Functions F_1^{SP}, F_2^{SP}, F_3^{SP}, and F_4^{SP} Defined by Eqs. (8-16)-(8-19) for the XYX (C_{2v}) Molecule)

$$F_1^{SP} = -\tfrac{1}{4}(B_1^{zz}\zeta_{31} - B_2^{zz}\zeta_{23})^2 = -I_z\zeta_{23}^2\zeta_{31}^2[(1/\lambda_1) - (1/\lambda_2)]^2$$

$$F_2^{SP} = -\tfrac{1}{4}(B_1^{xx}\zeta_{31} - B_2^{xx}\zeta_{23})^2 + \tfrac{1}{4}(B_1^{yy}\zeta_{31} - B_2^{yy}\zeta_{23})^2$$
$$+ \tfrac{1}{6}B_3^{xy}\{[\zeta_{31}B_1^{zz}(\lambda_3 - 2\lambda_1)/(\lambda_3 - \lambda_1)] - [\zeta_{23}B_2^{zz}(\lambda_3 - 2\lambda_2)/(\lambda_3 - \lambda_2)]\}$$

$$F_3^{SP} = -\tfrac{1}{2}(B_1^{xx}\zeta_{31} - B_2^{xx}\zeta_{23})(B_1^{yy}\zeta_{31} - B_2^{yy}\zeta_{23}) + \tfrac{1}{2}(B_3^{xy})^2$$
$$+ \tfrac{1}{6}B_3^{xy}\{[\zeta_{31}\Delta B_1(\lambda_3 - 2\lambda_1)/(\lambda_3 - \lambda_1)]$$
$$- [\zeta_{23}\Delta B_2(\lambda_3 - 2\lambda_2)/(\lambda_3 - \lambda_2)]\}$$

$$F_4^{SP} = -(B_1^{xx}\zeta_{31} - B_2^{xx}\zeta_{23})(B_1^{yy}\zeta_{31} - B_2^{yy}\zeta_{23}) + \tfrac{1}{2}(B_1^{zz}\zeta_{31} - B_2^{zz}\zeta_{23})^2$$
$$- (B_3^{xy})^2 - \tfrac{1}{2}(\sum_\alpha I^{\alpha\alpha}B_1^{\alpha\alpha})^2 - \tfrac{1}{2}(\sum_\alpha I^{\alpha\alpha}B_2^{\alpha\alpha})^2$$
$$- \tfrac{1}{6}I^{zz}B_3^{xy}\zeta_{31}[\Delta B_1(\lambda_1 + \lambda_3) + 3B_1^{zz}(\lambda_1 - 3\lambda_3)]/(\lambda_3 - \lambda_1)$$
$$+ \tfrac{1}{6}I^{zz}B_3^{xy}\zeta_{23}[\Delta B_2(\lambda_2 + \lambda_3) + 3B_2^{zz}(\lambda_2 - 3\lambda_3)]/(\lambda_3 - \lambda_2)$$
$$- B_3^{xy}\lambda_3\{[\zeta_{31}\Delta B_1/(\lambda_3 - \lambda_1)] - [\zeta_{23}\Delta B_2/(\lambda_3 - \lambda_2)]\}$$

Table (8-2). The Functions F_1^{AW}, F_2^{AW}, F_3^{AW}, and F_4^{AW} Defined by Eqs. (8-16)-(8-19) for the XYX (C_{2v}) Molecule

Replace terms with Coriolis-resonant denominators $(\lambda_3 - \lambda_1)$ and $(\lambda_3 - \lambda_2)$ of Table (8-1).

in F_2^{SP} by: $+ \frac{1}{4} B_3^{xy}(B_1^{zz}\zeta_{31} - B_2^{zz}\zeta_{23})$

in F_3^{SP} by: $+ \frac{1}{4} B_3^{xy}(\Delta B_1\zeta_{31} - \Delta B_2\zeta_{23})$

in F_4^{SP} by: $- \frac{1}{2} B_3^{xy}(\Delta B_1\zeta_{31} - \Delta B_2\zeta_{23}) + I^{zz}B_3^{xy}(B_1^{zz}\zeta_{31} - B_2^{zz}\zeta_{23})$

Table (8-3). The Functions F_1^{SP}, F_2^{SP}, F_3^{SP}, and F_4^{SP} Defined by Eqs. (8-16)-(8-19) for the XYZ (C_s) Molecule

$$F_1^{SP} = +\frac{1}{4}(B\zeta)^2_{zz} - \frac{1}{4}\sum_s (B_s^{zz})^2 + \frac{1}{16}(I_z/I_xI_y)\sum_s\sum_{s'} \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{zz}B_{s'}^{zz}$$

$$F_2^{SP} = +\frac{1}{4}(B\zeta)^2_{xx} - \frac{1}{4}(B\zeta)^2_{yy} - \frac{1}{4}\sum_s(B_s^{xx})^2 + \frac{1}{4}\sum_s(B_s^{yy})^2$$

$$+ \frac{1}{6}\sum_{s<s'}\sum [\zeta_{ss'}/(\lambda_s - \lambda_{s'})][B_s^{zz}B_{s'}^{xy}(\lambda_{s'} - 2\lambda_s) + B_{s'}^{zz}B_s^{xy}(\lambda_s - 2\lambda_{s'})]$$

$$- \frac{1}{16}(I_z/I_xI_y)\sum_s\sum_{s'}\lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_{s'}^{zz}\Delta B_s$$

$$- \frac{3}{8}[I_z/(I_y - I_x)^2]\sum_s\sum_{s'} \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{zz}[(I_yB_{s'}^{xx}/I_x) - (I_xB_{s'}^{yy}/I_y)]$$

$$F_3^{SP} = +\frac{1}{2}(B\zeta)_{xx}(B\zeta)_{yy} - \frac{1}{2}\sum_s B_s^{xx}B_s^{yy} + \frac{1}{2}\sum_s(B_s^{xy})^2$$

$$+ \frac{1}{6}\sum_{s<s'}\sum [\zeta_{ss'}/(\lambda_s - \lambda_{s'})][B_{s'}^{xy}\Delta B_s(\lambda_{s'} - 2\lambda_s) + B_s^{xy}\Delta B_{s'}(\lambda_s - 2\lambda_{s'})]$$

$$+ \frac{1}{8}[1/(I_y - I_x)]\sum_s\sum_{s'} \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}[(I_yB_s^{yy}B_{s'}^{xx}/I_x) - (I_xB_s^{xx}B_{s'}^{yy}/I_y)]$$

$$+ \frac{1}{8}[I_z/(I_y - I_x)^2]\sum_s\sum_{s'} \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}\Delta B_s[(I_yB_{s'}^{xx}/I_x) - (I_xB_{s'}^{yy}/I_y)]$$

$$F_4^{SP} = +(B\zeta)_{xx}(B\zeta)_{yy} - \frac{1}{2}(B\zeta)^2_{zz} - \sum_s B_s^{xx}B_s^{yy} + \frac{1}{2}\sum_s(B_s^{zz})^2 + 2(B\zeta)^2_{xy}$$

$$- \sum_s(B_s^{xy})^2 - \frac{1}{2}\sum_s(\sum_\alpha I^{\alpha\alpha}B_s^{\alpha\alpha})^2 - \sum_{s\neq s'}\sum \zeta_{ss'}B_{s'}^{xy}\Delta B_s\lambda_{s'}/(\lambda_{s'} - \lambda_s)$$

$$- \frac{1}{2}I^{zz}\sum_{s\neq s'}\sum \zeta_{s's}B_s^{xy}B_{s'}^{zz}(\lambda_{s'} - 3\lambda_s)/(\lambda_{s'} - \lambda_s)$$

$$- \frac{1}{6}I^{zz}\sum_{s<s'}\sum \zeta_{ss'}(B_s^{xy}\Delta B_{s'} + B_{s'}^{xy}\Delta B_s)(\lambda_s + \lambda_{s'})/(\lambda_s - \lambda_{s'})$$

$$+ \frac{1}{8}[1/(I_y - I_x)]\sum_s\sum_{s'} \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}[(I_y/I_x)(2B_s^{xx}B_{s'}^{xx} - B_s^{yy}B_{s'}^{yy})$$

$$- (I_x/I_y)(2B_s^{yy}B_{s'}^{yy} - B_s^{xx}B_{s'}^{xx})]$$

$$+ \frac{3}{4}[I_z/(I_y-I_x)^2]\sum_s\sum_{s'}\lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}\Delta B_s[(I_xB_{s'}^{yy}/I_y) - (I_yB_{s'}^{xx}/I_x)]$$

$$+ \frac{9}{4}[I_z/I_xI_y]\sum_s\sum_{s'}\lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{xx}B_{s'}^{yy}.$$

Table (8-4). The Functions F_1^{AW}, F_2^{AW}, F_3^{AW}, and F_4^{AW} Defined by Eqs. (8-16)-(8-19) for the XYZ (C_s) Molecule

$$F_1^{AW} = + \frac{1}{4}(B\zeta)^2_{zz} - \frac{1}{4}\sum_s (B_s^{zz})^2 + \frac{1}{16}(I_z/I_xI_y)\sum_s\sum_{s'} \lambda_s\lambda_{s'}B_s^{xx}B_{s'}^{xy}B_s^{zz}B_{s'}^{zz}$$

$$F_2^{AW} = + \frac{1}{4}(B\zeta)^2_{xx} - \frac{1}{4}(B\zeta)^2_{yy} - \frac{1}{4}\sum_s (B_s^{xx})^2 + \frac{1}{4}\sum_s (B_s^{yy})^2$$
$$+ \frac{1}{4}\sum_{s<s'}\sum \zeta_{ss'}(B_s^{xy}B_{s'}^{zz} - B_s^{zz}B_{s'}^{xy}) - \frac{1}{16}(I_z/I_xI_y)\sum_s\sum_{s'}\lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_{s'}^{zz}\Delta B_s$$
$$- \frac{3}{8}[I_z/(I_y - I_x)^2]\sum_s\sum_{s'} \lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{zz}[(I_yB_{s'}^{xx}/I_x) - (I_xB_{s'}^{yy}/I_y)]$$

$$F_3^{AW} = + \frac{1}{2}(B\zeta)_{xx}(B\zeta)_{yy} - \frac{1}{2}\sum_s B_s^{xx}B_s^{yy} + \frac{1}{2}\sum_s (B_s^{xy})^2 + \frac{1}{4}\sum_{s<s'}\sum \zeta_{ss'}(B_s^{xy}\Delta B_{s'}$$
$$- B_{s'}^{xy}\Delta B_s) + \frac{1}{8}[1/(I_y - I_x)]\sum_s\sum_{s'}\lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}[(I_yB_s^{yy}B_{s'}^{xx}/I_x)$$
$$- (I_xB_s^{xx}B_{s'}^{yy}/I_y)] + \frac{1}{8}[I_z/(I_y - I_x)^2]\sum_s\sum_{s'}\lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}\Delta B_s[(I_yB_{s'}^{xx}/I_x)$$
$$- (I_xB_{s'}^{yy}/I_y)]$$

$$F_4^{AW} = +(B\zeta)_{xx}(B\zeta)_{yy} - \frac{1}{2}(B\zeta)^2_{zz} - \sum_s B_s^{xx}B_s^{yy} + \frac{1}{2}\sum_s (B_s^{zz})^2 + 2(B\zeta)^2_{xy}$$
$$- \sum_s (B_s^{xy})^2 - \frac{1}{2}\sum_s(\sum_\alpha I^{\alpha\alpha}B_s^{\alpha\alpha})^2 - I^{zz}\sum_{s\neq s'}\sum \zeta_{ss'}B_{s'}^{xy}B_s^{zz}$$
$$- \frac{1}{2}\sum_{s<s'}\sum \zeta_{ss'}(B_s^{xy}\Delta B_{s'} - B_{s'}^{xy}\Delta B_s) + \frac{9}{4}[I_z/I_xI_y]\sum_s\sum_{s'}\lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}B_s^{xx}B_{s'}^{yy}$$
$$+ \frac{1}{8}[1/(I_y - I_x)]\sum_s\sum_{s'}\lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}[(I_y/I_x)(2B_s^{xx}B_{s'}^{xx} - B_s^{yy}B_{s'}^{yy})$$
$$- (I_x/I_y)(2B_s^{yy}B_{s'}^{yy} - B_s^{xx}B_{s'}^{xx})]$$
$$+ \frac{3}{4}[I_z/(I_y - I_x)^2]\sum_s\sum_{s'}\lambda_s\lambda_{s'}B_s^{xy}B_{s'}^{xy}\Delta B_s[(I_xB_{s'}^{yy}/I_y) - (I_yB_{s'}^{xx}/I_x)]$$

8.3 Constrained Empirical Constants

In order to utilize the sextic planarity relations in the analysis of vibration-rotation data, the theoretical constants Φ_i must be related to the corresponding empirical constant $\tilde{\Phi}_i$. (Again, the tilde symbol is used consistently in this chapter to denote empirical constants.) The relations existing between the theoretical and the experimental constants have been studied by Watson.[13] This work was discussed in Chapter 6, and we shall use the results in the form given by Yallabandi and Parker,[25] Eqs. (24-26).

