

TRANSITIONS WITH $\Delta k \neq 0, \pm 1$ AND DETERMINATION OF A_0 FOR SYMMETRIC TOP MOLECULES

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The conditions under which observation of the vibration-rotation transitions with $\Delta k \neq 0, \pm 1$ can be expected in infrared spectra of symmetric top molecules are discussed. Theoretical results are applied to fundamentals and first overtones of molecules of symmetry C_{3v} .

It is well known, that for symmetric top molecules accurate values of A_0 cannot be determined by the standard methods of analysis of vibration-rotation or pure rotation spectra. The selection rules for the infrared absorption spectra are $\Delta J = 0, \pm 1$ and $\Delta k = 0$, or $\Delta k = \pm 1$; the selection rules for Δk prevent^{1,2} the accurate determination of A_0 . However, since k is not a "good quantum number" for the symmetric top molecules, selection rules for Δk are not strict and are valid in the zeroth approximation only. This means that, in addition to the transitions with $\Delta k = 0, \pm 1$, transitions with $\Delta k \neq 0, 1$ can also be allowed. However, since they are forbidden in zeroth approximation, their intensity is usually too low for detection. In some cases these transitions can become observable and then it is possible to determine A_0 from the differences between the frequencies of the transitions with $\Delta k = 0, \pm 1$ and $\Delta k \neq 0, \pm 1$ terminating on the same upper state energy level. In this way A_0 was determined for CH_3I by Maki and Hexter³ and Matsuura and coworkers⁴, for CH_3D by Olson⁵; for SiH_3D by Lovejoy and Olson⁶; for AsH_3 by Olson and coworkers⁷; and for PH_3 by Maki and coworkers⁸.

Since the determination of A_0 is of principal spectroscopic interest *e.g.* for determination of the molecular structure, the conditions under which observation of the transitions with $\Delta k \neq 0, \pm 1$ can be expected will be discussed in this paper.

THEORETICAL

It will be supposed throughout this paper that the molecule is in a totally symmetric electronic state, and the lower states for all transitions discussed are the rotational levels of the ground vibrational state.

It was found useful to classify the states according to the quantum number G introduced by Hougen⁹ which is defined as follows:

For all groups containing symmetric top molecules except the groups D_{nd} (n even), S_{2n} (n even), (Groups I):

$$G = G_v - k, \quad 01460/777 \quad (1)$$

$$G_v = (n/2) \sum_{\mathbf{B}} v_{\mathbf{B}} + \sum_j s_j l_j. \quad (2)$$

For groups D_{nd} (n even), S_{2n} (n even) (Groups II):

$$G = G_v - k(1 + n), \quad (3)$$

$$G_v = n \sum_{\mathbf{B}} v_{\mathbf{B}} + \sum_j s_j l_j. \quad (4)$$

Notice that in the ground vibrational state $G'' = -k$, $G'' = -k(1 + n)$ for groups I and II, respectively, and also that G classifies the states only with respect to C_n (Groups I) or S_{2n} (Groups II) elements of symmetry. Thus, results obtained by using only the quantum number G for classification of the states give the maximum information obtainable for the groups C_n and S_{2n} (n even). For other symmetry groups additional restrictions must be imposed, following from the presence of symmetry elements other than C_n , S_{2n} . These restrictions can, however, be imposed as the last step.

The infrared vibration-rotation transitions can be divided with the help of G into the following groups: 1) Strictly forbidden are transitions for which $\Delta G \neq tn$ for groups I or $\Delta G \neq n(1 + 2t)$ for groups II, where t is an arbitrary integer including zero. 2) Strongly allowed are transitions for which $\Delta G = tn$ (Groups I) or $\Delta G = n(1 + 2t)$ (Groups II) and $\Delta k = 0$, or ± 1 . 3) Approximately forbidden are transitions for which $\Delta G = tn$ (Groups I) or $\Delta G = n(1 + 2t)$ (Groups II) but $\Delta k \neq 0, \pm 1$. These transitions are forbidden in the zeroth approximation but can be allowed in higher approximation. Since transitions 1) will never appear in the further discussion, the term forbidden will be used to mean type (3) transitions.

