

## Original Investigations

# The Jahn-Teller Effect in Icosahedral Molecules and Complexes

V. P. Khlopin, V. Z. Polinger, I. B. Bersuker

Department of Quantum Chemistry, Academy of Sciences, Moldavian SSR, 277028, Kishinev, USSR

The adiabatic potential surface for icosahedral systems having three-, four- and five-fold degenerate orbital states interacting with five-fold degenerate vibrations ( $T-v$ ,  $U-v$  and  $V-v$  problems) is investigated. It is shown that for the  $T-v$  and  $V-v$  Jahn-Teller cases the potential surface possesses respectively a two- or three-dimensional equipotential continuum of minima. For the  $U-v$  problem the potential surface contains 15 equivalent minima. The nature of the extremum points on the adiabatic potential surfaces is elucidated. In the linear approximation to the  $V-v$  problem in the minima points the lowest potential surface is double degenerate due to the accidental occurrence of axial symmetry.

**Key words:** Icosahedral molecules and complexes, Jahn-Teller effect in  $\sim$

### 1. Introduction

Almost all previous studies on the Jahn-Teller effect have been devoted to systems with a not higher than cubic symmetry [1–5]. Molecules with higher symmetry, *e.g.* icosahedral molecules, are much more complicated to treat, due to the high orbital and vibrational degeneracies of three, four and five. However, the number of polyatomic systems of icosahedral symmetry is increasing [6–9]. In each of these molecules the ground or first excited electronic states are degenerate and the analysis of their properties is impossible without investigation of the vibronic Jahn-Teller effects.

In this communication we present some results of the linear Jahn-Teller effect operating in polyatomic icosahedral systems possessing orbital three-, four- or five-fold degenerate electronic terms interacting with five-fold vibrations. We are thus treating the linear  $T-v$ ,  $U-v$  and  $V-v$  problem respectively. The first stage of the investigation consists in the examination of the topology of the adiabatic

potential. This makes it possible to resolve the energy spectrum problem and to estimate the manifestations of the effect in the observable properties. After the overall theoretical analysis of the Hamiltonian (Sect. 2) the interaction of the electronic states with five-fold degenerate vibrations is considered (Sects. 3–5). Finally we present an analysis of some possible experimental manifestations of the effect.

## 2. The Hamiltonian

The simplest species of icosahedral molecules are the proper icosahedron and the pentagonal dodecahedron. The reducible vibrational representation for these molecules may be expressed as a sum of irreducible representations. Making use of

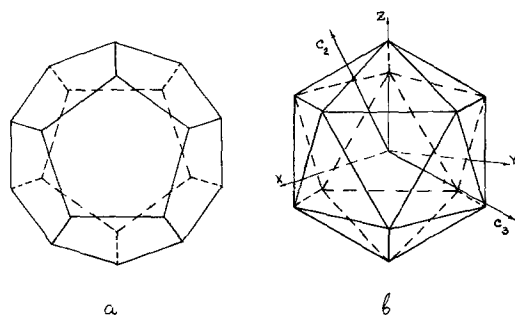


Fig. 1. The simplest polyhedra having icosahedral symmetry. **a** Pentagonal dodecahedron, **b** Icosahedron. The  $C_5$  axis coincides with the  $z$  axis.

McLellan's designations for the icosahedral irreducible representations [10] where  $U$  denotes a four-fold degenerate representation and  $V$  is a five-fold degenerate representation we find: for the pentagonal dodecahedron  $A_g + T_{1u} + T_{2g} + 2T_{2u} + 2U_g + 2U_u + 3V_g + 2V_u$  and for the icosahedron  $A_g + T_{1u} + T_{2u} + U_g + U_u + 2V_g + V_u$ . The symmetric products of the icosahedral irreducible representations are [11]:  $[T_{1,2}^2] = A + V$ ;  $[U^2] = A + U + V$ ;  $[V^2] = A + U + 2V$ . The following Jahn-Teller cases are therefore possible: an electronic triplet coupled to the five-fold vibrations ( $T \otimes (v_1 + v_2)$ ); the electronic quadruplet coupled to the four-fold and five-fold vibrations ( $U \otimes (u + v_1 + v_2)$ ), and the electronic quintet coupled with the five-fold and four-fold degenerate vibrations ( $V \otimes (u + v_1 + v_2)$ ).

The Hamiltonian of the molecule may be written as follows:

$$H = H_e(r) + \sum_{\Gamma\gamma} V_{\Gamma\gamma}(r) Q_{\Gamma\gamma} + H_n(Q). \quad (1)$$

Here  $H_e(r)$  is the electronic Hamiltonian in the high symmetry nuclear configuration. The second term in (1) is the vibronic interaction, being linear in the normal displacements  $Q_{\Gamma\gamma}$  of the nuclei.  $\Gamma$  and  $\gamma$  are indexes of the irreducible representations and their rows, contained in the reducible vibrational representation of the molecule. The  $H_n(Q)$  is the usual Hamiltonian of the harmonic vibrations of the nuclei:

$$H_n(Q) = \sum_{\Gamma\gamma} \left[ \left( -\frac{\hbar^2}{2m_\Gamma} \frac{\partial^2}{\partial Q_{\Gamma\gamma}^2} + K_\Gamma Q_{\Gamma\gamma}^2 / 2 \right) \right],$$

where  $m_{\Gamma}$  is the reduced mass and  $K_{\Gamma}$  is the force constant for the  $Q_{\Gamma\gamma}$  vibrations. Proceeding to the matrix representation of the electronic operators in the Hilbert space of the electronic wave functions within the degenerate electronic term manifold, and using the Wigner-Eckart theorem, one may rewrite the Hamiltonian (1) as follows:

$$H = \sum_{\Gamma\gamma} V_{\Gamma} Q_{\Gamma\gamma} C_{\Gamma\gamma} + H_n(Q) C_A. \quad (2)$$

Here  $C_A$  is a unit matrix,  $C_{\Gamma\gamma}$  are Clebsch-Gordan coefficient matrices as defined in electronic space,  $V_{\Gamma}$  are the reduced matrix elements (vibronic constants) for the vibronic interaction with five-fold degenerate vibrations only. The other coupling terms are put equal to zero.

