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The Dipole Moment Expansion for a Tetrahedral Molecule in the Ground Vibronic State[1]

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The expansion of the electric dipole moment operator in terms of angular momentum operators is examined in detail for a tetrahedral molecule in the ground vibronic state. The components of this centrifugal distortion moment in the molecule fixed frame are formally expanded to arbitrary order, with the expansion coefficients being given in terms of rotation matrices. For terms of rank j less than 15, general expressions are given for the matrix elements in the symmetric top basis of the space-fixed components of the dipole moment. The dependence of these matrix elements on the K-quantum number is shown to factor in such a way that previous first order calculations can be extended to second order by replacing the first order dipole coupling constant $\mu_2^{(2)}$ with a function of J which involves $\mu_2^{(2)}$ and two second order constants, $\mu_2^{(4)}$ and $\mu_4^{(4)}$. Different functions are required for Q- and R-branch matrix elements and explicit expressions are given for both. The third order terms are examined in detail in the Appendix. A recurrence relation is derived for $j < 15$ between the tetrahedral harmonics of types A_2 and F_2. The implications of this work for distortion moment spectroscopy in tetrahedral molecules are discussed.

1. INTRODUCTION

There has been considerable interest recently in the electric dipole moment that is generated in the ground vibronic state of a tetrahedral molecule by centrifugal distortion. The original theoretical works (*1–7*) on this problem inspired a series of experiments using a variety of techniques: molecular beams (*8*), far infrared spectroscopy (*9–14*), microwave-infrared double resonance (*15*) and microwave absorption (*16*). In opening up the field of distortion moment spectroscopy, these theoretical works were concerned with the first nonzero term in the dipole moment expansion and so considered only the term of lowest order.

There is now, however, strong experimental evidence that terms of higher order must be considered in the analysis of the various experiments, particularly those (*9–14, 16*) which involve states with large values of the rotational quantum number J. From Stark shift measurements on the ($J = 2$) level of CH_4, it has been found (*8*) that the effective distortion dipole moment μ_D is $(5.38 \pm 0.10) \times 10^{-6}$ D. On the other hand, if all the intensity measured in the R-branch spectrum is ascribed to the centrifugal distortion mechanism, it is found (*14*) that the effective moment from $J = 10$ to 15 is larger by a

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factor of ~ 1.4. It is quite reasonable (*14*) to attribute an increase of this order with J to the higher order terms in the dipole expansion.

It is the purpose of the current work to calculate the matrix elements of the dipole moment operator to high order and to discuss the implications for the analysis of R-branch and Q-branch spectra in tetrahedral molecules. In Section 2, the expansion of the dipole moment operator in the molecule fixed frame (MFF) to arbitrary order is put on a rigorous basis using arguments that can be applied to the Hamiltonian as well. The expansion is discussed in some detail because no treatment of this type has been previously presented for either the dipole moment or the Hamiltonian.[3] The general term in the expansion is given as a sum of spherical tensors, while the terms of first and second order are given explicitly as a sum of angular momentum operators.

In Section 3, the dipole moment in the space fixed frame (SFF) is obtained to high order and the matrix elements are calculated in the symmetric top basis. Explicit expressions are given for the matrix elements of first and second order. It is shown that earlier first order calculations can be extended to second order simply by replacing the lowest order moment μ_D by an appropriate effective moment which depends only on J. In the course of the calculation, a simple relationship is derived between the coefficients of the tetrahedral harmonics for the A_2 representation and those for the F_2 representation. The limitations on the results concerning the order of the expansion are described.

In Section 4, the implications of the work for distortion moment spectroscopy in tetrahedral molecules is discussed and the application of the current results to collision-induced absorption is considered briefly. An Appendix is included which treats the third order terms in the dipole moment expansion in some detail.

2. THE DIPOLE MOMENT EXPANSION FOR TETRAHEDRAL MOLECULES

1. The General Expansion

The components $\tilde{\mu}_\alpha$ of the dipole moment operator in the MFF can be expanded as

$$\tilde{\mu}_\alpha = \sum_{n=1}^{\infty} \tilde{A}_\alpha^{2n}, \tag{1}$$

where $\tilde{A}_\alpha^{2n}$ is the term of order n. Here α indicates the Cartesian component and the tilde shows explicitly that the operator is referred to the MFF. We will define the term "n-tuple" to mean a product of the form $\tilde{J}_\alpha \tilde{J}_\beta \cdots \tilde{J}_\delta$, where n factors appear, each one being a component of the rotational angular momentum **J**. The general term $\tilde{A}_\alpha^{2n}$ in Eq. (1) can be written as the sum of all possible linear combinations of $(2n)$-tuples which transform as the αth basis function of the irreducible representation (irrep) F_2 of the molecular point group T_d. Each independent linear combination in this sum is multiplied by its own coupling constant. Because of general symmetry considerations, odd n-tuples do not appear in this expansion of $\tilde{\mu}_\alpha$. The problem then is to find all the appropriate linear combinations of $(2n)$-tuples.

To solve this problem, we first consider the transformation properties of the $(2n)$-tuples under the full continuous rotation–reflection group $\mathbf{R(3)} \otimes \mathbf{I}$ and then apply the

[3] In high order, the problem arises of the determinability of the coupling constants from the observed data. This problem is not considered here. See Ref. (*17*).

condition that the required linear combinations of $(2n)$-tuples transform as the αth basis function of the irrep F_2 of the point group T_d. The components $\tilde{J}_\alpha$ form a basis (*18*) for the three-dimensional gerade irrep $D_g^{(1)}$ of $\mathbf{R(3)} \otimes \mathbf{I}$. All 3^{2n} possible $(2n)$-tuples in these components therefore form a basis for the $(2n)$th direct product representation

$$(D_g^{(1)})^{2n} \equiv D_g^{(1)} \otimes D_g^{(1)} \otimes \cdots \otimes D_g^{(1)}, \qquad 2n \text{ factors.} \tag{2}$$

Because the linear combinations of $(2n)$-tuples which are antisymmetric in the $(2n)$ indices do not contribute, we need consider only the symmetric combinations. These form a basis for the symmetrized $(2n)$th direct product representation $[D_g^{(1)}]^{2n}$ of the group $\mathbf{R(3)} \otimes \mathbf{I}$.

