

DETERMINABLE PARAMETERS OF THE EFFECTIVE ROTATIONAL HAMILTONIANS FOR EXCITED VIBRATIONAL STATES OF SEMIRIGID SYMMETRIC TOP MOLECULES OF C_{4v} , D_4 , D_{2h} , AND D_{2d} SYMMETRY

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A general method is described for obtaining the **S** functions which in the contact transformation of the vibration-rotation Hamiltonian of semirigid molecules with the fourfold symmetry axis eliminate the rotational and vibrational *l*-type operators and the $\Delta k = \pm 4$ centrifugal distortion operators from the λH_1 terms of the expanded Hamiltonian. Explicit expressions are given for the vibration-rotation energy levels with independent effective spectroscopic parameters. Expressions are also given for the splittings of energy levels with essential resonances.

The effect of the operators that are diagonal in *v*, but off-diagonal in *l*, *k* quantum numbers on the energy levels of excited vibrational states of C_{3v} molecules has been discussed recently¹⁻³. Increased attention that has been paid in the last years to molecules with the fourfold symmetry axis⁴⁻¹³, suggests that it would be worthwhile to extend this treatment also to molecules of symmetries C_{4v} , D_4 , D_{4h} , D_{2d} . The emphasis in this paper will be mainly on the discussion of the determinable parameters of these operators and on their contributions to the splittings of the degenerate energy levels.

THEORETICAL

In the standard method of the vibrational contact transformation¹⁴⁻¹⁶, the operators off-diagonal in *v* are transformed to the higher order operators that are diagonal in *v*. However, the transformed Hamiltonian still contains the operators which are diagonal in *v*, but off-diagonal in *l* or *k* or in both *l*, *k*. For molecules with the fourfold axis of symmetry, there are six such operators^{17,18}

a) L_- ($\Delta l_r = \pm 2$, $\Delta k = \mp 2$) operator,

$$L_- = \frac{1}{2} \sum_t G_t (\sigma_{t+}^2 J_+^2 + \sigma_{t-}^2 J_-^2), \quad (1)$$

where

$$\sigma_{t\pm}^2 = (\mathbf{q}_{ta} \pm i\mathbf{q}_{tb})^2 + (\mathbf{p}_{ta} \pm i\mathbf{p}_{tb})^2 \quad (2)$$

pertain to the vibrational dimensionless coordinates \mathbf{q} and the conjugate momenta \mathbf{p} of the doubly degenerate vibrational mode, and

$$\mathbf{J}_{\pm} = \mathbf{J}_x \pm i\mathbf{J}_y, \quad (3)$$

where $\mathbf{J}_x, \mathbf{J}_y$ are the components of the angular momentum operator with respect to the molecule-fixed system of axes.

Using the same phase conventions as in our previous paper³, we can also write

$$\begin{aligned} \langle v_t, l_t + 2, k - 2 | G_t \sigma_{t+}^2 \mathbf{J}_+^2 | v_t, l_t, k \rangle &= 2G_t \{ (v_t + l_t + 2) \times \\ &\times (v_t - l_t) [J, k - 1] [J, k - 2] \}^{1/2} \end{aligned} \quad (4)$$

where

$$[J, k] = J(J + 1) - k(k + 1). \quad (5)$$

b) \mathbf{L}_+ ($\Delta l_t = \pm 2, \Delta k = \pm 2$) operator,

$$\mathbf{L}_+ = \frac{1}{2} \sum_t F_t (\sigma_{t+}^2 \mathbf{J}_-^2 + \sigma_{t-}^2 \mathbf{J}_+^2) \quad (6)$$

and

$$\begin{aligned} \langle v_t, l_t + 2, k + 2 | F_t \sigma_{t+}^2 \mathbf{J}_-^2 | v_t, l_t, k \rangle &= 2F_t \{ (v_t + l_t + 2) (v_t - l_t) \times \\ &\times [J, k] [J, k + 1] \}^{1/2}, \end{aligned} \quad (7)$$

c) \mathbf{L}_3 ($\Delta k = \pm 4$) operator,

$$\mathbf{L}_3 = \frac{1}{2} [2d_2 (\mathbf{J}_+^4 + \mathbf{J}_-^4)] \quad (8)$$

and

$$\langle J, k - 4 | 2d_2 \mathbf{J}_+^4 | J, k \rangle = 2d_2 \{ [J, k - 4] [J, k - 3] [J, k - 2] [J, k - 1] \}^{1/2}. \quad (9)$$