In general, the planarity relations among the empirical coefficients are obtained when the Φ_i are replaced in Eqs. (8-16)-(8-19) by the corresponding $\tilde{\Phi}_i$ with the aid of the set of Eqs. (26) of Yallabandi and Parker.[25] After this replacement, however, the resulting equations are more complicated and contain four S-parameters viz., S_{111}, S_{113}, S_{131} and S_{311}. A more promising approach appears to be to let the planarity relations define a reduction of the sextic Hamiltonian by using an empirical Hamiltonian which includes all ten $\tilde{\Phi}_i$, but with these planarity constrained by our Eqs. (8-21)-(8-24) below. This reduction is specified by taking $S_{113} = S_{131} = S_{311} = 0$ which amounts to not applying the fourth-order part of the similarity transformation of the Hamiltonian. The advantage of this approach is that a reduction is obtained which has a natural and straightforward relation to the theoretical formulation, and that this relation can be explored without the necessity of determining non-zero numerical values for S_{113}, S_{131}, and S_{311} which tend to be very poorly determined in practice.

Another advantage is the immediate one that the equations relating the theoretical and empirical coefficients are much simplified by taking $S_{113} = S_{131} = S_{311} = 0$ in which case one finds from Eqs. (8-16)-(8-19) that

$$F_1 = \tfrac{3}{2}I_z^6\tilde{\Phi}_3 - I_y^2I_z^4\tilde{\Phi}_6 - I_x^2I_z^4\tilde{\Phi}_9 - 4\hbar S_{111}I_z^4[I_y^2(\tilde{T}_3 - \tilde{T}_4) + I_x^2(\tilde{T}_5 - \tilde{T}_3)]$$
$$- 4\hbar^2S_{111}^2I_z^4[-I_y^2(\tilde{C}-\tilde{B}) + I_x^2(\tilde{A}-\tilde{C})], \qquad (8\text{-}21)$$

$$F_2 = I_x^2I_z^4\tilde{\Phi}_9 - I_y^2I_z^4\tilde{\Phi}_6 - I_x^4I_z^2\tilde{\Phi}_8 + I_y^4I_z^2\tilde{\Phi}_7 - 4\hbar S_{111}I_z^2[I_y^2I_z^2(\tilde{T}_3 - \tilde{T}_4)$$
$$+ I_x^2I_z^2(\tilde{T}_3 - \tilde{T}_5) + I_x^4(\tilde{T}_1 - \tilde{T}_5) + I_y^4(\tilde{T}_2 - \tilde{T}_4)]$$
$$+ 4\hbar^2S_{111}^2I_z^2[I_x^2(I_x^2 + I_z^2)(\tilde{A}-\tilde{C}) + I_y^2(I_y^2 + I_z^2)(\tilde{C}-\tilde{B})], \qquad (8\text{-}22)$$

$$F_3 = I_x^6\tilde{\Phi}_1 + I_y^6\tilde{\Phi}_2 + \tfrac{1}{2}I_z^6\tilde{\Phi}_3 - I_y^4I_z^2\tilde{\Phi}_7 - I_x^4I_z^2\tilde{\Phi}_8 - 4\hbar S_{111}I_z^2[I_y^4(\tilde{T}_4 - \tilde{T}_2)$$
$$+ I_x^4(\tilde{T}_1 - \tilde{T}_5)] - 4\hbar S_{111}^2I_z^2[I_y^4(\tilde{C}-\tilde{B}) - I_x^4(\tilde{A}-\tilde{C})], \qquad (8\text{-}23)$$

$$F_4 = I_x^6\tilde{\Phi}_1 + I_y^6\tilde{\Phi}_2 - I_z^6\tilde{\Phi}_3 - 2I_x^2I_y^4\tilde{\Phi}_4 - 2I_x^4I_y^2\tilde{\Phi}_5 + 2I_x^2I_y^2I_z^2\tilde{\Phi}_{10}$$
$$- 8\hbar S_{111}I_x^2I_y^2[I_y^2(\tilde{T}_2 - \tilde{T}_6) + I_x^2(\tilde{T}_6 - \tilde{T}_1)]$$
$$- 8\hbar^2S_{111}^2I_x^2I_y^2[-I_y^2(\tilde{B}-\tilde{A}) + I_x^2(\tilde{B}-\tilde{A})]. \qquad (8\text{-}24)$$

Here $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$ are the experimentally determined effective rotational constants and the $\tilde{T}_i$ are the experimentally determined coefficients of the quartic part of the Hamiltonian,

$$\tilde{H}_4 = \tilde{T}_1P_x^4 + \tilde{T}_2P_y^4 + \tilde{T}_3P_z^4 + \tilde{T}_4(P_y^2P_z^2 + P_z^2P_y^2)$$
$$+ \tilde{T}_5(P_z^2P_x^2 + P_x^2P_z^2) + \tilde{T}_6(P_x^2P_y^2 + P_y^2P_x^2). \qquad (8\text{-}25)$$

The manner in which the reduction of $\tilde{H}_4$ is effected determines the value of the parameter. S_{111}. When $S_{113} = S_{131} = S_{311} = 0$, then the $\tilde{T}_i$ are related to the corresponding T_i by[41]

$$T_i = \tilde{T}_i + \mathcal{O}(4), \quad i = 1,2,3, \tag{8-26}$$

$$T_4 = \tilde{T}_4 + 2\hbar(\tilde{C}-\tilde{B})S_{111} + \mathcal{O}(4), \tag{8-27}$$

$$T_5 = \tilde{T}_5 + 2\hbar(\tilde{A}-\tilde{C})S_{111} + \mathcal{O}(4), \tag{8-28}$$

$$T_6 = \tilde{T}_6 + 2\hbar(\tilde{B}-\tilde{A})S_{111} + \mathcal{O}(4), \tag{8-29}$$

where $\mathcal{O}(4)$ are contributions of order four which also depend on S_{111}. In practice one is forced to neglect these contributions at the present time since the fourth-order contributions to the theoretical coefficients T_i are very complicated and have not yet been well developed. Consequently, the T_i need to be approximated by the theoretical expressions for the corresponding equilibrium quartic distortion constants τ_i. After a quartic reduction is specified, for example $\tilde{T}_6 = 0$, one can proceed to obtain a value for S_{111} from one or more of the Eqs. (8-27)-(8-29). Use of more than one equation for the determination of S_{111} amounts to a test for consistency, with the more reliable values of S_{111} probably those for which the difference in the rotational constants involved is of the same order of magnitude as the rotational constants themselves. Whereas, in principle, it is possible to determine the numerical value of S_{111} strictly from theory, in practice both experimental and theoretical input are required because the theoretical development remains incomplete.

It appears very attractive to attempt to take $S_{111} = 0$, as in that case the numerical values of <u>all</u> empirical constants would correspond to the numerical evaluation of the associated theoretical expressions, i.e.,

$$A = \tilde{A}, \quad B = \tilde{B}, \quad C = \tilde{C}, \quad T_i = \tilde{T}_i, \quad \Phi_i = \tilde{\Phi}_i \; . \tag{8-30}$$

For such a situation to apply it is, however, necessary to planarity-constrain the quartic constants $\tilde{T}_i$ in the data fit. These constraints, however, are known at the present time only for the corresponding equilibrium coefficients[33,35] τ_i, and thus an error of order four would be incurred in the data fit which may be acceptable in special cases[13,42], but almost certainly not in general.

Watson[39] has given a general sextic planarity relation involving only empirical rotational and distortion constants and valid for any reduction of the quartic and sextic portions of the Hamiltonian. The relation is, however, strictly valid only for the equilibrium values of these constants. With this proviso, we have confirmed that Watson's planarity relation is equivalent to the first planarity relation Eq. (8-16). This equivalence holds for both the XYX case and the XYZ case.

8.4 Cylindrical Tensor Form Hamiltonian

Cylindrical tensor forms of the Hamiltonian have been widely and successfully used for data analysis. Starting with such a Hamiltonian in the form cited by Yallabandi and Parker[25], Eqs. (5-2), (5-19)-(5-21), it is possible to develop the set of equations below. These are again based on a full ten-term sextic Hamiltonian with planarity contrained coefficients H_i. Use of Eqs. (5-22)-(5-43) leads to the following set of equations:

$$\Phi_1 + \Phi_2 = 2\tilde{H}_1 + \tilde{H}_6, \tag{8-31}$$

$$\Phi_1 - \Phi_2 = 2\tilde{H}_5 + 2\tilde{H}_{10}, \tag{8-32}$$

$$\Phi_3 = \tilde{H}_1 + \tilde{H}_2 + \tilde{H}_3 + \tilde{H}_4, \tag{8-33}$$

$$\Phi_4 + \Phi_5 = 3\tilde{H}_1 - \frac{5}{2}\tilde{H}_6 - 8\kappa S_{111}\tilde{D}_4, \tag{8-34}$$

$$\Phi_4 - \Phi_5 = -\tilde{H}_5 + 3\tilde{H}_{10} + 16\kappa S_{111}\tilde{D}_6 - 8\kappa^2 S_{111}^2(\tilde{B}-\tilde{A}), \tag{8-35}$$

$$\Phi_6 + \Phi_9 = 3\tilde{H}_1 + 2\tilde{H}_2 + \tilde{H}_3 + 4\kappa S_{111}(\tilde{D}_4 + 2\tilde{D}_5) - 4\kappa^2 S_{111}^2(2\tilde{C}-\tilde{A}-\tilde{B}), \tag{8-36}$$

$$\Phi_6 - \Phi_9 = -\tilde{H}_5 - 2\tilde{H}_7 - 2\tilde{H}_8 + 4\kappa S_{111}(\tilde{D}_2 + 2\tilde{D}_3) + 4\kappa^2 S_{111}^2(\tilde{B}-\tilde{A}), \tag{8-37}$$

$$\begin{aligned}\Phi_7 + \Phi_8 = {} & 3\tilde{H}_1 + \tilde{H}_2 + \frac{1}{2}\tilde{H}_6 + \tilde{H}_9 + 4\kappa S_{111}(\tilde{D}_4 - 2\tilde{D}_5) \\ & + 4\kappa^2 S_{111}^2(2\tilde{C}-\tilde{A}-\tilde{B}),\end{aligned} \tag{8-38}$$

$$\Phi_7 - \Phi_8 = -2\tilde{H}_5 - 2\tilde{H}_7 + 4\kappa S_{111}(\tilde{D}_2 - \tilde{D}_6) - 4\kappa^2 S_{111}^2(\tilde{B}-\tilde{A}), \tag{8-39}$$

$$\Phi_{10} = 3\tilde{H}_1 + \tilde{H}_2 - \frac{3}{2}\tilde{H}_6 - 3\tilde{H}_9. \tag{8-40}$$

If in Eqs. (8-16)-(8-19) the Φ_i are replaced in accordance with Eqs. (8-31)-(8-40) above, then the cylindrical tensor version of the planarity relations for the empirical coefficients, Eqs. (8-21)-(8-24), is obtained. If in these one takes $S_{111} = 0$ and removes the tilde symbols from the $\tilde{H}_i$, the cylindrical tensor version of the planarity relations for the theoretical coefficients, Eqs. (8-16)-(8-19) is obtained.

An experimental test of the planarity relations requires that the data fit be carried out in a particular way, viz., with the coefficients constrained as described. No such data fits have been carried out to date, but it may be hoped that they will be attempted at some future time.

9. THE CENTRIFUGAL DISTORTION COEFFICIENTS OF OZONE

A calculation of the centrifugal distortion constants of the ozone molecule was carried out and will be described in this chapter. For the sextic constants, both the Sumberg-Parker and the Aliev-Watson expressions were used. The calculated distortion constants were compared to experimental results in the literature with the aid of the reduced-Hamiltonian approach described in Chapter 6. The agreement between theory and experiment was found to be generally quite satisfactory.

9.1 The Fourth-Order Centrifugal Distortion Coefficients for an XYX-Type Molecule

The complete expressions for the ten sextic fourth-order centrifugal distortion coefficients for an XYZ-type molecule as calculated by Aliev-Watson[13] and Sumberg-Parker[7] are given in Tables (7-4) and (7-6) respectively. To specialize to the XYX-type molecule, we let $m_2 = m_3 = m$, $M_1 = M$, $a = b$, $\theta = 0$. The detailed expressions for $b_s^{\alpha\beta} = (a_s^{\alpha\beta}/\lambda_s^{3/4})$, $B_s^{\alpha\beta} = (a_s^{\alpha\beta}/\lambda_s)$, $(A_{ss'}^{\alpha\beta})'$ and $\zeta_{ss'}$ are obtained from Section 4.4 in a straightforward manner, and the expressions for the ten sextic centrifugal distortion coefficients for an XYX-type molecule can then be written out and are given in Table (9-1).

