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The Envelopes of Infrared Absorption Bands

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The *intensity formulae for the fine structure absorption lines of molecules of the symmetrical rotator type* are approximated by replacing the sums appearing therein by integrals. The resulting expressions are evaluated explicitly and may be used either to determine the intensity of an individual line or the envelope of all the fine structure lines. The envelopes of those bands corresponding to $\parallel$ type vibrations possess *P*, *Q*, and *R*-branches. The envelope may be characterized by two quantities, the relative intensity of the zero branch and the doublet separation which serve to fix the values of the moments of inertia *A* and *C*. The envelopes of the $\perp$ type vibrations are also determined and are plotted for a series of ratios of the moments of inertia. The range of validity of the approximation is discussed and the results applied to the infrared bands of the methyl halides. The doublet separations of the $\parallel$ type bands of these molecules are known and these (through the use of a plausible assumption regarding *C*) yield the following values of *A*, the moment of inertia $\perp$ to the symmetry axis. $A=32$, 61, 89, 99, $\times 10^{-40}$ for CH_3F, CH_3Cl, CH_3Br, CH_3I, respectively. The distances between the carbon and halide nuclei are computed and compared with the corresponding distances deduced by Pauling. The agreement is satisfactory.

§1. INTRODUCTION

THE absorption bands of molecules in the near infrared region of the spectrum exhibit a fine structure because of changes in the rotational energy of the molecule which occur simultaneously with a change in the vibrational energy. In the case of diatomic molecules the positions of the lines and also their relative intensities may be expressed in a very simple manner. By neglecting interaction terms, which are usually small, the positions of the lines are given by $\nu=\nu_0 \pm Jh/4\pi^2 A$, where J may take the values 1, 2, etc. The intensities of the lines on the high-frequency side of ν_0 are proportional to $Je^{-\sigma J(J-1)}$, while those on the low-frequency side are proportional to $Je^{-\sigma J(J+1)}$, where $\sigma=h^2/8\pi^2 AkT$.

In the case of the symmetrical rotator molecule (a molecule two of whose principal moments of inertia are equal, *viz.*, $A=B\neq C$) the positions and intensities of the fine structure lines may also be given explicitly.[1] The form in which the intensities are expressed is neither as simple nor as convenient to use as that for the diatomic molecule, since the formulae involve sums and double sums over a number of terms which may be large. These sums may be approximated by definite integrals, and it is the purpose of the present paper to evaluate these integrals. We believe that these expressions will be found useful and that in most cases they will lead to sufficiently accurate values for the intensities. They do, however, possess certain limitations which will be discussed in the final section of this paper.

§2. THE PARALLEL BANDS

In most molecules of the symmetrical rotator type the vibrations may be divided into two classes. In one of these the electric moment oscillates along, or parallel to, the symmetry axis; in the other the electric moment oscillates perpendicular to the symmetry axis. It is very convenient to discuss the fine structures of these two classes of bands separately. (Even if bands were observed for which the electric moment oscillated neither wholly $\parallel$ nor $\perp$ to the axis this method would still be applicable.)

The rotational energy of a symmetrical rotator molecule is given by $W_r=(h^2/8\pi^2 A)[J(J+1)+\beta K^2]$ where $\beta=(A/C)-1$. The selection rules for the $\parallel$ type bands are $\Delta J=\pm 1$, 0 and $\Delta K=0$. If ν_0 is the vibrational frequency the positions

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[1] Cf. D. M. Dennison, Rev. Mod. Phys. 3, 314 (1931). The squares of the amplitudes appearing on pp. 313 and 314 as well as the intensity formulae themselves should all be multiplied by the factor 4. This correction does not, of course, affect the relative intensities of the lines, but only their absolute intensities.

of the fine structure lines are then given by the following expressions, where the interaction terms between vibration and rotation have been neglected.

