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Theory of Microwave Transitions in the Vibronic Ground State of Tetrahedral Molecules*

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Vibration-rotation interactions in the motion of tetrahedral molecules, which are conventionally nonpolar in their ground vibrational and electronic states, permit pure rotational transitions. These transitions, which are electric dipole in nature, occur at microwave frequencies for the following changes in rotational quantum numbers: $\Delta J = 0$ and $\Delta K = \pm 2$. General expressions for spectral line positions and absolute intensities are calculated for $J = 0$–20. The effects of tetrahedral fine-structure splittings and nuclear-spin statistical weights have been included. Detailed results are established for methane, the prototype of molecules with tetrahedral symmetry. Possible competing transitions are discussed.

I. INTRODUCTION

A tetrahedral molecule in its ground vibrational and electronic state is conventionally assumed to have no permanent electric dipole moment, by virtue of the high symmetry in this state. Therefore, under ordinary circumstances, this class of molecules is not expected to have pure rotational transitions, i.e., transitions in which only its rotational quantum numbers change. However, recent theoretical calculations[1,2] have suggested that vibration-rotation interactions, which may be characterized as centrifugal distortion effects, can lead to a very small dipole moment in the vibronic ground state. Soon after these predictions were made by Fox[1] and by Watson,[2] the electric dipole moment of methane—the prototype of molecules with tetrahedral symmetry—was determined by Ozier[3] to have a magnitude of $(5.38 \pm 0.10) \times 10^{-6}$ D in the vibronic ground state. This determination was made by measuring Stark shifts in the ortho-para spectrum[4] of CH_4 in the $J = 2$ rotational level. The measured value of the dipole moment was considered[3] to be in excellent agreement with the earlier theoretical estimates of 4×10^{-6} D by Fox[1] and 5.8×10^{-6} D inferred[3] from Watson's[2] calculations.

The general theory of pure rotational transitions in the vibronic ground state of tetrahedral molecules,[1] and molecules of other symmetries,[2] has been discussed previously. The selection rules for the total-angular-momentum quantum number are the usual ones, $\Delta J = 0$ or ± 1, for electric dipole transitions. In Ref. 1, emphasis was placed on transitions arising from $\Delta J = +1$. In particular, a far-infrared absorption spectrum for CH_4 was calculated corresponding to the initial-state quantum numbers $J = 0$–10. An experiment is underway[3] to observe this spectrum.

The theoretical approach by Fox[1] was to calculate the admixture of infrared-active vibrational states into the vibronic ground state. Transition dipole moments were then calculated using an unperturbed dipole-moment operator between perturbed ground-state wave functions. In these quantum-mechanical calculations, considerable use was made of angular-momentum-coupled wave functions and the spherical tensor formalism, including Racah algebra and the Wigner-Eckart theorem.[5] The effects of nuclear-spin statistical weight factors on the calculated intensities were included. Tetrahedral fine-structure splittings were considered, but were summed over for each J value.

Watson's theoretical approach[2] was to calculate matrix elements of an effective dipole-moment operator which depends quadratically on components of the total angular momentum. The eigenfunctions used corresponded to the Wilson-Howard[6] rotational Hamiltonian. For molecules of D_{2d} symmetry, Watson[2] deduced the selection rules $\Delta J = 0$ or ± 1, and $\Delta K = \pm 2$. He calculated line strengths for T_d molecules by specializing his formulas for D_{2d} molecules. His results exhibit a strong J dependence, as is evident in Ref. 1 and again in the present work. The explicit expression for $\Delta J = +1$ transitions, obtained by summing over all allowed values of K, differs slightly from the corresponding one in Ref. 1. This difference is attributable, at least in part, to the omission of nuclear-spin statistical weight factors from Watson's calculations. As discussed in Ref. 1, a sum rule developed earlier[7] makes it possible to include nuclear-spin effects in a relatively simple way. For the observation of the $\Delta J = +1$ far-infrared absorption spectrum calculated in Ref. 1, it was not considered essential to determine the absolute intensity and spectral line position of each individual tetrahedral fine-structure component. In an experiment of sufficiently high spectral resolution, however, it would be desirable to have the parameters for individual components available.

These parameters may be readily calculated by the techniques to be described in the present work.

In this paper, detailed calculations and results will be displayed, for the entire class of T_d molecules, for the $\Delta J = 0$ transitions. These correspond to transitions in the microwave spectral region. It will be shown that the effects of T_d fine-structure splittings are crucial to the understanding and observation of the microwave spectrum.

In Sec. II, the theoretical framework of Ref. 1 will be reviewed and amplified. General expressions for absolute line intensities and spectral line positions will be calculated for the $\Delta J = 0$ transitions, for the entire class of T_d molecules, in Sec. III. In Sec. IV, the theory will be applied to predict a detailed microwave spectrum for CH_4; suitable modifications for other T_d molecules will also be considered. Some possible competing transitions and astrophysical applications will be discussed in Sec. V.

II. THEORETICAL FRAMEWORK

A. General

In the following quantum-mechanical calculations, only the electronic ground state will be considered. The *un*perturbed vibronic ground-state wave function is denoted by $\psi(g;\ RK_R)$. The perturbed vibronic ground-state wave function is[1]

$$\Psi(RK_R) = \psi(g;\ RK_R) - (\hbar\omega_3)^{-1} \sum_{R''K''_R} w_3(R''K''_R;\ RK_R)\psi(\nu_3;\ R''K''_R) - (\hbar\omega_4)^{-1} \sum_{R''K''_R} w_4(R''K''_R;\ RK_R)\psi(\nu_4;\ R''K''_R) + \cdots , \qquad (1)$$

where[8]

$$w_j(R''K''_R,\ RK_R) = \int \psi^*(\nu_j;\ R''K''_R)\sigma_j[x_j(J_yJ_z + J_zJ_y) + y_j(J_zJ_x + J_xJ_z) + z_j(J_xJ_y + J_yJ_x)]\psi(g;\ RK_R)\, d\tau_j\, d\Omega , \qquad (2)$$

in which $\sigma_j = \hbar\omega_j\zeta_{2j}\sqrt{2}(B_0/\omega_j)^{3/2}$ and $j = 3$ or 4. The rotational quantum numbers R and K_R specify the eigenvalues of $\vec{R}^2$ and R_z, respectively. The rotational angular momentum is related to $\vec{J}$ and $\vec{l}$, the total and the vibrational angular momentum respectively, through $\vec{J} = \vec{R} + \vec{l}$. The quantum number l takes the value 0 for the ground state, and 1 for the infrared-active fundamentals ν_3 and ν_4. These vibrational fundamentals occur[9] with the central spectral frequencies ω_3 and ω_4, respectively. The vectors $\vec{r}_3 \equiv (x_3,\ y_3,\ z_3)$ and $\vec{r}_4 \equiv (x_4,\ y_4,\ z_4)$ are the normal coordinates for ν_3 and ν_4. The differential $d\tau_j$ stands for $dx_j\,dy_j\,dz_j$, and $d\Omega$ corresponds to the differential for the Euler angles which are the arguments of the rotational wave functions.[5]

The physical picture contained in Eqs. (1) and (2) can be characterized as follows. Equation (1) represents a small but significant admixture of the vibration-rotation states $\psi(\nu_3;\ RK_R)$ and $\psi(\nu_4;\ RK_R)$ into the vibronic ground state $\psi(g,\ RK_R)$. Both $\psi(\nu_3;\ RK_R)$ and $\psi(\nu_4;\ RK_R)$ are of sufficiently polar character, owing to their respective normal modes of vibration, to produce strong and complicated vibration-rotation spectra[9] in the electronic ground state. The admixing thus attributes polar character to the vibronic ground state $\psi(g;\ RK_R)$. The amount of this polarity is determined primarily by Eq. (2). There the operator which connects $\psi(g;\ RK_R)$ to $\psi(\nu_j;\ RK_R)$ is vibration-rotation in nature, as it must be because of two basic requirements which must be met in order that $w_j \neq 0$. First, the operator must be linear in the components of $\vec{r}_j$ so that the vibrational part of the matrix element in Eq. (2) is nonzero. And second, the operator must be invariant under all symmetry operations of the tetrahedral point group; in other words, it must belong to the totally symmetric irreducible representation A_1 of T_d. These requirements lead to the operator in Eq. (2). In the coefficient σ_j; ζ_{2j} is the Coriolis coupling constant,[10] and B_0 is the ground-state rotational constant.[9]

The space-fixed Z component of the electric dipole-moment operator may be expressed conveniently as

$$\mu_Z = \lambda_{Zx}\mu_x + \lambda_{Zy}\mu_y + \lambda_{Zz}\mu_z , \qquad (3)$$

where $\lambda_{Z\alpha}$ is the direction cosine between the space-fixed Z axis and the molecule-fixed α axis,[11] and μ_α is the molecule-fixed α component of the dipole-moment operator. To second order in the normal coordinates.[10]

$$\mu_z = A_3z_3 + A_4z_4 + A'_3x_3y_3 + A'_4x_4y_4 + \cdots , \qquad (4)$$

with similar expressions for μ_x and μ_y. Here the A_i and A'_i are dipole-moment derivatives: $A_3 \equiv (\partial\mu_z/\partial z_3)_0$, $A'_3 \equiv (\partial^2\mu_z/\partial x_3\partial y_3)_0$,[11a] etc. In addition to the cubic and higher-order terms implied by Eq. (4), there are terms bilinear in the normal coordinates in which components of $\vec{r}_3$ and $\vec{r}_4$ occur only linearly.

