JOURNAL OF MOLECULAR SPECTROSCOPY **163**, 326–338 (1994)

The Symmetry of the Vibrational Components in T_d Molecules

B. I. ZHILINSKII[1] AND SVEND BRODERSEN[2]

Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark

The rotation–vibrational states of a methane-shaped molecule may be divided into vibrational components (S. G. Larsen and S. Brodersen, *J. Mol. Spectrosc.* **157**, 220-236, 1993), each characterized by a symmetry indicated as an irreducible representation of the full rotational group O_3. A simple group-theoretical method is presented, yielding the possible symmetries of the vibrational components for any vibrational state of a given symmetry. The method also indicates which changes may occur in the symmetries of two interacting vibrational components. Finally, local symmetry indices are introduced, and it is demonstrated that they represent an alternative description of the symmetry of vibrational components, leading to the same results for the possible symmetries and for the changes in these. The results are immediately valid for any T_d molecule, but the general ideas should be easy to transfer to other molecules.

INTRODUCTION

Spherical top molecules are characterized by a high vibrational degeneracy. Both doubly and triply degenerate fundamentals occur, and the overtone and combination states may be highly degenerate, as seen from the vibrational symmetry. Thus, in T_d molecules the overtone states $2\nu_3$ and $2\nu_4$ have the vibrational symmetry $A_1 + E + F_2$ and they are consequently six-fold degenerate in the harmonic approximation.

In some cases this high degeneracy is partly lifted due to anharmonic effects. The overtone state $2\nu_2$ has the symmetry $A_1 + E$ and is thus three-fold degenerate. In CF_4 this state is split by anharmonicity into a nondegenerate substate of symmetry A_1 and a doubly degenerate substate of symmetry E by 5 cm^{-1}. Correspondingly the $3\nu_2$ state of symmetry $A_1 + A_2 + E$ is split by anharmonicity into a doubly degenerate substate of symmetry E and another doubly degenerate substate of symmetry $A_1 + A_2$ by 9.5 cm^{-1}. Also this last substate may be considered as split into two nondegenerate substates of symmetry A_1 and A_2, although the splitting is only 0.1 cm^{-1}. These splittings have not been observed directly. They are found in an energy level diagram computed from a fairly accurate potential function (*1–3*).

If such an energy level diagram for CF_4 is computed for a large number of J values, it reveals a further splitting of all the rotation–vibrational energy levels belonging to the degenerate vibrational states (or substates) into as many vibrational components as the vibrational degeneracy indicates (*3*). Thus the six-fold degenerate $2\nu_4$ vibrational state is seen to split into six vibrational components, the doubly degenerate E substate of $3\nu_2$ is split into two vibrational components, and the six-fold degenerate $\nu_2 + \nu_4$ vibrational state is split into six vibrational components. Contrary to the anharmonic

---

[1] On leave of absence from Department of Chemistry, Moscow State University, Moscow 119899. Present address: Laboratoire de spectroscopie hertzienne, Université de Lille I, 59655 Villeneuve d'Ascq, France.

[2] Author to whom correspondence should be addressed.

0022-2852/94 $6.00

splitting this further splitting is often highly dependent on J; in general it increases with increasing values of J.

Each of the vibrational components for CF_4 is found empirically (*3*) to have a certain symmetry in the full rotation group O_3, in the sense that the correlation from O_3 to T_d (see Table I) for a given value of J is found to indicate the symmetry in T_d of all the rotation–vibrational states belonging to the vibrational component for that value of J. The symmetry is always of the form $D_g^{(J+\Delta)}$ or $D_u^{(J+\Delta)}$, where Δ is a small integer. For the 31 vibrational components of lowest energy in any of the three isotopic species of CF_4 all values of Δ have been found to be in the interval $-3 \leqslant \Delta \leqslant 3$, equally distributed over negative and positive values for a given vibrational state or substate. For instance, the six-fold degenerate $\nu_2 + \nu_4$ vibrational state of symmetry $F_1 + F_2$ is split into six vibrational components, which in order of increasing energy have the symmetries $D_u^{(J-1)}$, $D_g^{(J+3)}$, $D_g^{(J-2)}$, $D_u^{(J+2)}$, $D_u^{(J-3)}$, and $D_g^{(J+1)}$. In a way these symmetries form a nice pattern, but there is no obvious explanation why these six vibrational components have just these symmetries. The main purpose of the present paper is to present a group-theoretical method for predicting which symmetries may occur for the vibrational components of a vibrational state or substate of a given vibrational symmetry. The results presented are valid for any molecule of symmetry T_d, but the examples are taken from CF_4. The group-theoretical method as such may undoubtedly be extended to molecules of other symmetries.

The symmetry found empirically for a given vibrational component is not necessarily the same for all values of J. Such a change of symmetry is always the result of some

TABLE I

Correlation from O_3 to T_d

$J+\Delta$	$D_g^{(J+\Delta)}$	$D_u^{(J+\Delta)}$
$12t$	$t\Gamma + A_1$	$t\Gamma + A_2$
$1 + 12t$	$t\Gamma + F_1$	$t\Gamma + F_2$
$2 + 12t$	$t\Gamma + E + F_2$	$t\Gamma + E + F_1$
$3 + 12t$	$t\Gamma + A_2 + F_1 + F_2$	$t\Gamma + A_1 + F_1 + F_2$
$4 + 12t$	$t\Gamma + A_1 + E + F_1 + F_2$	$t\Gamma + A_2 + E + F_1 + F_2$
$5 + 12t$	$t\Gamma + E + 2F_1 + F_2$	$t\Gamma + E + F_1 + 2F_2$
$6 + 12t$	$t\Gamma + A_1 + A_2 + E + F_1 + 2F_2$	$t\Gamma + A_1 + A_2 + E + 2F_1 + F_2$
$7 + 12t$	$t\Gamma + A_2 + E + 2F_1 + 2F_2$	$t\Gamma + A_1 + E + 2F_1 + 2F_2$
$8 + 12t$	$t\Gamma + A_1 + 2E + 2F_1 + 2F_2$	$t\Gamma + A_2 + 2E + 2F_1 + 2F_2$
$9 + 12t$	$t\Gamma + A_1 + A_2 + E + 3F_1 + 2F_2$	$t\Gamma + A_1 + A_2 + E + 2F_1 + 3F_2$
$10 + 12t$	$t\Gamma + A_1 + A_2 + 2E + 2F_1 + 3F_2$	$t\Gamma + A_1 + A_2 + 2E + 3F_1 + 2F_2$
$11 + 12t$	$t\Gamma + A_2 + 2E + 3F_1 + 3F_2$	$t\Gamma + A_1 + 2E + 3F_1 + 3F_2$