The usual way to solve the Jahn-Teller problem is to investigate the topology of the adiabatic potentials and then to consider the vibronic equations using the Hamiltonian (2). The situation under consideration is extremely complicated due to the interaction with at least two active quintet modes. However the qualitative properties of the adiabatic potential may still be elucidated since the number of extremal points and their symmetry is independent of the number of the interacting quintet modes. In order to prove this statement one has to make the scale transformation for each degree of freedom  $q_{\Gamma\gamma} = Q_{\Gamma\gamma} \sqrt{K_{\Gamma}}$ . In so doing the operator for the potential energy of the elastic distortions becomes isotropic:  $\sum_{\Gamma\gamma} q_{\Gamma\gamma}^2/2$ . Now performing the orthogonal transformation in the space of the new coordinates  $q_{\Gamma\gamma}$ :

$$\begin{aligned} X_{\gamma} &= [(V_1/\sqrt{K_1})q_{1\gamma} + (V_2/\sqrt{K_2})q_{2\gamma}]/V \\ Y_{\gamma} &= [(V_1/\sqrt{K_1})q_{1\gamma} - (V_2/\sqrt{K_2})q_{2\gamma}]/V \end{aligned} \quad (3)$$

where

$$V = \sqrt{V_1^2/K_1 + V_2^2/K_2} \quad (3a)$$

one observes that due to its isotropy the operator for the potential energy of the elastic deformations is unchanged but the vibronic interaction takes the following changed form:

$$V \sum_{\gamma} X_{\gamma} C_{V\gamma}. \quad (4)$$

As one can see from Eq. (4) only five degrees of freedom  $X_{\gamma}$  are active in the Jahn-Teller effect. Actually the kinetic energy operator is not isotropic and so the orthogonal transformation (3) also produces a coupling term, bilinear in the impulses  $-\hbar(\partial/\partial X_{\gamma})$  and  $-\hbar(\partial/\partial Y_{\gamma})$ , describing the dynamic interaction between the coordinates  $X_{\gamma}$  and  $Y_{\gamma}$ . This is due to the fact that the coordinates  $X_{\gamma}$  and  $Y_{\gamma}$  are not normal modes in contrast to  $Q_{\Gamma\gamma}$ . If, however, we consider only the static problem, *i.e.* the extremal properties of the adiabatic potential, then the interaction between the  $X_{\gamma}$  and  $Y_{\gamma}$  modes does not affect the qualitative results and the problem is similar to the case of the one-mode Jahn-Teller effect. Therefore we shall now confine ourselves to the case where only one vibronic coupling constant among the  $V_i$  is nonzero.

### 3. The Icosahedral Triplet

A triplet representation of the icosahedral group can be generated by the reduction of the general rotation group. In so doing the seven-dimensional representation  $D^3$  of the  $R(3)$  group splits into the irreducible representations  $T_2$  and  $U$ , and the real wave functions for the electronic  $T_2$  triplet possess the following transformation properties:

$$\begin{aligned} |T_2\alpha\rangle &\sim x^3 - 3xy^2 + 3x^2z - 3y^2z, \\ |T_2\beta\rangle &\sim 3x^2y - y^3 + 6xyz, \\ |T_2\gamma\rangle &\sim z(3r^2 - 5z^2). \end{aligned} \quad (5)$$

The quintet representation results from the  $D^2$  representation of the  $R(3)$  group by reduction to the icosahedral one:  $D^2 \equiv V$ . Therefore the transformation properties of the real normal quintet coordinates  $Q_{\Gamma\gamma}$  are well known:

$$\begin{aligned} Q_u &\sim (3z^2 - r^2)/\sqrt{3}, & Q_v &\sim 2xz, \\ Q_\xi &\sim 2xy, & Q_\eta &\sim y^2 - x^2, & Q_\zeta &\sim 2yz. \end{aligned} \quad (6)$$

It can be easily shown that the Clebsch-Gordan coefficient matrices  $C_{V\gamma}$  for this case [12] have the same form as for the Jahn-Teller cubic triplet linearly coupled both to  $e_g$  and  $t_{2g}$  modes:

$$\begin{aligned} C_u &= (1/\sqrt{3}) \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, & C_v &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\ C_\xi &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, & C_\eta &= \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, & C_\zeta &= \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \end{aligned} \quad (7)$$

As one can see from Eqs. (2) and (7) the Hamiltonian describing the Jahn-Teller effect in the icosahedral triplet is similar to the cubic one if the force constant  $K_E$

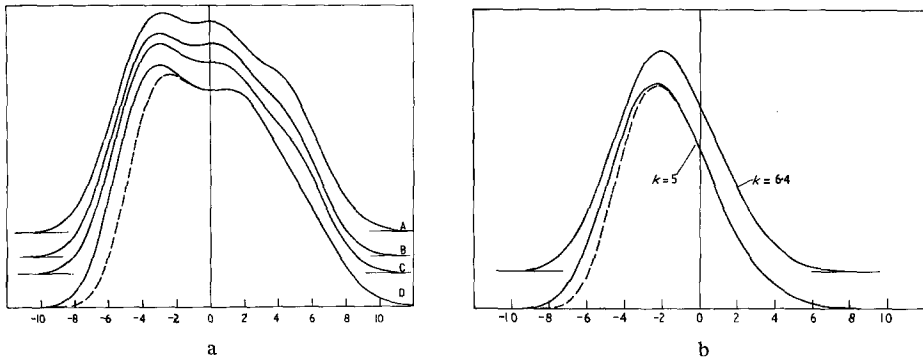
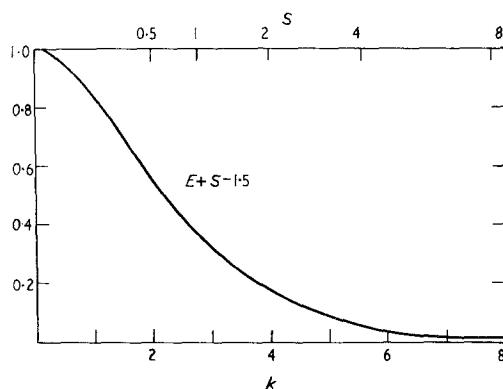
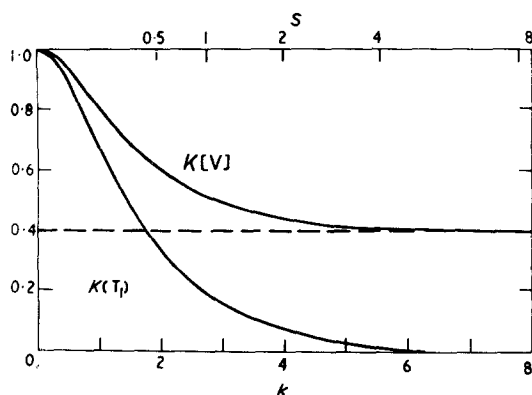