Table (9-1). The Fourth-order Centrifugal Distortion Coefficients for an XYX-type Molecule

$$I_x^6\Phi_1 = \frac{1}{4}N[(b_1^{xx})^3k_{111} + (b_2^{xx})^3k_{222} + (b_1^{xx})^2(b_2^{xx})k_{112}$$
$$+ (b_1^{xx})(b_2^{xx})^2k_{122}] + \frac{3}{8}(B_1^{xx}\sin\gamma + B_2^{xx}\cos\gamma)^2$$

$$I_y^2\Phi_2 = \frac{1}{4}N[(b_1^{yy})^3k_{111} + (b_2^{yy})^3k_{222} + (b_1^{yy})^2(b_2^{yy})k_{112}$$
$$+ (b_1^{yy})(b_2^{yy})^2k_{122}] + \frac{3}{8}(B_1^{yy}\cos\gamma - B_2^{yy}\sin\gamma)^2$$

$$I_z^6\Phi_3 = \frac{1}{4}N[(b_1^{zz})^3k_{111} + (b_2^{zz})^3k_{222} + (b_1^{zz})^2(b_2^{zz})k_{112}$$
$$+ (b_1^{zz})(b_2^{zz})^2k_{122}] + \frac{1}{2}[B_1^{zz}\zeta_{23} + B_2^{zz}\zeta_{31}]^2 - \frac{1}{8}[(B_1^{zz})^2 + (B_2^{zz})^2]$$

$$I_x^2I_y^4\Phi_4 = \frac{1}{8}N\{3(b_1^{xx})(b_1^{yy})^2k_{111} + 3(b_2^{xx})(b_2^{yy})^2k_{222} + 4(b_1^{yy})(b_3^{xy})^2k_{133}$$
$$+ 4(b_2^{yy})(b_3^{xy})^2k_{233} + [2(b_1^{xx})(b_1^{yy})(b_2^{yy}) + (a_2^{xx})(a_1^{yy})^2]k_{112}$$
$$+ [2(b_1^{yy})(a_2^{xx})(a_2^{yy}) + (a_1^{xx})(a_2^{yy})^2]k_{122}\}$$
$$+ \frac{3}{16}(B_1^{yy}\sin\gamma + B_2^{yy}\cos\gamma)^2 + \frac{3}{4}(I_y/I_z)(B_3^{xy})^2$$
$$+ \frac{3}{8}[B_1^{xx}B_1^{yy}\cos^2\gamma + B_2^{xx}B_2^{yy}\sin^2\gamma - \sin\gamma\cos\gamma(B_1^{xx}B_2^{yy}$$
$$+ B_2^{xx}B_1^{yy})] - \frac{3}{2}(I_y^2/I_z)^{1/2}B_3^{xy}\sin\gamma\cos\gamma(\frac{1}{\lambda_1} - \frac{1}{\lambda_2})$$
$$+ \frac{1}{12}I^{zz}B_3^{xy}[(\lambda_1 + \lambda_3)\zeta_{13}B_1^{yy}/(\lambda_1 - \lambda_3)$$
$$+ (\lambda_2 + \lambda_3)\zeta_{23}B_2^{yy}/(\lambda_2 - \lambda_3)]$$
$$- \frac{3}{2}B_3^{xy}(I_xI_y/I_z)^{1/2}(\cos^2\gamma/\lambda_1 + \sin^2\gamma/\lambda_2)$$

$$I_y^2I_x^4\Phi_5 = \frac{1}{8}N\{3(b_1^{yy})(b_1^{xx})^2k_{111} + 3b_2^{yy}(b_2^{xx})^2k_{222} + 4(b_1^{xx})(b_3^{xy})^2k_{133}$$
$$+ 4(b_2^{xx})(b_3^{xy})^2k_{233} + [2(b_1^{yy})(b_1^{xx})(b_2^{xx}) + (b_2^{yy})(b_1^{xx})^2]k_{112}$$

Table (9-1) (continued)

$$+ [2(b_1^{xx})(b_2^{yy})(b_2^{xx}) + (b_1^{yy})(b_2^{xx})^2]k_{122}\}$$

$$+ \frac{3}{16}(B_1^{xx}\cos\gamma - B_2^{xx}\sin\gamma)^2 + \frac{3}{4}(I_x/I_z)(B_3^{xy})^2$$

$$+ \frac{3}{8}[(B_1^{xx})(B_1^{yy})\sin^2\gamma + B_2^{xx}B_2^{yy}\cos^2\gamma + \sin\gamma\cos\gamma(B_1^{yy}B_2^{xx}$$

$$+ B_2^{yy}B_1^{xx})] - \frac{3}{2}(I_x^2/I_z)^{1/2}B_3^{xy}\sin\gamma\cos\gamma(1/\lambda_1 - 1/\lambda_2)$$

$$- \frac{3}{2}B_3^{xy}(I_xI_y/I_z)^{1/2}(\sin^2\gamma/\lambda_1 + \cos^2\gamma/\lambda_2)$$

$$- \frac{1}{12}I^{zz}B_3^{xy}[(\lambda_1 + \lambda_3)\zeta_{13}B_1^{xx}/(\lambda_1 - \lambda_3)$$

$$+ (\lambda_2 + \lambda_3)\zeta_{23}B_2^{xx}/(\lambda_2 - \lambda_3)]$$

$$I_y^2I_z^4\phi_6 = \frac{1}{8}N\{3(b_1^{yy})(b_1^{zz})^2k_{111} + 3(b_2^{yy})(b_2^{zz})^2k_{222}$$

$$+ [2b_1^{yy}b_1^{zz}a_2^{zz} + b_2^{yy}(b_1^{zz})^2]k_{112} + [2b_2^{yy}b_1^{zz}b_2^{zz}$$

$$+ b_1^{yy}(b_2^{zz})^2]k_{122}\} + \frac{3}{8}(B_1^{yy}B_1^{zz} + B_2^{yy}B_2^{zz}) - \frac{1}{2}[B_1^{yy}B_1^{zz}\zeta_{13}^2$$

$$+ B_2^{yy}B_2^{zz}\zeta_{23}^2 + \zeta_{23}\zeta_{13}(B_1^{yy}B_2^{zz} + B_2^{yy}B_1^{zz})]$$

$$+ \frac{3}{16}(B_1^{zz}\cos\gamma - B_2^{zz}\sin\gamma)^2 - \frac{1}{6}B_3^{xy}[(\lambda_3 - 2\lambda_1)\zeta_{13}B_1^{zz}/(\lambda_1 - \lambda_3)$$

$$+ (\lambda_3 - 2\lambda_2)\zeta_{23}B_2^{zz}/(\lambda_2 - \lambda_3)]$$

$$I_y^4I_z^2\phi_7 = \frac{1}{8}N\{3(b_1^{zz})(b_1^{yy})^2k_{111} + 3(b_2^{zz})(b_2^{yy})^2k_{222}$$

$$+ [2b_1^{yy}b_2^{yy}b_1^{zz} + (b_2^{zz})(b_1^{yy})^2]k_{112} + [2b_1^{yy}b_2^{yy}b_2^{zz}$$

$$+ b_1^{zz}(b_2^{yy})^2]k_{122}\} - \frac{1}{4}(B_3^{xy})^2 + \frac{3}{16}[(B_1^{yy})^2 + (B_2^{yy})^2]$$

$$- \frac{1}{4}[(B_1^{yy})^2\zeta_{13}^2 + (B_2^{yy})^2\zeta_{23}^2 + 2B_1^{yy}B_2^{yy}\zeta_{23}\zeta_{13}]$$

Table (9-1) (continued)

$$+ \frac{3}{8}[B_1^{yy}B_1^{zz}\cos^2\gamma + B_2^{yy}B_2^{zz}\sin^2\gamma - \sin\gamma\cos\gamma(B_1^{yy}B_2^{zz} + B_2^{yy}B_1^{zz})]$$

$$- \frac{1}{6}B_3^{xy}[(\lambda_3 - 2\lambda_1)B_1^{yy}\zeta_{13}/(\lambda_1 - \lambda_3) + (\lambda_3 - 2\lambda_2)B_2^{yy}\zeta_{23}/(\lambda_2 - \lambda_3)]$$

$$I_x^4I_z^2\Phi_8 = \frac{1}{8}N\{3b_1^{zz}(b_1^{xx})^2k_{111} + 3b_2^{zz}(b_2^{xx})^2k_{222} + [2b_1^{xx}b_2^{xx}b_1^{zz}$$

$$+ b_2^{zz}(b_1^{xx})^2]k_{112} + [2b_1^{xx}b_2^{xx}b_2^{zz} + b_1^{zz}(b_2^{xx})^2]k_{122}\}$$

$$- \frac{1}{4}(B_3^{xy})^2 + \frac{3}{16}[(B_1^{xx})^2 + (B_2^{xx})^2] - \frac{1}{4}[(B_1^{xx})^2\zeta_{13}^2 + (B_2^{xx})^2\zeta_{23}^2$$

$$+ 2B_1^{xx}B_2^{xx}\zeta_{23}\zeta_{13}] + \frac{3}{8}[B_1^{xx}B_1^{zz}\sin^2\gamma + B_2^{xx}B_2^{zz}\cos^2\gamma$$

$$+ \sin\gamma\cos\gamma(B_1^{xx}B_2^{zz} + B_2^{xx}B_1^{zz})]$$

$$+ \frac{1}{6}B_3^{xy}[(\lambda_3 - 2\lambda_1)\zeta_{13}B_1^{x}/(\lambda_1 - \lambda_3) + (\lambda_3 - 2\lambda_2)\zeta_{23}B_2^{xx}/(\lambda_2 - \lambda_3)]$$

$$I_x^2I_z^4\Phi_9 = \frac{1}{8}N\{3b_1^{xx}(b_1^{zz})^2k_{111} + 3b_2^{xx}(b_2^{zz})^2k_{222} + [2b_1^{xx}b_1^{zz}b_2^{zz}$$

$$+ b_2^{xx}(b_1^{zz})^2]k_{112} + [2b_2^{xx}b_1^{zz}b_2^{zz} + b_1^{xx}(b_2^{zz})^2]k_{122}\}$$

$$+ \frac{3}{8}(B_1^{xx}B_1^{zz} + B_2^{xx}B_2^{zz}) - \frac{1}{2}[B_1^{xx}B_1^{zz}\zeta_{13}^2 + B_2^{xx}B_2^{zz}\zeta_{23}^2$$

$$+ \zeta_{23}\zeta_{13}(B_1^{xx}B_2^{zz} + B_2^{xx}B_1^{zz})] + \frac{3}{16}(B_1\sin\gamma + B_2\cos\gamma)^2$$

$$+ \frac{1}{6}B_3^{xy}[(\lambda_3 - 2\lambda_1)\zeta_{13}B_1^{zz}/(\lambda_1 - \lambda_3)$$

$$+ (\lambda_3 - 2\lambda_2)\zeta_{23}B_2^{zz}/(\lambda_2 - \lambda_3)]$$

$$I_x^2I_y^2I_z^2\Phi_{10} = \frac{1}{8}N[6b_1^{xx}b_1^{yy}b_1^{zz}k_{111} + 6b_2^{xx}b_2^{yy}b_2^{zz}k_{222} + 2(b_1^{xx}b_1^{yy}b_2^{zz}$$

$$+ b_1^{xx}b_1^{zz}b_2^{yy} + b_1^{zz}b_1^{yy}b_2^{xx})k_{112} + 2(b_1^{xx}b_2^{yy}b_2^{zz} + b_1^{yy}b_2^{zz}b_2^{xx}$$

$$+ b_1^{zz}b_2^{yy}b_2^{xx})k_{122} + 4b_1^{zz}(b_3^{xy})^2k_{133} + 4b_2^{zz}(b_3^{xy})^2k_{233}]$$

