THE VIBRATIONAL PROBLEM IN MOLECULES WITH NEARLY FREE INTERNAL ROTATION

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In this paper we shall consider some of the recent work on the vibrational problem in molecules with nearly free internal rotation. The paper will be divided into two parts. In the first part we shall consider some of the group theoretical ideas currently being applied to the problem. In the second part we shall consider how normal modes can be algebraically described in such a molecule. To make the discussion more specific, we shall take as an example the dimethylacetylene molecule. In both parts of the paper we shall be concerned with the differences between the techniques suggested for dealing with dimethylacetylene-like molecules and the techniques employed for "ordinary" molecules.

GROUP THEORY

We could begin the first half of this talk with a review of the group theoretical material presented in various microwave papers concerning molecules with internal rotation. However, I think it is fair to say that none of the microwave workers describe adequately how their ideas concerning a given molecule could be generalized to apply to a whole host of similar molecules. Hence we begin here by considering the principal ideas involved in a paper by Longuet-Higgins¹.

Molecular symmetry group of Longuet-Higgins

Most spectroscopists are accustomed to thinking of the symmetry of a molecule in terms of geometrical operations on a three-dimensional solid object, i.e., in terms of rotations about an axis, reflections in a plane, the inversion, and rotation-reflections. The molecular symmetry group for any given molecule is composed of selected elements of this kind which have the property that they "convert the molecule in its equilibrium configuration into itself".

However, in a sense the fundamental reason why a molecule has symmetry is that it contains two or more identical atoms. Thus it is a natural step to consider the symmetry operations of a molecule, not in terms of some geometrical operation but rather as some permutation of the various identical nuclei within the molecule.

This brings us to the first important concept, namely, the difference between a geometrical symmetry operation and a permutational symmetry operation. Without presenting all the details of the arguments, we make the following observation. Every geometrical symmetry operation of the kind usually considered by molecular spectroscopists dealing with group theory
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is equivalent to some permutation of identical nuclei in the molecule, the nuclear permutation being accompanied by an inversion at the origin of the coordinates of all the particles of the molecule if the geometrical operation is one which converts a right-handed object into a left-handed object.\(^{3}\) The converse, however, is not true. Every permutation of identical nuclei in the molecule, with or without an accompanying inversion of all coordinates, is not equivalent to some geometrical symmetry operation of the usual kind.

As an example, consider the molecular structure depicted in Figure 1. A rotation of the molecule about the axis through atoms 1 and 4, represented by \(C_2(y)\), is equivalent according to the above rules to an exchange of the identical nuclei 2 and 6, represented by \((26)\), and an exchange of the identical nuclei 3 and 5. A reflection of the molecule in the plane perpendicular to the molecular plane and containing atoms 1 and 4, represented by \(\sigma(yz)\), is equivalent to the same permutations of identical nuclei as is \(C_2(y)\), but these permutations must be accompanied by an inversion at the origin of the coordinates of all the particles, represented by *, because reflection in a plane changes the handedness of an object. However, no geometrical symmetry operation is equivalent to an exchange of the two nuclei 2 and 6 only.

The group containing all possible permutations of identical nuclei and the inversion is determined solely by the chemical formula of a molecule. For example, this group for \(C_6H_5Cl\) contains \(2 \times 6! \times 5! \times 1!\) operations. However, Longuet-Higgins points out that it is undesirable to use this complete group of permutations together with the inversion when setting up a classification scheme for the energy levels of any given molecule. Rather, one wants to use a sub-group of this complete group which contains only feasible operations, i.e., operations corresponding to changes in the nuclear configuration which can be carried out without going over an "insurmountable" energy barrier. We shall here define the words feasible and insurmountable by example and shall postpone a discussion of the implications of classifying any given symmetry operation as feasible and any energy barrier as insurmountable until dealing with the correlation rule of Watson\(^4\).

Let us look at the dimethylacetylene molecule, as shown in Figure 2, and try to determine a few feasible and a few non-feasible symmetry operations. Consider first the permutation \((23)\), i.e., the exchange of hydrogens 2 and 3. This operation corresponds to the conversion of a right-handed carbon centre into a left-handed centre, and in general will not take place during the course of a normal experiment. Thus the barrier associated with this motion is insurmountable and the operation is not feasible. The same remark holds for the operation \((23)(56)\), which changes the handedness of two carbon centres. But the operation \((23)(56)*\) is different. The two permutations and the inversion (represented by *) both change the handedness of the two carbon centres, so that the composite operation \((23)(56)*\) leaves the handedness of each carbon centre unaltered. By drawing the molecule obtained from Figure 2 after the operation \((23)(56)*\) is performed, the reader can convince himself that a simple rotation of the molecule as a whole will bring the two configurations into coincidence. Since there are no forces

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Figure 1. An example of the relation between geometrical symmetry operations and permutational symmetry operations. The atoms labelled 1 through 6 are considered to be identical and are located at the corners of a regular hexagon. The symbol (26) represents an interchange of nuclei 2 and 6. The symbol * represents the inversion.

