The Interaction Between Vibration and Rotation for Symmetrical Molecules

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The explanation first proposed by Teller of the anomalous fine structure of the infrared bands of symmetrical molecules is discussed. The fine structure is closely related to an internal angular momentum of magnitude $\zeta h/2\pi$ which is due to the vibration of the molecule and arises from the degenerate character of the motion. A simple derivation is given for the spacing constant $[(1-\zeta)/C-1/A]h/4\pi^2$ of axially symmetric molecules and for the spacing constant $(1-\zeta)h/4\pi^2 A$ of tetrahedral molecules. A detailed calculation is made of the internal angular momenta to be associated with the $\perp$ frequencies ν_2 and ν_4 of the axial molecule YX_3. The resulting ζ's are found as functions of the moments of inertia and of the potential constants. The sum $\zeta_2+\zeta_4$ is shown to have the value $C/2A-1$. These results are applied to the molecules NH_3 and ND_3 and the line spacings of ν_2 and ν_4 are computed. The axial molecule ZYX_3 is treated and it is proved that the sum of the ζ's characterizing the three $\perp$ bands ν_2, ν_4, and ν_6 is equal to $C/2A$. The moment of inertia C of the methyl halides is computed and found to be, 5.61, 5.35, 5.44, and 5.44×10^{-40} for methyl fluoride to methyl iodide, respectively. The error is estimated to be around 5 percent. A calculation is made of the ζ's to be associated with the overtones of axial molecules possessing threefold symmetry. It is found that the ζ appropriate for the overtone $2\nu_i$ of a $\perp$ frequency is $-2\zeta_i$ while the ζ for $3\nu_i$ is ζ_i itself. The combination of two $\perp$ frequencies $\nu_2+\nu_4$ is next treated and the ζ is proved to be $-(\zeta_2+\zeta_4)=1-C/2A$. An application of these formulae to the observed spacings of the overtone bands of NH_3 and CH_3Cl results in a very satisfactory agreement. Expressions are obtained for the two ζ's which determine the line spacings of the active fundamentals ν_3 and ν_4 of the tetrahedral molecule YX_4. It is shown that $\zeta_3+\zeta_4=\frac{1}{2}$. The positions of the fundamental bands of methane together with the line spacings of ν_3 and ν_4 yield the moment of inertia $A=5.47\times 10^{-40}$ together with the five potential constants describing the molecule. A good agreement is found between these constants and those obtained by Ginsburg and Barker from the spectrum of methyl deuteride. The ζ's suitable for the overtones of YX_4 are next treated. It is found that the ζ to be used with $2\nu_i$, $i=3, 4$ is $-\zeta_i$ while the ζ belonging with the combination band $\nu_3+\nu_4$ is $-\frac{1}{2}(\zeta_3+\zeta_4)=-\frac{1}{4}$. The observations on the overtones of methane are in very good accord with these expressions. Less satisfactory agreement is obtained in the case of the silane spectrum where it appears that the higher order perturbation terms play a larger role.

§1. INTRODUCTION

DURING the past several years, great progress has been made in interpreting the spectra of polyatomic molecules. The molecule has been represented by a system of mass points whose equilibrium positions constitute the configuration of the molecule. It is assumed that, in zeroth approximation, the mass points are bound by elastic forces and that throughout their vibratory motion they remain essentially in the neighborhood of their equilibrium configuration. From this model it has been possible to understand the spectra of many molecules and to compute such physical constants as the potential energy function and the dimensions of the system. However, one grave difficulty has appeared in that the simple theory predicts that for a given molecule all the infrared bands which correspond to a particular type of vibration should show the same fine structure. This prediction is fulfilled for many types of vibration, for example, the $||$ bands of ammonia. However, it is flagrantly violated for others, notably the bands of methane and the $\perp$ bands of the methyl halides.

A solution to this problem has recently been given by Teller[1] who has pointed out that those vibrations which show anomalous fine structure are degenerate and may possess an angular momentum arising from the vibratory motion itself. The interaction between this angular momentum and that due to the rotation of the molecule will just account for the observed effects. The purpose of the present paper is to extend Teller's theory and to make detailed calculations for several molecular models.

The algebra involved in the computations is often rather complicated and may hide the simplicity of the underlying ideas. The vibratory motion of the nuclei may be regarded as a motion taking place on a slowly rotating turntable corresponding to the rotation of the molecule. This rotation of the system introduces a Coriolis force into the vibrational motion which in turn makes a contribution to the energy. In general, the con-

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[1] E. Teller, *Hand- und Jahrbuch d. chem. Physik* (1934), Vol. 9, p. 125.

tribution is very small (of second order) since the motion of each particle relative to the turntable is, to a high approximation, simple harmonic motion along a straight line. Thus the average Coriolis force is zero. However, for a degenerate vibration, which corresponds to the existence of two or more harmonic motions of equal frequency at right angles to each other, this is by no means the case. A suitable choice of amplitudes and phases renders the motion for each particle circular or at least elliptical. Here the average Coriolis force does not vanish but has the value $\pm k\omega$ where k is a proportionality factor and ω is the angular velocity of the turntable. The plus and minus signs relate to whether or not the circular motion of vibration is in the same direction as the rotation of the turntable. We shall now compute in detail the first order change in energy caused by the rotation.

It is convenient to introduce a moving coordinate system x, y, z whose axes are defined by the equilibrium positions of the nuclei and which coincide with the principal axes of inertia A, B, C. If the molecule possesses degenerate frequencies, there will be in general an angular momentum produced by the vibrational motion itself. The components of this internal angular momentum p, along the axes x, y, z will be designated by p_x, p_y, p_z. The eigenvalues of the internal angular momentum are not necessarily integral multiples of $h/2\pi$ since p relates to only part of the system, namely, the vibration, and does not take account of the rotation of the molecule. Following Teller we shall introduce ζ as the proportionality factor. In molecules having an axis of symmetry, such as the methyl halides, ammonia, etc., p lies along this axis and has the magnitude $\zeta h/2\pi$. For molecules having tetrahedral symmetry (methane) the vibrations in which we are interested possess spherical symmetry and consequently,

$$p^2 = l(l+1)\zeta^2 h^2/4\pi^2.$$

The quantity ζ is essentially dependent upon the vibrational properties of the molecule, that is, upon the relative dimensions, the masses, and the force constants. It has different values for the various normal modes of vibration. For this reason the individual bands of the same molecule may show different fine structure spacings. A knowledge of the ζ's as determined from the fine structure enables us to obtain information regarding the force constants of the molecule.

It is now necessary to consider the total angular momentum of the molecule P which includes the contributions due to the rotation and to the vibration. It has the components P_x, P_y, P_z along the moving axes and must be quantized. The formula for the rotational energy of a rotator involving an internal flywheel has appeared many times in the literature and has the form,

$$H_{\mathrm{rot}} = (P_x - p_x)^2/2A + (P_y - p_y)^2/2B + (P_z - p_z)^2/2C.$$

This expression has recently been carefully reexamined by Eckart,[2] Van Vleck,[3] and others, and appears to be entirely correct.

The rotational energy levels of the symmetric rotator, $A = B$, C may be readily obtained. The internal angular momentum for such a molecule must lie along the symmetry axis C and hence $p_x = p_y = 0$ and $p_z = \pm p$, the double sign indicating whether p is parallel or antiparallel to the C axis. We may write the rotational energy

$$H_{\mathrm{rot}} = (P_x^2 + P_y^2 + P_z^2)/2A + P_z^2(1/2C - 1/2A) \mp pP_z/C + p^2/2C.$$

The Hamiltonian may be diagonalized by using the representation for P such that P_z has only diagonal elements. $P_z = Kh/2\pi$ where K is a positive or negative integer. The total angular momentum is of course diagonal.

$$P_x^2 + P_y^2 + P_z^2 = J(J+1)h^2/4\pi^2.$$

Hence

$$W_{\mathrm{rot}} = J(J+1)h^2/8\pi^2 A + (1/C - 1/A)K^2 h^2/8\pi^2 \mp \zeta K h^2/4\pi^2 C.$$

The last term $p^2/2C$ may be omitted since it does not depend upon the rotation and hence may be absorbed into the vibrational energy.

In order to find the actual frequencies of the fine structure lines we must make use of the selection rules. These may be obtained by the rather laborious process of examining the matrix elements of the electric moment. However, they

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[2] C. Eckart, Phys. Rev. **47**, 552 (1935).

[3] J. H. Van Vleck, Phys. Rev. **47**, 487 (1935).

may be easily understood from the following argument. The electric moment depends upon the positions of the nuclei. In the coordinate system x, y, z which moves with the molecule, the electric moment executes circular motion about the axis of symmetry. Suppose that the direction of rotation of the electric moment is in the same sense as the direction of the angular momentum of vibration p. Now if p and P_z are in the same sense (in which case we use the upper or minus sign in the expression for W_{rot}) the motion of the electric moment may be described as a rotation about the symmetry axis with a frequency $\nu_0+\nu_K$ and a precession about the P axis with a frequency ν_J. Thus, if the vibrational quantum number goes from $0\rightarrow 1$ we have $K\rightarrow K+1$ and $J\rightarrow J-1$, $J\rightarrow J+1$, or $J\rightarrow J$ as the possible transitions. In the case where p and P_z are in opposite senses, the frequency of rotation is clearly $\nu_0-\nu_K$ and the selection rules are, vibrational number $0\rightarrow 1$, $K\rightarrow K-1$ and $J\rightarrow J-1$, $J\rightarrow J+1$, or $J\rightarrow J$. We must here use the plus sign in W_{rot}.

