Classification of Rotational Energy Levels for SymmetricTop Molecules

Jon T. Hougen

Additional information on J. Chem. Phys.

where

$$\delta = \langle \xi \rangle_{Av}/t + \langle x^2 + y^2 \rangle_{Av}/2t^2.$$

Using Eq. (13), at small λt

$$\langle \xi \rangle_{Av}/t = -\lambda t + O(\lambda t)^2.$$

For the limit of a short chain Daniels[9] has shown that the variances in the x and y direction equal $\frac{2}{3}\lambda t^3$. Therefore $\delta = -\frac{1}{3}\lambda t$ and $t^{-2}\langle r^2 \rangle = 1 - \frac{2}{3}\lambda t$ which is the limiting form of Eq. (13). This proves the assumption that $\langle \xi^2 \rangle_{Av}/t^2 \ll \langle x^2 \rangle_{Av}/t^2$ is correct, and that $t\langle r^{-1} \rangle = 1 + \frac{1}{3}\lambda t$.

Classification of Rotational Energy Levels for Symmetric-Top Molecules

JON T. HOUGEN*

Division of Pure Physics, National Research Council, Ottawa, Canada

(Received May 28, 1962)

It is shown that the rotational energy levels of a symmetric-top molecule can be classified according to symmetry species of the full symmetry group of the molecule. Useful selection rules for electric-dipole transitions between rotational energy levels thus classified are presented. It is shown that the rotational energy levels can be labeled in addition by a convenient quantum number G, which is essentially a generalization of the $+l$, $-l$ labels. Selection rules for this quantum number are presented, which, together with those for the symmetry species, allow one to determine easily the allowed branches for a transition between any two vibronic states in a symmetric-top molecule.

THIS paper represents an attempt to improve upon the existing classification scheme[1] for the rotational energy levels of symmetric-top molecules. Such levels are usually given four labels: J, specifying the total angular momentum; K, specifying the angular momentum about the top axis; $+l$ or $-l$, labels arising from a consideration of Coriolis splittings in degenerate vibronic states; and Γ, a symmetry species of the rotational subgroup of the full molecular point group, which is useful when considering the statistical weights of the rotational energy levels. This paper is divided into two parts. In part I we show that a symmetry species corresponding to an irreducible representation of the *full* point group of the molecule can be assigned to each rovibronic level of a symmetric top. We also derive useful selection rules involving these symmetry species for electric dipole transitions between pairs of rovibronic states. In part II we introduce a convenient quantum number G to replace the $\pm l$ designation, together with selection rules on G for the allowed and forbidden rotational branches in a transition between any two vibronic states of a symmetric-top molecule. An example of the use of this quantum number is given.

I. SYMMETRY SPECIES

Since the work of Wilson[2] on the statistical weights of rotational energy levels it has sometimes been assumed that only those symmetry species correspond-

ing to irreducible representations of the rotational subgroup of the full molecular point group provide useful labels for rovibronic levels.[1] It was pointed out by Jahn,[3] however, that a classification of levels according to irreducible representations of the full point group is very useful for investigations of the rotation–vibration spectrum of methane, a spherical-top molecule. Such a classification has been used in other papers on methane.[4,5] We now demonstrate that a classification of rotational energy levels according to the full point group of the molecule[6] is possible for any symmetric-top molecule in a singlet state. Even though spherical tops, asymmetric tops, and states of multiplicity two and higher will not be considered, one expects on the basis of the present work and the work on methane that a classification of rotational energy levels according to the full point group of the molecule will be possible for any molecule whatsoever.

Preliminary Formalism

The Hamiltonian $\mathcal{H}$ for a molecule can easily be written down in space-fixed Cartesian coordinates

$$\mathcal{H} = \mathcal{I}_e + \mathcal{I}_n + \mathcal{V}_{en}, \tag{1}$$

* National Research Council Postdoctorate Fellow 1960–62.
[1] G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945), pp. 400–446.
[2] E. B. Wilson, Jr., J. Chem. Phys. **3**, 276, 818 (1935).

[3] H. A. Jahn, Proc. Roy. Soc. (London) **A168**, 469 495 (1938).
[4] W. H. J. Childs and H. A. Jahn, Proc. Roy. Soc. (London) **A169**, 451 (1939).
[5] K. T. Hecht, J. Mol. Spectroscopy **5**, 355, 390 (1960).
[6] Essentially this classification of the rovibronic energy levels according to species of the full molecular point group is briefly discussed in Sec. 103 of the textbook *Quantum Mechanics* (English translation by J. B. Sykes and J. S. Bell, Pergamon Press, London, 1958) by L. D. Landau and E. M. Lifshitz. The author is indebted to Professor E. B. Wilson, Jr. for calling this fact to his attention.
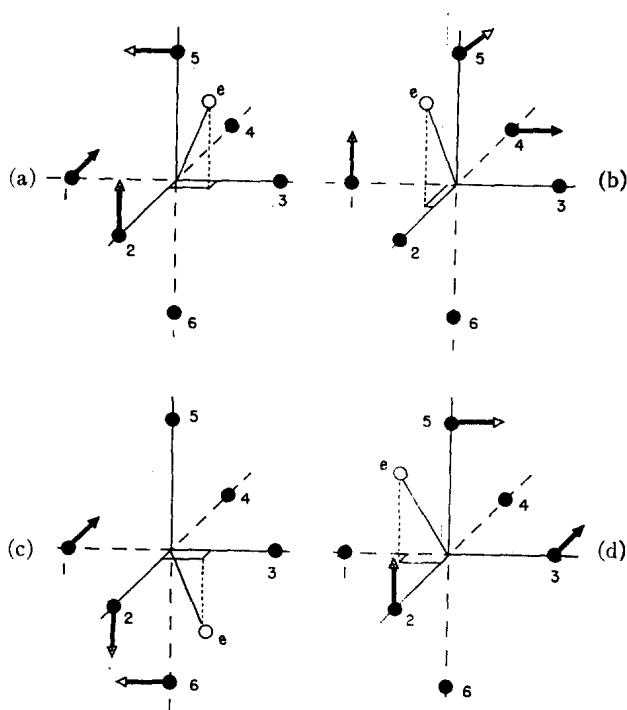
FIG. 1. The effect on a certain set (a) of nuclear displacements and electron positions of the operations: ^1C_n—(b), $^1\sigma_h$—(c), and $^1\sigma_v$—(d). The full circles represent nuclear reference positions, the arrows represent nuclear displacements, and the open circle represents the instantaneous position of an electron. In (a), (b), (c), and (d) the reference positions of nuclei 2, 3, and 5 lie on the positive x, y, and z axes, respectively. All nuclear displacements illustrated are parallel to coordinate axes.