The representation $[D_g^{(1)}]^{2n}$ is in general reducible and can be reduced into a direct sum of gerade irreps $D_g^{(L)}$ $(L = 0, 1, 2, \ldots)$ of the group $\mathbf{R(3)} \otimes \mathbf{I}$. Ungerade irreps do not appear in the reduction because all the factors in Eq. (2) are gerade. Let R represent a proper rotation by angle θ_R about an arbitrary axis and I represent the inversion. Further, let $\chi_L(R)$ and $\chi_L(IR)$ be the characters of the irrep $D_g^{(L)}$ for elements R and IR, respectively. Because we are considering only gerade representations, these two characters are equal. Then (*19*),

$$\chi_L(R) = \chi_L(IR) = \sin[(2L + 1)\theta_R/2]/\sin[\theta_R/2]. \tag{3}$$

Define $\chi^{2n}(R)$ and $\chi^{2n}(IR)$ to be the characters of $[D^{(1)}]^{2n}$ for elements R and IR, respectively. Again, these characters are equal. It then follows from work done (*20*) on the analysis of overtones of triply degenerate vibrational bands that

$$\chi^{2n}(R) = \chi^{2n}(IR) = \sum_{L=0}^{2n} \chi_L(R), \qquad L = 0, 2, 4, \ldots, 2n. \tag{4}$$

Thus each irrep $D_g^{(L)}$ for even rank $L \leq 2n$ occurs once and only once (*18*).

$$[D_g^{(1)}]^{2n} = \sum_{L=0}^{2n} D_g^{(L)} = D_g^{(0)} \oplus D_g^{(2)} \oplus \cdots \oplus D_g^{(2n)}. \tag{5}$$

The symmetrized $(2n)$-tuples can therefore be formed into independent linear combinations which are sets of basis functions for all the irreps $D_g^{(L)}$ appearing in Eq. (5).

For each irrep $D_g^{(L)}$ $(L = 0, 2, \ldots, 2n)$ of the group $\mathbf{R(3)} \otimes \mathbf{I}$, we now subduce a representation of the point group T_d and reduce this representation into a direct sum of irreps of the point group T_d. Let $N(L, F_2)$ denote the number of times the irrep F_2 of T_d is contained in the representation of T_d subduced from the irrep $D_g^{(L)}$ of $\mathbf{R(3)} \otimes \mathbf{I}$. Let $\tilde{B}_\alpha^{2n}(L, t)$ be the linear combinations of the basis functions of the irrep $D_g^{(L)}$ of group $\mathbf{R(3)} \otimes \mathbf{I}$ which transforms as the αth basis function of the irrep F_2 of group T_d. Here t labels the different independent functions which have identical transformation properties: $t = 1, 2, \ldots, N(L, F_2)$. Because each $D_g^{(L)}$ occurs only once in Eq. (5), the $\tilde{B}_\alpha^{2n}(L, t)$ are, for given $2n$ and L, unique to within a unitary transformation with respect to t. Therefore, the $\tilde{B}_\alpha^{2n}(L, t)$ for $L = 2, 4, \ldots, 2n$ include all possible linear combinations of $(2n)$-tuples which transform as the αth basis function of irrep F_2 and

include each such combination only once. As a result, we can write

$$\tilde{A}_\alpha^{2n} = \sum_{L=2}^{2n} \sum_{t=1}^{N(L,F_2)} \mu_{L,t}^{(2n)} \tilde{B}_\alpha^{2n}(L, t), \tag{6}$$

where the $\mu_{L,t}^{(2n)}$ form a complete set of independent coupling constants. These constants are real. The total number of constants is

$$N = \sum_{L=2}^{2n} N(L, F_2). \tag{7}$$

The sums on L in Eqs. (6) and (7) start at 2 because $N(0, F_2) = 0$.

To simplify Eq. (6), we define

$$\tilde{G}_\alpha(l, t) \equiv \tilde{B}_\alpha^{(l)}(l, t). \tag{8}$$

From the uniqueness of the $\tilde{B}_\alpha^{2n}(L, t)$ and the fact that $(\tilde{J}_x^2 + \tilde{J}_y^2 + \tilde{J}_z^2)$ is the only quadratic invariant that can be formed from the components of $\mathbf{J}$, it follows that

$$\tilde{B}_\alpha^{2n}(L, t) = [\mathbf{J}^2]^{(2n-L)/2} \tilde{G}_\alpha(L, t). \tag{9}$$

It is understood in writing Eq. (9) that, if $N(L, F_2)$ is >1, the appropriate unitary transformations must be chosen for both $\tilde{B}_\alpha^{2n}(L, t)$ and $\tilde{G}_\alpha(L, t)$. We can now express $\tilde{A}_\alpha^{2n}$ in terms of the $\tilde{G}_\alpha(L, t)$. From Eqs. (6) and (9),

$$\tilde{A}_\alpha^{2n} = \sum_{L=2}^{2n} [\mathbf{J}^2]^{(2n-L)/2} \sum_{t=1}^{N(L,F_2)} \mu_{L,t}^{(2n)} \tilde{G}_\alpha(L, t). \tag{10}$$

For each order n, the only new basis functions which are introduced in Eq. (10) are the $\tilde{G}_\alpha$ $(L = 2n, t)$. All the other $\tilde{G}_\alpha(L, t)$ have already appeared in the $\tilde{A}_\alpha^{2s}$ of order $s < n$.

The analysis which is presented here for the general term in the dipole moment expansion can be easily modified so as to apply to the terms in the Hamiltonian expansion. The analog of Eq. (10) for the Hamiltonian has been given previously (*21*) without detailed discussion of its basis.[4] The Hamiltonian expansion to specific values of n has also been used in various problems (*22*, *23*). However, to the authors' knowledge no general proof of Eq. (10) of the type given here for arbitrary order has appeared in the literature for the expansion of either the Hamiltonian or the dipole moment of a tetrahedral molecule. The essential point in the derivation of Eq. (10) lies in the fact that each $D_{0}^{(L)}$ $(L = 0, 2, 4, \ldots, 2n)$ appears in Eq. (5) once and only once.