Finally, there are three purely vibrational operators from $\mathbf{H}_{4,0}^T$,

d) \mathbf{L}_U ($\Delta l_t = \pm 4$) operator,

$$\mathbf{L}_U = \frac{1}{2} \sum_t \frac{1}{2} U_t (\sigma_{t+}^4 + \sigma_{t-}^4) \quad (10)$$

and

$$\begin{aligned} \langle v_t, l_t + 4 | \frac{1}{2} U_t \sigma_{t+}^4 | v_t, l_t \rangle &= 2U_t [(v_t - l_t - 2) (v_t - l_t) (v_t + l_t + 2) \times \\ &\times (v_t + l_t + 4)]^{1/2}, \end{aligned} \quad (11)$$

e) \mathbf{L}_R ($\Delta l_t = \pm 2, \Delta l_{t'} = \mp 2$) operator,

$$\mathbf{L}_R = \frac{1}{2} \sum_{t < t'} \frac{1}{2} R_{tt'} (\sigma_{t+}^2 \sigma_{t'-}^2 + \sigma_{t'+}^2 \sigma_{t-}^2) \quad (12)$$

and

$$\begin{aligned} & \langle v_t, v_{t'}, l_t + 2, l_{t'} - 2 | \frac{1}{2} R_{tt'} \sigma_{t+}^2 \sigma_{t'-}^2 | v_t, v_{t'}, l_t, l_{t'} \rangle = \\ & = 2R_{tt'} [(v_t + l_t + 2)(v_t - l_t)(v_{t'} - l_{t'} + 2)(v_{t'} + l_{t'})]^{1/2}, \end{aligned} \quad (13)$$

f) \mathbf{L}_S ($\Delta l_t = \pm 2, \Delta l_{t'} = \pm 2$) operator,

$$\mathbf{L}_S = \frac{1}{2} \sum_{t < t'} \frac{1}{2} S_{tt'} (\sigma_{t+}^2 \sigma_{t'+}^2 + \sigma_{t'-}^2 \sigma_{t-}^2) \quad (14)$$

and

$$\begin{aligned} & \langle v_t, v_{t'}, l_t + 2, l_{t'} + 2 | \frac{1}{2} S_{tt'} \sigma_{t+}^2 \sigma_{t'+}^2 | v_t, v_{t'}, l_t, l_{t'} \rangle = \\ & = 2S_{tt'} [(v_t + l_t + 2)(v_t - l_t)(v_{t'} + l_{t'} + 2)(v_{t'} - l_{t'})]^{1/2}. \end{aligned} \quad (15)$$

The subscripts t, t' denote the degenerate vibrations E . The explicit expressions for the parameters $G_t, F_t, U_t, R_{tt'}, S_{tt'}$ can be found in the paper by Grenier-Besson¹⁷ and for the parameter d_2 in ref.¹⁵. The operators $\mathbf{L}_+, \mathbf{L}_R$ are important also for C_{3v} molecules, while the operators $\mathbf{L}_-, \mathbf{L}_3, \mathbf{L}_U, \mathbf{L}_S$ appear in the expanded vibrational-rotational Hamiltonian of molecules with the fourfold symmetry axis. The operator \mathbf{L}_3 has to be considered for all energy levels; the operators $\mathbf{L}_+, \mathbf{L}_-$ must be considered if at least one vibrational state E is excited. Similarly, \mathbf{L}_U has to be considered if $v_t \geq 2$ and the operators \mathbf{L}_R and \mathbf{L}_S must be considered for combination energy levels $v_t \geq 1, v_{t'} \geq 1$.

