INTENSITIES OF PURE ROTATIONAL BAND SYSTEMS

OF SYMMETRIC TOP MOLECULES

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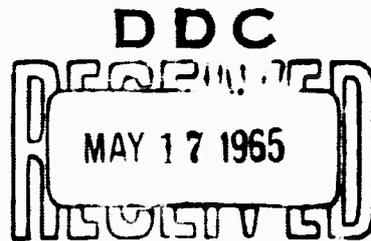
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GENERAL DYNAMICS | CONVAIR

Intensities of Pure Rotational Band Systems of Symmetric Top Molecules

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ABSTRACT

An exact expression for the total intensity of the pure
rotational band system of a rigid symmetric top molecule is
derived. An approximate expression for the mean spectral
absorption coefficient is obtained and is compared with
previously published results. The first-order effects of
non-rigidity and mechanical anharmonicity on the band intensity
are investigated in the special case of a diatomic molecule
and found to be small in general.

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INTRODUCTION

The total intensity of the pure rotational band system of a molecule
is defined as the sum of the intensities of all transitions of the molecule
in which the vibrational quantum number does not change. We will start
with the expression for the intensity of a single rotational transition
of a symmetric top molecule and sum this expression over all the quantum
numbers involved to obtain an exact expression for the total band intensity.
An approximate expression will be derived for the mean absorption coefficient
for which the exact summations involved cannot be performed.

For clarity of presentation, the following development neglects the
effect of alternating statistical weights, and strictly applies only to
an accidentally symmetric top molecule. However, the proof for the
general case of a symmetric top molecule of point group C_{pv} (such as the
C_{3v} molecules - NH_3, CH_3Cl, etc.) proceeds in exactly the same manner,
but requires more cumbersome equations and additional definitions.

TOTAL BAND INTENSITY

The intensity of a pure rotational line of a symmetric or asymmetric
top is given by[1]

$$S_{vJ\tau M'}^{vJ'\tau'M'} = \frac{8\pi^3}{3hc} \frac{N_{vJ\tau M}}{p} \mu_o^2 \, \omega[1-\exp(-\frac{hc}{kT}\omega)] \sum_F |\Phi_{Fg}|^2_{J\tau M, J'\tau'M'}, \qquad (1)$$

where

$$\frac{N_{vJ\tau M}}{p} = \frac{N}{p} \exp[-E(v,J,\tau,M)/kT]/Q \qquad (2)$$

is the number of molecules per unit volume and unit pressure in the
state described by the usual quantum numbers (v,J,τ,M),

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$$Q = \sum_{vJ\tau M} \exp[-E(v,J,\tau,M)/kT] \tag{3}$$

is the total partition function, and the Φ_{Fg} are the direction cosines between the space-fixed F and rotating g axes.

If Eq. (1) is summed over M and M', we obtain

$$S_{vJ\tau}^{vJ'\tau'} = \frac{8\pi^3}{3hc} \frac{N}{p} \mu_o^2 \frac{\exp[-E(v,J,\tau)/kT]}{Q} \omega[1-\exp(-\frac{hc}{kT}\omega)] \sum_{FMM'} |\Phi_{Fg}|^2_{J\tau M, J'\tau'M'}, \tag{4}$$

since the energy levels and frequencies are independent of M and M'.

If we consider the top rigid, i.e.,

$$E(v,J,\tau) = hc[G(v) + F(J,\tau)], \tag{5}$$

and sum over v, we obtain

$$S_{J\tau}^{J'\tau'} = \frac{8\pi^3}{3hc} \frac{N}{p} \mu_o^2 \frac{\exp[-\frac{hc}{kT}F(J,\tau)]}{Q_R} \omega[1-\exp(-\frac{hc}{kT}\omega)] \sum_{FMM'} |\Phi_{Fg}|^2_{J\tau M, J'\tau'M'}, \tag{6}$$

where Q_R is the rotational partition function

$$Q_R = \sum_{J\tau M} \exp[-\frac{hc}{kT}F(J,\tau)]. \tag{7}$$

We now specialize to the case of the symmetric top, for which we have[2]

$$F(J,K) = BJ(J+1) + (A-B)K^2, \tag{8}$$

where the symmetric top quantum number K (which runs from 0 to J) is now used in place of τ. For a $J \to J+1$ transition, we have (since $\Delta K = 0$)