2. *Specific Operators*

In order to expand $\tilde{\mu}_\alpha$ to order n, we require all $\tilde{G}_\alpha(L, t)$ for $L = 2, 4, \ldots, 2n$. These tetrahedral basis functions of species F_2 can be generated by methods used earlier (*22*, *23*) to obtain the tensor distortion terms in the rotational Hamiltonian. The

[4] In the current work, we are dealing specifically with the F_2 representation, while Ref. (*21*) deals only with the A_1 representation. However, it may be helpful to the reader to see which symbols in Ref. (*21*) play the same roles as those used here in Eq. (10). This correspondence is as follows, with current symbols listed first. $2n \leftrightarrow \Omega$; $L \leftrightarrow K$; $N(L, F_2) \leftrightarrow m$; $t \leftrightarrow n$.

tetrahedral harmonic R (L, $m = 0$; $\gamma\xi t\rho$) is constructed by standard methods (*24*, *25*) for component $\xi = \alpha$ of representation $(\gamma\rho) = F_2$ in terms of the spherical harmonics ${Y_k}^L$ which are then replaced by the operator equivalent $\lambda_L {\tilde{T}_k}^L$ written in terms of the MFF components of **J**. Here ${\tilde{T}_k}^L$ is component k in the MFF of a spherical tensor of rank L. Because the ${\tilde{T}_k}^L$ are referred to the MFF, the angles in the ${Y_k}^L$ used are measured in the MFF. The λ_L are numerical constants which depend only on L and are inserted to allow for the normalization condition used in the specific definition of the ${\tilde{T}_k}^L$.

The tetrahedral operators $\tilde{G}_\alpha(L, t)$ can be expressed in terms of the ${\tilde{T}_k}^L$ directly from (Ref. *25*, Eq. (3.15)) for $\alpha = \tilde{x}, \tilde{y}, \tilde{z}$. However, it is more convenient to introduce the spherical basis (*26*) and work with $\tilde{G}_\omega(L, t)$, where $\omega = +1, 0, -1$. Then

$$\begin{aligned}
\tilde{G}_{+1}(L, t) &= 2i\lambda_L[d_{1,{K_e}^L}{\tilde{T}_{-1}}^L + d_{3,{K_e}^L}{\tilde{T}_3}^L + d_{5,{K_e}^L}{\tilde{T}_{-5}}^L + d_{7,{K_e}^L}{\tilde{T}_7}^L + \cdots], \\
\tilde{G}_0(L, t) &= (i/\sqrt{2})\lambda_L[{\tilde{T}_{K_e}}^L - {\tilde{T}_{-K_e}}^L], \\
\tilde{G}_{-1}(L, t) &= -2i\lambda_L[d_{1,{K_e}^L}{\tilde{T}_1}^L + d_{3,{K_e}^L}{\tilde{T}_{-3}}^L + d_{5,{K_e}^L}{\tilde{T}_5}^L + d_{7,{K_e}^L}{\tilde{T}_{-7}}^L + \cdots],
\end{aligned} \tag{11}$$

where (*26*, *25*)

$$d_{KK'}{}^L \equiv D_{KK'}{}^L(0, \pi/2, 0). \tag{12}$$

K_e is defined as the one value of $|k|$ which appears in the ${\tilde{T}_k}^L$ for $\tilde{G}_0(L, t)$. Since L is even, K_e takes (*25*) the values 2, 6, 10, ... For the particular representation of the $\tilde{G}_\omega(L, t)$ given in Eq. (11), there is a one-to-one correspondence between t and K_e. In particular,[5]

$$t = (K_e + 2)/4. \tag{13}$$

All ${\tilde{T}_k}^L$ of odd $|k|$ appear in $\tilde{G}_{\pm 1}(L, t)$ with the sign pattern given in Eq. (11) subject to the restriction that $|k| < L$. Equation (11) can be summarized in the form

$$\tilde{G}_\omega(L, t) = \lambda_L \sum_k a_{\omega k}{}^{Lt} {\tilde{T}_k}^L, \tag{14}$$

where the range for k and the values of the constants $a_{\omega k}{}^{Lt}$ can be obtained by comparing Eqs. (11) and (14). One important property of these constants is that

$$a_{\omega k}{}^{Lt} = -a_{-\omega,-k}{}^{Lt}. \tag{15}$$

This property is invariant under a unitary transformation with respect to t.

The dipole moment operators of arbitrary order have now been expressed in terms of the ${\tilde{T}_k}^L$. Because the operators for first and second order are particularly important, these shall be written out explicitly in terms of $\tilde{J}_z$ and $\tilde{J}_\pm \equiv (\tilde{J}_x \pm i\tilde{J}_y)$ using Eqs. (1), (10), and (11). First, the $d_{k{K_e}^L}$ are calculated using Eq. (65) of Ref. (*24*). The ${\tilde{T}_k}^L$ are then expressed in terms of $\tilde{J}_z$ and $\tilde{J}_\pm$ using the tables available in the literature (*27*, *28*). Because these tables (and their extension in Ref. (*23*)) are written specifically for SFF components, the difference between the SFF and MFF commutation relations (*29*) must be taken into account. Because the table in Ref. (*27*) is explicitly symmetric in J_z and $J_\pm$, it can be used for the MFF simply by applying tildes and then treating $\tilde{J}_+$ and $\tilde{J}_-$, respectively, as lowering and raising operators (*30*). This is the procedure

[5] This definition of t agrees with that given in Ref. (*23*). Its relationship to the index n used in Ref. (*39*) is also given in Ref. (*23*).

used here. Because the tables in (*28*) and (*23*) do not have this same symmetry property, the more general procedure is used of replacing $\tilde{T}_k{}^L$ by its Hermitian adjoint (*29*, *31*). It is interesting to note that the distinction between SFF and MFF commutation relations does not affect the matrix elements of the operators Ω_L which appear (*23*) in the expansion of the Hamiltonian. On the other hand, this distinction must be carefully taken into account in calculating the matrix elements of the corresponding dipole operators $\tilde{G}_\omega(L, t)$.

