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Transfer of Clusters between the Vibrational Components of CF_4

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The pattern of the rotation–vibrational energy levels in isolated vibrational components of CF_4 has recently been described (B. I. Zhilinskii *et al., J. Mol. Spectrosc.* **160**, 192–216, 1993) in terms of the semiclassical model for the rotation of molecules. The present paper discusses the interaction between neighboring vibrational components due to a transfer from one component to the other of either one 6-fold cluster, one 8-fold cluster, one 12-fold cluster, or two 6-fold clusters. The rules for which transfers are possible are derived from a consideration of the formation of common points between the two corresponding classical rotational energy surfaces. These rules are conveniently stated in terms of the local symmetry indices (B. I. Zhilinskii and S. Brodersen, *J. Mol. Spectrosc.* **163**, 326–338, 1994) characterizing the symmetries of the two vibrational components. Three examples of such interactions are discussed in detail: first a crossing of one vibrational component from the ν_3 vibrational state with one of the components from the $2\nu_4$ state; second, a crossing of one vibrational component from the ν_3 vibrational state with the two components of the E substate of $3\nu_2$; and finally, the rearrangement of the vibrational components of the E and F_2 substates of the $2\nu_4$ vibrational state into five components of the combined $E + F_2$ substate.

INTRODUCTION

With CF_4 as an example, the pattern formed by the rotation–vibrational states of a heavy spherical top molecule has been discussed in two previous papers (*1*, *2*). It was found that the rotation–vibrational states belonging to one vibrational state are split, primarily by anharmonic splitting into *vibrational substates* and secondarily due to rotation–vibrational interaction into *vibrational components*, corresponding to a complete breakdown of the vibrational degeneracy. The collection of rotation–vibrational states within one vibrational component for one value of J was defined as a *manifold*. Most of the rotation–vibrational states within one manifold was found to collect in *clusters*, forming one series of 6-fold clusters, one of 8-fold clusters, sometimes one of 12-fold clusters, and in exceptional cases one series of 24-fold clusters. A *cluster index* τ was defined on the basis of the k-distribution, calculated from the wavefunctions of the states involved. Within each series of clusters τ always takes the values 0, 1, 2, 3, . . . , and each cluster within one manifold is completely specified by the degeneracy and the cluster index, collected in one symbol as, say, 12_0. The pattern of clusters within one manifold is often the one denoted *type I*, where a series of 6-fold clusters starts with the 6_0 cluster from the low energy end of the manifold and a series of 8-fold clusters starts from the high energy end with the 8_0 cluster, or the one denoted *type II*, where the order of the two series is reversed.

The semiclassical theory for the rotation of molecules was slightly redefined (*2*) and used to explain these patterns on the basis of a discussion of the possible shapes of the classical *rotational energy surface* (*3*). A corresponding discussion of the possible changes of these shapes as a function of J was used to explain the details of complicated patterns of clusters as a result of a transformation from type I to type II, or vice versa,

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as a function of J. Two cases were distinguished, the simple inversion, characterized by the appearance of a series of 12-fold clusters, and the complex inversion, where in addition the series of 6-fold and 8-fold clusters are folded as a function of energy and where 24-fold clusters may be formed.

The detailed discussion in Ref. (*2*) of the possible patterns of clusters within one manifold was limited to the case of isolated vibrational components, in which the influence from the neighboring vibrational components could be neglected. In the present paper this discussion is carried on to the more complicated case where vibrational components interact by a transfer of clusters. It will be shown that these cases also may be explained qualitatively in every detail by means of the semiclassical theory.

Each vibrational component may be characterized by a symmetry, indicated either by an irreducible representation in the full rotational group O_3, symbolized as, say, $D_u^{(J-3)}$ or $D_g^{(J+1)}$, or by means of the three local symmetry indices (n_4, n_3, n_2) defined in a recent publication (*4*). In this paper, two methods were indicated for finding the possible symmetries of the vibrational components into which a vibrational state or substate of a given vibrational symmetry is split. Further, a detailed analysis was given of the possible changes in the symmetries of two neighboring vibrational components as the result of a transfer of one or two clusters from one component to the other. The discussion in the present paper is based on this information.

The detailed analysis in Refs. (*1*, *2*) was possible because the potential function of CF_4 is very well known (*5*, *6*), and also because the energies and wavefunctions of all the rotation–vibrational states for $J \leqslant 70$ have been computed for the 10 vibrational states of lowest energy for all three isotopic species $^{12}CF_4$, $^{13}CF_4$, and $^{14}CF_4$. The examples given in the present paper are based on a highly refined potential function (*6*) and are therefore in close agreement with the presently known experimental data. The analysis given in Ref. (*2*) of isolated vibrational components was based on a potential function belonging to a slightly earlier step in the refinement process, but the differences between the results from the two potentials are quite small and they have no influence on the qualitative results and the general conclusions.

After the present work was finished, we were informed that Gabard *et al.* (*7*) have made a large number of assignments in the ν_3 and $2\nu_4$ bands for $J \leqslant 32$ by means of a high-order effective Hamiltonian. A comparison of the energies computed from this Hamiltonian and those from our Hamiltonian indicates a perfect qualitative agreement and small quantitative discrepancies. This demonstrates that the predictions based on our Hamiltonian are sufficiently accurate for the present purpose.

THE ROTATIONAL ENERGY SURFACES OF TWO NEIGHBORING VIBRATIONAL COMPONENTS

In the semiclassical model (*2*) a classical rotational energy surface is defined for each manifold, plotting the rotational energy as a function of the direction of the angular momentum in a molecule-fixed coordinate system. In this section, a short survey is given of the relations between the rotational energy surfaces of the two manifolds for one value of J of two neighboring vibrational components. This leads to a complete description of the rules for interactions between the components by means of a transfer of clusters, and the remaining sections of this paper are devoted to a discussion of examples of such interactions between the vibrational components of the CF_4 molecule.

If the two rotational energy surfaces are plotted in a common coordinate system, immediately there seem to be five different possibilities for their relative positions (*8*):

1. The energy values indicated by the two surfaces are completely separated, so that all energies of one manifold are well below all the energies of the other manifold. This is the case of two isolated vibrational components, discussed in detail in Ref. (*2*).

2. Some of the energy values of the low energy component are larger than some of the energy values of the high energy component, but the two surfaces are well separated from each other. This leads to a simple overlap of the energies within the two manifolds, and there is no interaction between the two components. It was discussed in Ref. (*1*) how it is possible by means of the cluster index to find which states (or clusters) belong to each of the two components.

3. The two surfaces are very close without actually touching each other. This leads to a complicated pattern of energy levels and to a strong coupling between the wavefunctions of both components. It is difficult to give a complete theory of the possible interactions, but some examples are discussed below.

4. The two surfaces may touch each other. Because of the O_h symmetry of both surfaces a touch will always take place at many points simultaneously, either at all 6 C_4 points, or at all 8 C_3 points, or at all 12 C_2 points, simultaneously. As discussed below, it is only these cases which lead to a transfer of one or two clusters between the two vibrational components. In principle, a touch at 24 σ points or at 48 C_1 points should also be a possibility, but from the previous discussion (*2*) of the possible shapes of the surface it seems clear that this is only a theoretical possibility.

