

The Vibration-Rotation Energies of Tetrahedral XY_4 Molecules

Part I. Theory of Spherical Top Molecules*

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The theory of vibration-rotational perturbations in tetrahedral XY_4 molecules has been reexamined in the light of the modern theory of angular momentum coupling. It is shown that, even to third order of approximation, the splitting of a vibration rotation level into its tetrahedral sublevels is governed only by perturbation terms of one basic symmetry in all states in which vibrational quanta of ν_1 , ν_2 , and ν_4 are excited and to a certain approximation in many of the infrared active states in which quanta of both ν_2 and ν_3 or ν_4 are excited. The perturbation term is identified as the tetrahedrally symmetric linear combination of fourth rank spherical tensor operators. In dominant approximation the rotational fine structure splitting patterns are characterized solely by the rotational angular momentum of the state. Only the overall extent of the patterns depends on the vibrational and total angular momentum quantum numbers and the vibrational character of the state. In next approximation the basic splitting patterns are all deformed to a certain extent by matrix elements off-diagonal in the rotational angular momentum quantum number. These cannot be neglected if theory is to account for the modern high resolution spectra.

The terms of the vibration-rotation Hamiltonian to third order of approximation are classified according to their symmetry. Explicit expressions are given for the pure vibrational energies of the simpler bands. Explicit numerical values are also given for the matrix elements of the rotational sublevels of types A_1 , A_2 , E , F_1 , and F_2 from which the rotational energies of the vibrational ground state and the infrared active fundamentals can be computed. These matrix elements also give the numbers for the basic splitting patterns of the dominant approximation for any state involving combinations of ν_1 , ν_2 , and ν_4 .

* A preliminary report on this work was given by the author at the 1957 Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio [*Appl. Spectroscopy* **11**, 203 (1957)]. A similar approach has been used by J. D. Louck [*Dissertation Abst.* **19**, 840 (1958)].

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INTRODUCTION

Advances in infrared spectroscopy in recent years have made it possible to completely resolve the complex rotational fine structure of many of the vibrational bands of the methane molecule (*1-4*). In order to account for the experimentally observed spectra it has proved useful to reexamine the theory of the vibration-rotation interactions in spherical top molecules in the light of the modern theory of angular momentum coupling and the concept of irreducible spherical tensor operators (*5, 6*).

The complete vibration-rotation Hamiltonian for tetrahedrally symmetric XY_4 molecules has been derived to second order of approximation by Shaffer *et al.* (*7, 8*) who have also computed the matrix elements of this Hamiltonian for the states which give rise to the fundamentals and the simpler combination and overtone bands. In order to compute the energies of the vibration-rotation levels, however, it is almost mandatory to make full use of the symmetry of the molecule to factor the Hamiltonian matrix as much as possible. This symmetry has been exploited by Jahn (*9, 10*) to facilitate the computation of the energy levels of the fundamental ν_4 . Jahn, however, has considered only the dominant perturbation for this band, the Coriolis interaction with the nearby fundamental ν_2 . In order to account for the modern high resolution spectra it is important to include the effects of all vibration-rotation interactions not only to second order but to third order of approximation. By classifying the perturbation terms according to their symmetry, however, it can be shown that the task of computing the vibration-rotation energy levels, even to third order, is not much more complicated than that undertaken by Jahn since the perturbation terms group themselves into a very few basic types. Since the Hamiltonian has spherical and inversion symmetry in zeroth approximation it is advantageous to classify the perturbation terms according to the irreducible representations of the full rotation-inversion group, where the possible types of perturbation terms are severely restricted by the additional requirement that they must transform according to the totally symmetric irreducible representation (A_1) of the point group of the regular tetrahedron (T_d). Because of this restriction it can be seen that most of the vibrational states of the molecule are influenced by only two types of perturbation terms. There are scalar perturbation terms which cannot remove the first order degeneracy of the vibration-rotation levels but merely shift the positions of the levels giving contributions to the effective B , D , and zeta values of the bands. There is in addition, in the case of most states, only one basic type of tensor perturbation operator which can split a vibration-rotation level into its A_1 , A_2 , E , F_1 , and F_2 sublevels without influencing its center of gravity. In dominant approximation this perturbation gives rise to a basic fine structure pattern which is characterized solely by the rotational angular momentum and is completely independent of the total angular momentum or the vibrational angular momentum of the level, the vibrational character of the state, or the

TABLE I
OBSERVED FINE STRUCTURE PATTERNS FOR STATES WITH A ROTATIONAL
ANGULAR MOMENTUM, $R = 4$

Theory (Dominant approximation)	$\nu_3 P(4)^a$	$\nu_3 Q(4)^a$
$A_1(A_2) + 14$	$A_1 + 14.0 \times (0.0138 \text{ cm}^{-1})$	$A_2 + 14.0 \times (-0.0173 \text{ cm}^{-1})$
$F_1(F_2) + 7$	$F_1 + 7.0$	$F_2 + 7.5$
$E + 2$	$E + 2.3$	$E + 4.4$
$F_2(F_1) - 13$	$F_2 - 13.3$	$F_1 - 15.0$
$\nu_1 + \nu_4 P(4)^b$	$\nu_4 P(4)^c$	$\nu_2 + \nu_3 R(4)^b$
$A_1 + 14.0 \times (0.061 \text{ cm}^{-1})$	$A_1 + 14.0 \times (.060 \text{ cm}^{-1})$	$A_1 + 14.0 \times (.022 \text{ cm}^{-1})$
$F_1 + 7.1$	$E_1 + 7.7$	$F_1 + 8.0$
$E + 1.8$	$F + 2.5$	$E + 3.8$
$F_2 - 13.0$	$F_2 - 14.0$	$F_2 - 15.2$

^a Reference 1. ^b Reference 2. ^c Reference 4.

dynamical nature of the dominant perturbation term (whether of Coriolis, centrifugal distortion, anharmonic, etc., type). Only the extent of the pattern depends on all these latter quantities. The effect is illustrated in Table I by some of the experimentally observed fine structure patterns where states with a rotational angular momentum of four units have been chosen. Such states have four rotational sublevels, either of symmetry A_1 , F_1 , E , and F_2 , or of symmetry A_2 , F_2 , E , and F_1 (9). In dominant approximation theory predicts that the four sublevels are split from their center of gravity in the ratios 14, 7, 2, and -13, respectively, where the A , E , and F sublevels are given weights of 1, 2, and 3, respectively, in determining their common center of gravity. It can be seen that the experimentally observed splittings follow the predicted patterns rather closely for states of very different vibrational character as well as for P , Q , and R branch transitions for which the total angular momentum quantum numbers of the upper state are 3, 4, and 5, respectively. (The observed splittings in these examples arise almost exclusively from the upper state). The differences between the experimentally observed splitting ratios and the theoretically predicted numbers may arise partly from experimental uncertainties (the overall separation of the four lines, determined by the numbers in parentheses, is considerably less than 1 cm^{-1} in some of the examples). However, theory predicts that the basic splitting patterns can be deformed if the splitting of a vibration-rotation level into its A_1 , A_2 , E , F_1 , and F_2 components is large compared with the first-order energy separation of states with the same total but different rotational angular momentum. In that case the fact that the rotational angular momentum is not a "good quantum number" becomes important. Matrix elements between nearby states of different rotational angular momentum (which were neglected by Jahn)

may give significant contributions to the energy and lead to states which are mixtures involving several rotational angular momenta. Since the basic theoretical splitting patterns of the dominant approximation are characterized by the rotational angular momentum quantum numbers such a mixing will lead to a deformation of the basic patterns which may become especially important for states with large angular momentum quantum numbers. Since the degree of mixing depends on the separations of states of different rotational angular momentum which in turn are functions of the B and zeta values of the band, the rotational fine structure patterns will differ somewhat from band to band.

In this first paper of a series an outline of the basic theory is given. The vibration-rotation perturbation terms to third order of approximation are classified according to their symmetry, and it is shown how this classification can be used to simplify the calculation of the energies. Explicit expressions are given for the pure vibrational energies of the simpler bands. Explicit numerical values are also given for the matrix elements of the Hamiltonian for the rotational sub-levels of types A_1 , A_2 , E , F_1 , and F_2 from which the rotational energies of the vibrational ground state and the infrared active fundamentals can be computed. In the second paper the numerical results for the fundamental ν_3 of CH_4 will be presented and compared with the experimentally observed spectrum which has recently been remeasured by Plyler *et al.* (1) under high resolution. In subsequent papers some of the simpler overtone and combination bands will be discussed.

CLASSIFICATION OF THE WAVE FUNCTIONS AND PERTURBATIONS TERMS

The complete vibration-rotation Hamiltonian can be written in the usual way (8) in terms of the P_α , the components of the total angular momentum along a molecule-fixed coordinate system, and the nine normal coordinates Q_1 , Q_{2a} , Q_{2b} , Q_{3x} , Q_{3y} , Q_{3z} , Q_{4x} , Q_{4y} , and Q_{4z} associated with the four fundamental frequencies. It is convenient to introduce dimensionless coordinates q_1 , e , f , x_3 , y_3 , z_3 , x_4 , y_4 , z_4 ,¹ which are related to the $Q_{i\alpha}$ as follows

$$\begin{aligned} Q_1 &= (h | 4\pi^2 c \omega_1)^{1/2} q_1, & Q_{2a} &= (h | 4\pi^2 c \omega_2)^{1/2} e, \\ Q_{2b} &= (h | 4\pi^2 c \omega_2)^{1/2} f, & Q_{3x} &= (h | 4\pi^2 c \omega_3)^{1/2} x_3, \end{aligned}$$

etc., in which the ω_i or (ν_i/c) are the normal frequencies expressed in cm^{-1} . In terms of these coordinates the zeroth order Hamiltonian becomes

$$\begin{aligned} \frac{H_0}{hc} &= \frac{\omega_1}{2} (p_1^2 + q_1^2) + \frac{\omega_2}{2} (p_2^2 + r_2^2) \\ &+ \frac{\omega_3}{2} (p_3^2 + r_3^2) + \frac{\omega_4}{2} (p_4^2 + r_4^2) + B_e P^2 \end{aligned} \quad (1)$$

¹ An attempt has been made to retain the notation of both Jahn and Shaffer *et al.* as much as possible.

in which $p_1^2 = -\partial^2/\partial q_1^2$, $r_2^2 = e^2 + f^2$, $p_2^2 = -(\partial^2/\partial e^2 + \partial^2/\partial f^2)$, $r_3^2 = x_3^2 + y_3^2 + z_3^2$, $p_3^2 = p_{3x}^2 + p_{3y}^2 + p_{3z}^2 = -(\partial^2/\partial x_3^2 + \partial^2/\partial y_3^2 + \partial^2/\partial z_3^2)$, etc., and $B_e = (\hbar | 8\pi^2 c I_e)$, while $P^2 = P_x^2 + P_y^2 + P_z^2$ is also a dimensionless quantity with eigenvalue $J(J + 1)$. In order to obtain the correct stabilized zeroth-order wave functions the Hamiltonian H_1' must be added to H_0

$$H_1'/\hbar c = -2B_e(\zeta_3 \mathbf{P} \cdot \mathbf{l}_3 + \zeta_4 \mathbf{P} \cdot \mathbf{l}_4), \quad (2)$$

in which \mathbf{l}_3 and \mathbf{l}_4 are the internal vibrational angular momentum vectors. The components along the molecule-fixed coordinate system are given by

$$l_{3x} = (y_3 p_{3z} - z_3 p_{3y}), \quad l_{3y} = (z_3 p_{3x} - x_3 p_{3z}), \quad l_{3z} = (x_3 p_{3y} - y_3 p_{3x})$$

with similar expressions for \mathbf{l}_4 . In states in which vibrational quanta of both normal modes ν_3 and ν_4 are excited the internal angular momenta couple quantum vectorially to a resultant total vibrational angular momentum \mathbf{l} . The eigenvalues of \mathbf{l}_3^2 , l_{3z} , \mathbf{l}_4^2 , and l_{4z} are $l_3(l_3 + 1)$, m_3 , $l_4(l_4 + 1)$, and m_4 , respectively, while the eigenvalues of \mathbf{l}^2 and l_z are $l(l + 1)$ and $m = m_3 + m_4$ where the integer l has the possible values $(l_3 + l_4), \dots, |l_3 - l_4|$, as usual. The vibrational angular momentum \mathbf{l} couples with the rotational angular momentum, to be denoted by \mathbf{R} , to give the resultant total angular momentum \mathbf{P} .² The eigenvalues of \mathbf{R}^2 , \mathbf{P}^2 and the molecule-fixed components R_z and P_z will be denoted by $R(R + 1)$, $J(J + 1)$, K_R , and K , respectively. The operators l_α satisfy the usual angular momentum commutation relations

$$[l_x, l_y] = +il_z \dots$$

The operators P_α (and similarly R_α), on the other hand, satisfy the commutation relations with the anomalous algebraic sign before i

$$[P_x, P_y] = -iP_z \dots$$

As a consequence it is natural to speak of quantum vector subtraction rather than quantum vector addition (see for example Van Vleck (11), or to build up the states by adding the vector (-1) to the vector \mathbf{P} to give a resultant $\mathbf{R} = \mathbf{P} - \mathbf{l}$. This is the natural way to perform the addition since all the components of \mathbf{P} commute with all the components of \mathbf{l} , whereas the components of \mathbf{R} do not commute with those of \mathbf{l} . The wave functions must therefore be built up from linear combinations of products of eigenfunctions of the vectors \mathbf{P} and \mathbf{l} , respectively. The wave function of a state characterized by the resultant rotational angular momentum quantum numbers R and K_R is given by

$$\psi(J_R^l)_{RK_R} = \sum_m \langle lJmK | lJRK_R \rangle \phi_{lm}^* \psi_{JK}, \quad (3)$$

² The angular momenta \mathbf{R} and \mathbf{l} are identical with Nielsen's \mathbf{P}_1 and \mathbf{P}_2 (Ref. 8). In this paper the subscripts 1 and 2 will be reserved for the normal modes 1 and 2.

in which the coupling coefficients $\langle lJmK | lJRK_R \rangle$ are the usual angular momentum *addition* or Clebsch-Gordan coefficients with $K = (K_R - m)$.³ The formula for the coupled wave function in the case of angular momentum subtraction is therefore the same as the usual addition formula with the exception that the eigenfunctions of the negative vector, -1 , are replaced by their complex conjugate, where

$$\phi_{lm}^* = (-1)^m \phi_{l-m}.$$

With this small modification the whole machinery of angular momentum addition theory (5, 6), can be applied to the problem of angular momentum subtraction of molecular physics. The ϕ_{lm} are the usual vibrational eigenfunctions. The dependence on all the principal vibrational quantum numbers v_i has not been written explicitly. For example, if only one vibrational quantum of ν_3 is excited, that is with $v_3 = 1, l_3 = 1, (v_1 = v_2 = v_4 = 0, l_4 = 0)$, the functions ϕ_{lm} are given by

$$\phi_{1\pm 1} = \mp \frac{1}{\sqrt{2}} [\phi(100) \pm i\phi(010)], \quad \phi_{10} = \phi(001),$$

in which $\phi(v_{3x} v_{3y} v_{3z})$ are products of one-dimensional harmonic oscillator functions in the coordinates x_3, y_3 , and z_3 with quantum numbers v_{3x}, v_{3y} , and v_{3z} , respectively. If vibrational quanta of both ν_3 and ν_4 are excited the vibrational wave functions ϕ_{lm} are themselves given by the angular momentum addition formula as linear combinations of products of eigenfunctions of \mathbf{l}_3 and \mathbf{l}_4 .

$$\phi_{lm} = \sum_{m_3} \langle l_3 l_4 m_3 m_4 | l_3 l_4 m \rangle \phi_{l_3 m_3} \phi_{l_4 m_4} \quad m_4 = (m - m_3). \quad (4)$$

The ψ_{JK} are the spherical (or symmetric) rotator eigenfunctions, functions of the three Euler angles which give the orientation of the molecular framework in space. In Eq. (3) the dependence of ψ_{JK} on the quantum number M , the eigenvalue of the space-fixed z -component of \mathbf{P} , has not been written explicitly. The rotational wave functions are related to the coefficients, D_{MK}^J , of the $(2J + 1)$ -dimensional irreducible representations of the rotation group as defined in (5), by

$$\psi_{JMK} = [(2J + 1)/8\pi^2]^{1/2} D_{MK}^J.$$

The wave functions ψ_{JK} transform according to the irreducible representations of the group of all rotations and reflections, according to D_o^J (for J even) and D_u^J (for J odd). Since the vibrational wave functions, ϕ_{lm} , transform according to the product representations of the eigenfunctions of \mathbf{l}_3 and \mathbf{l}_4 , they transform according to D_o^l (if $l_3 + l_4$ is even) or D_u^l (if $l_3 + l_4$ is odd). The eigenfunctions of the resultant rotational angular momentum, ψ_{RK_R} , therefore transform accord-

³ For the case $l = 1$ the wave functions (3) have been written out explicitly by Jahn.

ing to the representation D_g^R (if $J + l_3 + l_4$ is even) or D_u^R (if $J + l_3 + l_4$ is odd).

