

# Vibrationally induced nuclear quadrupole coupling in tetrahedral and octahedral molecules

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(Received 11 July 1980; accepted 22 September 1980)

Hyperfine splittings arising from the presence of a quadrupolar nucleus at the center of a molecule belonging to the point group  $T_d$  or  $O_h$  (e.g.,  $^{189}\text{OsO}_4$  or  $^{235}\text{UF}_6$ ) are symmetry forbidden to a high degree of approximation. Nevertheless, quadrupole splittings can be induced by either vibrational or rotational distortions of the molecule, i.e., by distortions similar to those responsible for inducing electric dipole moments in  $T_d$  molecules. Such hyperfine splittings have recently been observed in several laboratories using laser saturation spectroscopy. In this paper we investigate theoretically the quadrupole splittings induced by excitation of doubly and triply degenerate vibrations in  $T_d$  and  $O_h$  molecules. We find that much of the vibration-rotation formalism already present in the methane literature can be applied with only minor changes to the induced-quadrupole-coupling problem, and that rather simple theoretical relationships can be derived between the quadrupole splitting and the tetrahedral or octahedral vibration-rotation splitting of a given level. Values for the scalar and tensor contribution to the quadrupole coupling constant have been derived from the experimental data for  $^{189}\text{OsO}_4$  reported by Bordé *et al.*

## I. INTRODUCTION

A tetrahedral or octahedral molecule such as  $^{189}\text{OsO}_4$  or  $^{235}\text{UF}_6$ , having a central atom with nuclear spin  $I \geq 1$  and outer atoms with  $I \leq \frac{1}{2}$ , does not, to a first approximation, show nuclear quadrupole splittings in the rovibrational states of a totally symmetric electronic state. For even though the central nucleus may possess an electric quadrupole moment, the electric field gradient at the central position vanishes because of the high symmetry. In many excited vibrational and/or rotational states of a totally symmetric electronic state, however, the high symmetry is broken and a small electric quadrupole coupling is produced. Splittings due to such quadrupole couplings have recently been observed for  $^{189}\text{OsO}_4$  by using laser saturation spectroscopy<sup>1-3</sup> and radiofrequency spectroscopy inside a laser cavity,<sup>4</sup> although quantitative analyses have not yet been performed.

The mathematical condition requiring quadrupole coupling to vanish at equilibrium is much more stringent than that requiring the dipole moment to vanish, and is only satisfied by molecules with a high symmetry. However, the condition permitting a molecular-distortion induced quadrupole coupling is less stringent than that permitting a distortion induced dipole moment. For example, a molecule with a center of symmetry such as  $\text{UF}_6$  distorts under the influence of vibration and rotation in such a way that the dipole moment averaged over vibrational motion is always zero, even though a nonzero quadrupole coupling may be produced. We may thus anticipate practical applications of quadrupole coupling investigations when Lamb dip spectroscopy becomes applicable to  $\text{UF}_6$ , since observable quadrupole splittings will provide a very simple tool for discriminating between lines of  $^{238}\text{UF}_6$  ( $I=0$ ) and  $^{235}\text{UF}_6$  ( $I=\frac{7}{2}$ ).

In the present paper we attempt to formulate one aspect of the theory necessary for treating such quadrupole splittings. In particular, we consider quadrupole coupling effects arising from excitation of non-totally symmetric vibrations. Our problem is thus closely related to the vibrationally induced dipole moment problem first treated by Mizushima and Venkateswarlu<sup>5</sup> and later discussed more thoroughly by Mills, Watson, and Smith.<sup>6</sup> A second aspect of the theory necessary for treating these quadrupole splittings, which involves effects arising from the rotation of the molecule, is closely related to the rotationally induced dipole moment question investigated by Watson<sup>7,8</sup> and Fox.<sup>9,10</sup> We have recently learned that this aspect of the theory is being investigated by J. Bordé,<sup>11</sup> and hence will not deal with it here.

In the treatment below we first investigate the form of the quadrupole coupling Hamiltonian, and then discuss the determination of its matrix elements. The treatment is carried out for a molecule of symmetry  $O_h$ , but can easily be converted (as described in the text) to apply to a molecule of symmetry  $T_d$ .

## II. THE HAMILTONIAN

The Hamiltonian operator  $W_{\mathbf{Q}}$  for interaction of a nuclear quadrupole moment  $\mathbf{Q}$  with an electric field gradient  $\nabla \mathbf{E}$  at the position of the nucleus can be written<sup>12</sup> in the form

$$\begin{aligned} W_{\mathbf{Q}} &= -(1/6) \mathbf{Q} : \nabla \mathbf{E} = -(1/6) \sum_{\alpha\beta} \mathbf{Q}_{\alpha\beta} \nabla_{\alpha} E_{\beta} \\ &= -(1/6) \sum_{\alpha\beta} \mathbf{Q}_{\alpha\beta} q_{\alpha\beta}, \end{aligned} \quad (1)$$

where  $\alpha, \beta$  run over molecule-fixed coordinates  $x, y, z$ . Tensor components of the nuclear quadrupole moment

operator  $Q_{\alpha\beta}$  can be written<sup>12</sup> in terms of vector components of the nuclear spin operator  $I$  as follows:

$$Q_{\alpha\beta} = [eQ/I(2I-1)] \left[ \frac{3}{2}(I_\alpha I_\beta + I_\beta I_\alpha) - \delta_{\alpha\beta} I^2 \right]. \quad (2)$$

Components of the electric field gradient  $\nabla_\alpha E_\beta \equiv q_{\alpha\beta}$  at the instantaneous position of the nucleus in question for a nondegenerate electronic state can be expressed in some axis system fixed in the molecule as a power series in the vibrational coordinates  $Q_i$ :

$$q_{\alpha\beta} = (q_{\alpha\beta})_e + \sum_i (\partial q_{\alpha\beta} / \partial Q_i)_e Q_i + \frac{1}{2} \sum_{ij} (\partial^2 q_{\alpha\beta} / \partial Q_i \partial Q_j)_e Q_i Q_j + \dots \quad (3)$$

(In order to conform as closely as possible to standard notation and still avoid ambiguity, we use the sans serif  $Q$  to represent the nuclear quadrupole moment operator and normal  $Q$  to represent vibrational normal coordinates.) Note that Eq. (3) represents a power series expansion of the electric field gradient at the vibrationally displaced position of the nucleus, and that the first term  $(q_{\alpha\beta})_e$  is zero for molecules considered in this paper.

It can be seen from Eqs. (2) and (3) that the single nucleus quadrupole coupling operator  $W_Q$  in Eq. (1) contains components of the nuclear spin operator, vibrational normal coordinates, and constants. We now specialize our consideration of such operators to a molecule belonging to the point group  $O_h$  or  $T_d$ , with only one quadrupolar nucleus, located at its center. To the maximum extent possible we carry out the discussion for the point group  $O_h$ . Because of formal similarities in the symmetry operations and group theoretical notation, however, such discussion will also apply to molecules of symmetry  $T_d$ , if the  $O_h - T_d$  correlation table is used:  $(A_{1g}, A_{2u}) - A_1$ ,  $(A_{2g}, A_{1u}) - A_2$ ,  $(E_g, E_u) - E$ ,  $(F_{1g}, F_{2u}) - F_1$ , and  $(F_{2g}, F_{1u}) - F_2$ .

### A. Sign conventions and definitions

Numerous sign conventions must be specified in any detailed discussion of group theoretical transformation properties. We shall follow here the conventions of Ref.

TABLE I. Linear combinations<sup>a</sup> of quadratic products of functions ( $U_x, U_y, U_z$  and  $V_x, V_y, V_z$ ) belonging to the same triply degenerate ( $F$ ) representation, which transform according to the  $O_h$  representation matrices obtained from Ref. 13.

$$\begin{aligned} A_{1g}(UV) &= (3)^{-1/2} (U_x V_x + U_y V_y + U_z V_z) \\ E_{ga}(UV) &= (6)^{-1/2} (2U_x V_x - U_y V_y) \\ E_{gb}(UV) &= (2)^{-1/2} (U_x V_x - U_y V_y) \\ F_{1gx}(UV) &= (2)^{-1/2} (U_y V_x - U_z V_y) \\ F_{2gx}(UV) &= (2)^{-1/2} (U_y V_x + U_z V_y) \end{aligned}$$

<sup>a</sup>The  $F_{1gy}$  and  $F_{1gz}$  functions are generated by cyclic permutations of  $x, y, z$  in the  $F_{1gx}$  expression. A similar remark holds for the  $F_{2x}$  functions.