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$$\omega = 2B(J+1), \tag{9}$$

and[2]

$$\sum_{FMM'} |\Phi_{Fg}|^2_{JKM,J+1K\ M'} = (2-\delta_{OK}) \frac{(J+1)^2-K^2}{J+1} \ . \tag{10}$$

From Eq. (6), we obtain

$$S_J^{J+1}\ {}_K^K = \frac{8\pi^3}{3hc} \frac{N}{p} \mu_o^2 \frac{\exp\left\{-\frac{hc}{kT}[BJ(J+1) + (A-B)\ K^2]\right\}}{Q_R}$$

$$\times\ 2B(J+1)\ \left\{1-\exp[-\frac{hc}{kT}\ 2B(J+1)]\right\} \frac{(J+1)^2-K^2}{J+1}\ (2-\delta_{OK}). \tag{11}$$

The quantity S_J^{J+1} is now obtained by summation over K:

$$S_J^{J+1} = \frac{8\pi^3}{3hc} \frac{N}{p} \mu_o^2 \frac{2B}{Q_R} \left\{\exp[-\frac{hc}{kT}\ BJ(J+1)] - \exp[-\frac{hc}{kT}\ B(J+1)(J+2)]\right\}$$

$$\times\ \sum_{K=0}^{J} (2-\delta_{OK})\ [(J+1)^2-K^2]\ \exp[-\frac{hc}{kT}\ (A-B)\ K^2]. \tag{12}$$

The summations over K in Eq. (12) cannot be expressed in closed form. We will approximate the sums later by integrals, and derive an approximate expression for the absorption coefficient. However, we will continue the present development in order to obtain an (exact) expression for tne band intensity.

If we define the quantities $f(J)$ and $g(J)$ as follows:

$$f(J) = \sum_{K=0}^{J} (2-\delta_{OK})\ \exp[-\frac{hc}{kT}\ (A-B)\ K^2] \tag{13}$$

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and

$$g(J) = 2 \sum_{K=0}^{J} K^2 \exp\left[-\frac{hc}{kT}(A-B)K^2\right],$$ (14)

then we have

$$S_J^{J+1} = \frac{16\pi^3}{3hc} \frac{N}{p} \frac{\mu_o^2 B}{Q_R} \left\{ \exp\left[-\frac{hc}{kT}BJ(J+1)\right] - \exp\left[-\frac{hc}{kT}B(J+1)(J+2)\right] \right\} \left[(J+1)^2 f(J) - g(J) \right],$$ (15)

and Eq. (7) becomes

$$Q_R = \sum_{J=0}^{\infty} (2J+1) \exp\left[-\frac{hc}{kT}BJ(J+1)\right] f(J).$$ (16)

We note here that if the derivation is carried through for a non-accidentally symmetric top molecule, an additional nuclear spin-dependent factor in the statistical weights must be considered. (This factor has implicitly been assumed constant here and, hence, has been neglected.) This factor is dependent only^2 on the quantum number K. Extended definitions analogous to Eqs. (13) and (14) can then be made and carried through in the same manner to produce the same results.

The total rotational band intensity, given by

$$\alpha(T) = \sum_{J=0}^{\infty} S_J^{J+1},$$ (17)

is obtained by substituting Eq. (15) into Eq. (17) and rearranging terms:

$$\alpha(T) = \left(\frac{16\pi^3}{3hc} \frac{N}{p} \mu_o^2 B\right) \left[1 + \frac{\sum \exp[-hcBJ(J+1)/kT]\{J^2[f(J)-f(J-1)]-g(J)+g(J-1)\}}{\sum \exp[-hcBJ(J+1)/kT](2J+1)f(J)} \right].$$ (18)