5. One should immediately think that the two surfaces might cross each other by having a continuum of points in common, forming closed curves on the surfaces. As discussed in the Appendix, it may be proved that such a crossing cannot take place, and the two surfaces cannot pass each other as J changes. This statement is a generalization of the noncrossing rule for potential surfaces (*9*) and of the description of the intersection between eigenvalues of matrices, the elements of which depend on parameters (*10*).

A touch of the two surfaces may lead, in the corresponding quantum mechanical calculations, to a transfer of one or two clusters between the components as J changes, depending on the symmetries of the two components. A discussion of this is given in the Appendix. Here only a short review is given of the results, based on the use of local symmetry indices (*4*) to characterize the symmetries of the components.

If one of the local symmetry indices differs by 1 (here n_4 and n_3 have to be considered modulo 4 and 3, respectively, so that for instance $n_4 = 3$ and $n'_4 = 0$ belongs to this case), the two surfaces may touch each other at the 6 C_4 points if n_4 and n'_4 differ by 1, at the 8 C_3 points if n_3 and n'_3 differ by 1, or at the 12 C_2 points if n_2 and n'_2 differ by 1. This case includes the major part of the differences between the symmetries of two components. Such a touch of the two surfaces leads to the formation of a number of double cones with each of the points of contact as the common vertex, and the C_4 axes, the C_3 axes, or the C_2 axes, respectively, as the axes of the cones. The important consequence of this is that one cluster will have an energy equal to the energy $E_\times$ of the vertex, provided the maxima of the lower surface and the minima of the upper surface are prominent enough to allow the formation of clusters. If n_4 and n'_4 differ by 1 and the axes of the cones consequently are the 6 C_4 axes, this central cluster is a 6-fold cluster, etc.

This kind of contact between the two surfaces can only take place for one (generally not integer) value of J, say $J_\times$. For $J = J_\times$ the central cluster belongs to both manifolds. If J is changed slightly, the two surfaces cannot touch, and the energy of the central cluster will change slightly, in the first approximation linearly with J. This means that for $J < J_\times$ the cluster belongs to one of the manifolds, whereas for $J > J_\times$ it belongs to the other manifold. In other words, one cluster is being transferred from one vibrational component to the other as J varies through $J_\times$. The transferred cluster has always the cluster index $\tau = 0$ in both of the two components.

For $J = J_\times$ the central cluster belongs to two series of clusters, one in each of the two components. In the first approximation, where the double cone is symmetric with respect to a plane containing the vertex and perpendicular to the axis, the energies of the double series of clusters are given by

$$E = E_\times \pm \alpha \sqrt{t}, \tag{1}$$

where $t = 0, 1, 2, 3, \ldots$ and α is a constant.

If the two components have identical symmetries ($n_4 = n'_4$, $n_3 = n'_3$, and $n_2 = n'_2$), the two surfaces cannot touch each other.

If n_4 and n'_4 have the values 0 and 2, or 1 and 3, they differ by 2 (even if considered modulo 4), and a different kind of contact of the two surfaces may take place at the 6 C_4 points. This leads to a simultaneous transfer of two 6-fold clusters as J varies through $J_\times$. One of these clusters is a 6_0 cluster in both components, the other is a 6_1 cluster.

Clearly such a transfer of one or two clusters must have consequences for the symmetries of both components. These have been discussed in detail in Ref. (*4*). Here it is only necessary to mention that the transfer leads to an interchange of the two corresponding local symmetry indices of the two components. The local symmetry indices may be translated into the more familiar symbols for the symmetries in O_3 by means of Table IV of Ref. (*4*). A simple calculation of the changes in the degeneracies of the two manifolds from the Δ values in these symbols (the constants following J) will in most cases immediately indicate in which direction the transfer takes place, in other words, which of the two components is the "donor" and which is the "acceptor."

If two vibrational components converge in the energy diagram as a function of J so that they tend to cross, they do not cross in the usual sense, because the two surfaces cannot cross. Instead, they must separate again in a kind of avoided crossing. In most cases where the symmetries of the two components are different, this requires an exchange of the symmetries, which is precisely possible due to a transfer of one or more clusters. Which transfers are needed are easily seen if the two symmetries are expressed as local symmetry indices. Several examples of this are given in the following sections.

A CROSSING OF TWO VIBRATIONAL COMPONENTS

As a relatively simple example of a crossing of two vibrational components we shall give a detailed discussion of the crossing in $^{13}CF_4$ between the highest component of the ν_3 vibrational state, having $D_u^{(J+1)}$ symmetry, and the lowest component of the $2\nu_4$ vibrational state, having $D_g^{(J+2)}$ symmetry. They cross at about $J = 33$ because in $^{13}CF_4$ the $2\nu_4$ vibrational state has a higher energy than the ν_3 vibrational state.

The first to be discussed is what can be concluded about such a crossing exclusively on the basis of the symmetries of the two components. In order that the crossing shall take place without the components actually crossing each other, the symmetries of

the two components have to be interchanged as a function of J. For low J values, actually for $J \leq 30$, the component of highest energy (the upper component) has $D_g^{(J+2)}$ symmetry and the component of lowest energy (the lower component) has $D_u^{(J+1)}$ symmetry, but for some higher J values this must be reversed so that the upper component has $D_u^{(J+1)}$ symmetry and the lower component $D_g^{(J+2)}$ symmetry, and these changes should be the result of one or more transfers of clusters between the two components. The two symmetries may be rewritten in the form of local symmetry indices (4) as $(n_4, n_3, n_2) = (220)$ for the upper component and (310) for the lower component. This means that both n_4 and n'_4, and n_3 and n'_3, differ by 1, whereas $n_2 = n'_2$. Thus one 6-fold cluster and one 8-fold cluster may be transferred between the two components. The directions of these transfers is obtained by looking at the changes in the total degeneracy of each component. The upper component shifts its symmetry from $D_g^{(J+2)}$ to $D_u^{(J+1)}$ as J increases, and the total degeneracy correspondingly drops by 2 compared to a component with a constant Δ value. This is only possible if this component loses one 8-fold cluster and gains one 6-fold cluster, in other words, if the 8-fold cluster is transferred from the upper to the lower component and the 6-fold cluster is transferred from the lower to the upper component as J increases. A consideration of the Δ values for the lower component leads to the same result.