TABLE II. Linear combinations of quadratic products of functions ( $X_a, X_b$  and  $Y_a, Y_b$ ) belonging to the same doubly degenerate ( $E$ ) representation, which transform according to the  $O_h$  representation matrices obtained from Ref. 13.

$$\begin{aligned} \bar{A}_{1g}(XY) &= (2)^{-1/2} (X_a Y_a + X_b Y_b) \\ \bar{A}_{2g}(XY) &= (2)^{-1/2} (X_a Y_b - X_b Y_a) \\ \bar{E}_{ga}(XY) &= (2)^{-1/2} (X_b Y_b - X_a Y_a) \\ \bar{E}_{gb}(XY) &= (2)^{-1/2} (X_a Y_b + X_b Y_a) \end{aligned}$$

13 for an  $XY_4$  molecule of symmetry  $T_d$ . The material in Ref. 13 can also be used to fix many conventions for an  $XY_6$  molecule of symmetry  $O_h$  by placing the six identical Y atoms on the positive and negative  $x, y, z$  axes and noting that: (i) the symmetry operations of  $T_d$  given in Table 3.1 of Ref. 13, together with those obtained by multiplying each of these operations by the molecule-fixed inversion operation  $i$ , constitute the symmetry operations of the point group  $O_h$ ; (ii) the irreducible representation matrices in Table 3.3 of Ref. 13, together with those obtained by multiplying each symmetry operation by the molecule-fixed inversion operation and each corresponding representation matrix by  $(+1)$ , constitute the irreducible representation  $F_{1g}$  of  $O_h$ ; (iii) the irreducible representation matrices of Table 3.4 of Ref. 13, together with the equal number generated as in (ii) above, constitute the irreducible representation  $E_g$  of  $O_h$ ; (iv) matrices for the other triply degenerate irreducible representations of  $O_h$ , i.e.,  $F_{1u}$ ,  $F_{2g}$ , and  $F_{2u}$ , can be generated by multiplying the matrices from (ii) by the characters of the  $A_{1u}$ ,  $A_{2g}$ , or  $A_{2u}$  irreducible representations of  $O_h$ , respectively; and (v) matrices for the  $E_u$  irreducible representation of  $O_h$  can be generated by multiplying the matrices from (iii) by the characters of  $A_{1u}$ . Unfortunately, the Longuet-Higgins permutation-inversion operations<sup>14</sup> corresponding to the molecular point group operations in  $O_h$  cannot be generated directly from the tables in Ref. 13, but must be determined for  $XY_6$  using the methods described in Ref. 13.

It is convenient for later discussion in this paper to define a set of linear combinations which can be used to generate specific components of irreducible representations of  $O_h$  from quadratic products of functions belonging to the same triply degenerate ( $F$ ) representation, or to the same doubly degenerate ( $E$ ) representation. These linear combinations  $\Gamma_s(UV)$  and  $\bar{\Gamma}_s(XY)$  are given in Tables I and II, respectively, and can be used to write two useful identities. For any quantities  $A_\alpha, B_\beta, U_\alpha, V_\beta$ , where  $\alpha, \beta = x, y, z$ , it can be shown by direct substitution from Table I that

$$\sum_{\alpha\beta} (A_\alpha B_\beta)(U_\alpha V_\beta) \equiv \sum_s [\Gamma_s(AB)] [\Gamma_s(UV)]. \quad (4)$$

Nine terms occur in the sum on the left as  $\alpha, \beta$  run over the indices  $x, y, z$ , and nine terms occur in the sum on the right as  $\Gamma_s$  runs over the nine components of the three symmetry species (three irreducible representa-

tions) occurring in Table I. Similarly, for any quantities  $A_\alpha$ ,  $B_\beta$ ,  $X_\alpha$ ,  $Y_\beta$ , where  $\alpha, \beta = a, b$ , it can be shown by direct substitution from Table II that

$$\sum_{\alpha\beta} (A_\alpha B_\beta)(X_\alpha Y_\beta) \equiv \sum_s [\bar{\Gamma}_s(AB)] [\bar{\Gamma}_s(XY)]. \quad (5)$$

Four terms occur in the sum on the left as  $\alpha, \beta$  run over the indices  $a, b$ , and four terms occur in the sum on the right as  $\bar{\Gamma}_s$  runs over the four components of the three symmetry species given in Table II. Note that we specify symmetry species given in Table II by a bar throughout this paper; symmetry species without a bar should be taken as those listed in Table I.

### B. Application of group theory to $W_Q$

Both  $Q_{\alpha\beta}$  and  $q_{\alpha\beta}$  in Eq. (1) have subscripts which range over  $x, y, z$ , so that the identification  $A_\alpha, B_\beta - Q_{\alpha\beta}$  and  $U_\alpha, V_\beta - q_{\alpha\beta}$  in Table I leads to the identity

$$W_Q = - (1/6) \sum_{\alpha\beta} Q_{\alpha\beta} q_{\alpha\beta} \equiv - (1/6) \sum_s [\Gamma_s(Q)] [\Gamma_s(q)]. \quad (6)$$

Since  $W_Q$  in this paper is assumed to represent the quadrupole coupling operator for a nucleus located at the center of an octahedral (or tetrahedral) molecule, the molecule-fixed components of the nuclear spin operator  $I$  occurring in the operator equivalent for  $Q$  given in Eq. (2) transform like the molecule-fixed components of the rotation, i. e., like  $F_{1g}$  (or  $F_1$ ). It can thus be shown (with the sign conventions of Ref. 13) that each nonvanishing function  $\Gamma_s(Q)$  defined formally in Table I actually has the symmetry species  $\bar{\Gamma}_s$ .

From the form of  $Q$  in Eq. (2) it can be seen that some  $\Gamma_s(Q)$  on the right of Eq. (6) vanish identically, namely,

$$A_{1g}(Q) = F_{1g}(Q) = 0. \quad (7)$$

Consequently, only the functions  $E_g(q)$  and  $F_{2g}(q)$  of the electric field gradient expansion in Eq. (3) occur in  $W_Q$ . This conclusion can also be reached from simple electrostatic considerations and the assumption that the electric field  $E$  at the nucleus arises only from charges outside the nucleus. For then,  $\nabla \cdot E = \nabla \times E = 0$ , which implies that  $A_{1g}(q)$  and  $F_{1g}(q)$  vanish. Since  $W_Q$  must be totally symmetric, the functions  $E_g(q)$  and  $F_{2g}(q)$  defined in Table I and occurring in Eq. (6) must also be of species  $E_g$  and  $F_{2g}$ , respectively.

Consider now matrix elements of the linear combinations  $E_g(q)$  and  $F_{2g}(q)$  of the vibrational operators in Eq. (3) within a vibrational state of given symmetry species. Watson has discussed group theoretical criteria<sup>15</sup> from which it can be shown that such matrix elements will be nonvanishing only if the species of the operator is contained in the symmetric square of the species of the vibrational state. For octahedral molecules, the symmetric square of nondegenerate species does not contain either  $E_g$  or  $F_{2g}$ , the symmetric square of doubly degenerate species contains  $E_g$  but not  $F_{2g}$ , and the symmetric square of triply degenerate species contains both  $E_g$  and  $F_{2g}$ . For tetrahedral molecules the statements above are true if the subscript  $g$  is removed

everywhere. Vibrationally induced quadrupole coupling phenomena in  $XY_4$  and  $XY_6$  molecules can thus occur in doubly and triply degenerate vibrational states, and these phenomena will be characterized by one and two independent parameters (vibrational matrix elements), respectively.

In the remainder of this paper we shall consider quadrupole coupling effects only in vibrational states involving the excitation of one quantum of one degenerate vibrational mode.

