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Simple Model for Asymptotic Level Clusters in SF_6 Rotational Spectra*

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We construct a simple model to explain the qualitative features of level clusters in the asymptotic regions or limbs of centrifugally split J levels in SF_6, as observed in diode spectroscopy and computer experiments. Parametric formulas for cluster splittings are derived by use of methods which may be useful for analysis of other molecular and solid-state resonance effects.

The spectrum of SF_6 has received considerable attention recently in connection with problems involving laser isotope separation and self-induced transparency. The first clearly identifiable rotational lines were recently observed[1] with use of a diode laser and analyzed through computer reductions of certain approximate molecular Hamiltonians.[2,3] In the process Fox *et al.*[4] noticed a curious cycle pattern for clusters of levels belonging to octahedral-group (O) irreducible representations (IR's) that appeared in the splitting of each J manifold. A cycle of four sixfold, nearly degenerate clusters (A_1, E, T_1), (T_1, T_2), (A_2, E, T_2), and (T_1, T_2) may be repeated several times in the upper limb until it abruptly splits and forms a similar cycle of eightfold clusters (E, T_1, T_2), (A_1, A_2, T_1, T_2), and (E, T_1, T_2). A similar clustering was noticed earlier by Dorney and Watson[5] in their XY_4 model calculations. They explained the degeneracies of 6 and 8 from a classical point of view in which the rotation axis is localized on a fourfold or threefold symmetry axis, respectively.

We describe here a quantum model which, in its simplest form, indicates the exact composition of the clusters, and parametrizes the form of the splitting within them. The model has recently been extended to give accurate approximate formulas for the spectrum of cubic 2^k-pole operators ($k = 4$ and 6) as we will report in longer follow-up publications.

We introduce state vectors $|1\rangle_3$, $|2\rangle_3$, ..., $|8\rangle_3$ to describe the eight equivalent states of rotation about each of the eight threefold symmetry axes perpendicular to faces of the SF_6 octahedron. For high rotational momentum J, we may imagine that these states are nearly degenerate; i.e., we picture a molecule "stuck" in rotation on any one of the threefold axes, and hardly able to "tunnel" over to other equivalent choices since it has become centrifugally flattened. Since the radial bonds of SF_6 are much stronger than the bending ones, we expect the eight threefold axes to be "soft" and to correspond to lower centrifugal energy. On the other hand, the six fourfold axes will be "hard" axes, and we introduce six "hard" state vectors $|1\rangle_4$, $|2\rangle_4$, ..., $|6\rangle_4$ to describe rotation around the fourfold axes at the vertices

TABLE I. O to C_3 correlation.

	(0_3)	(1_3)	(2_3)
A_1	1	·	·
A_2	1	·	·
E	·	1	1
T_1	1	1	1
T_2	1	1	1

TABLE II. O to C_4 correlation.

	(0_4)	(1_4)	(2_4)	(3_4)
A_1	1	·	·	·
A_2	·	·	1	·
E	1	·	1	·
T_1	1	1	·	1
T_2	·	1	1	1

of SF_6.

For our model, fairly little needs to be said about the nature of a state $|i\rangle_3$ (with $i=1-8$) or $|j\rangle_4$ (with $j=1-6$) beyond its local symmetry properties with respect to its own threefold or fourfold axis, i.e., which IR of subgroup C_3 labels $|i\rangle_3$, and which IR of C_4 labels $|j\rangle_4$. Relating our notation (m_n) for the C_3 IR's to those of Herzberg, we have $A=(0_3)$, $E_{x+iy}=(1_3)$, and $E_{x-iy}=(2_3)$; and for the C_4 IR's, we have $A=(0_4)$, $E_{x+iy}=(1_4)$, $B=(2_4)$, and $E_{x-iy}=(3_4)$. Now a J-manifold state $|k\rangle_n$ belonging to IR (m_n) of C_n must be composed only of angular momentum states $|JM\rangle$ for which the k-axis component M (M is K in molecular notation) is given by

$$M \equiv m \pmod{n}. \tag{1}$$

We obtain the observed patterns by assuming that the principal components $|JM\rangle$ of asymptotic limb states $|k\rangle_n$ will have the largest M satisfying Eq. (1).

Each row of Table I gives the well-known reduction or "splitting" of an O IR into the C_3 IR's. Similarly, Table II shows the corresponding reduction of an O IR into the C_4 IR's. Now the *columns* of these two tables are seen to indicate exactly the seven observed types of clusters in just the order in which they make their cycle appearance! The reason for this is that, according to the Frobenius reciprocity theorem, each (m_n) column must give the IR (D^A) contents of representation $(D^{(m_n)}\uparrow O)$ of O *induced* from $D^{(m_n)}$ of C_n if the rows give the contents of representation $(D^A\downarrow C_n)$ of C_n *subduced* or "split" from (A). Indeed, induced representations are the key to a number of widely used but mostly unexplained molecular and solid-state methods such as the "correlation method."[6] We exhibit now some induced-representation bases by treating, as an example, the upper clusters in the $J=30$ manifold.