This is as far as one can get on the basis of pure symmetry considerations. They cannot tell in what order the two transfers take place as a function of J, and we are left with two possibilities as sketched in the two diagrams given in the two halves of Fig. 1. In order to distinguish which of these is the one actually occurring in the present case, one has first to look at the energy level diagram and second to study the k-

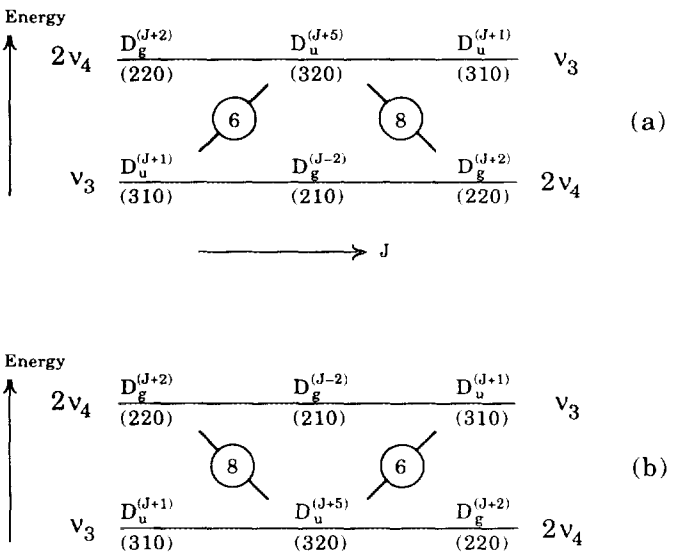

FIG. 1. Two possibilities for the diagram showing the effect on the symmetries of two vibrational components with symmetries $D_g^{(J+2)}$ and $D_u^{(J+1)}$ of the transfers of clusters as needed for a crossing of the components as J changes. Each diagram is a symbolic representation of the energy level diagram, indicating only the transfers of clusters and the resulting changes in symmetries of the two components. Each component is symbolized by a horizontal line. The symmetry of the component is given above this line using the conventional symbol and below the line using local symmetry indices. A transfer of a cluster is shown as a number giving the degeneracy of the cluster in a circle with two attached lines indicating the direction of the transfer.

distributions (J) of some of the clusters. In the following discussion, it is convenient to let $J_{\times 6}$ mean the (possibly noninteger) J value of the touch between the two surfaces leading to the transfer of the 6-fold cluster, and analogously for $J_{\times 8}$.

The energy level diagram is shown in Fig. 2. Here it is easy to see how the major parts of the two components avoid a crossing by bending off each other as J increases. Only one 6_0 cluster, marked by open circles in the figure, gradually leaves the lower component and transfers to the upper component as J increases. Also an 8_0 cluster, marked by squares, gradually leaves the upper component and is transferred to the lower one as J increases. It is, however, not possible on the basis of the energy level diagram alone to fix the values of $J_{\times 6}$ and $J_{\times 8}$ with an accuracy allowing one to distinguish between the two possibilities indicated in Fig. 1. If the two surfaces were

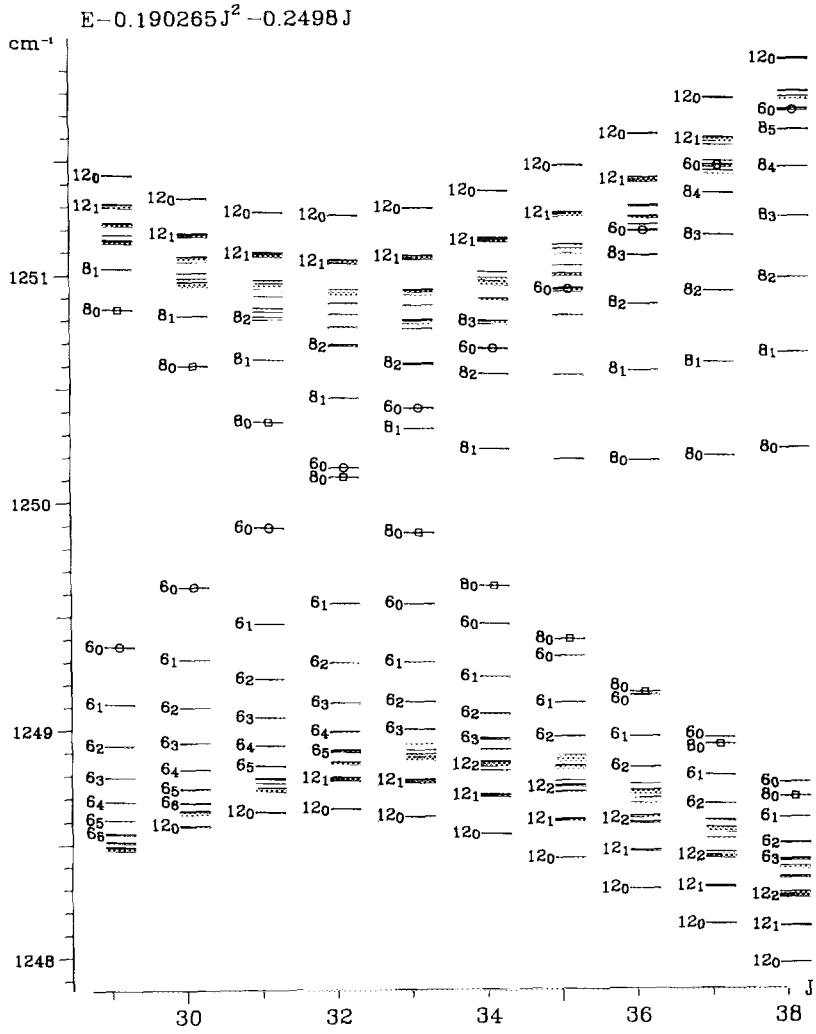

FIG. 2. A reduced energy level diagram showing the crossing of the $D_u^{(J+1)}$ component of the ν_3 vibrational state (lower component at low J; upper component at high J), and the $D_g^{(J+2)}$ component of the $2\nu_4$ vibrational state (upper component at low J; lower component at high J) in $^{13}CF_4$. The series of transferring 8-fold clusters is marked by squares. The series of transferring 6-fold clusters is marked by circles.

symmetrical in a region around the point of contact, corresponding to several clusters in both components, it would be possible to determine $J_{\times 6}$ or $J_{\times 8}$ as the J value for which the pattern of these clusters is symmetrical around the transferring cluster. This is, however, not the case here (and in many other cases), as may be seen from the fact that the series of 8-fold clusters is practically absent in the lower component, but rather well developed in the upper component, and vice versa for the 6-fold clusters.