According to the results described in detail in our previous paper³, if the off-diagonal part $\mathbf{H}_{\text{off-d}}$ of the Hamiltonian can be written as

$$\mathbf{H}_{\text{off-d}} = \frac{1}{2} \sum_j (\mathbf{H}_j + \mathbf{H}_j^\dagger), \quad (16)$$

where the superscript $+$ denotes the Hermitian conjugation and each \mathbf{H}_j (i.e., the first terms $\mathbf{L}_+, \mathbf{L}_-, \mathbf{L}_3, \dots$) has only one type of a nonzero matrix element characterized by $(\Delta l_t)_j, (\Delta l_{t'})_j, (\Delta k)_j$,

$$\langle v_t, v_{t'}, l_t - (\Delta l_t)_j, l_{t'} - (\Delta l_{t'})_j, k - (\Delta k)_j | \mathbf{H}_j | v_t, v_{t'}, l_t, l_{t'}, k \rangle, \quad (17)$$

then the operator \mathbf{S} of the contact transformation satisfying the commutator equation¹⁴⁻¹⁶

$$\mathbf{H}_{\text{off-d}} + i[\mathbf{S}, \mathbf{H}_0] = 0 \quad (18)$$

can be written in the following form:

$$\mathbf{S} = -\frac{i}{2} \sum_j (\mathbf{H}_j \mathbf{C}_j^{-1} - \mathbf{C}_j^{-1} \mathbf{H}_j^+), \quad (19)$$

where

$$\mathbf{C}_j = \mathbf{H}_0(\mathbf{V}_{2,t} \rightarrow \mathbf{V}_{2,t} - (\Delta l_t)_j, \mathbf{V}_{2,t'} \rightarrow \mathbf{V}_{2,t'} - (\Delta l_{t'})_j, \mathbf{J}_z \rightarrow \mathbf{J}_z - (\Delta k)_j) - \mathbf{H}_0. \quad (20)$$

The zeroth-order Hamiltonian \mathbf{H}_0 is the same as in ref.³, i.e.

$$\mathbf{H}_0 = \mathbf{H}_{\text{vib}} + \mathbf{B}_x \mathbf{J}^2 + (\mathbf{B}_z - \mathbf{B}_x) \mathbf{J}_z^2 - 2 \sum_t (\mathbf{B}_z \zeta_t^z) \mathbf{V}_{2,t} \mathbf{J}_z \quad (21)$$

and

$$\mathbf{V}_{2,t} = \frac{i}{4} (\mathbf{q}_{t+} \mathbf{p}_{t-} - \mathbf{p}_{t+} \mathbf{q}_{t-} + \mathbf{p}_{t-} \mathbf{q}_{t+} - \mathbf{q}_{t-} \mathbf{p}_{t+}). \quad (22)$$

We used the same notation in Eq. (20) as in ref.³, i.e., the first term on the right hand side of Eq. (20) means the operator \mathbf{H}_0 in which $\mathbf{V}_{2,t}$ should be replaced by $\mathbf{V}_{2,t} - (\Delta l_t)_j$, $\mathbf{V}_{2,t'}$ by $\mathbf{V}_{2,t'} - (\Delta l_{t'})_j$, and \mathbf{J}_z by $\mathbf{J}_z - (\Delta k)_j$. Note that \mathbf{B}_x , \mathbf{B}_z , and $(\mathbf{B}_z \zeta_t^z)$ in Eq. (21) are considered as vibrational operators and the only terms we have to consider from \mathbf{H}_{vib} are $x_{it}^{(l)} \mathbf{V}_{2,t} \mathbf{V}_{2,t'}$ (ref.³).

Substitution of the values of Δl_t , $\Delta l_{t'}$, Δk according to Eq. (17) and Eqs (4, 7, 9, 11, 13, 15) to Eq. (20) gives

$$\mathbf{C}_{L\pm,t} = 4 \left\{ \sum_{t'} [x_{it'}^{(l)} \mp (\mathbf{B}_z \zeta_{t'}^z)] (\mathbf{V}_{2,t'} + \delta_{it'}) \mp [\mathbf{B}_x - \mathbf{B}_z \pm (\mathbf{B}_z \zeta_{t'}^z)] \times \right. \\ \left. \times (\mathbf{J}_z \pm 1) \right\}, \quad (23)$$