Fig. 2. The optical band shape of the singlet-triplet transitions. a  $A \rightarrow T$  absorption, b  $T \rightarrow A$  luminescence,  $K$  is the nondimensional vibronic coupling constant:  $K = V(\hbar\omega^3 m)^{-1/2}$

equals  $K_T$  and the vibronic coupling constant  $V_E$  equals  $V_T$ . As it has been shown by O'Brien [13, 14] a two-dimensional variety of extrema points on the five-dimensional adiabatic potential surface with the Jahn-Teller energy  $E_{JT} = -2V^2/3K$  occurs in this case. Unfortunately it is impossible to make use of the O'Brien's result directly on the dynamic properties of the icosahedral molecule because of the bilinearity in the impulse interaction between the  $X_\gamma$  and  $Y_\gamma$  mentioned above. If, however, this interaction is weak (which is possible in the case of  $K_1/m_1 \approx K_2/m_2$ ) then in first approximation one can make an extension of O'Brien's results for the cubic system to our icosahedral case. In so doing one cannot make use of the detailed energy structure obtained numerically by O'Brien, since the mentioned interaction changes the vibronic energy levels. However integral characteristics, such as the optical band shape of an  $A \rightarrow T$  absorption and a  $T \rightarrow A$  emission (see Fig. 2), as well as the ground state energy and vibronic reduction factor dependence on the vibronic constant (Figs. 3, 4) can, especially in the case of strong vibronic coupling, be relied upon.



**Fig. 3.** The ground state energy in the  $\hbar\omega$  units;  $K$  is the nondimensional vibronic coupling constant:  $K = V(\hbar\omega^3 m)^{-1/2}$ ;  $S$  is the Jahn-Teller stabilization energy in the  $\hbar\omega$  units:  $S = |E_{JT}|/\hbar\omega$ .



**Fig. 4.** Dependence of the vibronic reduction factor of the electronic operators transforming as  $T$  and  $V$  irreducible representations on the nondimensional vibronic coupling constant  $K = V(\hbar\omega^3 m)^{-1/2}$  and on the nondimensional Jahn-Teller stabilization energy  $S = |E_{JT}|/\hbar\omega$ .

#### 4. The Adiabatic Potential for the Icosahedral Quadruplet

The quadruplet representation  $U$  occurs from the  $R(3)$  group rotational representation  $D^3: D^3 = T_2 + U$ . Hence the basis wave functions for the  $U$  representation transform as follows:

$$\begin{aligned} |U1\rangle &\sim y^3 - 3x^2y - 4xyz, \\ |U2\rangle &\sim x^3 - 3xy^2 - 2x^2z + 2zy^2, \\ |U3\rangle &\sim y(r^2 - 5z^2), \\ |U4\rangle &\sim x(5z^2 - r^2). \end{aligned} \quad (8)$$

The transformation properties (6) and (8) result in following Clebsch-Gordan coefficient matrices [12]:

$$\begin{aligned} C_u &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}, & C_v &= \begin{pmatrix} -2 & 0 & -1 & 0 \\ 0 & 2 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \\ C_\xi &= \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 2 \\ -1 & 0 & 2 & 0 \end{pmatrix}, & C_\eta &= \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & -2 & 0 \\ 0 & -1 & 0 & 2 \end{pmatrix}, \\ C_\zeta &= \begin{pmatrix} 0 & -2 & 0 & 1 \\ -2 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \end{aligned} \quad (9)$$

determined in the Hilbert space of the electronic wave functions of the icosahedral quadruplet. The Öpic-Pryce procedure [15] has been applied to the investigation of the extremal properties of the  $U$ - $v$  problem adiabatic potential. The adiabatic wave functions have been taken in the following form:  $\Psi = \sum_i a_i |Ui\rangle$ . In the extremal points the adiabatic potentials of the problem  $\mathcal{E}(Q) = \langle \Psi | U | \Psi \rangle$ ,  $U$  being the potential energy matrix, should satisfy the equation  $\partial \mathcal{E} / \partial Q_j = 0$ . By means of these equations we have obtained the following expressions for the extremal coordinates:  $Q_j^0 = -V \langle \Psi | C_j | \Psi \rangle / K$ . Substituting these expressions in the eigenvalue equation  $U\Psi = \mathcal{E}\Psi$ , one receives a set of four equations for the coefficients  $a_i$  and the potential energy  $\mathcal{E}(Q^0)$ . Solving these equations consistent with the normalization condition  $\sum_i a_i^2 = 1$  one can find the  $a_i$  and  $\mathcal{E}(Q^0)$ .