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But from the definitions of $f(J)$ and $g(J)$, we have

$$J^2[f(J)-f(J-1)] = 2J^2 \exp[-\frac{hc}{kT} (A-B) J^2] \tag{19}$$

and

$$[f(J)-g(J-1)] = 2J^2 \exp[-\frac{hc}{kT} (A-B) J^2] . \tag{20}$$

Thus the curly-bracketed term in Eq. (18) vanishes identically, leaving

$$\alpha(T) = \frac{16\pi^3}{3hc} \frac{N}{p} \mu_o^2 B. \tag{21}$$

Since $\frac{N}{p} = \frac{1}{kT}$, this can be written

$$\alpha(T) = \frac{16\pi^3 \mu_o^2 B}{3hc\ kT} , \tag{22}$$

or

$$\alpha(273°K) = 22.5 \mu_o^2 B\ cm^{-2}atm^{-1}, \tag{23}$$

where B is in cm^{-1} and μ_o is in debye units. Thus we find that

$$T_1 \alpha(T_1) = T_2 \alpha(T_2), \tag{24}$$

that is, the (density-corrected) intensity of a pure rotational band system of a rigid symmetric top molecule is independent of temperature.

We note here that the expression for the total band intensity is a function of B but not of A. This is related, at least in part, to the fact that the frequency of the radiation depends only on B. The limiting case A→∞ was treated by Golden,[3] who determined the absorption coefficient as a function of frequency for the rigid rotator model. Integration of Golden's Eq. (5)[3] over frequency yields an expression for total band

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intensity which is consistent with Eq. (22) within the approximation involved in replacing the summation over J by an integration.

APPROXIMATE MEAN ABSORPTION COEFFICIENT

The mean absorption coefficient $\bar{k}$ is given by S_J^{J+1}/d, where $d = 2B$ is the line spacing, so that we have from Eq. (15) and Eq. (9)

$$\bar{k} = S_J^{J+1}/d = \frac{8\pi^3}{3hc} \frac{N}{\nu} \frac{\mu_o^2}{Q_R} \left\{ \exp\left[-\frac{hc}{kT}BJ(J+1) \right] - \exp\left[-\frac{hc}{kT}B(J+1)(J+2) \right] \right\}$$

$$\times \left[(J+1)^2 f(J) - g(J) \right]. \tag{25}$$

The sums involved in the definitions of $f(J)$, $g(J)$ and Q_R cannot be performed exactly. If we approximate the sums by integrals, we obtain

$$f(J) \approx \int_{-(J+\frac{1}{2})}^{(J+\frac{1}{2})} \exp\left[-\frac{hc}{kT}(A-B) K^2 \right] dK$$

$$= \frac{\sqrt{\pi}}{\sqrt{\frac{hc}{kT}(A-B)}} \operatorname{erf}\left[\sqrt{\frac{hc}{kT}(A-B)} (J+\frac{1}{2}) \right] , \tag{26}$$

and, similarly,

$$g(J) \approx \frac{\sqrt{\pi}}{2[\frac{hc}{kT}(A-B)]^{3/2}} \operatorname{erf}\left[\sqrt{\frac{hc}{kT}(A-B)} (J+\frac{1}{2}) \right] - \frac{(J+\frac{1}{2})}{\frac{hc}{kT}(A-B)} \exp\left[-\frac{hc}{kT}(A-B)(J+\frac{1}{2})^2 \right]. \tag{27}$$

To the same degree of approximation, we have for the rotational partition function

$$Q_R = \int_{-\frac{1}{2}}^{\infty} (2J+1) \exp\left[-\frac{hc}{kT}BJ(J+1) \right] \int_{-(J+\frac{1}{2})}^{(J+\frac{1}{2})} \exp\left[-\frac{hc}{kT}(A-B)K^2 \right] dKdJ$$

or

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$$Q_R = \exp\left(\frac{1}{4}\frac{hc}{kT}B\right) \frac{\sqrt{\pi}}{\sqrt{\frac{hc}{kT}(A-B)}} \int_0^\infty 2I\exp\left[-\frac{hc}{kT}BI^2\right] \mathrm{erf}\left[\sqrt{\frac{hc}{kT}(A-B)}I\right] dI. \qquad (28)$$