$$\mathbf{C}_{L3} = 8 \left\{ (\mathbf{B}_x - \mathbf{B}_z) (\mathbf{J}_z - 2) + \sum_t (\mathbf{B}_z \zeta_t^z) \mathbf{V}_{2,t} \right\}, \quad (24)$$

$$\mathbf{C}_{U,t} = 8 \left\{ \sum_{t'} x_{it'}^{(l)} (\mathbf{V}_{2,t'} + 2\delta_{it'}) - (\mathbf{B}_z \zeta_{t'}^z) \mathbf{J}_z \right\}, \quad (25)$$

$$\mathbf{C}_{R,tt'} = 4 \left\{ \sum_{t''} (x_{it''}^{(l)} - x_{t't''}^{(l)}) (\mathbf{V}_{2,t''} + \delta_{it''} - \delta_{t't''}) + \right. \\ \left. + [(\mathbf{B}_z \zeta_{t'}^z) - (\mathbf{B}_z \zeta_{t''}^z)] \mathbf{J}_z \right\}, \quad (26)$$

$$\mathbf{C}_{S,tt'} = 4 \left\{ \sum_{t''} (x_{it''}^{(l)} + x_{t't''}^{(l)}) (\mathbf{V}_{2,t''} + \delta_{it''} + \delta_{t't''}) - \right. \\ \left. - [(\mathbf{B}_z \zeta_{t'}^z) + (\mathbf{B}_z \zeta_{t''}^z)] \mathbf{J}_z \right\}. \quad (27)$$

The contact transformation cannot be applied in those cases where the matrix elements of the operators which we wish to eliminate connect two states a, b that are degenerate in zeroth order (essential degeneracy). The interaction removes the

degeneracy of the level E_0 ,

$$E_{\pm} = E_0 \pm \frac{1}{2}\Delta_j, \quad (28a)$$

where the splitting $\Delta_j (\equiv E_+ - E_-)$ is

$$\Delta_j = \langle \Psi_a | \mathbf{H}_j | \Psi_b \rangle. \quad (28b)$$

There are six possible cases of this splitting for molecules with the fourfold symmetry axis:

a) Splitting of the energy levels $kl_t = +1$,

$$\Delta_{L-} = 2G_t(v_t + 1)J(J + 1). \quad (29)$$

b) Splitting of the energy levels $kl_t = -1$,

$$\Delta_{L+} = 2F_t(v_t + 1)J(J + 1). \quad (30)$$

c) Splitting of the $k = \pm 2$ levels (all $l_t = 0$),

$$\Delta_{L_3} = 2d_2J(J + 1)[J(J + 1) - 2]. \quad (31)$$

d) Splitting of the $l_t = \pm 2$, $k = 0$ energy levels,

$$\Delta_{L\nu} = 2U_t v_t(v_t + 2). \quad (32)$$

e) Splitting of the $l_t = \pm 1$, $l_{t'} = \mp 1$, $k = 0$ energy levels,

$$\Delta_{LR} = 2R_{t'}(v_t + 1)(v_{t'} + 1). \quad (33)$$

f) Splitting of the $l_t = l_{t'} = \pm 1$, $k = 0$ energy levels,

$$\Delta_{LS} = 2S_{t'}(v_t + 1)(v_{t'} + 1). \quad (34)$$

If any of the above splittings is observed in the spectra, then the corresponding parameter is clearly determinable. For example, if the splitting of the energy levels $k = l_t = \pm 1$ is observed, the magnitude of the splitting immediately determines the parameter F_t . It should also be noted that the contact transformation can be applied to all the other operators considered in this paper except those which must be considered separately for special vibrational-rotational states [cf. Eqs (29)–(34) and further discussion].

In all other cases the contact transformation can be applied and we obtain the following second order contribution E_2 to the energy of the state Ψ (cf. ref.³):

$$E_2 = \frac{i}{2} \langle \Psi | [\mathbf{S}, \mathbf{H}_{\text{off-d}}] | \Psi \rangle, \quad (35a)$$

where $\mathbf{H}_{\text{off-d}}$ and \mathbf{S} are given in Eqs (16) and (19).