Only a special kind of forbidden transition is of interest for the purpose of this paper, namely forbidden transitions which terminate on the same upper state energy levels as do other allowed transitions (Fig. 1).

Let the transition $S''_1 \rightarrow S'_1$ be allowed ($\Delta k = 0$ or $+1$ or -1), and let its observed frequency be ν_a . If in addition the forbidden transition $S''_2 \rightarrow S'_1$ can also be observed, then*

$$\begin{aligned} \Delta\nu &= \nu_f - \nu_a = \\ &= (A_0 - B_0)(k_1''^2 - k_2''^2) - D_0^{JK} J''(J'' + 1)(k_1''^2 - k_2''^2) - D_0^K(k_1''^4 - k_2''^4). \end{aligned} \quad (5)$$

Since accurate values of B_0 , D_0^{JK} are usually known, it is possible from Eq. (5) to determine accurate values of A_0 , D_0^K if a sufficient number of the forbidden transitions can be observed.

* Assuming that quantum number J has the same values for states S''_1 , S''_2 . Modification of Eq. (5) for $J''_1 \neq J''_2$ is obvious.

In the zeroth approximation (rigid rotor + harmonic oscillator) only one transition (with respect to Δk) is allowed from the ground state to any excited vibrational state. The forbidden transition $S_2'' \rightarrow S_1'$ then must be induced by perturbation of the state S_1' through interaction with another upper state S_2' , for which the transition $S_2'' \rightarrow S_2'$ is allowed (Fig. 2).^{*} Then also the forbidden transition $S_1'' \rightarrow S_2'$ is induced.

The first step is to find some relation between Δk values of allowed transitions and Δk value for matrix element of the perturbation. This relation should also reflect condition $k_1'' \neq k_2''$ necessary for determination of A_0 (see Fig. 1 and Eq. (5)). We shall try to find this condition using the quantum number G .

Groups I. The following equations must be obeyed⁹:

$$G_1' - G_1'' = t_1 n, \quad (6)$$

$$G_2' - G_2'' = t_2 n, \quad (7)$$

$$G_1' - G_2' = t_3 n, \quad (8)$$

where $t_1, t_2, t_3 = 0, \pm 1, \pm 2, \dots$ and for a given interaction the values of t_1, t_2 are fixed by the condition that transitions $S_1'' \rightarrow S_1'$, $S_2'' \rightarrow S_2'$ are allowed (See Appendix I).

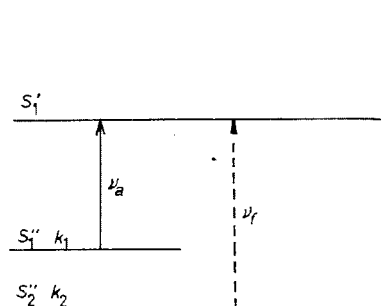


FIG. 1

Allowed ν_a and Forbidden ν_f Transitions Terminating on the Same Upper State Energy Level

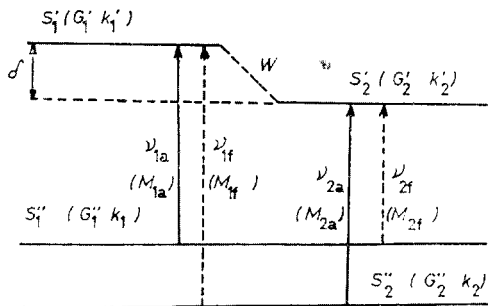


FIG. 2

Forbidden Transitions ν_{1f}, ν_{2f} Induced by Interaction W between the States S_1', S_2'

* Apparently forbidden transitions $S_2'' \rightarrow S_1'$, $S_1'' \rightarrow S_2'$ can be also induced, if there is a mixing of the wavefunctions of the states S_1', S_2' . Author is indebted to Professor Mills for this remark.

