Theory of Pure Rotational Transitions in the Vibronic Ground State of Methane

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It is shown that vibration-rotation interaction terms in the Hamiltonian of tetrahedral molecules like CH_4 permit transitions, in the ground vibrational and electronic states, in which only the rotational quantum numbers change. Selection rules, spectral line positions, and absolute intensities are calculated. Effects of tetrahedral fine-structure splittings and nuclear-spin statistical weights are considered. Possible competing transitions are discussed.

Methane, the prototype of molecules with tetrahedral symmetry, is known to have a complicated vibration-rotation spectrum in the electronic ground state.[1] Pure rotational transitions *from excited vibrational states* of tetrahedral molecules have been predicted,[2a] but these transitions have not been observed in methane.[2b] Similar transitions *from the vibronic ground state* have not been considered until now because tetrahedral molecules, by virtue of their high symmetry in this state, have no permanent dipole moment.[3] The purpose of this Letter is to establish that such transitions are possible *via* vibration-rotation interactions. Sufficient details of the predicted spectrum will be provided so that suitable experiments may be considered.

In the following quantum-mechanical calculations, only the electronic ground state will be considered. The perturbed vibronic ground-state wave function is

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

where

$$w_i(R''K_R''; RK_R) = \int \psi^*(\nu_i; R''K_R'')\sigma_i[x_i(J_yJ_z + J_zJ_y) + y_i(J_zJ_x + J_xJ_z) + z_i(J_xJ_y + J_yJ_x)]\psi(g; RK_R)d\tau_i d\Omega, \tag{2}$$

in which $\sigma_i = \hbar\omega_i\zeta_{2i}\sqrt{2}(B_0/\omega_i)^{3/2}$ and $i = 3$ or 4. The rotational quantum numbers R and K_R specify the eigenvalues of $\vec{R}^2$ and R_z, where $\vec{R} = \vec{J} - \vec{l}$; $\vec{J}$ and $\vec{l}$ are, respectively, the total and the vibrational angular momentum, the latter taking the values 0 for the ground state and 1 for the infrared-active fundamentals ν_3 and ν_4 at frequencies ω_3 and ω_4. The vibrational fundamentals ν_3 and ν_4 are mixed into the ground state by the vibration-rotation interaction term whose coefficient is σ_i, wherein ζ_{2i} is the Coriolis coupling constant.[4] The vectors $\vec{r}_3 = (x_3, y_3, z_3)$ and $\vec{r}_4 = (x_4, y_4, z_4)$ are the normal coordinates for ν_3 and ν_4. The differential $d\tau_i$ is $dx_i dy_i dz_i$ and $d\Omega$ corresponds to the differential for the Euler angles. The ground-state rotational constant is B_0.

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

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

where $\lambda_{Z\alpha}$ is the direction cosine between the space-fixed Z axis and the molecule-fixed α axis,[5] and μ_α is the molecule-fixed α component of the dipole-moment operator. To second order in the normal coordinates,[4]

$$\mu_z = A_3 z_3 + A_4 z_4 + A_3' x_3 y_3 + A_4' x_4 y_4 + \cdots, \tag{4}$$

with similar expressions for μ_x and μ_y; here $A_3 = (\partial\mu_z/\partial z_3)_0$, $A_3' = (\partial^2\mu_z/\partial z_3^2)_0$, 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

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

$$= -\sum_{i=3}^{4}\sum_{R''K_R''}(\hbar\omega_i)^{-1}[w_i(R''K_R''; RK_R)\int\psi^*(g; R'K_R')\mu_Z\psi(\nu_i; R''K_R'')d\tau_i d\Omega$$
$$+ w_i^*(R''K_R''; R'K_R')\int\psi^*(\nu_i; R''K_R'')\mu_Z\psi(g; RK_R)d\tau_i d\Omega]. \tag{6}$$

Terms proportional to ω^{-2}, and higher vibrational states than those explicit in Eq. (1) which would produce, at most, terms proportional to $A_i'/2\omega_i$, contribute $\lesssim 1\%$ and are therefore neglected in Eq. (6).