Now a normalization condition must be selected for the $\tilde{T}_k{}^L$ and a value for the constants λ_L for $L = 2$ and 4. Here we shall follow the normalization of Buckmaster *et al.* (*28*). This is related to the normalization of Smith and Thornley (*27*) in Ref. (*23*, Eq. (10)). The selection of λ_L then fixes the definition of $\mu_{L,t}{}^{(2n)}$ (for all n). For $\mu_2{}^{(2)}$, there are two commonly used definitions: that of Fox (*2*), who uses the symbol C_{34} and that of Watson (*3*) who uses the symbol $\theta_z{}^{xy}$. In Refs. (*10–13*, *16*), the symbol $\mu_D \equiv C_{34}$ is used. Here we shall set $\lambda_2 = -\sqrt{2}$ so that

$$\mu_2{}^{(2)} = \theta_z{}^{xy} = -(20)^{\frac{1}{2}}C_{34} = -(20)^{\frac{1}{2}}\mu_D. \tag{16}$$

The definition of $\mu_2{}^{(4)}$ given in Ref. (*14*) is consistent with this value of λ_2. $\mu_4{}^{(4)}$ was introduced in Ref. (*14*), but no explicit definition was given. Here we define it by setting λ_4 to unity. The constant $\mu_2{}^{(2)}$ has the physical meaning derived in Refs. (*2*) and (*3*). However, $\mu_2{}^{(4)}$ and $\mu_4{}^{(4)}$ are empirical constants whose interpretation in terms of higher order distortion effects has not yet been investigated.

The dipole moment can now be written out to second order:

$$\tilde{\mu}_\omega = [\mu_2{}^{(2)} + \mu_2{}^{(4)}\mathbf{J}^2]\tilde{G}_\omega(2) + \mu_4{}^{(4)}\tilde{G}_\omega(4): \tag{17}$$

$$\tilde{G}_0(2) = (+i/2)[\tilde{J}_-{}^2 - \tilde{J}_+{}^2], \tag{18a}$$

$$\tilde{G}_{\pm 1}(2) = (-i/\sqrt{2})[\tilde{J}_z\tilde{J}_\mp + \tilde{J}_\mp\tilde{J}_z], \tag{18b}$$

$$\tilde{G}_0(4) = [i/4(14)^{\frac{1}{2}}][(7\tilde{J}_z{}^2 - \mathbf{J}^2 - 5)(\tilde{J}_+{}^2 - \tilde{J}_-{}^2) + (\tilde{J}_+{}^2 - \tilde{J}_-{}^2)(7\tilde{J}_z{}^2 - \mathbf{J}^2 - 5)], \tag{19a}$$

$$\tilde{G}_{\pm 1}(4) = [-i/8(7)^{\frac{1}{2}}][7(\tilde{J}_z\tilde{J}_\pm{}^3 + \tilde{J}_\pm{}^3\tilde{J}_z) + (7\tilde{J}_z{}^2 - 3\mathbf{J}^2 - 1)\tilde{J}_z\tilde{J}_\mp + \tilde{J}_\mp\tilde{J}_z(7\tilde{J}_z{}^2 - 3\mathbf{J}^2 - 1)]. \tag{19b}$$

$\tilde{J}_+$ and $\tilde{J}_-$ here are lowering and raising operators, respectively. The index t has been dropped in Eqs. (17)–(19) because t can take only one value for $L = 2$ or 4 and so is redundant. It should be pointed out that the first order term in $\tilde{\mu}_\omega$ given here agrees with that given in Ref. (*3*, Eq. (3)).

3. THE DIPOLE MATRIX ELEMENTS

1. Definition of the Problem

In this section, we will calculate the matrix elements of the SFF components $G_\nu(L, t)$ of the tetrahedral dipole operators in the "unsymmetrized" representation (*12*) where the rotational wavefunctions are taken to be the normalized symmetric top functions (*25*):

$$|JKM\rangle = [(2J + 1)/8\pi^2]^{\frac{1}{2}}D_{MK}{}^{J*}(\Omega). \tag{20}$$

Here M and K are the eigenvalues of the projections of **J** along the SFF z-axis and the MFF $\tilde{z}$-axis, respectively. The Euler angles Ω which form the arguments of the rotation matrix (*26*) D_{MK}^{J*} are those through which the SFF must be rotated to be brought into coincidence with the MFF. These angles are measured in the SFF.

Of course, the rotational wavefunctions for a tetrahedral molecule are appropriate linear combinations of the $|JKM\rangle$. The matrix elements in this symmetrized representation (*12*, *23*) can be obtained from the $\langle J'K'M'|G_\nu(L, t)|JKM\rangle$ given here by using the tetrahedral harmonics (*24*) and standard matrix multiplication. However, the simple unsymmetrized representation has two direct uses. First it can provide valuable insight into problems being considered, and second it often provides the basis of an adequate approximation.

The rotation matrix $D_{mk}^{L}(\Omega)$ can also act as an operator. If k is held constant, D_{mk}^{L} will act as a spherical tensor (*18*) of rank L and component m. Similarly, if m is held constant, D_{mk}^{L} will act as a spherical tensor of rank L and component k. In $\langle J'K'M'|D_{mk}^{L}|JKM\rangle$, the D_{mk}^{L} acts as an (L, m) tensor to change M to $(M + m)$ and acts as an (L, k) tensor to change K to $(K + k)$. For this matrix element, $\Delta M = (M' - M) = m$ and $\Delta K = (K' - K) = k$. These simple properties of the operator D_{mk}^{L} will be useful in Section 3.2.

2. *The Dipole Moment in the SFF*

The first step in calculating the matrix elements is to obtain a convenient expression for the SFF components $G_\nu(L, t)$ from their MFF counterparts. Because the dipole moment operator is a first rank spherical tensor, it follows that (*26*, *3*)

$$G_\nu(L, t) = \tfrac{1}{2} \sum_{\omega} [D_{\nu\omega}^{(1)*} \tilde{G}_\omega(L, t) + \tilde{G}_\omega(L, t) D_{\nu\omega}^{(1)*}]. \tag{21}$$

It is necessary to symmetrize the transformation because $D_{\nu\omega}^{(1)*}$ and $\tilde{G}_\omega(L, t)$ do not commute in general. From Eq. (14),

$$G_\nu(L, t) = \tfrac{1}{2}\lambda_L \sum_{\omega k} a_{\omega k}^{Lt} [D_{\nu\omega}^{(1)*}, \tilde{T}_k^{L}]_+, \tag{22}$$

where we have introduced the symbol $[A, B]_+$ to represent the anticommutator of the operators A and B. The individual $\tilde{T}_k^{L}$ can be transformed back to the SFF by

$$\tilde{T}_k^{L} = \sum_{s} D_{sk}^{(L)} T_s^{L}. \tag{23}$$

In this case symmetrization is not necessary, because both orders give the same matrix elements. Then,

$$G_\nu(L, t) = \tfrac{1}{2}\lambda_L \sum_{\omega k} \sum_{s} (-1)^{\nu-\omega} a_{\omega k}^{Lt} [D_{-\nu,-\omega}^{(1)} D_{s,k}^{(L)}, T_s^{L}]_+. \tag{24}$$