$$+\text{ branch } \nu_{J}^{J-1}{}_{K}^{K}=\nu_0+Jh/4\pi^2A,$$

$$0\text{ branch } \nu_{J}^{J}{}_{K}^{K}=\nu_0,$$

$$-\text{ branch } \nu_{J-1}^{J}{}_{K}^{K}=\nu_0-Jh/4\pi^2A.$$

The intensities of the lines may then be determined with the aid of the following expressions, where σ has the same value as that already given, and $[2]$ is a symbol equal to 1 when $K=0$ and equal to 2 when $K\neq 0$.

$$+\text{ branch } I_J^{J-1}=rL\sum_{K=0}^{J-1}[[2](J^2-K^2)/J]e^{-\sigma J(J-1)-\sigma\beta K^2},$$

$$0\text{ branch } I_J^{J}=4rL\sum_{J=0}^{\infty}\sum_{K=0}^{J}[K^2(2J+1)/2J(J+1)]e^{-\sigma J(J-1)-\sigma\beta K^{\cdot}},$$

$$-\text{ branch } I_{J-1}^{J}=(I_J^{J-1})e^{-2\sigma J}.$$

For any given band rL is a constant which for convenience is split into two parts, r, which is a function of A and B, and L, which is independent of these constants. Thus

$$r=1/(\sum g_{JK}e^{-W_{JK}/kT})$$

and

$$L=[8\pi^3\nu_0N/3ch](V_{\xi V'}^{V''})^2(1-e^{-h\nu_0/kT}).$$

It may be shown that L is equal to the sum of the intensities of all the fine structure lines.

The approximation which will now be employed is equivalent to assuming that the values of J and K for the states in question are large compared with unity. In this case the quantity $J(J+1)$ may be replaced by J^2, $2J+1$ by $2J$, etc., and the sums may be replaced by integrals. Thus the intensity of the zero branch is given by the double integral

$$I_0=4rL\int_{J=0}^{\infty}\int_{K=0}^{J}(K^2/J)e^{-\sigma J^2-\sigma\beta K^2}dKdJ.$$

The intensity of the Jth line of the positive branch is, in the approximation, equal to that of the Jth line of the negative branch, and is equal to

$$I_J=2rL\int_0^J[(J^2-K^2)/J]e^{-\sigma J^2-\sigma\beta K^2}dK.$$

The constant r is determined by means of a double integral rather than a double sum and may be explicitly evaluated.

$$r=1\bigg/\int_{J=0}^{\infty}\int_{K=0}^{J}4Je^{-\sigma(J^2+\beta K^2)}dKdJ$$
$$=\sigma[\sigma(1+\beta)/\pi]^{\frac{1}{2}}.$$

It will be noticed that r is the approximate value of the reciprocal of the "Zustandsumme." L is a constant which is equal to the total intensity of the band, as may be seen by integrating over all the band lines.

The evaluation of the integrals determining I_0 and I_J may be carried out by standard methods. For I_0 the first integration, over K, may be rewritten with the substitution $K=Jt$ where J is now constant, and t is a variable running from 0 to 1. The integral becomes

$$I_0=4rL\int_{J=0}^{\infty}\int_{t=0}^{1}(J^2t^2/J)e^{-\sigma J^2-\sigma\beta J^2t^2}JdJdt$$

since the limits are constant the order of integration may be reversed, giving as a result

$$I_0=\frac{L\{\log[\beta^{\frac{1}{2}}+(1+\beta)^{\frac{1}{2}}]-[\beta/(1+\beta)]^{\frac{1}{2}}\}}{\beta[\beta/(1+\beta)]^{\frac{1}{2}}},\quad \beta>0$$

$$I_0=L/3,\quad \beta=0$$

$$I_0=\frac{L\{[-\beta/(1+\beta)]^{\frac{1}{2}}-\sin^{-1}(-\beta)^{\frac{1}{2}}\}}{-\beta[-\beta/(1+\beta)]^{\frac{1}{2}}},\quad \beta<0.$$

It is evident from these expressions that I_0 can be written as a certain fraction of L, which is a function of β alone, independent of σ.