where $\mathfrak{I}_e$ and $\mathfrak{I}_n$ are the kinetic energy operators for the electrons and nuclei, respectively, and where $\mathcal{V}_{en}$ is the interaction energy of the particles. Suppose now that the N nuclei of the molecule can be arranged so that the resultant configuration is a symmetric top, i.e., so that identical nuclei are carried into each other by operations belonging to a symmetric-top point group. Let us call this configuration of the molecule the reference configuration and the position occupied by a given nucleus its reference position. We now define a set of coordinates for the nuclei which replace their $3N$ Cartesian coordinates, namely the three coordinates of the center of mass of the nuclei, the three Eulerian angles θ, ϕ, χ, and $3N-6$ symmetry coordinates. These latter correspond to displacements of the nuclei from the symmetric-top reference configuration which leave unchanged the center-of-mass coordinates and the Eulerian angles; they are chosen in such a way that they transform according to irreducible representations of the molecular point group when the nuclear displacements are permuted according to some symmetry operation of the group.[7] The transformation from Cartesian coordinates to the new coordinates, which

leads to a separation of vibrational and rotational motion in the Hamiltonian, is well known.[8]

The three Eulerian angles mentioned above can be used to define a Cartesian axis system called the molecule-fixed axis system, which is essentially translating and rotating with the molecule.[9] It is convenient to transform the electronic Cartesian coordinates so that they are referred to this molecule-fixed axis system. (Note that such a change in the electronic variables also affects the operators involving differentiation with respect to the nuclear variables.)[10] After these changes in variables, the Hamiltonian for the molecule can be separated into two parts: a vibronic part $\mathcal{K}_{ev}$, which does not contain the Eulerian angles; and a rotational part $\mathcal{K}_r$, which does

$$\mathcal{K} = \mathcal{K}_{ev} + \mathcal{K}_r. \qquad (2)$$

The partitioning of the Hamiltonian is somewhat arbitrary. We choose to define

$$\mathcal{K}_{ev} = T_e + \sum_{k=1}^{3N-6} P_k^2 + V_{en},$$

$$\mathcal{K}_r = \tfrac{1}{2}\mu^{1/4}\sum_{\gamma\delta}(J_\gamma - p_\gamma)\mu_{\gamma\delta}\mu^{-1/2}(J_\delta - p_\delta)\mu^{1/4}$$

$$+ \sum_{k=1}^{3N-6}(\mu^{1/4}P_k\mu^{-1/2}P_k\mu^{1/4} - P_k^2). \qquad (3)$$

T_e is the kinetic energy operator for the electrons; it is simply the sum of Laplacian operators written in terms of the molecule-fixed Cartesian coordinates of the electrons. P_k is the momentum conjugate to the symmetry coordinate Q_k describing a nuclear displacement. V_{en} is the interaction energy of the particles with one another. J_x, J_y, and J_z are the components in the molecule-fixed axis system of the total angular momentum of the molecule; p_x, p_y, p_z are the components in the molecule-fixed axis system of the sum of the vibrational angular momentum of the nuclei[8] and the electronic orbital angular momentum. (Electronic spin angular momentum has been neglected.) μ and $\mu_{\gamma\delta}$ are quantities depending on the instantaneous moments and products of inertia of the molecule.[8] We note that the Hamiltonian of Eqs. (2) and (3) is a correct Hamiltonian regardless of whether or not the actual equilibrium positions of the nuclei coincide with their reference positions and regardless of the amplitudes of the vibrational motions within the molecule.

Species of Vibronic States

Let us define three operations ^1C_n, $^1\sigma_h$, and $^1\sigma_v$, which correspond to simultaneous transformations of the molecule-fixed electronic coordinates and the nuclear

[7] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955), Chap. 5, especially Sec. 5-5.

[8] Reference 7, Chap. 11.
[9] Reference 7, Appendix I.
[10] R. de L. Kronig, *Band Spectra and Molecular Structure* (Cambridge University Press, Cambridge, England, 1930), pp. 6–16.

symmetry coordinates. The operation ^1C_n is defined as that change in variables which corresponds to evaluating the wavefunction after (i) a rotation of the position of each electron through an angle of $-2\pi/n$ about the z axis and (ii) a rotation from its reference position of the displacement vector of each nucleus through an angle $-2\pi/n$ about the z axis. After rotating the displacement vectors, they are relabeled to agree with the nucleus for which they now measure a displacement. Figure 1(a) illustrates a particular reference configuration for the nuclei of a molecule, together with some arbitrary nuclear displacements,[11] as well as an electron at some arbitrary position. Figure 1(b) illustrates the effect of the operation ^1C_n. The operation $^1\sigma_h$ is defined as that change in variables which corresponds to evaluating the wavefunction after a reflection of the electron positions and the nuclear displacements in the xy plane, followed by an appropriate relabeling of the nuclear displacements. This operation is illustrated in Fig. 1(c). The operation $^1\sigma_v$ is defined as that change in variables which corresponds to evaluating the wavefunction after a reflection of the electron positions and the nuclear displacements in the xz plane, followed by an appropriate relabeling of the nuclear displacements. This operation is illustrated in Fig. 1(d). (If the reference configuration of the nuclei has vertical planes of symmetry, we can always arrange one of these to be the xz plane.)

The set of rotations and reflections which permute the nuclear displacements of identical nuclei constitutes the symmetry group to which the symmetric top reference configuration belongs. (This is also the set of rotations and reflections, which from another point of view would carry identical nuclei into each other.[7]) Only those operations are included in the molecular point group which carry the origins of the displacement vectors to the reference positions of identical nuclei, since only such transformations can be accomplished by changing the $3N-6$ symmetry coordinates alone. Any element of a symmetric top point group can be expressed as a product of the three operations ^1C_n, $^1\sigma_h$ and $^1\sigma_v$ defined above, i.e., in the general form $(^1C_n)^p \cdot (^1\sigma_h)^q \cdot (^1\sigma_v)^r$, where p, q and r are positive integers or zero. (The three operations ^1C_n, $^1\sigma_h$, and $^1\sigma_v$ need not themselves belong to the group.)