By using the Clebsch–Gordan series (*26*), we obtain

$$G_\nu(L, t) = \sum_{j} G_\nu(j, L, t), \tag{25}$$

where

$$G_\nu(j, L, t) = \tfrac{1}{2}\lambda_L(-1)^\nu \sum_\tau b_\tau{}^{jLt} \sum_s C(1, L, j; -\nu, s)[D_{-\nu+s,\tau}{}^{(j)}, T_s{}^L]_+, \tag{26}$$

and

$$b_\tau{}^{jLt} = \sum_{\omega k} (-1)^\omega a_{\omega k}{}^{Lt} C(1, L, j; -\omega, k)\delta(\tau, -\omega + k). \tag{27}$$

Here the $C(1, L, j; m, m')$ are Clebsch–Gordan coefficients. The sum in Eq. (25) on j is over the values $(L-1)$, L, $(L+1)$; while the sum in Eq. (26) on τ is over all values for which there are nonzero $a_{\omega k}{}^{Lt}$ in Eq. (14) with $\tau = (-\omega + k)$.

Considerable insight into the structure of the tetrahedral dipole operators $G_\nu(j, L, t)$ can be obtained from a close examination of Eq. (26). It is clear from Eq. (21) that $G_\nu(L, t)$ acts as a first rank tensor under the operations of **R(3)** applied to the SFF. The same conclusion can be drawn about the $G_\nu(j, L, t)$ from Eq. (26). The sum on s can be interpreted as adding a tensor of rank j with the tensor $T_s{}^L$ of rank L to get one of the first rank. This first rank tensor will act on J and M (but not K) when applied to the wavefunction $|JKM\rangle$ and will give the usual dipole selection rules $\Delta J = 0, \pm 1$ and $\Delta M = 0, \pm 1$. Under the operations of T_d applied relative to the MFF, the operator $D_{-\nu+s,\tau}{}^j$ acts as a tensor of rank j component τ, so that $G_\nu(j, L, t)$ acts as a linear combination of tensors with rank j but different components τ. The relative weight given the component with a particular value of τ is uniquely determined by the coefficient $b_\tau{}^{jLt}$.

Now the operator $G_\nu(j, L, t)$ must transform under the operations of T_d as an A_2 basis function[6] which results from subducing the irrep $D_\mu{}^{(j)}$ of the group **R(3)** $\otimes$ **I** into irreps of the point group T_d. The number of independent basis functions for given j will be denoted by $N(j, A_2)$. For $N(j, A_2) = 1$, there is a single, unique A_2 basis function of rank j. The property which characterizes $G_\nu(j, L, t)$ as this function is the relative weights $b_\tau{}^{jLt}$ given terms of different τ in Eq. (26). Consequently,

$$b_\tau{}^{jLt} = \beta^{jLt}\alpha_\tau{}^j, \tag{28}$$

where the $\alpha_\tau{}^j$ are the constants (*24*) that define the A_2 tetrahedral harmonics of rank j and β^{jLt} is a constant independent of τ which allows for the fact that the $b_\tau{}^{jLt}$ and the $\alpha_\tau{}^j$ can be normalized differently. The critical feature of Eq. (28) is the factorization of the Lt dependence from the τ dependence.

Equation (26) can now be written

$$G_\nu(j, L, t) = \tfrac{1}{2}\lambda_L(-1)^\nu\beta^{jLt} \sum_\tau \alpha_\tau{}^j \sum_s C(1, L, j; -\nu, s)[D_{-\nu+s,\tau}{}^j, T_s{}^L]_+. \tag{29}$$

Since the t dependence enters only through the multiplicative constant β^{jLt}, we can define

$$G_\nu(j, L) = \sum_t G_\nu(j, L, t), \tag{30}$$

where $G_\nu(j, L)$ is given by Eq. (29) with β^{jLt} replaced by $[\sum_t \beta^{jLt}]$. By combining Eqs.

[6] The definition of the irrep A_2 used here is that of Hougen (*32*) and Watson (*3*). The correlation with the alternative definition of Jahn (*33*) and Hecht (*34*) is given in Ref. (*23*).

(27) and (28), we obtain an explicit relationship between $\alpha_\tau{}^j$ and $a_{\omega k}{}^{Lt}$:

$$\beta^{jLt}\alpha_\tau{}^j = \sum_{\omega k} (-1)^\omega a_{\omega k}{}^{Lt} C(1, L, j; -\omega, k)\delta(\tau, -\omega + k). \tag{31}$$

Because only $j < 15$ is being considered, $N(j, A_2) \leq 1$. These results apply therefore to all ranks $j < 15$ for which $G_\nu(j, L)$ is not identically zero.

Equations (28)–(31) have several important implications. Equation (31) provides a mapping from t to j. It shows that a necessary condition for $G_\nu(j, L)$ to be nonzero is that $N(j, A_2) \geq 1$. For given L, the number of nontrivial values of j equals the number of values of t. That is, for given L, the number of nontrivial $G_\nu(j, L)$ equals the number of independent sets of $a_{\omega k}{}^{Lt}$.

$$N(L, F_2) = \sum_{j=L-1}^{L+1} N(j, A_2). \tag{32}$$

This result can be proved for all L directly from Ref. (*24*, Eqs. (11)–(15)). The mapping from t to j provided by Eq. (31) also provides a method of calculating the tetrahedral harmonics of rank j type A_2 (i.e., the $\alpha_\tau{}^j$) from the tetrahedral harmonics of rank L occurrence t type F_2 (i.e., the $a_{\omega k}{}^{Lt}$). This result provides a method of calculating the tetrahedral harmonics of type A_2 (e.g., see Appendix) and leads to relationships between the $d_{KK'}{}^L$ defined in Eq. (12) and the Clebsch–Gordan coefficients.

Another implication of Eq. (29) and the one of central importance here lies in the fact that the K dependence of $\langle J'K'M'|G_\nu(j, L, t)|JKM\rangle$ is independent of L and t. This result will be proved in Section 3.3 and its application to distortion moment spectroscopy will be discussed in Section 4.