Since the zeroth-order wave functions transform according to one of the irreducible representations of the full rotation-reflection group it is advantageous to classify the tetrahedrally symmetric vibration-rotation perturbation terms according to their transformation properties under this more extended group. It should be pointed out, however, that not all vibrational wave functions transform according to one of the irreducible representations of the full rotation-reflection group. For example, the vibrational wave functions of the doubly degenerate fundamental state ν_2 (a state of zero vibrational angular momentum) transform according to the irreducible representation E of the tetrahedral group. This is not one of the irreducible representations of the full rotation-reflection group. The rotational fine structure patterns for the "infrared forbidden" fundamental ν_2 are therefore very different from the basic patterns discussed in connection with Table I. In this paper the discussion will be restricted to vibrational states whose wave functions transform according to one of the irreducible representations of the full rotation-reflection group. This includes all possible combinations and overtones of the states ν_1 , ν_3 , and ν_4 . Although it does not include the fundamental ν_2 itself it does include many states in which quanta of both ν_2 and ν_3 or ν_4 are excited. (The excited states for all "infrared active" transitions originating from the vibrational ground state fall into this category.) The combination state $\nu_2 + \nu_3$, for example, has vibrational substates F_2 and F_1 whose wave functions transform according to the irreducible representations D_u^1 and D_g^1 , respectively. As a result the rotational fine structure patterns for this band are the basic ones discussed in connection with Table I.

The perturbation terms of the vibration-rotation Hamiltonian will be ordered according to the scheme of Nielsen *et al.* (12, 13) in which the ω_i and the rotational energy $BJ(J + 1)$ are considered to be quantities of the same order of magnitude.⁴ The Hamiltonian is subjected to the usual contact transformation (7, 12, 13) so that the transformed Hamiltonian, H_1' , contains only terms diagonal in the vibrational quantum numbers, v_i , Eq. (2). In order to exploit the symmetries of the zeroth-order wave functions the perturbation terms of H_2' , H_3' will be classified according to their tensor character. An examination of the transformed Hamiltonian, H' , shows that the individual perturbation terms in H_2' , H_3' , H_4' , \dots are at most tensors of rank 4, 5, or 6 \dots , respectively. Characteristic terms of H_3' , for example, have the form $q_a p_b P_\alpha P_\beta P_\gamma$ or $q_a q_b q_c p_d P_\alpha$ (12), in which the individual q_a , p_b , P_α , \dots transform at most as tensors of rank 1. Calculation of the vibration-rotation energies to third order of approximation will therefore involve only tensors of rank ≤ 5 . In order to apply the machinery

⁴ In this scheme quantities of order B , $(B^2/\omega)J^2$, $(B^3/\omega^2)J^4$, the quartic potential constants, and the squares of the cubic constants divided by ω are all considered to be of second order, whereas quantities of order $(B^2/\omega)J$, $(B^3/\omega^2)J^3$, \dots are considered to be of third order.

of angular momentum coupling theory the perturbation terms must be classified as irreducible spherical tensor operators ($\bar{5}$), but the possible types of tensor operators are restricted by the requirement that they must transform according to the totally symmetric irreducible representation (A_1) of the group T_d . Only those linear combinations of spherical tensor operators which remain invariant under all the symmetry operations of the tetrahedral group can occur in the Hamiltonian. The reduction of the representations D_g^j, D_u^j of the full rotation-inversion group into irreducible representations of T_d has been given by Jahn (9). The result is shown in Table II for small values of j . For $j \leq 5$ the only representations which contain A_1 are those with $j = 0, 3$, and 4. The only tetrahedrally symmetric linear combinations of spherical tensor operators of rank ≤ 5 therefore involve only tensors of rank 0, 3, and 4. The correct linear combinations have also been given by Jahn. They are

$$T(00),$$

$$[T(3-2) - T(32)],$$
(5)

and

$$\{(2 \cdot 5 \cdot 7)^{1/2} T(40) + 5[T(44) + T(4-4)]\},$$

in which the individual tensor operators $T(jm)$ transform under rotations and inversion as do the spherical harmonics Y_{jm} . It is to be noted that the inclusion of third-order perturbation terms (tensors of rank ≤ 5) cannot introduce any new types of spherical tensor operators, (D^5 does not contain A_1), so that the calculation of the vibration-rotation energies to third order of approximation involves terms of the same basic symmetries as the calculation to second order. Inclusion of fourth-order perturbation terms, on the other hand, would introduce entirely new types of tensor operators since the representations D^6 contain the irreducible representation A_1 . It is to be noted further that the third-rank tensor operator $[T(3-2) - T(32)]$ transforms according to a representation of type u . In calculating energies of the levels to third order, however, only matrix

TABLE II
REDUCTION OF D_g^j, D_u^j INTO IRREDUCIBLE REPRESENTATIONS OF T_d

j	D_g^j	D_u^j
0	A_1	A_2
1	F_1	F_2
2	$E + F_2$	$E + F_1$
3	$A_2 + F_1 + F_2$	$A_1 + F_2 + F_1$
4	$A_1 + E + F_1 + F_2$	$A_2 + E + F_2 + F_1$
5	$E + 2F_1 + F_2$	$E + 2F_2 + F_1$
6	$A_1 + A_2 + E + F_1 + 2F_2$	$A_2 + A_1 + E + F_2 + 2F_1$

elements diagonal in v_i and J are needed. For given v_i the angular momentum quantum numbers l_i are *either* even *or* odd. The required matrix elements of H' therefore connect states which are either *both* of type g (if $J + l_3 + l_4$ is even) or *both* of type u (if $J + l_3 + l_4$ is odd). Consequently matrix elements of an operator of type u are zero, and the operator [$T(3-2) - T(32)$] cannot contribute to the vibration-rotation energies. The spacing of the vibration-rotation levels is therefore governed by only two types of perturbation terms, scalars $T(00)$ which, as will be shown, cannot remove the first-order degeneracies of the levels, and one linear combination of fourth-rank tensors which can split a level into its $A_1, A_2, E, F_1,$ and F_2 fine structure components. The splitting patterns are therefore governed by perturbation terms of one basic symmetry. The above applies strictly only to states in which quanta of only $\nu_1, \nu_3,$ and ν_4 are excited. Combination bands involving ν_2 may have vibrational substates of both type g and u . The state $\nu_2 + \nu_3$, for example, has vibrational substates F_2 and F_1 with $l = 1$ which transform according to D_u^1 and D_g^1 , respectively (Table II). The third-rank tensor operator may make contributions to the energies of this state since it may have nonzero matrix elements connecting the vibrational substate F_2 with the substate F_1 . The scalar and fourth-rank operators on the other hand can connect only either the vibrational substate F_2 with F_2 or F_1 with F_1 . If the separation into the rotational fine structure components is small compared with the separation of the F_2 and F_1 vibrational substates, it might be expected, however, that the splitting patterns are dominated by the fourth-rank tensor operators. This seems to be the case for the states of small angular momentum so that the basic splitting patterns of $\nu_2 + \nu_3$ are very similar to those of all other infrared active bands (Table I). For states of large angular momentum, however, the effect of the third-rank tensor operator seems to become important and the splitting patterns diverge more and more from the basic ones (2).

THE VIBRATION-ROTATION HAMILTONIAN

To carry out the calculation of the energy levels of an XY_4 molecule to third order of approximation the tetrahedrally symmetric cubic and quartic potential terms must be added to the harmonic part of the potential function. These have been given by Shaffer *et al.* (7) but are listed again in Appendix I in order to establish the notation to be used in this paper. The individual terms of the transformed Hamiltonian are listed below. The only terms which can contribute to the energies to within third order of approximation are those terms of H_2' and H_3' whose matrix elements are diagonal in the principal vibrational quantum numbers v_i . These will be denoted by $H'(\text{diag})$. To pick out these terms from the complete Hamiltonian, H' , it is only necessary to rewrite the vibrational operators. The operator q_1^2 , for example, can be rewritten

$$q_1^2 = \frac{1}{2}(p_1^2 + q_1^2) - \frac{1}{2}(p_1^2 - q_1^2).$$

The only nonzero matrix elements of the first term are diagonal in the quantum number v_1 , whereas the diagonal matrix elements of the second term are zero. Since the second term has matrix elements off-diagonal in v_1 only, it can be neglected to within the approximation of interest. As another example of this process the operator $x_3^2 y_3^2$ can be written

$$\begin{aligned} x_3^2 y_3^2 = & \left\{ \frac{3}{8}(p_{3x}^2 + x_3^2)(p_{3y}^2 + y_3^2) - \frac{1}{4}l_{3z}^2 - \frac{1}{8} \right\} \\ & - \frac{1}{4}(p_{3x}^2 - x_3^2)(p_{3y}^2 + y_3^2) - \frac{1}{4}(p_{3x}^2 + x_3^2)(p_{3y}^2 - y_3^2) \\ & + \frac{1}{8}[(p_{3x}^2 - x_3^2)(p_{3y}^2 - y_3^2) - (p_{3x}x_3 + x_3p_{3x})(p_{3y}y_3 + y_3p_{3y})]. \end{aligned}$$

Only the first term, enclosed in braces $\{ \}$, is completely diagonal in v_3 whereas the remaining terms are completely off-diagonal in v_3 and can therefore be neglected.

For convenience the terms of H' (diag) are subdivided into pure vibrational perturbation terms and vibration-rotation terms which are classified according to their dependence on the angular momentum quantum number J .

$$\begin{aligned} H'(\text{diag}) = & H_2'(\text{vib, diag}) + H_2'(P^4) + H_2'(P^2, \text{diag}) + H_3'(P^3, \text{diag}) \\ & + H_3'(P, \text{diag}) + \dots \end{aligned} \quad (6)$$

The pure vibrational terms are given by

$$\begin{aligned} H_2'(\text{vib, diag}) = & X_{11} \frac{(p_1^2 + q_1^2)}{2} \frac{(p_1^2 + q_1^2)}{2} + X_{22} \frac{(p_2^2 + r_2^2)}{2} \frac{(p_2^2 + r_2^2)}{2} \\ & + X_{33} \frac{(p_3^2 + r_3^2)}{2} \frac{(p_3^2 + r_3^2)}{2} + X_{44} \frac{(p_4^2 + r_4^2)}{2} \frac{(p_4^2 + r_4^2)}{2} \\ & + X_{12} \frac{(p_1^2 + q_1^2)}{2} \frac{(p_2^2 + r_2^2)}{2} + X_{13} \frac{(p_1^2 + q_1^2)}{2} \frac{(p_3^2 + r_3^2)}{2} \\ & + X_{14} \frac{(p_1^2 + q_1^2)}{2} \frac{(p_4^2 + r_4^2)}{2} + X_{23} \frac{(p_2^2 + r_2^2)}{2} \frac{(p_3^2 + r_3^2)}{2} \\ & + X_{24} \frac{(p_2^2 + r_2^2)}{2} \frac{(p_4^2 + r_4^2)}{2} + X_{34} \frac{(p_3^2 + r_3^2)}{2} \frac{(p_4^2 + r_4^2)}{2} \\ & + G_{22}m_{2z}^2 + G_{33}l_3^2 + G_{44}l_4^2 + G_{34}(l_3 \cdot l_4) + S_{34}O_{34}(\text{scalar}) \\ & + T_{34}O_{34}(\text{tensor}) + T_{33}O_{33}(\text{tensor}) + T_{44}O_{44}(\text{tensor}) \\ & + T_{23}O_{23}(\text{tensor}) + T_{24}O_{24}(\text{tensor}). \end{aligned} \quad (7)$$

The operator m_{2z} is the angular momentum operator in the space of the two-fold degenerate normal coordinates (but not in three-dimensional space), $m_{2z} = -i(e\partial/\partial f - f\partial/\partial e)$. Its eigenvalues are $\pm v_2$, $\pm(v_2 - 2)$, $\pm(v_2 - 4)$, \dots .

The operators O_{34} , O_{33} , \dots are given by

$$\begin{aligned}
 O_{34}(\text{scalar}) &= (p_{3x}^2 + x_3^2)(p_{4x}^2 + x_4^2) + (p_{3y}^2 + y_3^2)(p_{4y}^2 + y_4^2) \\
 &\quad + (p_{3z}^2 + z_3^2)(p_{4z}^2 + z_4^2) + 2(p_{3x}p_{3y} + x_3y_3)(p_{4x}p_{4y} + x_4y_4) \\
 &\quad + 2(p_{3x}p_{3z} + x_3z_3)(p_{4x}p_{4z} + x_4z_4) \\
 &\quad + 2(p_{3y}p_{3z} + y_3z_3)(p_{4y}p_{4z} + y_4z_4) - \frac{1}{3}(p_3^2 + r_3^2)(p_4^2 + r_4^2), \\
 O_{34}(\text{tensor}) &= \frac{3}{2}(p_{3x}^2 + x_3^2)(p_{4x}^2 + x_4^2) + \frac{3}{2}(p_{3y}^2 + y_3^2)(p_{4y}^2 + y_4^2) \\
 &\quad + \frac{3}{2}(p_{3z}^2 + z_3^2)(p_{4z}^2 + z_4^2) \\
 &\quad - 2(p_{3x}p_{3y} + x_3y_3)(p_{4x}p_{4y} + x_4y_4) \\
 &\quad - 2(p_{3x}p_{3z} + x_3z_3)(p_{4x}p_{4z} + x_4z_4) \\
 &\quad - 2(p_{3y}p_{3z} + y_3z_3)(p_{4y}p_{4z} + y_4z_4) \\
 &\quad - \frac{1}{2}(p_3^2 + r_3^2)(p_4^2 + r_4^2), \\
 O_{33}(\text{tensor}) &= (p_{3x}^2 + x_3^2)(p_{3x}^2 + x_3^2) + (p_{3y}^2 + y_3^2)(p_{3y}^2 + y_3^2) \\
 &\quad + (p_{3z}^2 + z_3^2)(p_{3z}^2 + z_3^2) - 3(p_{3x}^2 + x_3^2)(p_{3y}^2 + y_3^2) \\
 &\quad - 3(p_{3x}^2 + x_3^2)(p_{3z}^2 + z_3^2) - 3(p_{3y}^2 + y_3^2)(p_{3z}^2 + z_3^2) \\
 &\quad + 2l_3^2 + 6, \\
 O_{23}(\text{tensor}) &= (p_e^2 + e^2 - p_f^2 - f^2)(p_3^2 + r_3^2 - 3p_{3z}^2 - 3z_3^2) \\
 &\quad + 2\sqrt{3} (p_e p_f + ef)(p_{3x}^2 + x_3^2 - p_{3y}^2 - y_3^2).
 \end{aligned} \tag{8}$$

The operators O_{44} , O_{24} , are obtained from O_{33} , and O_{23} by an interchange of indices 3 and 4. The coefficients X_{ij} , G_{ij} , S_{ij} , and T_{ij} are tabulated in terms of the molecular parameters in Appendix I.

The purely vibrational corrections to the zeroth order energies are

$$\Delta E_{\text{vib}} = \sum_{i < j} X_{ij}(v_i + d_i/2)(v_j + d_j/2) + W(m_{2z}, l_3, l_4, l, \text{symmetry}). \tag{9}$$

The first sum gives an anharmonicity correction similar to that found in less symmetrical molecules. The contribution W , which is a function of the vibrational angular momentum quantum numbers and the symmetries of the vibrational substates, gives the eigenvalues of the operators l_i^2 and O_{ij} and determines the splitting of a pure vibrational level into its possible tetrahedral sublevels. The energies W are listed in Table III for all vibrational states in which one, two, or three vibrational quanta have been excited. These energies have been computed by the techniques to be discussed in connection with the computation of the vibration-rotation energies.