### C. Contact transformation of the electric field gradient

When matrix elements of  $q_{\alpha\beta}(Q)$  in Eq. (3) are taken within a given vibrational state, nonzero contributions arise not only from the quadratic term, but also from the linear term, because of vibrational anharmonicity effects. It is convenient to treat the latter using the procedure given by Hanson, Nielsen, Shaffer, and Waggoner.<sup>16</sup> We apply to Eq. (3) a contact transformation  $T$  which eliminates the third order anharmonicity terms

$$(1/6) \sum_{ijk} \Phi_{ijk} Q_i Q_j Q_k \quad (8)$$

from the vibrational energy expression [see Eq. (7) of Ref. 17], and thus obtain [see Eq. (12) of Ref. 6]

$$\begin{aligned} T q_{\alpha\beta} T^{-1} = & \sum_i (\partial q_{\alpha\beta} / \partial Q_i)_e Q_i + \frac{1}{2} \sum_{ij} (\partial^2 q_{\alpha\beta} / \partial Q_i \partial Q_j)_e Q_i Q_j \\ & + \sum_{ijk} \Phi_{ijk} (\partial q_{\alpha\beta} / \partial Q_k)_e \left[ \frac{1}{2} (\lambda_i + \lambda_j - \lambda_k) Q_i Q_j \right. \\ & \left. + P_i P_j \right] / \Delta_{ijk}, \quad (9) \end{aligned}$$

where

$$\begin{aligned} \lambda_i &= (2\pi\nu_i)^2, \\ \Delta_{ijk} &= \lambda_i^2 + \lambda_j^2 + \lambda_k^2 - 2\lambda_j \lambda_k - 2\lambda_k \lambda_i - 2\lambda_i \lambda_j, \end{aligned} \quad (10)$$

and the  $\Phi_{ijk}$  are cubic constants from the unrestricted sum<sup>17</sup> in Eq. (8).

Because of the contact transformation, we can take matrix elements of the right hand side of Eq. (9) in a harmonic oscillator basis set. Obviously, terms linear in the  $Q_i$  give zero contributions to such matrix elements. Also, for matrix elements within a given degenerate fundamental vibrational state,  $Q_i$  and  $Q_j$ , or  $P_i$  and  $P_j$ , must both be components of the same vibration, so that we can make the substitutions

$$\begin{aligned} \lambda_j - \lambda_i, \\ Q_i Q_j - Q_{ir} Q_{is}, \\ P_i P_j - P_{ir} P_{is} - \lambda_i Q_{ir} Q_{is} \end{aligned} \quad (11)$$

in Eq. (9) to obtain an effective operator for the  $i$ th vibrational state of the form

$$\begin{aligned} (q_{\alpha\beta})_{\text{eff}} = & \frac{1}{2} \sum_{\gamma\delta} \left[ (\partial^2 q_{\alpha\beta} / \partial Q_{ir} \partial Q_{is})_e \right. \\ & \left. - \sum_k \Phi_{ir, is, k} (\partial q_{\alpha\beta} / \partial Q_k)_e / \lambda_k \right] Q_{ir} Q_{is}. \quad (12) \end{aligned}$$

Contributions to  $\sum_k$  vanish except for  $\Gamma_k = E_g$  when  $\Gamma_i$  is

doubly degenerate, and vanish except for  $\Gamma_k = E_g$  or  $F_{2g}$  when  $\Gamma_i$  is triply degenerate, because of the symmetry properties of  $q_{\alpha\beta}$  and  $\Phi_{ijk}$ .

**D. Application of group theory to the effective field gradient operator**

The effective field gradient operator for the  $i$ th degenerate fundamental vibrational state given in Eq. (12) can be written in a somewhat more compact notation by (i) dropping the vibrational state subscript  $i$ , (ii) defining a differential operator

$$D_{\gamma\delta} \equiv \frac{1}{2} \left[ (\partial^2 / \partial Q_\gamma \partial Q_\delta)_e - \sum_k \Phi_{\gamma\delta k} (\partial / \partial Q_k)_e / \lambda_k \right], \quad (13)$$

and (iii) rewriting Eq. (12) as

$$(q_{\alpha\beta})_{\text{eff}} = \sum_{\gamma\delta} Q_\gamma Q_\delta (D_{\gamma\delta} q_{\alpha\beta}). \quad (14)$$

Construct next from Table I a specific linear combination  $\Gamma_s(q_{\text{eff}})$  of the components of the effective field gradient tensor, and apply the identity of Eq. (4) or Eq. (5) to the sum over  $\gamma, \delta$  in Eq. (14) when the vibrational state under consideration is triply or doubly degenerate, respectively. One then obtains

$$\Gamma_s(q_{\text{eff}}) = \sum_t \Gamma_t(QQ) [\Gamma_t(D) \Gamma_s(q)], \quad (15)$$

$$\bar{\Gamma}_s(q_{\text{eff}}) = \sum_t \bar{\Gamma}_t(QQ) [\bar{\Gamma}_t(D) \Gamma_s(q)].$$

Since  $\Gamma_s(q_{\text{eff}})$  must be of species  $\Gamma_s$  under transformations of the vibrational coordinates, the coefficient of  $\Gamma_t(QQ)$  in the sum on the right of the first of Eqs. (15) must vanish except when  $t=s$ . A similar remark holds for the second (barred) equation. Thus,

$$\Gamma_s(q_{\text{eff}}) = \Gamma_s(QQ) [\Gamma_s(D) \Gamma_s(q)] = \Gamma_s(QQ) (a_{\Gamma_s}), \quad (16)$$

$$\bar{\Gamma}_s(q_{\text{eff}}) = \bar{\Gamma}_s(QQ) [\bar{\Gamma}_s(D) \Gamma_s(q)] = \bar{\Gamma}_s(QQ) (\bar{a}_{\Gamma_s}).$$

The numerical coefficients  $a_{\Gamma_s}$  and  $\bar{a}_{\Gamma_s}$  can be defined for the doubly and triply degenerate representations occurring in Tables I and II as

$$a_E = a_{E_{ga}} = a_{E_{gb}} = [E_{ga}(D) E_{ga}(q)],$$

$$a_F = a_{F_{2gx}} = a_{F_{2gy}} = a_{F_{2gz}} = [F_{2gx}(D) F_{2gx}(q)],$$

$$\bar{a}_E = \bar{a}_{E_{ga}} = \bar{a}_{E_{gb}} = [\bar{E}_{ga}(D) E_{ga}(q)],$$

$$\bar{a}_F = \bar{a}_{F_{2gx}} = \bar{a}_{F_{2gy}} = \bar{a}_{F_{2gz}} = 0. \quad (17)$$

**E. Transformation from molecule-fixed to laboratory-fixed components of I**

We now return to a consideration of the nuclear quadrupole operator  $\mathbf{Q}$  in Eq. (1). The discussion of the vibrational dependence of the electric field gradient  $\mathbf{q}$  was carried out in a molecule-fixed coordinate system to make possible the use of group theoretical arguments arising from the symmetry of the molecular equilibrium geometry. It is convenient, however, to use nuclear spin functions characterized by a projection quantum number quantized along a laboratory-fixed axis. Thus, it is necessary to transform from molecule-fixed vector components of  $\mathbf{I}$  in Eq. (2) to laboratory-fixed vector components, using the direction cosine matrix.<sup>18</sup>

If we consider only  $\Delta J=0$  matrix elements of the nuclear quadrupole operator (and we shall see in the next section that this is generally an appropriate restriction), then we can use an operator equivalent technique<sup>19</sup> to replace quadratic products of direction cosine functions of the Eulerian (rotational) angles by products of angular momentum operators. The operator equivalent to Eq. (2) for  $\Delta J=0$  matrix elements can be shown to be<sup>20</sup>

$$\begin{aligned} (\mathbf{Q}_{\alpha\beta})_{\text{eff}} = & [e\mathbf{Q}/I(2I-1)] [2/J(J+1)(2J-1)(2J+3)] \\ & \times [\frac{3}{2}(J_\alpha J_\beta + J_\beta J_\alpha) - \delta_{\alpha\beta} \mathbf{J}^2] [3(\mathbf{I} \cdot \mathbf{J})^2 + \frac{3}{2}(\mathbf{I} \cdot \mathbf{J}) \\ & - \mathbf{I}^2 \mathbf{J}^2]. \quad (18) \end{aligned}$$

The indices  $\alpha, \beta$  still represent molecule-fixed vector components, but the operators  $\mathbf{I}$  and  $\mathbf{J}$  in the last square brackets of Eq. (18) can now be expressed in terms of laboratory-fixed components if desired.