Instead, one has to look at the k-distributions. As mentioned previously (*4*), the transfer of, say, an 8_0 cluster from one component to the other must lead to a reorganization of the cluster indices in the series of 8-fold clusters in both components, and this must be seen in the k-distributions of the clusters in the two series. To demonstrate this, Table I indicates the essential part of the k-distributions for the 8-fold

TABLE I

Reorganization of a Series of 8-fold Clusters Due to the Transfer of One Cluster

J	E cm^{-1}	Symmetry	τ	k-distrubution × 1000 J–k = 0	1	2	3	4	5
31	1441.396	$E+F_1+F_2$	2	5	155	586	4	31	73
	1441.214	$E+F_1+F_2$	1	120	843	2	6	24	0
	1440.942	$A_1+A_2+F_1+F_2$	0	990	2	1	6	0	0
33	1466.047	$A_1+A_2+F_1+F_2$	2	10	317	590	1	22	39
	1465.764	$E+F_1+F_2$	1	255	715	1	5	17	0
	1465.312	$E+F_1+F_2$	0	988	2	1	7	0	0
34	1479.228	$A_1+A_2+F_1+F_2$	3	3	26	392	402	4	54
	1479.000	$E+F_1+F_2$	2	14	408	519	0	19	27
	1478.671	$E+F_1+F_2$	1	369	612	1	4	12	0
	1478.071	$A_1+A_2+F_1+F_2$	0	987	2	1	8	0	0
35	1492.820	$A_1+A_2+F_1+F_2$		1	8	40	386	259	13
	1492.633	$E+F_1+F_2$		3	32	485	379	2	43
	1492.372	$E+F_1+F_2$		17	501	449	0	14	17
	1492.004	$A_1+A_2+F_1+F_2$		494	493	1	4	8	0
	1491.213	$E+F_1+F_2$	0	986	3	2	8	0	0
36	1506.656	$E+F_1+F_2$	3	1	7	50	510	281	7
	1506.440	$E+F_1+F_2$	2	2	37	557	348	1	30
	1506.149	$A_1+A_2+F_1+F_2$	1	19	576	381	0	11	11
	1505.756	$E+F_1+F_2$	0	606	386	0	3	5	0
	1504.738	$E+F_1+F_2$	0	972	3	2	9	0	1
37	1521.066	$E+F_1+F_2$	4	0	5	12	65	502	212
	1520.881	$E+F_1+F_2$	3	1	6	56	574	280	4
	1520.636	$A_1+A_2+F_1+F_2$	2	2	39	606	315	1	21
	1520.323	$E+F_1+F_2$	1	21	636	327	0	8	7
	1519.914	$E+F_1+F_2$	0	691	303	0	2	3	0
	1518.646	$A_1+A_2+F_1+F_2$	0	983	3	2	10	0	0
40	1565.802	$E+F_1+F_2$	3	1	3	62	650	252	2
	1565.500	$A_1+A_2+F_1+F_2$	2	1	45	689	249	1	10
	1565.146	$E+F_1+F_2$	1	25	740	227	0	4	3
	1564.719	$E+F_1+F_2$	0	825	173	0	1	1	0
	1562.666	$A_1+A_2+F_1+F_2$	0	974	4	2	12	0	1

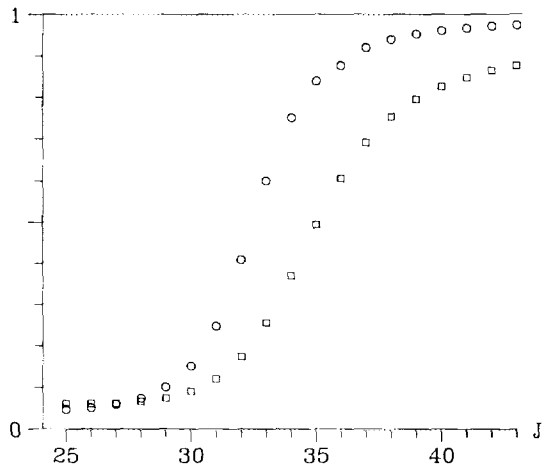

FIG. 3. The reorganization of the k-distributions of the nontransferring clusters illustrated by the k-distributions for $J - k = 0$ of the 8-fold clusters (indicated by squares) and 6-fold clusters (indicated by circles) nearest to the transferring clusters for the crossing shown in Fig. 2.

clusters for selected J values. However, as mentioned, all these clusters, except the transferring cluster, unfortunately belong to the upper component, so that the reorganization can only be seen in the upper component.

From Table I, it is seen that the determination of the value of the cluster index τ (I) represents no problem for $J = 31$ or $J = 33$, although the k-distributions are by no means ideal. For $J = 34$ the assignment of $\tau = 3$ to the cluster at 1479.228 cm^{-1} is only possible due to an extrapolation from the clusters with lower values of τ. Correspondingly, for $J = 35$ the τ value for the cluster at 1492.004 cm^{-1} can only be given if extrapolated from the clusters with higher τ values. For $J = 36$ the cluster at 1505.756 cm^{-1} definitely has $\tau = 0$, as seen both from its own k-distribution and from an extrapolation from the clusters with higher τ values. There are thus two 8-fold clusters with $\tau = 0$ for $J = 36$, out of which the one at 1504.738 cm^{-1} is the transferring cluster. This construction goes on for $J > 36$, the k-distributions being closer and closer to the ideal case as J increases. There can be no doubt that the transferring cluster belongs to the upper component for $J \leqslant 34$ and to the lower component for $J \geqslant 36$, so that $J_{\times 8}$ is close to 35. The reorganization of the series of 8-fold clusters in the upper component takes place over a rather large interval of J values, as seen from the pseudo-continuous changes in the k-distributions. It is important to note that these changes only apply to the nontransferring clusters. The k-distributions of the transferring cluster are almost ideal and nearly independent of J.

If one wishes to indicate a more precise value of $J_{\times 8}$, it seems reasonable to base this on the k-distributions of the nontransferring clusters with low values of τ, because the theory discussed in the Appendix applies best to the region closest to the point where the two surfaces touch. In the present case, this means that the almost identical k-distributions for $J - k = 0$ and 1 for the cluster at 1492.004 cm^{-1} ($J = 35$) indicate that $J_{\times 8}$ is approximately equal to 35. For the same reason we find it dubious to assign τ values to the remaining clusters for $J = 35$.

It is possible to get an overview of the reorganization of the nontransferring clusters by plotting, as a function of J, the value of the k-distribution for $J - k = 0$ for the

cluster nearest to the transferring cluster. Ideally this should be done for the cluster at both sides of the transferring one, but in the present case there are only 8-fold clusters above. This plot is given by the squares in Fig. 3. Several of these points may be found in Table I. It is seen that this value of the k-distribution has rather low values for low J because these clusters have $\tau = 1$, but high values for high J where these clusters have $\tau = 0$. At $J \approx 35$ the value passes 0.5, indicating that τ changes at this J value. The nontransferring cluster is above the transferring cluster; this means that the transferring cluster belongs to the upper component for $J < 35$ and to the lower component for $J > 35$, and $J_{\times 8} \approx 35$, as also found by means of Table I.

A corresponding study of the k-distributions for the 6-fold clusters shows an analogous reorganization of the k-distributions, as illustrated in Fig. 3 for the 6-fold cluster below the transferring one by means of circles. As these clusters all belong to the lower components, the plot shows that the transferring 6-fold cluster belongs to the lower component for $J < 32$ and to the upper component for $J \geqslant 33$, so that $J_{\times 6}$ is close to 32.5. This has the interesting consequence that for $J = 32$ the transferring 6_0 cluster belongs to the lower component, whereas the transferring 8_0 cluster belongs to the upper component, in apparent contradiction to their relative positions in the energy level diagram (Fig. 2). This only means, however, that the two surfaces touch for $J \approx 32.5$ at the C_4 points at a slightly higher energy than the energy of the minima at the C_3 points of the surface of the upper component. There is nothing special in this situation which just leads to a simple overlap of the energies of the two components.