In the $\perp$ bands of axial molecules it usually happens that only the so-called zero-branch lines for which $J\rightarrow J$ are observed. The frequency of the fine structure lines under *either* of the above sets of rules (p parallel or antiparallel to P_z) is then

$$\nu=\nu_0-(1/C-1/A)h/8\pi^2 +[(1-\zeta)/C-1/A]Kh/4\pi^2,\quad K=0,\ \pm 1,\ \pm 2,\ \cdots.$$

In deriving this formula it was assumed that the direction of rotation of the electric moment was parallel to the angular momentum p. However, it may occur that the rotation of the electric moment and the internal angular momentum are antiparallel. In this case the selection rules are just reversed and the spacing of the zero-branch lines may be shown to be $[(1+\zeta)/C-1/A]\times(h/4\pi^2)$. It is convenient to retain only the first formula and to consider that ζ is positive or negative according to whether the rotation of the electric moment and the vibrational angular momentum have the same or opposite senses.

Finally it must be remarked that we have here considered a transition from the normal state, where there is no vibrational angular momentum, and consequently $\zeta=0$, to an excited state $\zeta=\zeta$. These bands are the ones most frequently observed experimentally. However, transitions may occur between two excited levels, each of which has a ζ different from zero. In this case the above formula for the fine structure lines would be altered.

The second class of molecules to be treated in this paper is the group of molecules which have tetrahedral symmetry. For these all three moments of inertia are the same. The Hamiltonian may be written in the simple form

$$H_{\text{rot}}=P^2/2A-(P\cdot p)/A+p^2/2A.$$

The first term becomes $J(J+1)h^2/8\pi^2A$ in virtue of the diagonal nature of the total angular momentum P^2, while the third term may be absorbed into the vibrational energy. The second term, which contains the scalar product of the total angular momentum P and the internal angular momentum p, represents the interaction which we wish to evaluate.

The fundamental frequencies of the methane molecule which are active in the infrared are to be associated with a transition from the normal state where there is no internal angular momentum to the first excited state of a three-dimensional isotropic oscillator. This latter state possesses an internal angular momentum p which may have the three eigenvalues $\pm\zeta h/2\pi$ and 0. Thus the interaction term I may be written $I=-(\Pi\cdot\pi)\zeta h^2/4\pi^2A$ where Π is a vector having eigenvalues J, $J-1$, $\cdots -J$ and π has the values 1, 0, -1. The expression for the eigenvalues of $(\Pi\cdot\pi)$ is well known in spectroscopy and is

$$2(\Pi\cdot\pi)=J(J+1)+2-R(R+1).$$

R is a vector which, when compounded with π, will give the total momentum Π. Evidently it may take on the values $J-1$, J, and $J+1$ thus yielding the following three eigenvalues for $(\Pi\cdot\pi)$; $J+1$, 1, and $-J$. Now the vector R corresponds to a rotation of the molecular framework and the three values for $(\Pi\cdot\pi)$ are to be correlated with the three possibilities, p parallel to P, p perpendicular to P, and p antiparallel to P, respectively. These considerations furnish a key to the selection rules and show that in making a transition from the normal to the excited state we must use the first, second, or third eigenvalue of $(\Pi\cdot\pi)$ according as $J-1\rightarrow J$, $J\rightarrow J$, or $J\rightarrow J-1$. We thus obtain the following formulae for the fine structure lines

Positive branch $J-1\rightarrow J$ $\quad \nu=\nu_0-h\zeta/4\pi^2A+Jh(1-\zeta)/4\pi^2A$

Zero branch $J\rightarrow J$ $\quad \nu=\nu_0-h\zeta/4\pi^2A$

Negative branch $J\rightarrow J-1$. $\quad \nu=\nu_0-h\zeta/4\pi^2A-Jh(1-\zeta)/4\pi^2A$.

It thus appears that the form of the vibration-rotation bands has not been changed by the introduction of an internal angular momentum. However the actual spacing of the fine structure lines is altered by the factor $(1-\zeta)$. These results, which have also been obtained by Teller, we believe to be correct only up to the first-order approximation here treated. In higher approximation where the particular symmetry of the molecule must be taken into account it seems probable that the fine structure lines will be divided into multiplets.[4] It is hoped shortly to make calculations on this effect of which there are already some experimental indications.

The formulae which have been developed show that the line spacing depends essentially upon a quantity ζ without a knowledge of which the experimental data cannot be interpreted. $\zeta h/2\pi$ represents the angular momentum due to the vibratory motion of the nuclei relative to a coordinate system defined by the equilibrium positions of the nuclei. This internal angular momentum may always be computed as a function of the force constants, the masses, and the relative dimensions of the molecule, but in many cases the actual calculation becomes very laborious and involved. There exists, however, an important theorem discovered by Teller[1] which states that the sum of the ζ's of all the first excited states belonging to a given symmetry class is independent of the force constants and is a function only of the masses and the relative dimensions of the molecule. The quantity $\Sigma\zeta$ is thus relatively simple to compute since in making the calculation we may use any type of force field, in particular, such forces that the motion of the system may be readily visualized. Immediate use may be made of $\Sigma\zeta$ since the sum of the fine structure spacings of all the fundamental bands of a given category depends only upon $\Sigma\zeta$ and not upon the individual ζ's. This point will be illustrated later in the present paper.

§2. AXIALLY SYMMETRIC MOLECULES

We begin our discussion of molecules having an axis of symmetry by considering the system YX_3, of which ammonia is a representative. It is well known that the regular pyramid YX_3 possesses four normal frequencies which are separated into two symmetry classes, the two $||$ frequencies and the two $\perp$ frequencies. Since these belong to different symmetry classes the Hamiltonian falls into two parts and there exist no interaction terms. It is only the $\perp$ frequencies which are degenerate and which may exhibit an internal angular momentum. Consequently we shall treat them exclusively in what follows. In separating the $||$ and $\perp$ vibrations it is only necessary to introduce symmetry coordinates; coordinates which are capable of specifying all possible configurations of the system which belong to the desired symmetry class.

We shall begin by obtaining the kinetic energy and we will make use of the theorem that the kinetic energy of any system may be regarded as the sum of two terms, the energy relative to the center of gravity of the system and the translational energy of the center of gravity. We shall divide the YX_3 molecule into two parts, the Y atom and the X_3 group. The energy may thus be written as the energy of the Y atom, the translational energy of the center of gravity of the X_3 group and the energy of the X_3 group relative to its center of gravity. The method of calculation is made clearer by Fig. 1. The dotted horizontal line is the equilibrium position of the figure axis. The center of gravity of the X atoms is shown by the letter G and the quantity y_1 is the sum of the displacements of the Y atom and G. The inclination of the plane of the X atoms to the symmetry line is indicated by the angle θ.

The kinetic energy of the whole system is then

$$T=\tfrac{1}{2}\mu\dot{y}_1^2+\tfrac{1}{2}I\dot{\theta}^2+T_0,$$

where μ is the reduced mass of the Y atom and G, that is, $\mu=3mM/(3m+M)$; m and M being the masses of the X and Y atoms, respectively. The

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[4] See the concluding portion of the present paper.

second term represents the energy of tipping of the X_3 triangle and I is the moment of inertia of the triangle about an axis through G lying in the plane of the triangle. It will be more convenient to use the substitution $I=C/2$ where C is the moment of inertia of the X_3 atoms, and hence of the whole YX_3 molecule about the figure axis. T_0 denotes the kinetic energy of the X atoms within their plane and relative to G. We shall presently evaluate T_0; the only point to consider for the instant is that there can be no interaction terms between T_0 and the tipping term $\frac{1}{2}I\dot{\theta}^2$ since the displacements of the particles for the two motions are always perpendicular.

The first two terms of T may be combined because of the condition that the angular momentum of the system perpendicular to the symmetry axis must remain zero throughout the motion. (This is equivalent to the demand, explained earlier, that we examine the motion in a moving coordinate system x, y, z, which is fixed by the equilibrium configuration of the system.) Thus, $\mu h\dot{y}_1=I\dot{\theta}$ where h is the height of the pyramid. But $\mu h^2+I=A$, the moment of inertia of the molecule perpendicular to the symmetry axis. By substitution we obtain for the first two terms of the kinetic energy $\mu A\dot{y}_1^2/C$. It has appeared simplest to develop the kinetic energy as a function of y_1 and one might continue to treat the motion using this coordinate. Such a treatment would suffer a disadvantage, however, in that y_1 does not specify a geometric property of the system, since the actual geometric configuration is determined both by y_1 and by the tipping of the X_3 triangle. That is to say, it involves the momentum relation and hence implies that the positions of the particles are a function both of y_1 and of the masses. This difficulty, which becomes particularly important when we examine isotope effects, may be obviated by choosing a geometric coordinate, one which characterizes a geometric property of the system and is independent of the masses. For example we may use the perpendicular distance between the Y atom and the normal to the X_3 plane through G. Let this be called y. Clearly

$$y=y_1+h\theta \quad \text{or} \quad y=(1+2\mu h^2/C)y_1=(2A/C)y_1$$

by reason of the momentum relation.