Then

$$k_1'' - k_2'' = G_2'' - G_1'' = (t_1 - t_2 - t_3)n. \quad (9)$$

Since values of t_1, t_2 for a given interaction are fixed, $k_1'' \neq k_2''$ if and only if

$$t_3 \neq t_1 - t_2. \quad (10)$$

Groups II. The following relations must be obeyed⁹:

$$G_1' - G_1'' = n(1 + 2t_1), \quad (11)$$

$$G_2' - G_2'' = n(1 + 2t_2), \quad (12)$$

$$G_1' - G_2' = 2t_3n. \quad (13)$$

Again $t_1, t_2, t_3 = 0, \pm 1, \pm 2 \dots$ and t_1, t_2 are fixed by the same condition as for groups I and

$$k_1'' - k_2'' = \frac{1}{1+n} (G_2'' - G_1'') = \frac{2n}{1+n} (t_1 - t_2 - t_3). \quad (14)$$

Since $k_1'' - k_2''$ must be an integer $k_1'' \neq k_2''$ if and only if

$$t_3 = t_1 - t_2 + t_4(1+n), \quad (15)$$

where t_4 is arbitrary nonzero integer.

Equations (6-8, 10 or 11-13, 15) are basic conditions for perturbation which must be obeyed if forbidden transitions $S_2'' \rightarrow S_1', S_1'' \rightarrow S_2'$ become allowed. However these conditions do not say anything about the intensity of the induced transitions. Thus, the next step will be the inspection of the intensities of the induced forbidden transitions $S_2'' \rightarrow S_1', S_1'' \rightarrow S_2'$. The following two quantities will be defined (Fig. 2): $\delta = |E_1' - E_2'|$ where E_1', E_2' are energies of the unperturbed states S_1', S_2' and $W = |\langle S_1' | \mathbf{H} | S_2'' \rangle|$. The intensity of a transition is proportional to the square of the transition moment M ($M = |\langle S_1' | \mu | S_1'' \rangle|$). Let the unperturbed moments for the transitions $S_1'' \rightarrow S_1', S_2'' \rightarrow S_2'$ be M_{1a}, M_{2a} , respectively, and let the unperturbed moments for the transitions $S_2'' \rightarrow S_1', S_1'' \rightarrow S_2'$ be equal to zero. Then the squares of the transition moments M_{1f}, M_{2f} induced by perturbation are

$$M_{1f}^2 = \beta M_{2a}^2, \quad M_{2f}^2 = \beta M_{1a}^2, \quad (16)$$

where

$$\beta = \frac{1}{2} [1 - 1/(1 + 4W^2/\delta^2)^{1/2}]^2. \quad (17)$$

The ratio $M_{2a}^2/M_{1f}^2 = M_{1a}^2/M_{2f}^2$ was calculated for several values of W/δ and results are presented as follows:

| | | | | | | | |
|------------|-----|------|------|------|------|---------|-----------|
| W/δ | 30 | 2 | 1 | 0.5 | 0.3 | 0.1 | 0.03 |
| β | 0.5 | 0.29 | 0.13 | 0.04 | 0.01 | 0.00019 | 0.0000016 |

Particularly interesting are results for $W/\delta = 30, 1, 0.03$ since 30 is a typical value of the ratio $\mathbf{H}_n/\mathbf{H}_{n+1}$ in the usual rovibrational classification of the magnitudes of the terms of the Hamiltonian¹⁰. From above calculations it immediately follows that for the observation of forbidden transitions W must necessarily be of the order of δ .