This set of equations is nonlinear and therefore we must turn to symmetry considerations in order to solve it. The distortions of the molecule in the extremal points of the adiabatic potential are along the symmetry axes. The icosahedral symmetry of the molecule is reduced under such distortions to a subgroup. The operations  $R$  of

the subgroup includes the rotations in the electronic space such that the electronic wave function transform as a non-degenerate irreducible representation, i.e.  $R\Psi = \pm\Psi$ . Thus, for example the matrices  $R_2$ ,  $R_3$ ,  $R_5$  of the rotations about the axes  $C_2$ ,  $C_3$ ,  $C_5$  respectively (see Fig. 1) has in the electronic  $U$  term space the following form:

$$R_2 = \begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & -2/\sqrt{5} & 0 & -1/\sqrt{5} \\ -1 & 0 & 0 & 0 \\ 0 & -1/\sqrt{5} & 0 & 2/\sqrt{5} \end{bmatrix};$$

$$R_3 = \begin{bmatrix} 0 & 0 & (\sqrt{5}+1)/4 & -\sqrt{5-\sqrt{5}}/2\sqrt{2} \\ -\sqrt{5+\sqrt{5}}/\sqrt{10} & (\sqrt{5}-1)/2\sqrt{5} & -\sqrt{5-\sqrt{5}}/2\sqrt{10} & -(\sqrt{5}+1)/4\sqrt{5} \\ -(\sqrt{5}-1)/4 & -\sqrt{5+\sqrt{5}}/2\sqrt{2} & 0 & 0 \\ -\sqrt{5+\sqrt{5}}/2\sqrt{10} & (\sqrt{5}-1)/4\sqrt{5} & \sqrt{5-\sqrt{5}}/\sqrt{10} & (\sqrt{5}+1)/2\sqrt{5} \end{bmatrix};$$

$$R_5 = \begin{bmatrix} -(\sqrt{5}+1)/4 & -\sqrt{5-\sqrt{5}}/2\sqrt{2} & 0 & 0 \\ \sqrt{5-\sqrt{5}}/2\sqrt{2} & -(\sqrt{5}+1)/4 & 0 & 0 \\ 0 & 0 & (\sqrt{5}-1)/4 & \sqrt{5-\sqrt{5}}/2\sqrt{2} \\ 0 & 0 & -\sqrt{5-\sqrt{5}}/2\sqrt{2} & (\sqrt{5}-1)/4 \end{bmatrix}$$

Since the  $R_5$  matrices have only imaginary eigenvalues there are no extremal points on the adiabatic potential of the  $U$ - $v$  problem, hence no distortions of the molecule along the five-fold axes occurs. By rotating about the  $C_2$  axes one receives some additional equations for  $a_1$ :

$$R_2\Psi = \Psi; \quad a_3 = -a_1, \quad a_4 = -(\sqrt{5}+2)a_1 \quad (10)$$

$$R_2\Psi = -\Psi; \quad a_3 = a_1, \quad a_4 = (\sqrt{5}-2)a_1. \quad (11)$$

Substituting the Eqs. (10) and (11) in the Öpic-Pryce system of nonlinear equations we find the coefficients  $a_i$ , the coordinates  $Q_y^0$  of the extremal points and the energies  $\mathcal{E}(Q^0)$  of the adiabatic potential in the extremal points. The results are presented in Table 1. Similar considerations for the three-fold axes do not result in new types of extremal points.

The new normal frequencies and new normal coordinates in the extremal points one can also find by means of the Öpic-Pryce procedure. For a small displacement  $\Delta Q_y$  from the extremum,  $Q_y = Q_y^0 + \Delta Q_y$ , one obtains for the lowest adiabatic potential surface (in second order approximation of the perturbation theory in  $\Delta Q_y$ ):

$$\mathcal{E}(Q) = \mathcal{E}(Q^0) + K \sum_{\gamma} \Delta Q_{\gamma} / 2 - V^2 \sum_{\gamma\gamma'} W_{\gamma\gamma'} \Delta Q_{\gamma} \Delta Q_{\gamma'}, \quad (12)$$

$$W_{\gamma\gamma'} = \sum_{\kappa} [\langle \Psi | C_{\gamma} | \Psi_{\kappa} \rangle \langle \Psi | C_{\gamma'} | \Psi_{\kappa} \rangle] / [\varepsilon_{\kappa}(Q^0) - \varepsilon(Q^0)]. \quad (13)$$

The summation in (13) is performed over all adiabatic potentials but the lowest. The diagonalization of the quadratic sum (13) may be carried out by means of group theory. The nuclear configurations presented in Table 1 have the  $D_2$  symmetry for which the icosahedral quintet representation splits as follows:  $V = 2A + B_1 + B_2 + B_3$ . The two  $A$  representations can be separated by solving the quadratic equation. The symmetry combinations  $\Delta Q^{\Gamma} = \sum_{\gamma} C_{\gamma}^{\Gamma} \Delta Q_{\gamma}$  of the  $D_2$  group has been obtained by means of the projection operator technique. The coefficients  $C_{\gamma}^{\Gamma}$  and the new force constants  $K_{\Gamma}$  are given in the Table 1. As one can see, three types of 15-fold extrema corresponding to the  $C_2$  axes results for the adiabatic potential ( $U-v$ ). Types I and II are saddle points, whereas points of type III are minima with  $E_{J\Gamma} = -25V^2/6K$ .

### 5. The Adiabatic Potential of the Icosahedral Quintet

The Clebsch-Gordan coefficient matrices acting in the quintet electronic wave functions space and describing its interaction with the five-fold degenerate mode may be constructed by means of the transformation properties (6):

$$C_u = \begin{pmatrix} 2 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -2 & 0 & 0 \\ 0 & 0 & 0 & -2 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad C_v = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & -\sqrt{3} & 0 \\ 0 & 0 & 0 & 0 & \sqrt{3} \\ 0 & -\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 & 0 \end{pmatrix},$$

$$C_{\xi} = \begin{pmatrix} 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{3} \\ -2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{3} & 0 & 0 & 0 \end{pmatrix}, \quad C_{\eta} = \begin{pmatrix} 0 & 0 & 0 & -2 & 3 \\ 0 & -\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ -2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{3} \end{pmatrix},$$

$$C_{\zeta} = \begin{pmatrix} 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & \sqrt{3} & 0 & 0 \\ 0 & \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{3} \\ 1 & 0 & 0 & \sqrt{3} & 0 \end{pmatrix}. \quad (14)$$

In the absence of vibronic coupling the Hamiltonian (1) separates into the two  $H_e(r)$  and  $H_n(Q)$  terms. In the Hilbert space of the quintet electronic term the operator  $H_e(r)$  is represented by a  $5 \times 5$  matrix. The general symmetry group of this