where $t = 0, 1, 2, \ldots.$ and $\Gamma = A_1 + A_2 + 2E + 3F_1 + 3F_2$

interaction between two (or three) vibrational components close to one another in the energy level diagram, and the symmetries of the components involved are changed simultaneously according to certain rules which are deduced below. A more detailed treatment of these interactions between the different vibrational components of CF_4 will be given in a forthcoming paper (*4*), based on the present theoretical results.

THE POSSIBLE SYMMETRIES OF THE VIBRATIONAL COMPONENTS WITHIN ONE VIBRATIONAL STATE

Let us start by answering a relatively simple question: What is the sum Γ_{rv} of the symmetries in T_d of all the rotation–vibrational states belonging to a vibrational state or substate of a given vibrational symmetry Γ_{vib} for a certain value of J? Here we do not take the splitting into vibrational components into account.

For the vibrational ground state the answer to this question is well known (*5, 6*). It is given by the reduction of the irreducible representation $D_g^{(J)}$ of O_3 to T_d for any value of J. In other words, the vibrational ground state consists as a nondegenerate vibrational state of one vibrational component, and this has the symmetry $D_g^{(J)}$. The starting point of the present paper is that Γ_{rv} for any other vibrational state of symmetry Γ_{vib} is given by the direct product

$$\Gamma_{rv} = \Gamma_{vib} \otimes D_g^{(J)}, \tag{1}$$

where either $D_g^{(J)}$ must be reduced to T_d by means of Table I or Γ_{vib} must be correlated to O_3, also by means of Table I, before the direct product is formed. The first method is always applicable, whereas, as seen from Table I, the second method may be used only in rather few cases, including $\Gamma_{vib} = A_1$ or F_2, but not for the important case of $\Gamma_{vib} = E$. Equation (1) has been applied in several hundred cases for different isotopic species of CF_4, always indicating a splitting of the rotation–vibrational states in agreement with the coarse structure of the energy level diagram. As an example, Γ_{rv} computed from Eq. (1) for $\Gamma_{vib} = E$ is given in the second column of Table II for $J = 0$ through 11.

TABLE II

Two Solutions to Eq. (2) for $\Gamma_{vib} = E$

		1. Solution		2. Solution	
J	$\Gamma_{rv} = E \otimes D_g^{(J)}$	$D_u^{(J+2)}$	$D_g^{(J-2)}$	$D_g^{(J+2)}$	$D_u^{(J-2)}$
0	E	$E\,[+F_1]$	$[-F_1]$	$E\,[+F_2]$	$[-F_2]$
1	F_1+F_2	$[A_1+]\,F_1+F_2$	$[-A_1]$	$[A_2+]\,F_1+F_2$	$[-A_2]$
2	$A_1+A_2+E+F_1+F_2$	$A_2+E+F_1+F_2$	A_1	$A_1+E+F_1+F_2$	A_2
3	$E+2F_1+2F_2$	$E+F_1+2F_2$	F_1	$E+2F_1+F_2$	F_2
4	$A_1+A_2+2E+2F_1+2F_2$	$A_1+A_2+E+2F_1+F_2$	$E+F_2$	$A_1+A_2+E+F_1+2F_2$	$E+F_1$
5	$A_1+A_2+E+3F_1+3F_2$	$A_1+E+2F_1+2F_2$	$A_2+F_1+F_2$	$A_2+E+2F_1+2F_2$	$A_1+F_1+F_2$
6	$A_1+A_2+3E+3F_1+3F_2$	$A_2+2E+2F_1+2F_2$	$A_1+E+F_1+F_2$	$A_1+2E+2F_1+2F_2$	$A_2+E+F_1+F_2$
7	$A_1+A_2+2E+4F_1+4F_2$	$A_1+A_2+E+2F_1+3F_2$	$E+2F_1+F_2$	$A_1+A_2+E+3F_1+2F_2$	$E+F_1+2F_2$
8	$2A_1+2A_2+3E+4F_1+4F_2$	$A_1+A_2+2E+3F_1+2F_2$	$A_1+A_2+E+F_1+2F_2$	$A_1+A_2+2E+2F_1+3F_2$	$A_1+A_2+E+2F_1+F_2$
9	$A_1+A_2+3E+5F_1+5F_2$	$A_1+2E+3F_1+3F_2$	$A_2+E+2F_1+2F_2$	$A_2+2E+3F_1+3F_2$	$A_1+E+2F_1+2F_2$
10	$2A_1+2A_2+4E+5F_1+5F_2$	$A_1+2A_2+2E+3F_1+3F_2$	$A_1+2E+2F_1+2F_2$	$2A_1+A_2+2E+3F_1+3F_2$	$A_2+2E+2F_1+2F_2$
11	$2A_1+2A_2+3E+6F_1+6F_2$	$A_1+A_2+2E+3F_1+4F_2$	$A_1+A_2+E+3F_1+2F_2$	$A_1+A_2+2E+4F_1+3F_2$	$A_1+A_2+E+2F_1+3F_2$

Knowing Γ_{rv} from Eq. (1), it is possible to put an important restriction on the symmetries of the vibrational components for a vibrational state or substate of symmetry Γ_{vib}. For any J the sum of the symmetries of the vibrational components must equal Γ_{rv}, because the vibrational components only indicate a splitting of the rotation–vibrational states, the symmetries of which are given by Γ_{rv}. The symmetries of the vibrational components are, as mentioned above, always of the form $D_{\mathrm{g}}^{(J+\Delta)}$ or $D_{\mathrm{u}}^{(J+\Delta)}$, so this condition may be expressed mathematically as

$$\Gamma_{\mathrm{rv}} = \sum_{i=1}^{g_{\mathrm{vib}}} D_{\alpha_i}^{(J+\Delta_i)}, \tag{2}$$

where g_{vib} is the vibrational degeneracy of the vibrational (sub)state and α_i is either g or u. As before the symmetries of the vibrational components should be correlated from O_3 to T_d by means of Table I.