Each of the six operators considered [Eqs (1)–(15)] contributes to the energy separately. Thus using the expressions for \mathbf{H}_j and \mathbf{C}_j given above, we obtain for the individual contributions the following results. Each contribution ΔE to the vibrational-rotational state $\Psi = \prod_s |v_s\rangle \prod_t |v_t^l\rangle |J, k\rangle$ can be written as

$$\Delta E_j = E_j^+ - E_j^- \quad (35b)$$

where

$$E_{L-}^{\pm} = \sum_t G_t^2 (v_t \mp l_t + 2) (v_t \pm l_t) [J(J+1) - k(k \pm 1)] \times \\ \times [J(J+1) - (k \pm 1)(k \pm 2)] c_{L-,t}^{-1}(\pm) \quad (36)$$

where

$$c_{L-,t}(\pm) = 4 \sum_{t'} [x_{tt'}^{(1)} + (B_z \zeta_{t'}^z)] (l_{t'} \mp \delta_{tt'}) - 4 [B_z - B_x + (B_z \zeta_t^z)] (k \pm 1). \quad (37)$$

Analogously, we have the following contributions:

$$E_{L+}^{\pm} = \sum_t F_t^2 (v_t \mp l_t + 2) (v_t \pm l_t) [J(J+1) - k(k \mp 1)] \times \\ \times [J(J+1) - (k \mp 1)(k \mp 2)] c_{L+,t}^{-1}(\pm), \quad (38)$$

where

$$c_{L+,t}(\pm) = 4 \sum_{t'} [x_{tt'}^{(1)} - (B_z \zeta_{t'}^z)] (l_{t'} \mp \delta_{tt'}) - 4 [B_x - B_z + (B_z \zeta_t^z)] (k \mp 1); \quad (39)$$

$$E_{L3}^{\pm} = d_2^2 [J(J+1) - k(k \pm 1)] [J(J+1) - (k \pm 1)(k \pm 2)] [J(J+1) - \\ - (k \pm 2)(k \pm 3)] [J(J+1) - (k \pm 3)(k \pm 4)] c_{L3,t}^{-1}(\pm), \quad (40)$$

where

$$c_{L3,t}(\pm) = 8 (B_x - B_z) (k \pm 2) + 8 \sum_{t'} (B_z \zeta_{t'}^z) l_{t'}; \quad (41)$$

$$E_{Lv}^{\pm} = \sum_t U_t^2 (v_t \mp l_t + 2) (v_t \pm l_t) (v_t \mp l_t + 4) (v_t \pm l_t - 2) c_{Lv,t}^{-1}(\pm), \quad (42)$$

where

$$c_{Lv,t}(\pm) = 8 \sum_{t'} x_{tt'}^{(1)} (l_{t'} \mp 2\delta_{tt'}) - 8 (B_z \zeta_t^z) k; \quad (43)$$

$$E_{LR}^{\pm} = \sum_{t < t'} R_{tt'}^2 (v_t \mp l_t + 2) (v_t \pm l_t) (v_{t'} \mp l_{t'}) (v_{t'} \pm l_{t'} + 2) c_{LR,tt'}^{-1}(\pm), \quad (44)$$

where

$$c_{LR,tt'}(\pm) = 4 \left\{ \sum_{t''} (x_{tt''}^{(l)} - x_{t't''}^{(l)}) (l_{t''} \mp \delta_{tt''} \pm \delta_{t't''}) + [(B_z \zeta_t^z) - (B_z \zeta_{t'}^z)] k \right\}; \quad (45)$$

$$E_{LS}^{\pm} = \sum_{t < t'} S_{tt'}^2 (v_t \mp l_t + 2) (v_t \pm l_t) (v_{t'} \mp l_{t'} + 2) (v_{t'} \pm l_{t'}) c_{LS,tt'}^{-1}(\pm), \quad (46)$$

where

$$c_{LS,tt'}(\pm) = 4 \left\{ \sum_{t''} (x_{tt''}^{(l)} + x_{t't''}^{(l)}) (l_{t''} \mp \delta_{tt''} \mp \delta_{t't''}) - [(B_z \zeta_t^z) + (B_z \zeta_{t'}^z)] k \right\}. \quad (47)$$

In Eqs (36)–(47), B_x , B_z , and $(B_z \zeta_t^z)$ are the effective values of the corresponding rotational constants in a given vibrational state (cf. ref.³).