We can now prove a statement concerning the eigenfunctions of the vibronic Hamiltonian as defined in Eq. (3). *The vibronic wavefunctions can be characterized by symmetry species specifying the irreducible representation to which they belong with respect to the molecular point group of the symmetric-top reference configuration, since the vibronic Hamiltonian as defined in (3) can never mix functions of different symmetry species.* This statement is proved by showing that the vibronic Hamiltonian is invariant under the operations of the molecular point

group described above. V_{en} is certainly invariant, since it is physically evident that the interaction energy of the electrons and nuclei is not altered by transformations that effectively correspond to a rotation and/or reflection of all the electric charges in the system under consideration. The electronic kinetic-energy operator, being the sum of Laplacian operators, is invariant under transformations corresponding to rotations and/or reflections of the electronic molecule-fixed Cartesian coordinates. $\sum_k P_k^2$ is invariant under operations of the molecular point group since the Q_k, and consequently their conjugate momenta P_k, have been chosen to transform according to irreducible representations of this group. Thus, the italicized statement above is proved.

Species of Rovibronic States

Before discussing the rovibronic levels, let us define a new set of operations which act on the Eulerian angles θ, ϕ, χ and on the coordinates of the center of mass X, Y, Z as well as on the vibronic variables.

$$C_n = {}^1C_n{}^2C_n{}^3C_n, \qquad \sigma_h = {}^1\sigma_h{}^2\sigma_h{}^3\sigma_h, \qquad \sigma_v = {}^1\sigma_v{}^2\sigma_v{}^3\sigma_v, \qquad (4)$$

where

$$^2C_n f(\chi) = f(\chi + 2\pi/n),$$

$$^2\sigma_h f(\chi) = f(\pi + \chi),$$

$$^2\sigma_v f(\theta, \phi, \chi) = f(\pi - \theta, \pi + \phi, \pi - \chi),$$

$$^3C_n f(X, Y, Z) = f(X, Y, Z),$$

$$^3\sigma_h f(X, Y, Z) = f(-X, -Y, -Z),$$

$$^3\sigma_v f(X, Y, Z) = f(-X, -Y, -Z). \qquad (5)$$

It can be shown that, if any set of operations of the form $(^1C_n)^p \cdot (^1\sigma_h)^q \cdot (^1\sigma_v)^r$ form a group, then the set of operations formed by omitting the superscript 1 forms an isomorphic group.

We shall now prove a statement concerning eigenfunctions of the complete Hamiltonian which is analogous to that given above concerning eigenfunctions of the vibronic Hamiltonian. *The rovibronic (complete) wavefunctions for the molecule can be characterized by symmetry species specifying the irreducible representation to which they belong with respect to the full molecular point group of the symmetric-top reference configuration, since the complete Hamiltonian can never mix functions of different symmetry species.* This statement is proved by showing that the complete Hamiltonian is invariant under the set of operations of the form $(C_n)^p \cdot (\sigma_h)^q \cdot (\sigma_v)^r$ comprising the group isomorphic with the molecular point group of the vibronic problem.

The simplest way of showing the total Hamiltonian to be invariant under the combinations of the operations given in (4) which comprise the molecular point group involves relating the operations given in (4),

---

[11] To simplify the diagram, the displacements were not required to leave the center of mass of the nuclei and the Eulerian angles invariant.

and consequently any combinations thereof, to transformations of the space-fixed Cartesian coordinates of the particles in the molecule. The values of the space-fixed coordinates are related to the values of the molecule-fixed coordinates as follows[8]:

$$\mathbf{r}^{\alpha} = \mathbf{R} + S^{-1} \varrho^{\alpha},$$

$$\mathbf{r}^{i} = \mathbf{R} + S^{-1}(\mathbf{d}^{i} + \mathbf{a}^{i}), \tag{6}$$

where the $\mathbf{r}^{\alpha}$ represent the space-fixed coordinates of the electrons, the $\mathbf{r}^{i}$ those of the nuclei; the ϱ^{α} represent the molecule-fixed coordinates of the electrons; the $\mathbf{a}^{i}$ represent the reference positions of the nuclei in molecule-fixed coordinates; the $\mathbf{d}^{i}$ represent displacements therefrom; $\mathbf{R}$ represents the coordinates of the center of gravity of the nuclei. S is a matrix[9] involving the Eulerian angles.

It can be shown by a lengthy but straightforward calculation that the operation C_{n} corresponds to changing the variable quantities $\mathbf{R}$, ϱ^{α}, S, and $\mathbf{d}^{i}$ in Eqs. (6) such that the electronic space-fixed coordinates remain unchanged and such that the nuclear space-fixed coordinates $\mathbf{r}^{i}$ are replaced by $\mathbf{r}^{j}$. The index j is the label of the atom to which the displacement of atom i has been carried by the rotation $^{1}C_{n}$. The operations σ_{h} and σ_{v} correspond to changing the variable quantities in Eqs. (6) such that the electronic coordinates $\mathbf{r}^{\alpha}$ are replaced by $-\mathbf{r}^{\alpha}$ and such that the nuclear coordinates $\mathbf{r}^{i}$ are replaced by $-\mathbf{r}^{k}$. The index k is the label of the atom to which the displacement of atom i has been carried by the reflection σ_{h} or σ_{v}, as the case may be. The complete Hamiltonian is invariant to permutations of the coordinates of identical particles and to inversion of the coordinates of all the particles in the molecule, and consequently is invariant under those combinations of the operations given in (4) which comprise the molecular point group. (Only for these latter operations can indices on the nuclear coordinates analogous to j and k above be defined.) Thus, the italicized statement above is proved. Since motion associated with the center of mass of the nuclei can generally be ignored, we apply the italicized statement directly to rovibronic wave functions which do not involve the variables $\mathbf{R}$.

The italicized statements of the preceding paragraphs are valid regardless of the actual equilibrium configuration of the molecule or of the amplitude of the vibrational motions. Nevertheless, they will only really be useful when the reference configuration of the nuclei coincides or nearly coincides with the equilibrium configuration, and when displacements from the reference configuration during vibration are "small," i.e., when only those wavefunctions constructed from a single nuclear framework[2] need be considered. Two examples of phenomena which involve "large" departures from the equilibrium configuration are the inversion motion in ammonia and the internal rotation in ethane.