As the total degeneracy for a given J of a vibrational component with symmetry $D_{\alpha_i}^{(J+\Delta_i)}$ is $2(J + \Delta_i) + 1$ and the total degeneracy of the vibrational (sub)state is $g_{\mathrm{vib}}(2J + 1)$, it is easily seen that Eq. (2) cannot be satisfied unless

$$\sum_{i=1}^{g_{\mathrm{vib}}} \Delta_i = 0, \tag{3}$$

which explains the observation mentioned in the Introduction, that the values of Δ are equally distributed over positive and negative values. However, if Δ_i is negative, $2(J + \Delta_i) + 1$ is a negative quantity for very low values of J, giving no meaning as a degeneracy. This indicates that Eq. (2) should be understood in a special way for these very low values of J.

As an example we demonstrate how Eq. (2) is solved for $\Gamma_{\mathrm{vib}} = E$. First E is multipled on the reduction of $D_{\mathrm{g}}^{(J)}$ for $0 \leqslant J \leqslant 11$, as given in Table I. The result is given in the second column of Table II. From Eq. (3) it is clear that the two values of Δ must be numerically equal, and it is easily seen by means of Table I that neither 0, nor 1, may be used for the numerical value. Consequently, the simplest solution is obtained if one Δ is +2 and the other is −2. But there are still two solutions. If the first component has a g symmetry, it is found that the other must have a u symmetry, or vice versa. These two solutions are indicated in Table II, as found directly from Table I for $J \geqslant 2$. For $J = 0$ and 1, one has to use the formal value of $t = -1$ for the component with $\Delta = -2$, yielding negative contributions. When these are subtracted from the contents of the component with $\Delta = +2$, the result is the correct one. It seems reasonable to interpret this so that the component with $\Delta = -2$ starts at $J = 2$, whereas the component with $\Delta = +2$ starts at $J = 0$, containing the one state of symmetry E for $J = 0$ and the two states with symmetry F_1 and F_2 for $J = 1$.

Generally, if Δ is negative, the formally negative contents of the component should be found from Table I using $t = -1$ and subtracted from the contents of the component(s) with positive values of Δ.

In the example of $\Gamma_{\mathrm{vib}} = E$ there are more than the two solutions given in Table II. There are thus also two solutions for $\Delta = +4$ and −4. In fact there is an infinite number of solutions, which may be indicated mathematically in the form

$$E \otimes D_{\mathrm{g}}^{(J)} = D_{\alpha}^{(J+\delta)} + D_{\beta}^{(J-\delta)}, \tag{4}$$

where α and β equal g or u, but are always different in the two components, and δ may have the values $\delta = 2, 4, 8, 10, 14, 16$, etc. There is always a pair of solutions for each value of δ. This is basically caused by the invariance of the direct product of E with any irreducible representation of T_d to an interchange of the subscripts 1 and 2. Consequently Γ_{rv} is also invariant to such an interchange for any value of J. But an interchange of the subscripts 1 and 2 in T_d is equivalent to an interchange of the subscripts u and g in O_3, as seen from Table I, and any solution to Eq. (2) may be transformed into another solution by such an interchange of u and g. The results obtained here for $\Gamma_{\mathrm{vib}} = E$ are in agreement with previous results found by Michelot (*7*) by a different procedure.

For $\Gamma_{\mathrm{vib}} = A_1$, which is equal to $D_{\mathrm{g}}^{(0)}$, Eq. (1) indicates $\Gamma_{\mathrm{rv}} = D_{\mathrm{g}}^{(J)}$, as already discussed above. Equation (2) has consequently only one solution. The one component of a vibrational (sub)state of symmetry A_1 always has the symmetry $D_{\mathrm{g}}^{(J)}$.

For $\Gamma_{\mathrm{vib}} = A_2$, which is equal to $D_{\mathrm{u}}^{(0)}$ according to Table I, Eq. (1) indicates $\Gamma_{\mathrm{rv}} = D_{\mathrm{u}}^{(J)}$. Again Eq. (2) has only one solution. The one component of a vibrational (sub)state of symmetry A_2 always has the symmetry $D_{\mathrm{u}}^{(J)}$. These two cases are the only ones for which Eq. (2) has a limited number of solutions; in all other cases there is an infinite number.

For $\Gamma_{\mathrm{vib}} = F_2$, which is equal to $D_{\mathrm{u}}^{(1)}$ according to Table I, Eq. (1) indicates

$$\Gamma_{\mathrm{rv}} = D_{\mathrm{u}}^{(1)} \otimes D_{\mathrm{g}}^{(J)} = D_{\mathrm{u}}^{(J-1)} + D_{\mathrm{u}}^{(J)} + D_{\mathrm{u}}^{(J+1)} \tag{5}$$

from the usual rule for the reduction of direct products within O_3. This immediately indicates one solution to Eq. (2), but an infinite number of other solutions may be found if Γ_{rv} is rewritten in terms of the irreducible representations of T_d by means of Table I. The only other solutions for which all the Δ values are in the interval $-3 \leqslant \Delta \leqslant 3$ may be written in the form

$$\Gamma_{\mathrm{rv}} = F_2 \otimes D_{\mathrm{g}}^{(J)} = D_{\mathrm{g}}^{(J\pm3)} + D_{\mathrm{u}}^{(J\mp1)} + D_{\mathrm{g}}^{(J\mp2)} \tag{6}$$

$$\Gamma_{\mathrm{rv}} = F_2 \otimes D_{\mathrm{g}}^{(J)} = D_{\mathrm{u}}^{(J\pm3)} + D_{\mathrm{g}}^{(J\mp1)} + D_{\mathrm{g}}^{(J\mp2)}, \tag{7}$$

and these four solutions are probably those which will appear most often in practice in addition to the well-known (*5*) solution given by Eq. (5).