But since $\int_0^\infty x\,\exp(-x^2)\,\mathrm{erf}(ax)dx = \frac{1}{2}a(a^2+1)^{-\frac{1}{2}}$, we have

$$Q_R = \sqrt{\pi}\,\left(\frac{kT}{hc}\right)^{3/2} \frac{1}{\sqrt{AB^2}}\,, \qquad (29)$$

if we set $\exp\left(\frac{1}{4}\frac{hc}{kT}B\right) \approx 1$. Thus the use of this customary expression[4] for Q_R is completely consistent with the assumed model and approximations; further comment will be made on this point in discussing the limiting case $A \to \infty$.

Thus we obtain the following explicit expression for $\bar{k}$:

$$\bar{k} = \left(\frac{8\pi^3}{3hc}\frac{N}{p}\mu_o^2\right)\frac{1}{\sqrt{\pi}}\left(\frac{hc}{kT}\right)^{3/2}\sqrt{AB^2}\left\{\exp\left[-\frac{hc}{kT}BJ(J+1)\right]-\exp\left[-\frac{hc}{kT}B(J+1)(J+2)\right]\right\}$$

$$\times\left\{\frac{\sqrt{\pi}}{\sqrt{\frac{hc}{kT}(A-B)}}(J+1)^2\,\mathrm{erf}\left[\sqrt{\frac{hc}{kT}(A-B)}\,(J+\tfrac{1}{2})\right]\right.$$

$$\left.-\frac{\sqrt{\pi}}{2\left[\frac{hc}{kT}(A-B)\right]^{3/2}}\mathrm{erf}\left[\sqrt{\frac{hc}{kT}(A-B)}\,(J+\tfrac{1}{2})\right]+\frac{(J+\tfrac{1}{2})}{\sqrt{\frac{hc}{kT}(A-B)}}\exp\left[-\frac{hc}{kT}(A-B)(J+\tfrac{1}{2})^2\right]\right\}, \quad (30)$$

or, to a degree of accuracy consistent with the previous approximations,

$$\bar{k} = \left(\frac{8\pi^3}{3hc}\frac{N}{p}\mu_o^2\right)\frac{1}{\sqrt{\pi}}\left(\frac{hc}{kT}\right)\sqrt{\frac{AB^2}{A-B}}\left\{\exp\left[-\frac{hc}{kT}BJ(J+1)\right]-\exp\left[-\frac{hc}{kT}B(J+1)(J+2)\right]\right\}$$

$$\times\,(J+1)^2\,G\left[\sqrt{(A-B)\frac{hc}{kT}}\,(J+1)\right]\,, \qquad (31)$$

where

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$$G(z) = \sqrt{\pi} \left(1 - \frac{1}{2z^2}\right) \text{erf}(z) + \frac{1}{z} \exp(-z^2). \tag{32}$$

The power series representation of G is given by

$$G(z) = 4 \sum_{n=0}^{\infty} \frac{(-1)^n}{n!(2n+1)(2n+3)} z^{2n+1}. \tag{33}$$

Equation (31) is not consistent with the expression for the absorption coefficient presented by Penner[5] [Eq. (11-134)[5]]. There appear to be two causes of discrepancy.

First, the induced emission term $[1-\exp(-hc\omega/kT)]$ was implicitly assumed to be approximately unity in the derivation of Eq. (11-134)[5]. Such an approximation is not valid in gene. il for a pure rotational band as can be shown by the following argument: Consider a spherical top molecule (for simplicity). The population of a given J state is approximately proportional to $J^2 \exp(-\beta J^2)$, which is a maximum for $\beta J^2 = 1$. For this value of J, the induced emission term $[1-\exp(-2\beta J)]$ is equal to $[1-\exp(-2/J)]$. Even at temperatures low enough for the maximum population to lie in the $J = 3$ state, the induced emission term is equal to $[1-\exp(-2/3)] \approx 0.49$. With increasing temperature, the induced emission term decreases; thus approximating this term by unity is, in general, not reasonable.