Upper clusters belong to the "hard" C_4 axes; and since $30\equiv 2 \pmod 4$, the upper limit of the $J=30$ pattern should consist of a (2_4) cluster (for $M=30$), followed by a (1_4) cluster (for $M=29$), followed by a (0_4) cluster (for $M=28$), followed by a (3_4) cluster, followed again by a (2_4), and so on (see Fig. 1 in Ref. 2), until the sixfold clusters "melt" or merge into eightfold ones coming up from the lower limb. [Actually, either type of cycle can be traced from limb to limb, and each complete cycle $(3_42_41_40_4)$ or $(2_31_30_3)$ contains a regular representation: $R=A_1\oplus A_2\oplus 2E\oplus 3T_1\oplus 3T_2$ of O.] Cubic symmetry projection is used to compute the combination of some primitive

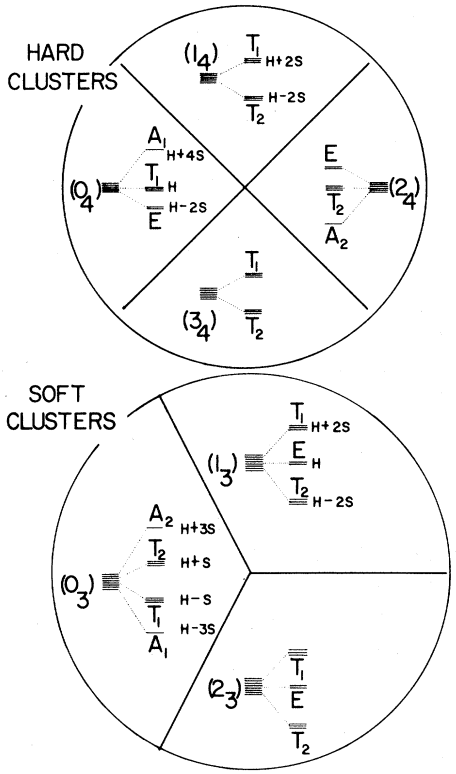

FIG. 1. Octahedral level clusters and cycles. The "soft clusters" of O IR are predicted by using the O to C_3 correlation table [Table I] and appear in the lower energy limb of the SF_6 rotational levels. The "hard clusters" [see the columns of Table II] appear in the upper limb. The form of the splitting of each cluster is predicted by the "nearest-neighbor" tunneling model [Eq. (5)], and has been observed repeatedly in computer reductions of SF_6 centrifugal Hamiltonians (Ref. 4).

TABLE III. Induced or cluster eigenvectors for fourfold cubic axes. Cubic symmetry defined eigenvectors $|m_4;{}^{A}_{a}\rangle$ are given in the primitive basis $|m_4;R\rangle = |j\rangle_4$ of the cubic representation induced by the IR (m_4) of C_4 for $m = 0, 1,$ and 2.

	$\|1\rangle_4 = \|m_4;1\rangle$	$\|2\rangle_4 = \|m_4;R_2{}^2\rangle$	$\|3\rangle_4 = \|m_4;R_1\rangle$	$\|4\rangle_4 = \|m_4;R_2\rangle$	$\|5\rangle_4 = \|m_4;R_1{}^3\rangle$	$\|6\rangle_4 = \|m_4;R_2{}^3\rangle$
$6^{1/2}\|0_4;{}^{A_1}_{\cdot}\rangle$	1	1	1	1	1	1
$2^{1/2}\|0_4;{}^{T_1}_{3}\rangle$	1	−1	0	0	0	0
$3^{1/2}\|0_4;{}^{E}_{1}\rangle$	1	1	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
$2\|1_4;{}^{T_1}_{1}\rangle$	1	−1	1	0	1	0
$2\|1_4;{}^{T_2}_{1}\rangle$	1	−1	−1	0	−1	0
$3^{1/2}\|2_4;{}^{E}_{2}\rangle$	1	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
$2^{1/2}\|2_4;{}^{T_2}_{3}\rangle$	1	−1	0	0	0	0
$6^{1/2}\|2_4;{}^{A_2}_{\cdot}\rangle$	1	1	−1	−1	−1	−1

cluster states $|j\rangle_n$ which are octahedral IR bases. Results for fourfold $(n = 4)$ axis clusters are given in Table III.

Table III shows only one component for each IR, and only one rotation operator $1, R_2{}^2, R_1, \ldots, R_2{}^3$ is used from each left coset $R_2{}^2C_4, R_1C_4, \ldots$ of $C_4 = \{1, R_3, R_3{}^2, R_3{}^3\}$ to label the six states $|1\rangle_4$, $|2\rangle_4, \ldots,$ and $|6\rangle_4$. The rotation operators are described in the caption of Fig. 2 which shows a Hamilton[7,8] vector-addition diagram[9] or "slide rule" for combining operations of the O double group, or, if you ignore the minus signs, the group O itself. By use of the latter, it is convenient to find any cosets such as the following ones of C_4:

$$R_2{}^2\{1, R_3, R_3{}^2, R_3{}^3\} = \{R_2{}^2, i_3, R_1{}^2, i_4\},$$
$$R_1\{1, R_3, R_3{}^2, R_3{}^3\} = \{R_1, r_4{}^2, i_5, r_2{}^2\}, \ldots . \quad (2)$$