Table (9-1) (continued)

$$+ \frac{3}{8}(B_1^{xx}B_1^{yy} + B_2^{xx}B_2^{yy}) + \frac{1}{4}(B_3^{xy})^2 - \frac{1}{2}[B_1^{xx}B_1^{yy}\zeta_{13}^2$$

$$+ B_2^{xx}B_2^{yy}\zeta_{23}^2 + (B_1^{xx}B_2^{yy} + B_2^{xx}B_1^{yy})\zeta_{23}\zeta_{13}]$$

$$+ \frac{3}{8}[B_1^{zz}B_1^{xx}\cos^2\gamma + B_2^{xx}B_2^{zz}\sin^2\gamma - \sin\gamma\cos\gamma(B_1^{zz}B_2^{zz}$$

$$+ B_1^{zz}B_2^{xx})] + \frac{3}{8}[B_1^{zz}B_1^{xx}\cos^2\gamma + B_2^{xx}B_2^{zz}\sin^2\gamma$$

$$- \sin\gamma\cos\gamma(B_1^{zz}B_2^{zz} + B_1^{zz}B_2^{xx})] + \frac{3}{8}[B_1^{zz}B_1^{yy}\sin^2\gamma$$

$$+ B_2^{zz}B_2^{yy}\cos^2\gamma + \sin\gamma\cos\gamma(B_1^{yy}B_2^{zz} + B_2^{yy}B_1^{zz})]$$

$$- \frac{1}{4}(I^{xx}B_1^{xx} + I^{yy}B_1^{yy} + I^{zz}B_1^{zz})^2 - \frac{1}{4}(I^{xx}B_2^{xx} + I^{yy}B_2^{yy}$$

$$+ I^{zz}B_2^{zz})^2 - \frac{3}{2}B_3^{xy}(I_z)^{-1/2}\{[(I_xI_y)^{1/2} + I_z\sin\gamma\cos\gamma]/\lambda_1$$

$$+ [(I_xI_y)^{1/2} - I_z\sin\gamma\cos\gamma]/\lambda_2\} - \frac{1}{2}B_3^{xy}\zeta_{13}(B_1^{xx}$$

$$- B_1^{yy})\lambda_3/(\lambda_3 - \lambda_1) - \frac{1}{2}B_3^{xy}\zeta_{23}(B_2^{xx} - B_2^{yy})\lambda_3/(\lambda_3 - \lambda_2)$$

$$- \frac{1}{4}I^{zz}B_3^{xy}[(\lambda_1 - 3\lambda_3)B_1^{zz}\zeta_{13}/(\lambda_1 - \lambda_3)$$

$$+ (\lambda_2 - 3\lambda_3)\zeta_{23}B_2^{zz}/(\lambda_2 - \lambda_3)]$$

9.2 Fundamental Molecular Constants of Ozone

The calculation of the theoretical centrifugal distortion constants requires the following input data: the equilibrium geometry of the molecule, the harmonic force field (which determines the normal frequencies), and in the case of the sextic constants, the cubic anharmonic portion of the molecular force field.

At equilibrium, ozone $^{16}O_3$ is known to have the geometry of an isosceles triangle. The equilibrium apex angle $2\alpha_e = 116°47(2)'$ and the bond lengths of the equal-length sides of the isosceles triangle, $r_e = 1.2717(2)$A, are well established through microwave spectroscopy[43,44], with the numbers in parenthesis representing the quoted uncertainties in units of the last decimal place given. The above values allow determination of the equilibrium moments of inertia for $^{16}O_3$ as

$$I_x = \frac{2}{3}mr_e^2\cos^2\alpha_e = 7.868(10) \times 10^{-40} \text{ g cm}^2, \tag{9-1}$$

$$I_y = 2mr_e^2\sin^2\alpha_e = 6.233(4) \times 10^{-39} \text{ g cm}^2, \tag{9-2}$$

$$I_z = I_x + I_y = 7.020(4) \times 10^{-39} \text{ g cm}^2. \tag{9-3}$$

For $^{18}O_3$, the above values scale by a factor of $(^{18}m/^{16}m) = 1.12531$.

The most reliable harmonic frequencies, harmonic force field, and cubic potential constants available for $^{16}O_3$ and $^{18}O_3$ at the present time are those determined by Barbe, Secroun, and Jouve,[45] obtained through an analysis of thirty-three band center positions, and these values were used for the present work. For the harmonic frequencies of $^{16}O_3$, Barbe et al. give

$$\omega_1 = 1134.9(2)\ \mathrm{cm}^{-1}, \tag{9-4}$$

$$\omega_2 = 716.0(2)\ \mathrm{cm}^{-1}, \tag{9-5}$$

$$\omega_3 = 1089.2(2)\ \mathrm{cm}^{-1}. \tag{9-6}$$

These are related to the corresponding λ_s by

$$\omega_s = \lambda_s^{1/2}/2\pi c, \quad s = 1,2,3. \tag{9-7}$$

The fourth parameter needed for the complete specification of the harmonic field was taken to be ζ_{31} as determined by Barbe et al,[46] viz.,

$$\zeta_{31} = 0.604(1). \tag{9-8}$$

This value of ζ_{31} is more precise than, and consistent with previous determinations by Tanaka and Morino[44] and also by Clough and Kneizys[47] who found

$$\zeta_{31} = 0.60(1). \tag{9-9}$$

Since

$$\zeta_{23}^2 + \zeta_{31}^2 = 1, \tag{9-10}$$

we obtain

$$\zeta_{23} = -\zeta_{32} = -0.797(1), \tag{9-11}$$

$$\zeta_{31} = -\zeta_{13} = +0.604(1). \tag{9-12}$$

With these values, use of Eqs. (4-144)-(4-148) now allows calculation of the angle γ associated with the normal coordinate transformation and one obtains

$$\sin\gamma = 0.836(2), \tag{9-13}$$

$$\cos\gamma = 0.549(2), \tag{9-14}$$

$$\gamma = 56°43(13)'. \tag{9-15}$$

The angle γ as well as the Coriolis constants have the same numerical values for $^{16}O_3$ and $^{18}O_3$ under the assumption of negligible nuclear size effects due to isotopic substitution.[48] The signs of the Coriolis coupling constants ζ_{23} and ζ_{31} as given by (9-9) and (9-10) are consistent with the arbitrary choice of placing γ in the first quadrant. Different choices of quadrant for γ correspond to other mutually consistent choices of phase for the two totally symmetric modes ν_1 and ν_2.

For the cubic potential constants, the set given by Barbe, et al.[45] was adopted. However, care must be exercised because the signs of the cubic potential constants depend, in general, on the choices of phase for the normal coordinates. In order to obtain signs consistent with those of our γ, ζ_{23}, and ζ_{31}, the cubic potential constants were recalculated from the rotation-vibration interaction constants α_s^α measured by Tanaka and Morino[44], and those of Barbe et al.[45] The theoretical expressions for the α_s^α are well-established and are reproduced in the paper by Tanaka and Morino[44]. As a sample calculation, we have:

$$\alpha_1^x = \frac{\hbar^{3/2}}{2I_x^2}\left\{\frac{3a_1^{xx}}{\lambda_1^{3/4}}k_{111} + \frac{a_2^{xx}}{\lambda_2^{3/4}}k_{112}\right\} + \frac{3\hbar^2\sin^2\gamma}{4\pi c\, I_x^2\lambda_1^{1/2}} \tag{9-16}$$

$$\alpha_1^y = \frac{\hbar^{3/2}}{2I_y^2}\left\{\frac{3a_1^{yy}}{\lambda_1^{3/4}}k_{111} + \frac{a_2^{yy}}{\lambda_2^{3/4}}k_{112}\right\} + \frac{3\hbar^2\cos^2\gamma}{4\pi c I_y^2\lambda_1^{1/2}} \tag{9-17}$$

$$\alpha_1^z = \frac{\hbar^{3/2}}{2I_z^2}\left\{\frac{3a_1^{zz}}{\lambda_1^{3/4}}k_{111} + \frac{a_2^{zz}}{\lambda_2^{3/4}}k_{112}\right\} + \frac{3\hbar^2}{4\pi c I_z^2 \lambda_1^{1/2}} + \frac{\hbar^2}{\pi c I_z^2 \lambda_1^{1/2}}\zeta_{13}^2\Gamma_{13} \tag{9-18}$$

with

$$\Gamma_{13} = \lambda_3/(\lambda_1 - \lambda_3) = 11.66977 \tag{9-19}$$

$$\frac{\hbar}{2\pi c} = 5.5987 \times 10^{-39} \text{ g - cm} \tag{9-20}$$

$$a_1^{xx} = 2I_x^{½} \sin\gamma = 4.690 \times 10^{-20} \text{ g}^{½} \text{ - cm} \tag{9-21}$$

$$a_1^{yy} = 2I_y^{½} \cos\gamma = 8.669 \times 10^{-20} \text{ g}^{½} \text{ - cm} \tag{9-22}$$

$$a_1^{zz} = -2I_z^{½}\zeta_{23} = 13.355 \times 10^{-20} \text{ g}^{½} \text{ - cm} \tag{9-23}$$

$$a_2^{xx} = 2I_x^{½} \cos\gamma = 3.080 \times 10^{-20} \text{ g}^{½} \text{ - cm} \tag{9-24}$$

$$a_2^{yy} = -2I_y^{½}\sin\gamma = -13.200 \times 10^{-20} \text{ g}^{½} \text{ - cm} \tag{9-25}$$

$$a_2^{zz} = 2I_z^{½}\zeta_{13} = -10.121 \times 10^{-20} \text{ g}^{½} \text{ - cm} \tag{9-26}$$

and

$$\lambda_1^{½} = 2.1378 \times 10^{14} \text{ radians/sec} \tag{9-27}$$

$$\lambda_2^{½} = 1.3487 \times 10^{14} \text{ radians/sec} \tag{9-28}$$

$$\lambda_3^{½} = 2.0517 \times 10^{14} \text{ radians/sec} \tag{9-29}$$

Thus we can write the following relations for α_1^x, α_1^y, and α_1^z:

$$\alpha_1^x = (1.2451\times 10^{-3})k_{111} + (0.5439 \times 10^{-3})k_{112} + 4.67705 \times 10^{-2} \tag{9-30}$$

$$\alpha_1^y = (3.6673 \times 10^{-5})k_{111} - (3.7146 \times 10^{-5})k_{112} + 3.21395 \times 10^{-4} \tag{9-31}$$

$$\alpha_1^z = (4.4539 \times 10^{-5})k_{111} - (2.2453 \times 10^{-5})k_{112} + 5.61252 \times 10^{-3} \tag{9-32}$$

Using Tanaka and Morino[44] data, we have

$$\alpha_1^x = -3.037 \times 10^{-3} \quad cm^{-1} \tag{9-33}$$

$$\alpha_1^y = 2.540 \times 10^{-3} \quad cm^{-1} \tag{9-34}$$

$$\alpha_1^z = 2.317 \times 10^{-3} \quad cm^{-1} \tag{9-35}$$

while Barbe et al. data determined

$$\alpha_1^x = -2.981 \times 10^{-3} \quad cm^{-1} \tag{9-36}$$

$$\alpha_1^y = 2.554 \times 10^{-3} \quad cm^{-1} \tag{9-37}$$

$$\alpha_1^z = 2.319 \times 10^{-3} \quad cm^{-1} \tag{9-38}$$

Thus these values are reasonably consistent. Using the newer data by Barbe et al.[45], one obtains

$$(1.2451)k_{111} + (0.5439)k_{112} = -43.79 \tag{9-39}$$

$$(3.6673)k_{111} + (-3.7146)k_{112} = -287.5 \tag{9-40}$$

$$(4.4539)k_{111} + (-2.2453)k_{112} = -285.3 \tag{9-41}$$

Solving for k_{111} and k_{112} in the three possible ways gives

$$k_{111} = -48.2,\ -48.6,\ -49.8 \quad cm^{-1}, \tag{9-42}$$

$$k_{112} = +29.8,\ +30.7,\ +28.2 \quad cm^{-1}. \tag{9-43}$$

The remaining cubic potential constants can be determined in a similar manner. Using the average values of these constants and attaching the appropriate uncertainties to these quantities, we obtain

$$k_{111} = -48.1(7) \ \text{cm}^{-1} \tag{9-44}$$

$$k_{222} = +19.2(6) \ \text{cm}^{-1} \tag{9-45}$$

$$k_{112} = +29.7(10) \ \text{cm}^{-1} \tag{9-46}$$

$$k_{122} = -25.5(30) \ \text{cm}^{-1} \tag{9-47}$$

$$k_{133} = -225.8(30) \ \text{cm}^{-1} \tag{9-48}$$

$$k_{233} = +59.3(10) \ \text{cm}^{-1} \tag{9-49}$$

This complete set of cubic potential constants is the same as that determined by Barbe et al[45], except that positive sign is obtained for k_{222}, k_{112}, and k_{233}.

For our calculations, the uncertainties limiting the precision of the final results are principally determined by those of $\sin\gamma$ and $\cos\gamma$ above, and by those of the cubic potential constants. When the cubic potential constants as well as the harmonic frequencies of $^{16}O_3$ are scaled by factors of $(^{16}m/^{18}m)^{3/4}$ and $(^{16}m/^{18}m)$, respectively, they are in satisfactory agreement with the corresponding experimental values for $^{18}O_3$ as determined by Barbe et al.[45] A recent study by Hennig and Strey[49] also confirms the anharmonic force field of Barbe et al.[45]

9.3 Calculated Centrifugal Distortion Constants

One is now ready to calculate the sextic centrifugal distortion coefficients Φ_i. The coefficients Φ_i will now be separated into three parts: a harmonic part, an anharmonic part, and a Coriolis part. The expressions for the Φ_i, as calculated by Aliev-Watson and Sumberg-Parker for XYX-type molecules, differ only in part of the Coriolis portion. The calculated values for ozone of the harmonic, anharmonic, Coriolis, and total Φ_i of Aliev-Watson and Sumberg-Parker are given in Table (9-2). The Coriolis entries list only the part of the Coriolis contribution which differs in the two formulations. The matching parts have been included in the harmonic contributions.