Selection rules and absolute intensities for transitions in the vibronic ground state are determined by integrals of the form

$$\langle\mu_z\rangle \equiv \int \Psi^*(R'K_R')\mu_Z\Psi(RK_R)\,d\tau_3 d\tau_4 d\Omega \tag{5}$$

$$\begin{aligned}= -\sum_{j=3}^{4}\sum_{R''K_R''}(\hbar\omega_j)^{-1}\Big[&w_j(R''K_R''; RK_R)\\ &\times\int \psi^*(g, R'K_R')\mu_Z\psi(\nu_j, R''K_R'')\,d\tau_j d\Omega\\ &+w_j^*(R''K_R''; R'K_R')\\ &\quad\times\int \psi^*(\nu_j; R''K_R'')\mu_Z\psi(g; RK_R)\,d\tau_j d\Omega\Big].\end{aligned} \tag{6}$$

Various terms which contribute $\lesssim 1\%$ have been neglected in obtaining Eq. (6) from Eq. (5). Terms of the type

$$\int \psi^*(\nu_j; R'K_R')x_j y_j \psi(\nu_j; RK_R)\,d\tau_j d\Omega$$

and

$$\int \psi^*(\nu_j; R'K_R')x_j y_k \psi(\nu_k; RK_R)\,d\tau_j d\tau_k d\Omega$$

are proportional to ω_j^{-2} and $(\omega_j\omega_k)^{-1}$, respectively. Higher vibrational states than those in Eq. (1) would lead to terms of the form, e.g.,

$$\int \psi^*(g; R'K_R')x_j y_j \psi(2\nu_j; R''K_R'')\,d\tau_j d\Omega,$$

which is proportional to $A_j'/2\omega_j$. The analog of the coefficient w_j which would admix the wave function $\psi(2\nu_j; RK_R)$ into the ground-state wave function $\psi(g; RK_R)$ is determined from a different vibration-rotation interaction than that displayed in Eq. (2). Higher-order corrections to Eq. (6) may be readily calculated by the formulation given in Ref. 8. These contributions may be required, e.g., by experimental data of sufficiently high precision.

B. Evaluation of Admixing Parameters

Evaluation of the integrals in Eqs. (2) and (6) is most efficiently done by expressing all operators in spherical tensor form,[5] and by using angular-momentum-coupled wave functions. The operator in Eq. (2) can be reconstituted from the spherical vectors

$$\begin{aligned}&(r_j)_{11} \equiv -(2)^{-1/2}(x_j + iy_j),\\ &(r_j)_{1-1} \equiv (2)^{-1/2}(x_j - iy_j), \qquad (r_j)_{10} \equiv z_j,\end{aligned} \tag{7}$$

and

$$\begin{aligned}&J_{11} \equiv -(2)^{-1/2}(J_x - iJ_y),\\ &J_{1-1} \equiv (2)^{-1/2}(J_x + iJ_y), \qquad J_{10} \equiv J_z.\end{aligned} \tag{8}$$

The sign differences in Eqs. (7) and (8) are a consequence of a complicated combination of circumstances. Vibration-rotation angular-momentum-coupled wave functions are formed by the usual vector-coupling methods,[5] with angular momentum addition coefficients, viz., Clebsch-Gordan coefficients or Wigner 3-j symbols. However, the corresponding angular momentum vectors $\vec{J}$ and $\vec{I}$ are subtracted,[12] rather than added, to form $\vec{R} = \vec{J} - \vec{I}$. Considerable care must be used in applying the techniques of Racah algebra and the Wigner-Eckart theorem.[5] Details have been discussed in the pioneering work of Hecht[13] and in Ref. 8. From the intermediate spherical tensor operator T_{2q} defined by

$$T_{2q} \equiv \sum_{q_1}(1\,1\,q_1 q_2|1\,1\,2q)J_{1q_1}J_{1q_2}, \tag{9}$$

it follows that

$$[x_j(J_yJ_z + J_zJ_y) + \text{cyclic}] = i(3)^{1/2}(\Omega_{32} - \Omega_{3-2}), \tag{10}$$

where the spherical tensor operator Ω_{3q} is defined by

$$\Omega_{3q} \equiv \sum_{q_1}(1\,2\,q_1 q_2|1\,2\,3\,q)(r_j)^*_{1q_1}T_{2q_2}. \tag{11}$$

The coefficients in Eqs. (9) and (11) are the usual Clebsch-Gordan coefficients for angular momentum addition.[5] In Eq. (11), the complex conjugate (*) is a consequence of the angular momentum subtraction[8,12,13] $\vec{R} = \vec{J} - \vec{I}$. Substitution of Eq. (10) into Eq. (2) yields, with the help of Eqs. (11) and (9),

$$\begin{aligned}w_j(R''K_R''; RK_R) = (\tfrac{1}{4}i\sigma_j)[&7(2J-1)(2J)(2J+1)\\ &\times(2J+2)(2J+3)]^{1/2}\begin{Bmatrix}J & R'' & 3\\ 1 & 2 & J\end{Bmatrix}\\ &\times[(R\,3\,K_R\,2|R\,3\,R''\,K_R'')\\ &-(R\,3\,K_R-2|R\,3\,R''\,K_R'')]\delta_{J''J},\end{aligned} \tag{12}$$

where the 6-j symbol,[5] arising from Racah algebra, has been used.

C. Evaluation of Dipole-Moment Matrix Elements

Similarly, by combining Eq. (3) with Eq. (4) and its analogs for μ_x and μ_y to write

$$\mu_Z = \sum_{j=3}^{4}A_j(\lambda_{Zx}x_j + \lambda_{Zy}y_j + \lambda_{Zz}z_j) + \cdots, \tag{13}$$

and by defining[8]

$$\begin{aligned}&\lambda_{11} \equiv -(2)^{-1/2}(\lambda_{Zx} - i\lambda_{Zy}),\\ &\lambda_{1-1} \equiv (2)^{-1/2}(\lambda_{Zx} + i\lambda_{Zy}), \qquad \lambda_{10} \equiv \lambda_{Zz},\end{aligned} \tag{14}$$

it can be shown that

$$\mu_Z = \sum_{j=3}^{4}A_j(-\sqrt{3})\sum_{q_1}(1\,1\,q_1 q_2|1\,1\,0\,0)(r_j)^*_{1q_1}\lambda_{1q_2}. \tag{15}$$

Then

$$\int \psi^*(g; R'K_R')\mu_Z\psi(\nu_j; R''K_R'')\,d\tau_j d\Omega$$

$$= -(A_j/\sqrt{2})(J'\,1M'\,0|J'\,1\,J''M'')\delta_{R''R'}\delta_{K_R''K_R'}\,, \tag{16}$$

with a similar expression for the other integral in Eq. (6). Here M' and M'' are the projections of $\vec{J}\,'$ and $\vec{J}\,''$, respectively, on the space-fixed Z axis; and δ is the Kronecker δ function. The rotational "reduced" matrix elements[5] required by the Wigner-Eckart theorem were calculated in Refs. 8 and 13.

The selection rules resulting from Eqs. (5), (6), (12), and (16) are $R'=R$, $R\pm 1$, $R\pm 2$, $R\pm 3$, subject to $R'+R\geqslant 3$; $K_R'=K_R\pm 2$; $J'=J$, $J\pm 1$, subject to $J'+J\geqslant 1$; and $K'=K\pm 2$ (K' and K are the projections of $\vec{J}\,'$ and $\vec{J}$, respectively, on the molecule-fixed z axis). The selection rule $\Delta J = 0, \pm 1$ is the familiar one for electric dipole transitions. These apply to the infrared-active vibration-rotation transitions in tetrahedral molecules. The selection rule $\Delta K = \pm 2$ already appears[7,8] to have been appropriate for the $2\nu_4$ overtone of CH_4. The more usual selection rule $\Delta K = 0$ applies to the fundamentals[13,14] ν_3 and[15] ν_4 of CH_4, and probably to[16] $3\nu_3$ of CH_4 to a good approximation.[17]

III. $\Delta J = 0$ TRANSITIONS

A. Absolute Line Intensities

Absolute line intensities for transitions in the vibronic ground state are determined from Eqs. (5) and (6), with the substitution of Eqs. (12) and (16). The case $\Delta J = +1$ was considered in some detail in Ref. 1. For the $\Delta J = 0$ transitions, Eqs. (5) and (6) become

$$\langle \mu_Z \rangle = -(\tfrac{1}{2}i)[(\hbar\omega_3)^{-1}\sigma_3 A_3 + (\hbar\omega_4)^{-1}\sigma_4 A_4] \times [\tfrac{3}{10}(2J-2)(2J-1)(2J+3)(2J+4)]^{1/2} \times f(JK)(J\,1M\,0|J\,1\,JM)\,, \tag{17}$$

where

$$f(JK) \equiv (J\,3K\,2|J\,3\,JK+2) - (J\,3K-2|J\,3\,JK-2)\,. \tag{18}$$

Equations (17) and (18) are the analogs of Eqs. (9) and (10), respectively, in Ref. 1. From the average and sum, respectively, over the initial- and final-state M values of $|\langle\mu_X\rangle|^2 + |\langle\mu_Y\rangle|^2 + |\langle\mu_Z\rangle|^2$, the following transition dipole moment is obtained:

$$\langle \mu_{JK}\rangle^2 = \tfrac{3}{2} C_{34}^2 (2J-2)(2J-1)(2J+1) \times (2J+3)(2J+4)[f(JK)]^2\,, \tag{19}$$

where

$$C_{34}^2 \equiv \tfrac{1}{20}(\sigma_3 A_3/\hbar\omega_3 + \sigma_4 A_4/\hbar\omega_4)^2\,. \tag{20}$$

Equation (19) is the analog of Eq. (11) in Ref. 1.

