Symmetry Considerations Concerning the Splitting of Vibration Rotation Levels in Polyatomic Molecules

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E. Bright Wilson, Jr.,* *Mallinckrodt Chemical Laboratory, Harvard University*

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The interaction of rotation and vibration and perhaps other effects may split degenerate vibration-rotation energy levels of symmetrical polyatomic molecules into a number of components. The permutation symmetry of molecules containing several identical atoms provides certain restrictions on this splitting. This paper discusses the maximum number of fine-structure components, their quantum weights when nuclear spins are taken into account, and the selection rule for transitions. All arguments are based solely on symmetry considerations so that no estimate of the magnitude of the splitting is given.

Definition of Coordinates

IN discussing the motions of the atoms in a polyatomic molecule (as distinct from the motion of the electrons) it is useful to use the Eulerian angles θ, φ, χ to describe the orientation of the molecule in space and the normal coordinates Q_1, Q_2, Q_3, $\cdots$, Q_N to describe the mutual positions of the atoms in the molecule. It is important to define these coordinates more definitely. Let the angles θ, φ, χ define a set of rotating Cartesian axes X, Y, Z, with origin at the center of gravity of the molecules. The position of any atom i can be specified by the Eulerian angles and the coordinates x, y, z relative to the rotating system. However, there are three too many coordinates so that three relations between the coordinates must be written down in order to define the rotating system uniquely. These relations are conveniently chosen to be[1a]

$$\Sigma m_i(a_i y_i - b_i x_i) = 0,$$
$$\Sigma m_i(b_i z_i - c_i y_i) = 0, \qquad (1)$$
$$\Sigma m_i(c_i x_i - a_i z_i) = 0,$$

where a_i, b_i, c_i are the coordinates (in terms of the rotating system) of the equilibrium position of the ith atom and m_i is the mass of the atom. A transformation from the coordinates x_i, y_i, z_i to normal coordinates Q_1, Q_2, $\cdots$, Q_N can then be carried out in the usual manner and it will be found that the relations (1) are equivalent to those usually made in normal coordinate treatments; namely, that to the first approximation

there is no rotational angular momentum with respect to the rotating system of coordinates.

An Approximate Wave Equation

It is natural to set up the wave equation in terms of these coordinates. This involves first expressing the kinetic energy in terms of θ, φ, χ, Q_1, Q_2, $\cdots$, Q_N and then using the result to construct the wave equation in the usual manner.[1] This is a possible, but complicated, procedure. However, if we assume that we can neglect in the classical Lagrangian expression for the kinetic energy those terms involving the normal coordinates to the first or higher powers (which means classically that we are assuming small vibrations), then the wave equation resulting from this approximate Lagrangian will be simply the sum of two parts; one the equation for the rigid rotator (coordinates θ, φ, χ), the other the equation for harmonic vibrations (coordinates Q_1, Q_2, $\cdots$, Q_N).*

The solutions of this equation are products of the type

$$\psi = R(\theta, \varphi, \chi) V(Q_1, \cdots, Q_N), \qquad (2)$$

where $R(\theta, \varphi, \chi)$ is the rotational wave function and $V(Q_1, \cdots, Q_N)$ is the vibrational wave function.

For molecules whose equilibrium configurations possess a certain minimum symmetry; namely, at least a threefold axis of symmetry,

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* Junior Fellow of the Society of Fellows.
[1a] C. Eckart, Phys. Rev. **47**, 552 (1935).

[1] B. Podolsky, Phys. Rev. **32**, 812 (1928).
* We assume here that the potential function is harmonic but this assumption does not change the final conclusions. This method of justifying the usual separation into rotational and vibrational parts does, however, depend on the choice of the rotating coordinate system defined by (1).

both the rotational and vibrational energy levels may be degenerate when the approximation considered here is used. Thus for CH_2F the functions R are the symmetrical top solutions with the energy levels

$$W_{J,\ K} = (h^2/8\pi^2)\{J(J+1)/ \\ A + K^2(1/C-1/A)\}, \quad (3)$$

so that levels with $|K| > 0$ are doubly degenerate. For this molecule certain of the fundamental vibrational levels are also doubly degenerate so that, to this approximation, CH_3F possesses some fourfold degenerate energy levels because of its threefold symmetry axis.

It will be shown that this high degeneracy is not really required by the symmetry so that these energy levels may be split by terms which have been omitted in obtaining this simple approximation. Some degeneracy, however, will remain on account of the symmetry.