As $J_{\times 6}$ is smaller than $J_{\times 8}$, the preceding discussion of the k-distributions indicates that the upper half of Fig. 1 gives the correct diagram for the crossing of the two components in the present case.

A CROSSING OF THREE VIBRATIONAL COMPONENTS

As the second and much more complicated example, this section presents an analysis of the crossing in $^{12}CF_4$ between the highest component of the ν_3 vibrational state, having $D_u^{(J+1)}$ symmetry, and the two components of the $3\nu_2(E)$ vibrational substate. Out of these the lower component has $D_g^{(J+2)}$ symmetry for low J values (below the crossing), but $D_g^{(J-2)}$ symmetry for high J values (above the crossing), whereas the upper component has $D_u^{(J-2)}$ symmetry for low J values and $D_u^{(J+2)}$ for high J values. This means that the two components of the E substate change from one of the two most common possibilities for the symmetries (*4*) to the other as a consequence of the crossing. It is thus not just a simple crossing leading to an exchange of the symmetries of the three components. A further complication, as compared to the first example, is that the transfers of the clusters are not so easily seen directly from the energy level diagram, given in Fig. 4. Consequently, it is essential to start the analysis with a determination of which transfers of clusters are able to produce the needed changes of the symmetries of all three components.

The result of this consideration is presented in Fig. 5, containing a diagram analogous to Fig. 1. The symmetries indicated to the left and to the right in this diagram are known, and the rest of the diagram is determined in the following way: The lowest component changes the local symmetry indices from (310) to (210). This calls for a transfer of one 6-fold cluster, which must leave the lower component as J increases because Δ is lowered by 3. The upper component changes the local symmetry indices from (011) to (310), necessitating a transfer of one 6-fold cluster and one 12-fold cluster (*4*). Again the increase of Δ by 3 with increasing J shows that the 6-fold cluster must leave this component, whereas the 12-fold cluster must go to this component as

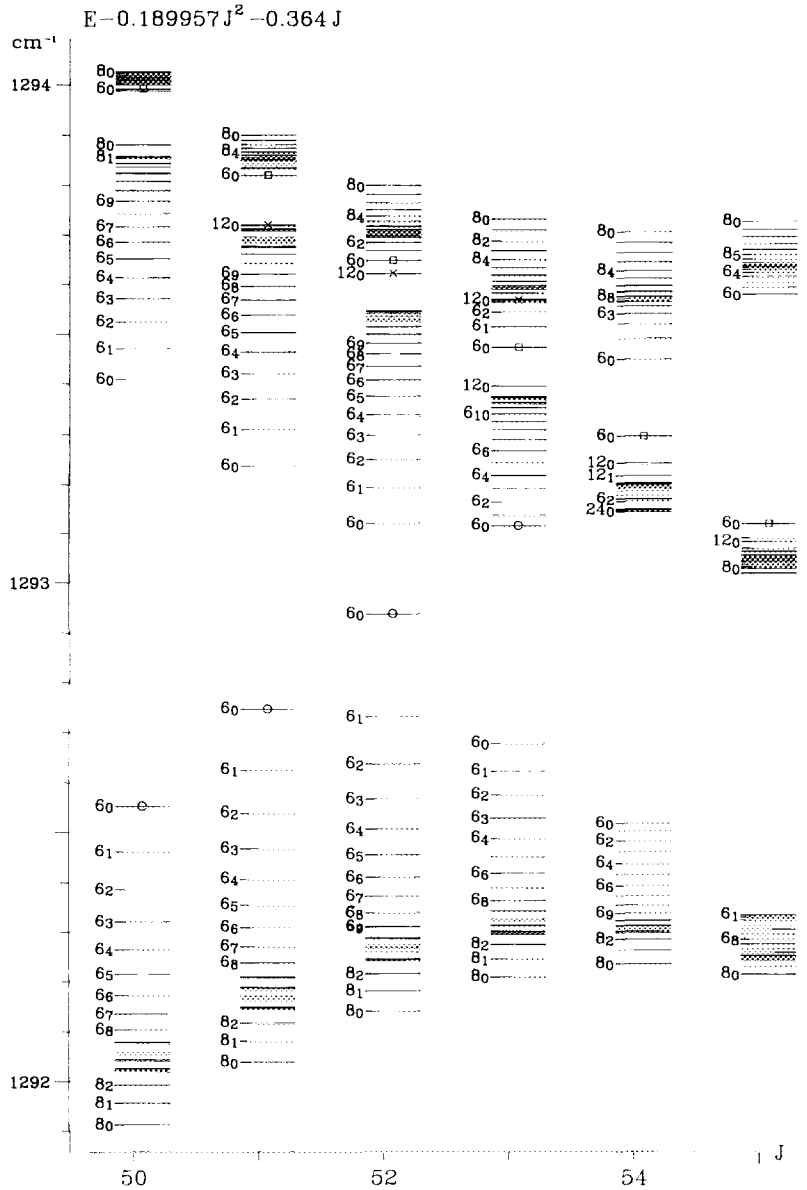

FIG. 4. A reduced energy level diagram showing the crossing of the $D_u^{(J+1)}$ component of the ν_3 vibrational state (lower component at $J = 50$; upper component at $J = 55$), and the two components of the $3\nu_2(E)$ vibrational substate in $^{12}CF_4$. The first series of transferring 6-fold clusters is marked by circles, that of 12-fold clusters by crosses, and the second series of transferring 6-fold clusters by squares.

J increases. As in the first example, this is as far as one can get exclusively on the basis of the symmetries of the three components before and after the crossing, whereas a choice between the six different ways these transfers may be ordered can only be made on the basis of a detailed study of the energy level diagram and the k-distributions of the clusters. The order given in Fig. 5, and the resulting intermediate symmetries, is the one resulting from this study.

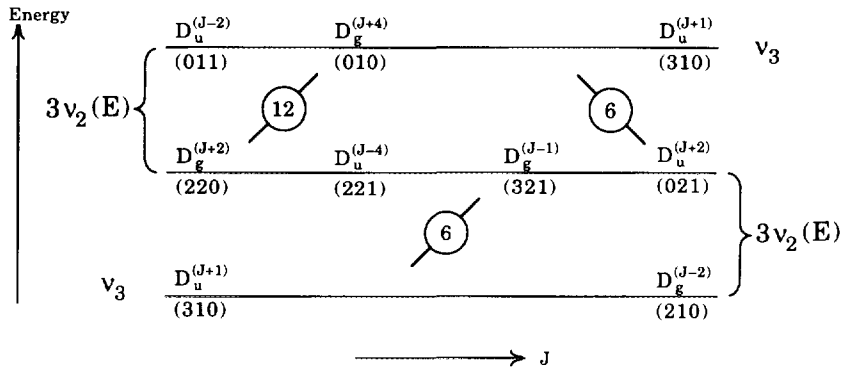

FIG. 5. A diagram, analogous to Fig. 1, showing the effect on the symmetries of three vibrational components of the transfers of three clusters, as needed for a crossing of the $D_u^{(J+1)}$ vibrational component of ν_3 with the $D_u^{(J-2)}$ and $D_g^{(J+2)}$ components of the $3\nu_2(E)$ substate, as J changes. As indicated, the crossing also results in a change in the symmetries of the two components of the $3\nu_2(E)$ substate. The corresponding energy level diagram is shown in Fig. 4.

