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Icosahedral $T_{1u}+T_{1g}$ Jahn-Teller problem

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The $T_{1u}+T_{1g}$ multimode Jahn-Teller problem in icosahedral symmetry is investigated. It is found that the pseudo-Jahn-Teller interaction between T_{1u} and T_{1g} can give rise to an increase of symmetry through the development of additional troughs in the space of ungerade modes. This result is related to a continuous group invariance of the Hamiltonian. The possible relevance to the Jahn-Teller instability of negatively charged fullerides is discussed.

There is currently a great interest in the study of icosahedral Jahn-Teller instabilities, especially in relationship to the mechanism of electron-phonon coupling in alkali-doped fullerides.[1–13] In the present communication we examine the adiabatic potential energy surface of the $T_{1u}+T_{1g}$ Jahn-Teller problem in icosahedral symmetry. This surface exhibits an interesting continuous group invariance. Its potential relevance to the Jahn-Teller activity of negatively charged fullerides will also be discussed.

C_{60} and all other closed-shell fullerenes of the leapfrog class have six low-lying empty orbitals matching the translational and rotational symmetries.[14] In the I_h point group this orbital sextuplet transforms as $T_{1u}+T_{1g}$. The corresponding Jahn-Teller problem is of the $(T_{1u}+T_{1g})\times(a_g+h_g+a_u+t_{1u}+h_u)$ type. The even modes in this model are due to vibronic coupling within the two triplets: a_g denotes totally symmetric modes and h_g represents fivefold degenerate modes. The odd modes arise through pseudo-Jahn-Teller interterm mixing: degeneracies of a_u, t_{1u}, h_u representations are 1, 3, 5, respectively. For a truncated icosahedral cage, as in C_{60}, the phonon part of the Hamiltonian should be written as: $2a_g+8h_g+a_u+4t_{1u}+7h_u$. The general multimode Hamiltonian for linear coupling with harmonic phonons is described as follows:

$$H=\Delta(C^{T_{1g}}_{A_g}-C^{T_{1u}}_{A_g})+\frac{1}{2}\sum_{\mu\Gamma\gamma}K_{\mu\Gamma}Q^2_{\mu\Gamma\gamma}+\sum_{\Gamma_i\Gamma_j\mu\Gamma\gamma}V^{\Gamma_i\Gamma_j}_{\mu\Gamma}C^{\Gamma_i\Gamma_j}_{\Gamma\gamma}Q_{\mu\Gamma\gamma},\tag{1}$$

where the first term describes the energies of the electronic T_{1g} and T_{1u} states, spaced by 2Δ, the second term is the elastic energy of the phonons, and the third term is the linear coupling. The index μ counts repeated irreducible representations Γ of the modes. The representations Γ_i and Γ_j run independently over the electronic T_{1u} and T_{1g} symmetries. The linear coupling constants V are reduced matrix elements that link levels of Γ_i and Γ_j under vibronic coupling to the $\mu\Gamma$ mode. They are independent of the mode component γ. Finally C's denote electronic operators in the $T_{1u}+T_{1g}$ space of the model. Their matrix elements correspond to Clebsch-Gordan coefficients for the icosahedral group:[15]

$$\langle\Gamma_i\gamma_i|C^{\Gamma_i\Gamma_j}_{\Gamma\gamma}|\Gamma_j\gamma_j\rangle=\langle\Gamma_i\gamma_i|\Gamma\gamma\Gamma_j\gamma_j\rangle.\tag{2}$$

For $\Gamma\in(\Gamma_i\times\Gamma_j)$ the following normalization condition holds:

$$\sum_{\gamma_i\gamma_j}|\langle\Gamma_i\gamma_i|\Gamma\gamma\Gamma_j\gamma_j\rangle|^2=|\Gamma_i|/|\Gamma|.\tag{3}$$

Hermiticity of H further implies

$$V^{\Gamma_i\Gamma_j}_{\mu\Gamma}\langle\Gamma_i\gamma_i|\Gamma\gamma\Gamma_j\gamma_j\rangle=V^{\Gamma_j\Gamma_i}_{\mu\Gamma}\langle\Gamma_j\gamma_j|\Gamma\gamma\Gamma_i\gamma_i\rangle.\tag{4}$$

We now introduce six directional cosines to express an arbitrary real electronic vector $|\psi_a\rangle$.