Equation (28) is a group theoretical result whose derivation does not depend on the numerical values of $\alpha_\tau{}^j$ and $a_{\omega k}{}^{Lt}$. It applies only for $N(j, A_2) = 1$. In cases where $N(j, A_2) > 1$, Eq. (28) and the results obtained from it would have to be generalized. However, since $N(j, A_2)$ exceeds unity only for $j \geq 15$, this limitation is of no physical interest here. The validity of Eq. (28) is not directly limited by the value of $N(L, F_2)$. Some interesting features arise when $N(L, F_2) > 1$, and these will be discussed in the Appendix where the $(L = 6)$ case is treated.

3. The Matrix Elements of $G_\nu(j, L, t)$

The matrix elements of $G_\nu(j, L, t)$ can be calculated from Eq. (26) using standard angular momentum theory (*18*, *26*, *28*, *31*). The result is

$$\langle J'K'M'|G_\nu(j, L, t)|JKM\rangle = (-1)^{J+J'+1}(\lambda_L/2)C(J, 1, J'; M, \nu, M')$$
$$\times[(2j+1)(2J+1)/(2J'+1)]^{\frac{1}{2}}F(L, j; J, J')\beta^{jLt}\sum_{\tau>0}\alpha_\tau{}^j[C(J, j, J'; K, -\tau, K')$$
$$+(-1)^j C(J, j, J'; K, \tau, K')], \tag{33}$$

where

$$F(L, j; J, J') = \langle J\|T_L\|J\rangle \begin{Bmatrix} J' & 1 & J \\ L & J & j \end{Bmatrix} + (-1)^{j+1}\langle J'\|T_L\|J'\rangle \begin{Bmatrix} J & 1 & J' \\ L & J' & j \end{Bmatrix}. \tag{34}$$

Here $\langle J\|T^L\|J\rangle$ is the reduced matrix element of the spherical tensor $T_s{}^L$ as defined in

terms of $3j$ symbols in Ref. (*28*, Eq. (7)). The explicit values of the reduced matrix elements are given in Ref. (*28*, Eq. (9)). The $\begin{Bmatrix} J' & 1 & J \\ L & J & j \end{Bmatrix}$ are $6j$ symbols (*31*). In deriving Eqs. (33) and (34), we have used Ref. (*31*, Eq. (6.2.8)) to introduce the $6j$ symbols and Eqs. (31) and (15) to change the sum on τ so that it runs over only positive values.

The fact that $F(L, j; J, J')$ contains two terms results directly from the symmetrization introduced in Eq. (21). For Q-branch transitions, the second term in Eq. (34) equals the first except for the sign $(-1)^{j+1}$. For j odd, the two terms are identical and the symmetrization has no effect on the Q-branch matrix elements. For j even, however, the two terms cancel and the Q-branch matrix elements vanish as a result of the symmetrization. This leads to the interesting result that for even j there is no Stark effect. This case arises first in third order (i.e., $L = 6$). For the R branch, the two terms in Eq. (34) are different in general, but are equal for the particular case of first order (i.e., $L = 2$). Consequently, the expressions given in Refs. (*2*, *6*) for the first order dipole operator agree with those obtained from Eq. (33) in spite of the fact that the symmetrization was neglected in Refs. (*2*, *6*).

Equation (33) shows explicitly that the K-dependence of the matrix element is fixed by j alone; it does *not* depend on L or t. To put this result into a form that is particularly useful here, consider two tetrahedral dipole operators $G_\nu(j, L, t)$ and $G_\nu(j, L', t')$ of the same j but different L and/or t. It follows from Eq. (33) that the ratio of the two sets of matrix elements is given by

$$W \equiv \langle G_\nu(j, L', t')\rangle / \langle G_\nu(j, L, t)\rangle = [\lambda_{L'} F(L', j; J, J')\beta^{jL't'}]/[\lambda_L F(L, j; J, J')\beta^{jLt}]. \tag{35}$$

This ratio can equally well be calculated using $b_\tau{}^{jL't'}$ and $b_\tau{}^{jLt}$ instead of the β's. The τ selected is arbitrary since the result is independent of τ. The factorization of the K dependence in Eq. (33) leads directly to the result given in Eq. (35) that W is independent of K.

Because the matrix elements to second order are of particular interest in studies to date of the centrifugal distortion moment, explicit expressions will be given here for the $(L = 2)$ and $(L = 4)$ matrix elements. For both of these L values, $N(L, F_2) = 1$ so that t is redundant and $G_\nu(j, L, t)$ reduces to $G_\nu(j, L)$. (See Eq. (30).) Furthermore, there can be only one nonzero G_ν $(j, L = 2)$ and one nonzero G_ν $(j, L = 4)$. Since $N(1, A_2)$ $= N(2, A_2) = N(4, A_2) = N(5, A_2) = 0$ and $N(3, A_2) = 1$, these two nonzero operators are G_ν $(j = 3, L = 2)$ and G_ν $(j = 3, L = 4)$. We shall write these at G_ν $(L = 2)$ and G_ν $(L = 4)$, respectively, suppressing the j.

It now follows immediately from Eq. (35) that the matrix elements of $G_\nu(4)$ are proportional to those for $G_\nu(2)$. The constant of proportionality W defined in Eq. (35) can be evaluated using Eq. (34) for the F's and Eq. (27) for the b's. The matrix elements of the dipole moment operator to second order can then be written

$$\langle J'K'M'|\mu_\nu|JKM\rangle = \mu(\text{eff})\langle J'K'M'|G_\nu(2)|JKM\rangle, \tag{36}$$

where for the Q branch:

$$\mu(\text{eff}) = \mu_Q(J) = \mu_2{}^{(2)} + J(J+1)\mu_2{}^{(4)} - [1/3(14)^{\frac{1}{2}}][4J(J+1) - 15]\mu_4{}^{(4)}; \tag{37a}$$

and for the R branch:

$$\mu(\text{eff}) = \mu_R(J) = \mu_2^{(2)} + (J+1)^2\mu_2^{(4)} + [1/(14)^{\frac{1}{2}}][(J+1)^2 + 5]\mu_4^{(4)}. \quad (37b)$$

$\mu_Q(J)$ and $\mu_R(J)$ were determined from the W's and Eq. (17).