Thus we can describe the effect of the off-diagonal operators on the energy levels as

$$E = E_{\text{diag}} + \sum_j \Delta E_j, \quad (48a)$$

where

$$E_{\text{diag}} = v_0 + B_x J(J+1) + (B_z - B_x) k^2 - 2 \sum_t (B_z \zeta_t^z) k l_t - D_J J^2 (J+1)^2 - D_{JK} J(J+1) k^2 - D_K k^4 + \dots \quad (48b)$$

[see also Eq. (66) in ref.³] and ΔE_j is defined by Eqs (35a)–(47) or Eqs (28)–(43) in special cases. For the energy levels with splittings [Eqs (29)–(34)], the individual splittings $\pm A_j/2$ replace ΔE_j corresponding to the operator \mathbf{H}_j which causes the splitting.

The above mentioned results can be easily used to find whether the parameters F_t , G_t etc. can be determined by simultaneous fitting of the experimental data or whether the inclusion of the matrix elements with these parameters would lead to nearly linear interdependence of the fitted parameters and therefore to numerical problems.

Example: $v_t = 1$, $l_t = \pm 1$ Fundamental Level

As an example, let us consider the $v_t = 1$, $l_t = \pm 1$ energy level of the E vibration. In this case, only the \mathbf{L}_- , \mathbf{L}_+ , and \mathbf{L}_3 operators have to be taken into account and their contributions are respectively ($K \equiv |k|$ in the following equations):

+l, K levels:

$$\Delta E_{L-} = \frac{G_t^2}{B_x - B_z - (B_z \zeta_t^2)} [J, K] [J, K + 1] (K + 1)^{-1}, \quad (49)$$

$$\Delta E_{L+} = \frac{F_t^2}{B_z - B_x - (B_z \zeta_t^2)} [J, K - 1] [J, K - 2] (K - 1)^{-1} \quad (K \neq 1), \quad (50a)$$

$$\Delta E_{L+} = \pm 2F_t J(J + 1) \quad (E_{\pm} \text{ levels}, K = 1); \quad (50b)$$

-l, K levels:

$$\Delta E_{L-} = - \frac{G_t^2}{B_x - B_z - (B_z \zeta_t^2)} [J, K - 1] [J, K - 2] (K - 1)^{-1} \quad (K \neq 1), \quad (51a)$$

$$\Delta E_{L-} = \pm 2G_t J(J + 1); \quad (51b)$$

$$\Delta E_{L+} = - \frac{F_t^2}{B_z - B_x - (B_z \zeta_t^2)} [J, K] [J, K + 1] (K + 1)^{-1}; \quad (52)$$

$\pm l, K$ levels:

$$\begin{aligned} \Delta E_{L_3} = & \frac{1}{8} d_2^2 \left\{ \frac{[J, K] [J, K + 1] [J, K + 2] [J, K + 3]}{(B_x - B_z)(K + 2) \pm (B_z \zeta_t^2)} \right. \\ & \left. - \frac{[J, K - 1] [J, K - 2] [J, K - 3] [J, K - 4]}{(B_x - B_z)(K - 2) \pm (B_z \zeta_t^2)} \right\} (1 - \delta_{2,K}) \pm \delta_{2,K} d_2 J(J + 1) \times \\ & \times [J(J + 1) - 2]. \end{aligned} \quad (53)$$

It is obvious from the above formulae that the constants G_t , F_t , and d_2 are determinable. On the other hand, d_2 is determinable only if the molecule is not a quasi-spherical top [$(B_x - B_z) = 0$]. If the molecule is a quasispherical top, then d_2 is determinable only if the splitting of the $K = 2$ levels is observed.