Two feasible operations: (23)(56)* (123)  
Two non-feasible operations: (23), (23)(56)

Figure 2. The dimethylacetylene molecule together with two feasible and two non-feasible symmetry operations.

opposing rotation of the entire molecule in free space, the barrier associated with this motion is surmountable (in fact, non-existent) and the operation (23)(56)* is feasible. We consider one more example, namely the cyclic permutation (123) of the three hydrogen atoms 1, 2 and 3, a motion which involves the rotation of one methyl group against the other. Since dimethylacetylene is generally believed to have a very small barrier to internal rotation (less than 10 cm⁻¹), the operation (123) is to be regarded as feasible for dimethylacetylene. Even in ethane derivatives, where the barrier to internal rotation is much higher, splittings due to tunnelling through the barrier are often observable in microwave studies, and for these cases the barrier must still be regarded as surmountable and the operations analogous to (123) as feasible. However, if the barrier to internal rotation were extremely high, or if the nuclei at the hydrogen positions were extremely heavy, so that no effects due to tunnelling through the barrier were observable in the experiment being performed, then the barrier should be regarded as insurmountable and the operation (123), or its analogue, as non-feasible.

The collection of all feasible symmetry operations for a given molecule forms the molecular symmetry group. Since most of these groups are not isomorphic with the familiar three-dimensional point groups, the investigator is faced at this point with an exercise in the theory of representations, i.e., faced with the problem of determining the symmetry species and
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Associated character table for each group under consideration. Thus, Longuet-Higgins\textsuperscript{1} has written down character tables appropriate for any molecules "having the same symmetry" as CH\textsubscript{3}BF\textsubscript{3}, C\textsubscript{5}H\textsubscript{6}, N\textsubscript{2}H\textsubscript{4} and B(CH\textsubscript{3})\textsubscript{3}, the tables for the first three of these molecules agreeing completely with the earlier results of microwave investigators. Bunker has done the same for any molecules having the same symmetry as ferrocene\textsuperscript{5}, methylsilylacetylene\textsuperscript{6}, and X\textsubscript{2}Y\textsubscript{8} (two square pyramids attached at their apexes)\textsuperscript{7}. Stone\textsuperscript{8} has considered the molecules C(CH\textsubscript{3})\textsubscript{4} and M(NH\textsubscript{3})\textsubscript{6}. When internal rotations are considered in the latter molecule, which represents an octahedral metal hexamine ion, its molecular symmetry group contains 34,992 symmetry operations and has 102 symmetry species. The symmetry species of highest degeneracy is 48-fold degenerate. It seems at the present time unlikely that any observed spectrum will fully illustrate the subtleties associated with such a complex group theoretical apparatus.

Use of the double group for the vibrational problem

Up to this point we have been discussing the operations of the molecular symmetry group in terms of permutations of identical nuclei. Let us imagine for a moment that the molecular wave-function is written in terms of the space-fixed Cartesian coordinates of each nucleus, and that each Cartesian coordinate is provided with a subscript indicating to which nucleus it refers. (Naturally the wave-function will also depend on the space-fixed Cartesian coordinates of each electron. We are not considering the electronic problem in this paper. Suffice it to say, that the electronic problem can be dealt with in a manner consistent with the ideas being presented here for the nuclear problem. It should also be mentioned at this point that we are not considering the dependence of the molecular wave-function on the nuclear spins, a dependence which is important when considering statistical weights.*) In any case, when the wave-function is expressed in terms of the space-fixed Cartesian coordinates of the nuclei, then we can perform the operations of Longuet-Higgins' molecular symmetry group simply by permuting the subscripts on various Cartesian coordinates, sometimes accompanying the permutation by a change in sign of all Cartesian coordinates.

However, the molecular wave-function is usually written in terms of a set of variables which do not explicitly indicate how they depend on the Cartesian coordinates of a given nucleus, making it difficult to determine exactly how to perform any permutational symmetry operation. In dimethylacetylene, for example, one must answer the question: what is the effect of the operation (23) (56)* on the three Eulerian angles (rotational variables) and on the normal coordinates (vibrational variables)?