The matrix elements of $G_\nu(2)$ can be found from Eqs. (33), (34), (31), (14), and (11). For the Q branch:

$$\langle JK'M'|G_\nu(2)|JKM\rangle = iC(J, 1, J; M, \nu, M') \times[3(2J-2)(2J-1)(2J+3)(2J+4)/40]^{\frac{1}{2}} f_0(J, K); \quad (38)$$

and for the R branch:

$$\langle J+1, K'M'|G_\nu(2)|JKM\rangle = iC(J, 1, J+1; M, \nu, M') \times\left[\frac{(2J-1)(2J)(2J+1)(2J+4)(2J+5)}{20(2J+3)}\right]^{\frac{1}{2}} f_1(J, K), \quad (39)$$

where

$$f_\Delta(J, K) = C(J, 3, J+\Delta; K, 2, K') - C(J, 3, J+\Delta; K, -2, K'). \quad (40)$$

Equation (38) agrees with Ref. (*6*, Eq. (17)). Equation (39) agrees with Ref. (*12*, Eq. (15)) and Ref. (*2*, Eq. (9)).

4. DISCUSSION

A general expansion to arbitrary order has been given for the MFF components $\tilde{\mu}_\omega$ of the centrifugal distortion dipole moment and explicit expressions have been given for the expansion coefficients $a_{\omega k}{}^{Lt}$. The derivations presented of the expansion procedure can be easily modified so that it applies to the Hamiltonian. Expressions have been derived for the SFF components μ_ν from which a recurrence relation has been obtained between the tetrahedral harmonics of type F_2 occurrence t rank L and the tetrahedral harmonics of type A_2 rank $j = (L-1)$, L, and $(L+1)$, provided $j < 15$. The matrix elements of the tetrahedral dipole operators $G_\nu(j, L, t)$ have been calculated in the unsymmetrized representation. The K dependence of these matrix elements has been shown to be independent of L and t. Explicit expressions have been obtained for the dipole matrix elements to second order.

The current work has many implications for past and future studies of distortion moment spectra of tetrahedral molecules. The importance of the higher order corrections has been previously established for CH_4 (*14*). The intensity observed in the six R-branch transitions for $J = 10$ to 15 was compared to that calculated from the value of $\mu_2^{(2)}$ determined earlier (*8*) from Stark shifts within the $(J = 2)$ manifold of levels. If all the observed intensity is ascribed to the centrifugal distortion mechanism, then the effective moment for the far-infrared measurements is $\sim$1.4 times that for the molecular beam Stark shift determination.

This increase is easily understood in the context of Eqs. (36) and (37). The far-infrared experiment measured $\mu_R(J)$ averaged from $(J = 10)$ to $(J = 15)$. The molecu-

lar beam experiment measured $\mu_Q(2)$. The observed difference in effective moments can be accounted for if the second order constants are the order of 2×10^{-3} of the first order moment in magnitude (*14*). This agrees with the estimate in Ref. (*2*) of the size of the higher order terms. If $|\mu_2^{(4)}|$ and $|\mu_4^{(4)}|$ are indeed $\sim 2 \times 10^{-3}$ of $|\mu_2^{(2)}|$, then their contribution to the molecular beam measurement of the ($J = 2$) Stark effect is smaller than the experimental error. However, with modest refinements in the ($J = 2$) experiment and/or extension of the work to the ($J = 3$) level, the contribution of the higher order terms to the molecular beam results would be significant.

The ν_4 and ν_2 fundamental bands of SiH_4 are currently being studied using high-resolution infrared laser spectroscopy (*35*). Stark shifts have been measured for high rotational levels and the centrifugal distortion moment is being determined from the data. If a first order analysis were adequate, then the value of $\mu_2^{(2)}$ obtained would equal that determined (*13*) from the intensity of the R-branch transitions for $J = 14$ to 19.

However, in second order, we see the laser experiment measures $\mu_Q(J)$ while the far-infrared value is $\mu_R(J)$ averaged from 14 to 19. If the second order terms are as important in SiH_4 as they appear to be in CH_4, then the values of μ(eff) in the two experiments might well be significantly different. For example, if $|\mu_4^{(4)}/\mu_2^{(2)}| = 2 \times 10^{-3}$ in SiH_4, then for $J = 18$, $\mu_Q(18)$ differs from $\mu_R(18)$ by the order of 40%. This difference is enhanced by the fact that the terms in $\mu_4^{(4)}$ have *opposite signs* in the expressions for $\mu_Q(J)$ and $\mu_R(J)$. In CH_4, the evidence (*8*, *14*) suggests that $\mu_2^{(2)}$ and $\mu_4^{(4)}$ have the same sign. If this is the case in SiH_4, then $|\mu_Q(J)|$ will be smaller than $|\mu_R(J)|$. In third order, the R-branch intensities receive contributions from two additional constants, while the Stark shifts receive contributions from only one of these. (See Appendix.) One of the most promising methods of determining the various dipole moment constants individually is to combine Stark shift measurements with intensity studies on the R-branch transitions.

The form of μ(eff) also has important implications for the frequency analysis of the R-branch transitions that have been observed in CH_4 (*9*, *14*), SiH_4 (*10*, *13*) and GeH_4 (*11*, *12*). For a given $J \rightarrow J + 1$, the many tetrahedral components were not resolved but were observed as a single R branch line. To analyse the frequencies ν_J observed for these lines, it was necessary to calculate the intensities of all these components. Because the second order effects can be taken into account simply by changing the effective moment from $\mu_2^{(2)}$ to $\mu_R(J)$ as was shown in Sec. 3.3, the relative intensities of the different tetrahedral components within a given ($J \rightarrow J + 1$) line do *not* change when we go to second order. As a result, the treatment developed in Refs. (*12*) and (*13*) for analyzing the observed frequencies is valid to second order. From the work in the Appendix, it is clear that third order terms *will* introduce additional frequency shifts.

In general, the earlier calculations on distortion moment spectra can be extended from first to second order simply by replacing $\mu_2^{(2)}$ with μ(eff) as given in Eq. (37). However, third and higher order effects cannot be taken into account in such a simple manner. To treat these effects, new matrix elements as given in Eq. (33) must be calculated. For each order above second, there is more than one independent dipole operator $\tilde{G}_\nu(L, t)$, i.e., $N(L, F_2) > 1$. The new features which arise from this are discussed in the Appendix, where the ($L = 6$) case is treated in some detail.