Contributions to the Splittings of Levels

Until now we have analyzed only the diagonal second order contributions to the energy levels [see Eq. (35a)]. However, the off-diagonal terms

$$\frac{i}{2} \langle \Psi | [\mathbf{S}, \mathbf{H}_{\text{off-d}}] | \Psi' \rangle \quad (54)$$

can also become important if Ψ , Ψ' are two states which are degenerate in the zeroth order (e.g. the $+l$, $+k$ and $-l$, $-k$ energy levels). Contributions of these terms [Eq. (54)] to the splittings of degenerate energy levels are summarized in Table I.

TABLE I
Higher-order contributions to the splittings of energy levels^a

| Vibrational states | Levels split | Splitting term ^b |
|----------------------------------------------------------------|------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Ground state and excited vibrational states with all $l_t = 0$ | $l_t = 0, k = \pm 4$ | $\frac{1}{16}d_2^2(B_z - B_x)^{-1} J(J+1) [J(J+1) - 2] \times [J(J+1) - 6] [J(J+1) - 12]$ |
| Excited vibrational states with $ l_t = 1, l_{t'} = 0$ | $l_t = \pm 1, k = \pm 1$ | $\left. \begin{aligned} &\frac{1}{4}d_2 G_t X_t^- \\ &\frac{1}{4}d_2 F_t X_t^+ \\ &-\frac{1}{4}d_2 F_t X_t^+ \\ &-\frac{1}{4}d_2 G_t X_t^- \end{aligned} \right\} \times (v_t + 1) J(J+1) [J(J+1) - 2] \times [J(J+1) - 6]$ |
| | $l_t = \pm 1, k = \mp 1$ | |
| | $l_t = \pm 1, k = \pm 3$ | |
| | $l_t = \pm 1, k = \mp 3$ | |
| Excited states of degenerate vibrations with v_t even | $l_t = 0, k = \pm 2$ | $\left. \begin{aligned} &-\frac{1}{2}G_t F_t Y_{tt} \\ &\frac{1}{2}G_t F_t Y_{tt} \\ &\frac{1}{4}(F_t^2 W_{tt}^- - d_2 U_t Z_{tt}) \\ &\frac{1}{4}(G_t^2 W_{tt}^+ + d_2 U_t Z_{tt}) \end{aligned} \right\} \times v_t(v_t + 2) J(J+1) \times [J(J+1) - 2]$ |
| | $l_t = \pm 2, k = 0$ | |
| | $l_t = \pm 2, k = \pm 2$ | |
| | $l_t = \pm 2, k = \mp 2$ | |
| Excited vibrational states with $ l_t = 1, l_{t'} = 1$ | $l_t = \pm 1, l_{t'} = \pm 1, k = 0$ | $\left. \begin{aligned} &\frac{1}{2}(G_t F_{t'} Y_{t't'} + G_{t'} F_t Y_{t't'}) \times M \\ &\frac{1}{2}(F_t F_{t'} W_{t't'}^- - \frac{1}{2}S_{t't'} d_2 Z_{t't'}) \times M \\ &\frac{1}{2}(G_t G_{t'} W_{t't'}^+ + \frac{1}{2}S_{t't'} d_2 Z_{t't'}) \times M \\ &-\frac{1}{2}\{G_t F_{t'} Y_{t't'} + \frac{1}{4}R_{t't'} d_2 [(B_z \zeta_t^z) - (B_z \zeta_{t'}^z)]^{-1}\} \times M \end{aligned} \right\}$ |
| | $l_t = \pm 1, l_{t'} = \pm 1, k = \pm 2$ | |
| | $l_t = \pm 1, l_{t'} = \pm 1, k = \mp 2$ | |
| | $l_t = \pm 1, l_{t'} = \mp 1, k = \pm 2$ | |

^a Splittings which occur only if $\sum v_t \geq 3$ were ignored and the following symbols were introduced: $M = (v_t + 1)(v_{t'} + 1) J(J+1) \times [J(J+1) - 2]$; $X_t^\pm = [B_x - B_z \pm (B_z \zeta_t^z)]^{-1}$; $Y_{t't'} = [x_{t't'}^{(l)} + B_x - B_z - (B_z \zeta_t^z) + (B_z \zeta_{t'}^z)]^{-1}$; $Z_{t't'} = [(B_z \zeta_t^z) + (B_z \zeta_{t'}^z)]^{-1}$; $W_{t't'}^\pm = [x_{t't'}^{(l)} - B_x + B_z \pm (B_z \zeta_t^z) \pm (B_z \zeta_{t'}^z)]^{-1}$. ^b Equivalent of $\Delta_j/2$ in Eq. (28a).