Since \mathbf{H}_0 is diagonal in all quantum numbers, W is the matrix element of \mathbf{H}_1 or \mathbf{H}_2 or still higher order Hamiltonian and since δ must be of the same order, the states S'_1, S'_2 must be in resonance. Notice also that if $W = \langle S'_1 | \mathbf{H}_1 | S'_2 \rangle \approx 30 \text{ cm}^{-1}$ then $\nu_1^0 \approx \nu_2^0$ (ν^0 is the vibrational frequency) satisfactory fulfills the condition $W \approx \delta$, while if $W = \langle S'_1 | \mathbf{H}_2 | S'_2 \rangle \approx 1 \text{ cm}^{-1}$ the states S'_1, S'_2 must be in almost exact resonance ($\delta \approx 1 \text{ cm}^{-1}$) which can be probably achieved at best only for a limited region of K values. For $W = \langle S'_1 | \mathbf{H}_n | S'_2 \rangle$ ($n > 2$) δ should be of the order $1/30^{n-2}$ ($\delta \approx 0.03$ for $n = 3$). Since the probability of this situation is very low, the interaction caused by \mathbf{H}_n ($n > 2$) can for the purpose of this paper be safely neglected. The conclusion is, then, that the states S'_1, S'_2 must be in resonance and must interact with each other through the operators from \mathbf{H}_1 or \mathbf{H}_2 . (If the resonance is a simple two level interaction.) Since forbidden transitions are induced by perturbation we want to find specifically which operators from Hamiltonian induce forbidden transitions.

The terms of \mathbf{H} can be represented as $\mathbf{h}_{v,r}$ where v is the power of the vibrational operators and r is the power of the rotational operators. Terms $\mathbf{h}_{v,0}$ can be excluded from the consideration since they cannot satisfy conditions (10) or (15) (for proof see Appendix II). Terms $\mathbf{h}_{1,r}$ can also be excluded since their matrix elements do not connect states with nearly equal energies. According to the Amat and Nielsen classification¹⁰ the order m of the term $\mathbf{h}_{v,r}$ is

$$m = v + r - 2 \quad (18)$$

and since m must be equal to 1 or 2 the only terms which have to be considered are:

$$\mathbf{h}_{2,1}; \mathbf{h}_{3,1}; \mathbf{h}_{2,2}; \mathbf{h}_{0,4}. \quad (19)$$

The discussion of conditions which must be satisfied if forbidden transitions are to be observed is now completed. These conditions can be summarized as follows:

a) Equations (6)–(8), (10) or (11)–(13), (15) must be obeyed; b) The states S'_1, S'_2 must be in resonance; c) The operator of perturbation coupling the states S'_1, S'_2 must be one of the operators in (19).

Application

In the preceding section we have derived the conditions necessary for observation of forbidden transitions which are required for determination of A_0 . In this section it will be shown how these conditions can be applied in a convenient way to observed infrared bands.

Let us suppose we have observed in the infrared spectrum that two assigned bands lie close to each other. We would like to know whether there is a chance to observe the forbidden transitions and to determine A_0 . Since we know G_v values for these bands (Eq. (2) or (4)), values t_1, t_2 immediately follow from Appendix I and Eqs (6, 7) or (11, 12) and these values can be substituted to Eq. (10) or Eq. (15). Value $\Delta G_v = (G'_v)_1 - (G'_v)_2$ of interaction is given by values $(G'_v)_1, (G'_v)_2$ which we know and all we have to do is to find out whether any of the operators in (19) can yield such values of $\Delta k = k'_1 - k'_2$ which combined with ΔG_v would satisfy Eqs (8), (10) or (13), (15). Hence, using only elementary algebra we can determine whether the forbidden transitions can become observable in the studied bands and if so, which perturbation induces forbidden transitions and also type of the forbidden transitions. Then we can predict the approximate frequencies of the forbidden transitions and if force constants for a given molecule are known, also their approximate intensities.

The most often studied bands of axially symmetric molecules are fundamental bands and the first overtones of molecules of symmetry C_{3v} . We shall now demonstrate the above described procedure on several examples of interaction between such bands.