The constant $\beta=(A/C)-1$ has a range of values from $-\frac{1}{2}$ to $+\infty$. For a disk-shaped molecule $\beta=-\frac{1}{2}$; for a spherical molecule $\beta=0$, and for a linear (e.g., diatomic) molecule $\beta=+\infty$. In the mathematical treatment the expressions containing positive values of β must be handled separately from those containing negative values. In general this leads to different functions of β (such as, for example, those giving I_0); these functions are, however, continuous at $\beta=0$, as one has a right to expect.

The expression for I_J involves only a single integration which may readily be evaluated according to the several ranges of β.

$$I_J=(L/\beta)[\sigma(1+\beta)/\pi]^{\frac{1}{2}}e^{-\sigma J^2}\left\{[(2\sigma\beta J^2-1)/J(\sigma\beta)^{\frac{1}{2}}]\int_0^{J(\sigma\beta)^{\frac{1}{2}}}e^{-u^2}du+e^{-\sigma\beta J^2}\right\}\quad\text{for }\beta>0,$$

$$I_J=(4/3)L\sigma(\sigma/\pi)^{\frac{1}{2}}J^2e^{-\sigma J^2}\quad\text{for }\beta=0,$$

$$I_J=(-L/\beta)[\sigma(1+\beta)/\pi]^{\frac{1}{2}}e^{-\sigma J^2}\left\{[(1-2\sigma\beta J^2)/J(-\sigma\beta)^{\frac{1}{2}}]\int_0^{J(-\sigma\beta)^{\frac{1}{2}}}e^{u^2}du-e^{-\sigma\beta J^2}\right\}\quad\text{for }\beta<0$$

The formulae just obtained give approximately the intensity of the Jth line. Some modifications may have to be made in the case of molecules possessing several like atoms, for here the weights will be influenced by the nuclear spins. Such modifications will usually not be difficult to perform.

The approximate intensity formulae depend on the assumption that J and K are both large. This condition will be best fulfilled for heavy molecules (i.e., molecules with large moments of inertia) where each band contains many rotational lines which are very closely spaced. In this case, however, the spectrometer may not be able to resolve the individual lines, but only determine their envelope.[2] We wish to show that the properties of this envelope will yield information concerning the moments of inertia of the molecule.

We shall first consider the intensity of the zero branch as compared with that of the whole band; the ratio function R is defined as $R=I_0/L$. It was shown earlier that the total intensity of the whole parallel band is equal to L; the ratio function R for the various ranges of β is thus simply the corresponding I_0, as given above, divided by L. This ratio has been calculated as a function of β and is plotted as such in Fig. 1. For a disk-shaped molecule, $\beta=-\frac{1}{2}$, the zero branch intensity is almost half that of the whole band. For a spherical molecule the intensities of the three branches are equal, $R=\frac{1}{3}$, and as β increases the zero branch intensity decreases steadily. In the limit where $\beta=\infty$ we have in effect a linear molecule, and $R=0$, as it should, because such a molecule shows no zero branch at all in its $\|$ type bands. Thus if the ratio R could be measured experimentally it would then be possible to determine β from Fig. 1.

We consider next the separation between the maxima of the positive and negative branches in the parallel bands. The doublet separation for the absorption bands of diatomic molecules is analogous to this, and is in fact a special case of the more general doublet separation to be discussed now.

The doublet separation may be connected with the values of J corresponding to the most intense lines of the positive and negative branches by

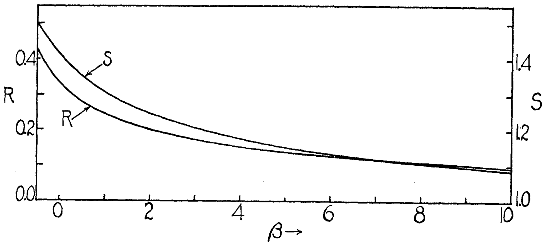

FIG. 1. The intensity ratio I_0/L for the zero branch and the separation function $S(\beta)$.