Evaluation of the integrals in Eqs. (2) and (6) is most efficiently done by expressing all operators in spherical tensor form,[6] and by using angular-momentum–coupled wave functions. Then the formalism of Racah algebra and the Wigner-Eckart theorem[6] can be used to obtain

$$\int \psi^*(g;R'K_R')\mu_Z\psi(\nu_i;R''K_R'')d\tau_i d\Omega = -(A_i/\sqrt{2})(J'\ 1\ M'\ 0|J'\ 1\ J''\ M'')\delta_{R''R'}\delta_{K_R''K_R'}, \tag{7}$$

where 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; and

$$w_i(R''K_R'';RK_R) = (i\sigma_i/4)[7(2J-1)(2J)(2J+1)(2J+2)(2J+3)]^{1/2}\begin{Bmatrix} J & R'' & 3 \\ 1 & 2 & J \end{Bmatrix}$$

$$\times[(R\ 3\ K_R\ 2|R\ 3\ R''\ K_R'') - (R\ 3\ K_R-2|R\ 3\ R''\ K_R'')]\delta_{J''J}, \tag{8}$$

where the 6-j symbol[6] has been used. Selection rules resulting from Eqs. (5)-(8) are $R'=R$, $R\pm1$, $R\pm2$, and $R\pm3$, subject to the triangle inequality; $K_R'=K_R\pm2$; $J'=J$, $J\pm1$; and $K'=K\pm2$ (K' and K are the projections of $\vec{J}'$ and $\vec{J}$, respectively, on the molecule-fixed z axis). In the remainder of this Letter, only transitions $\Delta J=+1$ will be considered.[7] Then, for $J\to J'=J+1$,

$$\langle\mu_Z\rangle = -(i/2)[(\hbar\omega_3)^{-1}\sigma_3 A_3 + (\hbar\omega_4)^{-1}\sigma_4 A_4][(2J-1)(2J)(2J+1)/2J+4)(2J+5)/5(2J+3)]^{1/2}$$

$$\times f(JK)(J\ 1\ M\ 0|J\ 1\ J+1\ M), \tag{9}$$

where

$$f(JK) \equiv (J\ 3\ K\ 2|J\ 3\ J+1\ K+2) - (J\ 3\ K-2|J\ 3\ J+1\ K-2). \tag{10}$$

Finally, 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:

$$\langle\mu_{JK}\rangle^2 = C_{34}^2(2J-1)(2J)(2J+3)(2J+4)(2J+5)[f(JK)]^2, \tag{11}$$

where

$$C_{34}^2 \equiv \tfrac{1}{20}(\sigma_3 A_3/\hbar\omega_3 + \sigma_4 A_4/\hbar\omega_4)^2. \tag{12}$$

The intensity of an absorption line is given by

$$\alpha_{abs} = (8\pi^3/3hc)(N/\mathfrak{z})[B_0(J+1)(J+2) - B_0 J(J+1)]\langle\mu_{JK}\rangle^2\epsilon_{JK}$$

$$\times\{\exp[-B_0 J(J+1)hc/kT] - \exp[-B_0(J+1)(J+2)hc/kT]\}, \tag{13}$$

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 which takes the values 5, 2, and 3 for rotational wave functions belonging to the irreducible representations A_1 (or A_2), E, and F_1 (or F_2), respectively, of the tetrahedral point group T_d. Tetrahedral fine-structure splittings, as well as centrifugal distortion effects have been neglected so far since they contribute at most a few percent to Eq. (13). The T_d splittings in the vibronic ground state[8] amount to only about 0.01 to 0.1 cm^{-1}, out of principal spacing of $2B_0 \approx 10.5$ cm^{-1}, for $J<10$. Moreover, to a good approximation, these splittings do not shift the "center of gravity" of the absorption features. Therefore, Eq. (13) will be summed over all K values to obtain α_{abs} for each J. It has been shown,[9] from the orthonormality of the vector-coupling coefficients, that