Essential Resonances

We shall discuss first "essential resonances"¹⁰. Matrix elements of operator $\mathbf{h}_{0,4}$ always couple rotational levels within the same vibrational state. Consequently interactions caused by this operator have always character of "essential resonance"¹⁰ which can be accidentally strengthened. Since $(G'_v)_1 = (G'_v)_2$ in this case, it follows that also $t_1 = t_2$ (Appendix I). Then $t_3 \neq 0, \Delta G_v = 0$ and conditions (8, 10) can be simplified as follows:

$$\Delta k = k'_1 - k'_2 = \pm 3, \pm 6, \dots \quad (20)$$

This condition is satisfied by the operator of the type \mathbf{J}_\pm^3 and matrix element of interaction is:

$$W = \langle k | \mathbf{H}_{\text{int}} | k \pm 3 \rangle. \quad (21)$$

The explicit expression for \mathbf{H}_{int} is given in a paper by Olson and coworkers⁷. If for example interacting bands are in parallel fundamental then energy difference δ (Fig. 2) is given by the equation:

$$\delta = (A - B) [k^2 - (k \pm 3)^2]. \quad (22)$$

From this equation it follows that "essential resonance" is accidentally strengthened if $A \approx B$ and forbidden transitions with $\Delta k = \pm 3$ can become observable. For $3\nu_2$ vibrational state of PH_3 condition $A \approx B$ is satisfied and Maki, Sams and Olson were indeed able to observe a number of forbidden transitions with $\Delta k = \pm 3$ in this band.

Another interaction which has the character of "essential resonance" is the so called "2, -1 resonance". Matrix element of this interaction has the form⁷:

$$W = \langle v, l, k | \mathbf{H}_{\text{int}} | v, l \mp 2, k \pm 1 \rangle. \quad (23)$$

For the degenerate fundamental $\delta = (A - B + 2A\zeta_1^z) (1 \pm 2k)$ and the "essential resonance" can be accidentally strengthened if $A - B + 2A\zeta_1^z \approx 0$. Then together with the allowed transitions also transitions with $\Delta l = \pm 1, \Delta k = \mp 2$ can be observed. For ν_3 band of AsH_3 (ref.⁷) $A - B + 2A\zeta_1^z = 0.36$ and many of forbidden transitions observed in this band are probably induced by this interaction.

The last type of "essential resonance" which will be discussed is "l-type doubling". Matrix elements of these interactions have the following form⁵:

$$W = \langle v, l, k | \mathbf{H}_{\text{int}} | v, l \pm 2, k \pm 2 \rangle. \quad (24)$$

From Eqs (1), (2), (8) it follows immediately that $t_3 = 0$ and Eq. (10) takes the form $t_1 \neq t_2$. From Appendix I it follows that for degenerate fundamental $E : t_1 = t_2 = 0$ and therefore this interaction does not induce forbidden transitions in fundamentals. On the other hand in the first overtone $2\nu(E)$ the upper state energy levels have $l = 0, \pm 2$. The transitions to $l = 0$ level have $t_1 = 0$ while for transitions to $l = \pm 2$ levels $t_1 = \pm 1$. Since $t_1 \neq t_2$ Eq. (10) is satisfied and in addition to allowed transitions $\Delta v = 2, \Delta l = 0, \Delta k = 0$ and $\Delta v = 2, \Delta l = \pm 2, \Delta k = \mp 1$ also forbidden transitions $\Delta v = 2, \Delta l = 0, \Delta k = \pm 3$; $\Delta v = 2, \Delta l = \Delta k = \mp 2$ can be induced. Forbidden transitions of this type were observed by Olson⁵ in $2\nu_5, 2\nu_6$ bands of CH_3D (forbidden bands observed in $\nu_5 + \nu_6$ combination band are caused by quite analogous interaction).

After discussing the "essential resonances" we shall turn our attention to remaining operators in (19) and present a few examples of interactions between bands of molecules of symmetry C_{3v} .

Accidental Resonances

Interaction between fundamentals. In infrared spectra only fundamentals belonging to symmetry species A_1 or E are allowed. From Eqs (1), (2), (6), (7) and Appendix I it follows that for these transitions is $t_1 = t_2 = 0$ and conditions (8, 10) reduce to a simple equation

$$G'_1 - G'_2 = (G'_v)_1 - (G'_v)_2 - (k'_1 - k'_2) = \pm 3, \pm 6, \dots \quad (25)$$

a) Interaction $\nu_i(A_1) \leftrightarrow \nu_j(A_1)$. This interaction could be important if two parallel fundamentals have nearly equal frequencies. Since $(G'_v)_1 = (G'_v)_2 = 0$ Eq. (25) reduces to Eq. (20). None of the operators in (19) can satisfy Eq. (20) in this case and therefore interaction between two parallel fundamentals does not induce forbidden transitions.