Numerically, the distortion constants range over more than four orders of magnitude, with the harmonic and anharmonic contributions of comparable magnitudes. Generally, the harmonic contributions are better determined than the anharmonic contributions. The quoted uncertainties were arrived at by elementary standard methods for propagating errors on the basis of the uncertainties specified for the input data.

Table (9-3) lists the values calculated for the six non-vanishing second-order centrifugal distortion constants τ_i. Since the smaller τ_i are of the order of $10^{-6}cm^{-1}$ and the largest Φ_i is of the order of $10^{-8}cm^{-1}$, the numerical separation by order of approximation of the perturbation calculation seems adequate.

9.4 Reduced Hamiltonian

In order to effect a comparison of the calculated distortion constants with the measured ground state constants of $^{16}O_3$ recently determined by Maki[50] from the $\nu_1 + \nu_3$ band and by Barbe et al.[45] from the ν_3 band, it is necessary to reconcile the

Table (9-2). Calculated Sumberg-Parker (SP) and Aliev -Watson (AW) Sextic Distortion Coefficients of $^{16}O_3$ in cm^{-1}

Coeff.	Anharmonic Contribution	Harmonic Contribution	SP Coriolis	AW Coriolis	SP Total Coefficient	AW Total Coefficient
Φ_1	-0.07(8)	+3.50(8)	0	0	+3.43(15)	+3.43(15) $\times 10^{-8}$
Φ_2	-1.67(11)	+2.24(3)	0	0	+0.57(15)	+0.57(15) $\times 10^{-12}$
Φ_3	-7.13(43)	+6.51(10)	0	0	-0.62(54)	-0.62(54) $\times 10^{-13}$
Φ_4	-2.74(25)	-0.02(1)	+2.56(4)	0	-0.21(29)	-2.76(25) $\times 10^{-11}$
Φ_5	-7.99(573)	-0.10(38)	-4.41(287)	0	-12.50(898)	-8.08(611) $\times 10^{-10}$
Φ_6	-1.37(9)	+1.35(3)	+0.354(4)	-0.0615(8)	+0.33(12)	-0.08(12) $\times 10^{-12}$
Φ_7	-1.82(12)	+1.10(4)	+0.278(4)	-0.136(2)	+0.45(16)	+0.04(16) $\times 10^{-12}$
Φ_8	-2.61(27)	-3.81(27)	-6.75(10)	-2.27(3)	-13.16(65)	-8.68(58) $\times 10^{-10}$
Φ_9	+0.92(87)	+1.34(47)	-22.24(28)	+3.86(6)	-20.98(163)	+6.12(141) $\times 10^{-12}$
Φ_{10}	-2.63(30)	-2.80(28)	+1.61(13)	-0.45(2)	-3.82(71)	-5.88(60) $\times 10^{-11}$

Table (9-3). Calculated Second-Order Distortion Coefficients τ_i of $^{16}O_3$ in cm^{-1}

$\tau_1 = -8.139(48) \times 10^{-4}$	$\tau_4 = -1.605(7) \times 10^{-6}$
$\tau_2 = -2.313(13) \times 10^{-6}$	$\tau_5 = +3.499(75) \times 10^{-6}$
$\tau_3 = -1.221(4) \times 10^{-6}$	$\tau_6^* = +0.23(13) \times 10^{-6}$

To obtain the corresponding values for $^{18}O_3$, all entries should be multiplied by $(^{16}m/^{18}m)^2 = 0.78969$.

Hamiltonians used by these authors with the one used by us. As discussed in Chapter 6, one must take into account Watson's theory which requires the Hamiltonian used to fit the data to be in a reduced form such that no redundant coefficients, or redundant combinations of coefficients, occur. The Hamiltonians used by Maki and by Barbe et al. are identical in structure and very similar in notation. Inspection of the Hamiltonian shows that the symmetric-top or H-form[25,51] is used, and that the reduction is carried out by choosing one of the six quartic coefficients and three of the ten sextic coefficients to be equal to zero. Since the molecule is taken to be in the zx plane, one cyclic permutation is required to bring the molecule into the xy plane. Carrying out the permutation and introducing the notation of Yallabandi and Parker[25] for the coefficients, it is determined that

$$H_2 = \tilde{A}P_x^2 + \tilde{B}P_y^2 + \tilde{C}P_z^2, \tag{9-50}$$

$$H_4 = \tilde{D}_1^*P^4 + \tilde{D}_2^*P^2P_x^2 + \tilde{D}_3^*P_x^4 + \tilde{D}_4^*P^2(P_y^2 - P_z^2)$$
$$+ \tilde{D}_5^*[P_x^2(P_y^2 - P_z^2) + (P_y^2 - P_z^2)P_x^2], \tag{9-51}$$

and

$$\mathcal{H}_6 = \tilde{H}_1 P^6 + \tilde{H}_2 P^4 P_x^2 + \tilde{H}_3 P^2 P_x^4 + \tilde{H}_4 P_x^6 + \tilde{H}_5 P^4 (P_y^2 - P_z^2)$$
$$+ \tilde{H}_7 P^2 [P_x^2 (P_y^2 - P_z^2) + (P_y^2 - P_z^2) P_x^2]$$
$$+ \tilde{H}_8 [P_x^4 (P_y^2 - P_z^2) + (P_y^2 - P_z^2) P_x^4]. \qquad (9.52)$$

As we have mentioned in Chapter 6, we use the tilde with the experimentally determined constants of the Hamiltonian, whereas all constants calculated on the basis of theory appear without the tilde. The particular reduction used is specified by

$$\tilde{D}_6^* = \tilde{H}_6 = \tilde{H}_9 = \tilde{H}_{10} = 0. \qquad (9\text{-}53)$$

The Hamiltonian, Eqs. (9-50)-(9-52), must be arranged into the form specified by Eqs. (5-2)-(5-5) in order to develop the relations between the two sets of coefficients. This is done by expanding (9-51) and (9-52), retaining all Hermitian groupings of operators, and comparing coefficients. The listing of angular momentum operator identities given by Kneizys, Freedman and Clough[51] in their Table II is quite helpful in carrying out this calculation expeditiously. We find that

$$\tilde{A} = \tilde{\mathcal{A}} + \hbar^4(-8\tilde{H}_1), \qquad (9\text{-}54)$$

$$\tilde{B} = \tilde{\mathcal{B}} + \hbar^4(-8\tilde{H}_1 - 4\tilde{H}_2 + 4\tilde{H}_5), \qquad (9\text{-}55)$$

$$\tilde{C} = \tilde{\mathcal{C}} + \hbar^4(16\tilde{H}_1 + 4\tilde{H}_2 - 4\tilde{H}_5). \qquad (9\text{-}56)$$

Also:

$$\tilde{T}_1 = \tilde{D}_1^* + \tilde{D}_2^* + \tilde{D}_3^*, \tag{9-57}$$

$$\tilde{T}_2 = \tilde{D}_1^* + \tilde{D}_4^*, \tag{9-58}$$

$$\tilde{T}_3 = \tilde{D}_1^* - \tilde{D}_4^*, \tag{9-59}$$

$$\tilde{T}_4 = \tilde{D}_1^* - 4\not{k}^2\tilde{H}_1, \tag{9-60}$$

$$\tilde{T}_5 = (\tilde{D}_1^* - \tilde{D}_5^*) + \frac{1}{2}(\tilde{D}_2^* - \tilde{D}_4^*) + \not{k}^2(-4\tilde{H}_1 - 2\tilde{H}_2 + 2\tilde{H}_5), \tag{9-61}$$

$$\tilde{T}_6 = (\tilde{D}_1^* + \tilde{D}_5^*) + \frac{1}{2}(\tilde{D}_2^* + \tilde{D}_4^*) + \not{k}^2(+8\tilde{H}_1 + 2\tilde{H}_2 - 2\tilde{H}_5). \tag{9-62}$$

Furthermore,

$$\tilde{\Phi}_1 = \tilde{H}_1 + \tilde{H}_2 + \tilde{H}_3 + \tilde{H}_4, \tag{9-63}$$

$$\tilde{\Phi}_2 = \tilde{H}_1 + \tilde{H}_5, \tag{9-64}$$

$$\tilde{\Phi}_3 = \tilde{H}_1 - \tilde{H}_5, \tag{9-65}$$

$$\tilde{\Phi}_4 = \frac{3}{2}\tilde{H}_1 + \frac{1}{2}\tilde{H}_2 + \tilde{H}_5 + \tilde{H}_7, \tag{9-66}$$

$$\tilde{\Phi}_5 = \frac{3}{2}\tilde{H}_1 + \tilde{H}_2 + \frac{1}{2}\tilde{H}_3 + \frac{1}{2}\tilde{H}_5 + \tilde{H}_7 + \tilde{H}_8, \tag{9-67}$$

$$\tilde{\Phi}_6 = \frac{3}{2}\tilde{H}_1 - \frac{1}{2}\tilde{H}_5, \tag{9-68}$$

$$\tilde{\Phi}_7 = \frac{3}{2}\tilde{H}_1 + \frac{1}{2}\tilde{H}_5, \tag{9-69}$$

$$\tilde{\Phi}_8 = \frac{3}{2}\tilde{H}_1 + \tilde{H}_2 + \frac{1}{2}\tilde{H}_3 - \frac{1}{2}\tilde{H}_5 - \tilde{H}_7 - \tilde{H}_8, \tag{9-70}$$

$$\tilde{\Phi}_9 = \frac{3}{2}\tilde{H}_1 + \frac{1}{2}\tilde{H}_2 - \tilde{H}_5 - \tilde{H}_7, \tag{9-71}$$

$$\tilde{\Phi}_{10} = 3\tilde{H}_1 + \tilde{H}_2. \tag{9-72}$$

The reduction, Eqs. (9-53), is specified alternatively by taking

$$\tilde{T}_2 + \tilde{T}_3 = 2\tilde{T}_4 + 8\not{k}^2\tilde{H}_1 = 2\tilde{T}_4 + 4\not{k}^2(\tilde{\Phi}_2 + \tilde{\Phi}_3), \tag{9-73}$$

$$\tilde{\Phi}_6 + \tilde{\Phi}_7 = \frac{3}{2}(\tilde{\Phi}_2 + \tilde{\Phi}_3), \tag{9-74}$$

$$\tilde{\Phi}_6 - \tilde{\Phi}_7 = -\frac{1}{2}(\tilde{\Phi}_2 - \tilde{\Phi}_3), \tag{9-75}$$

$$\tilde{\Phi}_{10} = \tilde{\Phi}_4 + \tilde{\Phi}_9. \tag{9-76}$$

Inverting Eqs. (9-57)-(9-62) and (9-63)-(9-72), and using Eqs. (9-73)-(9-76) to eliminate $\tilde{T}_4$, $\tilde{\Phi}_6$, $\tilde{\Phi}_7$, and $\tilde{\Phi}_{10}$ gives:

$$\tilde{D}_1^* = \frac{1}{2}(\tilde{T}_2 + \tilde{T}_3), \tag{9-77}$$

$$\tilde{D}_2^* = -(\tilde{T}_2 + \tilde{T}_3) + (\tilde{T}_5 + \tilde{T}_6) - 4\kappa^2\tilde{H}_1, \tag{9-78}$$

$$\tilde{D}_3^* = \tilde{T}_1 + \frac{1}{2}(\tilde{T}_2 + \tilde{T}_3) - (\tilde{T}_5 + \tilde{T}_6) + 4\kappa^2\tilde{H}_1, \tag{9-79}$$

$$\tilde{D}_4^* = \frac{1}{2}(\tilde{T}_2 - \tilde{T}_3), \tag{9-80}$$

$$\tilde{D}_5^* = -\frac{1}{4}(\tilde{T}_2 - \tilde{T}_3) - \frac{1}{2}(\tilde{T}_5 - \tilde{T}_6) - 2\kappa^2(3\tilde{H}_1 + \tilde{H}_2 - \tilde{H}_5), \tag{9-81}$$

$$\tilde{D}_6^* = 0, \tag{9-82}$$

and

$$\tilde{H}_1 = \frac{1}{2}(\tilde{\Phi}_2 + \tilde{\Phi}_3), \tag{9-83}$$

$$\tilde{H}_2 = -\frac{3}{2}(\tilde{\Phi}_2 + \tilde{\Phi}_3) + (\tilde{\Phi}_4 + \tilde{\Phi}_9), \tag{9-84}$$