Knowing that one 6-fold cluster must leave the lower component for increasing J, there is no difficulty in localizing this in the energy level diagram, as indicated by circles in Fig. 4. This interpretation is confirmed by the k-distributions of the 6-fold clusters of the two lowest components, which also fixes the $J_{\times 6}$ value to a little above 52, which means that the rather isolated 6_0 clusters for $J = 52$ definitely belong to the lower component, in agreement with the values for the cluster indices of the nontransferring clusters, as indicated in Fig. 4. For $J = 53$ the transferring cluster is clearly seen as the lowest one in the middle component, but for $J = 54$ it has already disappeared as a consequence of a beginning complex inversion (*2*) in this component.

Again, knowing that a 6-fold cluster must transfer from the upper to the middle component as J increases, it is possible to localize it, as indicated by squares in Fig. 4. Maybe the most convincing proof of this assignment is the fact that the k-distributions for all these clusters is ideal (*1*) for all the J values included in the figure, the k-distribution value for $J - k = 0$ being as high as 0.999 in all cases. The k-distributions of the neighboring 6-fold clusters show unambiguously that $J_{\times 6}$ in this case has a value slightly below 54.

The transferring 12-fold clusters are the most difficult ones to find, because they exist only for $J = 51$, 52, and 53, as shown by crosses in Fig. 4. Out of these three clusters, the first and the last are fairly broad, and there is no sign of neighboring 12-fold clusters. The series of 12-fold clusters seen in the middle component for $J \geqslant 53$ has nothing to do with this transfer. The value of $J_{\times 12}$ cannot be fixed with certainty, but the energy level diagram seems to indicate that the transferring cluster belongs to the middle component for $J = 51$ and to the upper component for $J = 52$, so that $J_{\times 12}$ probably is between 51 and 52. This leads to the order of the three transfers given in Fig. 5. It is interesting to note that the transfer for lowest J is between the two components of $3\nu_2(E)$, which means that the ν_3 component does not cross each of the two $3\nu_2(E)$ components separately, but all three components are interacting in a rather complicated way.

The present example offers a unique opportunity to test the validity of Eq. (1) for the energies of the double series of clusters formed for $J = J_{\times}$. The two series of 6-fold clusters in the lower and the middle component at $J = 52$ are unusually long

and $J_{\times 6}$ is close to the integer value of 52. In Fig. 6 the energies of this double series of 6-fold clusters, including the central cluster, are plotted against the integer number t from Eq. (1) on a symmetrical square root scale. Ideally this plot should show a straight line. In general, the comparison indicates a most satisfactory agreement, although two kinds of systematic deviations are seen. The first is an upward bend at $t = 0$. There may be several reasons for this, and presently we cannot indicate which is the most important. The second systematic deviation is a tendency for both series to bend off toward more constant energies for high values of t. This is to be expected, because the energy cannot increase and decrease infinitely, as required by Eq. (1). At some distance to the point of contact the two surfaces must flatten out to fit a more or less perfect sphere, which causes the clusters to appear with a smaller and smaller distance as t increases. The analogous effect is observed in long series of clusters in isolated components, as seen in the series of 6-fold clusters in Fig. 2 of Ref. (*1*).

REARRANGEMENT OF THE $2\nu_4$ STATE

As the third example of the effect of the transfer of clusters we shall discuss the change in the symmetries of the vibrational components of the $2\nu_4$ vibrational state for $^{13}CF_4$ from the isolated E and F_2 substates to the combined $E + F_2$ substate.

The $2\nu_4$ vibrational state has the symmetry $A_1 + E + F_2$. The corresponding anharmonic splitting into three substates at $J = 0$ is shown in Fig. 7.

At low J values the F_2 substate splits as usual into three components of symmetry $D_u^{(J+1)}$, $D_u^{(J)}$, and $D_u^{(J-1)}$ with decreasing energy, precisely as observed for the ν_3 vi-

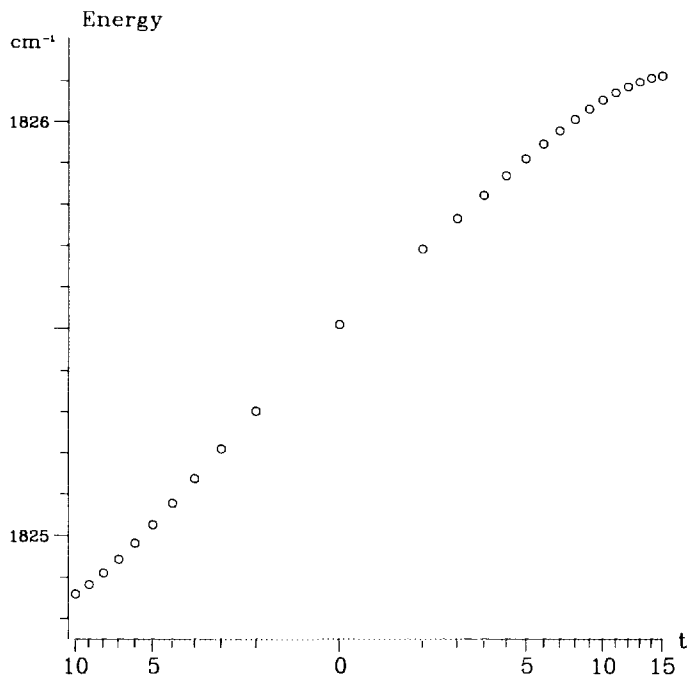

FIG. 6. The energies of the double series of 6-fold clusters from the lower and middle components of Fig. 4 for $J = 52$, plotted against the integer number t on a symmetrical square root scale. As required by Eq. (1), the points form an almost straight line.