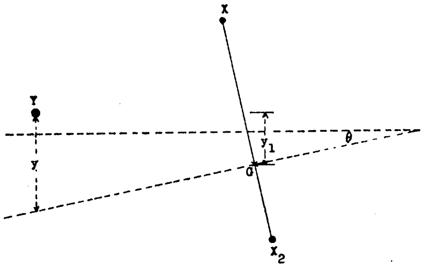

FIG. 1.

Up to the present we have considered a displacement y perpendicular to the symmetry axis and lying in the plane of the paper (Fig. 1). Let the corresponding displacement perpendicular to the plane of the paper be x. Making the indicated substitutions we obtain

$$T=\tfrac{1}{2}(\mu C/2A)(\dot{x}^2+\dot{y}^2)+T_0.$$

The kinetic energy T_0 of the X atoms within their plane and relative to their center of gravity G has appeared many times in the literature[5] since it is the kinetic energy for a triatomic molecule. We begin by expressing it as a function of q_1, q_2, and q_3, the changes in distance between pairs of atoms.

$$T_0=\tfrac{1}{2}m\{(5/9)(\dot{q}_1^2+\dot{q}_2^2+\dot{q}_3^2) -(2/9)(\dot{q}_1\dot{q}_2+\dot{q}_1\dot{q}_3+\dot{q}_2\dot{q}_3)\}.$$

A linear transformation may now be made which diagonalizes T_0 and at the same time introduces symmetric coordinates. Let

$$\xi=(q_1-q_2)/3^{\frac{1}{2}}, \quad \eta=\tfrac{1}{3}(q_1+q_2-2q_3), \quad \zeta=\tfrac{1}{3}(q_1+q_2+q_3),$$

in which case $T_0=\frac{1}{2}m(\dot{\xi}^2+\dot{\eta}+\dot{\zeta}^2)$. The displacements corresponding to ξ, η, and ζ are shown in Fig. 2 and it is at once evident that ξ and η form a degenerate pair capable of describing a ⊥ vibration. ζ belongs to the other symmetry class and hence for our present purpose it may be disregarded.

The motions corresponding to ξ and η are subject to the condition that the linear and angular momenta of the system must remain zero. This serves to determine both the direction and magnitude of the actual space displacements of the particles which may be characterized as fol-

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[5] N. Bjerrum, Verh. d. D. Phys. Ges. **16**, 737 (1914).

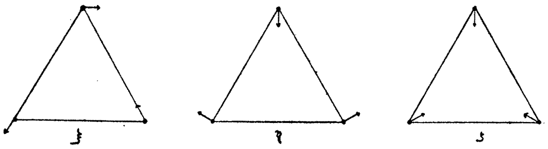

FIG. 2.

lows. (1) The displacement of any individual atom in the ξ motion is perpendicular to its displacement in the η motion. (2) The displacements of all the particles are the same and are given, respectively, by $d_i=\xi/3^{\frac{1}{2}}$ and $d_i=\eta/3^{\frac{1}{2}}$ where i is the number of the atom and runs from 1 to 3.

The total kinetic energy thus becomes

$$T=\tfrac{1}{2}m\{\alpha(\dot{x}^2+\dot{y}^2)+\dot{\xi}^2+\dot{\eta}^2\},$$

where $\alpha=\mu C/2mA$.

The potential energy may be written as a general quadratic form involving the arbitrary coefficients a, b, and c.

$$V=\tfrac{1}{2}\{a(x^2+y^2)+b(\xi^2+\eta^2)+2c(x\xi+y\eta)\}.$$

Although there are ten coefficients entering a general quadratic form containing four variables, the above expression is the most general one which may be used for the potential energy. This is due to the axial symmetry of the molecule, which insures first, that x and y and also ξ and η must enter on the same footing, and second, that the coefficients of such terms as xy, $x\eta$, etc., must vanish.

The Hamiltonian clearly may be divided into the sum of two identical Hamiltonians, the first a function of x and ξ and the second of y and η. Either of these may be treated by the method of normal vibrations, which yields the following relations between the λ's, where the normal frequency $\nu_i=\lambda_i^{\frac{1}{2}}/2\pi$:

$$m(\lambda_2+\lambda_4)=a/\alpha+b,\quad m^2\lambda_2\lambda_4=(ab-c^2)/\alpha.$$

This result is in agreement with the expressions obtained by J. E. Rosenthal[6] for the frequencies of the YX_3 molecule although the notation is somewhat different. We reproduce it here merely because it is one of the steps in the calculation of the internal angular momentum factors ζ_2 and ζ_4.

It is now necessary to transform to the normal coordinates x_2, x_4, y_2, and y_4 whereby

$$H=H_1(x_2,\,x_4)+H_1(y_2,\,y_4),$$

$$H_1(x_2,\,x_4)=\tfrac{1}{2}(p_{x_2}{}^2+p_{x_4}{}^2+\lambda_2x_2{}^2+\lambda_4x_4{}^2).$$

The normal coordinates x_2, x_4 are related to x and ξ by means of a linear transformation whose coefficients are proportional to the first minors of the determinant which gave the λ's. We find

$$x=\Sigma A_ix_i,\quad \xi=\Sigma B_ix_i,\quad i=2,\,4,$$

where $A_i=(m\lambda_i-b)/[m\alpha(m\lambda_i-b)^2+mc^2]^{\frac{1}{2}}$,

$$B_i=c/[m\alpha(m\lambda_i-b)^2+mc^2]^{\frac{1}{2}}.$$

Identical expressions connect y_2 and y_4 with y and η.

The angular momentum of the entire system might be determined by finding the angular momentum of each particle and summing. However it will be more convenient to divide the molecule into two parts, the Y atom and the X_3 group. Now, as is well known, the angular momentum of any group of particles (say X_3) is equal to the angular momentum of the particles relative to their center of gravity G, plus the contribution due to the center of gravity. Thus Y and G together, which constitute a two particle group, will possess an angular momentum $\mu(x_1\dot{y}_1-y_1\dot{x}_1)=\mu(C/2A)^2(x\dot{y}-y\dot{x})$. The angular momentum of the X_3 group relative to G may be found by considering the momentum of any one particle and multiplying by 3. We obtain $-m(\xi\dot{\eta}-\eta\dot{\xi})$. This expression is preceded by a minus sign since it is oppositely directed from the momentum of Y and G. The reader may easily verify this statement by drawing several phases of the motion illustrated in Fig. 2. The momentum due to Y and G has the same direction as the rotation of the electric moment, since Y and G are the carriers of the electric charges.

We may now transform to the normal coordinates and $(x\dot{y}-y\dot{x})$ becomes $A_2{}^2(x_2\dot{y}_2-y_2\dot{x}_2)+A_4{}^2(x_4\dot{y}_4-y_4\dot{x}_4)+A_2A_4(x_2\dot{y}_4-y_4\dot{x}_2+x_4\dot{y}_2-y_2\dot{x}_4)$. The eigenvalues of these terms may be found very easily when we recall that the wave functions are the usual Hermitian orthogonal functions in the variables $2\pi(\nu_i/h)^{\frac{1}{2}}x_i$ and $2\pi(\nu_i/h)^{\frac{1}{2}}y_i$. We obtain $A_2{}^2h/2\pi$ or $A_4{}^2h/2\pi$ for the first excited states of ν_2 and ν_4, respectively. Thus the

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[6] J. E. Rosenthal, Phys. Rev. **47**, 235 (1935). The relations between our constants and those of Dr. Rosenthal are $A=a$, $3D=b$, and $3E^2=c^2$.

contribution to ζ_i from the motion of Y and G is $\mu(C/2A)^2 A_i^2$. From similar reasoning one obtains the remaining part of ζ_i which is due to the momentum of the X_3 particles relative to G.

Adding these two terms and substituting for A_i and B_i we have finally

$$\zeta_i=(C/2A-\delta_i)/(1+\delta_i) \qquad i=2, 4,$$

where $$\delta_i=2mAc^2/\mu C(m\lambda_i-b)^2.$$

The sum $\zeta_2+\zeta_4$ may now be determined by direct substitution. The resulting complicated expression may be reduced by means of the relations between λ_2 and λ_4 to the simple form $\Sigma\zeta=C/2A-1$. The fact that $\Sigma\zeta$ turns out to be independent of the force constants a, b, and c, is both an example of the general theorem relating to $\Sigma\zeta$ and a verification that our calculations have been free from algebraic errors.

These formulae may be used in the analysis of the spectra of NH_3 and ND_3. The experimental data are as follows.

The long wave perpendicular band ν_4 of NH_3 has been mapped by E. F. Barker[7] and has its center at 1631 cm^{-1}. It shows an intense central region of absorption which is between 30 and 40 cm^{-1} wide. This no doubt corresponds to a clustering of zero branch lines whose spacing $\Delta\nu_4$ may be estimated at around 3 cm^{-1}. The spectrum of ND_3 has been studied by M. V. Migeotte and E. F. Barker[8] who have found both of the fundamental perpendicular bands, $\nu_2=2556$ and $\nu_4=1188$. The short wave bands consist of a set of equally spaced lines (the zero-branch lines) with a spacing $\Delta\nu_2\cong 5.2$ cm^{-1}. The long wave band ν_4 exhibits a strong central absorption corresponding to a spacing of from 1 to 2 cm^{-1}. We wish to express our gratitude to Professor Barker and Dr. Migeotte for allowing us to reproduce here a portion of their unpublished data.