For $\Gamma_{\mathrm{vib}} = F_1$, which is equal to $D_{\mathrm{g}}^{(1)}$ according to Table I, Eq. (1) indicates

$$\Gamma_{\mathrm{rv}} = D_{\mathrm{g}}^{(1)} \otimes D_{\mathrm{g}}^{(J)} = D_{\mathrm{g}}^{(J-1)} + D_{\mathrm{g}}^{(J)} + D_{\mathrm{g}}^{(J+1)}, \tag{8}$$

again indicating one out of an infinite number of solutions to Eq. (2). All these are obtained easily from the solutions to $\Gamma_{\mathrm{vib}} = F_2$ by substitution of all indices u by g and all g by u, as is obvious from Table I.

This example finishes the discussion of all vibrational states or substates for which the symmetry is given by one irreducible representation of T_d. If the symmetry Γ_{vib} of a given vibrational state is given by a sum of irreducible representations, two cases must be distinguished. If the anharmonic splitting is large enough to split the vibrational state completely into substates, the symmetry of each of which is given by one irreducible representation of T_d, the easiest way is to consider each substate separately. If, however, the anharmonic splitting is insufficient to split all the rotation–vibrational states completely, one gets immediately a number of solutions to Eq. (2) by adding one solution to each single irreducible representation to those of the other ones in all possible combinations. Thus, for $\Gamma_{\mathrm{vib}} = F_1 + F_2$ a total of 25 solutions are obtained by adding one of the five solutions given by Eqs. (5)–(7) to any of the corresponding five solutions for $\Gamma_{\mathrm{vib}} = F_1$. One of these solutions, obtained by use of Eq. (6) twice, once for $\Gamma_{\mathrm{vib}} = F_2$ and once for $\Gamma_{\mathrm{vib}} = F_1$, is the one mentioned in the Introduction as the solution observed in the $\nu_2 + \nu_4$ state of $^{12}CF_4$. In reality these solutions correspond to the assumption of a large anharmonic splitting, and this procedure will not give all the solutions. The simple example of $\Gamma_{\mathrm{vib}} = A_1 + A_2$ will demonstrate this. From the above given results one immediately gets the solution

$$\Gamma_{\mathrm{rv}} = (A_1 + A_2) \otimes D_{\mathrm{g}}^{(J)} = D_{\mathrm{g}}^{(J)} + D_{\mathrm{u}}^{(J)}, \tag{9}$$

but in fact there is an infinite number of solutions given by

$$\Gamma_{\mathrm{rv}} = (A_1 + A_2) \otimes D_{\mathrm{g}}^{(J)} = D_{\alpha}^{(J+6t)} + D_{\beta}^{(J-6t)}, \tag{10}$$

where t is any integer, and α and β are g or u, but are always different in the two components.

An alternative method for finding all the solutions to Eq. (2) is to use local symmetry indices as indicated in the last section of this paper.

CHANGES IN THE SYMMETRIES OF TWO NEIGHBORING COMPONENTS AS A FUNCTION OF J

The semiclassical model for the rotation of spherical top molecules has proved to be an excellent instrument for understanding the rather complicated pattern of clusters in isolated vibrational components of the CF_4 molecules (*8*). In the present section we discuss some consequences of this model for the possible changes in the symmetries of vibrational components due to a variation in J. In a forthcoming paper (*4*) we shall present a number of examples of such changes in $^{12}CF_4$ and $^{13}CF_4$, with interpretations based on the present results.

As shown previously (*3, 9–12*) the clusters within the manifold of rotation–vibrational states for one value of J in one vibrational component may be ordered in one series of 6-fold clusters, another series of 8-fold clusters, and possibly also a series of 12-fold clusters. Each cluster may be assigned a cluster index $\tau = 0, 1, 2$, etc., usually with clusters of index 0 at both limits of the manifold. The symmetry of any cluster is completely determined by τ, J, and the symmetry of the vibrational component (*3*).

The semiclassical model indicates important information of how the symmetry of a vibrational component may change due to a variation in J (*4, 13*). Such a change in the symmetry is the result of a transfer from one component to a neighboring component of one 6-fold cluster with cluster index $\tau = 0$ (termed 6_0), or of two such clusters, 6_0 and 6_1, or of one 8-fold cluster, 8_0, or of one 12-fold cluster, 12_0. This means that the symmetry of an isolated component cannot change with J, whereas the symmetries of two components may change simultaneously. In the following we present the rules for what changes are possible for a given transfer of one or two clusters. We refer to the component from which the cluster(s) is split off as the donor and to the other component as the acceptor.

It is immediately clear that the values of Δ for both components must change, depending on the degeneracy of the transferred cluster(s). Because the total degeneracy of a given manifold equals $2(J + \Delta) + 1$, the value of Δ for the donor must decrease by half of the degeneracy of the transferred cluster(s), and the value of Δ for the acceptor must increase by the same amount. Thus, by a transfer of an 8-fold cluster Δ for the donor is lowered by 4, and Δ of the acceptor is raised by 4. If two 6-fold clusters are transferred, the corresponding change in the Δ values is 6.