$$|\psi_a\rangle=\sum_{\Gamma_i\gamma_i}c^{\Gamma_i}_{\gamma_i}|\Gamma_i\gamma_i\rangle,\quad\text{with}\quad\sum_i|c^{\Gamma_i}_{\gamma_i}|^2=1.\tag{5}$$

The average energy of this state is minimized with respect to the nuclear coordinates. In this way one generates the isostationary function. The stationary points of this function in electronic space are images of the extrema of the adiabatic Jahn-Teller potential in actual coordinate space,[16–18] even in the multimode case.[19] The isostationary function of H is given by

$$\langle H\rangle_a=\Delta(\langle C^{T_{1g}}_{A_g}\rangle_a-\langle C^{T_{1u}}_{A_g}\rangle_a)-\frac{1}{2}\sum_{\mu\Gamma\gamma}\left[\sum_{\Gamma_i\Gamma_j}V^{\Gamma_i\Gamma_j}_{\mu\Gamma}(K_{\mu\Gamma})^{-1/2}\langle C^{\Gamma_i\Gamma_j}_{\Gamma\gamma}\rangle_a\right]^2,\tag{6}$$

where one has

$$\langle C^{\Gamma_i\Gamma_j}_{\Gamma\gamma}\rangle_a=\sum_{\gamma_i\gamma_j}c^{\Gamma_i}_{\gamma_i}c^{\Gamma_j}_{\gamma_j}\langle\Gamma_i\gamma_i|\Gamma\gamma\Gamma_j\gamma_j\rangle.\tag{7}$$

The functionals in Eq. (7) are easily obtained from the published tables of icosahedral coupling coefficients.[15] The result for $\langle H\rangle_a$ has a transparent form if we define two vectors **R** and **L** in a common three-dimensional space, as

$$\mathbf{R}=(c^{T_{1u}}_x,c^{T_{1u}}_y,c^{T_{1u}}_z),$$

$$\mathbf{L}=(c^{T_{1g}}_x,c^{T_{1g}}_y,c^{T_{1g}}_z).\tag{8}$$

The isostationary function only contains scalar and vector products of these vectors. This is a consequence of the sphericallike vector addition of T_1 representations in icosahedral symmetry.

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$$\begin{aligned}\langle H\rangle_a=\Delta(\mathbf{L}^2-\mathbf{R}^2)-\{&(A+A')\mathbf{R}^4+(B+B')\mathbf{L}^4\\&+2(C+C')\mathbf{R}^2\mathbf{L}^2+2(D+2F)(\mathbf{R}\cdot\mathbf{L})^2\\&+3(E+F-C)(\mathbf{R}\wedge\mathbf{L})^2\}.\end{aligned}\tag{9}$$

The coupling parameters in this expression are defined as follows:

$$A=\frac{1}{5}\sum_{\mu Hg}(V^{uu}_{\mu Hg})^2/K_{\mu Hg},\quad A'=\frac{1}{2}\sum_{\mu Ag}(V^{uu}_{\mu Ag})^2/K_{\mu Ag},$$

$$B=\frac{1}{5}\sum_{\mu Hg}(V^{gg}_{\mu Hg})^2/K_{\mu Hg},\quad B'=\frac{1}{2}\sum_{\mu Ag}(V^{gg}_{\mu Ag})^2/K_{\mu Ag},$$

$$C=\frac{1}{5}\sum_{\mu Hg}V^{uu}_{\mu Hg}V^{gg}_{\mu Hg}/K_{\mu Hg},\quad C'=\frac{1}{2}\sum_{\mu Ag}V^{uu}_{\mu Ag}V^{gg}_{\mu Ag}/K_{\mu Ag},$$

$$D=\sum_{\mu Au}\frac{(V^{ug}_{\mu Au})^2}{K_{\mu Au}},\quad E=\frac{1}{3}\sum_{\mu T_{1u}}(V^{ug}_{\mu T_{1u}})^2/K_{\mu T_{1u}},$$

$$F=\frac{1}{5}\sum_{\mu Hu}(V^{ug}_{\mu Hu})^2/K_{\mu Hu}.$$

Here the superscripts u and g refer to the T_{1u} and T_{1g} states, respectively. Note that the non-a_g parameter definitions include the degeneracy of the mode in the denominators. In this way the constants are scaled as Jahn-Teller stabilization energies.