It is by no means a trivial problem, in general, to find the answer to a question like this. First of all, the question cannot even be asked until one has decided upon exactly which variables are to be used in the molecular wave-function. In dimethylacetylene it seems natural enough to use three rotational variables (Eulerian angles), one internal rotation variable (torsional angle), 23 vibrational variables (normal coordinates), and three variables representing translation of the molecule as a whole. In certain
other problems, e.g., an ozone-like molecule in which the three oxygen atoms take turns in occupying the central position, the best choice of variables is less obvious. After the set of variables for the molecular wave-function has been chosen, the space-fixed Cartesian coordinates of the nuclei must be explicitly related to them and a set of transformations for the new variables must be found which reproduce the permutational symmetry operations on the space-fixed Cartesian coordinates which are required by Longuet-Higgins' molecular symmetry group.

Such a procedure has been carried out for dimethylacetylene. As it happens, it led to the somewhat surprising result that the appropriate group to use in classifying the wave-functions of dimethylacetylene contains twice as many elements as the group proposed by Longuet-Higgins. This larger group will be referred to as the double group of the Longuet-Higgins molecular symmetry group. It arises for the following reason. When discussing the nuclear motions of the dimethylacetylene molecule, it seems intuitively desirable to consider separately, at least in the zeroth approximation, the rotational motion, the torsional motion, and the motion associated with each normal mode of vibration. It thus also seems intuitively desirable to have a classification scheme which allows symmetry species to be assigned separately to rotational wave-functions, torsional wave-functions, and vibrational wave-functions. Now, the complete rotational–torsional–vibrational wave-function can in principle always be expressed as a single-valued function of the space-fixed Cartesian coordinates of the nuclei, and thus can always be classified according to symmetry species of Longuet-Higgins' molecular symmetry group. However, in principle it could happen that the torsional function by itself, say, might be expressible only as a multiple-valued function of these coordinates. This is in fact what happens in dimethylacetylene. Without going into details, it turns out that for the system of coordinates to be used in the second half of this talk, there are two different ways of choosing the Eulerian angle \( \chi \) and the torsional angle \( \gamma \) for any given arrangement in space of the nuclei of the dimethylacetylene molecule. If \( \chi, \gamma \) correspond to one choice, then \( \chi + \pi, \gamma + \pi \) correspond to an equally good second choice. The total nuclear wave-function always involves \( \chi \) and \( \gamma \) in such a way that the transformation \( \chi, \gamma \to \chi + \pi, \gamma + \pi \) leaves that wave-function unchanged. For the total wave-function this operation is thus equivalent to the identity. However, the torsional functions by themselves are of the form \( \exp(iL\gamma) \), where \( L \) is an integer. They are therefore not invariant to the transformation \( \chi, \gamma \to \chi + \pi, \gamma + \pi \). For the torsional wave-function by itself this operation must be considered different from the identity. Considerations of this kind ultimately lead to a doubling of each original molecular symmetry operation for dimethylacetylene. In my opinion, a similar phenomenon may well occur for other molecules, perhaps involving in some cases groups even larger than the double group of Longuet-Higgins' molecular symmetry group.

**Correlation rule of Watson**

Let us return for a moment to the question of feasible and non-feasible symmetry operations and consider the example of methane. Though it is
normally not explicitly taken into account, the rotational levels of methane (like those of \(\text{NH}_3\), say) occur as inversion doublets. This phenomenon is associated with the fact that if one labels the hydrogen atoms, then one can write for the equilibrium configuration two forms: a right-handed form and a left-handed form. However, these inversion doublets in methane cannot be resolved by any normal spectroscopic technique. It is therefore useless in a practical system of classifying the energy levels to distinguish between the two components of a doublet. It is in fact sufficient to have a classification scheme which distinguishes only between different doublets. For methane the complete permutation–inversion group is of order 48, with 10 symmetry species. A classification of the energy levels according to this group attaches a different species to the two components of each doublet. It turns out, however, that there are only five different kinds of doublets,

![Diagram](image)

*Figure 3 (a). The \(D_{3h}\) structure of a planar \(XY_3\) molecule; (b) three equivalent \(C_{2v}\) structures of a planar \(XY_3\) molecule*

and further that if one discards from the complete permutation–inversion group as non-feasible, those operations which convert a right-handed form into a left-handed form, then one is left with a group of 24 elements (corresponding to the point group \(T_d\)), with 5 symmetry species. A classification of the energy levels according to this latter group attaches a different species to each of the five kinds of doublets, but does not distinguish between the individual components of a doublet.

The situation in methane is in fact an example of a more general phenomenon. In many molecules energy levels occur in systematically degenerate sets, corresponding to the fact that the molecule can be thought of as existing in one of several frameworks between which interconversion is not feasible. If for some reason tunnelling between these frameworks becomes feasible, *i.e.*, if some interconversion takes place, then some of the degeneracy associated with the existence of several equivalent frameworks is removed. From the point of view of group theory, as we increase the number of feasible symmetry operations in the molecular symmetry group, levels which were previously degenerate split.