The vibration-rotation perturbation terms are given by

$$H_2'(P^4) - -D_s P^4 = D_t O_{PPPP}(\text{tensor}), \tag{10}$$

TABLE III
VIBRATIONAL ENERGIES

State	$W(m_{2z}, l_3, l_4, l, \text{symmetry})$
Ground state	0
$\nu_3 F_2 l_3 = 1$	$2G_{33}$
$2\nu_3 \begin{cases} A_1 l_3 = 0 \\ E l_3 = 2 \\ F_2 l_3 = 2 \end{cases}$	0 $6G_{33} + 12T_{33}$ $6G_{33} - 8T_{33}$
$3\nu_3 \begin{cases} A_1 l_3 = 3 \\ F_1 l_3 = 3 \\ 2F_2 l_3 = 3, 1^a \end{cases}$	$12G_{33} - 24T_{33}$ $12G_{33} - 4T_{33}$ $7G_{33} + 6T_{33} \pm [(5G_{33} + 6T_{33})^2 + 384T_{33}^2]^{1/2}$
$4\nu_3^b \begin{cases} 2A_1 l_3 = 4, 0 \\ 2E l_3 = 4, 2 \\ F_1 l_3 = 4 \\ 2F_2 l_3 = 4, 2 \end{cases}$	$10G_{33} + 12T_{33} \pm [(10G_{33} + 12T_{33})^2 + 1,536T_{33}^2]^{1/2}$ $13G_{33} + 18T_{33} \pm [(7G_{33} - (10/3)T_{33})^2 + (38.40/49)T_{33}^2]^{1/2}$ $20G_{33} + 12T_{33}$ $13G_{33} - 22T_{33} \pm [(7G_{33} - (2/3)T_{33})^2 + (9.60/49)T_{33}^2]^{1/2}$
$\nu_3 + \nu_4 \begin{cases} A_1 l = 0 \\ F_1 l = 1 \\ l_3 = 1 \\ l_4 = 1 \end{cases} \begin{cases} E l = 2 \\ F_2 l = 2 \end{cases}$	$2(G_{33} + G_{44}) - 2G_{34} + (20/3)S_{34}$ $2(G_{33} + G_{44}) - G_{34} - (19/3)S_{34}$ $2(G_{33} + G_{44}) + G_{34} + (2/3)S_{34} + 6T_{34}$ $2(G_{33} + G_{44}) + G_{34} + (2/3)S_{34} - 4T_{34}$
$n\nu_2 m_{2z}$	$m_{2z}^2 G_{22}$
$\nu_2 + \nu_3 \begin{cases} F_2 l_3 = 1 \\ m_{2z} = 1 \\ F_1 l_3 = 1 \end{cases}$	$G_{22} + 2G_{33} + 8T_{23}$ $G_{22} + 2G_{33} - 8T_{23}$
$2\nu_2 + \nu_3 \begin{cases} F_1 m_{2z} = 2 \\ l_3 = 1 \\ 2F_2 m_{2z} = 2, 0 \end{cases}$	$4G_{22} + 2G_{33}$ $2G_{22} + 2G_{33} \pm [(2G_{22})^2 + 256T_{23}^2]^{1/2}$
$\nu_2 + 2\nu_3 \begin{cases} A_1 l_3 = 2 \\ A_2 l_3 = 2 \\ F_1 l_3 = 2 \\ F_2 l_3 = 2 \\ m_{2z} = 1 \\ 2E l_3 = 2, 0 \end{cases}$	$G_{22} + 6G_{33} + 12T_{33} + 16T_{23}$ $G_{22} + 6G_{33} + 12T_{33} - 16T_{23}$ $G_{22} + 6G_{33} - 8T_{33} + 8T_{23}$ $G_{22} + 6G_{33} - 8T_{33} - 8T_{23}$ $G_{22} + 3G_{33} + 6T_{33} \pm [(3G_{33} + 6T_{33})^2 + 256T_{23}^2]^{1/2}$
$\nu_2 + \nu_3 + \nu_4 \begin{cases} A_1 l = 2 \\ A_2 l = 2 \\ 2E l = 2, 0 \\ 2F_2 l = 2, 1 \\ m_{2z} = 1 \\ l_3 = 1 \\ l_4 = 1 \end{cases} \begin{cases} F_1 l = 2, 1 \\ 2F_1 l = 2, 1 \end{cases}$	$G_{22} + 2(G_{33} + G_{44}) + G_{34} + (2/3)S_{34} + 6T_{34} + 8(T_{23} + T_{24})$ $G_{22} + 2(G_{33} + G_{44}) + G_{34} + (2/3)S_{34} + 6T_{34} - 8(T_{23} + T_{24})$ $G_{22} + 2(G_{33} + G_{44}) + (-1/2)G_{34} + 11/3 S_{34} + 3T_{34}$ $\pm [(3/2)G_{34} - 3S_{34} + 3T_{34}]^2 + 64(T_{23} + T_{24})^2]^{1/2}$ $G_{22} + 2(G_{33} + G_{44}) - 4/3 S_{34} - 2T_{34}$ $\pm [(G_{34} + 2S_{34} - 2T_{34} - 4T_{23} - 4T_{24})^2 + 48(T_{23} - T_{24})^2]^{1/2}$ $G_{22} + 2(G_{33} + G_{44}) - 4/3 S_{34} - 2T_{34}$ $\pm [(G_{34} + 2S_{34} - 2T_{34} + 4T_{23} + 4T_{24})^2 + 48(T_{23} - T_{24})^2]^{1/2}$
$2\nu_3 + \nu_4 \begin{cases} A_1 l_3 = 2, l = 3 \\ l_4 = 1 \\ E l_3 = 2, l = 2 \\ 2F_1 l_3 = 2; \\ l = 3, 2 \end{cases}$	$2G_{44} + 6G_{33} + 2G_{34} - 8T_{33} + (4/3)S_{34} - 8T_{34}$ $2G_{44} + 6G_{33} - G_{34} - 8T_{33} - (14/3)S_{34} - 2T_{34}$ $2G_{44} + 6G_{33} + (1/2)G_{34} + 2T_{33} - (5/3)S_{34}$ $\pm \left[\left(\frac{3}{2}G_{34} - \frac{10}{3}T_{33} - \frac{4}{3}T_{34} + 3S_{34} \right)^2 + \frac{800}{9} \left(T_{33} - \frac{T_{34}}{2} \right)^2 \right]^{1/2}$

TABLE III—Continued

State	$W(m_{2z}, l_3, l_4, l, \text{symmetry})$		
<i>Eigenvalues of the 3 × 3 matrix:</i>			
$2\nu_3 + \nu_4$ $\underline{3F_2}$			
$\left(\begin{smallmatrix} l_3 = 2 \\ l = 3 \end{smallmatrix}\right)$	$2G_{44} + 6G_{33} + 2G_{34} + 4T_{33} + (\frac{4}{3})S_{34} + 4T_{34}$	$-4\sqrt{6}[T_{33} + (\frac{1}{6})T_{34}]$	$\frac{4\sqrt{10}}{\sqrt{3}}T_{34}$
$l_4 = 1\left(\begin{smallmatrix} l_3 = 2 \\ l = 1 \end{smallmatrix}\right)$	$-4\sqrt{6}[T_{33} + (\frac{1}{6})T_{34}]$	$2G_{44} + 6G_{33} - 3G_{34} + (\frac{14}{3})S_{34}$	$-\frac{8}{3}\sqrt{5}S_{34}$
$\left(\begin{smallmatrix} l_3 = 0 \\ l = 1 \end{smallmatrix}\right)$	$\frac{4\sqrt{10}}{\sqrt{3}}T_{34}$	$-\frac{8}{3}\sqrt{5}S_{34}$	$2G_{44}$

^a The notation $3\nu_3 2F_2 l_3 = 3, 1$ is to be interpreted as follows: The state $3\nu_3$ has two sub-states of symmetry F_2 with eigenfunctions which are mixtures of wave functions with $l_3 = 3$ and $l_3 = 1$. In the limit in which $G_{33} \gg T_{33}$, the wave function of the state listed first ($l_3 = 3$) becomes the eigenfunction associated with the eigenvalue given by the upper sign in the expression for W .

^b Excited states involving ν_4 are obtained from those involving ν_3 by an interchange of subscripts 3 and 4. Combinations with ν_1 do not affect the energies W .

with

$$O_{PPP}(\text{tensor}) = 4(P_x^4 + P_y^4 + P_z^4) - 6(P_x^2 P_y^2 + P_y^2 P_x^2 + P_x^2 P_z^2 + P_z^2 P_x^2 + P_y^2 P_z^2 + P_z^2 P_y^2) + 2P^2, \quad (11)$$

$$H_2'(P^2, \text{diag}) = \frac{1}{2}[Y_1(p_1^2 + q_1^2) + Y_2(p_2^2 + r_2^2) + Y_3(p_3^2 + r_3^2) + Y_4(p_4^2 + r_4^2)]P^2 + Z_{3s}O_{PP33}(\text{scalar}) + Z_{4s}O_{PP44}(\text{scalar}) + Z_{3t}O_{PP33}(\text{tensor}) + Z_{4t}O_{PP44}(\text{tensor}) + Z_2O_{PP22}(\text{tensor}), \quad (12)$$

where the operators are given by

$$O_{PP33}(\text{scalar}) = \frac{1}{2}[(\mathbf{P} \cdot \mathbf{r}_3)(\mathbf{P} \cdot \mathbf{r}_3) + (\mathbf{P} \cdot \mathbf{p}_3)(\mathbf{P} \cdot \mathbf{p}_3) - \frac{1}{3}P^2(p_3^2 + r_3^2)],$$

$$O_{PP33}(\text{tensor}) = \left\{ \begin{array}{l} P_x^2[2(p_{3x}^2 + x_3^2) - (p_{3y}^2 + y_3^2) - (p_{3z}^2 + z_3^2)] \\ + P_y^2[2(p_{3y}^2 + y_3^2) - (p_{3x}^2 + x_3^2) - (p_{3z}^2 + z_3^2)] \\ + P_z^2[2(p_{3z}^2 + z_3^2) - (p_{3x}^2 + x_3^2) - (p_{3y}^2 + y_3^2)] \\ - 2(P_x P_y + P_y P_x)(p_{3x} p_{3y} + x_3 y_3) \\ - 2(P_x P_z + P_z P_x)(p_{3x} p_{3z} + x_3 z_3) \\ - 2(P_y P_z + P_z P_y)(p_{3y} p_{3z} + y_3 z_3) \end{array} \right\}, \quad (13)$$

$$O_{PP22} = -\frac{3}{8}[(P_x^2 + P_y^2 - 2P_z^2)(p_e^2 + e^2 - p_f^2 - f^2) + 2\sqrt{3}(P_x^2 - P_y^2)(p_e p_f + e f)].$$

The coefficients D_s and D_t are independent of the anharmonic potential constants. The coefficients Y_i and Z_i are functions of the unknown cubic potential constants. All these coefficients are again tabulated in terms of the molecular parameters in Appendix I.

The third-order vibration-rotation perturbation terms are given by

$$\begin{aligned}
 H_3'(P^3, \text{diag}) = & F_{3s}P^2(\mathbf{P}\cdot\mathbf{1}_3) + F_{4s}P^2(\mathbf{P}\cdot\mathbf{1}_4) \\
 & + F_{3t}O_{PP^3}(\text{tensor}) + F_{4t}O_{PP^4}(\text{tensor}) \\
 & + F_2(m_{2z}/\sqrt{3})(P_xP_yP_z + P_xP_zP_y + P_yP_xP_z \\
 & + P_yP_zP_x + P_zP_xP_y + P_zP_yP_x),
 \end{aligned} \tag{14}$$

$$\begin{aligned}
 H_3'(P, \text{diag}) = & [M_{311}(p_1^2 + q_1^2) + M_{322}(p_2^2 + r_2^2) + M_{333}(p_3^2 + r_3^2) \\
 & + M_{344}(p_4^2 + r_4^2)](\mathbf{P}\cdot\mathbf{1}_3) + [M_{411}(p_1^2 + q_1^2) \\
 & + M_{422}(p_2^2 + r_2^2) + M_{433}(p_3^2 + r_3^2) \\
 & + M_{444}(p_4^2 + r_4^2)](\mathbf{P}\cdot\mathbf{1}_4) \\
 & + M_{233}m_{2z}[P_x(p_{3y}p_{3z} + y_3z_3) + P_y(p_{3z}p_{3x} + z_3x_3) \\
 & + P_z(p_{3x}p_{3y} + x_3y_3)] + M_{244}m_{2z}[P_x(p_{4y}p_{4z} + y_4z_4) \\
 & + P_y(p_{4z}p_{4x} + z_4x_4) + P_z(p_{4x}p_{4y} + x_4y_4)] \\
 & + N_{344}O_{P344}(\text{scalar}) + N_{433}O_{P433}(\text{scalar}) \\
 & + N_{344t}O_{P344}(\text{tensor}) + N_{433t}O_{P433}(\text{tensor}) \\
 & + N_{333t}O_{P333}(\text{tensor}) + N_{444t}O_{P444}(\text{tensor}) \\
 & + N_{322}O_{P322} + N_{422}O_{P422},
 \end{aligned} \tag{15}$$

where the operators are

$$O_{PP^3}(\text{tensor}) = 10(P_x^3l_{3x} + P_y^3l_{3y} + P_z^3l_{3z}) - 6P^2(\mathbf{P}\cdot\mathbf{1}_3) + 2(\mathbf{P}\cdot\mathbf{1}_3), \tag{16}$$

$$O_{P344}(\text{scalar}) = \frac{1}{2}[(\mathbf{P}\cdot\mathbf{r}_4)(\mathbf{1}_3\cdot\mathbf{r}_4) + (\mathbf{P}\cdot\mathbf{p}_4)(\mathbf{1}_3\cdot\mathbf{p}_4) - \frac{1}{3}(\mathbf{P}\cdot\mathbf{1}_3)(p_4^2 + r_4^2)],$$

$$\begin{aligned}
 O_{P344}(\text{tensor}) = & 3P_xl_{3z}(p_{4x}^2 + x_4^2) + 3P_yl_{3y}(p_{4y}^2 + y_4^2) + 3P_zl_{3z}(p_{4z}^2 + z_4^2) \\
 & - 2(P_xl_{3y} + P_yl_{3x})(p_{4x}p_{4y} + x_4y_4) \\
 & - 2(P_xl_{3z} + P_zl_{3x})(p_{4x}p_{4z} + x_4z_4) \\
 & - 2(P_yl_{3z} + P_zl_{3y})(p_{4y}p_{4z} + y_4z_4) - (\mathbf{P}\cdot\mathbf{1}_3)(p_4^2 + r_4^2),
 \end{aligned} \tag{17}$$

$$\begin{aligned}
 O_{P333}(\text{tensor}) = & P_xl_{3x}[4(p_{3x}^2 + x_3^2) - (p_{3y}^2 + y_3^2) - (p_{3z}^2 + z_3^2)] \\
 & + P_yl_{3y}[4(p_{3y}^2 + y_3^2) - (p_{3x}^2 + x_3^2) - (p_{3z}^2 + z_3^2)] \\
 & + P_zl_{3z}[4(p_{3z}^2 + z_3^2) - (p_{3x}^2 + x_3^2) - (p_{3y}^2 + y_3^2)],
 \end{aligned}$$

$$\begin{aligned}
 O_{P322} &= \frac{P_x l_{3x}}{4} [(p_f^2 + f^2) - (p_e^2 + e^2) - 2\sqrt{3}(p_e p_f + ef)] \\
 &\quad + \frac{P_y l_{3y}}{4} [(p_f^2 + f^2) - (p_e^2 + e^2) + 2\sqrt{3}(p_e p_f + ef)] \\
 &\quad + \frac{P_z l_{3z}}{2} [(p_e^2 + e^2) - (p_f^2 + f^2)].
 \end{aligned}$$

The coefficients F_i are tabulated in Appendix I. The coefficients M_{ijk} and N_{ijk} are extremely complicated functions of both the cubic and quartic potential constants, and although their numerical value may be deduced from the experimentally observed rotational fine structures, these values will never be useful in the determination of the molecular parameters. For this reason these coefficients are not explicitly tabulated although one of the very simplest is given in Appendix I to illustrate their dependence on the potential constants. Third-order perturbation terms have to be included in order to get a good fit between theory and experiment and may even be important in making correct assignments of the rotational fine structure lines in regions where there is much overlapping of lines, but it is doubtful whether they give significant information about the molecule. Because of the breakdown of the Born–Oppenheimer approximation in this order it may in fact even be questioned whether the coefficients of these terms are meaningful when computed by the usual methods (12, 13). Because of symmetry considerations it may perhaps be expected that the omitted electronic-vibration-rotation corrections will give terms of the same general form and will thus merely alter the coefficients.

EVALUATION OF THE MATRIX ELEMENTS

The terms of the Hamiltonian, H' (diag), have been classified according to their irreducible spherical tensor character and will now be identified as tensors of rank k , with the possible values $k = 0, 3$, and 4 . The individual tensors are all built up from the vector \mathbf{P} and vectors such as \mathbf{r}_3 , \mathbf{p}_3 , and \mathbf{l}_3 . The spherical components of these vectors are given, for example, by

$$(r_3)_1 = -\frac{1}{\sqrt{2}}(x_3 + iy_3), \quad (r_3)_0 = z_3, \quad (r_3)_{-1} = \frac{1}{\sqrt{2}}(x_3 - iy_3).$$

On the other hand

$$P_1 = -\frac{1}{\sqrt{2}}(P_x - iP_y), \quad P_0 = P_z, \quad P_{-1} = \frac{1}{\sqrt{2}}(P_x + iP_y).$$

The anomalous sign before i is related to the anomalous sign in the commutation relations of the P_α . The vibration rotation tensor operators of rank k are built up from pure vibrational tensor operators of rank k_1 and commuting rotational

tensor operators of rank k_2 , where spherical vibration-rotational tensors of any rank k may be constructed by the usual vector coupling methods

$$T(k, q) = \sum_{q_1} \langle k_1 k_2 q_1 q_2 | k_1 k_2 k q \rangle T_{\text{vib}}(k_1 q_1) * T_{\text{rot}}(k_2 q_2) \text{ with } q_2 = (q - q_1). \quad (18)$$

The coefficients are the angular momentum *addition* coefficients. The anomalous complex conjugate sign arises from the anomalous behavior of the P_α and the related fact that the operators are to be applied to an angular momentum subtraction coupling scheme. [Compare with Eq. (3).] The vibrational and rotational tensor operators are themselves built up from the vibrational and rotational vectors by a repeated application of analogous vector coupling formulas.

Matrix elements of these tensor operators in the coupling scheme ($l J R$) are given by the Wigner-Eckart theorem

$$\begin{aligned} \langle v' l' J R' K_R' | T(kq) | v l J R K_R \rangle \\ = \frac{\langle R k K_R q | R k R' K_R' \rangle}{(2R' + 1)^{1/2}} \langle v' l' J R' || T(k) || v l J R \rangle. \end{aligned} \quad (19)$$

The dependence on K_R is given solely by the Clebsch-Gordan coefficient. The reduced or double-bar matrix element is a function only of the quantum numbers l, J, R , and v which stands as a collective label for the remaining vibrational quantum numbers. Since the A_1, A_2, E, F_1 , and F_2 fine structure components of a given vibration-rotation level differ only in their K_R values (the specific linear combinations of K_R values have been given by Jahn), it can now be seen that the relative splittings in the fine structure patterns are characterized solely by the rotational angular momentum quantum number, R . With $k = 0$ the Clebsch-Gordan coefficient is unity (independent of K_R). Scalar perturbation operators can therefore not split a vibration-rotation level into its fine structure components.