That one cluster with cluster index $\tau = 0$ is transferred from the donor component to the acceptor component means that the transferred cluster must have $\tau = 0$ both in the donor before the transfer and in the acceptor after the transfer. This implies of course that for any given J the symmetry of the cluster in the donor before the transfer must be the same as the symmetry in the acceptor after the transfer. As mentioned this symmetry may be found in Table IV of Ref. (*3*). Thus, for an 8_0 cluster the symmetry is found to be $A_1 + A_2 + F_1 + F_2$ if $J + \Delta = 3p$, where p is an integer, and $E + F_1 + F_2$ otherwise, independently of the subscript u or g in the symmetry symbol of the component. In order to maintain the symmetry this implies that if the superscript in the symmetry symbol for the donor before the transfer is $J + \Delta$, it must be $J + \Delta + 3t$ for the acceptor after the transfer, where t is any integer. The superscript for the donor after the transfer must then be $J + \Delta - 4$ and that of the acceptor before the transfer must be $J + \Delta - 4 + 3t$. These superscripts are included in the "reaction scheme" given in Table III for a transfer of one 8_0 cluster. The corresponding superscripts are a bit more complicated for a transfer of one 6_0 or one 12_0 cluster, because the symmetry of the cluster depends on the subscript u or g. The results are given in Table III.

Knowing the symmetry of the transferred cluster it is easy by means of Table I to show that the subtraction of one 8_0 cluster from the symmetry of any given manifold always leads to the symmetry of the manifold for a component with the same subscript g or u, but naturally with a superscript lowered by 4. This leads to the subscripts given in Table III for this case. A subtraction of a 6_0 or a 12_0 cluster always leads to a new component with the opposite subscript, from g to u or vice versa, and this leads to the subscripts given in Table III for these cases.

It is clear that the transfer of a cluster with $\tau = 0$ from one vibrational component to the other requires some rearrangements in the cluster indices of both vibrational components. This is precisely what has been observed in several cases in CF_4, as discussed in detail in a forthcoming publication (*4*).

TABLE III

Possible Changes in the Symmetries of Two Vibrational Components Due to a Change of J

By means of the transfer of one 6_0 cluster:

$$D_\alpha^{(J+\Delta)} + D_\beta^{(J+\Delta-3+4t)} \rightleftarrows D_\beta^{(J+\Delta-3)} + D_\alpha^{(J+\Delta+4t)} \qquad \alpha \neq \beta$$

$$D_\alpha^{(J+\Delta)} + D_\alpha^{(J+\Delta-1+4t)} \rightleftarrows D_\beta^{(J+\Delta-3)} + D_\beta^{(J+\Delta+2+4t)} \qquad \alpha \neq \beta$$

By means of the transfer of two 6-fold clusters:

$$D_\alpha^{(J+\Delta)} + D_\alpha^{(J+\Delta-2+4t)} \rightleftarrows D_\alpha^{(J+\Delta-6)} + D_\alpha^{(J+\Delta+4+4t)}$$

$$D_\alpha^{(J+\Delta)} + D_\beta^{(J+\Delta+4t)} \rightleftarrows D_\alpha^{(J+\Delta-6)} + D_\beta^{(J+\Delta+6+4t)} \qquad \alpha \neq \beta$$

By means of the transfer of one 8_0 cluster:

$$D_\alpha^{(J+\Delta)} + D_\beta^{(J+\Delta-4+3t)} \rightleftarrows D_\alpha^{(J+\Delta-4)} + D_\beta^{(J+\Delta+3t)} \qquad \alpha = \beta \text{ or } \alpha \neq \beta$$

By means of the transfer of one 12_0 cluster:

$$D_\alpha^{(J+\Delta)} + D_\beta^{(J+\Delta-6+2t)} \rightleftarrows D_\beta^{(J+\Delta-6)} + D_\alpha^{(J+\Delta+2t)} \qquad \alpha \neq \beta$$

$$D_\alpha^{(J+\Delta)} + D_\alpha^{(J+\Delta-5+2t)} \rightleftarrows D_\beta^{(J+\Delta-6)} + D_\beta^{(J+\Delta+1+2t)} \qquad \alpha \neq \beta$$

α and β are the subscripts g or u. t is any integer.

The transfer of two 6-fold clusters simultaneously is a bit more complicated than the transfer of one cluster. Immediately it looks like there would be two possibilities for such a transfer, one in which the cluster indices of both clusters are maintained during the transfer, and another in which the 6_0 cluster is transferred as a 6_1 cluster and vice versa. A detailed study of the symmetries of the clusters demonstrates, however, that the transfer is possible only if the cluster indices are maintained; i.e., the 6_0 cluster in the donor is transferred to the acceptor as a 6_0 cluster and the 6_1 cluster in the donor as a 6_1 cluster in the acceptor. The resulting reaction schemes are included in Table III.

The reaction schemes given in Table III are closely analogous to those for a chemical reaction due to a transfer of a cluster of atoms. Each scheme may be read from left to right or from right to left. In the first case the first symbol on each side of the two arrows represents the symmetry of the donor and the second one that of the acceptor, before and after the transfer, respectively. If read from right to left, this is reversed.

As an example of the use of Table III we may look at what changes are possible due to a transfer of an 8_0 cluster from a component of symmetry $D_{\mathrm{u}}^{(J+2)}$ and what could be the symmetry of the acceptor component. In this case $\Delta = 2$, and $\alpha = \mathrm{u}$, but β may be either g or u, and t may be any integer. This means that there is an infinite number of possibilities for the symmetry of the acceptor, out of which $D_{\mathrm{g}}^{(J-2)}$, $D_{\mathrm{u}}^{(J-2)}$, $D_{\mathrm{g}}^{(J+1)}$, and $D_{\mathrm{u}}^{(J+1)}$ may be the most interesting. With the first possibility as an example, the reaction scheme becomes

$$D_{\mathrm{u}}^{(J+2)} + D_{\mathrm{g}}^{(J-2)} \rightleftarrows D_{\mathrm{u}}^{(J-2)} + D_{\mathrm{g}}^{(J+2)}. \tag{11}$$

Knowing the symmetry of the transfered cluster, as indicated above, it is easy to verify this equation for any value of J by means of Table I.