We shall adopt the following procedure. By means of the observed band centers ν_4 of NH_3 and ν_2, ν_4 of ND_3, the potential constants a, b, and c may be determined. From a knowledge of these constants, the ζ's and finally the fine structure spacings may be computed and compared with the observed spacings. In making all these calculations we require the ratio of the moments of inertia $C/2A$. To find this we shall use the line spacings of the pure rotation spectra of the ammonias. Wright and Randall[9] obtained for NH_3 that $h/4\pi^2A=19.88$ whereas Barnes, Benedict and Lewis[10] found for ND_3 that $h/4\pi^2A=10.22$ cm^{-1}. These data yield $C/2A=0.825$ and 0.847 for NH_3 and ND_3, respectively. Unfortunately this ratio is extremely sensitive to small changes in the line spacings and appears to be determined with an accuracy of not better than 5 to 10 percent. The potential constants are then found to be $a=9.42$, $b=4.12$, $c=\pm 3.97\times 10^5$ dynes/cm. Here again the errors are considerable, amounting to at least 5 percent. This is due to two causes: first to the inaccuracy in $C/2A$; second, to the fact that we have used the observed positions of the fundamental bands rather than the normal frequencies which are demanded by the theory. The normal frequencies themselves may be found only when all the anharmonic constants are known.

TABLE I. *Values of the ζ's and line spacings.*

	ζ_2	$\Delta\nu_2$ COMP.	$\Delta\nu_2$ OBS.	ζ_4	$\Delta\nu_4$ COMP.	$\Delta\nu_4$ OBS.
NH_3	-0.004	7.15	–	-0.171	5.76	~3 to 4
ND_3	$+$ .104	4.81	5.2	$-$ .257	2.66	~1 to 2

The results of the calculations on the ζ's and the line spacings are shown in Table I.

The agreement between the computed and observed $\Delta\nu$ is not at all satisfactory although it appears to be best in the one case, $\Delta\nu_2$ of ND_3, where the experimental data are most precise. We feel that these results do not constitute any real test of the theory. They show rather that the $\Delta\nu$ are sensitive to the potential constants and to the ratio $C/2A$, and consequently it may be possible through them to obtain more exact values for the molecular constants. This must wait however in the case of the ammonias until further measurements are available on the line spacings.

The next class of molecules to be considered is the axial system ZYX_3 to which the methyl halides belong. There exist three perpendicular bands which are determined by six potential constants. The task of computing the individual ζ's in terms of the six constants becomes rather

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[7] To be published in the near future.

[8] M. V. Migeotte and E. F. Barker, Phys. Rev., in press.

[9] N. Wright and H. M. Randall, Phys. Rev. **44**, 391 (1933).

[10] R. B. Barnes, W. S. Benedict and C. M. Lewis, Phys. Rev. **45**, 347 (1934).

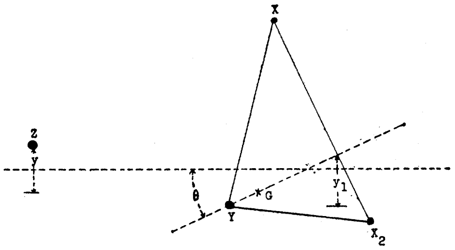

FIG. 3.

arduous and for the present we shall merely obtain an expression for $\Sigma\zeta$ over the three perpendicular fundamental bands. Now $\Sigma\zeta$ is independent of the potential constants and therefore may be calculated by using any limiting force field. The result is then correct for all force fields.

We have chosen the limiting field to be such that the YX_3 group is held together by very strong forces while the Z particle is very weakly bound to the YX_3 group. The three perpendicular frequencies may now be characterized by ν_2 and ν_4 which correspond to a motion within the YX_3 group itself, the Z atom standing still, and ν_6, which is to be correlated with a vibration of the Z atom against a rigid pyramid YX_3. In this latter mode of vibration, the Z atom moves in a path perpendicular to the symmetry line against the center of gravity G of the YX_3 pyramid. This motion is shown in Fig. 3. In order to preserve the constancy of the angular momentum the pyramid must tip through the angle θ.

In this extreme type of force field the frequencies ν_2 and ν_4 belong to a motion of the YX_3 group alone and hence we have $\zeta_2+\zeta_4=C/2A'-1$ where A' is the moment of inertia of the YX_3 pyramid about an axis perpendicular to the symmetry axis and drawn through G. C is the moment of inertia of the YX_3 group, or, in fact, of the entire molecule ZYX_3 along the symmetry axis. It remains now to compute ζ_6. The total kinetic energy for the motion ν_6 is the sum of the energies of Z, of G and of the tipping of the pyramid.

$$T=\tfrac{1}{2}(\mu_1\dot{y}^2+A'\dot{\theta}^2),$$

where y is the sum of the displacements of Z and of G and μ_1 is the reduced mass $\mu_1=M_1(M_2+3m)/M_1+M_2+3m$; M_1, M_2 and m are the masses of a Z, Y and X atom, respectively.

The coordinates y and θ are not independent but are connected by the momentum relation

$$u_1b\dot{y}=A'\dot{\theta}$$

where b is the equilibrium distance between Z and G. Thus

$$T=\tfrac{1}{2}(\mu_1+\mu_1^2b^2/A')\dot{y}^2.$$

This expression may be somewhat simplified by recalling that $A'+\mu_1b^2=A$, the moment of inertia of the whole molecule about an axis perpendicular to the symmetry axis. We shall also introduce the coordinate x, corresponding to a displacement of Z relative to G, out from the plane of the paper in Fig. 3.

$$T=\tfrac{1}{2}(\mu_1A/A')(\dot{x}^2+\dot{y}^2).$$

The kinetic energy may however be written as a function of the normal coordinates x_6 and y_6.

$$T=\tfrac{1}{2}(\dot{x}_6{}^2+\dot{y}_6{}^2)$$

and therefore we have the relations

$$x=(A'/\mu_1A)^{\frac{1}{2}}x_6 \quad\text{and}\quad y=(A'/\mu_1A)^{\frac{1}{2}}y_6.$$

The total angular momentum of the system about the symmetry axis is most easily obtained by decomposing it into two parts. First, consider the contribution due to the motion of Z and G. This is clearly $\mu_1(x\dot{y}-y\dot{x})$. The second contribution is that coming from the motion of the YX_3 pyramid relative to its center of gravity G. This becomes $\mu_2(x_1\dot{y}_1-y_1\dot{x}_1)$ where μ_2 is the reduced mass $3mM_2/(3m+M_2)$ and x_1, y_1 are the displacements of the Y atom relative to the center of gravity of the X_3 group, perpendicular to and in the plane of the paper (Fig. 3), respectively.[11] The coordinate $y_1=h\theta$ where, as earlier, h is the height of the YX_3 pyramid. Hence, through the momentum relation y_1 is connected with y. Thus $y_1=(\mu_1bh/A')y$ and the total angular momentum of the ZYX_3 molecule becomes

$$(\mu_1+\mu_2(\mu_1bh/A')^2)(x\dot{y}-y\dot{x})$$

or in terms of the normal coordinates

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[11] In considering this second contribution we have treated the YX pyramid as two units, the Y atom and the X_3 group. It might be thought that there would be a third contribution to the angular momentum coming from the motion of the X_3 group relative to its center of gravity. This term is however zero since, relative to their center of gravity, the displacements of each X atom are always parallel to the symmetry axis.

$$[\mu_1+\mu_2(\mu_1 bh/A')^2](A'/\mu_1 A)(x_6\dot{y}_6-y_6\dot{x}_6).$$

The eigenvalues of $(x_6\dot{y}_6-y_6\dot{x}_6)$ may be found by the method indicated in the calculations on the YX_3 molecules. For the first excited state they are $\pm h/2\pi$. Therefore

$$\zeta_6=[\mu_1+\mu_2(\mu_1 bh/A')^2](A'/\mu_1 A).$$

A simple calculation reduces this to the form

$$\zeta_6=C/2A-C/2A'+1.$$

The sum over all the ζ's therefore becomes $\Sigma\zeta=C/2A$. We wish to emphasize again that, although this result has been obtained from a computation using a limiting and physically unreal force field, it will hold true for any actual force field. The conditions for its strict validity are, harmonicity of the motion and no resonance relations between the frequencies. It is clear that this method of the limiting fields may be used to determine the $\Sigma\zeta$ for any axial molecule.