Although the current work has been concerned with centrifugal distortion moments, many of the results apply to dipole moments of other physical origin. For example, the integrated intensity for a given $(J \rightarrow J + 1)$ R-branch transition summed over all contributing tetrahedral components has been calculated for both the distortion moment (*12*) and the collision-induced moment (*36*). It has been shown (*37*) that the ratio of these intensities is a function only of J. This result follows directly arguments similar to those which showed that W in Eq. (35) is independent of K. In fact, it can be shown by such arguments that, except for this function of J, the collision-induced dipole matrix elements for the individual tetrahedral components in the R branch are given by Eq. (33). This application to collision-induced absorption will be discussed elsewhere (*38*).

APPENDIX

The magnitude of the second order terms observed for CH_4 indicates that third order terms $(n = 3, L = 6)$ may well be important. For this reason, the third order terms will be discussed briefly here. Because $N(6, F_2) = 2$, the expansion of the dipole moment to third order will introduce two new tetrahedral MFF dipole operators $\tilde{G}_\omega$ $(L = 6, t = 1)$ and $\tilde{G}_\omega$ $(L = 6, t = 2)$ with their associated constants $\mu_{6,1}{}^{(6)}$ and $\mu_{6,2}{}^{(6)}$, respectively. The matrix elements arising from these two operators are not simply proportional to those for $L = 2$ or 4, as can be seen from Eq. (33). There will be other third order terms (see Eq. (10)), but these are proportional to the lower order contributions. Here we shall confine our attention to the new operators.

It is convenient to introduce the operator $\tilde{V}_\omega$ $(L = 6, t)$ which includes the constant $\mu_{6,t}{}^{(6)}$ in its definition:

$$\tilde{V}_\omega\ (6, t) = \mu_{6,t}{}^{(6)}\tilde{G}_\omega(6, t). \tag{41}$$

The $\mu_{6,t}{}^{(6)}$ are defined so that $\lambda_6 = 1$. Expressions for the two sets of $\tilde{V}_\omega(6, t)$ can be obtained from Eq. (11). K_e takes the values 2 and 6 which correspond respectively to $t = 1$ and 2, as can be seen from Eq. (13).

When $\tilde{V}_\omega(6, t)$ is transformed to the SFF, it leads to two independent operators.

$$V_\nu(j, 6) = \sum_{t=1}^{2} \mu_{6,t}{}^{(6)}G_\nu(j, 6, t). \tag{42}$$

Here $j = 6$ or 7 since $N(6, A_2) = N(7, A_2) = 1$, but $N(5, A_2) = 0$. Equation (42) is analogous to Eq. (30). Because the two $G_\nu(J, 6, t)$ for fixed j differ only by a multiplicative factor, Eq. (42) can be written

$$V_\nu(j, 6) = \bar{\mu}(j, 6)\tilde{G}(j, 6), \tag{43}$$

where

$$\bar{\mu}(j, 6) \equiv \sum_{t=1}^{2} \beta^{j6t}\mu_{6,t}{}^{(6)} \tag{44}$$

and

$$\tilde{G}(j, 6) = \tfrac{1}{2}(-1)^\nu \sum_\tau \alpha_\tau{}^j \sum_s C(1, L, j; -\nu, s)[D_{-\nu+s,\tau}{}^j, T_s{}^L]_+. \tag{45}$$

[See Eq. (29).] From Eqs. (43) to (45) and (31), it has been found that

$$V_\nu(6,6) = \bar{\mu}(6,6)\left[\frac{-i}{8}\left(\frac{3}{2}\right)^{\frac{1}{2}}\right](-1)^\nu \sum_s C(1,6,6;-\nu,s)[-\sqrt{5}(D_{-\nu+s,6}^{(6)} + D_{-\nu+s,-6}^{(6)}) + (11)^{\frac{1}{2}}(D_{-\nu+s,2}^{(6)} + D_{-\nu+s,-2}^{(6)}), T_s^6]_+, \quad (46a)$$

$$V_\nu(7,6) = \bar{\mu}(7,6)\left(\frac{i}{8}\right)(-1)^\nu \sum_s C(1,6,7;-\nu,s)[(11)^{\frac{1}{2}}(D_{-\nu+s,6}^{(7)} - D_{-\nu+s,-6}^{(7)}) + (13)^{\frac{1}{2}}(D_{-\nu+s,2}^{(7)} - D_{-\nu+s,-2}^{(7)}), T_s^6]_+, \quad (46b)$$

where

$$\bar{\mu}(6,6) = (11/56)^{\frac{1}{2}}\mu_{6,1}^{(6)} - 3(5/56)^{\frac{1}{2}}\mu_{6,2}^{(6)}, \quad (47a)$$

$$\bar{\mu}(7,6) = 3(5/56)^{\frac{1}{2}}\mu_{6,1}^{(6)} + (11/56)^{\frac{1}{2}}\mu_{6,2}^{(6)}. \quad (47b)$$

Equations (46) and (47) give us explicitly the necessary dipole moment operators in the SFF. By using Eq. (33) with β^{j6t} replaced by $\bar{\mu}(j,6)$ the matrix elements of $V_\nu(j,6)$ can be calculated. From Eqs. (33) and (34), it is clear that $V_\nu(6,6)$ will have nonvanishing matrix elements only for the R branch, while $V_\nu(7,6)$ will have nonzero matrix elements for both the R and Q branches.

It is clear from Eq. (47) that the $\bar{\mu}(j,6)$ are related to the $\mu_{6,t}^{(6)}$ through a unitary matrix **M**. It was noted in Section 2 that the operators $\tilde{G}_\omega(L,t)$ are defined only to within a unitary transformation. If we had selected our representation with respect to t to be related to that given in Eq. (11) by the matrix **M**, then $\tilde{V}_\omega(6,1)$ would transform to $V_\nu(6,6)$ and $\tilde{V}_\omega(6,2)$ would transform to $V_\nu(7,6)$. The new unitary matrix relating $\bar{\mu}(j,6)$ to $\mu_{6,t}^{(6)}$ would be diagonal. The form of the operators $\bar{G}(j,6)$ is not affected by the representation actually used.

The α_τ^j in Eq. (45) were calculated from Eq. (31). Their values can be seen directly from a comparison of Eqs. (45) and (46). These α_τ^j can be compared with the coefficients defining corresponding tetrahedral harmonics for $j = 6$ and 7 given by Jahn (*33*). To within an overall normalization constant (which depends on j), the two sets of coefficients agree. This illustrates the use of Eq. (31) to generate tetrahedral harmonics.

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