**F. Final form of the effective quadrupole coupling Hamiltonian operator**

The effective Hamiltonian operator used in the next section to calculate nuclear quadrupole coupling matrix elements within a  $v=1$  state can now be written in the form

$$\begin{aligned} W_{\mathbf{Q}} = & - (1/6) \sum_{\alpha\beta} [(\mathbf{Q}_{\alpha\beta})_{\text{eff}}] [(q_{\alpha\beta})_{\text{eff}}] = - \{ a_E [E_{ga}(JJ) E_{ga}(QQ) + E_{gb}(JJ) E_{gb}(QQ)] \\ & + a_F [F_{2gx}(JJ) F_{2gx}(QQ) + F_{2gy}(JJ) F_{2gy}(QQ) + F_{2gz}(JJ) F_{2gz}(QQ)] \} [e\mathbf{Q}/I(2I-1) J(J+1)(2J-1)(2J+3)] \\ & \times [3(\mathbf{I} \cdot \mathbf{J})^2 + \frac{3}{2}(\mathbf{I} \cdot \mathbf{J}) - \mathbf{I}^2 \mathbf{J}^2] \quad (19) \end{aligned}$$

for a triply degenerate vibration, and in the form

$$\begin{aligned} W_{\mathbf{Q}} = & - \{ \bar{a}_E [E_{ga}(JJ) \bar{E}_{ga}(QQ) + E_{gb}(JJ) \bar{E}_{gb}(QQ)] \} \\ & \times [e\mathbf{Q}/I(2I-1) J(J+1)(2J-1)(2J+3)] \\ & \times [3(\mathbf{I} \cdot \mathbf{J})^2 + \frac{3}{2}(\mathbf{I} \cdot \mathbf{J}) - \mathbf{I}^2 \mathbf{J}^2] \quad (20) \end{aligned}$$

for a doubly degenerate vibration.

The numerical coefficients  $a_E, a_F,$  and  $\bar{a}_E$  are de-

defined in Eqs. (17), and the linear combinations of vector components  $\Gamma(JJ), \Gamma(QQ),$  and  $\bar{\Gamma}(QQ)$  are defined in Tables I and II.

**III. MATRIX ELEMENTS**

In this section we address the problem of calculating matrix elements of the effective quadrupole interaction operators  $W_{\mathbf{Q}}$  in Eqs. (19) and (20) for rotational levels

within a given vibrational state. The calculation can be divided into two separate parts: (i) determination of matrix elements of the vibration-rotation operator enclosed in braces  $\{ \}$  in Eqs. (19) and (20), and (ii) determination of the matrix elements of the spin-rotation operator enclosed in the final square brackets.

Matrix elements of the spin-rotation operator are quite simple and well known. In a basis set of the form  $| \gamma; J, I, F, M_F \rangle$ , where the two laboratory-fixed projections  $M_J$  and  $M_I$  have been coupled to give a total angular momentum  $F$  and projection  $M_F$ , these matrix elements are diagonal in all quantum numbers and have the form<sup>12</sup>

$$3(\mathbf{I} \cdot \mathbf{J})^2 + \frac{3}{2}(\mathbf{I} \cdot \mathbf{J}) - \mathbf{I}^2 \mathbf{J}^2 - \frac{3}{4} C_F(C_F + 1) - I(I + 1)J(J + 1), \quad (21)$$

where  $C_F \equiv F(F + 1) - J(J + 1) - I(I + 1)$ .

The vibration-rotation operators in Eqs. (19) and (20), while somewhat formidable in appearance (as such spherical top operators often are), can be expressed in terms of three vibration-rotation operators already studied in some detail in the literature. The details of the treatment are somewhat different for doubly and triply degenerate vibrational states.

## A. Excitation of a triply degenerate fundamental

### 1. Connection with the vibration-rotation literature

For a triply degenerate vibrational state, the two operators  $\sum_{\alpha} E_{g\alpha}(JJ) E_{g\alpha}(QQ)$  and  $\sum_{\alpha} F_{2g\alpha}(JJ) F_{2g\alpha}(QQ)$  in Eq. (19) can be related by straightforward but lengthy algebra to operators of the form  $O_{PP33}(\text{scalar})$  and  $O_{PP33}(\text{tensor})$  introduced by Hecht<sup>21</sup>:

$$\begin{aligned} (\hbar^2/h\nu_3)O_{PP33}(\text{scalar}) &= \sum_{\alpha} E_{g\alpha}(JJ) E_{g\alpha}(QQ) \\ &+ \sum_{\alpha} F_{2g\alpha}(JJ) F_{2g\alpha}(QQ), \\ (\hbar^2/h\nu_3)O_{PP33}(\text{tensor}) &= 6 \sum_{\alpha} E_{g\alpha}(JJ) E_{g\alpha}(QQ) \\ &- 4 \sum_{\alpha} F_{2g\alpha}(JJ) F_{2g\alpha}(QQ), \end{aligned} \quad (22)$$

where  $\alpha = a, b$  for the  $E_g$  sum,  $\alpha = x, y, z$  for the  $F_{2g}$  sum, and the quantities referring specifically to  $\nu_3$  in Hecht's expressions<sup>21</sup> must be considered instead to refer to the triply degenerate vibration under consideration here. Expressed in terms of the  $O_{PP33}$  quantities the vibration-rotation operator in braces in Eq. (19) becomes

$$\{ (\hbar^2/10h\nu_3) [ (4a_E + 6a_F)O_{PP33}(\text{scalar}) + (a_E - a_F)O_{PP33}(\text{tensor}) ] \}. \quad (23)$$

Matrix elements of  $O_{PP33}(\text{scalar})$  within the  $v = 1$  state of a triply degenerate vibration are particularly simple<sup>21</sup> when written in terms of quantum numbers describing the magnitudes of the total angular momentum  $J$  excluding nuclear spin, the vibrational angular momentum  $l$ , and the rotational angular momentum  $R$  obtained by coupling  $J$  and  $l$  ( $R \equiv J - 1$ ). (Note that be-

cause of the anomalous sign of  $l$  in the commutation relations for  $J$ , but not in the commutation relations for  $l$ , the angular momentum difference  $J - 1$  has many formal similarities to an angular momentum sum.<sup>22</sup>) Matrix elements of  $O_{PP33}(\text{scalar})$  are diagonal in the quantum numbers  $J, l, R$ , and  $k_R$  (the molecule-fixed  $z$  component of  $R$ ), and have the form<sup>21</sup>

$$O_{PP33}(\text{scalar}) \rightarrow - (1/3) \left[ \frac{3}{4} C_R(C_R + 1) - l(l + 1)J(J + 1) \right], \quad (24)$$

where  $C_R \equiv R(R + 1) - l(l + 1) - J(J + 1)$ .

Closed form expressions for the matrix elements of the operator  $O_{PP33}(\text{tensor})$  can be obtained from the literature by setting  $t_{044} = t_{134} = 0$  and  $t_{224} = 1$  in Tables VI and VII of Ref. 21, but eigenvalues of the resulting Hamiltonian matrices must be determined numerically. As a consequence of the Wigner-Eckart theorem (as illustrated by the form of Table VI of Ref. 21), matrix elements of  $O_{PP33}(\text{tensor})$  within the set of  $(2R + 1)$  functions characterized by fixed  $v, l, J, R$  and the range  $k_R = R, R - 1, \dots, -R$ , are proportional to the matrix elements of any other  $A_{1g}$  operator constructed from a fourth rank tensor in the vibration, rotation, or vibration-rotation variables. The proportionality constant depends on  $v, l, J, R$ , but not on  $k_R$ .