$$\sum_K \epsilon_{JK}[f(JK)]^2 = \frac{2(2J+3)}{7} + 4\sum_{K\sim A}[f(JK)]^2, \tag{14}$$

where $K\sim A$ implies a sum over only those K values corresponding to A_1 or A_2. This result simplifies the intensity calculations considerably. A calculation of the intensity of each of the T_d components of the absorption lines considered here will be presented elsewhere. The rotational partition function $\mathfrak{z}_r$, a good approximation to $\mathfrak{z}$ for temperatures $T \leqslant 300°K$, may be written[10]

$$\mathfrak{z}_r = \tfrac{4}{3}\pi^{1/2}(B_0 hc/kT)^{-3/2}\exp(B_0 hc/4kT), \tag{15}$$

which is accurate to 1% for $T>40°K$, for CH$_4$.

To obtain absolute intensities, the numerical value of the coefficient C_{34}^2 in Eq. (11) must be

determined. From Eq. (12) and the definition of σ_i following Eq. (2) we have

$$C_{34}{}^2 = \tfrac{1}{10} B_0{}^3(\zeta_{23}A_3\omega_3{}^{-3/2} + \zeta_{24}A_4\omega_4{}^{-3/2})^2. \qquad (16)$$

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,[4] it follows that $\zeta_{23}\zeta_{24}<0$. It has also been inferred,[11] from low-resolution infrared spectra and several calculations, that $A_3A_4<0$. Thus the two terms in Eq. (16) are additive, which is favorable for the observation of the transitions. The values B_0 $=5.240\,59$ cm^{-1},[12] $|\zeta_{23}| = 0.795$ and $|\zeta_{24}| = 0.605$,[4,8,12,13] $|A_3| \approx 0.07$ and $|A_4| \approx 0.05$ D,[11,14] $\omega_3 = 3019.48$ cm^{-1},[12] and $\omega_4 = 1305.95$ cm^{-1}[13] were used to obtain $C_{34} \approx 4 \times 10^{-6}$ D.

Equations (11)-(15) have been evaluated for T $=273°$K, with N replaced by $N_0 p$, wherein N_0 is Avogadro's number and p is the pressure in amagats.[15] The quantity $\sum_K \alpha_{abs}p^{-1}$ is given in Table I for $J = 0, 1, \cdots, 10$. The corresponding spectral-line positions have been calculated from[8]

$$E(J \to J+1) = 2B_0(J+1) - 4D_s(J+1)^3, \qquad (17)$$

with[12] $B_0 = 5.240\,59$ cm^{-1} and $D_s = 1.0855 \times 10^{-4}$ cm^{-1}, the latter being the coefficient of the scalar centrifugal stretching term in the Hamiltonian. The T_d splittings (produced by a fourth-rank spherical-tensor operator also corresponding to centrifugal effects[8]) discussed above have been neglected. The spectral-line positions, in the approximation Eq. (17), are given in Table I. For $J>10$, the intensities $\sum_K \alpha_{abs}p^{-1}$ decrease rapidly, and the T_d splittings are on the order of a few tenths to one cm^{-1} and greater. Therefore, these intensities will be distributed over many relatively widely spaced absorption lines.