THE USE OF LOCAL SYMMETRY INDICES

The symmetry of a vibrational component has so far been characterized by an irreducible representation of the full rotational group O_3, indicated as $D_{\alpha}^{(J+\Delta)}$, where α is either g or u. In this section we present an alternative description of the symmetry by means of the subgroups C_4, C_3, and C_2, leading to alternative methods for finding all the solutions to Eq. (2) and for finding the possible changes in the symmetries of neighboring vibrational components.

In order to do this, it is convenient to introduce an alternative symbolism for the irreducible representations of these subgroups. The new symbols are the small integers n appearing in the characters of the irreducible representations of the C_m group, written in the form $\exp(in\pi/m)$. Thus, for the subgroup C_4 this numerical symbol n_4 has the value $n_4 = 0, 1, 2$, or 3 as an alternative symbol for A, E_a, B, or E_b, respectively. For the subgroup C_3 the numerical symbol n_3 has the value $n_3 = 0, 1$, or 2 as an alternative symbol for A, E_a, or E_b, respectively. For the subgroup C_2 the numerical symbol n_2 has the value $n_2 = 0$ or 1 as an alternative symbol for A or B, respectively.

An irreducible representation of O_3 correlates to a sum of irreducible representations for any of the three C_∞ point groups with the axis chosen as a C_4, C_3, or C_2 axis. Each of these irreducible representations is characterized by an integer number, indicating the value of the projection of the rotational angular momentum on the axis. The maximum value of this projection differs from the projection of the total angular momentum due to the vibrational contribution. Selecting for each of the C_∞ point groups the irreducible representation characterized by the maximum integer number, a description of the vibrational contribution is obtained which characterize each vibrational component. The correlation from each of the C_∞ point groups to the corresponding C_4, C_3, or C_2 group then leads to a single irreducible representation. Each of these is characterized by one of the three numbers n_4, n_3, and n_2 defined above. These three numbers may be called the local symmetry indices of the vibrational component. In the semiclassical model they indicate the length of the projections of the vibrational angular momentum vector on one of each of the three axes, whereas $J + \Delta$ indicates the length of the angular momentum vector, resulting from the coupling of the J vector and the vibrational angular momentum vector.

This special correlation from O_3 to the three subgroups leads to the following general expressions for n_4, n_3, and n_2 as functions of Δ and α in the symbol $D_\alpha^{(J+\Delta)}$ for the symmetry in O_3 of the vibrational component

$$n_4 = \Delta \text{ modulo } 4 \qquad \text{if } \alpha = \text{g} \tag{12}$$

$$n_4 = (\Delta + 2) \text{ modulo } 4 \qquad \text{if } \alpha = \text{u} \tag{13}$$

$$n_3 = \Delta \text{ modulo } 3 \tag{14}$$

$$n_2 = \Delta \text{ modulo } 2 \qquad \text{if } \alpha = \text{g} \tag{15}$$

$$n_2 = (\Delta + 1) \text{ modulo } 2 \qquad \text{if } \alpha = \text{u}. \tag{16}$$

The result of these expressions is indicated in Table IV. For 12 consecutive values of Δ, there is a one-to-one correspondence between the symmetry in O_3, as given by Δ and α, and the local symmetry indices n_4, n_3, and n_2. Considering that Δ usually is confined to the interval $-3 \leqslant \Delta \leqslant 3$, so that t in Table IV is usually equal to zero, the

TABLE IV

The Local Symmetry Indices for a Vibrational Component of Symmetry $D_\alpha^{(J+\Delta)}$

	α = g			α = u		
Δ	n_4	n_3	n_2	n_4	n_3	n_2
−5+12t	3	1	1	1	1	0
−4+12t	0	2	0	2	2	1
−3+12t	1	0	1	3	0	0
−2+12t	2	1	0	0	1	1
−1+12t	3	2	1	1	2	0
12t	0	0	0	2	0	1
1+12t	1	1	1	3	1	0
2+12t	2	2	0	0	2	1
3+12t	3	0	1	1	0	0
4+12t	0	1	0	2	1	1
5+12t	1	2	1	3	2	0
6+12t	2	0	0	0	0	1

t is any integer

local symmetry indices give in practice a complete description of the symmetry of any vibrational component. The reverse relations to Eqs. (12)-(16) are

$$\Delta = (6n_4 + 8n_3 + 12n_2)/2 + 12t, \tag{17}$$

where t is any integer, provided that Eq. (3) is satisfied, and

$$\alpha = \mathrm{g} \quad \text{if } n_4 + n_2 \text{ is even,} \qquad \alpha = \mathrm{u} \quad \text{if } n_4 + n_2 \text{ is odd.} \tag{18}$$

The symmetry of a vibrational state or substate is given in the point group T_d, but may alternatively be given by the symmetries in the subgroups S_4, C_3, and C_s. These subgroups are isomorphic to the subgroups C_4, C_3, and C_2, and we use the same numerical symbols n_4, n_3, and n_2 to indicate the irreducible representations of these groups. The irreducible representations of T_d are in general reducible if correlated to these subgroups, as indicated in the left half of Table V by means of the traditional symbols and in the right half by means of the numerical symbols. Table V may be used to indicate the vibrational symmetry in the three subgroups of any vibrational state. If the symmetry in T_d is given by a reducible representation, the corresponding lines in the table are just added. The symmetry in any of the subgroups is always a sum of g_{vib} terms, where g_{vib} as above indicates the vibrational degeneracy of the vibrational state.

This correlation from the symmetry in T_d to the three subgroups for a given vibrational state is analogous to Eq. (2), and the solutions to this equation may be found by selecting all the vibrational components for which the sum of the local symmetry indices equals the result of the correlation.

