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Jahn-Teller effects in the fullerene anion C_{60}^{3-}

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The A_3C_{60} fullerides ($A \equiv$ alkali metal) are of considerable interest both experimentally and theoretically. One important consideration in understanding many of the observed results is the Jahn-Teller (JT) coupling between vibrations of C_{60}^{3-} anions and their electrons, and also of cooperative JT coupling between these anions. To understand the effects of these intermolecular and intramolecular couplings, it is necessary to have a good theoretical description of the JT effect experienced by isolated C_{60}^{3-} anions in both unstrained and strained environments. In this paper, we will determine analytical expressions for the energies and eigenstates of an isolated (unstrained) C_{60}^{3-} anion in terms of the JT coupling strength and the splitting between two different molecular terms. We will then look at the effect of strain as a perturbation on these states.

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I. INTRODUCTION

Much research has been undertaken on the fullerene molecule and its compounds. One particular area of interest is in the effect of the strong coupling between the motion of the electrons and vibrations of the fullerene molecule. For isolated molecules, this leads to a dynamic Jahn-Teller (JT) effect.[1] The molecule will locally distort into one of a number of equivalent lower-symmetry configurations, but tunneling between the equivalent configurations restores the original icosahedral symmetry of the C_{60} molecule. For fullerene-based solids, coupling to intermolecular vibrations between molecules can also be strong, leading to a cooperative JT effect.[1–3] In this case, distortions of neighboring molecules can be locked in place resulting in a macroscopic distortion of the solid as a whole at low temperatures.[4] At higher temperatures, the correlations between distortions are destroyed by thermal effects, leading to the possibility of structural phase transitions.[5,6] Indeed, structural phase transitions are seen in a number of fullerene materials.[5–7] Although not all of the observed structural changes will be due to JT effects, it is nevertheless important to investigate the possible JT effects that could occur in these systems.

Estimates of the JT coupling in a given fullerene material can be calculated[8,9] or deduced from experimental data,[10–12] but these are all obviously subject to certain assumptions. It is, therefore, important to calculate the quantum-mechanical states of an isolated ion and their energies as a function of the JT coupling strength. The results can be used to explain various (e.g., spectroscopic) data as well as used in further calculations

In this paper, we will consider the JT effects experienced by isolated C_{60}^{3-} anions. These ions occur in materials such as the A_3C_{60} fullerides (where A is an alkali metal), which are of particular interest in fullerene research as they can be superconducting at relatively high temperatures.[5] Various mechanisms have been proposed to help explain the observed superconductivity, and vibronic coupling involving the C_{60}^{3-} anions is an important feature of many of these models. The system may change from a Mott-Hubbard insulator to a band insulator through a JT effect.[13] Also, as the alkali atoms sit in symmetric positions within the A_3C_{60} lattice, vibronic hopping matrix elements may largely cancel, and the band gap may be widened due to a combination of electron-correlation and electron-phonon interactions.[14] In addition to being superconducting, the A_3C_{60} fullerides can also exhibit orientational phase transitions to states with merohedral disorder, in which rotations take place about an axis which is aligned in one of two standard orientations.[15]

The motion of the JT system experienced by C_{60}^{3-} ions can be understood by examining the lowest adiabatic potential energy surface (APES) formed due to vibrational and JT potential energy terms (and any electronic term splittings). This is a five-dimensional surface containing points of minimum energy in two dimensions and troughs of equivalent-energy points in the other three.[16–18] We will assume that the JT coupling is sufficiently strong that the potential barriers between the minimum-energy points are sufficiently high to localize the motion around the minimum-energy positions, then the motion can be described in terms of two vibrations and three pseudorotations. (It should be noted that "rotation" here refers to rotation of a distortion of a fullerene molecule rather than real rotations of the molecule itself.)

Our basic formalism for specifying the Hamiltonian and identifying the vibrations and rotations follows that of O'Brien,[17,18] which in turn carries on from the original work of Auerbach *et al.*[16] These three works then used numerical diagonalization methods to determine the spectrum of lower-lying energy levels as a function of the JT coupling strength. We will take a different approach, in which analytical expressions for the vibronic states are obtained in terms of integrals over all points on the lowest APES. The energies of the states are then determined by evaluating related integrals numerically. This work complements that on C_{60}^{2-} and C_{60}^{4-} anions already published.[19]

In order to understand the cooperative JT effects linking motion of individual C_{60} molecules in fullerene solids,[2,3] it will be necessary to understand JT effects experienced by ions in a distorted environment. Such distortions can be modeled as an effective strain.[20] We will, therefore, use our results for the undistorted case to predict the behavior of a system subject to a weak strain as a perturbation on the undistorted case.