In this way we associate each O operator with one of the $|k\rangle_n$ states in any cluster problem. For example, i_3 is associated with the second $(R_2{}^2)$ state as shown by the following:

$$|m_4; i_3\rangle = i_3|m_4;1\rangle = R_2{}^2R_3|m_4;1\rangle = R_2{}^2(e^{2\pi i/4})^m|m_4;1\rangle = e^{2\pi mi/4}|m_4;R_2{}^2\rangle . \quad (3)$$

Phases obtained in this way are needed to calculate nonscalar eigenvectors [cf. (1_4) and (2_4) in Table III] and the energy eigenvalues. To compute the energy eigenvalues we assume, following Feynman's procedure,[10] a tunneling-amplitude Hamiltonian matrix $H_{ij}{}^{(m_n)} = \langle m_n; i|H|m_n; j\rangle$. For the six "hard" axes we take the first row to be

$$H_{11}{}^{(m_4)} = H_m, \quad H_{12}{}^{(m_4)} = 0, \quad H_{13}{}^{(m_4)} = S_m, \quad H_{14}{}^{(m_4)} = S_m, \quad H_{15}{}^{(m_4)} = S_m, \quad H_{16}{}^{(m_4)} = S_m, \quad (4)$$

where S_m is the tunneling amplitude between adjacent octahedron axes and H_m is the cluster energy. We may assume a nonzero diagonal tunneling or reversal parameter $H_{12}{}^{(m_4)} = R_m$, too, but this "second-order" tunneling is not needed to explain the results of Ref. 4.

The states have been labeled in the top of Table III so that Eq. (4) is the correct first row for each cluster type (m_4). Also, the entries in Table III are chosen so that the first number is unity. Then "scalar products" of Eq. (4) with each row of Table III gives the desired eigenvalues for splitting of "hard" clusters:

$$\begin{aligned} &e^{A_1}(0_4) = H_0 + 4S_0, \quad e^{T_1}(0_4) = H_0, \quad e^{E}(0_4) = H_0 - 2S_0; \\ &e^{T_1}(1_4) = H_1 + 2S_1, \quad e^{T_2}(1_4) = H_1 - 2S_1; \\ &e^{E}(2_4) = H_2 + 2S_2, \quad e^{T_2}(2_4) = H_2, \quad e^{A_2}(2_4) = H_2 - 2S_2 . \end{aligned} \quad (5)$$

These results are recorded schematically in Fig. 1 along with similar ones for the "soft" clusters. The ordering and form of the splittings given by this simple tunneling model are very close to those found by Krohn in hundreds of computed eigenvalues. This sort of tunneling model is turning out to be a very powerful way to analyze a number of spectroscopic and quantum resonance effects.[11]

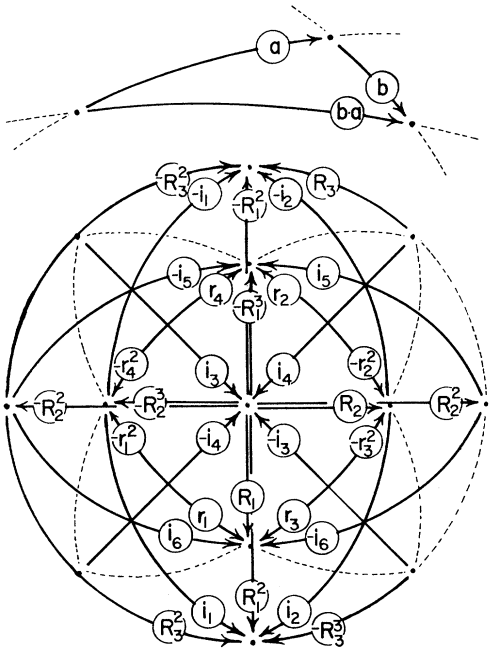

FIG. 2. Octahedral rotations on O-group slide rule. R_1, R_2, and R_3 are 90° counter-clockwise rotations around the (100), (010), and (001) axes, respectively. r_1, r_2, r_3, and r_4 are 120° rotations around the (111), $(\bar{1}\bar{1}1)$, $(1\bar{1}\bar{1})$, and $(\bar{1}1\bar{1})$ directions, respectively. i_1, i_2, i_3, i_4, i_5, and i_6 are 180° rotations around the (101), $(10\bar{1})$, (110), $(1\bar{1}0)$, $(0\bar{1}1)$, and (011) directions, respectively. To compute the product of two rotations, find their intersection on the diagram, and visually slide their vectors into a head-to-tail addition position as shown in the key. Their product corresponds to the resultant vector sum. Ignore the signs written in the diagram when working with boson or integral-spin systems, but keep track of the products of the signs when operating upon systems which have half-integral spin.

In the quantitative model to be reported later we find very accurate approximate formulas for the H parameters, and somewhat less accurate formulas for the S parameters. In addition we are able to extend the methods immediately to analyze half-integral J splitting.

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