b) Interaction $\nu_i(E) \leftrightarrow \nu_j(E)$. This interaction can become important if two perpendicular bands have nearly equal frequencies. Since $(G'_v)_1 = \pm 1$, $(G'_v)_2 = \pm 1$ (Eq. (2)) there are two possibilities:

$$(G'_v)_1 - (G'_v)_2 = 0 \quad \text{or} \quad \pm 2. \quad (26)$$

The first case (0) leads again to Eq. (20) which as was said cannot be satisfied by operators in (19), while in the second case (± 2) (Eq. (25)) can be satisfied by operator $\mathbf{h}_{2,1}$ with $k'_1 - k'_2 = \mp 1$. Matrix element of interaction is

$$W = \langle 1^{\mp 1}, 0^0, k | \mathbf{H}_c^{x,y} | 0^0, 1^{\pm 1}, k \mp 1 \rangle, \quad (27)$$

where $\mathbf{H}_c^{x,y}$ is well-known first-order Coriolis operator and together with the allowed transitions $\Delta l_i = \Delta k = \pm 1$; $\Delta l_j = \Delta k = \pm 1$, also forbidden transitions $\Delta l_i = \pm 1, \Delta k = \mp 2$; $\Delta l_j = \pm 1, \Delta k = \mp 2$ can be induced.

c) Interaction $\nu_i(A_1) \leftrightarrow \nu_j(E)$. This interaction is to be considered if parallel and perpendicular fundamentals have nearly equal frequencies. In this case $(G'_v)_1 = 0$, $(G'_v)_2 = \pm 1$ and Eq. (25) can be satisfied by operator $\mathbf{h}_{2,2}$ for which $k'_1 - k'_2 = \pm 2$. Matrix element of interaction is

$$W = \langle 1, 0^0, k | \mathbf{H}_{\text{int}} | 0, 1^{\pm 1}, k \mp 2 \rangle, \quad (28)$$

where \mathbf{H}_{int} is "K-type doubling" operator¹¹ and besides allowed transitions $\Delta v_i = 1, \Delta k = 0$; $\Delta v_j = 1, \Delta l_j = \Delta k = \pm 1$ also forbidden transitions $\Delta v_i = 1, \Delta k = \pm 3$ and $\Delta v_j = 1, \Delta l_j = \pm 1, \Delta k = \mp 2$ can be induced. Olson, Maki and Sams⁷ observed forbidden transitions of this type induced by interaction between ν_1 ($\approx 2115 \text{ cm}^{-1}$)

and ν_3 ($\approx 2126 \text{ cm}^{-1}$) bands of arsine. Lovejoy and Olson⁶ observed such transitions in ν_1 ($\approx 2187 \text{ cm}^{-1}$) and ν_4 ($\approx 2188 \text{ cm}^{-1}$) bands of SiH_3D .

Interactions between the fundamental and the first overtone. The upper state energy levels of the fundamental and the first overtone can be connected only by operator $\mathbf{h}_{3,1}$. No other operator in (19) can couple these levels. We shall present two examples of interactions of this type.

a) Interaction $\nu_i(A_1) \leftrightarrow 2\nu_j(E)$. The first overtone $2\nu_j$ is split into two vibrational levels: $2\nu_j(l=0)$ and $2\nu_j(l=\pm 2)$. As far as interaction $\nu_i \leftrightarrow 2\nu_j(l=0)$ is concerned, since $(G'_\nu)_1 = (G'_\nu)_2 = 0$ this is the same case as the interaction $\nu_i(A_1) \leftrightarrow \nu_j(A_1)$ which has been already discussed and therefore this interaction does not induce forbidden transitions. However for transitions $2\nu_j(l=\pm 2)$ is $\Delta l = \pm 2$, $\Delta k = \mp 1$ and $t_2 = \pm 1$. (See Eq. (2) and Appendix I). Since $t_1 = 0$ from Eq. (10) it follows that $t_3 \neq \pm 1$ and Eq. (8) takes the following form