SYMMETRY CONSIDERATIONS[2]

The true energy operator, H, is unchanged by any permutation of identical particles; it is therefore invariant under the group of permutations which are equivalent to rotations of the molecule. The wave functions RV are not in general invariant under these permutations since the coordinates θ, φ, χ, Q_1, $\cdots$, Q_N, are not. Thus the permutation (123) of the three H atoms in CH_3F changes χ into $\chi+2\pi/3$ and therefore $R(\chi)$ into $e^{2\pi iK/3}R(\chi)$.

The functions RV belonging to a given approximate energy level form a *representation*[3] of the group of permutations equivalent to rotations. This representation is in general *reducible* so that by forming the correct linear combinations of these functions RV the representation can be *reduced* and each combination will correspond to one of the *irreducible representations* of the group. The technique of finding the number

[2] This paper is an extension of a previous publication (J. Chem. Phys. 3, 276 (1935)), which considered the same symmetry questions but which obtained the total statistical weights of the unsplit energy levels. Here exactly the same methods are used, only the split levels will be considered and their separate statistical weights determined.

[3] For the meaning and use of the group theory terms employed here see E. Wigner, *Gruppentheorie* (Vieweg and Sohn); B. L. van der Waerden, *Die gruppentheoretische Methode in der Quantenmechanik* (Springer, Berlin).

of wave functions with each type of symmetry has been treated in detail in a previous paper[2] and will be assumed here.

If ψ_A, ψ_B, etc., are the linear combinations of the functions RV which reduce the representation then the perturbed energy levels are determined by integrals of the type $\int \psi_A H \psi_B d\tau$. It is a consequence of group theory that if ψ_A and ψ_B belong to different irreducible representations the integral is identically zero. Therefore the energy matrix, if set up in terms of ψ_A, ψ_B, etc., will factor into diagonal blocks, the elements of each block involving only functions of one symmetry type or irreducible representation. All other elements of the matrix will vanish. Furthermore, blocks corresponding to doubly degenerate representations of the group will occur twice, so that the energy levels which are the roots of such a block of the secular equation will be doubly degenerate. Similar remarks apply to triply degenerate representations.

CH_3F AS AN EXAMPLE

These statements may be better understood if illustrated by an example, CH_3F. From reference 2, Table X, it is found that if the rotational quantum number K has a value not divisible by three the rotational functions R for that level have the symmetry E with respect to the group of permutations equivalent to rotations. If the vibrational energy level under consideration is also doubly degenerate with the symmetry E, there will be four wave functions of the type RV, having the symmetry $E \times E = 2A + E$; that is, there can be formed four independent linear combinations of the four functions RV, such that two of them are symmetrical with respect to permutations equivalent to rotations whereas the other two form a degenerate pair. Applying the theorems of the previous paragraph we obtain the energy matrix (or secular equation) shown in Fig. 1, in which only the elements in the heavy squares are different from zero and the elements of the two squares marked E are equal. As far as the symmetry is concerned, therefore, the originally fourfold level may split, under the influence of coupling terms, etc., into three levels, two of which are the roots of the quadratic equation

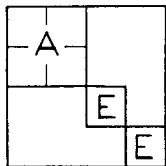FIG. 1.   FIG. 2.

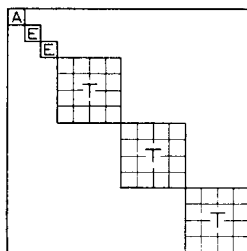FIG. 1. Energy matrix for a sample approximate level of CH_3F. Heavy lines enclose non-zero elements.
FIG. 2. Energy matrix for a sample approximate level of CH_4.

obtained from the upper block of Fig. 1, while the remaining level is doubly degenerate and comes from either of the two equal lower blocks of the secular equation.

METHANE AS AN EXAMPLE

Methane may be similarly treated. As a sample let us consider the level with J equal to 2 and with one quantum of one of the triply degenerate vibrations excited. From Table III, reference 2 we find that the symmetry of this level is $(E+T)\times T=A+E+4T$. The secular equation for this level therefore has the form shown in Fig. 2, in which the lower three blocks are identical and the two blocks above these are identical. This energy level may therefore split into one single level (A), one double level (E), and four triple levels (T).

In connection with methane it may be pointed out that it is possible, but not proved, that even the nonvibrating rotational levels of methane may be split. For example, the level with J equal to 5 has the symmetry $E+3T$ so that in the nonvibrating state it is possible for a perturbation with tetrahedral symmetry (such as conceivably the stretching terms) to split this eleven-fold level into one double level and three triple levels. It requires further study of a more quantitative nature in order to decide whether or not such a splitting actually occurs to an appreciable degree or not. This treatment merely shows that the symmetry of the molecule does not require such a high degree of degeneracy.