If the reference configuration is the equilibrium configuration and if the vibrational amplitudes are "small," then the wavefunctions will occur in almost perfectly degenerate sets, there being one wavefunction for each possible equivalent reference configuration of the molecule. The statistical weight of each degenerate set of levels can be found as described by Wilson.[2] The present paper in no way alters his work on that subject. The statistical weights of the components of levels which exhibit splittings due to inversion or to the exchange of identical nuclei (the general phenomenon which is sometimes equivalent to internal rotation) depend on the specific problem under consideration, i.e., on which degeneracies are removed and which are not. These statistical weights are not discussed here.

We shall now consider the transformation properties of the symmetric-top rotational functions.[12-14] (The vibronic wavefunctions must be multiplied by these rotational functions to form a complete wavefunction for the molecule.) Symmetric-top functions will be denoted by the symbol $|K J M\rangle$, where J specifies the total angular momentum of the system, K specifies the component of J along the molecule-fixed z axis (top axis), and M specifies the component of J along the space-fixed Z axis. We define the phases of all the functions having the same value of J by the following relations:

$$|\pm|K|, J, \pm|M|\rangle$$
$$= N'_{\pm} (J_{x} \mp i J_{y})^{|K|} (J_{X} \pm i J_{Y})^{|M|} |0 J 0\rangle,$$

$$|\pm|K|, J, \mp|M|\rangle$$
$$= N''_{\pm}(J_{x} \mp i J_{y})^{|K|} (J_{X} \mp i J_{Y})^{|M|} |0 J 0\rangle,$$

$$N'_{\pm}, N''_{\pm} > 0. \tag{7}$$

The functions $|0 J 0\rangle$, which have $K = M = 0$, are proportional to the Legendre polynomials $P_{J}(\cos\theta)$. The operators J_{x}, J_{y} are the x and y components of $\mathbf{J}$ in the molecule-fixed axis system; the operators J_{X}, J_{Y}, are the X and Y components of $\mathbf{J}$ in the space-fixed axis system. $J_{x} - i J_{y}$ and $J_{X} + i J_{Y}$ act on a wavefunction to increase the value of K and M, respectively, by unity; $J_{x} + i J_{y}$ and $J_{X} - i J_{Y}$ act on a wavefunction to decrease the value of K and M, respectively, by unity. A consistent set of phases for all wavefunctions having the same value of J is obtained by requiring that all the normalizing constants N be real and positive.

From the properties of the Legendre polynomials we see that $^{2}C_{n}$ and $^{2}\sigma_{h}$ take $|0 J 0\rangle$ into itself and that

[12] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1959), Chap. 3.

[13] J. H. Van Vleck, Revs. Modern Phys. **23**, 213 (1951).

[14] E. C. Kemble, *The Fundamental Principles of Quantum Mechanics with Elementary Applications* (Dover Publications, Inc., New York, 1958), Secs. 34d-f.

$^2\sigma_v$ takes $|0J0\rangle$ into $(-1)^J$ times itself. From the definitions of the angular momentum operators[13,14] we see that

$$^2C_n(J_x\mp iJ_y)=[\exp(\pm 2\pi i/n)](J_x\mp iJ_y)\,^2C_n,$$

$$^2\sigma_h(J_x\mp iJ_y)=-(J_x\mp iJ_y)\,^2\sigma_h,$$

$$^2\sigma_v(J_x\mp iJ_y)=-(J_x\pm iJ_y)\,^2\sigma_v,$$

$$^2C_n(J_X\pm iJ_Y)=(J_X\pm iJ_Y)\,^2C_n,$$

$$^2\sigma_h(J_X\pm iJ_Y)=(J_X\pm iJ_Y)\,^2\sigma_h,$$

$$^2\sigma_v(J_X\pm iJ_Y)=(J_X\pm iJ_Y)\,^2\sigma_v. \quad (8)$$

Thus, the effect of the operations ^2C_n, $^2\sigma_h$ and $^2\sigma_v$ on the symmetric-top rotational wavefunctions is

$$^2C_n\,|\,K\,J\,M\rangle=\exp(+2\pi iK/n)\,|\,K\,J\,M\,\rangle,$$

$$^2\sigma_h\,|\,K\,J\,M\rangle=(-1)^K\,|\,K\,J\,M\,\rangle,$$

$$^2\sigma_v\,|\,K\,J\,M\rangle=(-1)^{J-K}\,|\,-K\,J\,M\,\rangle. \quad (9)$$

The symmetry species to which the rotational wavefunctions belong for the particular molecular point group under consideration can be determined from Eqs. (9) by the usual procedures of group theory.

Selection Rules

Having shown that rovibronic energy levels can be classified according to certain symmetry species, we shall now derive the selection rules for electric dipole transitions between these levels for molecules in free space. Because free space is isotropic, it is sufficient to consider the selection rules for the component of the dipole moment operator along the space-fixed Z axis. This operator μ_Z is simply the sum of the charges e_i of all the particles in the molecule multiplied by their Z coordinates.

$$\mu_Z=\sum_i e_i Z_i. \quad (10)$$

Since this operator is invariant to a permutation of the coordinates of identical particles, we see from the statements following Eq. (6) that it remains invariant under C_n and simply changes sign under σ_h and σ_v.

In discussions of the normal vibrational modes of molecules, the transformation properties of two operations, namely translation and rotation, are generally included in tables giving the symmetry species of the molecular point group under consideration. We note that the transformation properties of μ_Z above are identical with those of the product $T_z R_z$, where T_z represents a translation in the z direction and R_z represents a rotation about the z axis. This statement can be made physically reasonable if we express μ_Z in terms of components of the dipole moment operator in the molecule-fixed axis system μ_x, μ_y, μ_z together with the appropriate direction cosines α_x, α_y, α_z.

$$\mu_Z=\alpha_x\mu_x+\alpha_y\mu_y+\alpha_z\mu_z$$

$$=-(\sin\theta\,\cos\chi)\mu_x+(\sin\theta\,\sin\chi)\mu_y+(\cos\theta)\,\mu_z. \quad (11)$$

Fig. 2. The rovibronic levels with $K=1$ and $J=1$, 2 for a vibronic E state of a molecule of symmetry C_{3v}. The transitions indicated by solid arrows have been observed in CH$_3$NC; those indicated by dashed arrows have not.
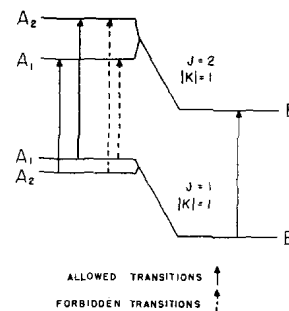
It is not difficult to show that the dipole-moment component μ_z transforms like the translation T_z and that the direction cosine α_z, which involves the Eulerian angles, transforms like the rotation R_z. The expression $\alpha_x\mu_x+\alpha_y\mu_y$ can be shown to transform in the same way.