Let φ be the angle between $\mathbf{L}$ and $\mathbf{R}$. From Eq. (5) one can further infer that $\mathbf{L}^2+\mathbf{R}^2=1$. The isostationary function can now be rewritten as a function of $\mathbf{R}$ only:

$$\langle H\rangle_a=-u\mathbf{R}^4-v\mathbf{R}^2+\Delta-B-B',\tag{10}$$

with

$$u=A+A'+B+B'-2C-2C'-f(\varphi),$$

$$v=2\Delta-2B-2B'+2C+2C'+f(\varphi),$$

$$f(\varphi)=2(D+2F)\cos^2\varphi+3(E+F-C)\sin^2\varphi.$$

This function must be minimized with respect to the electronic space coordinates $\mathbf{R}$ and φ, which is equivalent to finding extremal points of the eigenenergy surface of Eq. (1) in the space of nuclear coordinates.[16] The results can conveniently be represented in a (u,v) diagram as shown in Fig. 1. The corresponding energy expressions are given in Table I. Three qualitatively different distortion phases can occur. The T_{1g} phase arises when the stabilization energy of the excited ${}^2T_{1g}$ term in h_g and a_g modes overcomes the sum of the ${}^2T_{1u}\rightarrow{}^2T_{1g}$ energy spacing, 2Δ, and the Jahn-Teller stabilization energy of the ${}^2T_{1u}$ term. The T_{1u} phase is found whenever the pseudo-Jahn-Teller mixing is not strong enough to produce additional distortions along the odd nuclear coordinates. In this case there is no admixture of the upper term ($\mathbf{L}^2=0$). In both these phases the static vibronic problem reduces to the well-known $T\times h$ Jahn-Teller (JT) effect,[20–22] the equilibrium distortions forming a two-dimensional continuum, that is invariant under SO(3) symmetry. Finally a third phase establishes in the presence of a strong pseudo-Jahn-Teller effect. It is characterized by odd distortions which mix the two terms of opposite parity. Minimization of the isostationary function with respect to the angle φ between $\mathbf{R}$ and $\mathbf{L}$ yields three types of minimal energy surfaces, depending on the relative coupling strength of the odd-parity distortions and the interterm coupling element C of the even-parity h_g modes. These results are summarized in Table II.

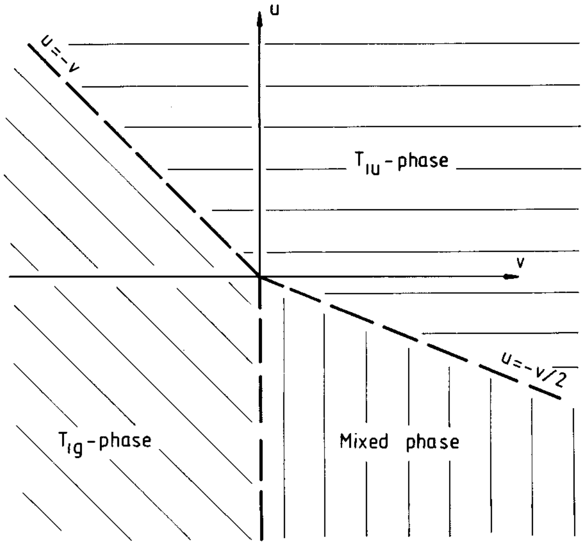

FIG. 1. Phase diagram for the $T_{1u}+T_{1g}$ problem.

For $\varphi=0$ odd distortions of the a_u and h_u type couple $\mathbf{R}$ and $\mathbf{L}$ in a parallel way. This orientation is maintained while the system rotates in the two-dimensional trough of the $T\times h$ JT problem. The symmetry of this solution therefore does not exceed the SO(3) symmetry of the T_{1u} or T_{1g} phases. A degenerate solution exists for $\varphi=\pi$, with the two vectors antiparallel. There is a saddle-point ridge between the $\varphi=0$ and $\varphi=\pi$ minimal troughs with a perpendicular orientation of the two vectors. In the second type of solutions with $\varphi=\pi/2$ this saddle point ridge has become a minimum. In this case coupling to t_{1u} modes prevails. There are now two different types of rotation which leave the isostationary function invariant: a three-dimensional rotation of the vector $\mathbf{R}$ which is driven by h_g distortions, and a precession of $\mathbf{L}$ about $\mathbf{R}$. The total symmetry of the system therefore increases to SO(3)×SO(2). The $\varphi=0,\pi$ solutions now correspond to local maxima. Finally in the third type of angular coupling, with $2D+F=3E-3C$, the isostationary function is independent of φ. This means that only the lengths of $\mathbf{R}$ and $\mathbf{L}$ remain fixed while both vectors are allowed to rotate freely. The total symmetry of this solution is SO(3) ×SO(3), which is isomorphic to SO(4).