The definition of the coefficient in Eq. (20) is identical to that in Eq. (12) of Ref. 1. The quantity C_{34} is a function only of molecular parameters, in addition to universal constants. Its magnitude was theoretically estimated[1] to be approximately 4×10^{-6} D for CH_4. A subsequent molecular-beam experiment[3] on CH_4 resulted in a measured magnitude of $(5.38\pm 0.10)\times 10^{-6}$ D. This value compared well with the value 5.8×10^{-6} D inferred[3] from Watson's[2] calculations. In Sec. IV C of the present work, upper limits to the parameter C_{34} for other T_d molecules will be estimated theoretically.

The intensity of an individual absorption line is given by

$$\alpha_{\text{abs}} = (8\pi^3/3hc)(N/\mathfrak{z})(E_f - E_i)\langle\mu_{JK}\rangle^2 \epsilon_{JK} \times (e^{-E_i hc/kT} - e^{-E_f hc/kT})\,, \tag{21}$$

where N is the number of molecules per cm^3, $\mathfrak{z}$ is the partition function, and ϵ_{JK} is the nuclear-spin statistical weight factor. The energies E_i and E_f refer to the initial and final states, respectively, involved in the transition. Equation (21) is the analog of Eq. (13) in Ref. 1. The values of E_i and E_f to be used both in evaluating Eq. (21) and in determining spectral line positions will be considered in detail in Sec. III B, and in Sec. IV for several T_d molecules.

B. Spectral Line Positions

The term values for the energy of the vibronic ground state of a tetrahedral molecule are given, except for additive constants independent of rotational quantum numbers, by[13]

$$E = B_0 J(J+1) - D_s J^2(J+1)^2 - D_t O_{PPPP}(\text{tensor}) + \cdots\,. \tag{22}$$

The coefficients B_0 and D_s are the usual[9] ground-state rotational and centrifugal distortion constants, respectively. The third term in Eq. (22) contains the spherical tensor operator, of fourth rank,[18] which transforms according to the irreducible representation ("rep"[18a]) A_1 of T_d. Its explicit form, as given by Hecht,[13] is

$$O_{PPPP}(\text{tensor}) = 4(J_x^4 + J_y^4 + J_z^4) - 6(J_x^2 J_y^2 + J_y^2 J_x^2 + J_y^2 J_z^2 + J_z^2 J_y^2 + J_z^2 J_x^2 + J_x^2 J_z^2) + 2\vec{J}^2\,. \tag{23}$$

The matrix elements of this operator have been calculated[13] as a function of J and K. There are, in principle, higher-order terms in Eq. (22) such as $H\vec{J}^6$ and a spherical tensor operator of sixth rank[18] in the angular momentum components. The matrix elements of the latter operator have also been calculated[15] as a function of rotational quantum numbers.

In the present calculations of spectral line positions, only the form given explicitly in Eq. (22) will be used. One reason for the neglect of higher-order terms is that it seems from a recent analysis of a high-resolution spectrum of ν_3 of CH_4, that the value of the ground-state constant H is "essentially zero."[19] Of course, a purely J-dependent term in Eq. (22) will not contribute to the spectral line positions for $\Delta J = 0$ in any case. Nevertheless, it may be supposed that the coefficient of the sixth-rank tensor is also essentially zero for the ground vibronic state. If this is not so, as might be demonstrated by an experimental spectrum, then the appropriate calculations may be done to determine an accurate value of this molecular constant. It is possible that for sufficiently high J, the sixth-rank tensor may make a measurable contribution.

In the approximation of Eq. (22), the spectral line positions for the $\Delta J = 0$ transitions in the vibronic ground state are simply given by

$$E(J,\ K \to J,\ K') = -D_t [\langle JK' \,|\, O_{PPPP}(\text{tensor}) \,|\, JK' \rangle - \langle JK \,|\, O_{PPPP}(\text{tensor}) \,|\, JK \rangle]\,. \quad (24)$$

Equation (24) is not the most useful form for calculating the term values, because the T_d molecular symmetry results in considerable degeneracy which is not removed in the absence of an applied external field. More appropriate than Eq. (24) is a form in which matrix elements of the operator are calculated between symmetry-adapted wave functions ("SAF's"[18a]), in this case called "tetrahedral harmonics." These T_d harmonics were calculated by Jahn[18] for $J = 0$–10, and extended by Hecht[13] to $J = 11$, 12, and 13. An explicit, detailed, and convenient algorithm has been developed recently[20,21] for constructing T_d harmonics for arbitrary J.

Hecht[14] calculated the analog of Eq. (24) as a function of D_t, for $J = 0$–8. In the remainder of his calculations for $J = 9$–13, he deduced only numerical values based on a "best value of D_t of 4.5×10^{-6} cm^{-1}." Hecht's choice of molecular parameters was based on an analysis of a spectrum[22] of ν_3 of CH_4. In Table I of the present work, only those transitions which contribute to the $\Delta J = 0$ spectrum will be listed. Some of the results follow directly from Table I of Ref. 14. For the purpose of microwave accuracy, it was necessary to recalculate the results in Table II of Ref. 14 for $J = 9$–13. This work was then extended to $J = 14$–20. The value of the molecular parameter D_t will be discussed in Sec. IV B.

A symmetry selection rule, implicit in Ref. 1, is effective for all transitions, and was applied in Ref. 1 to the $\Delta J = +1$ transitions. The electric-dipole-moment operator is of type A in the molecule-fixed coordinates. It follows, therefore, that the initial- and final-state wave functions, $\Psi(RK_R)$ and $\Psi(R'K_R')$, respectively, must both be of type A, E, or F in order for a transition between these states to be allowed. This selection rule is a necessary, but not sufficient, condition. The selection rule $\Delta K = \pm 2$, as evidenced by Eq. (18), excludes some of the $A \to A$, $E \to E$, and $F \to F$ transitions. Only the transitions which satisfy both selection rules are listed in Table I.

It may appear surprising that the first nonzero entry in Table I occurs for $J = 3$. As can be seen (e.g., in Table I of Ref. 14) $J = 0$ and $J = 1$ each consists of only a single symmetry entry in the ground vibronic state. Moreover, the J values do not satisfy the triangle inequality for quantum vector addition.[5] Although $J = 2$ satisfies the latter condition, it consists of only one entry in each of the symmetry types E and F_2. Therefore, $J = 2 \to 2$ transitions are forbidden in the vibronic ground state.[22a] The first allowed transition is $J = 3 \to 3$, $F_2 \to F_1$.

It should be stressed that, unlike the case of the $\Delta J = +1$ transitions,[1] there is no regular progression of spectral line positions with increasing J. Consequently, to map any portion of the microwave spectrum of any tetrahedral molecule it is necessary to go to sufficiently high J so that all transitions of appreciable strength are included. Table I contains these transitions, as required by the intensity calculations described in Sec. IV A.

IV. MICROWAVE SPECTRUM OF CH_4

A. Absolute Line Intensities

The intensity of an absorption line is given by Eq. (21). The energies E_i and E_f of the initial and final states, respectively, are determined from Eq. (24), with the matrix elements evaluated using tetrahedral harmonics.[13,18,20,21] Transition dipole moments between states of appropriate T_d symmetry, as shown in Table I, are calculated from Eqs. (18)–(20). It should be stressed that Eqs. (21) and (24), and the spectral line positions in units of D_t in Table I, are universal expressions for all tetrahedral molecules. The intensities for CH_4 are obtained by selecting appropriate values for the parameters D_t, C_{34}, and ϵ_{JK}, and for the partition function $\mathfrak{z}$.

For CH_4, the value of D_t is taken to be 4.403×10^{-6} cm^{-1}. This choice will be discussed in Sec. IV B. The measured value[3] of $C_{34} = 5.38 \times 10^{-6}$ D is used. The nuclear-spin statistical weight factor ϵ_{JK} takes the values 5, 2, and 3 for T_d harmonics belonging to the reps A_1 (or A_2), E, and F_1 (or F_2), respectively.[9,23] The rotational partition function $\mathfrak{z}_r$, a good approximation to $\mathfrak{z}$ for temperatures $T \lesssim 300\,^\circ$K, may be written[24]

$$\mathfrak{z}_r = \tfrac{4}{3}\pi^{1/2}(B_0 hc/kT)^{-3/2} e^{B_0 hc/4kT}\,, \quad (25)$$

which is accurate to 1% for $T > 40\,^\circ$K, for CH_4. The value[19] of B_0 used in Eq. (25) is 5.24 cm^{-1}.