The problem of changing the number of feasible operations in a molecular symmetry group arises because there is no absolute criterion for the feasibility
of a given element. For instance, if the energy in an appropriate vibrational mode is high enough to be comparable with the energy barrier, then the probability of penetrating the barrier, and therefore the associated splittings of the energy levels, will be greater for these higher vibrational energies than it is for lower energies. Symmetry operations which are not feasible for lower levels will therefore become feasible for higher levels. Furthermore, a high resolution spectroscopic technique may be able to resolve some or all of the nearly degenerate levels, and to interpret data obtained by this technique more feasible operations must be considered than for data obtained by a lower resolution technique. The choice of feasible operations is therefore to some extent arbitrary, and depends on which distinctions one wishes to preserve and which one wishes to ignore.

The question which Watson considered is the following: into what symmetry species does a given level split when the number of feasible operations in the molecular symmetry group is increased? Or in other words, how does one correlate the levels in the high barrier limit with the levels in the low barrier limit? A somewhat imprecise, but easy to remember phrasing of the answer to this question is simply: use the ordinary correlation table backwards. The best way of getting a feeling for what this correlation rule actually entails is to consider an example. Unfortunately, the case of dimethylacetylene is somewhat complicated because of the large number of symmetry operations. Therefore we consider the rotational levels of a planar \(XY_3\) molecule for the two limiting cases of a \(D_{2h}\) structure (Figure 3a) and three equivalent \(C_{2v}\) structures (Figure 3b). We consider only the rotational levels, rather than the more interesting vibrational levels, since it is possible, though I think not very likely, that the group to be used in discussing the vibrational problem of three interconverting \(C_{2v}\) structures may be larger than \(D_{2h}\), i.e., it is possible that some complication similar to that which leads to the use of the double group in dimethylacetylene may occur. For the rotational energy levels, however, we can use Longuet-Higgins’ molecular symmetry groups, which for the situation under consideration are equivalent to \(D_{2h}\) and \(C_{2v}\). Table 1 presents the usual correlation table relating the species of the group \(D_{2h}\) to the species of the group \(C_{2v}\). Table 2 presents Table 1 “read backwards”. It indicates how the rotational levels of the \(C_{2v}\) molecule are split as the barrier to interconversion of the three frameworks in Figure 3b is reduced.

**Table 1.** Ordinary correlation table for the sub-group \(C_{2v}\) of \(D_{2h}\)

<table>
<thead>
<tr>
<th>(D_{2h}) species</th>
<th>(C_{2v}) species</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1^i)</td>
<td>(A_1)</td>
</tr>
<tr>
<td>(A_2^i)</td>
<td>(A_2)</td>
</tr>
<tr>
<td>(A_3^i)</td>
<td>(B_1)</td>
</tr>
<tr>
<td>(A_4^i)</td>
<td>(B_2)</td>
</tr>
<tr>
<td>(E^i)</td>
<td>(A_1 + B_1)</td>
</tr>
<tr>
<td>(E^e)</td>
<td>(A_2 + B_2)</td>
</tr>
</tbody>
</table>

**Table 2.** The splitting of the \(C_{2v}\) levels of an \(XY_3\) molecule caused by tunnelling between the three equivalent \(C_{2v}\) frameworks (see Figure 3)

<table>
<thead>
<tr>
<th>(C_{2v}) levels</th>
<th>(D_{2h}) sub-levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1)</td>
<td>(A_1^i + E^i)</td>
</tr>
<tr>
<td>(A_2)</td>
<td>(A_2^i + E^i)</td>
</tr>
<tr>
<td>(B_1)</td>
<td>(A_3 + E^i)</td>
</tr>
<tr>
<td>(B_2)</td>
<td>(A_4 + E^i)</td>
</tr>
</tbody>
</table>
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It is common knowledge that a decrease in symmetry is associated with a splitting of degeneracies (see Table 1). We observe in this section, however, that an increase in symmetry is associated with a splitting of degeneracies (see Table 2). Both of these statements are true. The apparent paradox can only be resolved by a far more careful investigation, than we have time for, of the relationship between the degeneracy associated with having several equivalent frameworks and the degeneracy associated with having certain symmetry operations in the molecular symmetry group.

NORMAL MODES

The problem of normal modes in the dimethylacetylene molecule has been considered by Bunker\textsuperscript{10}, His treatment makes use of internal coordinates, \textit{i.e.}, of bond length changes and bond angle changes, as the fundamental basis set with which to express the normal modes, and leads to the result that the "degenerate normal coordinates depend on the torsional quantum number \( \ell^\prime \)." Bunker has applied similar ideas to the ferrocene molecule\textsuperscript{11}, and somewhat similar ideas to the methylsilylacetylene molecule\textsuperscript{6}.