$$\tilde{H}_3 = \frac{3}{2}(\tilde{\Phi}_2 + \tilde{\Phi}_3) - 2(\tilde{\Phi}_4 + \tilde{\Phi}_y) + (\tilde{\Phi}_5 + \tilde{\Phi}_8), \tag{9-85}$$

$$\tilde{H}_4 = -\frac{1}{2}(\tilde{\Phi}_2 + \tilde{\Phi}_3) + \tilde{\Phi}_1 + (\tilde{\Phi}_4 + \tilde{\Phi}_9) - (\tilde{\Phi}_5 + \tilde{\Phi}_8) \tag{9-86}$$

$$\tilde{H}_5 = \frac{1}{2}(\tilde{\Phi}_2 - \tilde{\Phi}_3), \tag{9-87}$$

$$\tilde{H}_7 = -\frac{1}{2}(\tilde{\Phi}_2 - \tilde{\Phi}_3) + \frac{1}{2}(\tilde{\Phi}_4 - \tilde{\Phi}_9), \tag{9-88}$$

$$\tilde{H}_8 = \frac{1}{4}(\tilde{\Phi}_2 - \tilde{\Phi}_3) - \frac{1}{2}(\tilde{\Phi}_4 - \tilde{\Phi}_9) + \frac{1}{2}(\tilde{\Phi}_5 - \tilde{\Phi}_8), \tag{9-89}$$

$$\tilde{H}_6 = \tilde{H}_9 = \tilde{H}_{10} = 0. \tag{9-90}$$

To relate the experimental to the theoretical constants, the required equations are the following[25]:

$$T_i = \tilde{T}_i + \mathcal{O}(4), \quad i = 1,2,3, \tag{9-91}$$

$$T_4 = \tilde{T}_4 + 2\hbar S_{111}(\tilde{C} - \tilde{B}) + \mathcal{O}(4), \tag{9-92}$$

$$T_5 = \tilde{T}_5 + 2\hbar S_{111}(\tilde{A} - \tilde{C}) + \mathcal{O}(4), \tag{9-93}$$

$$T_6 = \tilde{T}_6 + 2\hbar S_{111}(\tilde{B} - \tilde{A}) + \mathcal{O}(4), \tag{9-94}$$

and

$$\Phi_i = \tilde{\Phi}_i, \quad i = 1,2,3, \tag{9-95}$$

$$\Phi_4 = \tilde{\Phi}_4 + 2\hbar S_{113}(\tilde{B} - \tilde{A}) + 4\hbar S_{111}(\tilde{T}_2 - \tilde{T}_6) - 4\hbar^2 S_{111}^2(\tilde{B} - \tilde{A}), \tag{9-96}$$

$$\Phi_5 = \tilde{\Phi}_5 + 2\hbar S_{311}(\tilde{B} - \tilde{A}) + 4\hbar S_{111}(\tilde{T}_6 - \tilde{T}_1) + 4\hbar^2 S_{111}^2(\tilde{B} - \tilde{A}), \tag{9-97}$$

$$\Phi_6 = \tilde{\Phi}_6 + 2\hbar S_{131}(\tilde{C} - \tilde{B}) + 4\hbar S_{111}(\tilde{T}_3 - \tilde{T}_4) - 4\hbar^2 S_{111}^2(\tilde{C} - \tilde{B}), \tag{9-98}$$

$$\Phi_7 = \tilde{\Phi}_7 + 2\hbar S_{113}(\tilde{C} - \tilde{B}) + 4\hbar S_{111}(\tilde{T}_4 - \tilde{T}_2) + 4\hbar^2 S_{111}^2(\tilde{C} - \tilde{B}), \tag{9-99}$$

$$\Phi_8 = \tilde{\Phi}_8 + 2\hbar S_{311}(\tilde{A} - \tilde{C}) + 4\hbar S_{111}(\tilde{T}_1 - \tilde{T}_5) - 4\hbar^2 S_{111}^2(\tilde{A} - \tilde{C}), \tag{9-100}$$

$$\Phi_9 = \tilde{\Phi}_9 + 2\hbar S_{131}(\tilde{A} - \tilde{C}) + 4\hbar S_{111}(\tilde{T}_5 - \tilde{T}_3) + 4\hbar^2 S_{111}^2(\tilde{A} - \tilde{C}), \tag{9-101}$$

$$\Phi_{10} = \tilde{\Phi}_{10} + 6\hbar[(\tilde{C} - \tilde{B})S_{311} + (\tilde{B} - \tilde{A})S_{131} + (\tilde{A} - \tilde{C})S_{113}]. \tag{9-102}$$

As mentioned in Chapter 6, the coefficients S_{111}, of second order of approximation, and the coefficients S_{113}, S_{131}, and S_{311}, of fourth - order of approximation, are determined by the particular reduction chosen.

9.5 Comparison of the Quartic Distortion Coefficients

We first examine the quartic distortion coefficients $\tilde{D}_i^*$ given by Eqs. (9-77)-(9-82), with the $\tilde{T}_i$ related to the T_i by Eqs. (9-91)-(9-94). The T_i, in turn, are given by

$$T_i = \frac{1}{4}\tau_i + O(4), \quad i = 1,2,3,4,5, \tag{9-103}$$

$$T_6 = \frac{1}{4}(\tau_6 + 2\tau_9) + O(4)$$
$$= \frac{1}{4}\tau_6^* + O(4), \qquad (9\text{-}104)$$

in which the terms of $O(4)$ are not firmly established, other than that they are very complicated. This necessitates approximating the T_i by the corresponding τ_i, thereby incurring an error of $O(4)$. Because of this, the terms of $O(4)$ in Eqs. (9-77)-(9-82) and (9-91)-(9-94) should be dropped as well at this point, with the result that to $O(2)$ we have that

$$\tilde{D}_1^* = \frac{1}{8}(\tau_2 + \tau_3), \qquad (9\text{-}105)$$

$$\tilde{D}_2^* = -\frac{1}{4}(\tau_2 + \tau_3) + \frac{1}{4}(\tau_5 + \tau_6^*) + 2\hbar S_{111}(\tilde{C} - \tilde{B}) \qquad (9\text{-}106)$$

$$\tilde{D}_3^* = \frac{1}{4}\tau_1 + \frac{1}{8}(\tau_2 + \tau_3) - \frac{1}{4}(\tau_5 + \tau_6^*) - 2\hbar S_{111}(\tilde{C} - \tilde{B}), \qquad (9\text{-}107)$$

$$\tilde{D}_4^* = \frac{1}{8}(\tau_2 - \tau_3), \qquad (9\text{-}108)$$

$$\tilde{D}_5^* = -\frac{1}{16}(\tau_2 - \tau_3) - \frac{1}{8}(\tau_5 - \tau_6^*) + \hbar S_{111}(2\tilde{A} - \tilde{B} - \tilde{C}). \qquad (9\text{-}109)$$

In order to evaluate these, the value of S_{111} is needed. From Eqs. (9-91)-(9-94) and again dropping terms of $O(4)$, we obtain

$$\hbar S_{111} = (\tau_4 - 4\tilde{T}_4)/8(\tilde{C} - \tilde{B}) = (\tau_5 - 4\tilde{T}_5)/8(\tilde{A} - \tilde{C})$$
$$= (\tau_6^* - 4\tilde{T}_6)/8(\tilde{B} - \tilde{A}). \qquad (9\text{-}110)$$

Using Eqs. (9-57)-(9-62) and Maki's $\tilde{D}_i^*$ to evaluate the $\tilde{T}_i$, using Maki's rotational constants $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$ in place of $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$, and using the values of the τ_i as given in Table (9-3), we find from Eqs. (9-110) three independently determined values for the dimensionless quantity $\hbar S_{111}$, viz.,

$$\kappa S_{111} = -0.525(19) \times 10^{-6},\ -0.459(4) \times 10^{-6},\ -0.465(6) \times 10^{-6} \tag{9-111}$$

respectively. These values are reasonably consistent, although the error ranges do not overlap completely which can be attributed to the neglect of the terms of $O(4)$. To proceed, we chose to use the average value and the maximum uncertainty, viz.,

$$\kappa S_{111} = -0.483(19) \times 10^{-6}. \tag{9-112}$$

The distortion constants $\tilde{D}_i^*$ can now be evaluated. The calculated values are listed in Table (9-4) along with the two sets of observed values. In order to provide a common basis of comparison for these, the uncertainties shown with both data sets were taken to correspond to twice the reported standard deviations. The ratio of calculated to observed values are also given. These ratios are the "best" ones obtainable in the sense that the uncertainties are used in such a way as to give ratios as close to unity as possible. For two of the five coefficients, $\tilde{D}_i^*$, this ratio is equal to unity which corresponds to an overlap of the error bars of the calculated and observed values. For the remaining three coefficients the agreement is close, but not complete. This can again be attributed to the neglect of terms of $O(4)$, and on the basis of this assumption, the agreement may be considered satisfactory. From Eqs. (9-105)-(9-109) it is seen that S_{111} is not needed to determine $\tilde{D}_1^*$ and $\tilde{D}_4^*$, Numerically, the contribution of the S_{111}-term to the value of $\tilde{D}_3^*$ is negligible, and it is less than 3% for $\tilde{D}_2^*$. The contribution of the S_{111}-term to the value of $\tilde{D}_5^*$ is, however, the dominant one and amounts to almost 90% of the total value of $\tilde{D}_5^*$.

Table (9-4). Observed and Calculated Second-Order Distortion Coefficients of $^{16}O_3$ in cm^{-1}

Coeff.	Notation of Maki[a]	Observed[a]	Observed[b]	Observed[c]	Calculated	Exp.	Calc./Obs. a,b	(best) c
$\tilde{D}_1^*$	$-\Delta_o^J$	-4.54283(178)	-4.5427(12)	-4.569(93)	-4.418(20)	-7	+0.977	+0.992
$\tilde{D}_2^*$	$-\Delta_o^{JK}$	+1.84646(297)	+1.8461(22)	+1.51(22)	+1.865(57)	-6	+1.000	+1.045
$\tilde{D}_3^*$	$-\Delta_o^K$	-2.116475(201)	-2.11661(15)	-1.996(15)	-2.049(13)	-4	+0.974	+1.012
$\tilde{D}_4^*$	$-2\delta_o^J$	-1.395906(446)	-1.39593(21)	-1.393(21)	-1.365(20)	-7	+0.992	+1.000
$\tilde{D}_5^*$	$-\delta_o^K$	-3.23314(284)	-3.2331(15)	-2.91(12)	-3.367(146)	-6	+1.000	+1.063

[a] A.G. Maki, J. Mol. Spectrosc. 57, 416 (1975).

[b] A. Barbe et al., J. Mol. Spectrosc., Reference 46.

[c] Corrected for vibrational contributions. See text.

Uncertainties shown with the observed values are twice the estimated standard deviations.

The third column of observed values of Table (9-4) gives the values of the second-order distortion coefficients corrected for vibration. For this calculation we used the values of $\tilde{D}_i^*$ of the (100) and (001) vibrational states given by Barbe et al.[45], and the $\tilde{D}_i^*$ of (010) obtained by Bellet[52] and his group from microwave data. For the largest coefficient $\tilde{D}_3^*$, the agreement is thereby improved, but in general, the agreement is not substantially better. The vibrationally corrected values of the $\tilde{D}_i^*$ still do not fully represent the equilibrium second-order distortion constants, because there remains a vibration-independent fourth-order difference between these and the vibrationally corrected quartic ground state coefficients[25].