TABLE I. Equilibrium distorted configurations resulting from ${}^2T_{1u}+{}^2T_{1g}$ vibronic mixing.

Phase	Coupling conditions	Energy of stabilization
$T_{1g}(\mathbf{R}^2=0)$	$u>0, v\leqslant -u$	$\Delta-B-B'$
	$u<0, v\leqslant 0$	
$T_{1u}(\mathbf{L}^2=0)$	$u>0, v\geqslant -u$	$-\Delta-A-A'$
	$u<0, v\geqslant -2u$	
Mixed	$u<0, 0\leqslant v\leqslant -2u$	$\Delta-B-B'+v^2/4u$

TABLE II. Odd static distortions in the mixed phase.

Condition	Angular minimum	Symmetry
$2D+F>3E-3C$	$\varphi=0,\pi$	SO(3)
$2D+F<3E-3C$	$\varphi=\pi/2$	SO(3)×SO(2)
$2D+F=3E-3C$		SO(4)

The appearance of a symmetry increase as a result of a pseudo-Jahn-Teller interaction is a rather surprising result that can be accounted for by considering the continuous group invariance of the model in Eq. (1). For u and v equal to zero the isostationary function in Eq. (10) is a constant. This case corresponds to the limit of equal coupling with SO(6) symmetry. The SO(6) group is locally isomorphic to SU(4), which provides a convenient subduction route to SO(4). In SU(4) the electronic sextuplet corresponds to the sixfold-degenerate representation [1100]. The symmetrized square of [1100] yields an SU(4) scalar and the [2200] tensor with 20 components which can embed all Jahn-Teller couplings. The branching rules for reduction from SU(4) to SO(4) are as follows:

$$[1100]\rightarrow(1,0)+(0,1),$$

$$[2200]\rightarrow(0,0)+(2,0)+(0,2)+(1,1). \tag{11}$$

The (1,0) and (0,1) components are readily identified as the T_{1u} and T_{1g} systems with internal SO(3) symmetry. From Eq. (11) an SO(4) Hamiltonian can be constructed with the following ingredients: a (0,0) scalar corresponding to the spacing between T_{1u} and T_{1g}, (2,0) and (0,2) tensors representing intraterm coupling to h_g modes, and the (1,1) tensor which matches the odd mode $a_u+t_{1u}+h_u$ interactions under equal coupling, i.e., with $D=E=F$.

The actual SO(4) invariance case in Table II is slightly more involved due to the appearance of the coupling parameter C which represents interaction between the electronic terms via the common h_g modes. The physics of the model requires that in the absence of odd-parity mixing modes such interaction should not be able to induce a mixed phase ground state, since that would violate the parity rule. This requirement can indeed easily be established. From the definition of the coupling parameters one can infer $|2C|\leqslant A+B$ and $|2C'|\leqslant A'+B'$. These inequalities imply that for vanishing D, E, and F the parameter u will always be positive, which precludes a mixed phase solution (cf. Fig. 1).

In conclusion it has been shown that the pseudo-JT effect in a $T_{1u}+T_{1g}$ manifold can give rise to an interesting mixed phase ground state with high dynamic symmetries. Whether or not this effect will play a role in fullerides must be the subject of further investigation. For the case of the $C_{60}{}^{-}$ anion the separation 2Δ between T_{1u} and T_{1g} states is of the order of 1 eV, while JT couplings are probably of a lesser magnitude. As a result the ground state of $C_{60}{}^{-}$ is likely to exhibit a pure T_{1u} phase. Interterm vibronic constants have not yet been calculated but a coupling of t_{1u} modes to the $t_{1u}\rightarrow t_{1g}$ absorption has been observed in the IR spectra of A_6C_{60} (A=K,Rb).[23] Indirect evidence of nonvanishing t_{1u} and h_u coupling constants is also obtained from the intensities of the false origins in the fluorescence spectrum of neutral C_{60}.[24] This suggests that it should be possible to induce a phase transition to the mixed phase ground state, provided the orbital separation constant could be lowered. Further investigations are needed to see if this goal can be achieved by chemical tuning or by changing the surroundings of the fulleride. In multiply charged $C_{60}{}^{n-}$ vibronic mixing between t_{1u} and t_{1g} orbitals will probably be enhanced due to reduced $t_{1u}\rightarrow t_{1g}$ promotion energies.[25] The presence of a manifold of open-shell states in these ions will of course give rise to more intricate Jahn-Teller surfaces.

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