The fundamental perpendicular bands of the methyl halide molecules have all been observed by Bennett and Meyer[12] and their fine structure measured. Since in the present theory $\Sigma\zeta$ and not the individual ζ's themselves have been computed, it will be possible to make use of the sum of the line spacings only. Adding the line spacings of the three perpendicular bands we obtain evidently[13]

$$\Sigma\Delta\nu=[(3-\Sigma\zeta)/C-3/A]h/4\pi^2 = (3/C-7/2A)h/4\pi^2.$$

The observations of Bennett and Meyer yield $\Sigma\Delta\nu=24.65$, 27.15, 28.32 and 28.5 cm^{-1} for CH_3F, CH_3Cl, CH_3Br and CH_3I, respectively. The moment of inertia A has been measured directly from the line spacing of the parallel type bands in the case of methyl fluoride[12] and methyl chloride[14] and found to be 39.5 and 50×10^{-40}. For the remaining methyl halides we have only the estimates[15] based upon the envelopes of the parallel bands, namely, 89 and 99×10^{-40}, respectively. These values are admittedly not very accurate, but small errors in them will have almost no influence upon the computation of C since the term $3/C$ is so much larger than $7/2A$.

The indicated substitutions are easily made and give the following numbers for the moment of inertia C of methyl fluoride to methyl iodide: 5.61, 5.35, 5.44, and 5.44×10^{-40}. The corresponding $H-H$ distances are 1.84, 1.80, 1.81 and 1.81×10^{-8} cm. In the next section we shall find the moment of inertia of methane $A=5.47\times10^{-40}$ and $H-H=1.81\times10^{-8}$ through an analogous method. Direct measurements on the moment of inertia of methane through the line spacings of methyl deuteride[16] are now available and give $A=5.298$ and $H-H=1.785$. We feel that these results are to be interpreted by saying that, within the present limits of error, the dimensions of the H_3 triangle and presumably of the CH_3 group remain unchanged throughout the series of methane and the methyl halides. There are two principal sources of error: on the experimental side the line spacings of many of the methyl halide bands are not very accurately known; on the theoretical side we have taken no account of the departures from harmonic motion. The total error in C could be as high as 10 percent although probably it is nearer 5 percent. We do not mean to imply that the CH_3 group undergoes no change as we proceed from CH_4 to CH_3I, but only that our calculations show that whatever change does occur, must be smaller, possibly much smaller, than 5 to 10 percent.

§3. The Overtones of Axially Symmetric Molecules

Transitions from the normal state to excited states higher than the first result in overtone bands. The fine structure spacing of the perpendicular bands will evidently be given by the same formula as that for the fundamentals $\Delta\nu=[(1-\zeta)/C-1/A]h/4\pi^2$. It is our purpose to compute the ζ's appropriate for the lower overtones of the molecules YX_3 and ZYX_3. We shall begin by treating the overtones $2\nu_i$. As usual the

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[12] W. H. Bennett and C. F. Meyer, Phys. Rev. **32**, 888 (1928).

[13] In the preliminary note, Dennison and Johnston, Phys. Rev. **47**, 93 (1935), an error appeared in this formula which slightly affected the resulting values of the moments of inertia. Since the publication of the note, a more precise measurement has become available for the moment of inertia A of methyl chloride which is incorporated in the present paper.

[14] E. F. Barker and E. K. Plyler, J. Chem. Phys. **3**, 367 (1935).

[15] S. L. Gerhard and D. M. Dennison, Phys. Rev. **43** 197 (1933).

[16] N. Ginsburg and E. F. Barker, J. Chem. Phys. **3**, 668 (1935).

wave function in first approximation is separable in the normal coordinates. Consider that part which depends upon x_i and y_i. It is now simpler to transform to polar coordinates ρ_i, θ_i where ρ_i is proportional to a displacement say of the Y atom perpendicular to the symmetry axis, and θ_i gives the angle of turning about the symmetry axis. Thus $\rho_i^2=x_i^2+y_i^2$ and $\tan\theta_i=y_i/x_i$. These coordinates and the resulting wave functions are identical with those employed in describing the CO_2 molecule.[17] The wave function of the normal state (at least that part depending upon ρ_i and θ_i) is $R_{(\rho)}{}^{00}$ while the excited state in question is characterized by the three functions $R_{(\rho)}{}^{22}e^{\pm 2i\theta}$ and $R_{(\rho)}{}^{20}$. The coefficients of $i\theta$ show that the eigenvalues of $(x_i\dot{y}_i-y_i\dot{x}_i)$ for the excited state are ± 2 and 0.

Now the electric moment perpendicular to the symmetry axis is proportional to x_i or to y_i, that is, to $\rho e^{\pm i\theta}$. It is thus clear that the matrix elements of the electric moment all vanish since the integrand is periodic in θ. This is to be expected, for up until now we have considered only the lowest order approximation, in which the motion is strictly harmonic and in which no overtone bands can appear. We must therefore consider the modifications to the wave functions caused by deviations from harmonicity. The perturbing function $\lambda V'$ may be expanded as a periodic series in 3θ, the factor 3 signifying the threefold symmetry of the X_3 group. Thus

$$\lambda V'=\lambda\sum_m F_{(\rho)}{}^m e^{3im\theta}.$$

For the present discussion where we are interested in the possibility but not the actual probability of a transition, it is sufficient to consider the effect of the perturbation on the wave function of the normal state. By the usual formulae of perturbation theory we obtain $R^{00}+\lambda\sum_{m=-\infty}^{\infty}S^m\times e^{i3m\theta}$ where S^m is a function of ρ. It is now evident that no transitions resulting in perpendicular bands occur to the state R^{20}. The matrix element of the electric moment does however receive a contribution from the two wave functions $S^1e^{+i3\theta}$ and $R^{22}e^{+i2\theta}$ and also from the terms $S^1e^{-i3\theta}$ and $R^{22}e^{-i2\theta}$. These considerations give us an answer to the question of the appropriate ζ. It must have the magnitude $2\zeta_i$ (from the magnitude of the eigenvalue of $(x_i\dot{y}_i-y_i\dot{x}_i)$ and it must have the negative sign. This last conclusion, namely, that the direction of rotation of the electric moment is reversed may be seen from the fact that in the fundamental bands we connect R^{00} and $R^{11}e^{i\theta}$, and the coefficient of $i\theta$ goes $0\rightarrow 1$. In the present case the coefficient of $i\theta$ goes $3\rightarrow 2$ thus giving a reversal of direction.

The next overtone $3\nu_i$ corresponds to a transition from the normal state to an excited state described by the four wave functions $R^{31}e^{\pm i\theta}$ and $R^{33}e^{\pm i3\theta}$. By an application of the reasoning just employed, it appears that a transition resulting in a perpendicular type band may occur only to $R^{31}e^{\pm i\theta}$. The ζ characterizing the fine structure spacing is therefore just ζ_i itself. In this manner we could compute the ζ for any harmonic $n\nu_i$ but the result would be rather meaningless for large values of n since here the influence of the anharmonic terms will become appreciable. The reader must not confuse the fact that although we have made use of the existence of the anharmonicity in order to find the selection rules, we have not taken account of its effect on the fine structure.

One further type of overtone may be discussed profitably, namely, the combination band $\nu_i+\nu_k$. Three possibilities exist. First ν_i and ν_k may both be parallel bands, in which case $\nu_i+\nu_k$ is also parallel and hence not included in the present treatment. Secondly, one of the bands, say ν_i, is perpendicular while the other ν_k is parallel. The presence of energy in a parallel mode of vibration does not at all change the internal angular momentum and hence the ζ for the overtone $\nu_i+\nu_k$ is just ζ_i. The third case where ν_i and ν_k are both perpendicular is somewhat more complex. The excited state is fourfold degenerate and is specified by the wave functions $R_i{}^{11}R_k{}^{11}e^{\pm i(\theta_i+\theta_k)}$ and $R_i{}^{11}R_k{}^{11}e^{\pm i(\theta_i-\theta_k)}$. The internal angular momentum is additive and depends upon the coefficients of θ_i and θ_k; hence the angular momentum belonging with these wave functions is $\pm(\zeta_i+\zeta_k)h/2\pi$ and $\pm(\zeta_i-\zeta_k)h/2\pi$, respectively. The electric moment with components μ_x and μ_y is given by $\mu_x+i\mu_y=a_i\rho_ie^{i\theta_i}+a_k\rho_ke^{i\theta_k}$ where a_i and a_k are proportionality factors. We must now consider the influence of the anharmonicity on the wave func-

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[17] A. Adel and D. M. Dennison, Phys. Rev. **43**, 716 (1933).

tions. The perturbing energy $\lambda V'$ is composed of a sum of terms of the type

$$\lambda F(\rho_i\rho_k)e^{i[m_1\theta_i+(3m_2-m_1)\theta_k]}$$

where m_1 and m_2 are integers. The threefold symmetry of the molecule shows itself in the fact that the sum of the coefficients of θ_i and θ_k must be a multiple of three.

As before it will be sufficient to obtain the form of the perturbed wave function of the normal state. This is evidently

$$R_i^{00}R_k^{00}+\lambda \sum_{m_1,\, m_2} S^{m_1,\, m_2}e^{i[m_1\theta_i+(3m_2-m_1)\theta_k]}.$$

A simple trial now makes it clear that no transitions of the perpendicular type may occur from the normal state to the wave functions $R_iR_ke^{\pm i(\theta_i-\theta_k)}$ since the integral is always periodic either in θ_i or θ_k. Transitions may occur, however, to the states $R_iR_ke^{\pm i(\theta_i+\theta_k)}$. The particular terms of the perturbed normal state wave functions which furnish a nonperiodic integrand have the following dependence upon the angles, $e^{\pm i(\theta_i+2\theta_k)}$ or $e^{\pm i(2\theta_i+\theta_k)}$. From these considerations we see that the ζ appropriate for the band $\nu_i+\nu_k$ has the magnitude $\zeta_i+\zeta_k$ and that it has the negative sign. The reasoning which fixes the sign is identical with that employed in the case of the overtone $2\nu_i$.