Various authors have tabulated the eigenvalues of such  $A_{1g}$  fourth rank tensor operators within a given set of  $v, l, J, R$  functions, using various phase conventions and somewhat divergent group theoretical approaches. We cite first Table III of Dorney and Watson,<sup>8</sup> since their group theoretical treatment is the same as ours. Eigenvalues for the operator  $O_{PP33}(\text{tensor})$  in Eq. (22) above, for the  $2R + 1$  states characterized by  $v = l = 1$  (single excitation of a triply degenerate fundamental vibration), and by fixed values of  $J, M_J$ , and  $R$  can be obtained from Table III of Ref. 8 as follows: (i) Replace  $J$  by  $R$  everywhere in the table. (ii) Multiply the quantities  $f(R, \kappa)$  by  $2/R(2R - 1)$ ,  $-2/R(R + 1)$ , or  $2/(R + 1)(2R + 3)$  when  $J = R - 1, R$ , or  $R + 1$ , respectively, to obtain correct numerical values for the eigenvalues of  $O_{PP33}(\text{tensor})$ . (iii) For excitation of an  $F_1$  vibration in  $T_d$ , use the symmetry species given in the column labeled  $\kappa$ ; for excitation of an  $F_{1g}$  vibration in  $O_h$ , add a subscript  $g$  everywhere to these species. For excitation of a vibration of species  $F_2$  in  $T_d$  or  $F_{2g}, F_{1u}, F_{2u}$  in  $O_h$ , multiply everywhere the species appropriate for  $F_1$  or  $F_{1g}$  by  $A_2$  or by  $A_{2g}, A_{1u}, A_{2u}$ , respectively.

### 2. Connection with the microwave literature

The quadrupole interaction energy for the hyperfine levels of a given vibration-rotation state can be expressed in the form commonly used in microwave spectroscopy<sup>12</sup>

$$W_Q = -eqQ \left[ \frac{3}{4} C_F(C_F + 1) - I(I + 1)J(J + 1) \right] / [2I(2I - 1)(2J - 1)(2J + 3)] \quad (25)$$

by substituting into Eq. (19) above the matrix element expression in Eq. (21) and a parameter  $q$  equal to  $2/J(J + 1)$  times the vibration-rotation matrix element of the operator given in Eq. (23). In Eq. (25), the proton

charge  $e$  and the nuclear quadrupole moment  $Q$  are constants, but  $q$  is a function of the particular vibration-rotation state ( $JR\kappa$ ) under consideration.

Using Eqs. (23), (24), and the last statement of the last subsection, we can write  $eqQ$  as

$$\begin{aligned} eqQ(J=R+1, \kappa) &= -\frac{2R+5}{2R+2} \chi_s - \frac{f(R, \kappa)}{(R+1)^2(R+2)(2R+3)} \chi_t, \\ eqQ(J=R, \kappa) &= \frac{(2R-1)(2R+3)}{2R(R+1)} \chi_s + \frac{f(R, \kappa)}{R^2(R+1)^2} \chi_t, \\ eqQ(J=R-1, \kappa) &= -\frac{2R-3}{2R} \chi_s - \frac{f(R, \kappa)}{(R-1)R^2(2R-1)} \chi_t, \end{aligned} \quad (26)$$

where we have introduced the scalar and tensor nuclear quadrupole coupling constants  $\chi_s$  and  $\chi_t$ :

$$\begin{aligned} \chi_s &= (2/5)(\hbar^2/h\nu) eQ(a_F + \frac{2}{3}a_E), \\ \chi_t &= (2/5)(\hbar^2/h\nu) eQ(a_F - a_E). \end{aligned} \quad (27)$$

The function  $f(R, \kappa)$  in Eqs. (26) is the eigenvalue of the tensor operator mentioned earlier, and its values are given in Ref. 8 up to  $R=20$ . Values can be obtained up to  $R=100$  from the table of  $F_4$  coefficients by Krohn,<sup>23</sup> using the relation

$$f(J, \kappa) = -[(3/28)(2J+5)! / (2J-4)!]^{1/2} F_4(J, \kappa). \quad (28)$$

Equations (26) can also be expressed in terms of  $J$ , but the form given in  $R$  is convenient for actual use because  $R$  is equal to the ground state  $J$  value for strongly allowed transitions.

It is interesting to note, that for given  $R$  and  $\kappa$ ,

$$eqQ(J=R, \kappa) \approx -2eqQ(J=R\pm 1, \kappa). \quad (29)$$

Further, for given  $R$  and  $J$ , the principal contribution to the small tetrahedral or octahedral displacements of the various vibration-rotation levels ( $JR\kappa$ ) is proportional to  $f(R, \kappa)$ , so that to a good approximation we may expect the second term in the  $eqQ$  expressions of Eqs. (26) to be proportional to these vibration-rotation energy displacements. Finally, for fixed  $J$  and  $R$ , the quantities  $eqQ(JR\kappa)$  obey the following sum rules:

$$\begin{aligned} \sum_{\kappa} g_{R\kappa} eqQ(J=R+1, \kappa) &= -[(2R+1)(2R+5)/(2R+2)] \chi_s, \\ \sum_{\kappa} g_{R\kappa} eqQ(J=R, \kappa) &= +[(2R+1)(2R-1) \\ &\quad \times (2R+3)/2R(R+1)] \chi_s, \end{aligned} \quad (30)$$

$$\sum_{\kappa} g_{R\kappa} eqQ(J=R-1, \kappa) = -[(2R+1)(2R-3)/2R] \chi_s,$$

where  $g_{R\kappa}$  is the degeneracy of the level  $R, \kappa$ . For fixed  $J$ ,

$$\sum_{R\kappa} g_{R\kappa} eqQ(JR\kappa) = 0. \quad (31)$$

### 3. Rotational clustering effects

It is by now well known<sup>8,24,25</sup> that the high  $J$  rotational levels of spherical top molecules occur in clusters of

nearly degenerate states. For the purposes of this paper, the results of Refs. 24 and 25 on clustering can be summarized for a triply degenerate vibrational state as follows: (i) Sixfold degenerate clusters occur, corresponding to rotation with a given value of  $|k_R|$  about each of the three fourfold axes in  $O_h$  or  $T_d$ ; similarly, eightfold degenerate clusters occur corresponding to equivalent positive and negative rotations about the four threefold axes in  $O_h$  or  $T_d$ . (ii) The center of gravity of the energy levels within a cluster can be calculated with good accuracy by second order perturbation theory, considering only  $\Delta k_R = \pm n$  mixings for the threefold ( $n=3$ ) or fourfold ( $n=4$ ) axes into a state of given  $k_R$ ,  $|k_R| > (R+1) - (2R+1)n/24$ , rotating about a given axis. (iii) The symmetry species of the states within a cluster can be determined from the  $k_R$  value, and the Frobenius reciprocity theorem. (iv) Relative values for the splittings of the levels within a cluster can be determined from a simple tunneling model. (v) Absolute values for the splittings within a cluster (characterized by one parameter per cluster) must still be determined by computer diagonalization of the complete Hamiltonian matrix.

We shall now show that these rotational-cluster near degeneracies do not affect the results presented above, a somewhat surprising conclusion arising essentially because the quadrupolar nucleus is located at the center of the molecule. We note first<sup>24</sup> that no two states within a cluster have the same vibration-rotation symmetry species. We note further that the central atom nuclear spin functions characterized by a laboratory-fixed projection quantum number are totally symmetric with respect to all operations of the molecular point group.<sup>26,27</sup> Thus, ignoring nuclear spins other than that of the central atom, the symmetry species of a vibration-rotation-nuclear-spin function will be the same as that of the vibration-rotation factor it contains. Since the Hamiltonian must be totally symmetric, there will be no mixing of the nearly degenerate states within a cluster due to quadrupolar interactions of the central nucleus with vibrationally or rotationally induced molecular electric field gradients.

One effect of clustering is evident from Eqs. (26), however: All states within a cluster are predicted to exhibit nearly the same vibrationally induced quadrupole coupling constant  $eqQ(JR\kappa)$ .

If the noncentral atoms have nonzero spin (such as <sup>235</sup>UF<sub>6</sub> or <sup>73</sup>GeH<sub>4</sub>), the off-diagonal spin-rotation term mixes levels of different vibration-rotation symmetry species,<sup>3,28,29</sup> so that components of a cluster no longer possess definite vibration-rotation symmetry of  $A$ ,  $E$ , and  $F$ . For such cases, the  $eqQ$  term and the spin-rotation term should be dealt with simultaneously. For molecules with noncentral atoms with zero spin (such as <sup>180</sup>OsO<sub>4</sub>), the components  $A_1$  and  $A_2$  in a cluster have opposite parity<sup>30</sup> and  $eqQ$  matrix elements between them are strictly forbidden.