CONCLUSIONS

The effect of the operators diagonal in v , but off-diagonal in the l, k quantum numbers on the energy levels of molecules with the fourfold symmetry axis has been studied in this paper. It has been found that in principle F_v , G_v , and d_2 molecular constants are determinable from the analysis of the $v_i(E)$ vibrational-rotational bands. For d_2 this conclusion applies only if the molecule is not a quasi-spherical top. Contributions of the above described operators to the splittings of the degenerate energy levels have been also determined and are summarized in Table I.

It should be noted that our discussion holds for "isolated" vibrational levels of molecules with the fourfold symmetry axis. During the work on this problem, we learned that Sulakshina and Perevalov¹⁹ considered the same problem but extended the discussion to interacting vibrational states (see also ref.²⁰).

Because our approach is slightly different from that of Sulakshina and Perevalov¹⁹ (at least from the methodological point of view), it seems to be useful to present our results for an eventual future comparison (the more general approach¹⁹ should give results identical with ours for "isolated" vibrational levels).

REFERENCES

1. Urban Š., Papoušek D., Hernández M. G.: *J. Mol. Spectrosc.* **124**, 272 (1987).
2. Hernández M. G., Papoušek D., Urban Š.: *J. Mol. Spectrosc.* **128**, 564 (1988).
3. Sarka K., Papoušek D.: *Mol. Phys.* **65**, 829 (1988).
4. Bradley R. H., Brier P. N., Whittle M. J.: *J. Mol. Spectrosc.* **44**, 536 (1972).
5. Brier P. N., Winrow M. J.: *J. Mol. Spectrosc.* **107**, 21 (1984).
6. Brier P. N., Jones S. R., Baker J. G., Georghiou C.: *J. Mol. Spectrosc.* **64**, 415 (1977).
7. Kupeczek P.: *J. Phys. Radium* **25**, 831 (1964).
8. Balicki B., Brier P. N.: *J. Mol. Spectrosc.* **85**, 109 (1981).
9. Balicki B., Brier P. N.: *J. Mol. Spectrosc.* **89**, 254 (1981).
10. Georghiou C., Brier P. N., Baker J. G., Jones S. R.: *J. Mol. Spectrosc.* **72**, 282 (1978).
11. Brier P. N.: *J. Mol. Spectrosc.* **120**, 127 (1986).
12. Jurek R., Suzeau P., Chanussot J., Champion J. P.: *J. Phys.* **35**, 533 (1974).
13. Chanussot J., Jurek R., Bellet J.: *J. Phys.* **37**, 1129 (1976).
14. Papoušek D., Aliev M. R.: *Molecular Vibrational-Rotational Spectra*. Elsevier/Academia, Amsterdam/Prague 1982.
15. Aliev M. R., Watson J. K. G.: *Molecular Spectroscopy, Modern Research*, Vol. III (K. Narahari Rao, Ed.). Academic Press, New York 1985.
16. Makushkin Yu. S., Tyuterev V. I.: *Perturbation Methods and Effective Hamiltonians in Molecular Spectroscopy* (in Russian). Nauka, Novosibirsk 1984.
17. Grenier-Besson M. L.: *J. Phys. Radium* **21**, 555 (1960).
18. Cartwright G. J., Mills I. M.: *J. Mol. Spectrosc.* **34**, 415 (1970).
19. Sulakshina O. N., Perevalov V. I.: *Proceedings of the Xth Conference on High Resolution Infrared Spectroscopy*, (D. Papoušek, Ed.). *Liblice, September 5–9, 1988*.
20. Lobodenko E. I., Sulakshina O. N., Perevalov V. I., Tyuterev V. I.: *J. Mol. Spectrosc.* **126**, 159 (1987).

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