Secondly, Eq. (31) differs from Eq. (11-134)[5] by a factor of approximately 2 or 3. This appears to result from the use of a summation rule [Eq. (7.116a)[5]] in which a sum of matrix elements is taken over the upper state values of J-1, J, and J+1, by analogy to the case of a vibration-rotation band system. In such a system, a lower state J can go

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to an upper state J-1, J, or J+1. However, in the pure rotational band system under consideration, the only corresponding transition is $J \rightarrow J+1$.

In the limit of $A \rightarrow \infty$, Eq. (31) is consistent with Golden's Eq. (5),[3] to the degree of approximation previously noted. Since it can be seen that the approximate expressions for $f(J)$, $g(J)$ and Q_R become arbitrarily poor for large A, we will comment briefly on this point.

We note that in the limit as $A \rightarrow \infty$, we have from Eqs. (13), (14), and (16)

$$f(J) \rightarrow 1 , \tag{34}$$

$$g(J) \rightarrow 0 , \tag{35}$$

and

$$Q_R \rightarrow \sum_{J=0}^{\infty} (2J+1) \exp[- \frac{hc}{kT}BJ(J+1)], \tag{36}$$

i.e., the rotational partition function for a linear molecule. Approximating this sum by an integral in the usual way[4] yields

$$Q_R \rightarrow \frac{kT}{hcB} . \tag{37}$$

Thus, in this limit we have

$$f(J)/Q_R \rightarrow hcB/kT \tag{38}$$

and

$$g(J)/Q_R \rightarrow 0. \tag{39}$$

But exactly the same results are obtained by taking the ratios of the approximate expressions used (i.e., the ratios of Eqs. (26) and (27) to Eq. (29)). Only these ratios are used in the present work; thus the

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limiting case of A-∞ is a valid limit although the separate expressions for $f(J)$, $g(J)$ and Q_R became arbitrarily poor approximations for large A.

EFFECTS OF CENTRIFUGAL STRETCHING

We will consider here only the special case of a diatomic molecule; a general formulation for polyatomic molecules is not feasible since each different molecular configuration presents a different geometrical problem. It is felt that the magnitudes of the effects determined for the diatomic molecule will be representative at least of those of the simpler polyatomic molecules.

We will consider the effect of nonrigidity of the molecule on the band intensity through (a) its effect on the energy level structure (and, hence, on the emitted frequencies) and (separately) through (b) its effect on the electric dipole moment.

One would expect that since centrifugal stretching tends to lower the energy levels and decrease w_J^{J+1}, the net effect of (a) would be to lower the total band intensity. Also, since the stretching may tend to increase the dipole moment (at least, for diatomic molecules, in many cases), one would also expect that the net effect of (b) would be to increase the total band intensity. These two effects will be investigated quantitatively.

The energy levels of a diatomic molecule (with the first approximation to the effect of centrifugal stretching) are given by[6]

$$F(J) = BJ(J+1)-DJ^2(J+1)^2. \qquad (40)$$

The second term is assumed to be a small correction. For this simple model, D is related to the rotational and vibrational constants:[6]

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$$\frac{D}{B} = \left(\frac{2B}{\omega_v}\right)^2 = \gamma^2. \tag{41}$$

The frequency of radiation is then

$$\omega_J^{J+1} = F(J+1)-F(J) = 2B(J+1)-4D(J+1)^3. \tag{42}$$

We then have for the intensity of a $J \to J+1$ transition

$$S_J^{J+1} = \left[\frac{8\pi^3\mu_o^2}{3hc}\frac{N}{p}\right]\frac{1}{Q_R}[2B(J+1)-4D(J+1)^3](J+1)$$

$$\times \left\{\exp[-\beta J(J+1)]\exp[\delta J^2(J+1)^2]-\exp[-\beta(J+1)(J+2)]\exp[\delta(J+1)^2(J+2)^2]\right\} \tag{43}$$

(using the notation $\beta = \frac{hc}{kT}B$ and $\delta = \frac{hc}{kT}D$).