$\gamma$	$u$	$v$	$\xi$	$\eta$	$\zeta$	$K_\gamma/K$	$Q_i$	$\mathcal{E}(Q^0)$
I	$Q_\gamma^0$	0	2	0	2	0		
	$C_\gamma^A$	$-\sqrt{3}/\sqrt{5}$	$1/\sqrt{5}$	0	$-1/\sqrt{5}$	0	$-1/4$	$1/\sqrt{2}$
	$C_\gamma^H$	0	$-1/\sqrt{2}$	0	$-1/\sqrt{2}$	0	1	0
	$C_\gamma^{B_1}$	$2/\sqrt{10}$	$\sqrt{3}/\sqrt{10}$	0	$-\sqrt{3}/\sqrt{10}$	0	1	$1/\sqrt{2}$
	$C_\gamma^{B_2}$	0	0	0	0	1	$5/6$	0
	$C_\gamma^{B_3}$	0	0	1	0	0	$5/6$	0
II	$Q_\gamma^0$	$-\sqrt{3}/\sqrt{5}$	$-(3-\sqrt{5})/\sqrt{5}$	$-\sqrt{5+\sqrt{5}}/\sqrt{10}$	$(3+\sqrt{5})/\sqrt{5}$	$\sqrt{5-\sqrt{5}}/\sqrt{10}$		
	$C_\gamma^A$	$1/\sqrt{10}$	$\sqrt{3}(\sqrt{5}+1)/2\sqrt{10}$	0	$(3+\sqrt{5})/2\sqrt{10}$	0	-5	$1/2$
	$C_\gamma^H$	$-\sqrt{3}/\sqrt{10}$	$1/\sqrt{10}$	$\sqrt{5-\sqrt{5}}/2\sqrt{5}$	$-1/\sqrt{10}$	$\sqrt{5+\sqrt{5}}/2\sqrt{5}$	-5	$\sqrt{5+2\sqrt{5}}/2\sqrt{5}$
	$C_\gamma^{B_1}$	$\sqrt{3}/\sqrt{10}$	$(3-\sqrt{5})/2\sqrt{10}$	0	$-(3-\sqrt{5})/2\sqrt{10}$	0	1	$1/2$
	$C_\gamma^{B_2}$	0	0	$-\sqrt{5+\sqrt{5}}/\sqrt{10}$	0	$\sqrt{5-\sqrt{5}}/\sqrt{10}$	1	$\sqrt{5+2\sqrt{5}}/2\sqrt{5}$
	$C_\gamma^{B_3}$	$-\sqrt{3}/\sqrt{10}$	$1/\sqrt{10}$	$-\sqrt{5-\sqrt{5}}/2\sqrt{5}$	$-1/\sqrt{10}$	$-\sqrt{5+\sqrt{5}}/2\sqrt{5}$	1	$\sqrt{5+2\sqrt{5}}/2\sqrt{5}$
III	$Q_\gamma^0$	$\sqrt{5}/\sqrt{3}$	$(3\sqrt{5}-5)/6$	$-5\sqrt{5+\sqrt{5}}/3\sqrt{10}$	$-(3\sqrt{5}+5)/6$	$5\sqrt{5-\sqrt{5}}/3\sqrt{10}$		$1/2\sqrt{3}$
	$C_\gamma^A$	$1/\sqrt{10}$	$(3-\sqrt{5})/2\sqrt{30}$	$\sqrt{5+\sqrt{5}}/\sqrt{15}$	$-(3+\sqrt{5})/2\sqrt{30}$	$-\sqrt{5-\sqrt{5}}/\sqrt{15}$	$1/3$	$\sqrt{5+2\sqrt{5}}/2\sqrt{3}$
	$C_\gamma^H$	$-\sqrt{3}/\sqrt{10}$	$1/\sqrt{10}$	$\sqrt{5-\sqrt{5}}/2\sqrt{5}$	$-1/\sqrt{10}$	$\sqrt{5+\sqrt{5}}/\sqrt{20}$	$1/3$	$\sqrt{5+2\sqrt{5}}/2\sqrt{3}$
	$C_\gamma^{B_1}$	$1/\sqrt{10}$	$\sqrt{3}(\sqrt{5}+1)/2\sqrt{10}$	0	$\sqrt{3}(\sqrt{5}-1)/2\sqrt{10}$	0	1	$-1/2\sqrt{3}$
	$C_\gamma^{B_2}$	$1/\sqrt{5}$	$(3-\sqrt{5})/2\sqrt{15}$	$-\sqrt{5+\sqrt{5}}/\sqrt{30}$	$-(3+\sqrt{5})/2\sqrt{15}$	$\sqrt{5-\sqrt{5}}/\sqrt{30}$	1	$\sqrt{5+2\sqrt{5}}/2\sqrt{3}$
	$C_\gamma^{B_3}$	$-\sqrt{3}/\sqrt{10}$	$1/\sqrt{10}$	$-\sqrt{5-\sqrt{5}}/2\sqrt{5}$	$-1/\sqrt{10}$	$-\sqrt{5+\sqrt{5}}/2\sqrt{5}$	1	$\sqrt{5+2\sqrt{5}}/2\sqrt{3}$

**Table 1.** The features of the extrema on the lowest adiabatic potential sheet for the  $U-v$  problem. Coordinates  $Q_\gamma^0$  for one of the extrema points, electronic wave function in the extremum (the coefficients  $a_i$ ), the extremum potential energy  $\mathcal{E}(Q^0)$ , coefficients  $C_\gamma^f$  of the linear combinations, determining the new normal coordinates in the extremum, and the corresponding new force constants  $K_\gamma$  are given for three types of 15-fold extrema. The coordinates  $Q_{T\gamma}$  are given in  $V/K$  units and the extrema energies in  $V^2/K$  units.

matrix contains all the unitary transformations in the above electronic space. It is the  $U(5)$  symmetry group, and if we drop the nonessential phase factor operations then it reduces to the  $SU(5)$  group. The Hamiltonian  $H_{II}(Q)$  of the five-dimensional isotropic harmonic oscillator possesses also  $U(5)$  symmetry. It may also be reduced to  $SU(5)$ . Thus, the general symmetry group of the uncoupled  $V-v$  problem is at least  $SU(5) \times SU(5)$ . Among the 24 infinitesimal operators of the