The reduced or double-bar matrix element can itself be written in terms of vibrational and rotational reduced matrix elements and a 9- j symbol.

$$\begin{aligned} \frac{\langle v' l' J R' || T(k) || v l J R \rangle}{[(2k + 1)(2R + 1)(2R' + 1)]^{1/2}} \\ = \left\{ \begin{matrix} l' & l & k_1 \\ J & J & k_2 \\ R' & R & k \end{matrix} \right\} \langle v' l' || T_{\text{vib}}(k_1) || v l \rangle \langle J || T_{\text{rot}}(k_2) || J \rangle. \end{aligned} \quad (20)$$

The notation of Edmonds (5) is used throughout this section. The 9- j symbol can be evaluated in terms of 6- j symbols (or Racah coefficients) which are tabulated by Edmonds. The matrix elements are diagonal in J , (P^2 commutes with H), but not in general diagonal in R and l . If the vibrational tensor operator

of rank k_1 is itself built up from operators of rank k_3 and k_4 which are in turn built up from vectors \mathbf{r}_3 , \mathbf{p}_3 , \mathbf{l}_3 and \mathbf{r}_4 , \mathbf{p}_4 , \mathbf{l}_4 , respectively, the vibrational reduced matrix element can be further written as a product of reduced matrix elements

$$\frac{\langle v'l' \| T_{\text{vib}}(k_1) \| vl \rangle}{[(2k_1 + 1)(2l + 1)(2l' + 1)]^{1/2}} = \begin{Bmatrix} l_3' & l_3 & k_3 \\ l_4' & l_4 & k_4 \\ l' & l & k_1 \end{Bmatrix} \langle v_3 l_3' \| T_{\text{vib}}(k_3) \| v_3 l_3 \rangle \langle v_4 l_4' \| T_{\text{vib}}(k_4) \| v_4 l_4 \rangle. \quad (21)$$

The pure vibrational perturbation operators O_{34} (scalar) and O_{34} (tensor) are examples of such operators with $k_3 = k_4 = 2$, and $k_1 = 0$ or 4 , respectively; ($k_2 = 0$). The matrix elements of the pure vibrational states are again given by the Wigner-Eckart theorem, where the m dependence is given solely by a Clebsch-Gordan coefficient.

SCALAR PERTURBATION OPERATORS. THE EFFECTIVE ROTATIONAL CONSTANTS OF THE INFRARED ACTIVE FUNDAMENTALS

The effective rotational constants of a vibration-rotation band are determined by the scalar perturbation terms. For states in which only quanta of ν_3 are excited, for example, the rotational constants are determined by the following scalar perturbation terms

$$\begin{aligned} H'(\text{scalar}, \nu_3) = & H_0 - 2B_s \zeta_3(\mathbf{P} \cdot \mathbf{l}_3) - D_s P^4 + Z_{3s} O_{PP33}(\text{scalar}) \\ & + F_{3s} P^2(\mathbf{P} \cdot \mathbf{l}_3) + \frac{1}{2} [Y_1(p_1^2 + q_1^2) + Y_2(p_2^2 + r_2^2) \\ & + Y_3(p_3^2 + r_3^2) + Y_4(p_4^2 + r_4^2)] P^2 \\ & + [M_{311}(p_1^2 + q_1^2) + M_{322}(p_2^2 + r_2^2) \\ & + M_{333}(p_3^2 + r_3^2) + M_{344}(p_4^2 + r_4^2)] (\mathbf{P} \cdot \mathbf{l}_3). \end{aligned} \quad (22)$$

The simplest type of scalar vibration-rotation perturbation operators are those which are themselves built up from scalar perturbation operators, that is those for which $k_1 = k_2 = k = 0$. Operators such as $(p_3^2 + r_3^2)P^2$ fall into this category. Examples of operators with $k_1 = k_2 = 1$, $k = 0$ are given by $P^2(\mathbf{P} \cdot \mathbf{l}_3)$, $(p_3^2 + r_3^2) \cdot (\mathbf{P} \cdot \mathbf{l}_3)$, and operators such as O_{P344} (scalar). In all but combination states of ν_3 and ν_4 their matrix elements can be written down at once. A third class of scalar perturbation operators are those with $k_1 = k_2 = 2$, $k = 0$. The operator O_{PP33} (scalar) is an example [as defined by Eq. (13) O_{PP33} (scalar) = $(5)^{1/2} T(00)$]. Since this operator contributes to the energy of the rotational levels of the fundamental ν_3 its matrix elements will be evaluated explicitly. With $k = 0$, the 9- j

symbol of Eq. (20) reduces to a single 6- j symbol and the matrix element is diagonal in R and K_R

$$\begin{aligned} & \langle v_3 l' J R K_R | O_{PP33} | v_3 l J R K_R \rangle \\ &= (-1)^{l+J+R} \begin{Bmatrix} l' & l & 2 \\ J & J & R \end{Bmatrix} \left\langle v_3 l' \parallel T_{\text{vib}} \left(2, \frac{p_3^2 + r_3^2}{2} \right) \parallel v_3 l \right\rangle \\ & \qquad \cdot \langle J \parallel T_{\text{rot}}(2) \parallel J \rangle. \end{aligned}$$

The reduced matrix elements are listed in Table IV. They have been computed by application of the Wigner-Eckart theorem to specific vibrational and rota-

TABLE IV
REDUCED MATRIX ELEMENTS

$\langle J \parallel T_{\text{rot}}(0) \parallel J \rangle = (2J + 1)^{1/2}$	$\langle l \parallel T_{\text{vib}}(0) \parallel l \rangle = (2l + 1)^{1/2}$
$\langle J \parallel T_{\text{rot}}(1) \parallel J \rangle = [J(J + 1)(2J + 1)]^{1/2}$	
$\langle J \parallel T_{\text{rot}}(2) \parallel J \rangle = \frac{1}{2(6)^{1/2}} [(2J - 1)2J(2J + 1)(2J + 2)(2J + 3)]^{1/2}$	
$\langle J \parallel T_{\text{rot}}(3) \parallel J \rangle = \frac{1}{4(10)^{1/2}} [(2J - 2)(2J - 1)2J(2J + 1)(2J + 2)(2J + 3)(2J + 4)]^{1/2}$	
$\langle J \parallel T_{\text{rot}}(4) \parallel J \rangle = \frac{1}{4(70)^{1/2}} [(2J - 3)(2J - 2)(2J - 1)$	$\cdot 2J(2J + 1)(2J + 2)(2J + 3)(2J + 4)(2J + 5)]^{1/2}$
$\langle v_3 l_3 \parallel T_{\text{vib}}(1, l_3) \parallel v_3 l_3 \rangle = [l_3(l_3 + 1)(2l_3 + 1)]^{1/2}$	
$\langle v_3 l_3 \parallel T_{\text{vib}}[2, (p_3^2 + r_3^2)/2] \parallel v_3 l_3 \rangle = -(2v_3 + 3) \left[\frac{l_3(l_3 + 1)(2l_3 + 1)}{6(2l_3 - 1)(2l_3 + 3)} \right]^{1/2}$	
$\langle v_3(l_3 - 2) \parallel T_{\text{vib}}[2, (p_3^2 + r_3^2)/2] \parallel v_3 l_3 \rangle = - \left[\frac{(v_3 + l_3 + 1)(v_3 - l_3 + 2)l_3(l_3 - 1)}{(2l_3 - 1)} \right]^{1/2}$	
$\langle v_3 l_3 \parallel T_{\text{vib}}[4, (p_3^2 + r_3^2)^2/4] \parallel v_3 l_3 \rangle$	$= \frac{[3(2v_3 + 3)^2 - (2l_3 - 1)(2l_3 + 3)][(2l_3 + 4)(2l_3 + 2)(2l_3 + 1)2l_3(2l_3 - 2)]^{1/2}}{8[70(2l_3 + 5)(2l_3 + 3)(2l_3 - 1)(2l_3 - 3)]^{1/2}}$
$\langle v_3(l_3 - 2) \parallel T_{\text{vib}}[4, (p_3^2 + r_3^2)^2/4] \parallel v_3 l_3 \rangle$	$= \frac{(2v_3 + 3)[(v_3 + l_3 + 1)(v_3 - l_3 + 2)(2l_3 + 2)2l_3(2l_3 - 2)(2l_3 - 4)]^{1/2}}{4[7(2l_3 - 5)(2l_3 - 1)(2l_3 + 3)]^{1/2}}$
$\langle v_3(l_3 - 4) \parallel T_{\text{vib}}[4, (p_3^2 + r_3^2)^2/4] \parallel v_3 l_3 \rangle$	$= \frac{[(v_3 - l_3 + 4)(v_3 - l_3 + 2)(v_3 + l_3 - 1)(v_3 + l_3 + 1)(2l_3 - 6)(2l_3 - 4)(2l_3 - 2)2l_3]^{1/2}}{4[(2l_3 - 5)(2l_3 - 3)(2l_3 - 1)]^{1/2}}$

tional tensor operators. Since the 6- j symbol is zero unless $(l', l, 2)$ satisfy the triangular condition of quantum vector addition the operator O_{PP33} does not contribute to the vibrational ground state energies ($l = l' = 0$). The 6- j symbols with $l, l' > 0$ can be evaluated from the tables of Edmonds (5). In the fundamental state ν_3 , with $l = l_3 = l'_3 = 1$, the operator O_{PP33} has the following eigenvalues

$$\begin{aligned} -\frac{1}{3}J(J+1) + \frac{1}{2}J & \quad \text{for states } R = J+1, \\ +\frac{2}{3}J(J+1) - \frac{1}{2} & \quad \text{for states } R = J, \\ -\frac{1}{3}J(J+1) - \frac{1}{2}(J+1) & \quad \text{for states } R = J-1. \end{aligned}$$

Since the eigenvalues of $(\mathbf{P} \cdot \mathbf{l}_3)$ are $-J, 1$, and $(J+1)$ for the states

$$R = (J+1), J, \quad \text{and } (J-1),$$

respectively, it can be seen that the operator O_{PP33} gives contributions to both the effective B -value (coefficient of the $J(J+1)$ term), and the effective $(B\zeta)$ -value (coefficient of the $(\mathbf{P} \cdot \mathbf{l}_3)$ term) of the fundamental state. It is to be noted, however, that the effective B -value for the J_J levels ($R = J$) differs from that of the J_{J+1} and J_{J-1} levels.

The eigenvalues of the operator $P^2(\mathbf{P} \cdot \mathbf{l}_3)$ can be written in similar fashion and are

$$\begin{aligned} -(J+1)^3 + 2J(J+1) + J & \quad + 1 \quad \text{for states } R = J+1, \\ J(J+1) - 1 & \quad + 1 \quad \text{for states } R = J, \\ + J^3 & \quad + 2J(J+1) - (J+1) + 1 \quad \text{for states } R = J-1, \end{aligned}$$

so that this operator contributes not only to the effective B and $(B\zeta)$ -values but also to the vibrational energy (through the constant $+1$) and to a term cubic in the angular momentum quantum numbers. Since the scalar centrifugal distortion term gives a contribution $+4D_s(J+1)^3$ to the allowed P -branch frequencies of the vibrational fundamentals (transitions to states J_{J+1}) and a contribution $-4D_sJ^3$ to the allowed R -branch frequencies (transitions to states J_{J-1}) while it does not affect the allowed Q -branch lines (transitions to states J_J), it can be seen that the operator $P^2(\mathbf{P} \cdot \mathbf{l}_3)$ in practice also makes a contribution to the effective D -value. The eigenvalues of the remaining operators of Eq. (22) can be written down at once and together with the above give the expression for the effective rotational constants of the infrared active fundamentals which are written out in Table V.

TENSOR PERTURBATION OPERATORS. THE SPLITTING PATTERNS

In a state in which only vibrational quanta of ν_1, ν_3 , and ν_4 are excited the splitting of the vibration-rotation levels into tetrahedral sublevels is governed

TABLE V

EFFECTIVE ROTATIONAL CONSTANTS OF THE INFRARED ACTIVE FUNDAMENTALS

Rotational constant	Value
$B_{\text{eff}} \quad v_3 = 1^* \quad R = (J - 1)$ or $(J + 1)$	$B_e + (\frac{1}{2})Y_1 + Y_2 + (\frac{3}{2})Y_4 + (\frac{5}{2})Y_3 - (\frac{1}{3})Z_{3s} + 2F_{3s}$
$B_{\text{eff}} \quad v_3 = 1 \quad R = J$	$B_e + (\frac{1}{2})Y_1 + Y_2 + (\frac{3}{2})Y_4 + (\frac{5}{2})Y_3 + (\frac{2}{3})Z_{3s} + F_{3s}$
$B_{\text{eff}} \quad v_3 = 0$	$B_e + (\frac{1}{2})Y_1 + Y_2 + (\frac{3}{2})Y_4 + (\frac{3}{2})Y_3$
$(B_{3s}^{\dagger})_{\text{eff}} \quad v_3 = 1$	$B_e \delta_3 - (\frac{1}{2})M_{311} - M_{322} - (\frac{3}{2})M_{344} - (\frac{5}{2})M_{333} + (\frac{1}{4})Z_{3s}$ + $(\frac{1}{2})F_{3s}$
D_{eff}	$D_s - (\frac{1}{4})F_{3s}$

* Constants for the fundamental $v_4 = 1$ are obtained from the above through an interchange of the indices 3 and 4.

solely by the fourth-rank tensor operators. In states in which only vibrational quanta of v_3 are excited, for example, the splitting patterns are determined entirely by the following perturbation terms

$$H'(4, v_3) = -D_t O_{PPPP}(\text{tensor}) + F_{3t} O_{PPP3}(\text{tensor}) + Z_{3t} O_{PP33}(\text{tensor}) \\ + N_{333t} O_{P333}(\text{tensor}) + T_{33} O_{33}(\text{tensor}), \quad (23)$$

where the operators, which are defined by Eqs. (8) through (17), are all normalized in the same way and are of the basic type

$$\{(2 \cdot 5 \cdot 7)^{1/2} T(40) + 5[T(44) + T(4-4)]\}.$$

They are again built up from vibrational operators of rank k_1 and rotational operators of rank k_2 . In $O_{PPPP} k_1 = 0, k_2 = 4$; in $O_{PPP3} k_1 = 1, k_2 = 3$; in $O_{PP33} k_1 = 2, k_2 = 2$; in $O_{P333} k_1 = 3, k_2 = 1$; while in $O_{33} k_1 = 4, k_2 = 0$. The matrix elements of these operators between states $vlJR$ and $v'l'JR'$ are zero unless (l', l, k_1) satisfy the triangular condition of quantum vector addition. In the vibrational ground state therefore the only operator with nonzero matrix elements is the operator O_{PPPP} since $l' = l = 0$ implies $k_1 = 0$. The splitting patterns of the vibrational ground state are therefore governed solely by this operator and increase essentially in proportion to J^4 . With $k_1 = 0, l' = l = 0, R = J$, the 9-j symbol of Eq. (20) reduces to $\frac{1}{3}(2J + 1)$. The reduced matrix elements are given in Table IV, and the nonzero matrix elements of O_{PPPP} in the vibrational ground state become

$$\langle 0JJK | O_{PPPP} | 0JJK \rangle = g_{0J}(J; J) \langle J4K0 | J4JK \rangle, \\ \langle 0JJ(K \pm 4) | O_{PPPP} | 0JJK \rangle \\ = g_{0J}(J; J) (\frac{5}{14})^{1/2} \langle J4K(\pm 4) | J4J(K \pm 4) \rangle. \quad (24)$$

with

$$g_{0J} = [(2J - 3)(J - 1)(2J - 1)J(J + 1)(2J + 3)(J + 2)(2J + 5)]^{1/2}.$$

In the state of the vibrational fundamental, $l = l' = 1$. The triangular condition is satisfied only by operators with $k_1 = 0, 1$, or 2 , hence only by the operators O_{PPPP} , O_{PPP3} , and O_{PP33} . The operators O_{P333} and O_{33} cannot contribute to the energies of ν_3 . With the reduced matrix elements of Table IV and the 9- j symbols evaluated through the use of the 6- j symbols tabulated by Edmonds (5), the nonzero matrix elements of the tensor operators for the state $\nu_3 = 1$ become

$$\begin{aligned} \langle 1JR'K_R | H'(4) | 1JRK_R \rangle &= f_{1J}(R'; R) \langle R4K_{R0} | R4R'K_R \rangle, \\ \langle 1JR'(K_R \pm 4) | H'(4) | 1JRK_R \rangle &= f_{1J}(R'; R) (\xi'_{14})^{1/2} \langle R4K_R(\pm 4) | R4R'(K_R \pm 4) \rangle, \end{aligned} \quad (25)$$

in which the coefficients $f_{1J}(R'; R)$ are listed in Table VI as functions of the pos-