If we expand the exponential functions involving D, retaining the first-order terms, and proceed as before, we obtain for the band intensity $\alpha = \sum S_J^{J+1}$:

$$\alpha = \left[\frac{8\pi^3\mu_o^2}{3hc}\frac{N}{p}\right]\frac{1}{Q_R}\left\{2B\sum (2J+1)\exp[-\beta J(J+1)]\right.$$

$$- 8D\sum (2J+1)J(J+1)\exp[-\beta J(J+1)]$$

$$\left.+ 2B\delta\sum (2J+1)J^2(J+1)^2\exp[-\beta J(J+1)]\right\}. \tag{44}$$

To the same approximation we have

$$Q_R = \sum (2J+1)\exp[-\beta J(J+1)][1+\delta J^2(J+1)^2]$$

$$= Q_R^o + \delta\frac{\partial^2}{\partial\beta^2} Q_R^o, \tag{45}$$

where $Q_R^o = Q_R(D = 0) = \beta^{-1}$. Thus we have

$$Q_R = Q_R^o[1+2\delta\beta^{-2}]. \tag{46}$$

In terms of Q_R^o, we have for the band intensity

$$\alpha = \left[\frac{8\pi^3\mu_o^2}{3hc}\frac{N}{p}\right]\frac{1}{Q_R^o(1+2\delta\beta^{-2})}\left[2BQ_R^o-8D\left(-\frac{\partial}{\partial\beta}Q_R^o\right)+2B\delta\frac{\partial^2}{\partial\beta^2}Q_R^o\right], \tag{47}$$

from which we obtain

$$\alpha = \left[\frac{8\pi^3\mu_o^2}{3hc}\frac{N}{p}\right]\frac{1}{1+2\delta\beta^{-2}}\left[2B-8D\beta^{-1}+2B\delta\beta^{-2}\right] \tag{48}$$

or

$$\alpha = \left[\frac{8\pi^3\mu_o^2}{3hc}\frac{N}{p}\right]2B[1-4\frac{D}{B}\frac{kT}{hcB}]. \tag{49}$$

We now consider the effect of the varying dipole moment. We write

$$\mu = \mu_o + \mu_1\,\Delta r, \tag{50}$$

and express Δr in terms of the molecular constants:

$$\Delta r = \frac{4B^2}{\omega_v^2}r_e\,J(J+1) = \gamma^2 r_e J(J+1). \tag{51}$$

Thus we find

$$\mu = \mu_o[1+\frac{\mu_1 r_e}{\mu_o}\gamma^2\,J(J+1)] \tag{52}$$

or

$$\mu^2 = \mu_o^2\,[1+2\frac{\gamma^2}{\theta}\,J(J+1)]\,, \tag{53}$$

where

$$\theta = \mu_o/\mu_1 r_e. \tag{54}$$

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If this value of μ_o^2 is substituted for μ_o^2 in Eq. (11), we obtain after similar manipulation,

$$\alpha = \left[\frac{8\pi^3 \mu_o^2}{3hc} \frac{N}{p}\right] 2B\left[1 + 4 \frac{\gamma^2}{\theta} \frac{kT}{hcB}\right]. \tag{55}$$

If we combine Eqs. (49) and (55), we find, for the net effect of centrifugal stretching,

$$\alpha = \left[\frac{8\pi^3 \mu_o^2}{3hc} \frac{N}{p}\right] 2B\left[1 - 4 \frac{D}{B} \frac{kT}{hcB} + 4 \frac{\gamma^2}{\theta} \frac{kT}{hcB}\right]. \tag{56}$$

If we assume further that $\frac{D}{B} = \left(\frac{2B}{\omega_v}\right)^2 \ (=\gamma^2)$ [Eq. (41)], we have

$$\alpha = \left[\frac{8\pi^3 \mu_o^2}{3hc} \frac{N}{p}\right] 2B\left[1 - 4 \gamma^2 \left(1 - \frac{1}{\theta}\right) \frac{kT}{hcB}\right]. \tag{57}$$

Investigating orders of magnitude, we find that since $4\gamma^2 \frac{kT}{hcB} \sim T \times 10^{-5}$ for most diatomic molecules, the correction is small for $T \sim 10^3$. We note that $\left(1 - \frac{1}{\theta}\right)$ is not large unless $\theta \approx 0$, which implies that μ_o (and α) are small. Although then $\left|\left(1 - \frac{1}{\theta}\right)\right| \propto \mu_o^{-1}$, there is a multiplicative factor of μ_o^2 in Eq. (57), which will still dominate. Hence, for $\theta \approx 0$, the percent correction may be large, but it is small on an absolute basis. For the other special case of $\theta = +1$ (which is approximately true for HCℓ and HF), the net effect of centrifugal stretching vanishes.