$SU(5)$  electronic group there are three components of the electronic orbital momentum:

$$\begin{aligned}
 \mathbf{S}_x &= \begin{pmatrix} 0 & 0 & 0 & 0 & i\sqrt{3} \\ 0 & 0 & i & 0 & 0 \\ 0 & -i & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -i \\ -i\sqrt{3} & 0 & 0 & i & 0 \end{pmatrix}, & \mathbf{S}_y &= \begin{pmatrix} 0 & i\sqrt{3} & 0 & 0 & 0 \\ -i\sqrt{3} & 0 & 0 & i & 0 \\ 0 & 0 & 0 & 0 & i \\ 0 & -i & 0 & 0 & 0 \\ 0 & 0 & -i & 0 & 0 \end{pmatrix}; \\
 \mathbf{S}_z &= \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -i \\ 0 & 0 & 0 & -2i & 0 \\ 0 & 0 & 2i & 0 & 0 \\ 0 & i & 0 & 0 & 0 \end{pmatrix}.
 \end{aligned} \tag{15}$$

Similarly among the 24 infinitesimal operators of the vibrational  $SU(5)$  group there are three components of the vibrational momentum:

$$\begin{aligned}
 L_x &= \sqrt{3}(Q_u P_\zeta - Q_\zeta P_u) + (Q_v P_\xi - Q_\xi P_v) - (Q_\eta P_\zeta - Q_\zeta P_\eta), \\
 L_y &= -\sqrt{3}(Q_u P_v - Q_v P_u) + (Q_v P_\eta - Q_\eta P_u) + (Q_\zeta P_\xi - Q_\xi P_\zeta), \\
 L_z &= -(Q_v P_\zeta - Q_\zeta P_v) - 2(Q_\zeta P_\eta - Q_\eta P_\zeta).
 \end{aligned} \tag{16}$$

It can easily be shown that when the vibronic coupling is taken into account only three constants of motion – the three components of the full angular momentum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$  – remain of the initial 48 in the zero order problem. This means that the symmetry of the problem is reduced to the  $R(3)$  rotation group. In a way the operator of the vibronic coupling is analogous to the spin-orbit coupling operator which reduces the  $R(3) \times R(3)$  group (describing the orbital momentum and the free spin of electrons) to the  $R(3)$  group describing the full momentum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ . An analogous situation was investigated for the first time by Moffitt and Thorson [16] for the cubic (trigonal)  $E-e$  problem.

The kinetic energy operator and therefore the so-called operator of nonadiabaticity, which appears when passing to the adiabatic electronic basis, are the invariants of the initial  $SU(5) \times SU(5)$  group. Hence the adiabatic potentials of the problem also possess the  $R(3)$  symmetry. As a matter of fact the constant of motion  $\mathbf{J}$ , when subjected to a unitary transformation which diagonalizes the potential energy matrix, is readily seen to become equal to  $\mathbf{L}$  acting in the nuclear space only. It follows that the five-dimensional surfaces of the adiabatic potentials possess the three-dimensional equipotential characteristics. In particular the extremum points form a three-dimensional potential trough.

It seems therefore natural to try to separate the three degrees of freedom  $\varphi_x$ ,  $\varphi_y$  and  $\varphi_z$ , conjugated to three components of  $\mathbf{J}$  and then to investigate the extremum points of the adiabatic potential in the subspace of the remainder two coordinates. The  $E-e$  problem, in which the axial symmetry makes it possible to investigate the

extremum points but in the radial direction, is analogous to the above one. In order to separate the  $\varphi_x$ ,  $\varphi_y$  and  $\varphi_z$  coordinates it is necessary to know the dependence of the coordinates  $Q_\gamma$  on the new curvilinear coordinates  $\varphi_x, \varphi_y, \varphi_z, \rho_1, \rho_2$ :

$$Q_\gamma = Q_\gamma(\varphi_x, \varphi_y, \varphi_z, \rho_1, \rho_2). \quad (17)$$

The unitary shift operation

$$\begin{aligned} S Q_\gamma S^{-1} &= \tilde{Q}_\gamma(\varphi_x + \alpha_x, \varphi_y + \alpha_y, \varphi_z + \alpha_z, \rho_1, \rho_2) \\ S &= \prod_{l=x,y,z} \exp(i\alpha_l L_l) \end{aligned} \quad (18)$$

gives us the former five variables  $Q_\gamma$  in terms of the new eight variables  $\varphi_x, \varphi_y, \varphi_z, \rho_1, \rho_2, \alpha_x, \alpha_y, \alpha_z$ , the  $\alpha_x, \alpha_y, \alpha_z$  being the additives to  $\varphi_x, \varphi_y, \varphi_z$  respectively. It is of course necessary to impose the three restricting conditions  $\alpha_x = \alpha_y = \alpha_z = 0$ , or, similarly,  $\varphi_x = \varphi_y = \varphi_z = 0$ . As there are no restrictions in the choice of the  $Q_\gamma(\rho_1, \rho_2)$  function (the  $Q_\gamma(\alpha_x, \alpha_y, \alpha_z)$  function being the one sought for) they may be chosen arbitrarily provided they do not affect the variables  $\alpha_x, \alpha_y, \alpha_z$ . The equations

$$\begin{aligned} \tilde{Q}_\xi(\varphi_x + \alpha_x, \varphi_y + \alpha_y, \varphi_z + \alpha_z, \rho_1, \rho_2)|_{\alpha_x = \alpha_y = \alpha_z = 0} &= Q_\xi = 0 \\ \tilde{Q}_\eta(\varphi_x + \alpha_x, \varphi_y + \alpha_y, \varphi_z + \alpha_z, \rho_1, \rho_2)|_{\alpha_x = \alpha_y = \alpha_z = 0} &= Q_\eta = 0 \\ \tilde{Q}_\zeta(\varphi_x + \alpha_x, \varphi_y + \alpha_y, \varphi_z + \alpha_z, \rho_1, \rho_2)|_{\alpha_x = \alpha_y = \alpha_z = 0} &= Q_\zeta = 0 \end{aligned} \quad (19)$$

are consistent with these requirements. The transformations (19) can be readily performed in the  $Q_u, Q_v, Q_\xi, Q_\eta, Q_\zeta$  coordinate representation in which the operator  $L$  is known (see (16)). For example  $Q_u$  takes the following form