$$(G'_\nu)_1 - (G'_\nu)_2 - (k'_1 - k'_2) = 0, \pm 6, \pm 9, \dots \quad (29)$$

After substituting $(G'_\nu)_1 = 0$, $(G'_\nu)_2 = \pm 2$ to Eq. (29) we obtain:

$$k'_1 - k'_2 = \pm 2, \pm 4, \dots \quad (30)$$

Eq. (30) cannot be satisfied by operator $\mathbf{h}_{3,1}$ (maximum Δk in matrix elements of this operator is ± 1) and this interaction does not induce forbidden transitions either.

b) Interaction $\nu_i(E) \leftrightarrow 2\nu_j(E)$. In this case there are again two possible interactions $\nu_i \leftrightarrow 2\nu_j(l=0)$ and $\nu_i \leftrightarrow 2\nu_j(l=\pm 2)$. As far as the former interaction is concerned it is easy to see that this is the same case as already discussed interaction $\nu_i(A_1) \leftrightarrow \nu_j(E)$. However, requirement $k'_1 - k'_2 = \pm 2$ cannot be satisfied by operator $\mathbf{h}_{3,1}$ and therefore this interaction does not induce forbidden transitions. For the interaction $\nu_i(E) \leftrightarrow 2\nu_j(l=\pm 2)$ $t_1 = 0$, $t_2 = \pm 1$ and Eq. (29) must be obeyed. Since $(G'_\nu)_1 = \pm 1$, $(G'_\nu)_2 = \pm 2$ there are two possibilities:

$$(G'_\nu)_1 - (G'_\nu)_2 = \mp 1 \quad \text{or} \quad \pm 3. \quad (31)$$

After substituting these values to Eq. (29) we find that in the first case $k'_1 - k'_2$ must be equal to ∓ 1 while in the second case $(k'_1 - k'_2)$ must be equal to ± 3 . Condition $k'_1 - k'_2 = \mp 1$ can be satisfied by operator $\mathbf{h}_{3,1}$ while the condition $k'_1 - k'_2 = \pm 3$ cannot. Thus the matrix element of interaction is

$$W = \langle 1^{\pm 1}, 0^0, k | \mathbf{H}_{\text{int}} | 0^0, 2^{\pm 2}, k \pm 1 \rangle \quad (32)$$

and together with allowed transitions $\Delta v_i = 1$, $\Delta l = \Delta k = \pm 1$ and $\Delta v_j = 2$, $\Delta l = \pm 2$, $\Delta k = \mp 1$ also the forbidden transitions $\Delta v_i = 1$, $\Delta l = \pm 1$, $\Delta k = \mp 2$ and $\Delta v_j = 2$, $\Delta l = \pm 2$, $\Delta k = \pm 2$ are induced. Olson⁵ observed transitions of this type induced by interaction between $v_4(E)$ and $2v_5(E)$ bands of CH_3D .

DISCUSSION

The problem of the indeterminacy of the constant A_0 of symmetric top molecules is well-known^{1,2,12,13}. The uncertainty of the constants A_0 determined from the values $[A_i(1 - \zeta_i^2) - B_i]$ and the ζ -sum rule is estimated to be less than five percent^{1,12} while the uncertainty of the constants A_0 determined by the Barnett and Edwards method¹³ can be estimated to be $\approx 1\%$. These uncertainties are several orders of magnitude higher than those of the constants B_0 determined from the microwave or high resolution infrared spectra. As a consequence also our knowledge of the geometries of simple symmetric top molecules is much less accurate than for linear molecules.