9.6 Comparison of the Sextic Distortion Coefficients

Calculation of the seven non-zero sextic distortion coefficients $\tilde{H}_i$ is based on Eqs. (9-83)-(9-90) with the $\tilde{\Phi}_i$ replaced by the corresponding Φ_i of Table (9-1) according to the scheme described by Eqs. (9-95)-(9-102). In Eqs. (9-95)-(9-102), the coefficient S_{111} is used as given by Eqs. (9-110), and the $\tilde{T}_i$ can be calculated from the experimental results with the aid of Eqs. (9-57)-(9-62). Correlation effects among the $\tilde{T}_i$ are not considered in the present calculation. The coefficients $\tilde{\Phi}_6$, $\tilde{\Phi}_7$, and $\tilde{\Phi}_{10}$ are eliminated from Eqs. (9-95)-(9-102) through the use of applicable constraints, Eqs. (9-73)-(9-76). According to Eq. (9-95), $\tilde{\Phi}_1$, $\tilde{\Phi}_2$, and $\tilde{\Phi}_3$ in Eqs. (9-83)-(9-90) can be replaced by Φ_1, Φ_2, and Φ_3 respectively. The remaining seven Eqs. (9-96)-(9-102) are used to determine the four combinations

$(\tilde{\Phi}_5 \pm \tilde{\Phi}_8)$ and $(\tilde{\Phi}_4 \pm \tilde{\Phi}_9)$ needed in Eqs. (9-83)-(9-90) along with the three coefficients S_{113}, S_{131}, and S_{311}. Carrying out the indicated calculations, we find

$$\hbar S_{113} = +1.45(275) \times 10^{-12}, \tag{9-113}$$

$$\hbar S_{131} = -0.19(200) \times 10^{-12}, \tag{9-114}$$

$$\hbar S_{311} = +2.30(415) \times 10^{-10}, \tag{9-115}$$

$$\tilde{\Phi}_5 + \tilde{\Phi}_8 = -2.15(15) \times 10^{-9} \ \text{cm}^{-1}, \tag{9-116}$$

$$\tilde{\Phi}_5 - \tilde{\Phi}_8 = +3.62(530) \times 10^{-9} \ \text{cm}^{-1}, \tag{9-117}$$

$$\tilde{\Phi}_4 + \tilde{\Phi}_9 = -1.63(345) \times 10^{-11} \ \text{cm}^{-1}, \tag{9-118}$$

$$\tilde{\Phi}_4 - \tilde{\Phi}_9 = +3.36(335) \times 10^{-11} \ \text{cm}^{-1}. \tag{9-119}$$

It is seen that, with the exception of $(\tilde{\Phi}_5 + \tilde{\Phi}_8)$, the above quantities are very poorly determined. This is principally due to the occurrence of near-cancellation of the calculated sextic distortion coefficients in the determination of S_{113} and S_{131} which, in turn, leads to the remaining large uncertainties. As a consequence, we obtain poorly determined values for $\tilde{H}_2$, $\tilde{H}_7$, and $\tilde{H}_8$. Since $(\tilde{\Phi}_5 + \tilde{\Phi}_8)$ constitutes the principal contribution to $\tilde{H}_3$, this coefficient is much better determined, as are $\tilde{H}_1$ to $\tilde{H}_5$ which do not depend on any of the Eqs. (9-113)-(9-119), and $\tilde{H}_4$ for which the $\tilde{\Phi}_1$ and $(\tilde{\Phi}_5 + \tilde{\Phi}_8)$ contributions dominate. The calculated values of the $\tilde{H}_i$ are listed in Table (9-5) along with the experimental values of Maki[50] and Barbe et al.[46] which are in remarkably good agreement. In Fig. (9-1) we compare the calculated values with the experimental values. The

Table (9-5). Observed and Calculated Fourth-order Distortion Coefficients of $^{16}O_3$ in cm^{-1}

Coeff.	Notation of Maki	Observed[a]	Observed[b]	Calculated (Sumberg-Parker)	Calculated (Aliev-Watson)	
$\tilde{H}_1$	H_o^J	+0.362(154)	+0.377(106)	+0.25(10)	+0.25(10)	$\times 10^{-12}$
$\tilde{H}_2$	H_o^{JK}	-0.564(597)	-0.59(42)	-0.98(418)	-0.98(409)	$\times 10^{-11}$
$\tilde{H}_3$	H_o^{KJ}	-0.18704(422)	-0.1839(34)	-0.25(11)	-0.17(8)	$\times 10^{-8}$
$\tilde{H}_4$	H_o^K	+0.39313(594)	+0.3929(44)	+0.37(3)	+0.36(2)	$\times 10^{-7}$
$\tilde{H}_5$	$2h_o^J$	+0.3510(498)	+0.3532(228)	+0.32(1)	+0.32(1)	$\times 10^{-12}$
$\tilde{H}_7$	h_o^{JK}	-0.701(640)	-0.60(40)	-1.05(213)	-1.06(209)	$\times 10^{-11}$
$\tilde{H}_8$	h_o^K	+0.2329(316)	+0.223(24)	+0.14(38)	+0.19(36)	$\times 10^{-8}$

[a] A.G. Maki, J. Mol. Spectrosc., 57, 416(1975). The exponent of $\tilde{H}_4$ is -7 as given above, not -8 as given in Maki's paper. Dr. Maki has confirmed this typographical error.

[b] A. Barbe et al., J. Mol. Spectrosc., Reference 46.

Uncertainties shown with the observed values are twice the estimated standard deviations.

Fig. (9-1). Comparison of the Experimental and Theoretical Values of $\tilde{H}_i$ of Ozone

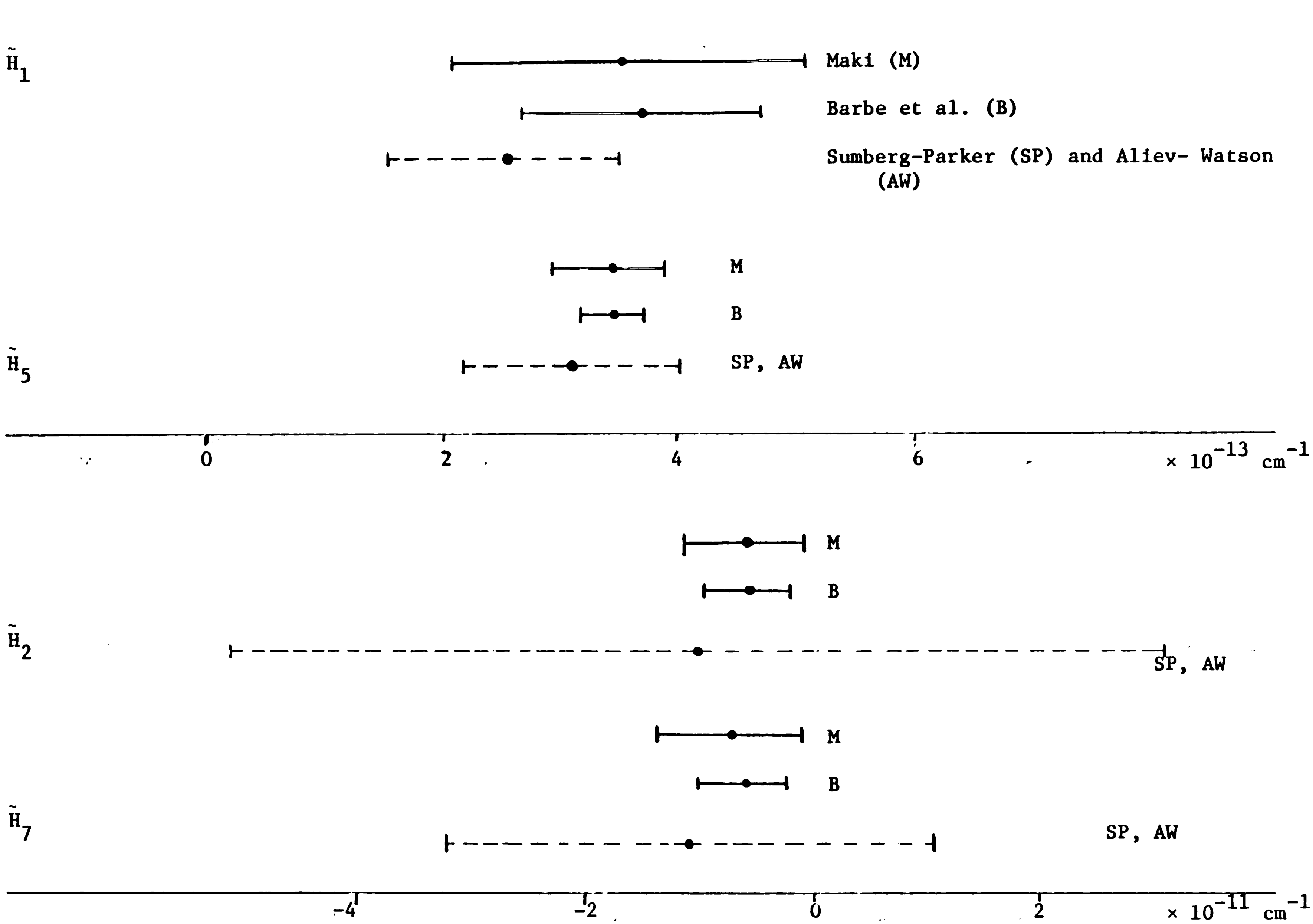
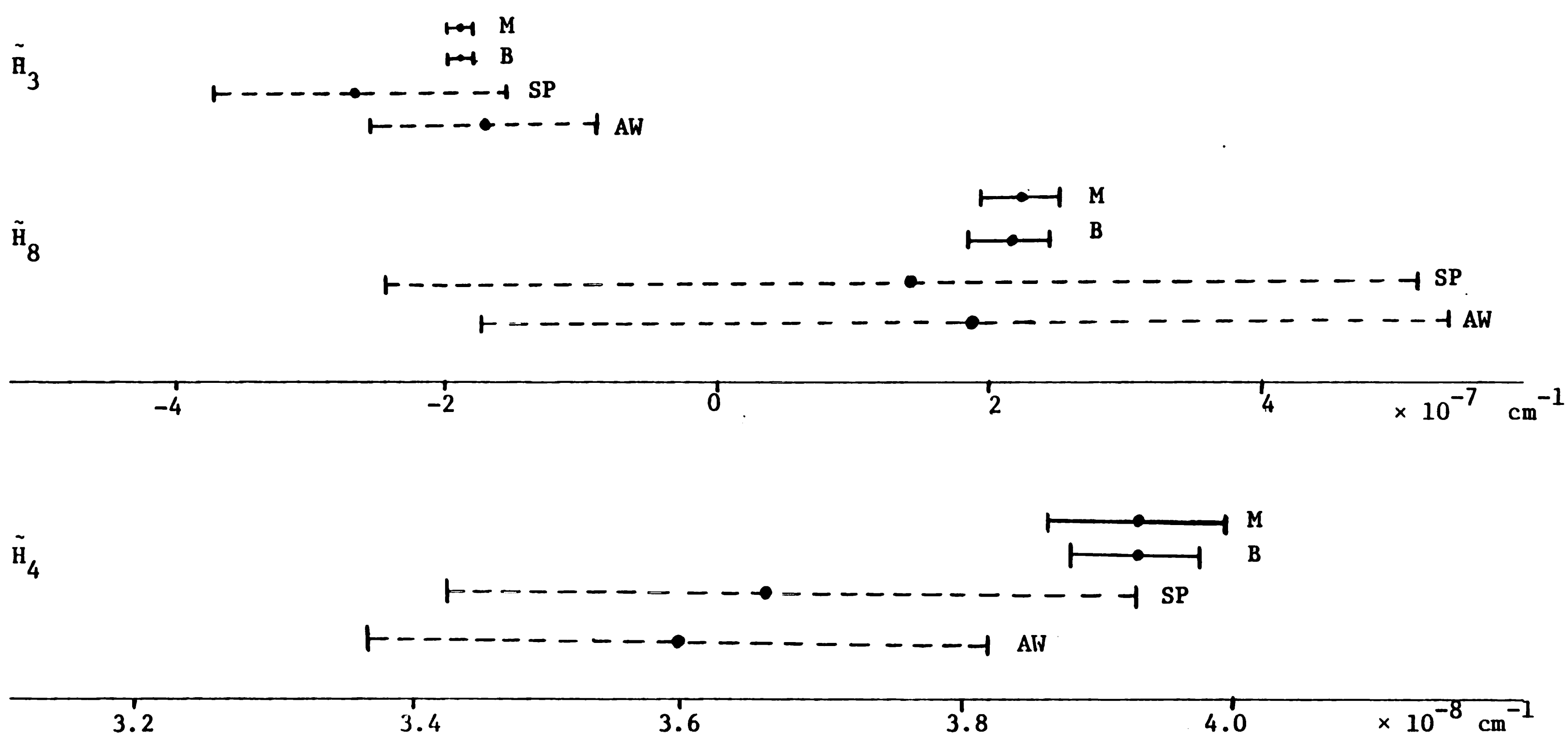


Fig. (9-1) (continued)



agreement between observed and calculated values is quite good, with the experimental values generally much more precise than the calculated ones. The Sumberg-Parker and Aliev-Watson theories generally give comparable results.