TABLE VI
 $f_{1J}(R'; R) = g_{1J}(R'; R) \{ \sum l_{ijk} f_{ijk}(J, R', R) \}$

R'	R	$f_{1J}(R'; R)$
$(J + 1)$	$(J + 1)$	$\left[\frac{(2J + 7)(2J + 6)(2J + 5)(2J + 4)2J(2J - 1)}{(2J + 1)(2J + 2)} \right]^{1/2}$ $\{ \frac{1}{2}(2J^2 - 5J + 3)t_{044} + (J - 1)t_{134} - t_{224} \}$
J	$(J + 1)$	$-\left[\frac{5(2J + 6)(2J + 5)(2J + 4)(2J + 3)(2J - 1)(2J - 2)}{2(2J + 1)(2J + 2)} \right]^{1/2}$ $\{ (2J - 3)t_{044} - \frac{1}{2}(J - 3)t_{134} + t_{224} \}$
$(J - 1)$	$(J + 1)$	$\left[\frac{5(2J + 5)(2J + 4)(2J + 3)(2J - 2)(2J - 3)}{2(2J + 1)} \right]^{1/2}$ $\{ 3t_{044} - \frac{3}{2}t_{134} - t_{224} \}$
J	J	$\left[\frac{(2J + 5)(2J + 4)(2J + 3)(2J - 1)(2J - 2)(2J - 3)}{2J(2J + 2)} \right]^{1/2}$ $\{ (J^2 + J - 10)t_{044} + 4t_{134} + 2t_{224} \}$
$(J - 1)$	J	$-\left[\frac{5(2J + 4)(2J + 3)(2J - 2)(2J - 3)(2J - 4)}{2 \cdot 2J} \right]^{1/2}$ $\{ (2J + 5)t_{044} - \frac{1}{2}(J + 4)t_{134} - t_{224} \}$
$(J - 1)$	$(J - 1)$	$\left[\frac{(2J + 3)(2J + 2)(2J - 2)(2J - 3)(2J - 4)(2J - 5)}{2J(2J + 1)} \right]^{1/2}$ $\left\{ \frac{(2J^2 + 9J + 10)}{2} t_{044} - (J + 2)t_{134} - t_{224} \right\}$

sible rotational angular momentum quantum numbers R and R' . It is convenient to use the following notation in addition:

$$f_{1J}(R'; R) = g_{1J}(R'; R) \left\{ \sum_{ijk} t_{ijk} f_{ijk}(J, R', R) \right\},$$

in which the t_{ijk} are the coefficients of the perturbation operators with subscripts $i = k_1$, $j = k_2$, and $k = 4$ to indicate their specific tensor character. To third order of approximation $t_{044} = -D_t$, $t_{134} = F_{3t}$, and $t_{224} = Z_{3t}$. The Clebsch-Gordan coefficients which occur in Eqs. (24) and (25) are given as functions of J and K in Table VII. The matrix elements of the Hamiltonian, $H'(4)$, can connect only vibration-rotational substates of the same tetrahedral symmetry, for example A_1 states with A_1 , E_e states with E_e , \dots . Tetrahedrally irreducible harmonic functions have been tabulated by Jahn (9) up to the tenth angular momentum quantum number. Since they involve specific linear combinations of the vibration-rotation wave functions, ψ_{RK_R} , with different values of K_R , the matrix elements of $H'(4)$ between the tetrahedral substates always involve

TABLE VII
CLEBSCH-GORDAN COEFFICIENTS

$$\langle J4K0 | J4JK \rangle = \frac{6J(J-1)(J+1)(J+2) - 10K^2(6J^2 + 6J - 5) + 70K^4}{[(2J+5)(2J+4)(2J+3)(2J+2)2J(2J-1)(2J-2)(2J-3)]^{1/2}}$$

$$\langle J4K0 | J4(J-1)K \rangle = \frac{K(3J^2 - 5 - 7K^2)[5(J-K)(J+K)]^{1/2}}{[(2J+4)(2J+3)(J+1)(2J+1)J(J-1)(2J-3)(J-2)]^{1/2}}$$

$$\langle (J+1)4K0 | (J+1)4(J-1)K \rangle = \frac{-2(J^2 + J - 2 - 7K^2)[10(J-K)(J+K)(J-K+1)(J+K+1)]^{1/2}}{[(2J+5)(2J+4)(2J+3)(2J+2)(2J+1)2J(2J-2)(2J-3)]^{1/2}}$$

$$\langle J4(K+4) -4 | J4JK \rangle = \frac{[70(J-K)(J-K-1)(J-K-2)(J-K-3)(J+K+1)(J+K+2)(J+K+3)(J+K+4)]^{1/2}}{[(2J+5)(2J+4)(2J+3)(2J+2)2J(2J-1)(2J-2)(2J-3)]^{1/2}}$$

$$\langle J4(K+4) -4 | J4(J-1)K \rangle = \frac{2[14(J+K)(J+K+1)(J+K+2)(J+K+3)(J+K+4)(J-K-1)(J-K-2)(J-K-3)]^{1/2}}{[(2J+4)(2J+3)(2J+2)(2J+1)2J(2J-2)(2J-3)(2J-4)]^{1/2}}$$

$$\langle (J+1)4(K+4) -4 | (J+1)4(J-1)K \rangle = \frac{2[7(J+K)(J+K+1)(J+K+2)(J+K+3)(J+K+4)(J+K+5)(J-K-1)(J-K-2)]^{1/2}}{[(2J+5)(2J+4)(2J+3)(2J+2)(2J+1)2J(2J-2)(2J-3)]^{1/2}}$$

specific linear combinations of the Clebsch–Gordan coefficients of Eqs. (24) and (25). For example, the wave function for the state $3_4 F_{2z}$ the (F_{2z} vibration-rotational substate of the level with $J = 3$, $R = 4$) has the form

$$\frac{1}{i\sqrt{2}} (\psi_{4-2} - \psi_{42}). \quad (26)$$

The matrix element, diagonal in R , for this particular substate, is therefore proportional to the following linear combination of Clebsch–Gordan coefficients

$$g_{13}(4; 4) \cdot \frac{1}{2} \left\{ \begin{aligned} &\langle 44 - 20 | 444 - 2 \rangle + \langle 4420 | 4442 \rangle \\ & - (5/4)^{1/2} [\langle 44 - 24 | 4442 \rangle + \langle 442 - 4 | 444 - 2 \rangle] \end{aligned} \right\} \quad (27)$$

with the numerical value $-(390/7)$. Numerical values such as this one are given in Table VIII where the numbers listed are $g_{1J}(R'; R)$ multiplied by the specific linear combinations of Clebsch–Gordan coefficients required by the symmetry of the tetrahedral substate. Only matrix elements connecting states J_{J+1} with J_{J+1} , J_J , and J_{J-1} are tabulated, since matrix elements connecting states $(J+1)_{J+1}$ with $(J+1)_{J+1}$ and $(J+1)_J$, for example, or those connecting states $(J+2)_{J+1}$ with $(J+2)_{J+1}$ involve exactly the same linear combinations of Clebsch–Gordan coefficients as those listed and differ from the numbers given in Table VIII only by the ratios of the g_{1J} values. For example, the wave functions for the states $5_4 F_{2z}$ and $4_4 F_{1z}$, with $R = 4$, also involve the linear combination of K_R values of Eq. (26).⁵ The matrix elements, diagonal in R , for these two states are therefore given by $(g_{15}/g_{13})(-390/7)$ and $(g_{14}/g_{13})(-390/7)$, respectively.

As an example the complete Hamiltonian matrix for the substates F_2 of $J = 3$ is exhibited on page 378 (I).

If the values of the t_{ijk} are small compared with $B\zeta J$; that is, if the elements off-diagonal in R are small compared with the differences between the diagonal matrix elements, the energies of the three states $3_R F_2$ are given to good approximation by the diagonal matrix elements. The off-diagonal matrix elements give contributions to the energies of the order of $(B^3/\zeta\omega^2)J^3$, a quantity which is formally of third order in the Nielsen *et al.* (12, 13) ordering scheme; but the off-diagonal matrix elements may in some cases give sizable contributions to the energies. In dominant approximation, in which the off-diagonal matrix elements are neglected, the tetrahedral substate $3_4 F_2$ is split from its unperturbed position by an amount $-(390/7)(3t_{044} + 2t_{134} - t_{224})$. From Table VIII it can be seen

⁵ It must be remembered that the wave functions for states 3_4 and 5_4 with $J + l_3$ even transform according to D_p^4 , whereas those for 4_4 with $J + l_3$ odd transform according to D_u^4 . Those linear combinations of spherical harmonics which transform according to F_2 in a g representation transform according to F_1 in a u representation and vice versa. A change from g to u also involves an interchange of A_1 with A_2 and E_g with E_f .

J_R	3_4F_2	3_3F_2	3_2F_2
$J_{R'}$			
3_4F_2	$12B_{\text{eff}} - 144D + 6B\zeta$ $- \frac{390}{7} (3t_{044} + 2t_{134} - t_{244})$	$\frac{i150}{(7)^{1/2}} (3t_{044} + t_{224})$	$\frac{60(5)^{1/2}}{7} \left(3t_{044} - \frac{3}{2} t_{134} - t_{224} \right)$
3_3F_2	$- \frac{i150}{(7)^{1/2}} (3t_{044} + t_{224})$	$12B'_{\text{eff}} - 144D - 2B\zeta$ $- 5(2t_{044} + 4t_{134} + 2t_{224})$	$- \frac{i20(5)^{1/2}}{(7)^{1/2}} \left(11t_{044} - \frac{7}{2} t_{134} - t_{224} \right)$
3_2F_2	$\frac{60(5)^{1/2}}{7} \left(3t_{044} - \frac{3}{2} t_{134} - t_{224} \right)$	$\frac{i20(5)^{1/2}}{(7)^{1/2}} \left(11t_{044} - \frac{7}{2} t_{134} - t_{224} \right)$	$12B_{\text{eff}} - 144D - 8B\zeta$ $- \frac{16}{7} \left(\frac{55}{2} t_{044} - 5t_{134} - t_{224} \right)$

(D)

TABLE VIII
MATRIX ELEMENTS OF FOURTH-RANK TENSORS^a

l_0		l_1		l_2		l_3		l_4	
A_1	F_1	A_1	F_1	A_1	F_1	A_1	F_1	A_1	F_1
l_0	0	0	0	0	0	0	0	0	0
l_1	0	0	0	0	0	0	0	0	0
l_2	0	0	0	0	0	0	0	0	0
l_3	0	0	0	0	0	0	0	0	0
l_4	0	0	0	0	0	0	0	0	0

2_3	A_1	F_1	F_2
2_3	-4/8	-8	24
2_2		$i20/\sqrt{2}$	
2_1			$-4/\sqrt{6}$

3_4	A_1	E	F_1	F_2
3_4	60	60	30	$-390/7$
3_3			$-i10/\sqrt{15}$	$-i150/\sqrt{7}$
3_2			$-i20/\sqrt{5}$	$60/\sqrt{7}$

4_5	A_1	A_2	E	F_1	$F_2^{(1)}$	$F_2^{(2)}$
$4_5^{(1)}$	$-i260/11$	60	$1140/11$	$-960/11$	$-590/11$	$30/\sqrt{5}$
$4_5^{(2)}$					$30/\sqrt{5}$	90
4_4			$i20/\sqrt{2}$	$-i60/\sqrt{35}$	$-i170/\sqrt{10}$	$-i30/\sqrt{2}$
4_3				$i60/\sqrt{11}$		

5_6	A_1	A_2	E	F_1	$F_2^{(1)}$	$F_2^{(2)}$
$5_6^{(1)}$	$-240/\sqrt{35}$		$-240/\sqrt{7}$	$420/\sqrt{6}$	$-60/\sqrt{35}$	$60/\sqrt{7}$
$5_6^{(2)}$						

6_7	A_1	E	$F_1^{(1)}$	$F_1^{(2)}$	$F_2^{(1)}$	$F_2^{(2)}$
$6_7^{(1)}$	$-i248/91$	$-8448/91$	$10572/91$	$300/\sqrt{143}$	$9072/91$	$600/\sqrt{231}$
$6_7^{(2)}$			$300/\sqrt{143}$	$-5148/91$	$600/\sqrt{231}$	$-8448/91$
6_6		$i1200/\sqrt{35}$	$i50/\sqrt{30}$	$i30/\sqrt{330}$	$-i300/\sqrt{6}$	$i300/\sqrt{22}$
$6_6^{(1)}$		$7/\sqrt{13}$	$7/\sqrt{13}$	7	$\sqrt{91}$	$7/\sqrt{13}$
$6_6^{(2)}$		$-i50/\sqrt{66}$	$-i50/\sqrt{66}$			
6_5		$-360/\sqrt{110}$	$180/\sqrt{15}$	$60/\sqrt{165}$	$-200/\sqrt{42}$	$300/\sqrt{22}$
$6_5^{(1)}$		$13/\sqrt{7}$	$13/\sqrt{7}$	$\sqrt{91}$	13	13
$6_5^{(2)}$					$60/\sqrt{30}$	$360/\sqrt{110}$

7_8	A_1	$E^{(1)}$	$E^{(2)}$	$F_1^{(1)}$	$F_1^{(2)}$	$F_2^{(1)}$	$F_2^{(2)}$
$7_8^{(1)}$	196	1596	$640/\sqrt{15}$	$-84/\sqrt{455}$	-91	$21/\sqrt{15}$	$2/\sqrt{21}$
$7_8^{(2)}$		$840/\sqrt{15}$	$-728/31$	$\sqrt{455}$	182	$21/\sqrt{15}$	$-273/2$
7_7		$i120/\sqrt{55}$	$-i160/\sqrt{55}$	$-i15/\sqrt{65}$	0	$-i1425/2$	$-i15/\sqrt{715}$
$7_7^{(1)}$		$\sqrt{51}$	$\sqrt{217}$	$-i15/\sqrt{13}$		$2/\sqrt{7}$	$2/\sqrt{3}$
$7_7^{(2)}$				$-i150/\sqrt{5}$		$115/\sqrt{143}$	$i195/\sqrt{5}$
7_6		$-888/\sqrt{51}$	$40/\sqrt{2145}$	$58/\sqrt{22}$	$2/\sqrt{430}$	$-270/\sqrt{3}$	$3/\sqrt{430}$
$7_6^{(1)}$			$\sqrt{217}$			$\sqrt{14}$	$\sqrt{330}$
$7_6^{(2)}$						$\sqrt{7}$	$33/\sqrt{26}$

^a The numbers tabulated are $g_{J_1}(R, R)$ times the linear combination of Clebsch-Gordan coefficients required by the symmetry.

TABLE VIII—Continued

8_9	A_1	A_2	E	$F_1^{(1)}$	$F_1^{(2)}$	$F_2^{(1)}$	$F_2^{(2)}$	$F_2^{(3)}$
8_9 (1)	$\frac{-3,720}{17}$	$\frac{-4,760}{51}$	$\frac{40}{51}$	$\frac{11,140}{51}$	$\frac{700\sqrt{13}}{17\sqrt{3}}$	$\frac{2,640}{17}$	$\frac{40\sqrt{5,005}}{17}$	0
(2)				$\frac{700\sqrt{13}}{17\sqrt{3}}$	$\frac{-3,020}{17}$	$\frac{40\sqrt{5,005}}{17}$	$\frac{-1,120}{17}$	$\frac{200\sqrt{7}}{3\sqrt{17}}$
(3)						0	$\frac{200\sqrt{7}}{3\sqrt{17}}$	$\frac{-1,360}{51}$
8_8 (1)		$\frac{i40\sqrt{455}}{3}$	$\frac{-i280\sqrt{715}}{\sqrt{1581}}$	$\frac{-i25\sqrt{154}}{3\sqrt{17}}$	$\frac{-i25\sqrt{2,002}}{\sqrt{51}}$	$\frac{i10\sqrt{3,850}}{\sqrt{17}}$	$\frac{-i70\sqrt{130}}{\sqrt{17}}$	$\frac{-i10\sqrt{910}}{3}$
(2)			$\frac{-i8,200\sqrt{7}}{3\sqrt{527}}$	$\frac{i35\sqrt{130}}{\sqrt{51}}$	$\frac{i35\sqrt{10}}{\sqrt{17}}$	0	$\frac{+i50\sqrt{14}}{\sqrt{17}}$	$\frac{i700\sqrt{2}}{3}$
8_7 (1)	$\frac{-40\sqrt{15,015}}{17}$		$\frac{-120\sqrt{455}}{17}$	$\frac{-5\sqrt{2,310}}{17}$	$\frac{25\sqrt{10,010}}{17}$	$\frac{2,100\sqrt{2}}{17}$	$\frac{30\sqrt{10,010}}{17}$	0
(2)				$\frac{5\sqrt{2,730}}{17}$	$\frac{455\sqrt{70}}{17}$	$\frac{50\sqrt{462}}{17}$	$\frac{70\sqrt{390}}{17}$	$\frac{10\sqrt{2,730}}{\sqrt{17}}$