EFFECTS OF MECHANICAL ANHARMONICITY

We next consider the fact that the rotational constants may vary with the vibrational quantum number (as a result of the mechanical anharmonicity of a real molecule).

If, in the previous development, the rotational constants are not

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considered independent of v as in Eqs. (5) and (8), and, instead, the expression

$$B(v) = B_o - \alpha_e v \tag{58}$$

is used, we obtain (after a similar sequence of manipulations and approximations)

$$\alpha = \left[\frac{8\pi^3 \mu_o^2}{3hc} \frac{N}{p} \right] 2B_o \left\{ 1 - \frac{\alpha_e}{B_c} \left[\exp\left(\frac{hc}{kT} w_o\right) - 1 \right]^{-1} \right\} . \tag{59}$$

In effect, the rotational constant B is replaced by the (population-weighted) average value of $B(v)$ at temperature T. The correction term is of the order of $1-.0002$ for $T \sim 10^3$.

In order to obtain the corresponding correction for the dipole moment, we note that in a vibrational state defined by the quantum number v, we have

$$\langle \mu^2 \rangle_{av} = \langle [\mu_o^2 + \mu_1 \, \Delta r]^2 \rangle_{av}$$

$$\approx \mu_o^2 \left(1 + 2 \frac{\mu_1}{\mu_o} \langle \Delta r \rangle_{av} \right). \tag{60}$$

To relate $\langle \Delta r \rangle_{av}$ to v, we note that since $B \propto \langle r^{-2} \rangle_{av}$, we have

$$B(v) = B_o - \alpha_e v \propto \langle r^{-2} \rangle_{av} \approx r_e^{-2} \left(1 - 2 \langle \Delta r \rangle_{av} / r_e \right). \tag{61}$$

Thus, we have, approximately

$$2 \langle \Delta r \rangle_{av} / r_e = \alpha_e v / B_o \tag{62}$$

and

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$$\langle\mu^2\rangle_{av} = \mu_o^2 \left(1 + \frac{1}{\theta}\frac{\alpha_e}{B_o} v\right). \tag{63}$$

Proceeding as before, we find that we have (considering only the effect of the dipole moment varying with each vibrational state)

$$\alpha = \left[\frac{8\pi^3\mu_o^2}{3hc}\frac{N}{p}\right]2B_o \left\{1 + \frac{1}{\theta}\frac{\alpha_e}{B_o} \left[\exp\left(\frac{hc}{kT}\omega_o\right)-1\right]^{-1}\right\} . \tag{64}$$

On combining the effects of variable B and μ, we obtain

$$\alpha = \left[\frac{8\pi^3\mu_o^2}{3hc}\frac{N}{p}\right]2B_o \left\{1 - \left(1-\frac{1}{\theta}\right)\frac{\alpha_e}{B_o} \left[\exp\left(\frac{hc}{kT}\omega_o\right)-1\right]^{-1}\right\} . \tag{65}$$

The comments made after Eq. (57) also apply here, although the magnitude of the correction is considerably smaller, in general.

Thus the expression for the rotational band intensity combining the corrections for the variation of B and μ with both v and J can be written as follows:

$$\alpha = \left[\frac{8\pi^3\mu_o^2}{3hc}\frac{N}{p}\right]2B_o \left\{1 - \left(1-\frac{1}{\theta}\right)\left(4\gamma^2\frac{kT}{hcB_o} + \frac{\alpha_e}{B_o}\left[\exp\left(\frac{hc}{kT}\omega_o\right)-1\right]^{-1}\right)\right\}. \tag{66}$$

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