Recently another method was suggested² for accurate determination of A_0 . This method requires the data on higher overtones and the uncertainty of the constant A_0 determined in this way can be estimated to be $\approx 0.01\%$. However this method thus far has not been applied in practice. On the other hand recently several papers appeared⁵⁻⁸, where the constant A_0 was determined with the precision $\approx 0.001\%$ comparable with the precision obtained for the constants B_0 . In these papers the constants A_0 were determined from the differences between the frequencies of allowed and forbidden transitions terminating on the same upper state energy level, *i.e.* from the ground state differences in K . This method requires the knowledge of frequencies of forbidden transitions with $\Delta k \neq 0, \pm 1$. Since this method gives the most accurate values of the constants A_0 , we thought that it would be useful to determine the conditions necessary for observation of forbidden transitions. There are two possible approaches to this problem. The first, more rigorous would be the derivation of complete expressions for intensities of forbidden transitions using the perturbation method. In the second, simpler approach which was actually used in this paper, it is assumed that contribution of the nonresonant interactions to the intensity of forbidden transition is negligible and that observation of forbidden transition is caused by dominant interaction between the states having nearly equal energies.

It was demonstrated on several examples that application of the conditions necessary for observation of forbidden transitions which were derived in this paper is very easy requiring in fact only simple algebra and it is believed that these conditions could serve as a useful guide in determining whether the search for forbidden transitions in measured bands would be successful or not.

APPENDIX I

Allowed transition i from the ground vibrational state must obey the relations:

Groups I:

$$(G_v)_i - \Delta k_i = t_i n \quad (A1)$$

Groups II:

$$(G_v)_i - \Delta k_i(1 + n) = n(1 - 2t_i) \quad (A2)$$

All groups:

$$\Delta k_i = 0 \text{ or } 1 \text{ or } -1. \quad (A3)$$

Since minimal n is equal to 3 (Groups I) or 2 (Groups II) there are only two possibilities for given $(G_v)_i$: a) Neither one of the allowed Δk_i satisfies the condition (A1 or A2) and transition is forbidden; b) Only one of the allowed Δk_i (A3) satisfies the condition (A1 or A2). Then apparently the value of $(G_v)_i$ determines the values Δk_i , t_i .

APPENDIX II

The following statement will be proved: If operator connecting the states S'_1, S'_2 is diagonal in k then $k''_1 = k''_2$ (Fig. 2).

Proof for groups I:

$$(G'_v)_1 - k'_1 + k''_1 = t_1 n, \quad (B1)$$

$$(G'_v)_2 - k'_2 + k''_2 = t_2 n, \quad (B2)$$

$$(G'_v)_1 - (G'_v)_2 = t_3 n, \quad (B3)$$

Then:
$$(k'_1 - k''_1) - (k'_2 - k''_2) = pn, \quad (B4)$$

where $p = t_3 - t_1 + t_2$ is integer or zero. Minimal value of n is equal to 3. Since transitions $S''_1 \rightarrow S'_1, S''_2 \rightarrow S'_2$ are allowed

$$|k'_1 - k''_1| \leq 1, \quad |k'_2 - k''_2| \leq 1. \quad (B5)$$

The Eq. (B4) can be obeyed only for $p = 0$ and since $k'_1 = k'_2$ also k''_1 must be equal to k''_2 q.e.d.

Proof for groups II:

$$(G'_v)_1 - (k'_1 - k''_1)(1 + n) = n(1 + 2t_1), \quad (B6)$$

$$(G'_v)_2 - (k'_2 - k''_2)(1 + n) = n(1 + 2t_2), \quad (B7)$$

$$(G'_v)_1 - (G'_v)_2 = 2t_3 n, \quad (B8)$$

Then:
$$(k'_1 - k''_1) - (k'_2 - k''_2) = 2n(t_3 - t_1 + t_2)(1 + n). \quad (B9)$$

Right-hand side of Eq. (B9) must be integer and then $(t_3 - t_1 + t_2)/(1 + n)$ must be integer let us say k . Since minimal n is equal to 2 and again $|k'_1 - k''_1| \leq 1, |k'_2 - k''_2| \leq 1$, in the same way as for groups I it can be proved that $k''_1 = k''_2$.

Since $k''_1 \neq k''_2$ is necessary condition for application of Eq. (5) all operators diagonal in k can be excluded from consideration for the purposes of this paper.

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