9_{10}	A_1	A_2	$E^{(1)}$	$E^{(2)}$	$F_1^{(1)}$	$F_1^{(2)}$	$F_2^{(1)}$	$F_2^{(2)}$	$F_2^{(3)}$
9_{10} (1)	$\frac{-1,980}{19}$	300	$\frac{7,164}{29}$	$\frac{2,016\sqrt{2,210}}{19\cdot 29}$	$\frac{-780}{19}$	$\frac{180\sqrt{51}}{19}$	$\frac{-660}{19}$	$\frac{420\sqrt{26}}{19}$	0
(2)			$\frac{2,016\sqrt{2,210}}{19\cdot 29}$	$\frac{-86,700}{19\cdot 29}$	$\frac{180\sqrt{51}}{19}$	$\frac{-3,060}{19}$	$\frac{420\sqrt{26}}{19}$	$\frac{-3,690}{19}$	$\frac{6\sqrt{255}}{\sqrt{19}}$
(3)							0	$\frac{6\sqrt{255}}{\sqrt{19}}$	306
9_9 (1)	$\frac{-i48\sqrt{1,309}}{\sqrt{19}}$	$i16\sqrt{39}$	$\frac{-i336\sqrt{65}}{\sqrt{551}}$	$\frac{i1,489\sqrt{17}}{\sqrt{1,102}}$	$\frac{-i28\sqrt{2,145}}{\sqrt{19}}$	0	$\frac{-i686\sqrt{6}}{\sqrt{19}}$	$\frac{-i140\sqrt{39}}{\sqrt{19}}$	0
(2)					$\frac{-i244\sqrt{21}}{\sqrt{19}}$	$\frac{-i60\sqrt{119}}{\sqrt{19}}$	$\frac{i70\sqrt{26}}{\sqrt{19}}$	$\frac{-i344}{\sqrt{19}}$	$\frac{-i4\sqrt{255}}{\sqrt{19}}$
(3)					$\frac{i20\sqrt{51}}{\sqrt{19}}$	$\frac{i1,224}{\sqrt{19}}$			
9_8 (1)	$\frac{-480\sqrt{143}}{19}$		$\frac{-480\sqrt{165}}{899}$	$\frac{1,120\sqrt{14,586}}{19\cdot 899}$	$\frac{40\sqrt{546}}{19}$	$\frac{60\sqrt{3,094}}{19}$	$\frac{-140\sqrt{1,155}}{19}$	$\frac{20\sqrt{30,030}}{19}$	0
(2)			$\frac{4,800\sqrt{91}}{19\cdot 899}$	$\frac{360\sqrt{1,190}}{19\cdot 899}$	$\frac{20\sqrt{30}}{19}$	$\frac{360\sqrt{170}}{19}$	$\frac{140\sqrt{13}}{19}$	$\frac{3,280\sqrt{2}}{19}$	$\frac{20\sqrt{510}}{\sqrt{19}}$

10_{11}	A_1	$E^{(1)}$	$E^{(2)}$	$F_1^{(1)}$	$F_1^{(2)}$	$F_1^{(3)}$	$F_2^{(1)}$	$F_2^{(2)}$	$F_2^{(3)}$
10_{11} (1)	$\frac{5,360}{77}$	$\frac{-878,000}{8,239}$	$\frac{960\sqrt{33,915}}{1,177}$	$\frac{2,400}{7}$	$\frac{120\sqrt{170}}{11}$	0	$\frac{17,160}{77}$	$\frac{600\sqrt{13}}{\sqrt{77}}$	0
(2)		$\frac{960\sqrt{33,915}}{1,177}$	$\frac{-177,840}{1,177}$	$\frac{120\sqrt{170}}{11}$	$\frac{-14,940}{77}$	$\frac{300\sqrt{19}}{11\sqrt{7}}$	$\frac{600\sqrt{13}}{\sqrt{77}}$	$\frac{-120}{11}$	$\frac{40\sqrt{4,845}}{11\sqrt{7}}$
(3)				0	$\frac{300\sqrt{19}}{11\sqrt{7}}$	$\frac{380}{11}$	0	$\frac{40\sqrt{4,845}}{11\sqrt{7}}$	$\frac{-19,000}{77}$
10_{10} (1)	$\frac{-i480\sqrt{969}}{11\sqrt{7}}$	$\frac{i50,400\sqrt{39}}{11\sqrt{21,721}}$	$\frac{i1,440\sqrt{20,995}}{11\sqrt{3,103}}$	0	$\frac{i40\sqrt{4,641}}{11}$	0	$\frac{-i60\sqrt{182}}{\sqrt{11}}$	$\frac{i2,460\sqrt{2}}{11}$	$\frac{i60\sqrt{9,690}}{11\sqrt{7}}$
(2)		$\frac{i4,800\sqrt{510}}{\sqrt{21,721}}$	$\frac{i10,920\sqrt{38}}{11\sqrt{3,103}}$	$\frac{-i120\sqrt{105}}{11}$	$\frac{i530\sqrt{102}}{11\sqrt{7}}$	$\frac{i30\sqrt{1,938}}{11}$	0	$\frac{-i60\sqrt{102}}{11}$	$\frac{-i360\sqrt{190}}{11\sqrt{7}}$
(3)				0	$\frac{-i30\sqrt{190}}{11\sqrt{7}}$	$\frac{-i1,710\sqrt{10}}{11}$			
10_9 (1)	$\frac{-240\sqrt{663}}{7\sqrt{11}}$	$\frac{-3,960\sqrt{50}}{7\sqrt{77}}$	$\frac{80\sqrt{6,783}}{\sqrt{1,177}}$	$\frac{-100\sqrt{195}}{7\sqrt{11}}$	$\frac{20\sqrt{1,326}}{\sqrt{11}}$	0	$\frac{-180\sqrt{110}}{7}$	$\frac{60\sqrt{130}}{\sqrt{7}}$	0
(2)				$\frac{60\sqrt{5}}{\sqrt{11}}$	$\frac{960\sqrt{34}}{7\sqrt{11}}$	$\frac{60\sqrt{646}}{\sqrt{77}}$	$\frac{60\sqrt{26}}{\sqrt{7}}$	$\frac{20\sqrt{2}}{\sqrt{11}}$	$\frac{20\sqrt{9,690}}{\sqrt{77}}$
(3)							0	$\frac{20\sqrt{34}}{\sqrt{77}}$	$\frac{340\sqrt{570}}{7\sqrt{11}}$

TABLE VIII—Continued

I_{12}	$A_1^{(1)}$	$A_1^{(2)}$	A_2	$E^{(1)}$	$E^{(2)}$	$F_1^{(1)}$	$F_1^{(2)}$	$F_1^{(3)}$	$F_2^{(1)}$	$F_2^{(2)}$	$F_2^{(3)}$
I_{12} (1)	$\frac{-1,706,796}{4,715}$	$\frac{-24\sqrt{1,939,938}}{205\sqrt{23}}$	$\frac{-6,244}{23}$	$\frac{-235,676}{23 \cdot 89}$	$\frac{120\sqrt{49,742}}{23 \cdot 89}$	$\frac{546}{23}$	$\frac{25\sqrt{13,566}}{23}$	0	$\frac{-504}{23}$	$\frac{150\sqrt{714}}{23}$	0
I_{12} (2)	$\frac{-24\sqrt{1,939,938}}{205\sqrt{23}}$	$\frac{95,172}{205}$		$\frac{120\sqrt{49,742}}{23 \cdot 89}$	$\frac{943,404}{23 \cdot 89}$	$\frac{25\sqrt{13,566}}{23}$	$\frac{-6,874}{23}$	$\frac{5\sqrt{462}}{\sqrt{23}}$	$\frac{150\sqrt{714}}{23}$	$\frac{-4,179}{23}$	$\frac{25\sqrt{4,389}}{23}$
I_{12} (3)	$\frac{205\sqrt{23}}{205\sqrt{23}}$			$\frac{23 \cdot 89}{23 \cdot 89}$	$\frac{23 \cdot 89}{23 \cdot 89}$	0	$\frac{5\sqrt{462}}{\sqrt{23}}$	$\frac{10,626}{23}$	0	$\frac{25\sqrt{4,389}}{23}$	$\frac{-3,619}{23}$
I_{11} (1)			$\frac{i,600\sqrt{14}}{\sqrt{253}}$	$\frac{-i,141,680\sqrt{5}}{\sqrt{89 \cdot 107 \cdot 253}}$	$\frac{-i,240\sqrt{22,610}}{\sqrt{23 \cdot 89 \cdot 107}}$	$\frac{-i,150\sqrt{182}}{\sqrt{23}}$	0	0	$\frac{-i,1380\sqrt{35}}{\sqrt{253}}$	$\frac{-i,210\sqrt{510}}{\sqrt{253}}$	0
I_{11} (2)				$\frac{-i,9,600\sqrt{6,783}}{\sqrt{89 \cdot 107 \cdot 253}}$	$\frac{i,6,400\sqrt{6}}{\sqrt{23 \cdot 89 \cdot 107}}$	$\frac{-i,4,200\sqrt{2}}{\sqrt{253}}$	$\frac{-i,50\sqrt{6,783}}{\sqrt{253}}$	0	$\frac{i,150\sqrt{238}}{\sqrt{253}}$	$\frac{-i,2,625\sqrt{5}}{\sqrt{253}}$	$\frac{-i,75\sqrt{133}}{\sqrt{23}}$
I_{11} (3)				$\frac{\sqrt{89 \cdot 107 \cdot 253}}{\sqrt{89 \cdot 107 \cdot 253}}$	$\frac{\sqrt{23 \cdot 89 \cdot 107}}{\sqrt{23 \cdot 89 \cdot 107}}$	$\frac{i,5\sqrt{67,830}}{\sqrt{253}}$	$\frac{i,280\sqrt{5}}{\sqrt{253}}$	$\frac{-i,5\sqrt{210}}{\sqrt{253}}$	0	$\frac{i,25\sqrt{399}}{\sqrt{253}}$	$\frac{i,2,275}{\sqrt{23}}$
I_{10} (1)	$\frac{6,408\sqrt{130}}{23\sqrt{41}}$	$\frac{-8\sqrt{373,065}}{\sqrt{23 \cdot 41}}$	$\frac{120\sqrt{33,915}}{23\sqrt{11}}$	$\frac{186,600\sqrt{78}}{23\sqrt{89 \cdot 319}}$	$\frac{200\sqrt{88,179}}{23\sqrt{29 \cdot 89}}$	$\frac{-360\sqrt{70}}{23\sqrt{11}}$	$\frac{300\sqrt{4,845}}{23\sqrt{11}}$	0	$\frac{-840\sqrt{1365}}{23\sqrt{11}}$	$\frac{420\sqrt{2,210}}{23\sqrt{11}}$	0
I_{10} (2)				$\frac{-28,560\sqrt{255}}{23\sqrt{89 \cdot 319}}$	$\frac{-1,920\sqrt{3,990}}{23\sqrt{29 \cdot 89}}$	$\frac{30\sqrt{3,570}}{23\sqrt{11}}$	$\frac{3180\sqrt{95}}{23\sqrt{11}}$	$\frac{10\sqrt{3,990}}{23}$	$\frac{300\sqrt{210}}{23\sqrt{11}}$	$\frac{1,830\sqrt{85}}{23\sqrt{11}}$	$\frac{30\sqrt{3,915}}{23}$
I_{10} (3)									0	$\frac{50\sqrt{57}}{23\sqrt{11}}$	$\frac{2,850\sqrt{7}}{23}$

TABLE VIII—Continued

12_{13}	A_1	A_2	$E^{(1)}$	$E^{(2)}$	$F_1^{(1)}$	$F_1^{(2)}$	$F_1^{(3)}$	$F_2^{(1)}$	$F_2^{(2)}$	$F_2^{(3)}$	$F_2^{(4)}$
(1)	$\frac{-14,424}{65}$	$\frac{7,080}{65}$	$\frac{58,920}{1,105}$	$\frac{-576\sqrt{144,210}}{1,105}$	$\frac{31,800}{65}$	$\frac{72\sqrt{35,530}}{65}$	0	$\frac{19,656}{65}$	$\frac{120\sqrt{2,618}}{5\sqrt{13}}$	0	0
(2)			$\frac{-576\sqrt{144,210}}{1,105}$	$\frac{-330,648}{1,105}$	$\frac{72\sqrt{35,530}}{65}$	$\frac{-10,404}{65}$	$\frac{84\sqrt{253}}{13}$	$\frac{120\sqrt{2,618}}{5\sqrt{13}}$	$\frac{4,056}{65}$	$\frac{756\sqrt{190}}{65}$	0
(3)					0	$\frac{84\sqrt{253}}{13}$	$\frac{-19,044}{65}$	0	$\frac{756\sqrt{190}}{65}$	$\frac{-21,240}{65}$	$\frac{12\sqrt{2,530}}{13}$
(4)								0	0	$\frac{12\sqrt{2,530}}{13}$	$\frac{8,280}{65}$
(1)	$\frac{i12\sqrt{3,553}}{13}$	$\frac{-i72\sqrt{4,522}}{\sqrt{535}}$	$\frac{-i888\sqrt{770}}{13\sqrt{89}}$	$\frac{-i240\sqrt{9,177}}{13\sqrt{89}}$	$\frac{-i72\sqrt{55}}{13}$	$\frac{i180\sqrt{646}}{13}$	0	$\frac{-i60\sqrt{462}}{\sqrt{13}}$	$\frac{i780\sqrt{51}}{13}$	$\frac{i42\sqrt{9,690}}{13}$	0
(2)		$\frac{-i2,008\sqrt{759}}{13\sqrt{41}}$	$\frac{i30,888\sqrt{95}}{13\sqrt{1,513}}$	$\frac{-i424\sqrt{1,518}}{13\sqrt{1,513}}$	$\frac{-i168\sqrt{2,805}}{13\sqrt{14}}$	$\frac{i250\sqrt{399}}{13}$	$\frac{i10\sqrt{100,947}}{13}$	0	$\frac{-190\sqrt{266}}{13}$	$\frac{i216\sqrt{35}}{13}$	$\frac{i30\sqrt{3,542}}{13}$
(3)					0	$\frac{-i210\sqrt{11}}{13}$	$\frac{-i990\sqrt{23}}{13}$	0	0	$\frac{-i2\sqrt{7,590}}{13}$	$\frac{-i5,060\sqrt{3}}{13}$
(1)	$\frac{-48\sqrt{49,742}}{5\sqrt{13}}$		$\frac{-1,392\sqrt{154}}{\sqrt{1,391}}$	$\frac{-288\sqrt{9,177}}{\sqrt{6,955}}$	$\frac{-48\sqrt{77}}{\sqrt{13}}$	$\frac{504\sqrt{323}}{\sqrt{910}}$	0	$\frac{-4004\sqrt{3}}{5\sqrt{13}}$	$\frac{4\sqrt{7,854}}{5\sqrt{13}}$	0	0
(2)			$\frac{672\sqrt{1,254}}{\sqrt{118,235}}$	$\frac{-23,688\sqrt{23}}{5\sqrt{23,647}}$	$\frac{12\sqrt{2,618}}{\sqrt{65}}$	$\frac{294\sqrt{133}}{5\sqrt{13}}$	$\frac{6\sqrt{35,649}}{\sqrt{13}}$	$\frac{12\sqrt{231}}{5\sqrt{13}}$	$\frac{-168\sqrt{102}}{5\sqrt{13}}$	$\frac{84\sqrt{969}}{\sqrt{65}}$	0
(3)					0	$\frac{42}{\sqrt{13}}$	$\frac{546\sqrt{253}}{5\sqrt{13}}$	0	$\frac{18\sqrt{266}}{\sqrt{65}}$	$\frac{588\sqrt{7}}{\sqrt{13}}$	$\frac{6\sqrt{17,710}}{\sqrt{13}}$