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[2] Experimentally an infrared absorption band is determined by a curve giving the percentage transmission of the substance as a function of frequency. From these data a curve may be calculated giving the absorption coefficient P_ν as a function of ν. When the individual lines of the band are not resolved the value of P_ν found represents an average absorption coefficient and is equal to the average intensity of the lines in this region divided by the interval between them. In the present case the spacing of the lines is uniform and equal to α and therefore $P_\nu=I/\alpha$.

means of the following expression, where $\alpha = h/4\pi^2 A$.

$$\Delta\nu = \alpha(J^{+}_{\max} + J^{-}_{\max}).$$

To the approximation being considered in this paper $J^{+}_{\max} = J^{-}_{\max}$ and accordingly $\Delta\nu = 2\alpha J_{\max}$. The problem thus resolves itself into finding the number J of the most intense line. This may be done by setting the first derivative of I_J with respect to J equal to zero and solving for $J_{\max}$.[3] $J_{\max}$ and consequently $\Delta\nu$ is a function both of A and of β, fortunately, however, this function may be divided into two factors, the first of which, $S(\beta)$, contains β alone, and is simply connected with the root of the transcendental equation obtained by setting $\partial I_J/\partial J = 0$, the second factor is the doublet separation for a diatomic molecule.

$$\Delta\nu = S(\beta)[(kT/A)^{\frac{1}{2}}/\pi].$$

The separation function, $S(\beta)$, is plotted as S in Fig. 1, it decreases from about 1.5 for $\beta = -\frac{1}{2}$ to $2^{\frac{1}{2}}$ for $\beta = 0$ and approaches unity as β becomes infinite. The relation between S and β is given by the following empirical formula, which is accurate to within 0.5 percent for all values of β from $\beta = -\frac{1}{2}$ to $\beta = 100$.

$$\log_{10} S = 0.721/(\beta+4)^{1.13}.$$

The envelope of a single parallel band yields two data from which can be obtained the moments of inertia of the molecule under investigation. The ratio of the intensity of the zero branch to that of the whole band gives at once the value of β, by means of the ratio function R. This value of β determines the appropriate value of S to use in the above expression for $\Delta\nu$, which is the other experimental datum. The moment of inertia A is thereby determined, and this in conjunction with β gives the moment of inertia C.

When one of the moments of inertia is already known, the doublet separation can be used for finding the other. If A is known S can be calculated directly from the expression for $\Delta\nu$ and this in turn gives β, and hence C. If, on the other hand C is known, then the following expression will give β, and finally A.

$$S/(1+\beta)^{\frac{1}{2}} = [(\Delta\nu)\pi C^{\frac{1}{2}}]/(kT)^{\frac{1}{2}}.$$

§3. PERPENDICULAR BANDS

The perpendicular type bands are those bands for which the electric moment oscillates perpendicular to the figure axis. The selection rules of the rotational quantum numbers are $\Delta J = 0, \pm 1$, and $\Delta K = \pm 1$. The fine structure lines for which $\Delta J = 0$, $\Delta K = \pm 1$ are multiple because the frequency of this transition does not depend upon the particular value of J. These lines are often called the zero branch lines and their intensities are given by formulae of the following type,

$$I^{J\,K}_{J\,K-1} = rL \sum_{J=K}^{\infty} [(2J+1)(J-K+1)(J+K)/2J(J+1)] e^{-\sigma[J(J+1)+\beta K^2]}.$$

The line whose intensity is given above has the frequency $\nu = \nu_0 - (h\beta/4\pi^2 A)(K+\frac{1}{2})$.

In the approximation to which we are working the intensity expression becomes

$$I_0 = rL \int_K^{\infty} [(J^2-K^2)/J] e^{-\sigma(J^2+\beta K^2)} dJ.$$

The first part of the integrand may be integrated directly; the second part may be transformed into the logarithmic integral for which tables are available. In this way the intensity of the Kth zero branch line may be readily approximated,

$$I_0 = (L/2)[\sigma(1+\beta)/\pi] e^{-\sigma\beta K^2} \left[e^{-\sigma K^2} + \sigma K^2 \int_{\infty}^{\sigma K^2} u^{-1} e^{-u} du \right].$$

In order to obtain the envelope of the zero branch lines the quantity P, absorption coefficient, must be introduced. The position of the

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[3] In making the computations the substitution $z = J(\sigma\beta)^{\frac{1}{2}}$ was made, and the differentiation carried out with respect to z.