### 4. Other second order effects

Off-diagonal matrix elements of the  $eqQ$  Hamiltonian between levels ( $JR\kappa$ ) and ( $JR\kappa'$ ) having the same sym-

metry species are allowed on the basis of symmetry considerations alone. However, such matrix elements will probably be negligible except for special cases, because the  $eq\mathbf{Q}$  Hamiltonian is diagonal in the set of tetrahedrally or octahedrally split wave functions, to the extent that the latter are obtained by diagonalizing  $\Delta J = \Delta R = \Delta l = 0$  matrices of  $O_{PP33}$  (tensor). Off-diagonal elements between different  $J$  or  $R$  levels exist, but their effects will be negligible except in cases of accidental degeneracy. Such cases are better dealt with individually.

### B. Excitation of a doubly degenerate fundamental

The discussion of Sec. III. A can be applied with relatively minor modification to a doubly degenerate fundamental vibrational state, as described below. For the  $v=1$  state of an  $E$  vibration, the operator  $\sum_{\alpha} E_{g\alpha}(JJ) \times \bar{E}_{g\alpha}(QQ)$  in Eq. (20) can be related easily to the operator  $N$  introduced by Herranz and Thyagarajan<sup>31</sup>:

$$(\hbar^2/h\nu_2)N = 2\sqrt{3} \sum_{\alpha} E_{g\alpha}(JJ) \bar{E}_{g\alpha}(QQ), \quad (32)$$

apart from a difference in sign for the phase choice of  $Q_b$ . Expressed in terms of  $N$ , the vibration-rotation operator in braces in Eq. (20) becomes simply  $(\sqrt{3}/6) \times (\hbar^2/h\nu_2) \bar{a}_E N$ . Numerical eigenvalues of  $N_J^{(0)}$ , the matrix obtained<sup>31</sup> from the operator  $N$  in a basis set containing the  $2(2J+1)$  functions of given  $J$  and  $M_J$  in a doubly degenerate fundamental vibrational state, are given in Table I of Ref. 31. Vibration-rotation symmetry species for even  $J$  levels of  $T_d$  molecules can be obtained directly from that table; for odd  $J$  levels, the subscripts 1 and 2 must be interchanged. Species for  $E_g$  or  $E_u$  vibrational states of  $O_h$  molecules can be obtained from the altered  $T_d$  species described above by adding a subscript  $g$  or  $u$  everywhere.

A quadrupole coupling constant  $eq\mathbf{Q}$  for each vibration-rotation state can again be used in Eq. (25) to obtain hyperfine energies. For a doubly degenerate state the quantum number  $R$  is not used,<sup>31</sup> and  $eq\mathbf{Q}$  is a function only of  $J, \kappa$ :

$$eq\mathbf{Q}(J\kappa) = \frac{n(J, \kappa)}{J(J+1)} \bar{\chi}_t, \quad (33)$$

where  $n(J, \kappa)$  are the dimensionless eigenvalues of  $N_J^{(0)}$  given in Table I of Ref. 31, and

$$\bar{\chi}_t = (1/\sqrt{3}) (\hbar^2/h\nu) eq\mathbf{Q} \bar{a}_E. \quad (34)$$

Equation (34) shows that the magnitude of  $eq\mathbf{Q}$  induced by the doubly degenerate vibration is proportional to the tetrahedral or octahedral displacements of the individual vibration-rotation components of a given  $J$  manifold. The quantity  $eq\mathbf{Q}(J\kappa)$  obeys a sum rule of the form

$$\sum_{\kappa} g_{\kappa} eq\mathbf{Q}(J\kappa) = 0, \quad (35)$$

where  $g_{\kappa}$  is the degeneracy of the level  $\kappa$ .

Rotational clustering also occurs upon excitation of a doubly degenerate vibration, as can be seen from the high  $J$  patterns in Table I of Ref. 31. It has been found<sup>32</sup> for given  $J$  that the entire energy level cluster

pattern is symmetric about its center of gravity, that outer clusters are sixfold degenerate, and that central clusters are eightfold degenerate. We again observe, as in Sec. III. A, that (i) rotational-cluster near degeneracies do not affect the results given above, and (ii) states within a cluster are expected to exhibit nearly the same vibrationally induced quadrupole coupling constant  $eq\mathbf{Q}(J\kappa)$ .

## IV. APPLICATION TO $^{189}\text{OsO}_4$ AND $^{235}\text{UF}_6$

### A. Analytical expressions for $XY_4(T_d)$ and $XY_6(O_h)$ molecules

We consider as specific examples the tetrahedral  $XY_4$ -type molecule, with vibrational modes  $\nu_1(A_1)$ ,  $\nu_2(E)$ ,  $\nu_3(F_2)$ , and  $\nu_4(F_2)$ , and the octahedral  $XY_6$ -type molecule, with modes  $\nu_1(A_{1g})$ ,  $\nu_2(E_g)$ ,  $\nu_3(F_{1u})$ ,  $\nu_4(F_{1u})$ ,  $\nu_5(F_{2g})$ , and  $\nu_6(F_{2u})$ . Excitation of the totally symmetric vibrational mode  $\nu_1$  does not produce an  $eq\mathbf{Q}$  in either type of molecule, but excitation of any other vibrational mode does produce an  $eq\mathbf{Q}$ . The quantities  $a_E$ ,  $a_F$ , and  $\bar{a}_E$  given in Eqs. (17) in general form can be expressed in more detail for each vibrational excitation using Eq. (13), Tables I and II, and relations among various mechanical and electric constants obtained from symmetry considerations.

We first note, for  $XY_4$  molecules, that the following are the nonvanishing cubic potential constants  $\Phi_{kr6}$  and the relationships among them:

$$\begin{aligned} \Phi_{111}, \\ \Phi_{12a2a} = \Phi_{12b2b} \equiv \Phi_{122}, \\ \Phi_{1t_x t_x'} = \Phi_{1t_y t_y'} = \Phi_{1t_z t_z'} \equiv \Phi_{1tt'}, \\ \Phi_{2a2a2a} = -\Phi_{2a2b2b} \equiv \Phi_{222}, \\ \Phi_{2at_z t_z'} = -2\Phi_{2at_x t_x'} = -2\Phi_{2at_y t_y'} = 2\Phi_{2bt_x t_x'} / \sqrt{3} \\ = -2\Phi_{2bt_y t_y'} / \sqrt{3} \equiv \Phi_{2tt'}, \\ \Phi_{t_x t_y t_z} \equiv \Phi_{ttt}, \\ \Phi_{t_x t_y t_z'} = \Phi_{t_y t_z' t_x'} = \Phi_{t_z' t_x' t_y'} = \Phi_{t_x t_z' t_y'} \\ = \Phi_{t_z' t_y' t_x'} = \Phi_{t_y' t_x' t_z'} \equiv \Phi_{t't't'}, \end{aligned} \quad (36)$$

where the subscripts  $t, t',$  and  $t''$  denote triply degenerate vibrations. Since these force constants are to be used in the unrestricted sum of Eq. (8),  $\Phi_{kr6}$  can be chosen to be invariant to any permutation of its subscripts. The relations given in Eqs. (36) then result from the invariance of various cubic expressions of normal coordinates under the symmetry operations (see for example Ref. 21). To obtain a complete set of all allowed values for the subscripts  $t, t',$  and  $t''$ , it is convenient to use the procedure described by Watson.<sup>33</sup> For  $XY_4$  we find that  $(t, t') = (3, 3), (3, 4), (4, 4)$  for  $\Phi_{1tt'}$  and  $\Phi_{2tt'}$ ;  $t=3$  and  $4$  for  $\Phi_{ttt}$ ; and  $(t, t' = t'') = (3, 4)$  and  $(4, 3)$  for  $\Phi_{t, t', t''}$ .