As an example the local symmetry indices are used to find all the symmetries of the vibrational components for $\Gamma_{\mathrm{vib}} = E$. One starts by selecting out of the sums in the third line of Table V three local symmetry indices for the first vibrational component. One choice is $(n_4, n_3, n_2) = (0, 2, 1)$. The sums in Table V then immediately indicate that the local symmetry indices of the other component must be $(n_4, n_3, n_2) = (2, 1, 0)$ because these are the only symbols left. Another choice for the first component would be $(n_4, n_3, n_2) = (0, 1, 1)$, with $(n_4, n_4, n_2) = (2, 2, 0)$ left for the other component. But there are still two other solutions as shown in Table VI. The symmetries in O_3 are found either from Table IV or by use of Eqs. (17) and (18), in each case giving an infinite number of solutions for different values of t. The symmetries given in Table VI are those having the smallest numerical values of Δ. It is seen that the

TABLE V

Reduction of the Irreducible Representations of T_d

	Traditional Symbols			Numerical Symbols		
T_d	S_4	C_3	C_s	S_4 (C_4)	C_3	C_s (C_2)
A_1	A	A	A'	0	0	0
A_2	B	A	A"	2	0	1
E	A+B	E_a+E_b	A'+A"	0+2	1+2	0+1
F_1	A+E_a+E_b	A+E_a+E_b	A'+2A"	0+1+3	0+1+2	0+1+1
F_2	E_a+B+E_b	A+E_a+E_b	2A'+A"	1+2+3	0+1+2	0+0+1

TABLE VI

Solutions for the Symmetries of Vibrational Components
Based on Local Symmetry Indices

Γ_{vib}	n_4	n_3	n_2	$D_{\alpha}^{(J+\Delta)}$	n_4	n_3	n_2	$D_{\alpha}^{(J+\Delta)}$	n_4	n_3	n_2	$D_{\alpha}^{(J+\Delta)}$
A_1	0	0	0	$D_{g}^{(J)}$								
A_2	2	0	1	$D_{u}^{(J)}$								
E	0	2	1	$D_{u}^{(J+2)}$	2	1	0	$D_{g}^{(J-2)}$				
	0	1	1	$D_{u}^{(J-2)}$	2	2	0	$D_{g}^{(J+2)}$				
	0	2	0	$D_{g}^{(J-4)}$	2	1	1	$D_{u}^{(J+4)}$				
	0	1	0	$D_{g}^{(J+4)}$	2	2	1	$D_{u}^{(J-4)}$				
F_2	3	1	0	$D_{u}^{(J+1)}$	2	0	1	$D_{u}^{(J)}$	1	2	0	$D_{u}^{(J-1)}$
	3	1	0	$D_{u}^{(J+1)}$	2	2	0	$D_{g}^{(J+2)}$	1	0	1	$D_{g}^{(J-3)}$
	3	0	1	$D_{g}^{(J+3)}$	2	1	0	$D_{g}^{(J-2)}$	1	2	0	$D_{u}^{(J-1)}$
	3	0	0	$D_{u}^{(J-3)}$	2	2	0	$D_{g}^{(J+2)}$	1	1	1	$D_{g}^{(J+1)}$
	3	2	1	$D_{g}^{(J-1)}$	2	1	0	$D_{g}^{(J-2)}$	1	0	0	$D_{u}^{(J+3)}$
	3	1	0	$D_{u}^{(J+1)}$	2	2	1	$D_{u}^{(J-4)}$	1	0	0	$D_{u}^{(J+3)}$
	3	0	0	$D_{u}^{(J-3)}$	2	1	1	$D_{u}^{(J+4)}$	1	2	0	$D_{u}^{(J-1)}$
	3	1	1	$D_{g}^{(J-5)}$	2	2	0	$D_{g}^{(J+2)}$	1	0	0	$D_{u}^{(J+3)}$
	3	0	0	$D_{u}^{(J-3)}$	2	1	0	$D_{g}^{(J-2)}$	1	2	1	$D_{g}^{(J+5)}$
	3	0	1	$D_{g}^{(J+3)}$	2	2	0	$D_{g}^{(J+2)}$	1	1	0	$D_{u}^{(J-5)}$
	3	2	0	$D_{u}^{(J+5)}$	2	0	1	$D_{u}^{(J)}$	1	1	0	$D_{u}^{(J-5)}$
	3	2	0	$D_{u}^{(J+5)}$	2	1	0	$D_{g}^{(J-2)}$	1	0	1	$D_{g}^{(J-3)}$
	3	1	1	$D_{g}^{(J-5)}$	2	0	0	$D_{g}^{(J+6)}$	1	2	0	$D_{u}^{(J-1)}$
	3	1	0	$D_{u}^{(J+1)}$	2	0	0	$D_{g}^{(J-6)}$	1	2	1	$D_{g}^{(J+5)}$
	3	2	1	$D_{g}^{(J-1)}$	2	0	0	$D_{g}^{(J+6)}$	1	1	0	$D_{u}^{(J-5)}$
	3	2	0	$D_{u}^{(J+5)}$	2	0	0	$D_{g}^{(J-6)}$	1	1	1	$D_{g}^{(J+1)}$
	3	0	0	$D_{u}^{(J-3)}$	2	2	1	$D_{u}^{(J-4)}$	1	1	0	$D_{u}^{(J+7)}$
	3	2	0	$D_{u}^{(J+5)}$	2	1	1	$D_{u}^{(J+4)}$	1	0	0	$D_{u}^{(J-9)}$

Each line indicates one solution.

solutions found in this way are precisely those indicated by Eq. (4), demonstrating that the two methods yield the same solutions, the advantage of the present method being that it is easier to find all possible solution in less trivial cases. As a further example all the solutions for $\Gamma_{vib} = F_2$ are included in Table VI.