The selection rule can now be formulated. *The electric dipole transition between two rovibronic states, of species Γ' and Γ'', is allowed if and only if $\Gamma'\times\Gamma''$ contains $\Gamma_{T_z}\times\Gamma_{R_z}$.* ($\Gamma_{T_z}$ and Γ_{R_z} are, of course, the species of T_z and R_z, respectively. They correspond to one-dimensional representations.)

Example

To conclude part I let us briefly consider the example of a C_{3v} molecule. The symmetry species for this point group are A_1, A_2, and E. The species of the rovibronic energy levels for an A_1 vibronic state and an E vibronic state are those shown[15] on p. 408 of reference 1 in Figs. 118(a) and 118(b), respectively. (Contrary to the caption of this figure, the subscript 1 or 2 of A is *not* to be dropped for C_{3v} molecules.) A small portion of Fig. 118(b) is reproduced here in Fig. 2. The species of the dipole moment operator μ_Z for C_{3v} is $\Gamma_{T_z}\times\Gamma_{R_z}=A_1\times A_2=A_2$. Hence, the allowed transitions are $A_1\leftrightarrow A_2$ and $E\leftrightarrow E$.

The three transitions between the levels shown in Fig. 2 allowed by the considerations presented above are indicated by solid arrows. In the classification scheme previously used, the A_1 and A_2 levels would both have been classified as A levels of the pure rotation group C_3, with the selection rule $A\leftrightarrow A$, so that one might expect in general two additional transitions between the levels in Fig. 2. namely those indicated by dashed arrows. A set of transitions involving the $K=1$, $J=1$ and the $K=1$, $J=2$ rotational levels of a degenerate vibrational state has been observed in the microwave spectrum of CH$_3$NC by Kessler, Ring, Trambarulo, and Gordy[16] and has been discussed

[15] The nearly degenerate pairs of A_1 and A_2 states are split by second and higher order Coriolis interactions. The A_1 rovibronic state for a series of fixed K and varying J will in general lie alternately above and below the A_2 state with which it is nearly degenerate, a phenomenon which is directly related to the occurrence of the factor $(-1)^J$ in the last of Eqs. (9). The order of states in the A_1, A_2 pairs for a series of fixed J and varying K has not been investigated by the author.

[16] M. Kessler, H. Ring, R. Trambarulo, and W. Gordy, Phys. Rev. **79**, 54 (1950).

theoretically by Nielsen.[17] It is clear from Nielsen's discussion that only those transitions indicated by solid arrows in Fig. 2 were actually observed.

The author considers these experimental observations on CH_3NC to be an indication of the correctness and usefulness of the results of this section.

II. CONVENIENT QUANTUM NUMBER

There is an additional useful classification of the rotational energy levels of symmetric-top molecules, besides that according to symmetry species of the appropriate point group, namely the division into so-called $+l$ and $-l$ levels.[1] Selection rules for the $+l$, $-l$ labels have been discussed in several papers[18-21] for particular types of transitions. It is the purpose of the present section to formulate the information concerning selection rules which is explicitly discussed or implicitly contained in these papers in such a way that it is easier to remember and easier to use.

The symmetry axis of any symmetric-top molecule will be an n-fold axis of rotation (C_n) and an m-fold axis of rotation-reflection (S_m). In the discussion to follow we shall consider molecules for which $m \leq n$ separately from molecules for which $m > n$. (Actually the relationship between m and n for symmetric top molecules is not arbitrary; either $m=0$, $m=n$, or $m=2n$.) In each case a quantum number G will be defined, which corresponds to a generalization of the $+l$, $-l$ labels. The selection rules on G which electric dipole transitions obey in the two cases will also be determined.

First Case: $m=0$ or n

Consider a complete wavefunction ψ_{evr} having the form of a simple product $\psi_{ev}\psi_r$. The vibronic wavefunction ψ_{ev} for a molecule with an axis of rotation C_n can be characterized by a vibronic quantum number G_{ev}, such that

$$^1C_n\,\psi_{ev}(G_{ev}) = [\exp(-2\pi i G_{ev}/n)]\,\psi_{ev}(G_{ev}), \quad (12)$$

where ^1C_n is defined following Eq. (3) above. Note that G_{ev} need only be defined modulo n (i.e., $G_{ev}\pm n$ is equivalent to G_{ev}), and that G_{ev} is not necessarily equal to $-G_{ev}$ mod n.[22] The value of G_{ev} is simply related to the symmetry species of the level. For point groups with $m \leq n$, A states have $G_{ev}=0$; B states have $G_{ev}=\frac{1}{2}n$; and E_s states $(s=1, 2, 3,$ etc.$)$, which are doubly degenerate, have $G_{ev}=\pm s$. We now define

[17] H. H. Nielsen, Phys. Rev. 77, 130 (1950). The absolute order of the A_1 and A_2 levels in Fig. 2 has been assigned according to the splitting mechanism given in this paper.
[18] E. Teller, Hand- und Jahrbuch d. chem. Phys. (Akademische Verlagsgesellshaft, Leipzig, 1934), Vol. 9, II, pp. 43-160.
[19] E. Teller and L. Tisza, Z. Physik 73, 791 (1932).
[20] R. S. Mulliken and E. Teller, Phys. Rev. 61, 283 (1942).
[21] D. R. J. Boyd and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) A213, 55 (1952).
[22] The quantities G_{ev}, G, K, G_e, G_v, and l_j, are all considered to be signed quantities in part II.

the desired rovibronic quantum number $G_{evr} \equiv G$ for the complete wavefunction as

$$G=G_{ev}-K, \quad (13)$$

where K is the (signed) quantum number for angular momentum about the top axis. G characterizes the transformation properties of the complete rovibronic wave function ψ_{evr} under the operation C_n.

$$C_n\,\psi_{evr}(G) = [\exp(-2\pi iG/n)]\,\psi_{evr}(G). \quad (14)$$

Note that G also need only be defined modulo n, and that the relation between $G \equiv G_{evr}$ and the rovibronic symmetry species is the same as that between G_{ev} and the vibronic symmetry species.