Equations (36), together with

$$\begin{aligned} \Phi_{2bt_z t_z'} = -2\Phi_{2bt_x t_x'} = -2\Phi_{2bt_y t_y'} = -2\Phi_{2at_x t_x'} / \sqrt{3} \\ = +2\Phi_{2at_y t_y'} / \sqrt{3} \equiv \Phi_{2t't'}, \end{aligned} \quad (37)$$

$$\begin{aligned}\Phi_{t_x t_y t_z} &= \Phi_{t_y t_x t_z} = \Phi_{t_x t_z t_y} = -\Phi_{t_x t_z t_y} \\ &= -\Phi_{t_x t_y t_z} = -\Phi_{t_y t_x t_z} \equiv \Phi_{t t' t''}\end{aligned}$$

give the nonvanishing cubic potential constants  $\Phi_{t' t''}$  and relationships among them for  $XY_6$  molecules. We find<sup>33</sup> for Eqs. (36) that  $(t, t') = (3, 3), (3, 4), (4, 4), (5, 5), (6, 6)$  for  $\Phi_{1 t t'}$  and  $\Phi_{2 t t'}$ ;  $t=5$  for  $\Phi_{t t t}$ ; and  $(t, t', t'') = (3, 3, 5), (3, 4, 5), (4, 4, 5)$ , and  $(5, 6, 6)$  for  $\Phi_{t t' t''}$ . We find<sup>33</sup> for Eqs. (37) that  $(t, t') = (3, 6)$  and  $(4, 6)$  for  $\Phi_{2 t t'}$ ; and  $(t, t', t'') = (3, 5, 6)$  and  $(4, 5, 6)$  for  $\Phi_{t t' t''}$ .

Relations between the various electric field gradient derivatives occurring in Eq. (14) can also be obtained by symmetry considerations (similar to those of Sec. II. D). Nonvanishing first derivatives take the form

$$\begin{aligned}\partial q_{xx} / \partial Q_{2a} &= -2(\partial q_{xx} / \partial Q_{2a}) = -2(\partial q_{yy} / \partial Q_{2a}) \\ &= (2/\sqrt{3})(\partial q_{xx} / \partial Q_{2b}) = -(2/\sqrt{3})(\partial q_{yy} / \partial Q_{2b}) \\ &\equiv \partial q / \partial Q_2, \quad (38)\end{aligned}$$

$$\partial q_{yz} / \partial Q_{tx} = \partial q_{zx} / \partial Q_{ty} = \partial q_{xy} / \partial Q_{tz} \equiv \partial q / \partial Q_t,$$

where  $Q_2$  represents the  $E$  or  $E_g$  vibration of an  $XY_4$  or  $XY_6$  molecule, respectively, and where  $Q_t$  in Eqs. (38) represents an  $F_2$  or  $F_{2g}$  vibration.

Nonvanishing second derivatives take the form

$$\begin{aligned}\partial^2 q_{xx} / \partial Q_{2a}^2 &= -2(\partial^2 q_{xx} / \partial Q_{2a}^2) = -2(\partial^2 q_{yy} / \partial Q_{2a}^2) \\ &= -(\partial^2 q_{xx} / \partial Q_{2b}^2) = 2(\partial^2 q_{xx} / \partial Q_{2b}^2) \\ &= 2(\partial^2 q_{yy} / \partial Q_{2b}^2) = -(2/\sqrt{3})(\partial^2 q_{xx} / \partial Q_{2a} \partial Q_{2b}) \\ &= (2/\sqrt{3})(\partial^2 q_{yy} / \partial Q_{2a} \partial Q_{2b}) \equiv \partial^2 q / \partial Q_2^2, \quad (39)\end{aligned}$$

$$\begin{aligned}\partial^2 q_{xx} / \partial Q_{tx}^2 &= \partial^2 q_{yy} / \partial Q_{ty}^2 = \partial^2 q_{zz} / \partial Q_{tz}^2 \\ &= -2(\partial^2 q_{xx} / \partial Q_{ty}^2) = -2(\partial^2 q_{yy} / \partial Q_{tx}^2) \\ &= -2(\partial^2 q_{zz} / \partial Q_{tx}^2) = -2(\partial^2 q_{xx} / \partial Q_{tz}^2) \\ &= -2(\partial^2 q_{yy} / \partial Q_{tz}^2) = -2(\partial^2 q_{zz} / \partial Q_{ty}^2) \\ &\equiv (\partial^2 q / \partial Q_t^2)_e,\end{aligned}$$

$$\begin{aligned}\partial^2 q_{yz} / \partial Q_{ty} \partial Q_{tz} &= \partial^2 q_{zx} / \partial Q_{tx} \partial Q_{tz} = \partial^2 q_{xy} / \partial Q_{tx} \partial Q_{ty} \\ &\equiv (\partial^2 q / \partial Q_t^2)_f,\end{aligned}$$

where  $Q_2$  again represents the  $E$  or  $E_g$  vibration, but where  $Q_t$  in Eqs. (39) now represents any  $F$  vibration.

Using the mechanical relations given in Eqs. (36) and (37) and the electrical relations given in Eqs. (38) and (39), we obtain from Eqs. (17) expressions for  $\bar{a}_E$ ,  $a_E$ , and  $a_F$  as follows:

$$\bar{a}_E(2) = -(\sqrt{3}/2) [\partial^2 q / \partial Q_2^2 - (\Phi_{222} / \lambda_2)(\partial q / \partial Q_2)] \quad (40)$$

for the  $\nu_2$  state of both  $XY_4$  and  $XY_6$ ;

$$a_E(t) = (3/4) [(\partial^2 q / \partial Q_t^2)_e - (\Phi_{2tt} / \lambda_2)(\partial q / \partial Q_2)] \quad (41)$$

for  $t=3$  and 4 of  $XY_4$  and  $t=3, 4, 5, 6$  of  $XY_6$ ; and

$$a_F(t) = (\partial^2 q / \partial Q_t^2)_f - \sum_{t'} (\Phi_{t' t t'} / \lambda_{t'}) (\partial q / \partial Q_{t'}) \quad (42)$$

for  $t=3$  ( $t'=3, 4$ ) and  $t=4$  ( $t'=3, 4$ ) of  $XY_4$ , and for  $t=3, 4, 5, 6$  ( $t'=5$ ) of  $XY_6$ . All other constants are zero.

## B. Numerical analysis of the observed hyperfine structure of $^{189}\text{OsO}_4$

Recently, Bordé and co-workers<sup>3</sup> have reported hyperfine patterns for three transitions of the  $\nu_3$  fundamental of  $^{189}\text{OsO}_4$  observed by laser saturation spectroscopy. Based on the extensive spectroscopic study of this band by McDowell *et al.*,<sup>34</sup> the three transitions were assigned to the  $A_1^0$  component (in the notation used by McDowell *et al.*) of the  $R(26)$  transition and to the  $A_2^2$  and  $A_1^3$  components of the  $P(49)$  transition. [The superscript numbering scheme of Refs. 3, 23, and 34 differs from two others also employed extensively in the literature; in the notation of Dorney and Watson,<sup>8</sup> which we wish to follow in this paper, the three transitions above become  $A_1^{(2)}$  of  $R(26)$  and  $A_2^{(4)}$  and  $A_1^{(4)}$  of  $P(49)$ , respectively.]

In the absence of more extensive data, a complete treatment of spin-rotation effects, rotationally induced quadrupole coupling effects, and vibrationally induced quadrupole coupling effects cannot be carried out. As a first approximation, spin rotation effects can be neglected in the allowed ( $\Delta R=0$ ) transitions of a fundamental band.<sup>3</sup> A least squares fit of each of the three observed hyperfine patterns, using the  $F$  assignments of Ref. 3, to an expression of the form

$$k - eqQ \cdot f(I, J, F), \quad (43)$$

where  $k$  is a constant, and  $f(I, J, F)$  is Casimir's function<sup>12</sup> [i.e., the function to the right of  $eqQ$  in Eq. (25)] then yields effective values for the vibration-rotation induced quadrupole coupling constants  $eqQ(J, R, \kappa)$  of

$$\begin{aligned}eqQ(27, 26, A_1^{(2)}) &= 6.03 \pm 0.10 \text{ MHz}, \\ eqQ(48, 49, A_2^{(4)}) &= 7.44 \pm 0.16 \text{ MHz}, \\ eqQ(48, 49, A_1^{(4)}) &= 7.43 \pm 0.16 \text{ MHz},\end{aligned} \quad (44)$$

where the quoted uncertainties are standard deviations  $\sigma$  from the fits. [Our effective  $eqQ(27, 26, A_1^{(2)})$  value is twice as large and opposite in sign from that given in Ref. 3; this difference is essentially notational, arising from the fact that Eq. (25) is similar to the linear molecule expression in Eq. (6-4) of Ref. 12, whereas the authors of Ref. 3 have used<sup>11</sup> an equation similar to the atomic expression in Eq. (6-1) of Ref. 12.] The rather large standard deviations on the coupling constants in Eqs. (44) reflect discrepancies between observed and calculated frequencies in the fits of the order of 30 kHz. As already noted by Bordé *et al.*,<sup>3</sup> these discrepancies can probably be eliminated by a consideration of spin rotation interactions.