The absolute line intensities for CH_4 have been

TABLE I. Spectral line positions, in units of the molecular parameter D_t [defined by Eqs. (22) and (23)], for pure rotational transitions $J \longleftrightarrow J$ from the vibronic ground state of tetrahedral molecules.

Transition^{a}	Position	Transition^{a}	Position	Transition^{a}	Position	Transition^{a}	Position
$0\longleftrightarrow 0$	none^{b}	$12\longleftrightarrow 12$		$16\longleftrightarrow 16$		$19\longleftrightarrow 19$	
$1\longleftrightarrow 1$	none^{b}	$A1(1)\longleftrightarrow A2$	101724	$A1(1)\longleftrightarrow A2$	240234	$A1(1)\longleftrightarrow A2$	328169
$2\longleftrightarrow 2$	none^{b}	$A2\longleftrightarrow A1(2)$	12683.6	$A2\longleftrightarrow A1(2)$	67671.7	$A2\longleftrightarrow A1(2)$	77845.7
$3\longleftrightarrow 3$		$E(1)\longleftrightarrow E(2)$	79570.2	$E(1)\longleftrightarrow E(2)$	222538	$E(1)\longleftrightarrow E(2)$	283574
$F2\longleftrightarrow F1$	240.000	$F1(1)\longleftrightarrow F2(1)$	50590.1	$E(1)\longleftrightarrow E(3)$	364600	$E(1)\longleftrightarrow E(3)$	511988
$4\longleftrightarrow 4$		$F1(1)\longleftrightarrow F2(2)$	83171.3	$E(2)\longleftrightarrow E(3)$	142062	$E(2)\longleftrightarrow E(3)$	228414
$F1\longleftrightarrow F2$	1200.00	$F1(2)\longleftrightarrow F2(2)$	28614.4	$F1(1)\longleftrightarrow F2(1)$	133234	$F2(1)\longleftrightarrow F1(1)$	46.824
$5\longleftrightarrow 5$		$F1(2)\longleftrightarrow F2(3)$	53048.6	$F1(1)\longleftrightarrow F2(2)$	281549	$F1(1)\longleftrightarrow F2(2)$	403023
$F2(1)\longleftrightarrow F1$	809.727	$F2(3)\longleftrightarrow F1(3)$	3604.26	$F1(2)\longleftrightarrow F2(2)$	91868.2	$F1(2)\longleftrightarrow F2(2)$	170539
$F1\longleftrightarrow F2(2)$	2489.73	$13\longleftrightarrow 13$		$F1(2)\longleftrightarrow F2(3)$	146307	$F1(2)\longleftrightarrow F2(3)$	293538
$6\longleftrightarrow 6$		$A2\longleftrightarrow A1$	53759.5	$F2(3)\longleftrightarrow F1(3)$	12527.1	$F1(3)\longleftrightarrow F2(3)$	115778
$A2\longleftrightarrow A1$	5760.00	$E(1)\longleftrightarrow E(2)$	86145.2	$F1(3)\longleftrightarrow F2(4)$	75067.9	$F1(3)\longleftrightarrow F2(4)$	193118
$F2(1)\longleftrightarrow F1$	5942.19	$F2(1)\longleftrightarrow F1(1)$	324.034	$F1(4)\longleftrightarrow F2(4)$	9186.38	$F2(4)\longleftrightarrow F1(4)$	17985.3
$F2(2)\longleftrightarrow F1$	1017.81	$F1(1)\longleftrightarrow F2(2)$	68108.2	$17\longleftrightarrow 17$		$F1(4)\longleftrightarrow F2(5)$	127938
$7\longleftrightarrow 7$		$F2(2)\longleftrightarrow F1(2)$	46336.0	$A2\longleftrightarrow A1$	172801	$F1(5)\longleftrightarrow F2(5)$	8910.70
$F2(1)\longleftrightarrow F1(1)$	802.531	$F2(3)\longleftrightarrow F1(2)$	7299.62	$E(1)\longleftrightarrow E(2)$	207402	$20\longleftrightarrow 20$	
$F1(1)\longleftrightarrow F2(2)$	11842.5	$F2(3)\longleftrightarrow F1(3)$	41429.4	$E(1)\longleftrightarrow E(3)$	307605	$A1(1)\longleftrightarrow A2$	488364
$F1(2)\longleftrightarrow F2(2)$	3202.53	$F1(3)\longleftrightarrow F2(4)$	8147.77	$E(2)\longleftrightarrow E(3)$	100203	$A2\longleftrightarrow A1(2)$	209239
$8\longleftrightarrow 8$		$14\longleftrightarrow 14$		$F2(1)\longleftrightarrow F1(1)$	97.594	$E(1)\longleftrightarrow E(2)$	479377
$E(1)\longleftrightarrow E(2)$	19499.2	$A2\longleftrightarrow A1$	134400	$F1(1)\longleftrightarrow F2(2)$	163019	$E(1)\longleftrightarrow E(3)$	759212
$F1(1)\longleftrightarrow F2(1)$	11903.1	$E(1)\longleftrightarrow E(2)$	149588	$F2(2)\longleftrightarrow F1(2)$	120913	$E(1)\longleftrightarrow E(4)$	921552
$F1(1)\longleftrightarrow F2(2)$	21060.9	$E(1)\longleftrightarrow E(3)$	209597	$F2(3)\longleftrightarrow F1(2)$	8530.87	$E(2)\longleftrightarrow E(3)$	279835
$F1(2)\longleftrightarrow F2(2)$	4896.93	$E(2)\longleftrightarrow E(3)$	60008.4	$F2(3)\longleftrightarrow F1(3)$	82894.6	$E(2)\longleftrightarrow E(4)$	442175
$9\longleftrightarrow 9$		$F2(1)\longleftrightarrow F1(1)$	88521.8	$F1(3)\longleftrightarrow F2(4)$	34806.6	$E(3)\longleftrightarrow E(4)$	162340
$A2\longleftrightarrow A1$	9599.91	$F2(2)\longleftrightarrow F1(1)$	2812.76	$F2(4)\longleftrightarrow F1(4)$	71286.7	$F1(1)\longleftrightarrow F2(1)$	273231
$F2(1)\longleftrightarrow F1(1)$	756.303	$F2(2)\longleftrightarrow F1(2)$	58012.4	$F1(4)\longleftrightarrow F2(5)$	9331.71	$F1(1)\longleftrightarrow F2(2)$	482183
$F1(1)\longleftrightarrow F2(2)$	19435.1	$F1(2)\longleftrightarrow F2(3)$	26096.1	$18\longleftrightarrow 18$		$F1(2)\longleftrightarrow F2(2)$	208253
$F2(2)\longleftrightarrow F1(2)$	13581.3	$F2(3)\longleftrightarrow F1(3)$	33977.2	$A2(1)\longleftrightarrow A1(1)$	331651	$F1(2)\longleftrightarrow F2(3)$	347912
$F2(3)\longleftrightarrow F1(2)$	2290.85	$F1(3)\longleftrightarrow F2(4)$	8941.57	$A2(1)\longleftrightarrow A1(2)$	601483	$F2(3)\longleftrightarrow F1(3)$	18536.7
$10\longleftrightarrow 10$		$15\longleftrightarrow 15$		$A1(1)\longleftrightarrow A2(2)$	255885	$F1(3)\longleftrightarrow F2(4)$	144355
$A2\longleftrightarrow A1$	38400.0	$A1(1)\longleftrightarrow A2$	163705	$A2(2)\longleftrightarrow A1(2)$	13947.2	$F1(4)\longleftrightarrow F2(4)$	43213.2
$E(1)\longleftrightarrow E(2)$	50436.6	$A2\longleftrightarrow A1(2)$	14187.8	$E(1)\longleftrightarrow E(2)$	343425	$F1(4)\longleftrightarrow F2(5)$	183923
$F2(1)\longleftrightarrow F1(1)$	30178.0	$E(1)\longleftrightarrow E(2)$	110301	$E(1)\longleftrightarrow E(3)$	489466	$F1(5)\longleftrightarrow F2(5)$	8268.54
$F2(2)\longleftrightarrow F1(1)$	3216.58	$F2(1)\longleftrightarrow F1(1)$	180.599	$E(2)\longleftrightarrow E(3)$	146042		
$F2(2)\longleftrightarrow F1(2)$	20398.1	$F1(1)\longleftrightarrow F2(2)$	176603	$F2(1)\longleftrightarrow F1(1)$	196361		
$F1(2)\longleftrightarrow F2(3)$	5865.55	$F1(2)\longleftrightarrow F2(2)$	67729.6	$F2(2)\longleftrightarrow F1(1)$	1210.55		
$11\longleftrightarrow 11$		$F1(2)\longleftrightarrow F2(3)$	117832	$F2(2)\longleftrightarrow F1(2)$	143938		
$E(1)\longleftrightarrow E(2)$	35076.9	$F1(3)\longleftrightarrow F2(3)$	37670.6	$F1(2)\longleftrightarrow F2(3)$	84421.4		
$F2(1)\longleftrightarrow F1(1)$	518.655	$F1(3)\longleftrightarrow F2(4)$	87431.4	$F2(3)\longleftrightarrow F1(3)$	30334.0		
$F1(1)\longleftrightarrow F2(2)$	57359.9	$F2(4)\longleftrightarrow F1(4)$	4417.22	$F1(3)\longleftrightarrow F2(4)$	45532.3		
$F1(2)\longleftrightarrow F2(2)$	18398.0			$F2(4)\longleftrightarrow F1(4)$	98269.0		
$F1(2)\longleftrightarrow F2(3)$	39386.7			$F2(5)\longleftrightarrow F1(4)$	4528.51		
$F1(3)\longleftrightarrow F2(3)$	7320.51						

[a] For convenience in tabulation, $F2(1)$ denotes $F_2^{(1)}$, etc. (see Refs. 7, 8, 13, and 14).