We shall consider here a different approach to the vibrational problem\textsuperscript{9,12}, which uses Cartesian displacements of the nuclei from their equilibrium positions as the fundamental basis set with which to express the normal modes, and which was designed to facilitate a rigorous algebraic derivation of certain quantities and statements of interest in the vibrational problem in dimethylacetylene. It seems very likely on physical grounds that we can consider the vibrational problem in dimethylacetylene by itself, and even that some sort of normal modes must exist, since the molecule has a superficially normal vibrational spectrum. We shall now examine an algebraic formalism which can hopefully be used to discuss that vibrational spectrum.

Definition of the nuclear displacement coordinates

Before discussing the problem of vibrational symmetry coordinates and normal modes in dimethylacetylene, we consider the definition of a set of Cartesian displacement coordinates \( \mathbf{d}_i \) for the nuclei of the molecule. The symmetry coordinates and normal modes of the molecule will ultimately be expressed as linear combinations of these displacement coordinates. Now, it is obvious that the definition of a set of displacement coordinates is only useful if we simultaneously define a set of "reference" positions for the atoms of the molecule from which these displacements are to be measured; but this is the essential difficulty for any molecule which, like dimethylacetylene, has nearly free internal rotation. Should one take as a reference configuration of the molecule a structure in which the two methyl groups are staggered, eclipsed, or at some intermediate torsional position? Intuitively, of course, one would like a set of reference positions which did not favour any particular value for the torsional angle. The set of coordinates we shall now describe satisfies this intuitive desire. In addition, it leads to a set of nuclear displacements \( \mathbf{d}_i \) which, like their analogues in ordinary molecules, remain small when the molecule vibrates.

Consider the following equation:

\[
\mathbf{r}_i = \mathbf{R} + S^{-1}(\chi, \theta, \phi) \cdot S^{-1}(\gamma, 0, 0) \cdot (\mathbf{a}_i + \mathbf{d}_i)
\]  

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Here $\mathbf{r}_i$ represents the space-fixed coordinates of the "$i$"th nucleus, i.e., the coordinates in an axis system fixed in the laboratory; $\mathbf{R}$ represents the space-fixed coordinates of the centre of mass of the nuclei; $\chi$, $\theta$ and $\phi$ represent three Eulerian angles which relate the space-fixed axis system to an axis system locked in the molecule; $\gamma$ is the torsional angle; the $\mathbf{a}_i$ represent reference positions of the nuclei in dimethylacetylene and the $\mathbf{d}_i$ represent displacements from these reference positions. The reference positions $\mathbf{a}_i$ are arbitrarily taken to correspond to an eclipsed configuration of the two methyl groups. We can most easily get a feeling for the meaning of equation (1) by reading it from right to left. Assume that the values of the variables on the right-hand side of the equality are known, and that we wish to determine the coordinates of the nuclei in the laboratory-fixed axis system. We begin with the quantities $\mathbf{a}_i$, i.e., each atom is placed at its reference position. Then each atom is displaced from its reference position by the amount $\mathbf{d}_i$. At this point the twisting matrix $S^{-1}_t(\gamma,0,0)$, is applied, which in reality represents two $3 \times 3$ matrices, one for each half of the molecule. These matrices are constructed in such a way that they twist the top half and the bottom half of the molecule in opposite directions, both halves being turned through an angle $\gamma$ from their original (reference) position. The molecule now has its final shape. We then apply the rotation matrix $S^{-1}(\chi,\theta,\phi)$, which is a $3 \times 3$ matrix constructed so that the entire molecule is rotated until it has the proper orientation in the laboratory. Last of all we move the centre of mass of the molecule-fixed axis system to the point $\mathbf{R}$. Each atom of the molecule is now in its correct position in the laboratory-fixed axis system.

We note at this point that even though the reference position was taken to correspond to an eclipsed configuration of the two methyl groups, we have not really favoured this configuration as far as the nuclear displacements $\mathbf{d}_i$ are concerned. In fact, the real purpose of the twisting matrix is to convert the eclipsed reference configuration of the molecule into an internally rotated configuration corresponding to the particular value of the torsional angle $\gamma$ under consideration, so that the nuclear displacements can be measured from this internally rotated reference configuration rather than from some arbitrarily chosen fixed reference configuration. This procedure evidently allows the nuclear displacement $\mathbf{d}_i$ to remain small at all times, because the large change in the hydrogen atom positions during internal rotation is accounted for by changing the value of the angle $\gamma$ and not by invoking large displacement vectors $\mathbf{d}_i$.