If the three vibration-rotation induced quadrupole coupling constants in Eqs. (44) are now ascribed solely to vibrational effects, we can perform a  $(1/\sigma^2)$ -weighted least squares fit to Eqs. (26) to obtain the two rotational-state-independent quantities

$$\begin{aligned}\chi_s &= -4.29 \pm 0.17 \text{ MHz}, \\ \chi_t &= -3.14 \pm 0.23 \text{ MHz}\end{aligned} \quad (45)$$

for the  $\nu_3$  vibrational state of  $\text{OsO}_4$ , where the quoted uncertainties are 30 times the standard deviations obtained from the fit, and represent an attempt to allow



for the large uncertainties in the input  $eqQ$  values. The  $\chi_s$  and  $\chi_t$  values in Eqs. (45) should be considered as tentative until more experimental data are available, and until the spin rotation and rotation-induced quadrupole coupling effects neglected here are treated properly. Furthermore, if the  $F$ - $J$  assignments of Ref. 3 are changed in a way (i.e.,  $\pm 3/2 \leftrightarrow \mp 1/2$ ) which cannot be ruled out from the preliminary results presented in Ref. 3, then all quantities in Eqs. (44) and (45) change sign.

The values of  $\chi_s$  and  $\chi_t$  obtained above can be used to illustrate the variation of effective  $eqQ$  values with rovibrational level. Thus, calculated values of  $eqQ(JR\kappa)$  for  $R=50$ , and for components  $\kappa$  of the tetrahedral splitting with symmetry species  $A$ , are plotted in Fig. 1 as a function of  $f(R, \kappa)$ ; the latter is proportional to the shift of energy levels from the center of gravity of a given  $J, R$  manifold. It is noted that  $eqQ(JR\kappa)$  is reduced in magnitude and eventually changes sign as  $\kappa$  ranges over the components from the  $C_{3v}$  extreme ( $A_1^{(4)}$ ) to the  $D_{2d}$  extreme ( $A_2^{(1)}$ ). This is somewhat similar to the case of symmetric rotors, where the effective  $eqQ$  varies as  $[3K^2/J(J+1) - 1]$ . As indicated in Eq. (29), corresponding  $eqQ(JR\kappa)$  values for  $J=R+1$  levels and  $J=R-1$  levels in Fig. 1 are similar to each other, but values for the  $J=R$  levels are opposite in sign and approximately twice as large. Other molecular examples, such as  $^{235}\text{UF}_6$  or  $^{73}\text{GeH}_4$ , have many more component levels than those shown in Fig. 1 (i.e., have  $E$  and  $F$  components, in addition to  $A$ ) because  $I = \frac{1}{2}$  for  $F$  and  $H$  nuclei, but straight-line patterns similar to those plotted in Fig. 1 will hold for these molecules as well.

In order to see the variation of  $eqQ(JR\kappa)$  with  $R$ , effective  $eqQ$  values in  $^{189}\text{OsO}_4$  for the levels with highest

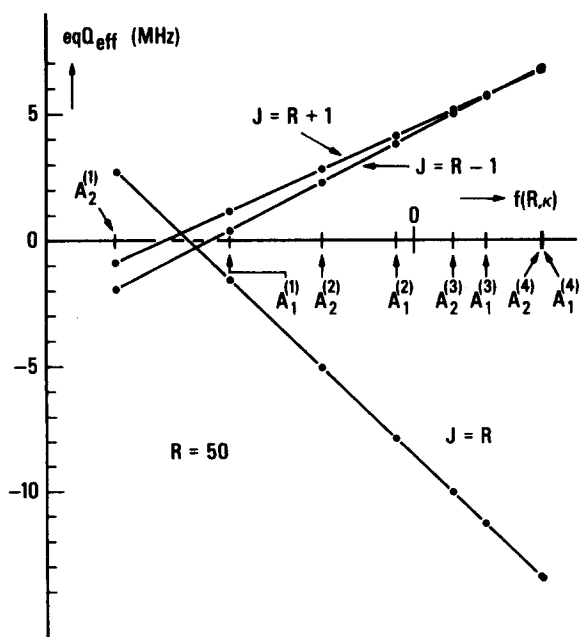


FIG. 1. An example of the dependence of  $(eqQ)_{\text{eff}}$  on energy levels. Values of  $(eqQ)_{\text{eff}}$  for  $^{189}\text{OsO}_4$  are plotted for  $J=R+1$ ,  $R$ , and  $R-1$  states with  $v_3=1$  and  $R=50$  against an abscissa proportional to the tetrahedral splitting energy.

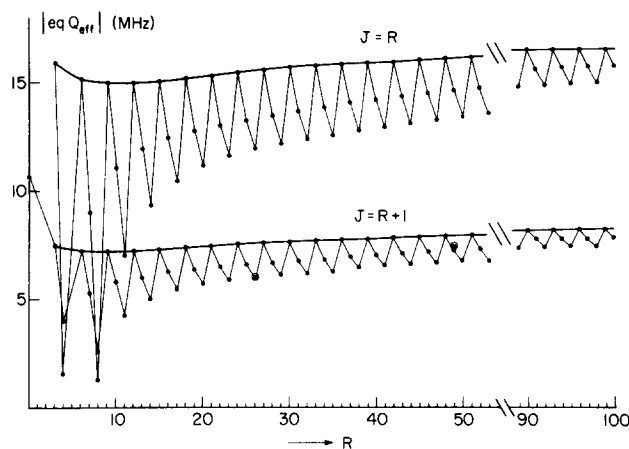


FIG. 2. Variation with  $R$  of values of  $|eqQ)_{\text{eff}}|$  for  $^{189}\text{OsO}_4$  at the  $C_{3v}$  limit, i.e., of values for the rovibrational  $A$  state with largest positive  $f(R, \kappa)$  in the tetrahedral splitting pattern. Note that values for  $J=R$  are approximately twice as large as those for  $J=R+1$ , and are opposite in sign. (Values for  $J=R-1$ , which are similar to those for  $J=R+1$ , are omitted for clarity.) The two points  $\circ$  represent the observed values of Bordé *et al.*<sup>3</sup> used in our analysis ( $J=R+1$  for  $R=26$ ;  $J=R-1$  for  $R=49$ ). The zigzag nature of the  $eqQ$  values is due to a periodic variation of the  $f(R, \kappa)_{\text{max}}$  value for rovibrational  $A$  species. For molecules such as  $^{235}\text{UF}_6$  or  $^{73}\text{GeH}_4$ , for which the  $A$ ,  $E$ , and  $F$  rovibrational species are all allowed, the curve will be much smoother, approximating the solid line connecting the  $R=3n$  values in Fig. 2.

$f(R, \kappa)$  value (the  $C_{3v}$  extreme) are plotted in Fig. 2 for  $J=R$  and  $J=R+1$ . (Values for  $J=R-1$ , which are close to those for  $J=R+1$ , are omitted for clarity.) Only the absolute values  $|eqQ(JR\kappa)|$  are plotted; the actual values for  $J=R$  and  $J=R+1$  have opposite sign. The zigzag variation with period  $\Delta R=3$  is due to the variation of the relative position of the highest  $A$  level in the tetrahedral splitting pattern; for molecules like  $^{235}\text{UF}_6$  and  $^{73}\text{GeH}_4$ , the curves connecting effective  $eqQ$  values for levels with highest  $f(R, \kappa)$  are much smoother, since for such molecules a consideration of only  $A$  rovibronic species is not appropriate. It is to be noted that the  $\text{OsO}_4$  values vary considerably for low  $R$  levels, but converge for high  $R$  levels to  $(\chi_s + 4\chi_t/3)$  or  $2(\chi_s + 4\chi_t/3)$  because  $f(R, \kappa)_{\text{max}} \rightarrow +8R^4/3$ .

## ACKNOWLEDGMENTS

Just prior to submission of this manuscript for publication, a very general treatment of the Hamiltonian for hyperfine interactions in spherical top molecules by Michelot and Moret-Bailly<sup>35</sup> has come to the attention of the authors. The relationship between our work and theirs is not yet clear.

The authors would like to thank Dr. J. K. G. Watson for his critical reading of the manuscript.

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