[b] Forbidden by symmetry. Also, $0\longleftrightarrow 0$ and $1\longleftrightarrow 1$ are forbidden by the triangle inequality for quantum vector addition [see Ref. 5, and Eqs. (17) and (18) in the present work].

evaluated for $T = 0\ ^\circ\mathrm{C}$, with N in Eq. (21) replaced by $N_0 p$, where N_0 is Loschmidt's number, and p is the pressure in amagats. (The number of amagats of a gas equals the ratio of its density to that at STP.) The quantities $\alpha_{\mathrm{abs}} p^{-1}$ are given in Table II. In comparison with the calculated intensities for the $\Delta J = +1$ transitions[1] in CH_4, the transitions in the microwave for $\Delta J = 0$ are substantially weaker.

For the far-infrared $\Delta J = +1$ transitions, the absolute line intensities are greatest[1,2] in the neighborhood of $J \approx 10$. As is apparent from Table II, the strongest lines occur in the range $J = 12$–18 for the microwave $\Delta J = 0$ transitions. The decrease in intensity for these transitions is comparatively slow with increasing J. The reason for this is that the strong J dependence of the transition dipole moment in Eq. (19) is only mildly offset by the

Boltzmann factors in Eq. (21).

B. Spectral Line Positions

The crucial parameter for determining spectral line positions is the molecular constant D_t in Eqs. (22) and (24). For the purpose of detecting the predicted spectral lines in the microwave region, it is important to know D_t accurately. A theoretical expression for D_t has been deduced by Hecht[14]: It is

$$D_t = (\tfrac{1}{5}B_0^3)(\omega_2^{-2} - \zeta_{23}^2\omega_3^{-2} - \zeta_{24}^2\omega_4^{-2}) . \qquad (26)$$

The molecular parameters in Eq. (26) have already been discussed in Sec. II A. An intrinsic limitation to the theoretical expression for D_t is that it was deduced on the basis of a theory which is valid only to third order in perturbation theory.[13] Nevertheless, Eq. (26) is useful, especially for obtaining a good estimate of D_t. From the values of B_0 and the ζ's and ω's known in 1960, Hecht[14] found $D_t = 4.0 \times 10^{-6}$ cm^{-1} from Eq. (26) compared with a "best value of D_t of 4.5×10^{-6} cm^{-1}" based on his analysis of an infrared spectrum[22] of ν_3 of CH_4. Over a decade later, the most accurately known values of the molecular parameters in Eq. (26), derived from high-resolution infrared spectra,[19,25–27] yield $D_t = (4.0142 \pm 0.004) \times 10^{-6}$ cm^{-1} from Eq. (26).

However, three accurate values of D_t have been determined recently directly from experimental data. In two instances,[19,25] the contribution of $D_t O_{PPPP}$(tensor) [see Eqs. (22) and (23)] to the line positions in high-resolution infrared spectra[19,28] of ν_3 of CH_4 has been calculated. In Ref. 19, $D_t = (4.453 \pm 0.038) \times 10^{-6}$ cm^{-1}; in Ref. 25, $D_t = (4.353 \pm 0.061) \times 10^{-6}$ cm^{-1}. In the third instance, an analysis of ortho-para transitions[4] in CH_4, observed by the molecular-beam magnetic-resonance method,[29] yielded[30] $D_t = 132.0$ kHz ($\equiv 4.403 \times 10^{-6}$ cm^{-1}). For the purpose of calculating microwave spectral line positions, the mean value $D_t = 4.403 \times 10^{-6}$ cm^{-1} will be adopted. The calculated frequencies may be expected to be accurate to four significant figures.

When a more accurate value of D_t becomes available, the spectral line positions in Table II can be recalculated from the more fundamental quantities in Table I.

C. Other Tetrahedral Molecules

Although CH_4 is the most intensively and thoroughly studied of all tetrahedral molecules, it is of interest to consider the theory discussed here for other T_d molecules such as SiH_4, GeH_4, $^{13}CH_4$, CD_4, CF_4, and CCl_4. The results in Sec. III apply to all T_d with the appropriate choice of parameters.

The expression for C_{34}^2 in Eq. (20) can be conveniently rewritten in the form[1]

$$C_{34}^2 = \tfrac{1}{10}B_0^3(\zeta_{23}A_3\,\omega_3^{-3/2} + \zeta_{24}A_4\,\omega_4^{-3/2})^2 . \qquad (27)$$

The relative sign of the $\zeta_{2i}A_i\omega_i^{-3/2}$ terms is important because these two terms are roughly equal. From the definition of the ζ_{2i}, as functions of masses and force constants,[10] it follows that $\zeta_{23}\zeta_{24} < 0$. In the case of CH_4, it has also been inferred[31–34] from low-resolution infrared spectra and several calculations that $A_3A_4 < 0$. It appears that the latter result may not hold generally for all T_d molecules, so that even an order-of-magnitude estimate of C_{34} may be precluded.

However, a useful upper limit to C_{34} may be obtained by assuming that the $\zeta_{2i}A_i\omega_i^{-3/2}$ terms in Eq. (27) have the same sign. In this case, the following approximate upper limits to C_{34} have been estimated for SiH_4, GeH_4, $^{13}CH_4$, CD_4, CCl_4, and CF_4, respectively, in units of 10^{-6} D: 8, 8, 4, 2, 0.1, and 0.1.

The appropriate partition function $\mathfrak{z} \approx \mathfrak{z}_r$ to be used in Eq. (21) has the form of Eq. (25), with two required modifications. First, obviously, the value of the ground-state rotational constant B_0 appropriate to the molecule under consideration must be used. And second, for tetrahdral XY_4 molecules with nuclear spin $I_Y = 1$ (as in CD_4) and $I_Y = \frac{3}{2}$ (as in CCl_4), the coefficient $\frac{4}{3}$ in Eq. (25) becomes[24] $\frac{27}{4}$ and $\frac{64}{3}$, respectively. Furthermore, the nuclear-spin statistical weight factor ϵ_{JK} in Eq. (21) takes the values {15, 12, 18} and {36, 40, 60} for T_d harmonics belonging to the reps {A_1 or A_2, E, F_1 or F_2} for $I_Y = 1$ and $I_Y = \frac{3}{2}$, respectively.[9,23,35]

The last and most delicate factor affecting especially the spectral line positions, as well as the absolute line intensities, is the molecular parameter D_t. This has been determined from analyses of high-resolution infrared spectra only for[7,36] CD_4 and $^{13}CH_4$,[37] in addition to $^{12}CH_4$ as discussed in Sec. IV B. The values are 1.1×10^{-6} cm^{-1} and 4.7×10^{-6} cm^{-1}, respectively, for CD_4 and $^{13}CH_4$. The nature of microwave spectroscopy probably requires more accurate values of D_t than can be determined from Eq. (26) at present. Analysis of high-resolution infrared spectra of various T_d molecules may yield molecular constants of sufficient precision to make estimates of D_t from Eq. (26) more useful. Alternatively, molecular-beam magnetic-resonance experiments, such as those already carried out[3,4] for $^{12}CH_4$, may yield more precise values of D_t. In any event, it was considered worthwhile for the present to estimate D_t from Eq. (26) for several T_d molecules. The results for SiH_4, GeH_4, $^{13}CH_4$, CD_4, CCl_4, and CF_4, respectively are as follows: 2.3, 2.2, 4.0, 1.3 (in units of 10^{-6} cm^{-1}), and 2.8, 4.8 (in units of 10^{-9} cm^{-1}). For the first four molecules of this series, the values of D_t are of the same order-of-magnitude as that for $^{12}CH_4$. In contrast, D_t for CCl_4 and CF_4 is three orders-of-magnitude smaller. This suggests that the lines of the microwave spectra of these two molecules will be much more closely spaced, and lie at much lower frequencies than those for CH_4.

V. DISCUSSION

A. Possible Competing Transitions

In addition to the usual difficulty in measuring extremely weak microwave transitions, it is also possible that competing transitions would mask the predicted ones. Several effects which might compete with the $\Delta J = +1$ transitions were considered briefly in Ref. 1. It appears, as for $\Delta J = +1$, that pure $\Delta J = 0$ rotational transitions from excited vibrational states[38–40] will also offer the most serious competition in the present context. This effect will be discussed in some detail below and in future work.[40] Other possible competing effects which will be considered here are "hot-band" transitions and collision-induced absorption.

TABLE II. Spectral line positions and absolute line intensities for pure-rotational transitions $J \longleftrightarrow J$ from the vibronic ground state of CH_4. The molecular parameter $D_t = 4.403 \times 10^{-6}$ cm^{-1} [see Eqs. (22) and (24), and Sec. IV B]. The transition dipole moment $C_{34} = 5.38 \times 10^{-6}$ D [as measured in Ref. 3; see Eqs. (19) and (20) in the present work].