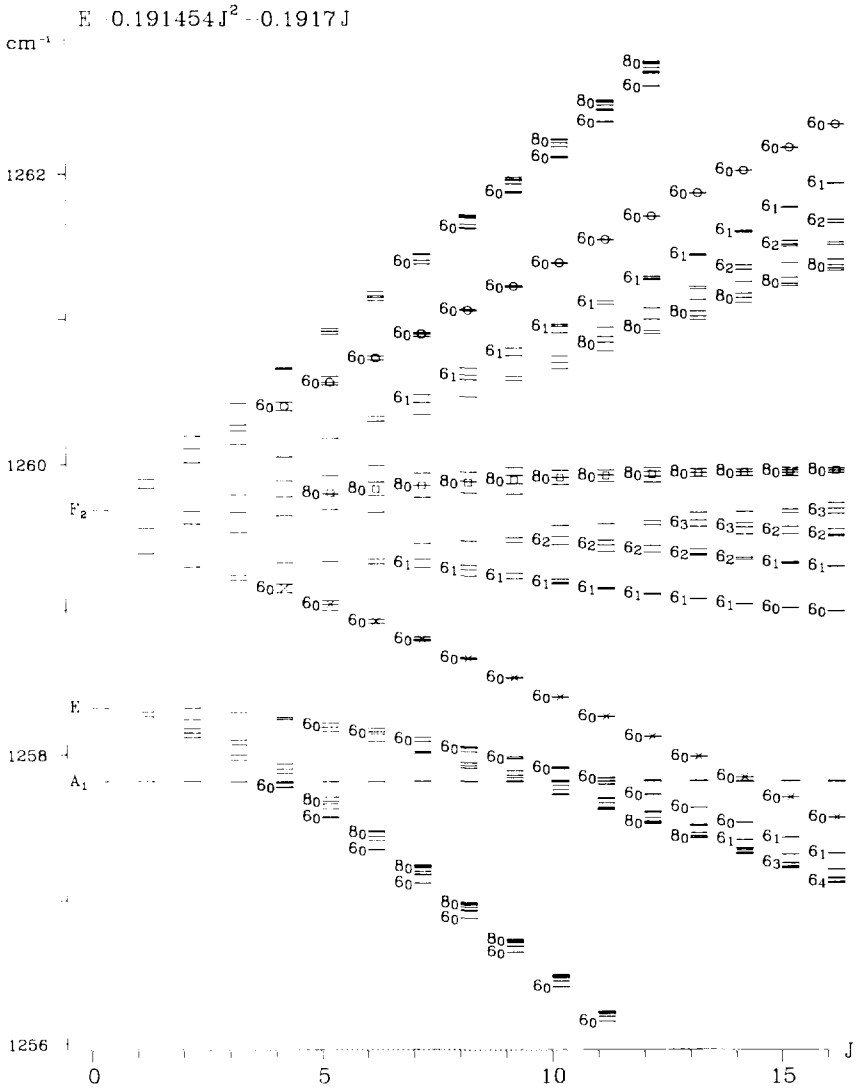

FIG. 7. A reduced energy level diagram illustrating the rearrangement of the five vibrational components of the F_2 and E substates of the $2\nu_4$ vibrational state of $^{13}CF_4$. The three series of transferring clusters are indicated by a circle, a square, and a cross, respectively.

brational state. This splitting is best seen in Fig. 7 for $J = 2$, 3, and 4. All of these three components change their symmetries as J increases.

At low J values the E substate splits into two vibrational components, the upper one having $D_u^{(J-2)}$ symmetry and the lower one having $D_g^{(J+2)}$ symmetry. This splitting is easily seen in Fig. 7. It is interesting to note that this is not the usual splitting for most E states or substates of CF_4 (*11*) but an alternative possibility (*4*) which seems as probable as the more usual one. The symmetry of the upper component changes as J increases, whereas the lower component keeps the $D_g^{(J+2)}$ symmetry up to very high J values.

The $D_g^{(J)}$ vibrational component corresponding to the A_1 substate is extremely nar-

row for all the values of J. It is seen in Fig. 7 as a series of levels running precisely horizontal as a function of J (because the energy reduction parameters were chosen to obtain this). This component and its interaction with the other components will not be discussed in the present paper.

For higher J values, for instance for $J = 16$, the five components from the E and F_2 substates have changed their symmetries into $D_g^{(J-2)}$, $D_g^{(J-1)}$, $D_g^{(J)}$, $D_g^{(J+1)}$, and $D_g^{(J+2)}$, respectively, for decreasing energy, clearly acting as one vibrational substate of symmetry $E + F_2$. This is in agreement with the well-known treatment of the interacting ν_2 and ν_4 vibrational states of spherical top molecules as one vibrational state with the vibrational angular momentum $l = 2$ (*12–15*).

The changes of the symmetries are caused by three transfers of clusters, as sketched in Fig. 8. The first of these is a transfer of a 6_0 cluster, marked by circles in Fig. 7, from the upper component of symmetry $D_u^{(J+1)}$ to the next component of symmetry $D_u^{(J)}$, causing the upper component to obtain the final symmetry of $D_g^{(J-2)}$. The symmetry of the other component is changed once more by a transfer of an 8_0 cluster, marked by squares in Fig. 7, to the following component, causing the second component to obtain its final symmetry of $D_g^{(J-1)}$. However, the third component also changes its symmetry once more by a transfer of a 6_0 cluster, marked in Fig. 7 by a cross, in order to obtain its final symmetry of $D_g^{(J)}$. Finally, the upper component of the E substate changes its symmetry from $D_u^{(J-2)}$ to $D_g^{(J+1)}$ because of the transfer of the 6-fold cluster.

Because of the low J value it is difficult to fix the value of $J_\times$ for the first two of these transfers. The most probable value seems to be between 6 and 7 in both cases. For the transfer of the 6_0 cluster marked by crosses a study of the k-distributions of the neighboring clusters clearly indicates a $J_\times$ value a little above 14.

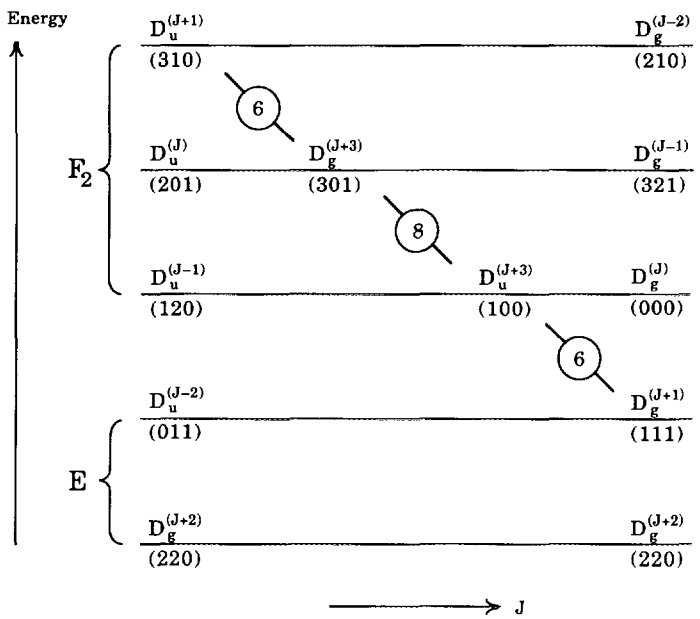

FIG. 8. A diagram, analogous to Figs. 1 and 5, showing how the symmetries of four of the five vibrational components of the F_2 and E substates of the $2\nu_4$ vibrational state of $^{13}CF_4$ are changed by three consequtive transfers of one cluster. The corresponding energy level diagram is shown in Fig. 7.

It is interesting to note that this change of the symmetries of four components is carried out by only three transfers of cluster, which is the minimum needed for such a complicated change. Also, the unusual splitting of the E substate into two components of symmetries $D_u^{(J-2)}$ and $D_g^{(J+2)}$ contributes to keep the number of transfers low.

APPENDIX

In this Appendix we consider two vibrational components which may interact with each other, whereas the interactions with all other components are neglected. The two components may belong to the same or to different vibrational states.