Kth line (in our approximation) is $\nu=\nu_0+\alpha\beta K$, where $\alpha=h/4\pi^2A$. The spacing of the lines is uniform and equal to $\alpha\beta$, and consequently the average absorption coefficient at a given frequency is equal to the intensity of the line nearest this frequency divided by $\alpha\beta$. For computational purposes it is convenient to introduce instead of the frequency a quantity x proportional to it; $x=(\nu/\alpha)\sigma^{\frac{1}{2}}$. The contribution to the absorption coefficient made by the zero branch lines may be obtained from I_0 by the transformations indicated,

$$P_0=(L/2\alpha|\beta|)\sigma^{\frac{1}{2}}[(1+\beta)/\pi]^{\frac{1}{2}}e^{-x^2/\beta}\left[e^{-(x/\beta)^2}+(x/\beta)^2\int_{\infty}^{(x/\beta)^2}u^{-1}e^{-u}du\right].$$

The absorption coefficient is thus given as a function of x, the distance from the center of the band expressed in units of $\sigma^{\frac{1}{2}}/\alpha$. This formula is valid for both the positive and negative values of β.

The remaining lines of the $\perp$ bands correspond to the changes of the quantum numbers $\Delta J=\pm1$, $\Delta K=\pm1$. Taken together they will form a practically continuous region of absorption, which we will designate as background absorption. As before, we shall first treat the intensities exactly, and later approximate them in the region where J and K are large compared with unity.

Consider the background absorption at a point ν frequency units to the high-frequency side of the band center ν_0. The lines which contribute to this absorption may be divided into three classes. First there are the lines where $\Delta K=+1$, $\Delta J=+1$, whose position relative to the center of the band is

$$\nu^{J\ \ K}_{J+1\ K+1}=\alpha(J+1)+\alpha\beta(K+\tfrac{1}{2}),$$

second the lines $\Delta K=-1$, $\Delta J=1$, $\nu=\alpha(J+1)-\alpha\beta(K-\frac{1}{2})$, and third the lines $\Delta K=1$, $\Delta J=-1$, $\nu=-\alpha J+\alpha\beta(K+\frac{1}{2})$. We shall compute the absorption coefficient arising from the first class of lines. The wave-mechanical intensity of a line in this class is

$$I^{J\ \ K}_{J+1\ K+1}=rL[(J+K+2)(J+K+1)/2J]e^{-\sigma J(J+1)-\sigma\beta K^2}.$$

For a given value of K the lines of this class are uniformly spaced in frequency with an interval between them of α. The absorption coefficient is therefore $P=I/\alpha$. There will, however, be contributions to the absorption coefficient at this point from transitions involving various values of J and K in all those cases where the quantum numbers satisfy the relation[4]

$$\nu=\alpha(J+1)+\alpha\beta(K+\tfrac{1}{2}).$$

The total background absorption at the point ν of the class I lines may be found by eliminating J from the above intensity expression and summing over all the allowed values of K, thus

$$(P_b)_1=(rL/2\alpha)\sum_{K=0}^{K=(\nu/\alpha-1-\beta/2)/(1+\beta)}\frac{[\nu/\alpha+1-\beta/(K+\frac{1}{2})][\nu/\alpha-\beta(K+\frac{1}{2})]}{\nu/\alpha-1-\beta(K+\frac{1}{2})}e^{-f(\nu,\,\alpha,\,K)},$$

where

$$f(\nu,\alpha,K)=\sigma\{[\nu/\alpha-\beta(K+\tfrac{1}{2})]^2-(3\nu/\alpha)\beta(K+\tfrac{1}{2})+2+\beta K^2\}.$$