SELECTION RULES

The electric moment of a molecule is a function of the coordinates of the nuclei and is unaffected by interchange of coordinates of identical nuclei. It is thus symmetrical. The integral $\int \psi_A \mu \psi_B d\tau$, determining the transition probability, is therefore zero if ψ_A and ψ_B are in different irreducible representations. The selection rule is that transitions occur only between levels of the same symmetry. This rule does not replace the ordinary selection rules but is an additional restriction.

STATISTICAL WEIGHTS OF COMPONENT LEVELS[2]

The calculation of the statistical weights of the components of a level (important for the computation of relative intensities) is carried out in exactly the same manner as in reference 2. Thus for methane the nuclear-spin functions have the symmetry $5A+E+3T$. The total wave function must have the symmetry A. Therefore the components of the sample vibration-rotation level previously discussed will have the weights shown in Fig. 3 (multiplied by $2J+1$).

MOLECULES WITH SEVERAL FRAMEWORKS

Both of the examples above are molecules possessing two "frameworks" in the sense used in reference 2. As discussed in that reference, however, this fact does not need to be taken into account in calculating the statistical weights of the levels since the total wave function must have one definite symmetry with respect to interchanges of identical particles and there will

FIG. 3. Number of components, their symmetries and statistical weights (factor $2J+1$ omitted) for a sample level of methane. Regions I and II give the symmetries before and after splitting, spins not included. Region III gives the symmetries when the spin function $\psi s(5A+E+3T)$ is included. Region IV gives the statistical weights of the components when the exclusion principle is applied (A only). The vertical order and relative spacing of the components has no significance.

be only one linear combination of the functions based on the various frameworks which will have the correct symmetry.

CONCLUSION

It is to be emphasized that only symmetry considerations have been used in this paper so that the results are necessarily incomplete since they do not yield any information regarding the magnitudes of the splittings to be expected. Actual energy levels may not be split to an observable extent or they may show the splitting indicated here only incompletely. It is possible also that certain of the perturbations, especially the rotation-vibration coupling, may split the approximate energy levels to such an extent that a component of one approximate level may nearly coincide with a component of another approximate level. In spite of these complications, however, the symmetry does restrict the maximum number of components which are possible and gives the selection rules and statistical weights involved. Experimental results[4] exist which may be capable of interpretation in terms of these effects but further work is necessary.

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

The Molecular Structures of Sulfur Dioxide, Carbon Disulfide, and Carbonyl Sulfide

PAUL C. CROSS* AND L. O. BROCKWAY, *Gates Chemical Laboratory, California Institute of Technology*†

The structures of the molecules SO_2, CS_2, and COS have been investigated by the electron diffraction method with the following results; SO_2, $S-O = 1.46 \pm 0.02 A$; CS_2, $C-S = 1.54 \pm 0.03 A$; COS, $C-O = 1.16 \pm 0.02 A$, $C-S = 1.56 \pm 0.03 A$. The types of bond arrangement compatible with these interatomic distances are discussed. In SO_2 the molecule resonates between the structures having single-double and double-single bonds between the sulfur and the two oxygen atoms, with a bond angle of $122° \pm 5°$. CS_2 is a linear molecule with the structure having the two double bonds predominating over those having a single and a triple bond. In COS the double-double bond arrangement and the structure having the triple carbon-oxygen bond predominate.

THE molecular structures of sulfur dioxide, carbon disulfide, and carbonyl sulfide have been studied by the method of electron diffraction of gases. A jet of vapor is made to intersect a beam of forty-kilovolt electrons whose diffraction pattern is registered on x-ray film. Visual measurements on the maxima and minima are correlated with those on the theoretical curves based on various molecular models. In these curves the scattering power of an atom for electrons is assumed to be constant with angle and the inelastic scattering is neglected. A detailed discussion of the procedure used in interpreting electron diffraction photographs has already been published.[1]

* National Research Fellow in Chemistry.
† No. 501.

[1] L. Pauling and L. O. Brockway, J. Chem. Phys. **2**, 867 (1934).

SULFUR DIOXIDE

The sample of sulfur dioxide was redistilled from the purest commercial product.

The heavier photographs showed four maxima. The first was very strong; the second, strong and rather broad; the third and fourth were weaker but very sharp. The theoretical intensity curve, Fig. 1, is based upon a triangular model with an angle of 120° between the sulfur-oxygen bonds. No other curves are shown since the theoretical diffraction pattern is very insensitive to changes in bond angle. This effect in molecules with heavy central atoms and light outer atoms has been discussed for chlorine dioxide.[2]

The values obtained for the sulfur-oxygen distance are given in Table I. The third column

[2] L. O. Brockway, Proc. Nat. Acad. Sci. **19**, 303, 874 (1933).