An application of this result may be made to the band of NH_3 which lies at about 2μ. The band,[18] which is of the perpendicular variety, is composed of a set of equispaced lines with a spacing constant $\Delta\nu=9.98$ cm^{-1}. The position of the band center would be consistent with its identification as either $\nu_1+\nu_4$ or $\nu_2+\nu_4$ where ν_2 and ν_4 are the perpendicular fundamentals and ν_1 is the high frequency parallel band. In the first case $\nu_1+\nu_4$, the ζ would be equal to ζ_4 and the fine structure should resemble that of the fundamental ν_4. However, this is not what is observed since ν_4 shows a strong central region of absorption corresponding to $\Delta\nu\sim3$ or 4. Under the second identification, $\nu_2+\nu_4$, the appropriate ζ would be $-(\zeta_2+\zeta_4)=1-C/2A$. Substituting in the formula for the line spacing we obtain $\Delta\nu=-h/8\pi^2A$. That is to say, the spacing should be just half the spacing of a parallel type band or 9.94 cm^{-1}, in very good agreement with the observations.

The only other existing data on the fine structure of overtones of axial molecules appear to be those by Nielsen and Barker[19] on methyl chloride. The methyl chloride molecule possesses three fundamental perpendicular bands ν_2, ν_4, and ν_6. The fine structure of each has been measured by Bennett and Meyer[12] and found to be 8.2, 12.0 and 6.95 cm^{-1}, respectively. From these values, together with the moments of inertia A and C already cited, we obtain $\zeta_2=0.100$, $\zeta_4=-0.268$ and $\zeta_6=0.220$.

Nielsen and Barker observed a perpendicular band at about 6100 cm^{-1} which they identify with $2\nu_2$. The appropriate ζ for this overtone we computed to be $-2\zeta_2=-0.200$, which yields $\Delta\nu=11.3$ cm^{-1}. The experimental value of the spacing was 12.0 cm^{-1}.

The next perpendicular bands which they resolved lie at about 4360 and 4460 cm^{-1} and were labeled $\nu_2+\nu_3$ and $\nu_2+2\nu_5$. These correspond to the sum of a perpendicular ν_2 with a parallel frequency ν_3 or $2\nu_5$ and accordingly should have the $\zeta=\zeta_2$ and $\Delta\nu=8.2$ cm^{-1}. Actually they were found to have the spacings 8.4 and 8.6 cm^{-1}, respectively.

The final perpendicular region observed by Nielsen and Barker lies at 2462 cm^{-1} and shows a spacing of 9.7 cm^{-1}. They identified this band as $\nu_6+2\nu_5$ in which case $\zeta=\zeta_6$ and $\Delta\nu=6.95$ cm^{-1} in bad agreement with the measurements. A second identification which would yield essentially the same position for the band center is $\nu_4+\nu_6$. The appropriate ζ for such a combination is $-(\zeta_4+\zeta_6)=+0.048$ giving $\Delta\nu=8.74$ cm^{-1}.

The agreements which have been obtained between the predicted and observed line spacings of the perpendicular overtone bands of ammonia and methyl chloride we regard as very satisfactory. The deviations which are in no case larger than 10 percent are no doubt caused by the effect of the anharmonic terms whose influence is of course greater on the overtone bands than on the fundamentals.

§4. Spherically Symmetric Molecules

The symmetrical molecule YX_4 possesses four fundamental frequencies ν_1, ν_2, ν_3, and ν_4 which are single, doubly, triply and triply degenerate,

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[18] Stinchcomb and Barker, Phys. Rev. **33**, 305 (1929).

[19] A. H. Nielsen and E. F. Barker, Phys. Rev. **46**, 970 (1934).

respectively. The first two, ν_1 and ν_2 involve no motion of the Y atom and are consequently inactive in the infrared. On the other hand ν_3 and ν_4 are both active and correspond in first approximation to isotropic harmonic oscillators in space. Each of these latter may possess an internal angular momentum $\zeta_i h/2\pi$ and we shall first sketch the method of calculating ζ_3 and ζ_4 as functions of the potential constants.

The tetrahedral system YX_4 has nine degrees of vibrational freedom and hence must be described by nine coordinates. It seems very convenient and straightforward to specify them in the following manner. The positions of the four X particles may be fixed relative to their center of gravity G by means of the mutual displacements $q_1, q_2, \cdots q_6$ of the particles along the edges of the tetrahedron defined by the equilibrium configuration X_4. Let q_1 and q_2, q_3 and q_4, q_5 and q_6 relate to opposite edges of the tetrahedron. Finally, the displacement of Y relative to G may be given by three Cartesian coordinates x, y, z. These rectangular axes may be chosen in any manner, but it is convenient to let x, y, and z be lines perpendicular to the opposite edges of the equilibrium tetrahedron X_4 1 and 2, 3 and 4, and 5 and 6, respectively. This numbering of the edges corresponds with the subscripts of the q's.

The potential energy of the system V can now be written as a general quadratic form in the nine coordinates. The number of independent constants is greatly reduced, however, by reason of the tetrahedral symmetry and has been shown to be only five.[20] The number and the nature of these constants may be explained by the following description. The axes x, y and z are all equivalent and hence x^2, y^2, and z^2 have the same coefficient, say a. Similarly all the q^2 have the same coefficient, b. There are two types of cross products between the q's, first, cross products between adjacent edges (for example q_1q_3) and second, cross products between opposite edges, as q_1q_2. These two classes require the constants c and d, respectively. Finally, the tetrahedral symmetry is unchanged by reversing the direction of one of the Cartesian axes, say the x axis, and simultaneously interchanging the two opposite edges in this case q_1 and q_2. Thus there may be a cross product term of the sort $x(q_1-q_2)$ but no terms such as xy. Hence

$$\begin{aligned}V=\tfrac{1}{2}\{&a(x^2+y^2+z^2)+b(q_1^2+q_2^2+q_3^2+q_4^2+q_5^2+q_6^2)\\&+2c(q_1q_3+q_1q_4+q_1q_5+q_1q_6+q_2q_3+q_2q_4\\&+q_2q_5+q_2q_6+q_3q_5+q_3q_6+q_4q_5+q_4q_6)\\&+2d(q_1q_2+q_3q_4+q_5q_6)+2e[x(q_1-q_2)\\&+y(q_3-q_4)+z(q_5-q_6)]\}.\end{aligned}$$

The kinetic energy of the YX_4 molecule was found by Dennison[21] using coordinates identical with those defined here, except for a nonessential charge in the orientation of the xyz axes.

$$\begin{aligned}T=\tfrac{1}{2}\{&\mu(\dot{x}^2+\dot{y}^2+\dot{z}^2)+(5m/8)(\dot{q}_1^2+\dot{q}_2^2+\dot{q}_3^2\\&+\dot{q}_4^2+\dot{q}_5^2+\dot{q}_6^2)-2(m/8)(\dot{q}_1\dot{q}_3+\dot{q}_1\dot{q}_4+\dot{q}_1\dot{q}_5\\&+\dot{q}_1\dot{q}_6+\dot{q}_2\dot{q}_3+\dot{q}_2\dot{q}_4+\dot{q}_2\dot{q}_5+\dot{q}_2\dot{q}_6+\dot{q}_3\dot{q}_5+\dot{q}_3\dot{q}_6\\&+\dot{q}_4\dot{q}_5+\dot{q}_4\dot{q}_6)+2(m/8)(\dot{q}_1\dot{q}_2+\dot{q}_3\dot{q}_4+\dot{q}_5\dot{q}_6)\},\end{aligned}$$

where $\mu=4mM/(4m+M)$ and m and M are the masses of the X and Y particles, respectively. The determinant giving the normal frequencies $\nu_i=\lambda_i^{\frac{1}{2}}/2\pi$ may be readily solved and yields,

$$m\lambda_1=4b+4d+16c,\quad m\lambda_2=b+d-2c,$$

$$m(\lambda_3+\lambda_4)=ma/\mu+2b-2d,$$

$$m^2(\lambda_3\lambda_4)=2m(ab-ad-2e^2)/\mu.$$

The normal frequencies of the YX_4 molecule have already been computed by J. E. Rosenthal[20] as a function of five constants, A, B, C, D and E which are connected with our constants by the linear relations, $A=a$, $B=(b-d)/4$, $C=(b+d)/4-c/2$ and $D^2=e^2/2$. $E=(b+d)/4+c$.

The internal angular momentum associated with the frequencies ν_3 and ν_4 may be calculated by a method essentially similar to that employed in the treatment of the YX_3 molecule. The first minors of the normal determinant will give the coordinates x, y, z, $q_1 \cdots q_6$ as linear functions of the normal coordinates. These functions in the case of the motions ν_3 and ν_4 are indeterminate to the extent of the threefold degeneracy. This degeneracy may be removed if we assume that the angular momentum lies along some definite axis,

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[20] J. E. Rosenthal, Phys. Rev. **45**, 538 (1934).