$$\begin{aligned} \tilde{Q}_u &= \{Q_u(-1 + 3 \cos 2\alpha_x + 3 \cos 2\alpha_y + 3 \cos 2\alpha_x \cos 2\alpha_y) + \\ &+ Q_v[-2\sqrt{3}(1 + \cos 2\alpha_x) \sin 2\alpha_y \cos \alpha_z + 4\sqrt{3} \sin 2\alpha_x \cos \alpha_y \\ &\sin \alpha_z] + Q_\xi\sqrt{3}[-4 \sin 2\alpha_x \sin \alpha_y \cos 2\alpha_z + (1 - 3 \cos 2\alpha_x + \cos 2\alpha_y + \\ &\cos 2\alpha_x \cos 2\alpha_y) \sin 2\alpha_z] + Q_\eta\sqrt{3}[4 \sin 2\alpha_x \sin \alpha_y \sin 2\alpha_z + (1 - 3 \\ &\cos 2\alpha_x + \cos 2\alpha_y + \cos 2\alpha_x \cos 2\alpha_y) \cos 2\alpha_z] + Q_\zeta 2\sqrt{3}[(1 + \cos 2\alpha_x) \\ &\sin 2\alpha_y \sin \alpha_z + 2 \sin 2\alpha_x \cos \alpha_y \cos \alpha_z]\}/8. \end{aligned}$$

Analogous expressions can be obtained for  $\tilde{Q}_v, \tilde{Q}_\xi, \tilde{Q}_\eta, \tilde{Q}_\zeta$ . Using the conditions (19) and taking into account that  $Q_u$  and  $Q_v$  correspond to  $\rho_1$  and  $\rho_2$ , we can pass from the normal coordinates  $Q_\gamma$  to the new curvilinear coordinates  $\alpha_x, \alpha_y, \alpha_z, \rho_1, \rho_2$  as follows:

$$\begin{aligned} Q_u &= \{\rho_1(-1 + 3 \cos 2\alpha_x + 3 \cos 2\alpha_y + 3 \cos 2\alpha_x \cos 2\alpha_y) + \\ &+ \rho_2[-2\sqrt{3}(1 + \cos 2\alpha_x) \sin 2\alpha_y \cos \alpha_z + 4\sqrt{3} \sin 2\alpha_x \cos \alpha_y \sin \alpha_z]\}/8, \\ Q_v &= [\sqrt{3} \rho_1 \cos \alpha_x \sin 2\alpha_y + 2\rho_2(\cos \alpha_x \cos 2\alpha_y \cos \alpha_z + \sin \alpha_x \sin \alpha_y \sin \alpha_z)]/2, \\ Q_\xi &= [-\sqrt{3} \rho_1 \sin \alpha_x \sin 2\alpha_y + 2\rho_2(-\sin \alpha_x \cos 2\alpha_y \cos \alpha_z + \cos \alpha_x \sin \alpha_y \\ &\sin \alpha_z)]/2, \\ Q_\eta &= \{\sqrt{3} \rho_1(-1 - \cos 2\alpha_x \cos 2\alpha_y - \cos 2\alpha_x + 3 \cos 2\alpha_y) - \\ &- 2\rho_2[(3 - \cos 2\alpha_x) \sin 2\alpha_y \cos \alpha_z + 2 \sin 2\alpha_x \cos \alpha_y \sin \alpha_z]\}/8, \\ Q_\zeta &= [-\sqrt{3} \rho_1(1 + \cos 2\alpha_x) \sin 2\alpha_y + 2\rho_2(\sin 2\alpha_x \sin 2\alpha_y \cos \alpha_z + \\ &+ 2 \cos 2\alpha_x \cos \alpha_y \sin \alpha_z)]/4. \end{aligned}$$

This procedure is similar to the one which in the Jahn-Teller  $E-e$  problem introduces the polar coordinates. The analogous result here is that the secular equation determining the adiabatic potentials is dependent only on  $\rho_1, \rho_2$ , *i.e.* the rotational variables  $\alpha_x, \alpha_y, \alpha_z$  are separated. It takes the following form:

$$\begin{aligned} \mathcal{E}^5 - 7(\rho_1^2 + \rho_2^2)\mathcal{E}^3 + \rho_1(2\rho_1^2 + 3\rho_2^2)\mathcal{E}^2 + 12(\rho_1^2 + \rho_2^2)^2\mathcal{E} - \\ - 4\rho_1(2\rho_1^2 + 3\rho_2^2)(\rho_1^2 + \rho_2^2) = 0. \end{aligned} \quad (20)$$

The roots of this equation are:

$$\begin{aligned} \mathcal{E}_{1,2} = [-\rho_1 \pm \sqrt{3(3\rho_1^2 + 4\rho_2^2)}]/2 \\ \mathcal{E}_{3,4} = \pm 2\sqrt{\rho_1^2 + \rho_2^2}, \quad \mathcal{E}_5 = \rho_1. \end{aligned} \quad (21)$$

The adiabatic potentials may be obtained from Eq. (21) by adding the potential energy of the elastic distortions,

$$U_i(\rho) = K(\rho_1^2 + \rho_2^2)/2 + \mathcal{E}_i.$$

As one can see from Eq. (21) the two potential sheets  $U_{3,4}$ , corresponding to  $\mathcal{E}_{3,4}$ , have the well known form of an axially symmetrical "Mexican hat" (Fig. 5),

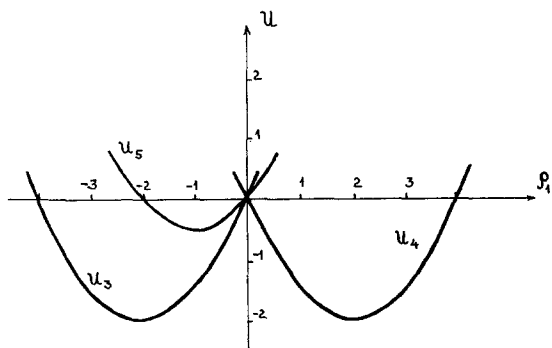
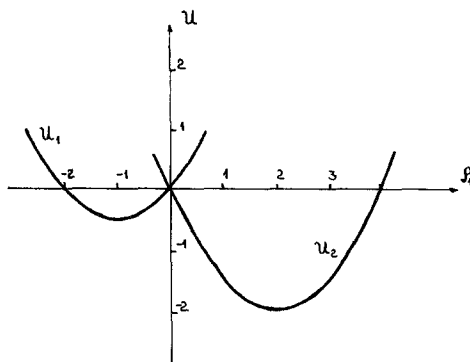