It is significant to compare the intensities calculated here with those of possible competing transitions in the frequency range below 120 cm^{-1} (see Table I). The lowest-lying vibrational state of CH_4 from which pure rotational transitions could arise is[1,13] at $\omega_4 \approx 1306$ cm^{-1}. At $T = 273°$K, the Boltzmann factor $\exp(-\omega_4 hc/kT)$ is roughly 1×10^{-3}; the intensity is also proportional to $A_4'^2$ instead of $A_4{}^2$ [see Eq. (4)]. The product of these two factors still leaves this effect several orders of magnitude greater than the transitions predicted in this Letter. However, at $T = 120°$K, the effects become comparable. These two types of transitions should be readily distinguishable by means of (1) the strong temperature dependence, i.e., a doubling of intensity for a $10°$ change in T,

TABLE I. Spectral line positions and absolute intensities for pure rotational transitions $J \to J+1$ from the vibronic ground state of CH_4. The rotational constants[a] $B_0=5.240\,59$ cm^{-1} and $D_s=1.0855\times10^{-4}$ cm^{-1} [see Eq. (17)] were used; tetrahedral splittings were neglected. The value $C_{34}=4\times10^{-6}$ D in the transition dipole moment [see Eqs. (11) and (16)] was used.

Transition $(J \to J+1)$	Position (cm^{-1})	Intensity $(10^{-6}$ cm^{-2} amagat$^{-1})$[b]
$0 \to 1$	none[c]	none[c]
$1 \to 2$	20.959	0.000 43
$2 \to 3$	31.432	0.017
$3 \to 4$	41.897	0.30
$4 \to 5$	52.352	0.76
$5 \to 6$	62.793	2.4
$6 \to 7$	73.219	7.3
$7 \to 8$	83.627	13
$8 \to 9$	94.014	19
$9 \to 10$	104.378	31
$10 \to 11$	114.715	33

[a]See Ref. 12.

[b]See Ref. 15.

[c]The rotational wave functions for $J=0$ and 1 do not permit a transition satisfying the selectron rule $\Delta K = \pm 2$.

of only one, and (2) markedly different rotational line spacings. (A vibration-rotation "hot band" may be expected to occur[1] at $\omega_2 - \omega_4 \approx 220$ cm^{-1}. This band, in addition to its strong temperature dependence, is about an order of magnitude weaker than the other possible competing transition considered above. Furthermore, its rotational line spacing should also be much different from that in Table I.)

The other important possible competing effect is the collision-induced absorption spectrum of CH_4. This spectrum consists[16] of a large number of rotational lines corresponding to transitions with $\Delta J = 0, 1, 2, 3$; each of the lines is many tens of cm^{-1} broad. The collision-induced absorption would constitute a kind of continuum background for the effect calculated in this Letter. From the room-temperature spectrum measured[17] at 24.1 amagat it may be inferred that at 1 amagat the peak absorption $\leq 4 \times 10^{-6}$ cm^{-1}. Peak absorptions may be deduced from Table I, provided that a line shape is assumed. In this Letter, a triangular line shape having a half-intensity width[18] of 0.17 cm^{-1} at STP was used to obtain peaks estimated to be 14, 43, and 78×10^{-6} cm^{-1} for the transitions $5 \to 6$, $6 \to 7$, and $7 \to 8$, respectively. These peaks are well above those of the collision-induced absorption spectrum.

Finally, from the experimental standpoint, it is worth considering what the absorption path is required to produce, e.g., a 10% decrease in the intensity of radiation transmitted according to Lambert's law. For $J = 7 \rightarrow 8$, from the intensity in Table I it may be inferred that at $T = 120°K$, 200 m amagat is required. At 1 amagat this value implies a path of 200 m, which is attainable in a multitraversal tube with base length of several meters. It is also possible that the phenomenon described in this Letter may produce effects detectable[19] by molecular-beam resonance techniques.

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[6]See, for example, A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. Press, Princeton, N. J., 1960).

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[15]The number of amagats of a gas equals the ratio of its density to that at STP.

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[17]Birnbaum and Rosenberg, Ref. 3.

[18]A summary of measurements of collision-broadened widths and shapes of CH_4 lines of vibration-rotation bands in the near infrared appears in P. Varanasi, to be published.

[19]The author is grateful to I. Ozier for suggestions on this point.