[21] D. M. Dennison, Astrophys. J. **62**, 84 (1925).

say the z axis. This means that the amplitude of z is zero while the amplitude of x and y are equal but ninety degrees out of phase. The amplitudes of all the q's, and hence the actual space displacements of all particles, are then completely defined. The angular momentum may be divided into the two parts: that caused by the motion of the Y particle and G, namely, $\mu(x\dot{y}-y\dot{x})$ and that caused by the motion of the X particles relative to G. These two contributions are then added and evaluated in terms of the normal coordinates exactly as was done in the case of the YX_3 molecule. The calculation is somewhat complicated but eventually leads to the simple result[22]

$$\zeta_i=(\delta_i-\tfrac{1}{2})/(\delta_i+1),$$

where $\delta_i=4\mu e^2/m(\mu\lambda_i-a)^2$; $i=3, 4$.

The frequencies ν_3 and ν_4 belong to the same symmetry class and are the only fundamental frequencies of this class. Hence according to Teller's theorem $\zeta_3+\zeta_4$ should be independent of the force constants. Upon making the addition and using the relations between λ_3 and λ_4 we find $\zeta_3+\zeta_4=\frac{1}{2}$. This result may also be obtained from the formula $\Sigma\zeta=C/2A$ for the ZYX_3 molecule. In this latter system as the Z atom is changed into an X atom and the molecule assumes the tetrahedral form, the frequencies ν_2, ν_4 and ν_6, go over into the frequencies ν_3, ν_2 and ν_4 of YX_4, respectively.[23] Therefore the $\zeta_2+\zeta_4+\zeta_6=C/2A$ of ZYX_3 becomes $\zeta_3+\zeta_2+\zeta_4=C/2A=\frac{1}{2}$ for YX_4. We must now consider the following question. What is the internal angular momentum to be associated with the inactive frequency ν_2 of YX_4? By drawing the displacements of the particles it is easy to show that each X particle does indeed possess an angular momentum, but that these angular momenta are all equal and all directed either towards, or directly away from the central Y atom. Consequently the total angular momentum vanishes and hence $\zeta_2=0$. Thus $\zeta_3+\zeta_4=\frac{1}{2}$ in agreement with the result obtained by direct calculation.

The formulae for the ζ's are of great practical importance in the interpretation of the spectrum of methane. In the first place, they enable one to calculate the moment of inertia by summing the line spacings of the bands ν_3 and ν_4. Thus $\Delta\nu_3+\Delta\nu_4=(2-\zeta_3-\zeta_4)h/4\pi^2A=3h/8\pi^2A$. Secondly, they supply a fifth datum which together with the values of the four fundamental frequencies just allows us to determine the five potential constants of the molecule. The measurements of Cooley[24] gave the following values for the line spacings. $\Delta\nu_3=9.771$ cm^{-1} and $\Delta\nu_4=5.409$ cm^{-1}. Following through the indicated substitutions we find $A=5.47\times10^{-40}$, $\zeta_3=0.0345$, $\zeta_4=0.4655$. The molecular dimensions are $H-H=1.81\times10^{-8}$ and $C-H=1.11\times10^{-8}$ cm.

The values of the fundamental frequencies $\nu_1=2914$, $\nu_2=1520$, $\nu_3=3014$, and $\zeta_4=1304$ cm^{-1} together with either ζ_3 or ζ_4 (the ζ's are not independent since $\Sigma\zeta=\frac{1}{2}$) serve to fix the potential constants. We find

$a=7.670\times10^5$ dynes/cm $c=-0.018$ $e=\pm1.807$
$b=1.616$ $d=-0.289$

or in Dr. Rosenthal's notation

$A=7.670\times10^5$ dynes/cm $C=0.341$ $E=0.313$
$B=0.476$ $D=\pm1.278$.

These data do not determine the sign of e or of D, but the recent paper of Ginsburg and Barker[16] on the spectrum of methyl deuteride shows conclusively that the positive sign is the one to be chosen. The work just cited is extremely important from our point of view since the values of the fundamental frequencies of CH_3D together with the line spacing of the parallel bands yield independent values for the moment of inertia and the potential constants of methane. It turns out that $A=5.298\times10^{-40}$, which is about 3 percent lower than our figure. This agreement is quite as good as could be expected from a theory which neglects second-order perturbations. The potential constants obtained by Ginsburg and Barker differ from ours by amounts around 5 percent. We regard a divergence of this order of magnitude as being inevitable for the following reason. Ginsburg and Barker in their calculations were forced to use the observed positions of the fundamental bands and not the actual normal frequencies themselves. The difference between these two is of the order of 10 to 50 cm^{-1} and will introduce

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[22] The formula for ζ_i appears to be slightly different from that published by us earlier. The difference is due solely to a small change in the notation and to the fact that we there employed Dr. Rosenthal's constants.

[23] D. M. Dennison, Rev. Mod. Phys. **3**, 304 (1931).

[24] J. P. Cooley, Astrophys. J. **62**, 73 (1925).

errors into the potential constants of around 5 percent. Thus we do not believe that the constants derived from the spectrum of methyl deuteride are essentially more accurate than those quoted here. A second way to make this clear is to calculate the frequencies of CH_3D by using our potential constants and the formulae of Dr. Rosenthal.[25] The differences between the calculated and observed frequencies are 18, 39, 22, 17, 7 and 5 cm^{-1}. But these are just of the order of magnitude of the shift in the position of a band caused by the existence of anharmonic terms in the potential.

The spectrum of methyl deuteride presents one further point where we may apply our theory and that is the fine structure spacing of the perpendicular bands ν_2, ν_4 and ν_6. In the formula $\Delta\nu_i=[(1-\zeta_i)/C-1/A]h/4\pi^2$ the moments of inertia A and C are known. The internal angular momentum factors ζ_i are completely fixed by the potential constants of methane and the masses of the particles. The actual computation of the ζ's was carried out by means of the method used previously, but eventually became so involved that recourse was had to a numerical evaluation. The only check that we have on the calculation is that the sum of the ζ's turns out to have its expected value $C/2A=0.370$. We obtained, $\zeta_2=0.03$, $\zeta_4=-0.25$, and $\zeta_6=0.59$ from which the line spacings $\Delta\nu_2=2.3$ $\Delta\nu_4=5.2$ and $\Delta\nu_6=-3.3$ cm^{-3} are readily deduced.

The observations of Ginsburg and Barker are as follows. The frequency ν_2 lies at 2983.0 cm^{-1} and has a strong central region of absorption indicating $\Delta\nu_2\sim 1$ cm^{-1}. This band, however, is in strong resonance interaction with the band $2\nu_4$ and consequently its line spacing will be greatly perturbed and no agreement with the theoretical spacing is to be expected.

The band ν_4 occurs at 1477.1 cm^{-1}. Its line spacing is somewhat irregular but appears to lie between 5 and 6 cm^{-1}, in good agreement with our estimate of 5.2 cm^{-1}. The frequency ν_6 at 1156.3 cm^{-1} consists of regularly spaced lines whose constant ranges from 3.8 to 4.5 cm^{-1}. Our value of 3.3 does not seem to be seriously in error.

§5. THE OVERTONES OF SPHERICALLY SYMMETRIC MOLECULES

A treatment of the overtones of the YX_4 molecule may be made along the same lines as that used in the discussion of the overtones of ZYX_3, but it is somewhat more complicated in that we are here concerned with tetrahedral rather than threefold symmetry. We shall consider only two types of overtone, $2\nu_i$, $i=3$, 4, and $\nu_3+\nu_4$.

Dennison and Ingram[26] in their paper on the overtones $n\nu_i$ of methane, calculated the multiplicity of the excited states. They showed that since the motion is similar to that of a three-dimensional isotropic oscillator, the wave functions may be expanded in terms of functions $\psi_{(x)}{}^{n_1}\psi_{(y)}{}^{n_2}\psi_{(z)}{}^{n_3}$ where $n_1+n_2+n_3=n$ the quantum number of the state. ψ is one of the Hermitian orthogonal functions and the rectangular coordinates x, y, z are proportional to the normal coordinates. (Because of the degeneracy the motions corresponding to ν_3 and ν_4 each require three normal coordinates.) The function $\psi_{(x)}{}^{n_1}\psi_{(y)}{}^{n_2}\psi_{(z)}{}^{n_3}$ is conveniently abbreviated by the symbol $(n_1n_2n_3)$ and it was shown that a perturbing function having tetrahedral symmetry will connect $(n_1n_2n_3)$ with $(n_1'n_2'n_3')$ providing n_1+n_1', n_2+n_2' and n_3+n_3' are either all even or all odd integers. One further statement must be made before beginning the analysis. A transition which is active must connect two wave functions for which one of the quantum numbers changes by one unit while the other two remain unchanged. Thus $(n_1n_2n_3)\rightarrow(n_1-1,\ n_2,\ n_3)$ corresponds to a nonvanishing electric moment in the x direction.

The normal state is characterized in first approximation by (000) but the perturbation will add terms of the sort $\lambda(n_1n_2n_3)$ where n_1, n_2, and n_3 are either all even or all odd integers. The first excited state is given (in first approximation) by the three functions (100), (010) and (001). Clearly, transitions to it from the normal state may occur resulting in the fundamental band ν_i. The internal angular momentum of this excited state is $\zeta_i h/2\pi$ and it is easy to show that its component, say along the z axis, is $(x\dot{y}-y\dot{x})\zeta_i h/2\pi$

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[25] In the letter by Dennison and Johnston the frequencies of all the heavy methanes are computed and presented in a table which we omit in the present paper.