Transition[a]	Spectral position (MHz)[b]	Absolute intensity (cm^{-2} amagat^{-1})[c]
$0 \longleftrightarrow 0$	none[d]	
$1 \longleftrightarrow 1$	none[d]	
$2 \longleftrightarrow 2$	none[d]	
$3 \longleftrightarrow 3$		
$F2 \longleftrightarrow F1$	31.6797	5.01(−17)
$4 \longleftrightarrow 4$		
$F1 \longleftrightarrow F2$	158.398	3.24(−15)
$5 \longleftrightarrow 5$		
$F2(1) \longleftrightarrow F1$	106.883	1.52(−15)
$F1 \longleftrightarrow F2(2)$	328.641	3.33(−14)
$6 \longleftrightarrow 6$		
$A2 \longleftrightarrow A1$	760.312	8.56(−13)
$F2(1) \longleftrightarrow F1$	784.361	2.88(−13)
$F2(2) \longleftrightarrow F1$	134.350	5.73(−15)
$7 \longleftrightarrow 7$		
$F2(1) \longleftrightarrow F1(1)$	105.933	1.92(−15)
$F1(1) \longleftrightarrow F2(2)$	1563.19	1.37(−12)
$F1(2) \longleftrightarrow F2(2)$	422.730	1.18(−13)
$8 \longleftrightarrow 8$		
$E(1) \longleftrightarrow E(2)$	2573.87	8.51(−13)
$F1(1) \longleftrightarrow F2(1)$	1571.19	1.41(−12)
$F1(1) \longleftrightarrow F2(2)$	2780.01	6.78(−12)
$F1(2) \longleftrightarrow F2(2)$	646.388	1.57(−13)
$9 \longleftrightarrow 9$		
$A2 \longleftrightarrow A1$	1267.17	5.21(−12)
$F2(1) \longleftrightarrow F1(1)$	99.8310	1.38(−15)
$F1(1) \longleftrightarrow F2(2)$	2565.41	3.40(−12)
$F2(2) \longleftrightarrow F1(2)$	1792.71	2.94(−12)
$F2(3) \longleftrightarrow F1(2)$	302.389	6.39(−14)
$10 \longleftrightarrow 10$		
$A2 \longleftrightarrow A1$	5068.75	1.76(−11)
$E(1) \longleftrightarrow E(2)$	6657.56	6.13(−13)
$F2(1) \longleftrightarrow F1(1)$	3983.45	6.65(−12)
$F2(2) \longleftrightarrow F1(1)$	424.584	1.47(−13)
$F2(2) \longleftrightarrow F1(2)$	2692.52	5.95(−12)
$F1(2) \longleftrightarrow F2(3)$	774.245	1.68(−13)
$11 \longleftrightarrow 11$		
$E(1) \longleftrightarrow E(2)$	4630.10	2.33(−11)
$F2(1) \longleftrightarrow F1(1)$	68.4617	3.66(−16)
$F1(1) \longleftrightarrow F2(2)$	7571.43	1.77(−11)
$F1(2) \longleftrightarrow F2(2)$	2428.51	3.84(−12)
$F1(2) \longleftrightarrow F2(3)$	5198.99	2.06(−11)
$F1(3) \longleftrightarrow F2(3)$	966.297	4.34(−13)
$12 \longleftrightarrow 12$		
$A1(1) \longleftrightarrow A2$	13427.4	4.16(−10)
$A2 \longleftrightarrow A1(2)$	1674.22	6.08(−13)
$E(1) \longleftrightarrow E(2)$	10503.2	1.16(−11)
$F1(1) \longleftrightarrow F2(1)$	6677.82	9.40(−12)
$F1(1) \longleftrightarrow F2(2)$	10978.5	5.60(−11)
$F1(2) \longleftrightarrow F2(2)$	3777.06	8.64(−12)
$F1(2) \longleftrightarrow F2(3)$	7002.34	2.39(−11)
$F2(3) \longleftrightarrow F1(3)$	475.757	3.27(−14)
$13 \longleftrightarrow 13$		
$A2 \longleftrightarrow A1$	7096.18	2.78(−11)
$E(1) \longleftrightarrow E(2)$	11371.0	9.90(−12)
$F2(1) \longleftrightarrow F1(1)$	42.7720	5.90(−17)
$F1(1) \longleftrightarrow F2(2)$	8990.19	1.07(−11)
$F2(2) \longleftrightarrow F1(2)$	6116.29	1.13(−11)
$F2(3) \longleftrightarrow F1(2)$	963.540	3.95(−13)
$F2(3) \longleftrightarrow F1(3)$	5468.62	1.20(−11)
$F1(3) \longleftrightarrow F2(4)$	1075.49	2.47(−13)
$14 \longleftrightarrow 14$		
$A2 \longleftrightarrow A1$	17740.6	3.04(−11)
$E(1) \longleftrightarrow E(2)$	19745.4	8.93(−11)
$E(1) \longleftrightarrow E(3)$	27666.5	1.75(−10)
$E(2) \longleftrightarrow E(3)$	7921.03	1.44(−11)
$F2(1) \longleftrightarrow F1(1)$	11684.8	2.44(−11)
$F2(2) \longleftrightarrow F1(1)$	371.280	2.45(−14)
$F2(2) \longleftrightarrow F1(2)$	7657.56	1.04(−11)
$F1(2) \longleftrightarrow F2(3)$	3444.65	2.11(−12)
$F2(3) \longleftrightarrow F1(3)$	4484.94	3.58(−12)
$F1(3) \longleftrightarrow F2(4)$	1180.27	2.48(−13)
$15 \longleftrightarrow 15$		
$A1(1) \longleftrightarrow A2$	21608.8	1.88(−10)
$A2 \longleftrightarrow A1(2)$	1872.77	1.41(−12)
$E(1) \longleftrightarrow E(2)$	14559.6	3.05(−11)
$F2(1) \longleftrightarrow F1(1)$	23.8388	5.77(−17)
$F1(1) \longleftrightarrow F2(2)$	23311.4	5.51(−11)
$F1(2) \longleftrightarrow F2(2)$	8940.51	8.11(−12)
$F1(2) \longleftrightarrow F2(3)$	15553.7	2.45(−11)
$F1(3) \longleftrightarrow F2(3)$	4972.47	2.50(−12)
$F1(3) \longleftrightarrow F2(4)$	11540.8	1.35(−11)
$F2(4) \longleftrightarrow F1(4)$	583.067	3.44(−14)

TABLE II. (*Continued*)