**Constraints**

A careful examination of equation (1) reveals the following difficulty. The $\mathbf{r}_i$ on the left-hand side of the equality correspond to $3N$ degrees of freedom: three Cartesian coordinates for each of the $N$ nuclei. The variables on the right hand side of the equality correspond to $3N + 7$ degrees of freedom: three Cartesian coordinates for the centre of mass, three Eulerian angles, one torsional angle $\gamma$, and $3N$ displacement vectors $\mathbf{d}_i$. (The reference positions $\mathbf{a}_i$, of course, do not represent variables in the wave-function, but are given some fixed values at the beginning of the problem.) The
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difficulty of having too many degrees of freedom in the set of variables on
the right-hand side of the equality in equation (1) is overcome by applying
seven constraint equations:

\[
0 = \sum_i m_i S_i^{-1} \cdot d_i
\]

\[
0 = \sum_i m_i [S_i^{-1} \cdot a_i] \times [S_i^{-1} \cdot d_i]
\]

\[
0 = k \left( \sum_i - \sum_f \right) m_i [S_i^{-1} \cdot a_i] \times [S_i^{-1} \cdot d_i]
\]

(2)

Here, \( S_i^{-1} \) represents \( S_i^{-1}(\gamma,0,0) \); \( \sum_i \) represents a sum over all the nuclei
in the molecule; and \( \left( \sum_i - \sum_f \right) \) represents the difference of a sum over
the nuclei in one half of the molecule and a sum over the nuclei in the other
half. We do not have time to examine these equations in detail, but will
content ourselves with a qualitative feeling of what they mean.

The first vector equation represents the three constraint equations
associated with the condition that only those sets of the \( d_i \) must be con-
sidered which do not change the centre of mass of the nuclei. The vectors
\( S_i^{-1} \cdot d_i \) rather than the \( d_i \) are used in this equation, because the former, and
not the latter, represent the actual displacements of the nuclei from their
twisted reference configuration. The second vector equation represents the
three constraint equations associated with the condition that only those
sets of the \( d_i \) must be considered which do not correspond to a rotation of
the molecule as a whole. This constraint is often called the Eckart condition.
Note that the instantaneous twisted reference positions \( S_i^{-1} \cdot a_i \) have been
used, rather than some arbitrarily chosen fixed reference positions, in
writing down the Eckart condition for dimethylacetylene. This is in keeping
with our desire not to favour any particular value of the torsional angle.
The third equation represents the single constraint equation (it involves
only the \( z \) component of a vector equation) associated with the condition
that only those sets of the \( d_i \) must be considered which do not correspond to
an internal rotation of the molecule. This constraint is often called the
Sayvetz condition.

Vibrational symmetry coordinates

Before discussing vibrational symmetry coordinates, I would like to
remark that it is the attempt to obtain operations corresponding to the
operations of Longuet-Higgins' molecular symmetry group for the coordi-
nates defined in equation (1) that leads to the introduction of the double
group. However, once the double group has been introduced, it is found
that the symmetric-top rotational wave-functions and also the torsional
wave-functions transform according to irreducible representations of this
double group. The "species of the constraint equations", which correspond
to the species of the three translations, the three overall rotations, and the
torsion, are also uniquely defined with respect to the double group. The
species of the three translations are the same as the species of the dipole
moment operator, and a rigorous statement of selection rules for spectro-
scopic transitions can be made. In addition, an exact expression for the
quantum mechanical nuclear kinetic energy operator can be derived.
While these topics are both interesting and important, we shall not discuss
them here.

Let us now consider a set of vibrational symmetry coordinates
$S_s(s = 1,2, \ldots, 3N-7)$ defined as linear combinations of the Cartesian
displacements $d_i$ of the nuclei:

$$S_s = \sum_i m_i \mathbf{f}_i^s(\gamma) \cdot \mathbf{d}_i$$  (3)

The coefficients in this linear combination, i.e., the $\mathbf{f}_i^s(\gamma)$, are considered for
dimethylacetylene to be functions of the torsional angle $\gamma$, even though such
coefficients for ordinary molecules are taken to be constants. The vibrations
in dimethylacetylene are expected to correspond to much faster motions
than does the torsion. The $\gamma$-dependence of the coefficients in (3) can thus
be thought of as allowing for the fact that the nature of the vibrational modes
may vary as the vibrating molecule internally rotates through eclipsed,
intermediate, staggered, intermediate, etc. torsional configurations.