The labels G are a generalization of the labels $\pm l$. The exact relationship between the two sets of labels can be made clearer if G_{ev} is expressed in terms of vibrational and electronic quantum numbers. Suppose ψ_{ev} can be written as a simple product $\psi_e\psi_v$. Then G_{ev} can be written as a sum

$$G_{ev}=G_e+G_v$$
$$=G_e+(n/2)\sum_B v_B+\sum_j s_j l_j. \quad (15)$$

G_e and G_v characterize the transformation properties of the electronic portion of the wavefunction ψ_e and the vibrational portion of the wavefunction ψ_v, respectively, such that if ψ_{ev} is replaced by ψ_e or ψ_v in Eq. (12), then G_{ev} must be replaced by G_e or G_v, respectively. G_e and G_v need be defined only modulo n and are related to the symmetry species of ψ_e and ψ_v respectively just as G_{ev} is related to the symmetry species of ψ_{ev}. G_e is analogous to the electronic quantum number Λ in linear molecules. G_v is analogous to the vibrational quantum number l in linear triatomic molecules. In nonlinear molecules it is composed of two parts. If n is even, the molecule may have vibrational modes of species B, the normal coordinates for which go into their negatives under ^1C_n. The first term in G_v adds up the total number of quanta of such vibrations excited for the state in question. If n is odd, there can be no B vibrations, and this term vanishes. The second term in G_v involves a sum over the (signed) vibrational quantum numbers l_j associated with degenerate vibrations; s_j specifies the representation E_{s_j} to which the jth degenerate vibration belongs. G_r, which characterizes the transformation properties of the symmetric-top rotational functions ψ_r in an equation analogous to (12), is given by $-K$.

Consider now a C_{3v} molecule in a totally symmetric electronic state with one quantum of an E vibration excited. For the resultant energy level

$$G_e=0, \quad \sum v_B=0, \quad \sum s_j l_j=l=\pm 1, \quad (16)$$

so that this level contains two vibronic wavefunctions, with $G_{ev}=\pm |l| =\pm 1$, respectively. For each $|K|>0$ there will be four rovibronic wavefunctions, with

$G = \pm(|l| - |K|)$ and $\pm(|l| + |K|)$, respectively. The pair characterized by $G = \pm(|l| - |K|)$ is the "$+l$" pair; both l and K have the same sign [note the minus sign in Eq. (13)], corresponding to the physical situation in which the vibrational angular momentum about the top axis and the total angular momentum about the top axis point in the same direction. The pair characterized by $G = \pm(|l| + |K|)$ is the "$-l$" pair; l and K have opposite signs, the angular momenta point in opposite directions.

We now show how the value of the quantum number G is related to the contribution of first-order Coriolis interaction to the rovibronic energies. The operator giving rise to first-order Coriolis interaction is $-2A\hbar^{-2}J_z p_z$, which occurs in the rotational Hamiltonian given in (3) when μ and $\mu_{\gamma\delta}$ are given their equilibrium (constant) values and when energies are expressed in cm^{-1}. A is the usual spectroscopic rotational constant for rotation about the top axis; J_z is the component of the total angular momentum along the top axis; and p_z is the component of the sum of the electronic and vibrational angular momenta along the top axis. The rotational energy of a level of a symmetric top molecule (neglecting centrifugal distortion, second-order Coriolis effects, perturbations, etc.) can be written as

$$E_r = BJ(J+1) + (A-B)K^2 - 2AK\langle\hbar^{-1}p_z\rangle_{\text{Av}}, \qquad (17)$$

where $\langle p_z\rangle_{\text{Av}}$ is the expectation value of p_z for the wave function under consideration. If we choose quantities $G_{ev}{}^0 = G_{ev}$ mod n, such that $0 < |G_{ev}{}^0| < \frac{1}{2}n$, and also define an effective Coriolis coupling constant ζ_{eff} as the expectation value of p_z for that member of the degenerate pair of wave functions characterized by the quantum number $+|G_{ev}{}^0|$,

$$\zeta_{\text{eff}} = \int \psi^*(+|G_{ev}{}^0|)\, p_z\, \psi(+|G_{ev}{}^0|)d\tau, \qquad (18)$$

then we find that

$$E_r = BJ(J+1) + (A-B)K^2 \mp 2A|K|\zeta_{\text{eff}}, \qquad (19)$$

when

$$|G| = |(|G_{ev}{}^0| \mp |K|)|, \qquad (20)$$

where, of course, either the upper sign or the lower sign must be used in both (19) and (20). The levels for which the minus (upper) sign has been used in Eq. (20) will for convenience be called the G_a levels; those for which the plus sign has been used will be called the G_b levels. The G_a levels are the levels of lower energy if $\zeta_{\text{eff}} > 0$, and correspond to the $+l$ levels in the limiting case of a state arising when one quantum of a degenerate vibration is excited in a nondegenerate electronic state.

Having defined the quantum number G and related it to the rotational energies, we now proceed to determine selection rules for it. Since the complete Hamiltonian is invariant with respect to the operation

C_n, it can only mix states with the same value of G, i.e., G is always a good quantum number for a molecule in free space.[23] Furthermore, the component of the dipole moment operator along the space-fixed Z axis is invariant with respect to the operation C_n. [See Eq. (10) and the succeeding discussion.] Consequently: *the electric dipole transition between two states is allowed if and only if* $G' - G'' \equiv \Delta G = 0$ mod n. This rule alone is not enough, however. We must say also that the branches in a transition which derives its intensity from the perpendicular components of the molecular dipole moment operator will correspond to transitions between states for which $\Delta K = \pm 1$. (Note that this is not to be read $\Delta|K| = \pm 1$.) The branches in a transition which derives its intensity from the parallel component of the molecular dipole moment operator will correspond to transitions between states for which $\Delta K = 0$. Thus: *the electric dipole transition between two states will obey the selection rule* $\Delta K = \pm 1$ *for perpendicular transitions and* $\Delta K = 0$ *for parallel transitions, where K is taken to be a signed quantity.*

Transitions or branches made allowed only by Coriolis interactions need not obey the selection rules on K just stated above, though they must still obey the selection rules on G. Such transitions will normally be exceedingly weak compared to vibronically allowed transitions. In general, the further the value of ΔK for a transition lies from the values given in the preceding paragraph, the weaker the transition will be.