Transition[a]	Spectral position (MHz)[b]	Absolute intensity (cm^{-2} $amagat^{-1}$)[c]
$16 \leftrightarrow 16$		
$A1(1) \leftrightarrow A2$	31710.6	9.48(−11)
$A2 \leftrightarrow A1(2)$	8932.57	7.52(−12)
$E(1) \leftrightarrow E(2)$	29374.7	6.15(−11)
$E(1) \leftrightarrow E(3)$	48126.7	1.65(−10)
$E(2) \leftrightarrow E(3)$	18752.0	2.50(−11)
$F1(1) \leftrightarrow F2(1)$	17586.7	1.90(−11)
$F1(1) \leftrightarrow F2(2)$	37164.1	8.46(−11)
$F1(2) \leftrightarrow F2(2)$	12126.5	9.01(−12)
$F1(2) \leftrightarrow F2(3)$	19312.3	2.28(−11)
$F2(3) \leftrightarrow F1(3)$	1653.56	1.67(−13)
$F1(3) \leftrightarrow F2(4)$	9908.86	6.02(−12)
$F1(4) \leftrightarrow F2(4)$	1212.58	9.01(−14)
$17 \leftrightarrow 17$		
$A2 \leftrightarrow A1$	22809.5	1.74(−11)
$E(1) \leftrightarrow E(2)$	27376.8	3.68(−11)
$E(1) \leftrightarrow E(3)$	40603.4	8.09(−11)
$E(2) \leftrightarrow E(3)$	13226.7	8.59(−12)
$F2(1) \leftrightarrow F1(1)$	12.882	5.04(−18)
$F1(1) \leftrightarrow F2(2)$	21518.3	1.41(−11)
$F2(2) \leftrightarrow F1(2)$	15960.4	7.75(−12)
$F2(3) \leftrightarrow F1(2)$	1126.06	3.86(−14)
$F2(3) \leftrightarrow F1(3)$	10942.0	3.64(−12)
$F1(3) \leftrightarrow F2(4)$	4594.42	6.42(−13)
$F2(4) \leftrightarrow F1(4)$	9409.74	2.69(−12)
$F1(4) \leftrightarrow F2(5)$	1231.77	4.61(−14)
$18 \leftrightarrow 18$		
$A2(1) \leftrightarrow A1(1)$	43777.5	6.42(−11)
$A2(1) \leftrightarrow A1(2)$	79394.9	2.11(−10)
$A1(1) \leftrightarrow A2(2)$	33776.5	3.82(−11)
$A2(2) \leftrightarrow A1(2)$	1841.01	1.13(−13)
$E(1) \leftrightarrow E(2)$	45331.6	2.17(−11)
$E(1) \leftrightarrow E(3)$	64608.8	4.41(−11)
$E(2) \leftrightarrow E(3)$	19277.3	3.93(−12)
$F2(1) \leftrightarrow F1(1)$	25919.4	1.06(−11)
$F2(2) \leftrightarrow F1(1)$	159.791	4.05(−16)
$F2(2) \leftrightarrow F1(2)$	18999.6	5.73(−12)
$F1(2) \leftrightarrow F2(3)$	11143.5	1.96(−12)
$F2(3) \leftrightarrow F1(3)$	4004.05	2.54(−13)
$F1(3) \leftrightarrow F2(4)$	6010.20	5.74(−13)
$F2(4) \leftrightarrow F1(4)$	12971.4	2.67(−12)
$F2(5) \leftrightarrow F1(4)$	597.757	5.67(−15)
$19 \leftrightarrow 19$		
$A1(1) \leftrightarrow A2$	43317.9	2.70(−11)
$A2 \leftrightarrow A1(2)$	10275.5	1.52(−12)
$E(1) \leftrightarrow E(2)$	37431.4	1.39(−11)
$E(1) \leftrightarrow E(3)$	67581.7	4.52(−11)
$E(2) \leftrightarrow E(3)$	30150.3	9.00(−12)
$F2(1) \leftrightarrow F1(1)$	6.181	2.64(−19)
$F1(1) \leftrightarrow F2(2)$	53198.5	1.96(−11)
$F1(2) \leftrightarrow F2(2)$	22510.9	3.50(−12)
$F1(2) \leftrightarrow F2(3)$	38746.6	1.03(−11)
$F1(3) \leftrightarrow F2(3)$	15282.5	1.61(−12)
$F1(3) \leftrightarrow F2(4)$	25491.3	4.49(−12)
$F2(4) \leftrightarrow F1(4)$	2374.04	3.86(−14)
$F1(4) \leftrightarrow F2(5)$	16887.6	1.97(−12)
$F1(5) \leftrightarrow F2(5)$	1176.20	9.58(−15)
$20 \leftrightarrow 20$		
$A1(1) \leftrightarrow A2$	64463.4	1.12(−11)
$A2 \leftrightarrow A1(2)$	27619.3	2.07(−12)
$E(1) \leftrightarrow E(2)$	63277.1	1.10(−11)
$E(1) \leftrightarrow E(3)$	100215.	2.77(−11)
$E(1) \leftrightarrow E(4)$	121644.	4.07(−11)
$E(2) \leftrightarrow E(3)$	36937.8	3.76(−12)
$E(2) \leftrightarrow E(4)$	58366.5	9.39(−12)
$E(3) \leftrightarrow E(4)$	21428.7	1.26(−12)
$F1(1) \leftrightarrow F2(1)$	36066.1	4.07(−12)
$F1(1) \leftrightarrow F2(2)$	63647.5	1.27(−11)
$F1(2) \leftrightarrow F2(2)$	27489.1	2.37(−12)
$F1(2) \leftrightarrow F2(3)$	45923.9	6.60(−12)
$F2(3) \leftrightarrow F1(3)$	2446.82	1.87(−14)
$F1(3) \leftrightarrow F2(4)$	19054.7	1.13(−12)
$F1(4) \leftrightarrow F2(4)$	5704.08	1.01(−13)
$F1(4) \leftrightarrow F2(5)$	24277.6	1.85(−12)
$F1(5) \leftrightarrow F2(5)$	1138.96	4.06(−15)

[a] For convenience in tabulation, $F2(1)$ denotes $F_2^{(1)}$, etc. (see Refs. 7, 8, 13, and 14).

[b] See Ref. 30.

[c] Powers of 10 are indicated in parentheses, e.g., $5.01(-17) \equiv 5.01 \times 10^{-17}$.

[d] Forbidden by symmetry. Also, $0 \leftrightarrow 0$ and $1 \leftrightarrow 1$ are forbidden by the triangle inequality for quantum vector addition [see Ref. 5, and Eqs. (17) and (18) in the present work].

1. Mizushima-Venkateswarlu Transitions

Pure rotational transitions arising from excited vibrational, but ground electronic, states of conventionally nonpolar molecules with D_{2d} or T_d symmetry were first postulated theoretically by Mizushima and Venkateswarlu[38] (MV). Their ideas were later extended by Mills *et al.*[39] to molecules of other symmetries. In 1968, two rotational spectral lines of allene C_3H_4 arising from the MV effect were reported.[41] However, shortly afterward serious questions were raised[42,43] about the interpretation of the observed effect, leaving the outcome in doubt. More recently, a partial confirmation of the MV theory for T_d molecules has been reported[44-46] in the form of measurements of vibrationally induced polar character in one of the triply degenerate states of CH_4, CCl_4, CF_4, and $SiCl_4$. The work[44,45] on CH_4 utilized Stark effect measurements achieved with laser absorption, and yielded[45]

0.0200 ± 0.0001 D for the dipole moment in the ν_3 vibrational state. The polar behavior of the other T_d molecules was observed[46] using a technique of electric deflection in a molecular beam. The interpretation of these results was confirmed by the dependence of the polar behavior on temperature, and on isotopic substitution of the chlorine atoms in the case of CCl_4. However, corresponding absorption spectra for T_d molecules have not yet been reported.

Sufficient details of the absorption spectra based on $\Delta J = 0$ MV transitions will be presented here to exhibit the essential features of these competing transitions. Complete results will be presented elsewhere.[40] Referring to Eqs. (3) and (4), it is apparent that the quantum-mechanical expectation value of μ_Z will be nonzero only for the triply degenerate vibrational states ν_3 and ν_4 of T_d molecules. The basic results of Ref. 38 will be developed briefly in the notation used here earlier.

For the ν_3 state (the following results are easily generalized to the ν_4 state also), the analog of Eq. (5) is

$$\langle \mu_Z \rangle \equiv \int \psi^*(\nu_3;\, R'K_R')\, \mu_Z \psi(\nu_3;\, RK_R)\, d\tau_3 \; d\Omega, \tag{28}$$

where the wave functions and quantum numbers are the same as defined in Sec. II A. From the computational techniques developed in Refs. 7, 8, 13, and 14 the analog of Eq. (19) can be shown to be

$$\langle \mu \rangle^2 = \tfrac{105}{4} (A_3')^2 \, (2J'+1)^2 \, (2R+1) \begin{Bmatrix} 1 & 1 & 2 \\ J' & J & 1 \\ R' & R & 3 \end{Bmatrix}^2 \times [f(RK_R)]^2 , \tag{29}$$

where

$$f(RK_R) \equiv (R\,3\,K_R\,2\,|\,R\,3\,R'\,K_R') - (R\,3\,K_R - 2\,|\,R\,3\,R'\,K_R') \tag{30}$$

is the analog of Eq. (18). The 9-*j* symbol,[5] arising from Racah algebra, appears in Eq. (29). The basic molecular parameter in the MV transition dipole moment in Eq. (29) is $A_3' \equiv (\partial^2 \mu_z / \partial x_3 \partial y_3)_0$. This same parameter determines the strength of absorption in the infrared-active overtone $2\nu_3$ of T_d molecules.[7,8] Consequently, a rough estimate of the relative magnitudes of $\langle \mu \rangle^2$ and $\langle \mu_{JK} \rangle^2$ can be made. However, the different J dependence is important, as is the strong temperature-dependence of the MV effect. These will be discussed briefly below.

Selection rules may be inferred directly from Eqs. (29) and (30). From the properties of 9-*j* symbols,[5] it follows that $R' = R$, $R \pm 1$, $R \pm 2$, $R \pm 3$, subject to $R' + R \geqslant 3$; and $J' = J$, $J \pm 1$, subject to $J' + J \geqslant 1$. In addition, from Eq. (30), $K_R' = K_R \pm 2$. Also, as discussed in Sec. III B, both the initial- and final-state wave functions must be of type A, E, or F. The intensity of an individual absorption line is given by

$$\alpha_{\text{abs}}' = (8\pi^3 / 3hc)\, (N/\mathcal{V})\, (E_f - E_i) \times \langle \mu \rangle^2 \epsilon \left(e^{-E_i hc/kT} - e^{-E_f hc/kT}\right) , \tag{31}$$

where the quantities in this equation have similar meanings as in the analogous Eq. (21).

Of the allowed MV transitions, those which lie in the microwave spectral region arise from $\Delta J = 0$ and primarily $\Delta R = 0$: $J_R \to J'_{R'} \equiv J_R$. In this case, the term values are determined mainly by $-D_t O_{PPPP}$ (tensor) + $Z_{3t} O_{PP33}$ (tensor), where the explicit form of the second operator is given in Ref. 13. The latter operator occurs, in principle, in Eq. (22) as well. However, its contribution to Eq. (24) is negligible because of the small coefficient of the corresponding wave function $\psi(2\nu_3;\, R''K_R'')$ required in Eq. (1).[7,8] The magnitude of the molecular parameter Z_{3t} has been found[14,19,25] to be about six hundred times that of D_t for CH_4. Thus, O_{PP33} (tensor) will dominate the run of spectral line positions for the MV microwave transitions until the higher J dependence of O_{PPPP}(tensor) becomes more effective. This may occur near $5 \times 10^{-6} J^4 \approx 3 \times 10^{-3} J^2$, i.e., at $J \sim 25$.