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II. THE HAMILTONIAN

The three electrons in a C_{60}^{3-} ion occupy triplet electronic states t_{1u}. These are coupled to h_g-type vibrations in what can be referred to as a $p^3 \otimes h$ JT effect.[17,18] The angular-momentum notation p for the t_{1u} state is chosen because when linear JT couplings only are considered, the system has SO(3) symmetry (as proved in general terms by Pooler[21]). This is accidentally higher than the I_h symmetry of the C_{60} molecule. Furthermore, all angular momentum states up to $L=2$ are not split under the icosahedral group.[17,18] Angular momentum notation provides the most convenient way to allow for interelectron Coulomb energies, which competes with the JT interaction to determine the ordering of energy levels.[17]

In general, we will take the total Hamiltonian $\mathcal{H}$ to be

$$\mathcal{H} = \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{vib}} + \mathcal{H}_{\text{term}} + \mathcal{H}_{\text{strain}}, \tag{1}$$

where $\mathcal{H}_{\text{int}}$ is the JT interaction, $\mathcal{H}_{\text{vib}}$ represent the vibrational terms, $\mathcal{H}_{\text{term}}$ is a contribution to account for any splitting between different terms and $\mathcal{H}_{\text{strain}}$ is a distorting strain. For the real C_{60}^{3-} ion, it may be necessary to include both first-order and higher-order contributions to $\mathcal{H}_{\text{int}}$. However, it is expected that a good indication of the behavior can be obtained by restricting the calculations to linear coupling only, and this is the approach we will adopt in this paper.

Before developing a theory for the $p^3 \otimes h$ JT system, it is first necessary to define some notation to label the five components of the vibrational h_g mode. We will follow Ref. 22 and use the labels $\{Q_\theta, Q_\epsilon, Q_4, Q_5, Q_6\}$ to represent the collective displacements, which correspond to the labels $\{Q_1, Q_4, Q_5, Q_2, Q_3\}$ used in Refs. 17 and 18. Due to the accidental SO(3) symmetry in linear coupling, it is irrelevant whether a C_2 axis or a C_5 axis is defined as the z-axis of the icosahedron.

In units in which the reduced mass of the mode, the mode frequency and $\hbar$ are set to unity, the vibrational term is

$$\mathcal{H}_{\text{vib}} = \frac{1}{2}\sum_{\lambda} (P_\lambda^2 + Q_\lambda^2), \tag{2}$$

where λ is summed over all of the components of the vibrational mode and the P_λ are the momenta conjugate to the Q_λ. The electronic terms arising from a $p^3 \otimes h$ JT interaction are ^4S, ^2D, and ^2P. As the high spin state is an S state, there is no JT coupling and this state need not be considered any further. It is also found that there is no JT coupling within either the ^2D or the ^2P states as all the required matrix elements are zero, but there is a nonzero coupling between the ^2P and ^2D states.[17,18,23,24] To first order, the resulting interaction Hamiltonian $\mathcal{H}_{\text{int}}$ can be written in the form

$$\mathcal{H}_{\text{int}} = k\sum_{\lambda} Q_\lambda \sigma_\lambda, \tag{3}$$

where the σ_λ are electronic operators whose representation in terms of 8×8 matrices can easily be deduced from Refs. 17 and 18, noting that our coupling constant k is equivalent to $\sqrt{3}k$ in these references (as their k is that applicable to the $T\otimes h$ [or $p^1 \otimes h$] JT system). An alternative but equivalent form for the Hamiltonian in terms of a coupling constant g and coordinates Q_m that transform as the spherical harmonics Y_{2m} is given in Ref. 26.

We will take the the ^2P term to be at an energy δ above the ^2D term, so that $\mathcal{H}_{\text{term}}$ is a diagonal matrix with the first three diagonal elements having the value δ and the remaining values zero. Recent calculations[25] indicate that the ^2P term is around 0.191 eV above the ^2D term, so we will use this value for δ in plots of our final results. However, the results themselves apply for any value of δ.