Fig. 5. Cross-section of the adiabatic potentials  $U_3, U_4, U_5$  along the  $\rho_1$  direction (see (19));  $\rho_1$  is given in the  $V/K$  units

quite similar to the  $E-e$  problem. The Jahn-Teller energy in the lowest surface trough is  $E_{JT} = -2V^2/K$ . Taking into account the three degrees of freedom, separated out above, one can see that the lowest surface possesses a four-dimensional variety of extrema. The potential surface  $U_5$ , corresponding to the root  $\mathcal{E}_5$  (see Eq. (21)), gives us a paraboloid shape with the minimum coordinates  $\rho_1 = -V/K, \rho_2 = 0$  (Fig. 5). Two potential surfaces,  $U_{1,2}$ , corresponding to  $\mathcal{E}_{1,2}$ , have the form of an asymmetrical (sloping) "Mexican hat", *i.e.* the lowest of these two potential sheets represents the sloping trough with one absolute minimum at  $\rho_1 = 2V/K, \rho_2 = 0, E_{JT} = -2V^2/K$ , and one saddle point  $\rho_1 = -V/K, \rho_2 = 0, E_{JT} = -V^2/2K$  (see Fig. 6). Notice that these two potential sheets  $U_{1,2}$  are degenerate with the  $U_{3,4,5}$  sheets along the  $\rho_2 = 0$  axis. While the degeneracy of the sloping trough  $U_{1,2}$  with the  $U_5$  sheet does not seem unusual (the minimum of the  $U_5$  sheet is not an absolute one), the existence of two-fold degeneracy in the point of the absolute minimum of the sloping trough seems to be very strange. Indeed, according to the Jahn-Teller theorem a further distortion of the molecule, resulting



**Fig. 6.** Cross-section of the adiabatic potentials  $U_1$ ,  $U_2$  along the  $\rho_1$  direction;  $\rho_1$  is given in the  $V/K$  units

in a splitting of this two-fold degeneracy, may be expected in this case. However, this situation is due to considering only the linear Jahn-Teller coupling terms in the Hamiltonian. The effective vibronic Hamiltonian for the system under consideration with the point  $\rho_1 = 2V/K$ ,  $\rho_2 = 0$  taken as the initial nuclear configuration has the symmetry of  $U(2) \times U(2)$  which is much higher than axial. This dramatic situation is owing to the “accidentally” high initial symmetry  $U(5) \times U(5)$  containing the  $U(2) \times U(2)$  group as subgroup. The unexpected degeneracy should obviously disappear if the second-order vibronic terms are taken into account.

## 6. Discussion

The above analysis of the topology of the Jahn-Teller adiabatic potentials for icosahedral molecules with triplet, quadruplet and quintet degenerate electronic terms makes it possible to understand the dynamics of the coupled motions of the electrons and nuclei. Also we may venture to predict certain observable physical effects using some analogies to the more simple cases investigated earlier [1–5]. For example, in the case of an icosahedral quadruplet with reasonably strong vibronic coupling the tunnelling through the potential barriers between the 15 equivalent minima of the adiabatic potential results in a splitting of the vibronic levels (tunnelling or inversion splitting [1]). This splitting can manifest itself in the optical, infrared and microwave absorption and luminescence and in the Raman scattering as well as in the temperature dependence of the EPR anisotropic spectra for paramagnetic centers, *e.g.* in double nitrates [3]. A small overlap of the nuclear vibrational states, localized in the near-neighbour Jahn-Teller minima, leads to the so-called Ham effect, that is a reduction of the matrix elements of the electronic operators and hence, to a reduction of the calculated physical magnitudes.

In the more complicated situation of a multidimensional trough, as in the cases of  $T$  and  $V$  terms, it is necessary to take into account the next (quadratic) terms in the vibronic coupling. This second-order approximation can be shown to result in a warping of the adiabatic potential sheets, *i.e.* in occurrence of alternating minima and saddle points along the bottom on the trough (quite similar to the  $E-e$  problem case [17]).

Some qualitative conclusions about the experimental features may however be obtained on the base of the linear approximation results of this paper. For instance, in the case of strong vibronic coupling the multiphonon optical absorption band for the  $A \rightarrow T$  and  $A \rightarrow V$  transitions must show a three-hump and five-hump structure respectively. The random strain in the nearest neighbourhood of a paramagnetic center may lead, as in the icosahedral quadruplet, to an anisotropy of the EPR spectra, the symmetry being reduced to  $D_2$ , and to a temperature dependence of the  $g$ -tensor. The influence of the Ham effect on the coupling constant is in the case of an icosahedral quintet expected to be qualitatively similar to the  $T$  term case (see Fig. 4).

The following two circumstances have to be taken into account when comparing our results with experimental data. First of all after the orthogonal transformation (3) the force constant  $K$  of the effective interacting five-fold degenerate mode is  $K=1$ , and the vibronic coupling constant  $V$  is given by Eq. (3a). Secondly, the interaction between the effective modes mentioned in Sect. 2 must be taken into account when solving the dynamic problem. This interaction can be neglected only if  $K_1/m_1 \approx K_2/m_2$ , which reduces the problem to a one-mode interaction. In addition to the simple icosahedral molecules discussed above (Fig. 1), there are more complicated ones spanning more than two  $v$  type representations. In these cases the breakdown of the requirement  $K_i/m_i \approx K_j/m_j$  leads to an essential multimodal situation. At last in analogy with the  $T-(e+t_2)$  problem for cubic molecules one can hope that in the linear coupling case the interaction of the icosahedral  $U$  and  $V$  terms with the quadruplet vibrations, ignored above, will not essentially alter our results, provided this interaction is weaker than the coupling to the quintet modes.

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