The corresponding effective quantum Hamiltonian operator may be represented by a 2×2 matrix where each element is a rotational operator. By replacing the angular momentum operators by their classical analogs, this operator is converted into a 2×2 Hermitian matrix, the eigenvalues of which are the classical rotational energies described by the rotational energy surfaces of the two manifolds for a given J (*2, 3, 8, 15–18*). The elements R_{ij} of this matrix depend on J and the two angles indicating the direction of the angular momentum in a molecule-fixed coordinate system. The two eigenvalues are

$$E_{1,2}(J, \theta, \phi) = \frac{1}{2}(R_{11} + R_{22}) \pm \sqrt{(R_{11} - R_{22})^2 + |R_{12}|^2}. \tag{A1}$$

The two surfaces can only have common points if the square root vanishes, requiring that

$$R_{11} = R_{22} \tag{A2}$$

and

$$|R_{12}|^2 = 0, \tag{A3}$$

where (A3) splits into two equations, one for the real part and one for the imaginary part, showing that three real equations must be satisfied simultaneously in order that the two surfaces may have points in common (*9*). Whether this is the case depends on the symmetries of the vibrational components, for convenience expressed by the local symmetry indices (n_4, n_3, n_2).

We shall for the moment concentrate on the conditions that common points are formed at the C_3 points. These depend exclusively on the local symmetry index n_3, numbering the irreducible representations A $(n_3 = 0)$, E_a $(n_3 = 1)$, and E_b $(n_3 = 2)$ of the subgroup C_3 of O_3. As C_3 is also a subgroup of the invariance group of the quantum operator, it may be shown that all four elements R_{ij} have A symmetry if the two vibrational components have identical values of n_3 $(n_3 = n_3')$, whereas if they have different values of $n_3 (n_3 \neq n_3')$ the diagonal elements have A symmetry and the off-diagonal elements have E_a or E_b symmetry. If the angles θ and ϕ are defined with respect to the C_3 axis, with θ indicating the angle between the angular momentum and C_3, any element R_{ij} may be expanded, if it has A symmetry, as

$$R_{ij}^A = f_0(J) + f_2(J) \sin^2\theta + \cdots, \tag{A4}$$

where the leading term is independent of θ, and, if it has E_a or E_b symmetry, as

$$R_{12}^E = g_{12}(J, \phi) \sin\theta + \cdots \tag{A5a}$$

and

$$R_{21}^E = g_{21}(J, \phi) \sin\theta + \cdots \tag{A5b}$$

with no term independent of θ and $g_{12}(J, \phi) = g_{21}(J, \phi)^*$ (where * means complex conjugation).

As we consider only the C_3 points on the rotational surfaces, we have to insert $\theta = 0$. If $n_3 = n'_3$, all four elements are of the form (A4) with a J-dependent value for $\theta = 0$. Obviously it is impossible in general to satisfy all three equations between the four elements given by (A2) and (A3) by varying J. Consequently, the two surfaces cannot touch at the C_3 points if $n_3 = n'_3$. If, on the other hand, $n_3 \neq n'_3$, the off-diagonal elements vanish and the two equations given by (A3) are automatically satisfied, leaving only one equation which in practice may be satisfied only for one value of $J = J_\times$. This means that for $n_3 \neq n'_3$ the two surfaces may touch at the C_3 points for the one value of $J = J_\times$.

It is further possible to find the form of the two surfaces close to the points of contact for $J = J_\times$ by inserting (A4) and (A5) into (A1). The result is

$$E_{1,2}(J = J_\times, \theta, \phi) = E_\times \pm g(J_\times) \sin \theta + \cdots, \tag{A6}$$

where $g(J_\times) = \sqrt{g_{12}(J_\times, \phi)\, g_{21}(J_\times, \phi)}$ is independent of ϕ due to a compensation of the two conjugated phases. For small values of θ this is a double cone with C_3 as the axis.

The corresponding approximate quantization condition may be derived in analogy with the derivation given in the Appendix of Ref. (*2*). A quantum rotational Hamiltonian, having in the classical limit (A6) as the form of the energy, may be expressed as a 2×2 matrix with $E_\times$ in the diagonal and $J_x \pm iJ_y$ as the off-diagonal terms. This Hamiltonian has $2(2J + 1)$ analytical solutions for each value of J, but we are only interested in the solutions corresponding to a small precession of the angular momentum around the C_3 axis. These are

$$E = E_\times \pm \text{const.}\, g(J_\times) \sqrt{t}, \tag{A7}$$

where $t = 0, 1, 2, 3, \ldots$. This means that a double series of 8-fold clusters may be formed having these energies, with the consequences outlined in the text.

Next we concentrate on the conditions that common points are formed at the C_2 points. These depend exclusively on the local symmetry index n_2, numbering the irreducible representations A ($n_2 = 0$) and B ($n_2 = 1$) of the subgroup C_2 of O_3. The same procedure as for the C_3 points leads to the analogous results: the two surfaces cannot touch if $n_2 = n'_2$, whereas a double cone is formed at each of the C_2 points if $n_2 \neq n'_2$, leading to a double series of 12-fold clusters with energies given by (A7).

Finally, we discuss the conditions that common points are formed at the C_4 points. These depend exclusively on the local symmetry index n_4, numbering the irreducible representations A ($n_4 = 0$), E_a($n_4 = 1$), B($n_4 = 2$), and E_b($n_4 = 3$) of the subgroup C_4 of O_3. Here it is necessary to distinguish three cases: (i) $n_4 = n'_4$, (ii) $n_4 = n'_4 \pm 1$ modulo 4, and (iii) $n_4 = n'_4 \pm 2$. In the first two cases the same procedure as for the C_3 and C_2 points leads to the analogous results: the two surfaces cannot touch if $n_4 = n'_4$, whereas a double cone is formed at each of the C_4 points if $n_4 = n'_4 \pm 1$ modulo 4, leading to a double series of 6-fold clusters with energies given by (A7). In the third case the diagonal elements R_{ij} have A symmetry and the form indicated by (A4). The off-diagonal elements have B symmetry and their forms are

$$R^B_{12} = h_{12}(J, \phi) \sin^2\theta + \cdots \tag{A8a}$$

and

$$R_{21}^{B} = h_{21}(J, \phi) \sin^2\theta + \cdots \tag{A8b}$$

with no term independent of θ, and $h_{12}(J, \phi) = h_{21}(J, \phi)^*$.

This means that the two surfaces may have the C_4 points in common, but the form of the surface is in this case given by

$$E_{1,2}(J = J_\times, \theta, \phi) = E_\times \pm h(J_\times) \sin^2\theta + \cdots, \tag{A9}$$

where $h(J_\times) = \sqrt{h_{12}(J, \phi)\, h_{21}(J, \phi)}$ is independent of ϕ due to a compensation of the two conjugated phases. For small values of θ, (A9) indicates two paraboloids with a common top point. The corresponding quantum Hamiltonian has many quasi-degenerate solutions near $E_\times$, and this probably leads to a transfer of two 6-fold clusters, but several mathematical details of this case are not known at present.

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