Due to the SO(3) invariance of the linear JT Hamiltonian, all directions in Q space are equivalent. A transformation of coordinates[27] can be used to convert the general Hamiltonian representing a strain in any direction into a Hamiltonian for a strain in the θ direction. We, therefore, only need to consider the case of a strain in the θ direction, with a strain Hamiltonian

$$\mathcal{H}_{\text{strain}} = -w\sigma_\theta, \tag{4}$$

where the coefficient w can be positive or negative. A strain in any other direction can be made equivalent to this by a rotation of the electronic and vibrational operators.[28] If higher-order coupling terms were to be considered in the Hamiltonian, then this equivalence would no longer hold and strains in different directions would need to be considered explicitly.

III. ADIABATIC POTENTIAL ENERGY SURFACES

As in Refs. 18 and 17, we start by examining the potential energy terms in the Hamiltonian to determine the structure of the adiabatic potential energy surfaces (APESs) around which the motion of the system will be based, using a parametrization involving a radial coordinate Q and four angles, θ, ϕ, γ, and α to rewrite the Q_λ. This is the usual parametrization in θ and ϕ for d-state functions, with the additional angles γ and α added to reflect the full five degrees of freedom. In Refs. 17 and 18, it was shown that a series of rotations in each of the four angles could then be used to reduce the potential to a form involving the angle α and the term splitting δ only (noting some errors in their original matrices[19]). When the result is diagonalized, it is found that two of the eight APES energies are zero, and the remaining six are of the form

$$V = \tfrac{1}{2}\left(Q^2 + \delta \pm \sqrt{4k^2Q^2\sin^2\beta + \delta^2}\right), \tag{5}$$

where $\beta = \alpha$, $\alpha + \pi/3$, and $\alpha - \pi/3$. The values of α and Q are chosen to minimize V. The APESs are independent of θ, ϕ, and γ. This corresponds to troughs of equivalent minimum-energy points. If the results depended on these angles, we would need to choose specific values of the angles to determine positions of minimum energy. The orientation of the trough is determined by the value of α.

The value of $Q \equiv \rho$ for which V is a minimum can now be determined. It is found that when $\delta' \equiv \delta/k^2 < 2$,

$$\rho = k\sqrt{1 - \delta'^2/4}, \tag{6}$$

resulting in a minimum in energy of

$$V = -\frac{1}{8}k^2(\delta' - 2)^2. \tag{7}$$

When $\delta' > 2$, the minimum is at the origin $(Q=0)$. As this corresponds to a term splitting much larger than the JT interaction, we will not consider this case any further in this paper, although this factor does determine the range of couplings over which results can be obtained. An equivalent result for the existence of a finite JT distortion was also found in Ref. 26.

When there is no strain, values of α can be chosen to make any of the three APESs in Eq. (5) with the negative sign a minimum. In Ref. 17, $\alpha = \pi/2$ was chosen as the simplest solution. Although this lies outside the $0 \leqslant \alpha < \pi/3$ range, it just represents a different copy of phase space. However, the strain term $\mathcal{H}_{\text{strain}}$ does not affect all of the APESs in the same way. In fact, the solution with $\alpha = \pi/2$ is unaffected by a θ-type strain. We could circumvent the problem by choosing the strain to be in a different direction. However, it would be much more difficult to convert the general problem of a strain in an arbitrary direction into this new problem as the known five-dimensional rotation matrix[27] favors the θ direction. We will, therefore, choose a different value of α so that a different eigenvalue is the lowest in energy. We will, therefore, set $\alpha = \pi/6$, even when there is no strain present. The APES involving $\sin(\alpha + \pi/3)$ then determines the minimum energy, and the electronic state at a point $\Omega \equiv (\theta, \phi, \gamma)$ on the lowest APES is