The L in this expression corresponds exactly to the L appearing in the formula for the $\parallel$ bands and is equal to the total intensity of the complete band. We may now proceed to approximate the above expression; as before, we take J and K to be large compared with unity, and replace the summation by an integration:

$$(P_b)_1=(rL/2\alpha)\int_0^{\nu/\alpha(1+\beta)}\{[(\nu/\alpha)+K(1+\beta)]^2/[(\nu/\alpha)-\beta K]\}e^{-\sigma\{[(\nu/\alpha)-\beta K]^2-\beta K\}}dK.$$

The contributions to the absorption coefficient arising from the lines in classes II and III may

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[4] Of course, if β is irrational only one set of values of J and K will satisfy this relation, i.e., only one line falls

be treated in a similar manner. The total absorption coefficient, P_b, is then the sum of these three terms. We introduce the variable $x=(\nu/\alpha)\sigma^{\frac{1}{2}}$, together with the following symbols, $B=(1-\beta)/(1+\beta)$; $C=x/[|\beta|(1+\beta)]^{\frac{1}{2}}$ $y=2C|\beta|/(1-\beta)$. For computational purposes three ranges of β must be considered separately, $\beta<0$, $0\leq\beta\leq 1$, $\beta>1$.

$\beta<0$,

$$P_b=(L\sigma^{\frac{1}{2}}/2\alpha\pi^{\frac{1}{2}})\beta^{-2}(1+\beta)^{\frac{3}{2}}e^{-x^2/(1+\beta)}\left[B^2(1-e^{y^2})/2+(B^2C-2B)\int_0^y e^{-\nu^2}d\nu+C^2\int_{-y}^0(\nu+c)^{-1}e^{\nu^2}d\nu\right].$$

$0\leq\beta\leq 1$,

$$P_b=(L\sigma^{\frac{1}{2}}/2\alpha\pi^{\frac{1}{2}})\beta^{-2}(1+\beta)^{\frac{3}{2}}e^{-x^2/(1+\beta)}\left[B^2(1-e^{-y^2})/2+(B^2C-2B)\int_0^y e^{-\nu^2}d\nu+C^2\int_0^y(\nu+c)^{-1}e^{-\nu^2}d\nu\right].$$

$\beta>1$,

$$P_b=(L\sigma^{\frac{1}{2}}/2\alpha\pi^{\frac{1}{2}})\beta^{-2}(1+\beta)^{\frac{3}{2}}e^{-x^2/(1+\beta)}\left[B^2(1-e^{-y^2})/2+(B^2C-2B)\int_0^{-y} [e^{-\nu^2}d\nu\right.$$

$$\left.+C^2\left\{e^{-C^2}\int_{y^2-C^2}^{\infty}u^{-1}e^{-u}du+\int_0^{-y}(\nu+C)^{-1}e^{-\nu^2}d\nu\right\}\right].$$

These expressions may be readily evaluated with the exception of the final definite integrals. Even here the integrands are relatively simple functions and accordingly the values of the integrals may be obtained rather easily by means of numerical quadrature.

The results of these computations have been collected in Fig. 2, which represents the envelopes of the ⊥ type bands for $\beta=-\frac{1}{2}$, $-\frac{1}{3}$, $\frac{1}{2}$, 1, and 4, respectively.

For each value of β the full line represents the total absorption coefficient (zero branches plus background) as a function of x, while the dotted line gives the absorption coefficient due to the zero branch lines alone. The two vertical lines along the axis indicate the doublet separation of the parallel type band for the same value of β.

For $\beta=-\frac{1}{2}$ the envelope presents the appearance of three almost equal maxima with a doublet spacing considerably smaller than that of the corresponding parallel band. As β grows the central peak becomes sharper and higher, while the doublet spacing increases. At $\beta=0$ we have all three moments of inertia of the molecule equal, and there is no distinction between a ⊥ and a || type band. For larger values of β the