An important mathematical consequence of the $\gamma$-dependence of the
coefficients is that the symmetry species of the vibrational symmetry co-
ordinates are not uniquely determined. By changing the $\gamma$-dependence
of the coefficients in (3), vibrational coordinates of certain species can be
changed into coordinates of certain other species, though there are group
theoretical restrictions upon exactly what can and cannot be done. This
indeterminacy, of course, is not found at all in ordinary molecules, where
the number and kind of normal vibrations can be determined uniquely from
the equilibrium structure of the molecule.

An important physical consequence of the $\gamma$-dependence of the coeffi-
cients in (3) can best be illustrated by considering Figure 4, which represents
a view of the dimethylacetylene molecule along the axis containing the
carbon atoms, each methyl group being represented by a triangle. In
Figure 4(a) the two methyl groups are in an eclipsed configuration. In
Figures 4(b) and 4(c) the two methyl groups have been rotated in opposite
directions through an angle of 30 degrees from their original eclipsed
configuration. Suppose now that we are considering a vibrational motion of
the two central carbon atoms of the molecule, which for the eclipsed con-
figuration corresponds to a motion of the two carbon atoms in the direction
indicated by the small double-headed arrow in Figure 4(a). It is now natural
to wonder in which direction each carbon atom will be vibrating when the
molecule has undergone an internal rotation corresponding to a change in
the torsional angle $\gamma$ of 30 degrees. Figure 4(b) illustrates the case in which
the direction of motion of the two carbon atoms remains unchanged,
corresponding to a vibrational motion which effectively ignores the internal
rotation of the two methyl groups. Figure 4(c) illustrates the case in which
the direction of the motion of each carbon atom maintains its original orien-
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tation relative to the three hydrogens of the methyl group nearest it, cor-
responding to a vibrational motion which effectively follows exactly the
internal rotation of the two methyl groups. By suitably choosing the γ-
dependence of the coefficients \( \mathbf{F}_r(\gamma) \) in (3) we can construct vibrational
symmetry coordinates corresponding to the motions illustrated in either
Figure 4(b) or Figure 4(c), or even corresponding to motions in which the
double-headed arrows of Figure 4 rotate faster than the methyl groups, in

![Diagram](image)

*Figure 4.* (a) An end-on view of a dimethylacetylene molecule in an eclipsed configuration,
with the two central carbon atoms vibrating as indicated by the double-headed arrow. (b) and
(c) This same molecule after transition via internal rotation to the staggered configuration:
(b) illustrates the case in which the vibrational motion of the two carbon atoms ignores the
internal rotation and (c) illustrates the case in which the vibrational motion of the two car-
bon atoms follows the internal rotation

the opposite direction from the nearest methyl group, etc. It seems in-
tuitively clear that vibrations involving mainly atoms in the centre of a
long chain between two internally rotating groups will ignore the internal
rotation. It also seems clear that hydrogenic motions, for example, will
follow exactly the internal rotation of the methyl group to which the
hydrogens belong. Thus the extra flexibility in the vibrational coordinates
which the \( \gamma \)-dependence of the coefficients in (3) allows is essential for
a good description of the normal modes in a molecule with nearly free
internal rotation.

**Vibrational potential energy expression**

Having discussed the problem of vibrational symmetry coordinates, we
must now consider the form of the vibrational potential energy expression
when written in terms of these coordinates. In particular, we shall con-
consider only those terms in the potential energy expression which are quadratic
in the symmetry coordinates, thus neglecting anharmonic effects. The
quadratic part of the potential energy expression \( V \) can be written in terms of
the symmetry coordinates \( S_s \) as:

\[
V = \frac{1}{2} \sum_{r,s} F_{rs}(\gamma) S_r S_s \tag{4}
\]

The difference between this expression and that for an ordinary molecule
lies in the fact that here all the force constants \( F_{rs} \) are allowed to depend
on the torsional angle \( \gamma \), while for an ordinary molecule they are taken to
be constants. I want to point out here quite emphatically, that the \( 3N-7 \)
symmetry coordinates \( S_s \) in (4) are not to be considered as functions of \( \gamma \),
but rather as part of the set of \( 3N \) independent variables \((\mathbf{R}; \chi, \theta, \phi; \gamma; S_s)\) in
molecular configuration space. In this scheme the nuclear displacement
vectors $\mathbf{d}_i$ are taken to be dependent variables, dependent in general on both the symmetry coordinates $S_s$ and on $\gamma$. In any case, as a consequence of the $\gamma$-dependent force constants, terms quadratic in the vibrational symmetry coordinates can occur in $V$ which involve vibrations of different symmetry species. Thus, subject to some group theoretical restrictions, vibrations of different species can interact in the quadratic part of the vibrational potential energy expression. In ordinary molecules, vibrations of different species can only interact in the cubic and higher terms of the potential energy expression.