It should be pointed out that the quantum number G by itself contains no more information than is contained in the symmetry species label of the rovibronic level. It is only when the (rigorous) selection rule on G is combined with the (approximate) selection rules on K that the strongly allowed transitions can be distinguished from the strongly forbidden (though symmetry allowed) transitions. A systematic way of simultaneously applying the selection rules on G and K is suggested in the example section.

Second Case: $m = 2n$

The procedure here is similar but not identical to that for the first case. The vibronic functions for a molecule with a rotation–reflection axis S_m can be

---

[23] A selection rule equivalent to $\Delta G = 0$ for matrix elements of the vibration-rotation Hamiltonian has already been given by G. Amat in Compt. rend. **250**, 1439 (1960). In this reference point groups having $m = 2n$ for which n is odd are considered together with point groups having $m = 0$ or n. No information is lost in this way, provided that the selection rules on the g, u symmetry labels are also taken into account; and the information contained in the subscripts s of the E_{sg} and E_{su} symmetry labels is more easily dealt with. In view of these facts, it may be more convenient to define the quantum number G for groups with $m = 2n$ where n is odd just as it is defined for groups having $m = 0$ or n, and to obtain the necessary additional information from the g, u subscripts of the symmetry labels. The entire discussion of the quantum number G for groups with $m = 0$ or n can be applied unchanged to groups with $m = 2n$ where n is odd, thus eliminating from consideration the rather cumbersome relationships between the subscripts s and the quantities $G_{s,n}$ and t discussed in the next section.

characterized by a number G_{ev}, defined modulo m, such that

$$^{1}S_{m}\psi_{ev}(G_{ev}) = [\exp(-2\pi iG_{ev}/m)]\psi_{ev}(G_{ev}). \quad (21)$$

It is important to note that all of the "G" quantum numbers used in this section ($m=2n$) are different from the quantum numbers with the same symbols used in the preceding section ($m=0$ or n). For a given molecule, only one set of "G" quantum numbers will be in use, however, so that no confusion between the two sets should arise.

If $\frac{1}{2}m$ is even ($m=2n$ must itself be even), then G_{ev} is related to the symmetry species of the wavefunctions in the way described in the preceding section. If $\frac{1}{2}m$ is odd, the relationship is somewhat different: A_{g} states have $G_{ev}=0$; A_{u} states have $G_{ev}=\frac{1}{2}m$; E_{sg} states have $G_{ev}=\pm(1+\frac{1}{2}m)s$; and E_{su} states have $G_{ev}=\pm[(1+\frac{1}{2}m)s-\frac{1}{2}m]$. G_{ev} can also be calculated from an equation analogous to (15).

$$G_{ev}=G_{e}+(\tfrac{1}{2}m)\sum_{B}v_{B}+\sum_{j}t_{j}l_{j} \quad (22)$$

The first term G_{e} must be defined in this case with respect to the operation S_{m} not C_{m}. If $\frac{1}{2}m$ is even, the second term adds up the total number of quanta of B vibrations which are excited; if $\frac{1}{2}m$ is odd, the second term adds up the total number of quanta of A_{u} vibrations which are excited in the state in question. If $\frac{1}{2}m$ is even, $l_{j}=s_{j}$, where s_{j} specifies the representation $E_{s_{j}}$ to which the jth degenerate vibration belongs. If $\frac{1}{2}m$ is odd, t_{j} is related to the representation E_{sg} or E_{su} to which the jth degenerate vibration belongs in the following way: for an E_{sg} state, t is chosen such that $t=(1+\frac{1}{2}m)s$ mod m and such that $-\frac{1}{2}m<t<\frac{1}{2}m$; for an E_{su} state t is chosen such that $t=(1+\frac{1}{2}m)s-\frac{1}{2}m$ mod m and such that $-\frac{1}{2}m<t<\frac{1}{2}m$. We now define the desired quantum number G as

$$G=G_{ev}-K(1+\tfrac{1}{2}m), \quad (23)$$

which differs from the analogous definition of G for $m=0$ or n by the term $-\frac{1}{2}mK$. G characterizes the transformation properties of the complete rovibronic wavefunction ψ_{evr} under the operation S_{m}.

$$S_{m}\psi_{evr}(G) = [\exp(-2\pi iG/m)]\psi_{evr}(G). \quad (24)$$

Note that G need only be defined modulo m, and that the relation between G and the rovibronic symmetry species is the same as that between G_{ev} and the vibronic symmetry species.

G for $m=2n$ is related to the rotational energy in a similar fashion to G for $m=0$ or n. If we choose quantities $G_{ev}^{0}=G_{ev}$ mod m, such that $0<|G_{ev}^{0}|<\frac{1}{2}m$, and also define an effective Coriolis coupling constant ζ_{eff} as the expectation value of p_{z} for that member of the degenerate pair of wavefunctions characterized by the quantum number $+|G_{ev}^{0}|$, then the rotational energy is given by Eq. (19) when

$$|G| = |[\,|G_{ev}^{0}| \mp |K|\,(1+\tfrac{1}{2}m)]|. \quad (25)$$

Again, the levels for which the minus sign has been used in Eq. (25) will be called the G_{a} levels; those for which the plus sign has been used will be called the G_{b} levels.

Because the complete Hamiltonian is invariant with respect to the operation S_{m}, the quantum number G is always good for molecules in free space. The component of the dipole moment operator along the space-fixed Z axis goes into its negative under S_{m}. Consequently: *the electric dipole transition between two states is allowed if and only if $G'-G''\equiv\Delta G=\frac{1}{2}m$ mod m.* Also: *the selection rule $\Delta K=\pm1$ will be obeyed for perpendicular transitions and the selection rule $\Delta K=0$ will be obeyed for parallel transitions.* Both G and K are considered to be signed quantities.

The two quantum numbers G (for $m=0$ or n, and for $m=2n$) actually serve only one purpose. They determine whether or not the electric dipole transition between wavefunctions for which $\Delta K=\pm1$ or 0 is allowed, when K is considered a signed quantity. This indicates why, for $m=n$, we need only consider the properties of the wavefunctions with respect to. either C_{n} or S_{m}, but not both.

Example

To illustrate the ideas presented in this section we consider the example of one perpendicular transition in a molecule of symmetry $S_{8v}=D_{4d}$. It is convenient when using the results of part II to follow the following procedure.

(1) Determine $|G_{ev}^{0}|$ for the vibronic states involved.

(2) Draw a schematic energy level diagram with Coriolis splittings. Assign values of the quantum number G to the levels, in the proper sense for positive values of the ζ_{eff}'s. Use the values of G for positive values of K only, as determined from Eq. (19) and either Eq. (20) or (25).