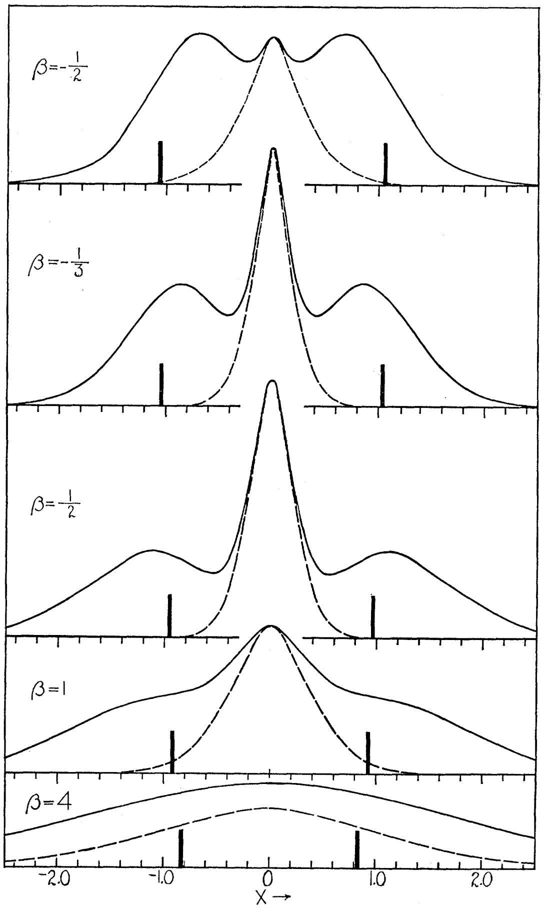

FIG. 2. Envelopes of the ⊥ type bands for various values of β.

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exactly at a given point, ν. We are, however, not interested in the intensity at a point, but rather in the average absorption coefficient in its immediate neighborhood. Thus for any particular K we are interested in the Jth line which most nearly satisfies the frequency relation.

central peak becomes broader and lower, while the doublet separation increases over that of the $\|$ type band. For values of β greater than unity the envelope no longer presents the appearance of three maxima, and for sufficiently large values of β the envelope resembles a Gauss error curve. In fact it may be shown that in the limit of large β the total absorption coefficient is given by

$$P=(L/\alpha\beta)[\sigma(1+\beta)/\pi]^{\frac{1}{2}}e^{-x^2(1+\beta)/\beta^2}.$$

§4. Discussion and Application

Before proceeding to apply the results of the foregoing calculations we shall discuss the region in which they are valid. The intensity formulae for those lines near the center of the band (or their envelope) may well be somewhat in error, because our approximation has been one which implies that K and J are large compared with unity. This limitation is not at all a serious one since the intensities of these lines may be readily computed from the exact formulae (i.e., the summations consist of only a few terms).

A second limitation of a much more serious character affects our formulae for the intensities (or envelopes) of the lines of the perpendicular bands. If the symmetry of the symmetrical rotator is a result of a geometrical symmetry of the atoms forming the molecule the lines of the perpendicular bands may suffer certain anomalies. Thus it is well known that the spacing of the fine structure lines of the infrared bands of methane is not a constant, but varies from band to band. The same phenomenon is observed in the $\perp$ bands of the methyl halides. A theory of this effect based on an interaction between vibration and rotation has been proposed by Teller and Tisza.[5] Their general conclusions may be stated very simply, *viz.*, the position of a line corresponding to the transition $\Delta K=\pm 1$, $\Delta J=0$, ± 1 will be given by the following expressions respectively

$$\nu=\nu_0\pm\alpha J\pm\alpha(\beta+\beta')(K\pm\tfrac{1}{2});\quad \Delta J=\pm 1$$

$$\nu=\nu_0\pm\alpha(\beta+\beta')(K\pm\tfrac{1}{2});\qquad \Delta J=0.$$

As before $\beta=(A/C)-1$ but β', which may be of the same order of magnitude as β, depends upon the anharmonic terms in the potential energy and cannot be evaluated without a more detailed knowledge of the molecular structure than we now possess.