A comparison of the absolute line intensities from Eqs. (21) and (31) yields, for transitions at comparable spectral positions,[40]

$$\alpha_{\text{abs}}' / \alpha_{\text{abs}} \approx [(A_3')^2 / 5C_{34}^2]\, [(2J)\,(2J+2)]^{-2}\, e^{-\omega_3 hc/kT} . \tag{32}$$

A rough estimate indicates that $\alpha_{\text{abs}}' \approx \alpha_{\text{abs}} / [32 J^2 \times (J+1)^2]$ for CH_4 at $T = 0\,^\circ\mathrm{C}$. However, for the lower-lying vibrational fundamental[9] at $\omega_4 \approx 1306\ \mathrm{cm}^{-1}$, $\alpha_{\text{abs}}' \approx 8 \times 10^3\ \alpha_{\text{abs}} / [32 J^2 (J+1)^2]$. This suggests, for CH_4, that at $T = 0\,^\circ\mathrm{C}$ the MV transitions will be stronger than the others for $J \lesssim 4$ only, after which the transitions calculated in the present work begin to dominate. The temperatures at which the two effects become comparable for each J are readily calculated.

In any event, as pointed out in Ref. 1 for the $\Delta J = +1$ transitions, the two types of transitions should be readily distinguishable by means of (i) the strong temperature dependence of the MV transitions, as indicated by Eq. (32), and (ii) markedly different spectral line positions in most cases. For $\Delta J = 0$, there may be a few near-accidental line coincidences between the two types of transitions.[40] These are expected to be distinguishable with microwave resolution.

2. *Hot-Band Transitions*

The most intense lowest-frequency vibration-rotation band originating from an excited vibrational state may be expected to occur[9] at $\omega_2 - \omega_4 \approx 220\ \mathrm{cm}^{-1}$ for CH_4, where frequency here is expressed in wave-number units. Individual lines, arising from $\Delta J = -$ transitions, are displaced from this band center by at most approximately[7] $2B_0(1+2\zeta_4)J$. This suggests that $J \gtrsim 11$ is required for a spectral line in this hot band to fall in the microwave spectral region. The Boltzmann factor, for $T = 0\,^\circ\mathrm{C}$, corresponding to $J = 11$ is about 50 times smaller than that corresponding to $J \approx 0$ at band center. The latter transitions are already expected to be weaker than the MV transitions because of the involvement of the relatively weak fundamental ν_2. Thus, hot-band transitions should be negligible compared to the transitions calculated in the present work. For other T_d molecules, the corresponding hot bands occur at lower frequencies[9] than for CH_4. However, their rotational constants are smaller than that of CH_4, so that their hot-band lines in the microwave should also be negligible.

transitions,[1] that the intensities of hot-band transitions have a strong temperature dependence. Furthermore, the rotational line spacings will be different from those calculated in the present work.

3. *Collision-Induced Absorption*

The collision-induced rotational spectra of several T_d molecules have been measured[47,48] to frequencies as low as about 10 cm^{-1}. A microwave collision-induced absorption (CIA) spectrum has not been reported for any molecule of this symmetry. The general theory of induced absorption resulting from binary collisions has been extended and applied to the pressure-induced rotational spectrum of a gas of T_d molecules.[49–52] The theory of Refs. 49 and 50 predicts the shape as well as the total absorption of the CIA spectrum. These predictions were found to be in good agreement with experiment.[47,48,53] However, the model used in Refs. 49 and 50 neglects the absorption due to the overlap moment and that due to the energy absorbed by the translational degrees of freedom. These limitations may seriously affect the calculation of microwave CIA for tetrahedral molecules.

However, it is possible to infer an approximate upper limit to the microwave CIA from a search[54] for dielectric loss in CH_4. A rough upper limit to the absorption coefficient in this spectral region has been estimated to be $\alpha_{\mathrm{CIA}} \lesssim 1.5\times10^{-10}$ cm^{-1} amagat^{-2}. Thus, at $T = 25\,^\circ\mathrm{C}$ and a pressure of 1 amagat, the integrated absorption is $\lesssim 1.5\times10^{-10}$ cm^{-1}. The CIA spectrum of T_d molecules is known to be very broad and to contain many rotational lines.[49,50] At any point in the microwave spectrum, it is therefore estimated that the intensity $\lesssim 10^{-11}$ cm^{-1}, conservatively. From Table II of the present work, it is apparent that there are many lines with $\alpha_{\mathrm{abs}} \gtrsim 10^{-11}$ $\mathrm{cm}^{-2}\,\mathrm{amagat}^{-1}$. For the present purpose, it is sufficient to assume a triangular line shape having a half-intensity width[55] of 0.17 cm^{-1} at STP. In this case, absorption peaks are estimated to have intensities $\approx 10^{-10}$ cm^{-1}, well above the upper limit to the microwave CIA.

B. Astrophysical Applications

CH_4 is known to be an important constituent of the atmospheres of the outer planets, e.g., Jupiter, with abundance increasing with heliocentric distance.[56] Because it is conventionally nonpolar, CH_4 is not ordinarily considered as a possible source of atmospheric opacity in the microwave spectral range. Ammonia, which has been detected only in the atmosphere of Jupiter, is considered to be the major source of microwave opacity there. However, it is interesting to note that many of the more intense lines in Table II fall in the frequency range 20.5–35.5 GHz, of measurements[57] made recently of Jupiter. In the absence of an NH_3 atmospheric constituent on Saturn, Uranus, or Neptune, CH_4 may be promoted as a source of microwave opacity there.

The expectation that CH_4 should be present in the interstellar medium[58] has not been actualized yet in the form of a definite detection. A possible observation was reported[59] on the basis of a near-infrared absorption spectrum. However, this identification has not been confirmed. Part of the difficulty is that the observed feature rests among the complicated vibration-rotation lines in a combination band which itself has not been completely analyzed theoretically. Two radio emission lines, for which no definite identification has been made, have been reported recently.[60–62] These have been named, presumably temporarily, xogen[60] and[61] X_2 with frequencies at 89.190 and 90.665 GHz, respectively. These frequencies do not correspond to any of the spectral positions in Table II, through $J = 20$. It is possible that the unidentified lines may arise from CH_4 (perhaps in the $^{13}CH_4$ form) emissions starting at $J = 21$. Finally, it has been noted[63] that CH_4 can equilibrate with a radiational environment through weak radiative rotational transitions.

C. Concluding Remarks

The measurement of pure rotational transitions from the vibronic ground state of tetrahedral molecules is of potentially fundamental importance. Ground-state rotational constants such as B_0 and D_s, and fine-structure splitting parameters such as D_t [see Eq. (22)], may be determined with unprecedented accuracy from $\Delta J = 1$ and $\Delta J = 0$ transitions, respectively.

After the present work was submitted for publication, a paper by Dorney and Watson treating some similar problems appeared.[64]

Note added in proof. A far-infrared spectrum of CH_4 interpreted as a series of pure rotational transitions[1,2] with $\Delta J = +1$, arising from the dipole moment[3] in the ground vibronic state, has been reported by A. Rosenberg, I. Ozier, and A. K. Kudian in J. Chem. Phys. 57, 568 (1972). Possible competing transitions were eliminated on the basis of considerations[1] described, in part, in Sec. V A of the present work. In particular, Eq. (29) was used to estimate the intensities of $J \rightarrow J' = J+1$ transitions predicted[38] to occur in the ν_4 state. I wish to thank I. Ozier for a preprint of the far-infrared work.

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Variational Principles for Single-Particle Expectation Values in the Hartree Approximation*

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The application of Delves's variational principle for the calculation of the expectation value of single-particle operators W is investigated in the Hartree approximation. In this approximation the auxiliary function is taken to be of the form $\psi_{1T}=\sum_i f_i(\vec{r}_i)\,\psi_{0T}$, where ψ_{0T} is the trial ground-state wave function. For a given ψ_{0T}, a set of coupled integrodifferential equations satisfied by the $f_i(\vec{r}_i)$ is derived by minimizing an auxiliary functional containing ψ_{0T}, ψ_{1T}, W, and the Hamiltonian of the system. The resulting equations are uncoupled in two different approximations each valid for one- and two-particle systems and are compared to those employed by others and to those previously suggested by us on the basis of certain self-consistency considerations. The uncoupled equations are solved exactly for single-particle operators that depend on the radial distance only. The utility of the technique is demonstrated by showing that for a model hydrogen-atom problem it leads to highly accurate results for the electron density at the origin and the Fourier transform of the electron density even when the calculation of these quantities employing ψ_{0T} alone is substantially in error. The results of applying the technique to the helium atom for the calculation of $\langle r^n\rangle$, $n=-2, -1, 1, 2$, and the electron density at the origin employing an energy-minimized product of hydrogenic wave functions for ψ_{0T} are reviewed and compared with those of Pekeris and found to have an accuracy equivalent to a numerical Hartree-Fock calculation. Finally, the decoupling approximations are extended to systems containing more than two particles.

I. INTRODUCTION AND CONCLUSIONS

The use of the Rayleigh-Ritz variational principle[1] with a many-parameter wave function for the determination of the ground-state energy of a quantum-mechanical system has two important characteristics. First of all, the calculated energy always overestimates the exact ground-state energy of the assumed Hamiltonian and thus enables us to determine which of two calculations for the energy is more accurate. Second, if the trial wave function is in error by $O(\delta)$, the calculated energy is in error by only $O(\delta^2)$ which leads to the result that good estimates of the en-