(3) Determine from the selection rules on G and K the allowed transitions and draw them in.

(4) From the equations mentioned in step 2, determine the spacing of the Q branch origins in the band.

(5) Express the ζ_{eff}'s for each vibronic state in terms of vibrational Coriolis coupling constants (ζ_{v}'s) and electronic Coriolis coupling constants (ζ_{e}'s), if enough is known about the vibronic wavefunctions to accomplish this.

In step 2, only positive values of K are used, since this automatically prevents us from considering transitions for which $\Delta|K|=\pm1\neq\Delta K$. In step 4, we are determining an algebraic expression for a quantity which often characterizes the qualitative appearance of the experimentally observed spectral

band.[1] Step 5 can be carried out easily if the vibronic wavefunction can be written as a simple product of an electronic wavefunction and vibrational wavefunctions for each normal coordinate. If, for example, there is significant Fermi resonance or Jahn–Teller interaction, the vibronic wavefunction will be the sum of such products and step 5 can be carried out only when the details of these interactions are known.

Let us now consider a vibronic E_2-E_1 transition in a molecule of symmetry $S_{8v}=D_{4d}$. This is a perpendicular transition, since the perpendicular and parallel components of the molecular dipole moment operator are of species E_1 and B_2, respectively, and since $E_2 \times E_1$ contains E_1 but not B_2. For the E_2 vibronic state, $|G_{ev}^0|=2$; for the E_1 vibronic state $|G_{ev}^0|=1$. Figure 3 is a schematic energy-level diagram, indicating the energy levels for one value of J, and values of K less than or equal to the order $(m=8)$ of the rotation–reflection axis. The values of G and also the symmetry species of the levels (see below) are dependent on K but independent of J and M. The values of G assigned to the levels are correct for positive values of K and of the ζ_{eff}'s. Transitions obeying the selection rules $\Delta G=4 \bmod 8$ and $\Delta K=\pm 1$ have been drawn in. The selection rules derived can be stated in a simple fashion in terms of the G_a, G_b labels. In this example, for $\Delta|K| = |K'| - |K''| =1$, the G_a' levels combine with the G_a'' levels; for $\Delta|K| = -1$, the G_b' levels combine with the G_b'' levels. The spacing of the Q branch origins, if for simplicity we assume that the rotational constants of the two states are identical, is given by

$$2A(1-\zeta_{eff}'+\zeta_{eff}'')-2B, \qquad (26)$$

where ζ' refers to the upper (E_2) state and ζ'' refers to the lower (E_1) state.

The symmetry species of the rovibronic energy levels, as discussed in part I, are shown in Fig. 3. The splitting of the A_1A_2 and B_1B_2 pairs because of second- and higher-order Coriolis interactions has not been indicated, but two arrows have been drawn for $A_1A_2 \leftrightarrow B_1B_2$ transitions, representing the $A_1 \leftrightarrow B_1$ and $A_2 \leftrightarrow B_2$ transitions allowed by the symmetry selection rules. $(\Gamma_{T_z,R_z}=B_1)$. Figure 3 offers an opportunity to make a final point concerning the results of part I. If the rovibronic levels were to be labeled according to the irreducible representations of the rotational subgroup D_4 of S_{8v}, then it would be necessary to make the substitutions: $B_1B_2 \rightarrow A_1A_2$; $E_1E_3 \rightarrow E$; and $E_2 \rightarrow B_1B_2$ in Fig. 3. Since the $J=K=0$ level of the E_2 vibronic state is now labeled as a B_1B_2 pair, this alternative notation suggests that this level, which is effectively rotationless, might split under certain circumstances. The results of part I, on the other hand, demand that
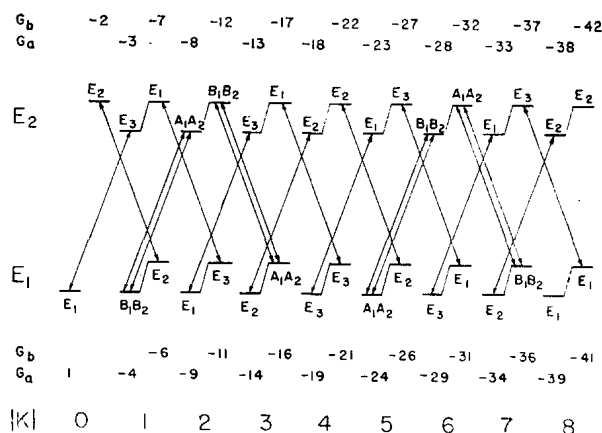

FIG. 3. The rovibronic energy levels for an E_2 and an E_1 vibronic state in a molecule of symmetry $D_{4d}=S_{8v}$. The symmetry labels have been assigned as described in part I. Values of the quantum number G are given for positive values of K as described in part II. Allowed transitions are indicated by arrows.

this level remain doubly degenerate under all circumstances for molecules in free space.

Finally we consider five examples in which ζ_{eff} for the E_1 vibronic state above is expressed in terms of electronic and vibrational Coriolis coupling constants. In what follows, we define ζ_v for a particular vibration as the expectation value of the operator p_z for the vibrational wavefunction with $v=l=+1$. We define ζ_e for a particular electronic state as the expectation value of p_z for the electronic wavefunction with $0 \leq G_e \leq \frac{1}{2}m$. (i) If the E_1 vibronic state is an E_1 electronic state with no vibrations excited, then $\zeta_{eff}=+\zeta_e$. (ii) If the E_1 vibronic state has arisen from the excitation of one quantum of an E_1 vibration in an A_1 electronic state, then $\zeta_{eff}=+\zeta_v$. (iii) If the E_1 vibronic state has arisen from the excitation of one quantum of an E_3 vibration in an E_2 electronic state, then $\zeta_{eff}=+\zeta_v-\zeta_e$. (iv) If the E_1 vibronic state has arisen from the excitation of two quanta of an E_3 vibration in an E_1 electronic state, then $\zeta_{eff}=-\zeta_e-2\zeta_v$. (v) If the E_1 vibronic state has arisen from the excitation of two quanta of an E_3 vibration in an E_3 electronic state, then $\zeta_{eff}=+\zeta_e+2\zeta_v$. The statements above are only valid as limiting cases, when Fermi resonance and Jahn–Teller interaction are small, but they serve to illustrate how ζ_{eff} can be expressed in terms of ζ_e's and ζ_v's.