[26] D. M. Dennison and S. B. Ingram, Phys. Rev. **36**, 1451 (1930).

Thus the eigenvalues of $(x\dot{y}-y\dot{x})$ for this state are $+1$, 0, -1.

Dennison and Ingram obtained the result that the second excited state $n=2$ is broken up into three states. The first and second of these are single and doubly degenerate, respectively, and both are described by linear combinations of the wave functions (200), (020) and (002). No transitions may occur to either of these states since it is impossible to select a wave function $(n_1n_2n_3)$ entering the perturbed part of the normal state wave function which will combine actively with the functions (200), (020) or (002). The third part of the state $n=2$ is triply degenerate and uses the functions (011), (101) and (110). A transition may occur from the normal state to this state by means of the particular term $\lambda(111)$ in the normal state wave function. Since the quantum number decreases rather than increases in going from the normal to the excited states, we would expect the ζ of $2\nu_i$ to be negative. This may be verified by direct calculation. The magnitude of the ζ depends upon the eigenvalues of $(x\dot{y}-y\dot{x})$ for the states (011), (101), and (110). A simple computation shows these to be $+1$, 0, and -1. Thus we obtain the result that the fine structure of the overtone $2\nu_i$, $i=3, 4$ has a spacing constant $(1-\zeta)h/4\pi^2A$ where $\zeta=-\zeta_i$.

The excited state leading to the overtone $n\nu_3+m\nu_4$ may be characterized by the symbol $(n_1n_2n_3)[m_1m_2m_3]$ where $n_1+n_2+n_3=n$ and $m_1+m_3+m_3=m$. The subscripts 1, 2, 3 refer to the xyz directions, respectively. The excited state of $\nu_3+\nu_4$ is ninefold degenerate; the wave functions consisting of functions of the type (100)[100], (010)[001], etc. The first problem is to find how the tetrahedral symmetry will regroup the nine functions. This is easily done by writing out the secular determinant, using any perturbing function $\lambda V'$ of tetrahedral symmetry. It soon appears that the only nonvanishing elements are those for which the changes in n_1+m_1, n_2+m_2 and n_3+m_3 are either all even or all odd integers. The secular determinant now shows that the nine degenerate levels arrange themselves into two triple states, one double, and one single state. Tetrahedral symmetry will not further reduce the degeneracy.

The first triple state is described by the wave functions

$$1/2^{\frac{1}{2}}\{(100)[001]+(001)[100]\},$$
$$1/2^{\frac{1}{2}}\{(010)[001]+(001)[010]\}$$

and

$$1/2^{\frac{1}{2}}\{(100)[010]+(010)[100]\}.$$

The second triple state is given by three functions of the type $1/2^{\frac{1}{2}}\{(100)[001]-(001)[100]\}$ while the double and single states are given by certain linear combinations of the functions (100)[100], (010)[010] and (001)[001]. To find the selection rules we must consider the perturbed part of normal state wave functions, the most significant terms of which for our purpose are of the type

$$\lambda\{(100)[011]+(010)[101]+(001)[110]\}.$$

These show that transitions may take place to the first triple state but not to the second triple state nor to the double or single state. Moreover in the term giving rise to the allowed transition, the quantum number decreases rather than increases, showing that the ζ will have the negative sign.

To obtain the magnitude of the ζ it is only necessary to calculate the eigenvalues of the angular momentum along some particular axis, say the z axis. The displacements used in computing the momentum are linear combinations of the normal coordinates with proportionality factors depending upon ζ_3 and ζ_4. Thus the angular momentum of the system about the z axis in units of $h/2\pi$ is,

$$(\zeta_3^{\frac{1}{2}}x_3+\zeta_4^{\frac{1}{2}}x_4)(\zeta_3^{\frac{1}{2}}\dot{y}_3+\zeta_4^{\frac{1}{2}}\dot{y}_4)$$
$$-(\zeta_3^{\frac{1}{2}}y_3+\zeta_4^{\frac{1}{2}}y_4)(\zeta_3^{\frac{1}{2}}\dot{x}_3+\zeta_4^{\frac{1}{2}}\dot{x}_4).$$

The eigenvalues of this function for the triple state in question are easily found to be $\pm\frac{1}{2}(\zeta_3+\zeta_4)$ and 0. Thus the ζ appropriate for the band $\nu_3+\nu_4$ is $-\frac{1}{2}(\zeta_3+\zeta_4)=-\frac{1}{4}$ and the line spacing of this overtone should be $5h/16\pi^2A$.

These results may now be compared with the experimental data. Although Cooley observed the positions of a number of the overtone bands of methane, he succeeded in resolving the fine structure of only one. He found a faint series of lines in the neighborhood of 3.5μ with a line spacing of about 15.3 cm^{-1}. This series he assumed to be the negative branch of a band with its center at 2824 cm^{-1} and hence he identified it as $\nu_2+\nu_4$.

Now the state ν_2 has no angular momentum and therefore $\nu_2+\nu_4$ should have the same line spacing as ν_4, that is, 5.4 cm^{-1}, in direct disagreement with the observations. A plausible way out of this difficulty is to assume that the faint series of lines found by Cooley is really the positive branch of the overtone $2\nu_4$ with its center lying at about 2608 cm^{-1}. Such an assumption is quite consistent with the observed data as far as it is now known. In that case the line spacing should be $(1+\zeta_4)h/4\pi^2A=14.8\ \text{cm}^{-1}$, which is in very good agreement with the experimental determination.

The overtone bands of methane have also been studied by Moorhead.[27] He was able to resolve the fine structure of two bands; a band at 1.66μ which gave $\Delta\nu=10.4\ \text{cm}^{-1}$ and a band at 2.20μ with a spacing of 10.7 cm^{-1}. The first of these Moorhead identified as $2\nu_3$, which according to our theory should have a spacing of $(1+\zeta_3)h/4\pi^2A=10.5\ \text{cm}^{-1}$. The band at 2.20μ which was also located by Cooley is probably $\nu_2+\nu_3$. Its line spacing should be the same as that of the fundamental ν_3 itself or about 9.8 cm^{-1}. This agreement, while less good, is still satisfactory.

In a recent paper Steward and Nielsen[28] report on the infrared absorption spectrum of silane, SiH_4. The general features of the spectrum are very similar to those of methane with the exception of the fact that the fine structure lines are not single but show satellites. This is probably due to the influence of the higher order perturbing terms which have not been included in the present theory. Ignoring as far as possible the multiplet structure, they obtain for the line spacing of the fundamentals ν_3 and ν_4 the values 5.7 and 3.5 cm^{-1}, respectively. From these data it follows that $\zeta_3=0.07$ and $\zeta_4=0.43$. Steward and Nielsen also observed the positions of a number of the overtones of silane and succeeded in partially resolving the fine structure of two of them, namely, the bands at 3095 cm^{-1} and 3153 cm^{-1}. These showed spacings of about 9.7 and 4.7 cm^{-1}, respectively. The band at 3095 cm^{-1} they identified as $\nu_3+\nu_4$. According to our theory it should have a spacing of $5h/16\pi^2A=7.7\ \text{cm}^{-1}$. The second band they consider to be $\nu_1+\nu_4$, in which case it would have the same spacing as ν_4, that is, 3.5 cm^{-1}. The agreements in neither case are very satisfactory and certainly not as good as those found for methane. This is perhaps just what is to be expected since, if the higher order terms are sufficiently large to produce a splitting of the fine structure lines, they will no doubt appreciably affect the values of the line spacing.

Note added in proof: Very recently A. H. Nielsen and H. H. Nielsen have succeeded in resolving the two overtone bands of methane $\nu_1+\nu_4$ and $\nu_3+\nu_4$ (Phys. Rev., this issue). They obtain the spacing constants 5.3 and 13.5 cm^{-1}, respectively. According to our theory the spacing of $\nu_1+\nu_4$ should be just that of ν_4, namely, 5.4 cm^{-1} while the spacing of $\nu_3+\nu_4$ is $5h/16\pi^2A=12.6\ \text{cm}^{-1}$. We wish to express our appreciation to the authors of this paper for allowing us to see and use their unpublished data.

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[27] G. J. Moorhead, Phys. Rev. **39**, 83 (1932).

[28] W. B. Steward and H. H. Nielsen, Phys. Rev. **47**, 828 (1935).

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Geiger-Counter Characteristics with Applied Potentials Reversed

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The paper describes experiments made with Geiger-Müller counters in which the cylinder potential is positive with respect to the wire instead of negative as ordinarily used. The counter operates under reduced efficiency with this reversed condition. When used as a double coincidence set the reduction in efficiency is greater than for a single counter. The paper also describes experiments confirming a view that the inefficiency of the reversed counter may be explained by supposing the counter action to be produced when a positive ion strikes the wire and liberates from it a secondary electron. Whenever such an electron is liberated a discharge takes place, but the probability of liberation is low. However, it seems reasonable that the probabilities of such liberation of secondary electrons as found by Penning and others stands in agreement with the efficiency observed in the counter experiments cited above.