The local symmetry indices are also useful in the study of the changes in the symmetries of vibrational components due to an exchange of one or two clusters. Two components will always form a basis of a reducible representation for all three subgroups, and this cannot change as a result of an interaction. Consequently, any change of symmetry can only be the result of an interchange of local symmetry indices between the two components. If, say, the index n_3 for one component is changed from 0 to 1, the index n'_3 of the other component must necessarily change from 1 to 0.

According to Eq. (17) such changes in n_3 and n'_3 lead to changes in the values of Δ for both components, which again result in changes in the total degeneracies and, according to Table IV of Ref. (*3*), also to changes in the symmetries of the 8-fold clusters. All of these changes agree with a transfer of 8-fold clusters from one of the components to the other, and due to the presence of the $12t$ in Eq. (17) there is always an infinite number of different solutions for how many clusters are transferred, including the transfer of one cluster only. Similar results are obtained if the index n_3 is changed from 1 to 2, or from 0 to 2, the important point being that a transfer of one cluster is always included in the solutions. This means that a transfer of one eightfold cluster is always sufficient to produce the changes in the symmetries of both components indicated by an exchange of the values of n_3 and n'_3.

Analogous results are obtained for an exchange of the values of n_2 and n'_2, where a transfer of one 12-fold cluster is always sufficient to produce the corresponding changes in the symmetries of the two components. The situation is slightly more complicated if the values of n_4 and n'_4 are exchanged. In most cases the transfer of one 6-fold cluster is sufficient, but if the values of n_4 and n'_4 are 0 and 2, or 1 and 3, a simultaneous transfer of two 6-fold clusters is needed to produce the corresponding changes in the symmetries of both components.

These results may be used to formulate the reaction schemes given in Table VII. If the value of any local symmetry index n_4, n_3, or n_2 gets outside its range according to this table, it should be brought back by the addition or subtraction of 4, 3, or 2, respectively. These reaction schemes are analogous to those given in Table III, except that the order of donor and acceptor is not necessarily the one used in Table III. It is possible to formulate some rather complicated rules for what is what, but it seems easier to use Eq. (17) or Table IV to determine the Δ values, giving this information immediately as discussed above in most cases. For a transfer of one 12-fold or two 6-fold clusters the transfer may in principle always go both ways, because of the $12t$ in Eq. (17) and in Table IV, but in practice one of these possibilities is often rather unrealistic because of the numerically high Δ values.

Inserting Eqs. (17) and (18) it is possible to change the expressions given in Table VII to those given in Table III, demonstrating once more that the local symmetry

TABLE VII

Possible Changes in the Symmetries of Two Vibrational Components Due to a Change of J, Expressed by Local Symmetry Indices

By means of the transfer of one 6_0 cluster:

$$(n_4, n_3, n_2) + (n_4\pm1, n_3', n_2') \rightleftarrows (n_4\pm1, n_3, n_2) + (n_4, n_3', n_2')$$

By means of the transfer of two 6-fold clusters:

$$(n_4, n_3, n_2) + (n_4\pm2, n_3', n_2') \rightleftarrows (n_4\pm2, n_3, n_2) + (n_4, n_3', n_2')$$

By means of the transfer of one 8_0 cluster:

$$(n_4, n_3, n_2) + (n_4', n_3\pm1, n_2') \rightleftarrows (n_4, n_3\pm1, n_2) + (n_4', n_3, n_2')$$

By means of the transfer of one 12_0 cluster:

$$(n_4, n_3, n_2) + (n_4', n_3', n_2\pm1) \rightleftarrows (n_4, n_3, n_2\pm1) + (n_4', n_3', n_2)$$

indices lead to the same results as the purely group-theoretical method presented above. When analyzing complicated interactions between vibrational components (*4*) it seems, however, easier to use Table VII, or the equivalent rules formulated above, together with Table IV than to use Table III, because the contents of Table VII are easy to remember. In reality this means that one works simultaneously with both kinds of symbols for the symmetry of the vibrational components.

The local symmetry indices indicate immediately that any pair of vibrational components of different symmetries may interact by means of an exchange of clusters. Thus, a crossing of any pair of two vibrational components may take place as a "modified avoided crossing" exclusively by means of transfers of clusters. Examples of such crossings will be given in a forthcoming publication (*4*).

ACKNOWLEDGMENT

The stay of B.I.Z. in Aarhus was financed by the Danish Natural Science Research Council.

RECEIVED: August 26, 1993

REFERENCES

1. S. Brodersen, *J. Mol. Spectrosc.* **145,** 331–351 (1991).
2. S. Brodersen, to be published.
3. S. G. Larsen and S. Brodersen, *J. Mol. Spectrosc.* **157,** 220–236 (1993).
4. S. Brodersen and B. I. Zhilinskii, to be published.
5. D. Papoušek and M. R. Aliev, "Molecular Vibrational-Rotational Spectra," Chap. 11, Academia, Prague, 1982.
6. L. D. Landau and E. M. Lifshitz, "Quantum Mechanics," Pergamon, Oxford, 1965.
7. F. Michelot, *J. Mol. Spectrosc.* **63,** 227–240 (1976).
8. B. I. Zhilinskii, S. Brodersen, and M. Madsen, *J. Mol. Spectrosc.* **160,** 192–216 (1993).
9. W. G. Harter and C. W. Patterson, *J. Chem. Phys.* **80,** 4241–4261 (1984).
10. W. G. Harter, *Comput. Phys. Rep.* **8,** 319–394 (1988).
11. L. C. Biedenharn and J. D. Louck, *in* "Encyclopedia of Mathematics" (G. C. Rota, Ed.), Vol. 8, Addison–Wesley, Reading, MA, 1981.
12. I. M. Pavlichenkov, *Phys. Rep.* **226,** 173–279 (1993).
13. V. B. Pavlov-Verevkin, D. A. Sadovskii, and B. I. Zhilinskii, *Europhys. Lett.* **6,** 573–578 (1988).