**Normal modes**

For the vibrational symmetry coordinates under consideration, the kinetic energy operator is already diagonal, so the problem of determining normal modes reduces to the problem of diagonalizing the quadratic expression given in equation (4). In principle this can be done for each value of the torsional angle $\gamma$, to obtain a set of normal modes $Q_s$ and a set of force constants $k_s$:

$$V = \frac{1}{2} \sum_s k_s(\gamma) Q_s^2$$  \hspace{1cm} (5)

The normal modes $Q_s$ will be linear combinations of the vibrational symmetry coordinates $S_s$, with coefficients which are in general functions of $\gamma$. The $Q_s$ now replace the $S_s$ in the set of $3N$ independent variables in molecular configuration space mentioned above. The relation between the normal modes $Q_s$ and the Cartesian displacement vectors of the nuclei is unique for a given force field and clearly will not depend on the choice of vibrational symmetry coordinates. However, it is advantageous to choose the symmetry coordinates at the beginning in such a way that they resemble closely the final normal modes of the molecule. Such a judicious choice of symmetry coordinates for molecules with nearly free internal rotation will only be possible after some experience has been gained from experimental observations coupled with normal mode calculations. It can be shown, and this I believe is an important point, that the normal modes $Q_s$ obtained by diagonalizing the quadratic form (4) must belong to some symmetry species of the molecular double group, although, as it turns out, the species of the normal modes $Q_s$ need not match exactly the species of the symmetry coordinates $S_s$ in terms of which the vibrational potential energy was first expressed.

We have now discussed the normal coordinates occurring in (5), but we have not yet decided what is to be done with the $\gamma$-dependent force constants in that equation. In fact, the problem is not too difficult. The $k_s(\gamma)$ can be expanded in a series involving $\cos n\gamma$, where $n$ is an integer. Group theoretical considerations can be used to demonstrate that only those values of $n$ divisible by 6 can occur in the series. The important point is the following. The part of $k_s(\gamma)$ which is independent of $\gamma$ is considered to be the force constant for the normal mode under consideration and the vibrational problem is solved in the usual way. The part of $\frac{1}{2}k_s(\gamma)Q_s^2$ remaining after the term involving the $\gamma$-independent part of $k_s(\gamma)$ is removed, is now reclassified. This remaining part, instead of representing the dependence
of the quadratic force constant on $\gamma$, is now thought of as representing the
dependence of the barrier to internal rotation on the vibrational coordinate $Q_s$. In a molecule like dimethylacetylene with nearly free internal rotation,
it is expected that the dependence of the barrier to internal rotation on the
vibrational coordinates will be small, and so such effects can be neglected
in the early stages of any calculation.

Selection rules

We shall not consider the selection rules here in any detail. Suffice it to
say that selection rules for allowed and forbidden vibrational transitions
can be set up just as for ordinary molecules, and furthermore that the
selection rules on the rotational and torsional quantum numbers associated
with any given type of vibrational transition can also be determined. The
principal difference from the situation in ordinary molecules is the existence
of a torsional quantum number $L$ which is associated with energy changes
comparable to rotational energy changes. Thus, instead of observing experi-
mentally only two types of bands in the symmetric-top dimethylacetylene,
i.e., instead of observing either parallel bands ($\Delta K = 0$) or perpendicular
bands ($\Delta K = \pm 1$), there is now in principle the possibility of observing
several kinds of parallel bands and several kinds of perpendicular bands,
corresponding to various selection rules on the torsional quantum number
($\Delta L =$ some integer).

Comparison with experiment

Now I think it is time to ask what all of this rather complicated theorizing
has done to increase our understanding of real experimental data. I am
afraid that at the moment this theory has done little to clarify experimental
observations, though part of the difficulty lies in the nature of the experi-
mental data. What we really need are spectra of vibrational transitions
in molecules exhibiting nearly free internal rotation which are well enough
resolved that a reasonable amount of the associated rotational and torsional
structure can be identified. It is in dealing with such spectra that we will
discover whether the theoretical developments described in this paper are
useful or not, and also I would add, whether they are correct or not.

There is some experimental data concerning the individual rotational
levels of molecules with nearly free internal rotation available from micro-
wave studies. In particular, Kirchhoff and Lide have studied the micro-
wave spectrum of methylsilylacetylene and have determined certain cen-
trifugal distortion constants. It is possible in ordinary molecules to calculate
the centrifugal distortion constants from a knowledge of certain force
constants and vibrational frequencies of the molecule, and I had hoped to
sketch a similar formalism here and compare calculated and observed
quantities. Unfortunately, this work is still rather incomplete.

References

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