Another method of comparing calculated and observed results is more indirect, but has the advantage that it does not require the evaluation of S_{113}, S_{131}, and S_{311}. As a consequence, this method leads to more precise calculated values and hence constitutes a more exacting test of the theory. In this procedure, the constants S_{113}, S_{131}, and S_{311} are first eliminated from the ten Eqs. (9-95)-(9-102), leaving seven linearly independent equations relating the Φ_i to the $\tilde{\Phi}_i$, valid for any reduction of H_6 provided only that the reduction exists. Such a set of seven reduction-invariant relations I_i is

$$I_i:\quad \Phi_i = \tilde{\Phi}_i, \quad i = 1,2,3, \tag{9-120}$$

$$I_4:\quad \sum_{i=4}^{9} (\Phi_i) + \frac{1}{3}\Phi_{10} = \sum_{i=4}^{9} (\tilde{\Phi}_i) + \frac{1}{3}\tilde{\Phi}_{10}, \tag{9-121}$$

$$I_5:\quad 2\Phi_7 + (1 + \tilde{\sigma})\Phi_4 = 2\tilde{\Phi}_7^* + (1 + \tilde{\sigma})\tilde{\Phi}_4^*, \tag{9-122}$$

$$I_6:\quad 2\Phi_8 + (1 - \tilde{\sigma})\Phi_5 = 2\tilde{\Phi}_8^* + (1 - \tilde{\sigma})\tilde{\Phi}_5^*, \tag{9-123}$$

$$I_7:\quad (1 - \tilde{\sigma})\Phi_9 - (1 - \tilde{\sigma})\Phi_6 = (1 + \tilde{\sigma})\tilde{\Phi}_9^* - (1 - \tilde{\sigma})\tilde{\Phi}_6^*, \tag{9-124}$$

where

$$\tilde{A} = 3.553666 \quad \mathrm{cm}^{-1} \tag{9-125}$$

$$\tilde{B} = 0.445283 \quad \mathrm{cm}^{-1} \tag{9-126}$$

$$\tilde{C} = 0.394752 \quad \mathrm{cm}^{-1} \tag{9-127}$$

$$\tilde{\sigma} = (2\tilde{C} - \tilde{A} - \tilde{B})/(\tilde{A} - \tilde{B}) = -1.032513, \tag{9-128}$$

and

$$\tilde{\Phi}_4^* = \tilde{\Phi}_4 + 4\text{ЖS}_{111}(\tilde{T}_2 - \tilde{T}_6) - 4\text{Ж}^2 S_{111}^2(\tilde{B} - \tilde{A}), \tag{9-129}$$

with $\tilde{\Phi}_5^*$ through $\tilde{\Phi}_9^*$ given by similar expressions, easily determined by reference to Eqs. (9-95)-(9-102) and (9-120)-(9-124). The $\tilde{\Phi}_i$ were obtained from the experimental results with the aid of Eqs. (9-63)-(9-72). Considering the left-hand sides of Eqs. (9-120)-(9-124) as the calculated values and the right-hand sides as the observed values, and carrying out the computations just described, one obtains the results summarized in Table (9-6). The precision of the calculated values is much improved over that in Table (9-5). However, since some manipulation of the experimental constants is required, the attendant accumulation of errors leads to a loss in precision of the experimental quantities. In Fig. (9-2), we compare the experimental values of the I_i with the calculated values. The algebraic signs of six invariants are reproduced correctly by the theory. With the exception of I_1, all error bars overlap and the agreement can be considered satisfactory.

Table (9-6). Observed and Calculated Fourth-order Invariants of $^{16}O_3$ in cm^{-1}

Invariant	Observed[a]	Observed[b]	Calculated (Sumberg-Parker)	Calculated (Aliev-Watson)	
I_1	+3.744(64)	+3.745(48)	+3.43(15)	+3.43(15)	$\times 10^{-8}$
I_2	+0.713(204)	+0.730(129)	+0.57(15)	+0.57(15)	$\times 10^{-12}$
I_3	+0.11(204)	+0.24(129)	-0.62(54)	-0.62(54)	$\times 10^{-13}$
I_4	-1.886(64)	-1.855(49)	-2.60(97)	-1.72(68)	$\times 10^{-9}$
I_5	+1.140(838)	+1.158(564)	+0.97(42)	+0.97(41)	$\times 10^{-12}$
I_6	-3.716(121)	-3.656(95)	-5.17(196)	-3.38(137)	$\times 10^{-9}$
I_7	-0.276(882)	-0.283(598)	-0.02(30)	-0.03(29)	$\times 10^{-12}$

[a] A.G. Maki, J. Mol. Spectrosc., 57, 416(1975).

[b] A. Barbe et al., J. Mol. Spectrosc., Reference 46.

Fig. (9-2). Comparison of the Experimental and Theoretical Values of the Invariants I_i for Ozone

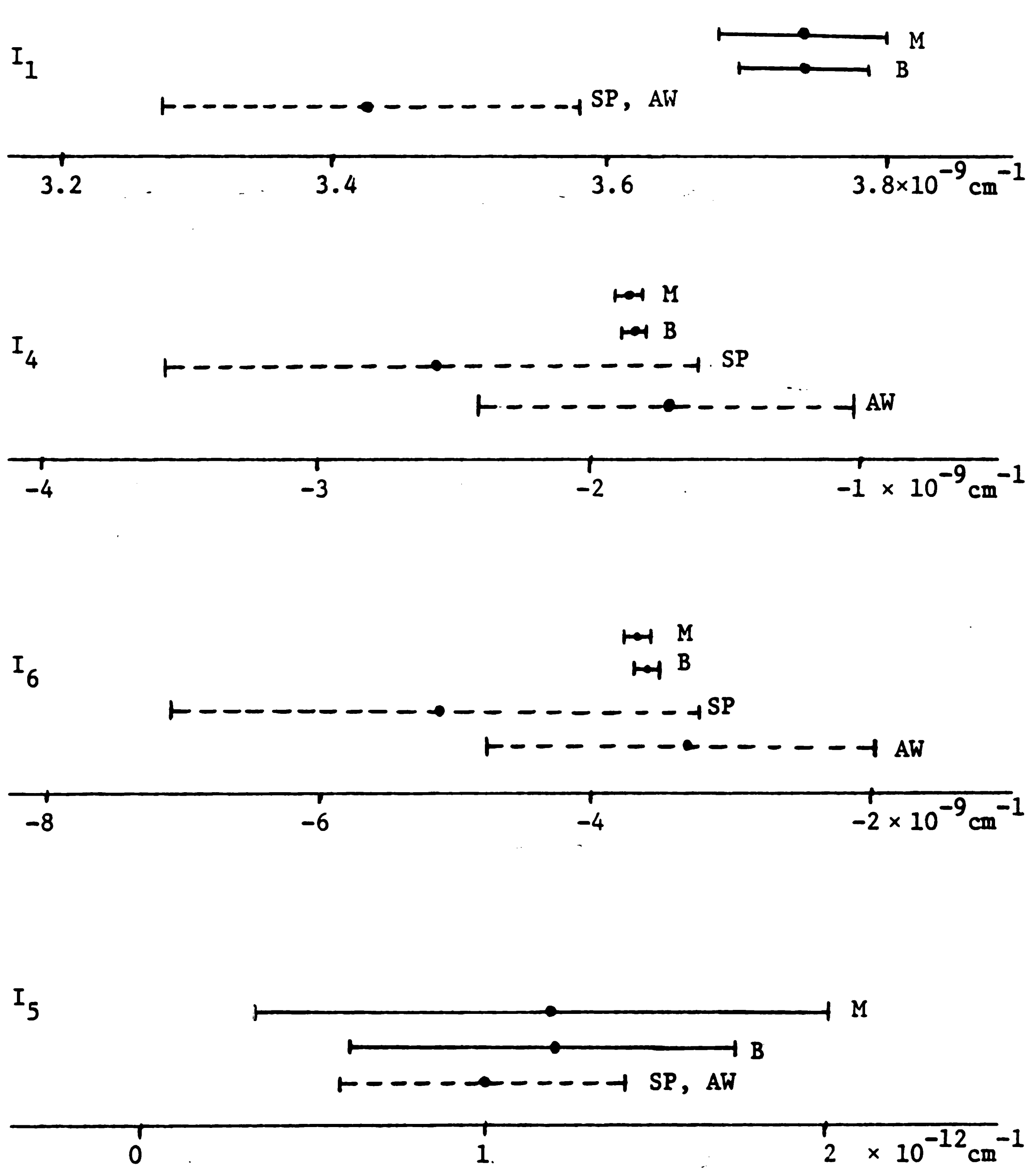
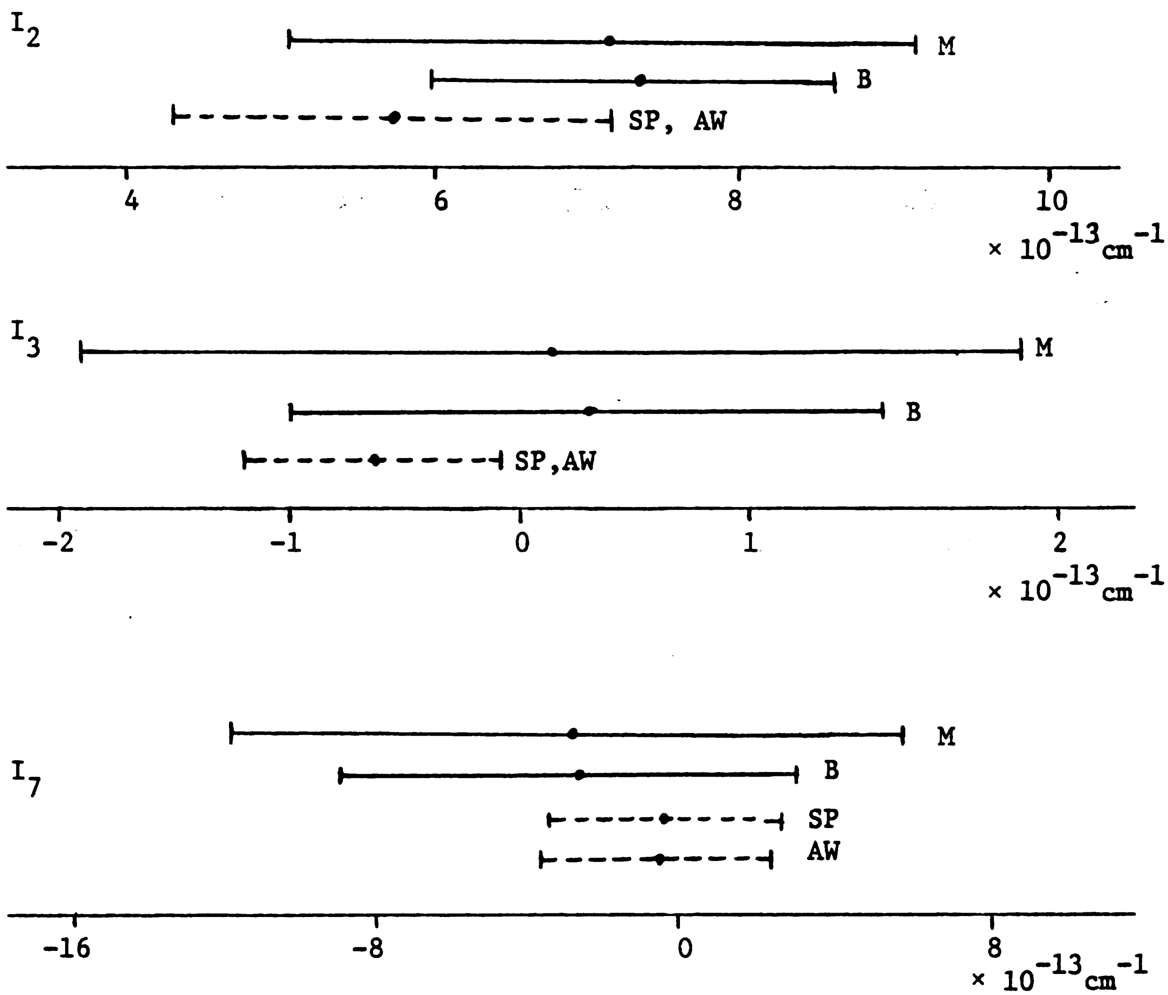


Fig. (9-2) (continued)



10. CONCLUSION

The Darling-Dennison molecular vibration-rotation Hamiltonian and an order-of magnitude expansion of this Hamiltonian appropriate for asymmetric-top molecules were presented. After outlining the contact transformation technique as applicable to the expanded Hamiltonian, the calculation by this technique of the second-order (quartic) and fourth-order (sextic) centrifugal distortion coefficients was described.

The results of the calculation of the theoretical expressions for the sextic centrifugal distortion coefficients for triangular triatomic molecules by Sumberg and Parker were compared with the results of the more recent calculation by Aliev and Watson. All discrepancies between the two calculations were determined and fully accounted for.

The complete set of quartic and sextic distortion coefficients was calculated for the ozone molecule and compared to experimental determinations appearing in the recent literature. To carry through this comparison, extensive use was made of Watson's theory of reduced Hamiltonians. Agreement between theory and experiment was found to be quite satisfactory.

Also in this dissertation, four linearly independent linear combinations of the ten sextic centrifugal distortion coefficients of triangular traitomic molecules are developed. These are independent of the cubic anharmonic potential constants and depend only on the equilibrium geometry and the harmonic force field parameters of the molecule. These expressions appear potentially useful as planarity-conditioned constraints on the ten sextic centrifugal distortion coefficients. Such sum-rule type constraints should normally reduce the uncertainty of the experimental constants without interfering with the deduction of the potential constants from them and lead to Hamiltonians devoid of indeterminable coefficients or combinations of coefficients. The manner in which these original results might be useful in the analysis of high-resolution vibration-rotation data was discussed.

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