TABLE IX
TETRAHEDRAL HARMONICS. $J = 11, 12, 13$

D_u^{11}	A_1	$\frac{\sqrt{5 \cdot 17}}{8\sqrt{3}} V_2^{11} + \frac{3\sqrt{3}}{8\sqrt{2}} V_6^{11} + \frac{\sqrt{7 \cdot 19}}{8\sqrt{6}} V_{10}^{11}$
	$E_e^{(1)}$	$-\frac{\sqrt{7 \cdot 15}}{2\sqrt{107}} V_4^{11} - \frac{\sqrt{17 \cdot 19}}{2\sqrt{107}} V_8^{11}$
	$E_f^{(1)}$	$-\frac{\sqrt{107}}{8\sqrt{3}} V_2^{11} + \frac{3\sqrt{15 \cdot 17}}{8\sqrt{2 \cdot 107}} V_6^{11} + \frac{\sqrt{5 \cdot 7 \cdot 17 \cdot 19}}{8\sqrt{6 \cdot 107}} V_{10}^{11}$
	$E_e^{(2)}$	$-\frac{\sqrt{17 \cdot 19}}{2\sqrt{107}} V_4^{11} + \frac{\sqrt{7 \cdot 15}}{2\sqrt{107}} V_8^{11}$
	$E_f^{(2)}$	$-\frac{\sqrt{7 \cdot 19}}{\sqrt{2 \cdot 107}} V_6^{11} + \frac{9}{\sqrt{2 \cdot 107}} V_{10}^{11}$
$F_{2z}^{(1)}, F_{2z}^{(2)}, F_{2z}^{(3)}$		$W_0^{11}, U_4^{11}, U_8^{11}$
$F_{1z}^{(1)}, F_{1z}^{(2)}, F_{1z}^{(3)}$		$U_2^{11}, U_6^{11}, U_{10}^{11}$
D_g^{12}	$A_1^{(1)}$	$-\frac{9\sqrt{11}}{20\sqrt{41}} W_0^{12} + \frac{4\sqrt{13 \cdot 14}}{20\sqrt{41}} U_4^{12} - \frac{\sqrt{17 \cdot 19 \cdot 39}}{20\sqrt{41}} U_8^{12}$
	$A_1^{(2)}$	$\frac{\sqrt{2 \cdot 7 \cdot 13 \cdot 17 \cdot 19 \cdot 23}}{160\sqrt{3 \cdot 41}} W_0^{12} + \frac{\sqrt{3 \cdot 11 \cdot 17 \cdot 19 \cdot 23}}{160\sqrt{41}} U_4^{12} + \frac{\sqrt{2 \cdot 7 \cdot 11 \cdot 23}}{160\sqrt{41}} U_8^{12} + \frac{1,025}{160\sqrt{3 \cdot 41}} U_{12}^{12}$
	A_2	$-\frac{\sqrt{2 \cdot 17}}{16\sqrt{3}} U_2^{12} + \frac{5\sqrt{21}}{16\sqrt{3}} U_6^{12} - \frac{\sqrt{11 \cdot 19}}{16\sqrt{3}} U_{10}^{12}$
	$E_e^{(1)}$	$-\frac{7\sqrt{21}}{24\sqrt{89}} U_2^{12} + \frac{39\sqrt{17}}{24\sqrt{2 \cdot 89}} U_6^{12} + \frac{\sqrt{3 \cdot 7 \cdot 11 \cdot 17 \cdot 19}}{24\sqrt{2 \cdot 89}} U_{10}^{12}$
	$E_f^{(1)}$	$-\frac{\sqrt{3 \cdot 11 \cdot 13}}{4\sqrt{89}} W_0^{12} + \frac{\sqrt{2 \cdot 3 \cdot 7}}{\sqrt{89}} U_4^{12} + \frac{\sqrt{17 \cdot 19}}{4\sqrt{89}} U_8^{12}$
	$E_e^{(2)}$	$\frac{\sqrt{2 \cdot 3 \cdot 11 \cdot 17 \cdot 19}}{16\sqrt{89}} U_2^{12} + \frac{\sqrt{7 \cdot 11 \cdot 19}}{16\sqrt{89}} U_6^{12} + \frac{\sqrt{3}}{16\sqrt{89}} U_{10}^{12}$
	$E_f^{(2)}$	$-\frac{\sqrt{2 \cdot 7 \cdot 13 \cdot 17 \cdot 19}}{32\sqrt{3 \cdot 89}} W_0^{12} - \frac{\sqrt{3 \cdot 11 \cdot 17 \cdot 19}}{32\sqrt{89}} U_4^{12} - \frac{\sqrt{2 \cdot 7 \cdot 11}}{32\sqrt{89}} U_8^{12} + \frac{\sqrt{89 \cdot 23}}{32\sqrt{3}} U_{12}^{12}$
$F_{2z}^{(1)}, F_{2z}^{(2)}, F_{2z}^{(3)}$		$V_2^{12}, V_6^{12}, V_{10}^{12}$
$F_{1z}^{(1)}, F_{1z}^{(2)}, F_{1z}^{(3)}$		$V_4^{12}, V_8^{12}, V_{12}^{12}$
D_u^{13}	A_1	$\frac{\sqrt{2 \cdot 5 \cdot 19}}{16\sqrt{3}} V_2^{13} - \frac{\sqrt{11 \cdot 17}}{16\sqrt{3}} V_6^{13} - \frac{\sqrt{17 \cdot 23}}{16\sqrt{3}} V_{10}^{13}$
	A_2	$\frac{5\sqrt{19}}{16\sqrt{3}} V_4^{13} + \frac{2\sqrt{10}}{16\sqrt{3}} V_8^{13} - \frac{\sqrt{11 \cdot 23}}{16\sqrt{3}} V_{12}^{13}$
	$E_e^{(1)}$	$\frac{3\sqrt{55}}{16\sqrt{17}} V_4^{13} + \frac{\sqrt{2 \cdot 11 \cdot 19}}{8\sqrt{17}} V_8^{13} + \frac{\sqrt{5 \cdot 19 \cdot 23}}{16\sqrt{17}} V_{12}^{13}$
	$E_f^{(1)}$	$-\frac{17\sqrt{34}}{16\sqrt{51}} V_2^{13} - \frac{\sqrt{5 \cdot 11 \cdot 19}}{16\sqrt{51}} V_6^{13} - \frac{\sqrt{5 \cdot 19 \cdot 23}}{16\sqrt{51}} V_{10}^{13}$
	$E_e^{(2)}$	$-\frac{\sqrt{2 \cdot 19 \cdot 23}}{8\sqrt{51}} V_4^{13} + \frac{\sqrt{5 \cdot 23}}{2\sqrt{51}} V_8^{13} - \frac{5\sqrt{22}}{8\sqrt{51}} V_{12}^{13}$
	$E_f^{(2)}$	$\frac{\sqrt{23}}{\sqrt{34}} V_6^{13} - \frac{\sqrt{11}}{\sqrt{34}} V_{10}^{13}$
$F_{2z}^{(1)}, F_{2z}^{(2)}, F_{2z}^{(3)}, F_{2z}^{(4)}$		$W_0^{13}, U_4^{13}, U_8^{13}, U_{12}^{13}$
$F_{1z}^{(1)}, F_{1z}^{(2)}, F_{1z}^{(3)}$		$U_2^{13}, U_6^{13}, U_{10}^{13}$

that the E , F_1 , and A_1 tetrahedral substates of 3_4 are similarly split from their unperturbed position by amounts of $+(60/7)$, $+30$, and $+60$, all times

$$(3t_{044} + 2t_{134} - t_{224}).$$

The four levels are therefore split from their common center of gravity in the ratios -13 , 2 , 7 , and 14 , the splitting pattern used as an example in connection with Table I. In the same approximation the F_2 , F_1 , E , and second F_2 substates of 4_5 are split from their unperturbed position by the amounts $+16(21)^{1/2}$, $(112/3)$, -56 , and $-16(21)^{1/2}$ all times $[(15/2)t_{044} + 3t_{134} - t_{224}]$, see Tables VI and VIII, where the splitting ratios are characteristic of any state with $R = 5$. The numbers $\pm 16(21)^{1/2}$ are the eigenvalues of the 2×2 F_2 matrix, diagonal in R . The examples show that the fourth-rank tensor operators do not shift the center of gravity of a vibration-rotation level and therefore cannot make any contribution to the effective B , D , and zeta values of the bands. (The A , E , and F levels are of course given weights of 1, 2, and 3, respectively, in determining their common center of gravity.)

In the second paper of this series the theoretical predictions will be compared with the recent high resolution spectra of the fundamental ν_3 of CH_4 (1). In order to get good agreement between theory and experiment the matrix elements off-diagonal in the quantum number R must be taken into account. The basic splitting patterns are therefore all deformed to a certain extent. This effect may become particularly significant in the case of large angular momentum quantum numbers. The true wave functions are mixtures of the wave functions for the three types of states J_{J+1} , J_J , and J_{J-1} . As a result some of the lines in the infrared-forbidden P^0 , P^- , Q^- , Q^+ , R^0 , and R^+ branches become active. Such lines have been observed by Plyler and Allen (1, 14). Since the most severe test of the theory is given by states of large angular momentum the calculations have been carried out to include states with angular momenta of 13. The tetrahedrally irreducible harmonic functions for $J = 11$, 12, and 13 are listed in Table IX, an extension of the table of tetrahedral harmonic functions given by Jahn (9). The notation of Jahn has been used in connection with Table IX. The U_K^J , V_K^J , W_o^J are real spherical harmonics as defined in (9).

APPENDIX I. COEFFICIENTS OF THE VIBRATION-ROTATION HAMILTONIAN

The cubic and quartic parts of the potential function, V_1 and V_2 , have been given by Shaffer *et al.* (7) but are listed again below in order to establish the notation. There are some minor differences between V_2 and that listed in Ref. 7.

$$\begin{aligned} V_1 = & c_{111}q_1^3 + c_{122}q_1r_2^2 + c_{133}q_1r_3^2 + c_{144}q_1r_4^2 + c_{134}q_1(r_3 \cdot r_4) + c_{333}x_3y_3z_3 + c_{444}x_4y_4z_4 \\ & + c_{344}(x_3y_4z_4 + y_3x_4z_4 + z_3x_4y_4) + c_{334}(x_4y_3z_3 + y_4x_3z_3 + z_4x_3y_3) \\ & + c_{222}(3e^2f - f^3) + c_{233}[e(x_3^2 - y_3^2) + (f/\sqrt{3})(x_3^2 + y_3^2 - 2z_3^2)] \\ & + c_{244}[e(x_4^2 - y_4^2) + (f/\sqrt{3})(x_4^2 + y_4^2 - 2z_4^2)] \\ & + c_{234}[e(x_3x_4 - y_3y_4) + (f/\sqrt{3})(x_3x_4 + y_3y_4 - 2z_3z_4)]. \end{aligned}$$

$$\begin{aligned}
V_2 = & d_{1111}q_1^4 + d_{1122}q_1^2r_2^2 + d_{1133}q_1^2r_3^2 + d_{1144}q_1^2r_4^2 + d_{2222}r_2^4 + d_{2233}r_2^2r_3^2 \\
& + d_{2244}r_2^2r_4^2 + d_{3333}r_3^4 + d_{4444}r_4^4 + d_{3344}r_3^2r_4^2 + d_{2344}(\mathbf{r}_3 \cdot \mathbf{r}_4)^2 \\
& + d_{2233}[ef(x_3^2 - y_3^2) + (e^2 - f^2)(x_3^2 + y_3^2 - 2z_3^2)/2\sqrt{3}] \\
& + d_{2244}[ef(x_4^2 - y_4^2) + (e^2 - f^2)(x_4^2 + y_4^2 - 2z_4^2)/2\sqrt{3}] \\
& + d_{3333}(x_3^4 + y_3^4 + z_3^4 - 3x_3^2y_3^2 - 3x_3^2z_3^2 - 3y_3^2z_3^2) \\
& + d_{4444}(x_4^4 + y_4^4 + z_4^4 - 3x_4^2y_4^2 - 3x_4^2z_4^2 - 3y_4^2z_4^2) \\
& + d_{3344}(3x_3^2x_4^2 + 3y_3^2y_4^2 + 3z_3^2z_4^2 - r_3^2r_4^2 - 4x_3y_3x_4y_4 - 4x_3z_3x_4z_4 \\
& - 4y_3z_3y_4z_4) + d_{1134}q_1^2(\mathbf{r}_3 \cdot \mathbf{r}_4) + d_{2234}r_2^2(\mathbf{r}_3 \cdot \mathbf{r}_4) + d_{3334}r_3^2(\mathbf{r}_3 \cdot \mathbf{r}_4) \\
& + d_{3444}r_4^2(\mathbf{r}_3 \cdot \mathbf{r}_4) + d_{2234}[ef(x_3x_4 - y_3y_4) + (e^2 - f^2)(x_3x_4 + y_3y_4 \\
& - 2z_3z_4)/2\sqrt{3}] + d_{2344}[(-\sqrt{3}e - f)x_3y_4z_4 + (\sqrt{3}e - f)y_3x_4z_4 \\
& + 2fz_3x_4y_4] + d_{2334}[(-\sqrt{3}e - f)x_4y_3z_3 + (\sqrt{3}e - f)y_4x_3z_3 \\
& + 2fz_4x_3y_3] + d_{3334}[5(x_4x_3^3 + y_4y_3^3 + z_4z_3^3) - 3r_3^2(\mathbf{r}_3 \cdot \mathbf{r}_4)] \\
& + d_{3444}[5(x_3x_4^3 + y_3y_4^3 + z_3z_4^3) - 3r_4^2(\mathbf{r}_3 \cdot \mathbf{r}_4)] + d_{1222}q_1(3e^2f - f^3) \\
& + d_{1333}q_1x_3y_3z_3 + d_{1444}q_1x_4y_4z_4 + d_{1233}q_1[e(x_3^2 - y_3^2) \\
& + (f/\sqrt{3})(x_3^2 + y_3^2 - 2z_3^2)] + d_{1234}q_1[e(x_3x_4 - y_3y_4) \\
& + (f/\sqrt{3})(x_3x_4 + y_3y_4 - 2z_3z_4)] + d_{1244}q_1[e(x_4^2 - y_4^2) \\
& + (f/\sqrt{3})(x_4^2 + y_4^2 - 2z_4^2)] + d_{1344}q_1(x_3y_4z_4 + y_3x_4z_4 + z_3x_4y_4) \\
& + d_{1334}q_1[x_4y_3z_3 + y_4x_3z_3 + z_4x_3y_3].
\end{aligned}$$

The coefficients of the pure vibrational perturbation terms are given below as functions of the cubic and quartic potential constants.

$$\begin{aligned}
X_{11} &= \frac{3}{2}d_{1111} - \frac{15}{4}\frac{c_{111}^2}{\omega_1}, \\
X_{22} &= \frac{3}{2}d_{2222} - \frac{15}{4}\frac{c_{222}^2}{\omega_2} + \frac{c_{122}^2}{4\omega_1}\frac{(3\omega_1^2 - 8\omega_2^2)}{(4\omega_2^2 - \omega_1^2)}, \\
X_{12} &= d_{1122} - \frac{2c_{122}^2\omega_2}{(4\omega_2^2 - \omega_1^2)} - \frac{3c_{111}c_{122}}{\omega_1}, \\
X_{13} &= d_{1133} - \frac{2c_{133}^2\omega_3}{(4\omega_3^2 - \omega_1^2)} \\
&+ \frac{c_{134}^2\omega_4(\omega_4^2 - \omega_3^2 - \omega_1^2)}{2(\omega_1 + \omega_3 + \omega_4)(\omega_1 + \omega_3 - \omega_4)(\omega_1 + \omega_4 - \omega_3)(\omega_3 + \omega_4 - \omega_1)} \\
&- \frac{3c_{111}c_{133}}{\omega_1},
\end{aligned}$$

$$X_{23} = d_{2233s} - \frac{4}{3} \frac{c_{233}^2 \omega_3}{(4\omega_3^2 - \omega_2^2)} - \frac{c_{122} c_{133}}{\omega_1} + \frac{B}{2} \frac{\zeta_{23}^2 (\omega_2^2 + \omega_3^2)}{\omega_2 \omega_3} \\ + \frac{1}{3} \frac{c_{234}^2 \omega_4 (\omega_4^2 - \omega_3^2 - \omega_2^2)}{(\omega_2 + \omega_3 + \omega_4)(\omega_3 + \omega_4 - \omega_2)(\omega_2 + \omega_4 - \omega_3)(\omega_2 + \omega_3 - \omega_4)},$$

$$X_{33} = \frac{3}{2} d_{3333s} - \frac{c_{333}^2}{12\omega_3} + \frac{c_{133}^2 (3\omega_1^2 - 8\omega_3^2)}{4\omega_1 (4\omega_3^2 - \omega_1^2)} + \frac{2c_{233}^2 (3\omega_2^2 - 8\omega_3^2)}{15\omega_2 (4\omega_3^2 - \omega_2^2)} \\ + \frac{c_{334}^2 (3\omega_4^2 - 8\omega_3^2)}{20\omega_4 (4\omega_3^2 - \omega_4^2)},$$

$$X_{34} = d_{3344sa} + \frac{1}{3} d_{3344sb} - \frac{1}{3} \left(\frac{c_{344}^2 \omega_4}{4\omega_4^2 - \omega_3^2} + \frac{c_{334}^2 \omega_3}{4\omega_3^2 - \omega_4^2} \right) \\ - \frac{c_{133} c_{144}}{\omega_1} + \frac{2}{3} B \zeta_{34}^2 \frac{(\omega_3^2 + \omega_4^2)}{\omega_3 \omega_4} \\ + \frac{c_{134}^2 \omega_1 (\omega_1^2 - \omega_3^2 - \omega_4^2)}{6(\omega_1 + \omega_3 + \omega_4)(\omega_1 + \omega_3 - \omega_4)(\omega_1 + \omega_4 - \omega_3)(\omega_3 + \omega_4 - \omega_1)} \\ + \frac{2c_{234}^2 \omega_2 (\omega_2^2 - \omega_3^2 - \omega_4^2)}{9(\omega_2 + \omega_3 + \omega_4)(\omega_2 + \omega_3 - \omega_4)(\omega_2 + \omega_4 - \omega_3)(\omega_3 + \omega_4 - \omega_2)},$$

$$G_{22} = -\frac{1}{2} d_{2222} + \frac{21}{4} \frac{c_{222}^2}{\omega_2} - \frac{1}{4} \frac{c_{122}^2}{(4\omega_2^2 - \omega_1^2)},$$

$$G_{33} = -\frac{1}{2} d_{3333s} + \frac{1}{12} \frac{c_{333}^2}{\omega_3} - \frac{1}{4} \frac{c_{133}^2 \omega_1}{(4\omega_3^2 - \omega_1^2)} + B \zeta_3^2 + \frac{2c_{233}^2 (6\omega_3^2 - \omega_2^2)}{15\omega_2 (4\omega_3^2 - \omega_2^2)} \\ + \frac{1}{20} \frac{c_{334}^2 (6\omega_3^2 - \omega_4^2)}{(4\omega_3^2 - \omega_4^2)},$$