Thus the spacing of the lines in a $\perp$ band of this class of molecule gives no direct information concerning the moments of inertia of the molecule. The envelope of these lines depends directly upon β' and consequently it also cannot be predicted *a priori.* However, Teller and Tisza's theory shows that while the positions of the lines depend upon β', their intensities are just what they would be if β' were zero. Consequently if β' were known the envelope would be given through a simple modification of our expressions. Fortunately this second limitation does not at all apply to the lines of the parallel bands. Although the infrared spectra of a considerable number of molecules of the symmetrical rotator class have been investigated only one group, the methyl halides, has so far yielded data to which our theory may be applied. It is true that in addition to these the spectrum of ammonia has been observed, but the moments of inertia of this molecule are so small that the fine structure lines are relatively few in number and completely separated. It is more suitable in the case of this molecule to use the exact expressions for the intensities of the lines. The spectra of other symmetrical molecules with large moments of inertia have been mapped, but not with spectroscopes of sufficiently high resolving power to reveal the structure of the envelopes. There seems, however, to be no reason why these envelopes cannot eventually be obtained.

The infrared spectra of the methyl halides have been observed by Bennett and Meyer[6] in the region from 3μ to 14μ and by Moorhead[7] in the region from 1.5μ to 3μ. A considerable number of parallel type bands were found by both investigators, but only one, the 9.55μ band of methyl fluoride, was resolved into its fine structure lines. The methods by which the bands were obtained were such that the ratio of intensity of the zero branch to that of the whole band is not given with sufficient accuracy to use in our formulae. The measured values of the

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[5] Teller and Tisza, Zeits. f. Physik **73**, 791 (1932).

[6] Bennett and Meyer, Phys. Rev. **32**, 888 (1928).

[7] J. G. Moorhead, Phys. Rev. **39**, 788 (1932).

TABLE I. *Measured values of doublet separation.*

	B. and M.	M.	$\Delta\nu$	$A\times10^{40}$
CH_3F	43, 44	—	43.5	32
CH_3Cl	35, 28, 28, 23	35, 33, 28	30.0	61
CH_3Br	25, 23, 23	26, 25, 24	24.2	89
CH_3I	23, 21, 21	27, 24, 21	22.8	99

doublet separation seem to be fairly concordant and these we have collected in Table I. The first column gives the measurements of Bennett and Meyer and, the second the measurements of Moorhead, while the third column represents their average in waves/cm. These experimental values for the doublet separation are each determined independently since the bands in question lie in quite different regions of the spectrum.

This one datum, the doublet separation, does not serve to determine either A or C but does constitute a relation between them. In the case of the methyl halides we may obtain an additional relation by assuming that the moment of inertia along the symmetry axis C, is the same for each molecule and is equal to the moment of inertia of methane. This assumption seems very plausible and is equivalent to assuming that the methyl group is relatively little influenced by the halide atom. In any case since β is large the value of A as determined from the doublet separation is relatively insensitive to small changes in C.

Teller and Tisza have estimated the moment of inertia of methane to be 5.3×10^{-40}. With this value and the relation between C, β and S mentioned previously, we obtain the values for the moment of inertia A which are given in the fourth column of Table I. No great accuracy can be claimed for these values and it would be very desirable to have a check on them. In the case of methyl fluoride this is possible since the fine structure of one of the bands has been resolved, yielding the value $A=39.5\times10^{-40}$. The agreement is not good but may be regarded as fairly satisfactory.

An estimate of the distance between the carbon and the halide nuclei may be made if we continue to use the assumption that the methyl group is identical in all the methyl halide molecules and is equal to the methyl group in methane. On this basis our values for A and C determine the following distances in Angstroms $C-Cl=1.80$; $C-Br=1.99$; $C-I=2.05$.

The $C-Cl$ distance in methyl chloride has been measured by R. Wierl,[8] from electron diffraction patterns and found to be 1.85 ± 0.06. Our results for the internuclear distances may also be compared with the atomic radii as determined by Pauling.[9] According to Pauling's work $C-Cl=1.76$, $C-Br=1.91$, and $C-I=2.10$.

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[8] R. Wierl, Ann. d. Physik **8**, 521 (1931).

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