$$G_{34} = \frac{B}{2} \zeta_{34}^2 + 2B \zeta_3 \zeta_4 + \frac{1}{2} \frac{c_{344}^2 \omega_4^2}{\omega_3 (4\omega_4^2 - \omega_3^2)} + \frac{1}{2} \frac{c_{433}^2}{\omega_4 (4\omega_3^2 - \omega_4^2)} \\ - \frac{1}{2} \frac{c_{134}^2 \omega_1 \omega_3 \omega_4}{(\omega_1 + \omega_3 + \omega_4)(\omega_1 + \omega_3 - \omega_4)(\omega_1 + \omega_4 - \omega_3)(\omega_3 + \omega_4 - \omega_1)} \\ + \frac{1}{3} \frac{c_{234}^2 \omega_2 \omega_3 \omega_4}{(\omega_2 + \omega_3 + \omega_4)(\omega_2 + \omega_3 - \omega_4)(\omega_2 + \omega_4 - \omega_3)(\omega_3 + \omega_4 - \omega_2)},$$

$$S_{34} = \frac{1}{4} d_{3344sb} - \frac{1}{40} \left[\frac{\omega_4 c_{344}^2}{(4\omega_4^2 - \omega_3^2)} + \frac{\omega_3 c_{334}^2}{(4\omega_3^2 - \omega_4^2)} \right] - \frac{c_{233} c_{244}}{5\omega_2} \\ - \frac{1}{4} B \zeta_{34}^2 \frac{(\omega_3^2 + \omega_4^2)}{\omega_3 \omega_4} - \frac{3}{40} \left(\frac{c_{444} c_{334}}{\omega_4} + \frac{c_{333} c_{344}}{\omega_3} \right) \\ + \frac{c_{134}^2 \omega_1 (\omega_1^2 - \omega_3^2 - \omega_4^2)}{8(\omega_1 + \omega_3 + \omega_4)(\omega_1 + \omega_3 - \omega_4)(\omega_1 + \omega_4 - \omega_3)(\omega_3 + \omega_4 - \omega_1)} \\ + \frac{c_{234}^2 \omega_2 (\omega_2^2 - \omega_3^2 - \omega_4^2)}{60(\omega_2 + \omega_3 + \omega_4)(\omega_2 + \omega_3 - \omega_4)(\omega_2 + \omega_4 - \omega_3)(\omega_3 + \omega_4 - \omega_2)},$$

$$\begin{aligned}
 T_{34} &= d_{3344t} + \frac{1}{10} \left[\frac{\omega_4 c_{344}^2}{(4\omega_4^2 - \omega_3^2)} + \frac{\omega_3 c_{334}^2}{(4\omega_3^2 - \omega_4^2)} \right] - \frac{c_{233}c_{244}}{5\omega_2} - \frac{1}{20} \left(\frac{c_{444}c_{334}}{\omega_4} + \frac{c_{333}c_{344}}{\omega_3} \right) \\
 &\quad + \frac{c_{234}^2 \omega_2 (\omega_2^2 - \omega_3^2 - \omega_4^2)}{10(\omega_2 + \omega_3 + \omega_4)(\omega_2 + \omega_3 - \omega_4)(\omega_2 + \omega_4 - \omega_3)(\omega_3 + \omega_4 - \omega_2)}, \\
 T_{33} &= \frac{3}{8} d_{3333t} + \frac{1}{48} \frac{c_{333}^2}{\omega_3} + \frac{1}{20} \frac{c_{233}^2 (3\omega_2^2 - 8\omega_3^2)}{\omega_2 (4\omega_3^2 - \omega_2^2)} + \frac{c_{334}^2 (8\omega_3^2 - 3\omega_4^2)}{80\omega_4 (4\omega_3^2 - \omega_4^2)}, \\
 T_{23} &= \frac{d_{2233t}}{8\sqrt{3}} - \frac{\sqrt{3}}{4} \frac{c_{222}c_{233}}{\omega_2} - \frac{c_{233}^2 \omega_3}{6(4\omega_3^2 - \omega_2^2)} - \frac{B}{16} \zeta_{23}^2 \frac{(\omega_2^2 + \omega_3^2)}{\omega_2 \omega_3} \\
 &\quad + \frac{c_{234}^2 \omega_4 (\omega_4^2 - \omega_2^2 - \omega_3^2)}{24(\omega_2 + \omega_3 + \omega_4)(\omega_2 + \omega_3 - \omega_4)(\omega_2 + \omega_4 - \omega_3)(\omega_3 + \omega_4 - \omega_2)}.
 \end{aligned}$$

The coefficient X_{44} is obtained from X_{33} by replacing the index 3 by 4, etc.

The scalar and tensor D values and the second-order vibration-rotation interaction constants are listed next.

$$\begin{aligned}
 D_s &= \left(\frac{8}{3} \frac{1}{\omega_1^2} + \frac{8}{15} \cdot \frac{1}{\omega_2^2} + \frac{4}{5} \frac{\zeta_{23}^2}{\omega_3^2} + \frac{4}{5} \frac{\zeta_{24}^2}{\omega_4^2} \right) B^3, \\
 D_t &= \frac{1}{5} \left(\frac{1}{\omega_2^2} - \frac{\zeta_{23}^2}{\omega_3^2} - \frac{\zeta_{24}^2}{\omega_4^2} \right) B^3 \\
 Y_1 &= \sqrt{6} \left(\frac{2B}{\omega_1} \right)^{3/2} c_{111} + \frac{4B^2}{\omega_1}, \\
 Y_2 &= \frac{\sqrt{2}}{\sqrt{3}} \left(\frac{2B}{\omega_1} \right)^{3/2} c_{122} + \frac{B^2}{\omega_2} + \frac{B^2}{\omega_2} \left[\frac{\zeta_{24}^2 (\omega_4^2 + 3\omega_2^2)}{(\omega_2^2 - \omega_4^2)} + \frac{\zeta_{23}^2 (\omega_3^2 + 3\omega_2^2)}{(\omega_2^2 - \omega_3^2)} \right], \\
 Y_3 &= \frac{\sqrt{2}}{\sqrt{3}} \left(\frac{2B}{\omega_1} \right)^{3/2} c_{133} + \frac{B^2}{\omega_3} \zeta_{23}^2 - \frac{2B^2 \zeta_{23}^2 (\omega_2^2 + 3\omega_3^2)}{3\omega_3 (\omega_2^2 - \omega_3^2)} + \frac{4B^2 \zeta_{34}^2 (3\omega_3^2 + \omega_4^2)}{3\omega_3 (\omega_3^2 - \omega_4^2)}, \\
 Z_{3s} &= \frac{3}{10} \frac{B^2}{\omega_3} \zeta_{23}^2 - \frac{B^2 \zeta_{23}^2 (\omega_2^2 + 3\omega_3^2)}{5\omega_3 (\omega_2^2 - \omega_3^2)} - \frac{2B^2 \zeta_{34}^2 (3\omega_3^2 + \omega_4^2)}{\omega_3 (\omega_3^2 - \omega_4^2)} + \frac{2}{5} c_{233} \left(\frac{2B}{\omega_2} \right)^{3/2} \\
 &\quad - \frac{3}{10} \zeta_{23} c_{333} \left(\frac{2B}{\omega_3} \right)^{3/2} - \frac{3}{10} \zeta_{24} c_{334} \left(\frac{2B}{\omega_4} \right)^{3/2}, \\
 Z_{3t} &= -\frac{3}{10} \frac{B^2}{\omega_3} \zeta_{23}^2 - \frac{3B^2 \zeta_{23}^2 (\omega_2^2 + 3\omega_3^2)}{10\omega_3 (\omega_2^2 - \omega_3^2)} + \frac{c_{233}}{10} \left(\frac{2B}{\omega_2} \right)^{3/2} + \frac{1}{20} \zeta_{23} c_{333} \left(\frac{2B}{\omega_3} \right)^{3/2} \\
 &\quad + \frac{1}{20} \zeta_{24} c_{334} \left(\frac{2B}{\omega_4} \right)^{3/2}, \\
 Z_2 &= -\frac{2}{3} \frac{B^3}{\omega_2} + \frac{2}{3} \frac{B^2}{\omega_2} \left[\frac{\zeta_{23}^2 (\omega_3^2 + 3\omega_2^2)}{(\omega_2^2 - \omega_3^2)} + \frac{\zeta_{24}^2 (\omega_4^2 + 3\omega_2^2)}{(\omega_2^2 - \omega_4^2)} \right] \\
 &\quad - \frac{2}{\sqrt{3}} c_{222} \left(\frac{2B}{\omega_2} \right)^{3/2}.
 \end{aligned}$$

Finally, some of the third-order interaction constants are listed. Only the very simplest coefficient M_{ijk} is listed as an example since these coefficients are very complicated functions of both the cubic and quartic potential constants.

$$\begin{aligned}
 F_{3s} &= \frac{32}{3} \zeta_3 \frac{B^3}{\omega_1^2} + \frac{B_3}{\omega_2^2} \left(\frac{32}{15} \zeta_3 + \frac{8}{5} \zeta_{23}^2 \right) + \frac{B^3}{\omega_3^2} \left(\frac{48}{5} \zeta_3 \zeta_{23} - \frac{4}{5} \zeta_{23}^2 \right) \\
 &+ \frac{B^3}{\omega_4^2} \left(\frac{32}{5} \zeta_3 \zeta_{24} + \frac{16}{5} \zeta_{23} \zeta_{34} \right) + \frac{12}{5} \frac{B^3 \zeta_{23}^2}{(\omega_2^2 - \omega_3^2)} + \frac{24}{5} \frac{B^3 \zeta_{34}^2}{(\omega_3^2 - \omega_4^2)} \\
 &+ \frac{24}{5} B^3 \frac{\zeta_3 \zeta_{23} (\omega_2^2 + \omega_3^2)}{(\omega_2^2 - \omega_3^2)^2} + 16 (\zeta_3 - \zeta_4) \zeta_{34}^2 \frac{B^3 (\omega_3^2 + \omega_4^2)}{(\omega_3^2 - \omega_4^2)^2} \\
 &- \frac{24}{5} \frac{B^3 \zeta_{23} \zeta_{24} \zeta_{34} (\omega_2^2 + \omega_4^2 + 2\omega_3^2)}{(\omega_3^2 - \omega_4^2) (\omega_3^2 - \omega_2^2)} - \frac{4}{5} \frac{c_{233} (2B)^{5/2} \zeta_{23}^2 (\omega_2)^{1/2}}{\omega_3 (\omega_2^2 - \omega_3^2)} \\
 &- \frac{2}{5} \frac{c_{234} (2B)^{5/2} \zeta_{23} \zeta_{24} (\omega_2 \omega_3)^{1/2}}{\omega_4 (\omega_2^2 - \omega_3^2) \left(\frac{\omega_2 \omega_3}{\omega_4} \right)^{1/2}} + \frac{4 (2B)^{5/2} c_{234} \zeta_{34}}{15 \omega_2 (\omega_3^2 - \omega_4^2) \left(\frac{\omega_3 \omega_4}{\omega_2} \right)^{1/2}} \\
 &- \frac{2\sqrt{2}}{\sqrt{3}} \frac{(2B)^{5/2} c_{134} \zeta_{34} (\omega_3 \omega_4)^{1/2}}{\omega_1 (\omega_3^2 - \omega_4^2) \left(\frac{\omega_3 \omega_4}{\omega_1} \right)^{1/2}} - \frac{2 (2B)^{5/2} [c_{334} \zeta_{23} (\omega_4)^{3/2} + c_{344} \zeta_{24} (\omega_3)^{3/2}]}{5 \omega_3 \omega_4 (\omega_3^2 - \omega_4^2)}, \\
 F_{3t} &= \frac{B^3}{\omega_2^2} \left(\frac{4}{5} \zeta_3 + \frac{3}{5} \zeta_{23}^2 \right) - \frac{B^3}{\omega_3^2} \left(\frac{12}{5} \zeta_3 \zeta_{23} + \frac{4}{5} \zeta_{23}^2 \right) - \frac{B^3}{\omega_4^2} \left(\frac{8}{5} \zeta_3 \zeta_{24} + \frac{4}{5} \zeta_{23} \zeta_{34} \right) \\
 &- \frac{3}{5} \frac{B^3 \zeta_{23}^2}{(\omega_2^2 - \omega_3^2)} + \frac{4}{5} \frac{B^3 \zeta_{34}^2}{(\omega_3^2 - \omega_4^2)} - \frac{6}{5} \frac{B^3 \zeta_3 \zeta_{23}^2 (\omega_2^2 + \omega_3^2)}{(\omega_2^2 - \omega_3^2)^2} \\
 &+ \frac{6}{5} \frac{B^3 \zeta_{23} \zeta_{24} \zeta_{34} (\omega_2^2 + \omega_4^2 + 2\omega_3^2)}{(\omega_3^2 - \omega_4^2) (\omega_3^2 - \omega_2^2)} + \frac{(2B)^{5/2} c_{233} \zeta_{23}^2 (\omega_2)^{1/2}}{5 \omega_3 (\omega_2^2 - \omega_3^2)} \\
 &+ \frac{(2B)^{5/2}}{10} c_{234} \left[\frac{\zeta_{23} \zeta_{24}}{\omega_4 (\omega_2^2 - \omega_3^2) \left(\frac{\omega_2 \omega_3}{\omega_4} \right)^{1/2}} + \frac{\zeta_{34}}{\omega_2 (\omega_3^2 - \omega_4^2) \left(\frac{\omega_3 \omega_4}{\omega_2} \right)^{1/2}} \right] \\
 &+ \frac{1}{10} \frac{(2B)^{5/2} \zeta_{34}}{\omega_3 \omega_4 (\omega_3^2 - \omega_4^2)} [c_{334} \zeta_{23} (\omega_4)^{3/2} + c_{344} \zeta_{24} (\omega_3)^{3/2}], \\
 F_2 &= 4B^3 \left[\frac{1}{\omega_2^2} - \frac{\zeta_{23}}{\omega_3^2} - \frac{\zeta_{24}}{\omega_4^2} - \frac{3\zeta_{23}^2}{2(\omega_2^2 - \omega_3^2)} - \frac{3\zeta_{24}^2}{2(\omega_2^2 - \omega_4^2)} \right] \\
 &- 12B^3 \left[\frac{\zeta_3 \zeta_{23}^2 (\omega_2^2 + \omega_3^2)}{(\omega_2^2 - \omega_3^2)^2} + \frac{\zeta_4 \zeta_{24}^2 (\omega_2^2 + \omega_4^2)}{(\omega_2^2 - \omega_4^2)^2} + \frac{\zeta_{23} \zeta_{24} \zeta_{34} (2\omega_2^2 + \omega_3^2 + \omega_4^2)}{(\omega_2^2 - \omega_3^2) (\omega_2^2 - \omega_4^2)} \right] \\
 &+ \frac{2(2B)^{5/2} \zeta_{23}^2 c_{233} (\omega_2)^{1/2}}{\omega_3 (\omega_2^2 - \omega_3^2)} + \frac{2(2B)^{5/2} \zeta_{24}^2 c_{244} (\omega_2)^{1/2}}{\omega_4 (\omega_2^2 - \omega_4^2)} \\
 &+ c_{234} (2B)^{5/2} \zeta_{23} \zeta_{24} \left[\left(\frac{\omega_2 \omega_3}{\omega_4} \right)^{1/2} \frac{1}{\omega_4 (\omega_2^2 - \omega_3^2)} + \left(\frac{\omega_2 \omega_4}{\omega_3} \right)^{1/2} \frac{1}{\omega_3 (\omega_2^2 - \omega_4^2)} \right],
 \end{aligned}$$

$$\begin{aligned}
M_{311} = & -\frac{4B^2}{\omega_1} \zeta_3 - \sqrt{6} \left(\frac{2B}{\omega_1} \right)^{3/2} \zeta_3 c_{111} - \frac{(4B)^{3/2}}{\sqrt{3}} \left(\frac{\omega_3 \omega_4}{\omega_1} \right)^{1/2} \\
& \cdot \frac{c_{134} \zeta_{34} (\omega_3^2 - \omega_4^2)}{(\omega_1 + \omega_3 + \omega_4)(\omega_1 + \omega_3 - \omega_4)(\omega_1 + \omega_4 - \omega_3)(\omega_3 + \omega_4 - \omega_1)} \\
& + \frac{12B \zeta_{34} c_{111} c_{134} (\omega_3 \omega_4)^{1/2}}{\omega_1 (\omega_3^2 - \omega_4^2)} \\
& + \frac{24B \zeta_{34} c_{133} c_{134} (\omega_3 \omega_4)^{1/2} \omega_3 (\omega_1^2 - \omega_3^2 - \omega_4^2)}{(\omega_3 - \omega_4)(\omega_1 + \omega_3 + \omega_4)(\omega_1 + \omega_3 - \omega_4)(\omega_1 + \omega_4 - \omega_3)(\omega_3 + \omega_4 - \omega_1)} \\
& - \frac{2B(\zeta_3 - \zeta_4) c_{134}^2 \omega_3 \omega_4 [3\omega_1^4 - (\omega_3^2 - \omega_4^2)^2 - 2\omega_1^2(\omega_3^2 + \omega_4^2)]}{(\omega_1 + \omega_3 + \omega_4)^2 (\omega_1 + \omega_3 - \omega_4)^2 (\omega_1 + \omega_4 - \omega_3)^2 (\omega_3 + \omega_4 - \omega_1)^2} \\
& - \frac{4B \zeta_{34} d_{1134} (\omega_3 \omega_4)^{1/2}}{(\omega_3^2 - \omega_4^2)}.
\end{aligned}$$

In these expressions the quantities ζ_{23} and ζ_{24} have the opposite sign from that defined by Shaffer, *et al.* (7).

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