$$\psi_g(\Omega) = \frac{1}{2}\begin{pmatrix} \sqrt{2-\delta'}(\cos\gamma\cos\theta\cos\phi - \sin\gamma\sin\phi) \\ \sqrt{2-\delta'}(\cos\gamma\cos\theta\sin\phi + \sin\gamma\cos\phi) \\ -\sqrt{2-\delta'}\cos\gamma\sin\theta \\ \dfrac{\sqrt{3(2+\delta')}}{2}\sin 2\theta\sin\gamma \\ -\sqrt{2+\delta'}(\cos 2\theta\cos\phi\sin\gamma + \cos\gamma\cos\theta\sin\phi) \\ \sqrt{2+\delta'}\sin\theta(\cos\gamma\cos 2\phi - \cos\theta\sin\gamma\sin 2\phi) \\ -\sqrt{2+\delta'}\sin\theta(\cos\theta\cos 2\phi\sin\gamma + \cos\gamma\sin 2\phi) \\ \sqrt{2+\delta'}(\cos\gamma\cos\theta\cos\phi - \cos 2\theta\sin\gamma\sin\phi) \end{pmatrix}. \tag{8}$$

IV. KINETIC ENERGY

When $\alpha = \pi/2$, the kinetic energy part of $\mathcal{H}_{\text{vib}}$ has been shown to have the form[17,18]

$$\mathcal{H}_{\text{KE}} = -\frac{1}{2}\left[\frac{1}{Q}\frac{\partial}{\partial Q}\left(Q\frac{\partial}{\partial Q}\right) + \frac{1}{Q^2}\frac{\partial^2}{\partial\alpha^2} + \frac{9}{4Q^2}\right] + \frac{1}{8Q^2}[4\lambda_x^2 + 4\lambda_y^2 + \lambda_z^2] \tag{9}$$

where $\{\lambda_x, \lambda_y, \lambda_z\}$ are the three components of an angular momentum operator in the subspace involving θ, ϕ, and γ. (Note that Refs. 17 and 18 erroneously give the wrong sign for the angular momentum terms.) The first line is the Hamiltonian for two vibrations and the second line is the Hamiltonian for a symmetric top. The motion in the five-dimensional space of the h vibrations is, therefore, comprised of vibrations in two directions and pseudorotations in three directions. This is different from the motion in the other $p^n \otimes h$ JT systems,[16–19] where there are vibrations in three directions and pseudorotations in two directions. Alternatively, in order to distinguish the rotational directions from the vibrational ones, the Hamiltonian can be written in terms of rotating coordinates

$$Q'_\nu = \sum_\mu D_{\mu\nu}(\theta, \phi, \gamma, \alpha) Q_\mu, \tag{10}$$

where the $D_{\mu\nu}(\theta, \phi, \gamma, \alpha)$ are rotation matrix elements.[27] Setting $Q'_\theta = Q$ and taking the inverse recovers the parametrization of the Q'_λ, so Q'_θ is clearly a vibrational coordinate. Using the method of Öpik and Pryce[29] and considering the conjugate momenta, it can be shown that Q'_ϵ is the other vibrational coordinate and Q'_4, Q'_5, and Q'_6 are the pseudorotations.

The wave functions for a symmetric top are well known.[30] They are functions of the same angles θ, ϕ, and γ used in the parametrization of the Q'_λ, which are related to the representations of finite rotations. The states, whose form can be found in Refs. 17 and 18, will be written as $\Phi^{(L,M,K)}(\Omega)$, where L, M, and K are integer quantum numbers with $|M| \leqslant L$ and $|K| \leqslant L$. (It should be noted that Refs. 17 and 18 erroneously state that the required eigenstates involve $\cos K\gamma$ or $\sin K\gamma$ rather than $e^{iK\gamma}$.) Now the electronic state changes signs under the transformation $\gamma \rightarrow \gamma + \pi$, so the pseudorotational state must also change signs under this transformation. Also, the electronic state is invariant under the inversion operations $\theta \rightarrow \pi - \theta$, $\phi \rightarrow \phi + \pi$, and $\gamma \rightarrow -\gamma$ and so the pseudorotational state must also be invariant.[17,18] As a result, K

TABLE I. Eigenstates $\Phi_{\mathrm{rot}}^{(L,M,K)}$ of the x-axis symmetric top $(\lambda_x^2+4\lambda_y^2+4\lambda_z^2)/8Q^2$ with K even. The algebraic form given must be multiplied by the common factor $e^{iM\phi}\cos\gamma\sin\theta$ if L is odd and $e^{iM\phi}\sin\gamma\sin 2\theta$ if L is even. Note that the states are a linear combination of the odd-K eigenstates $\Phi_i^{(L,M,K)}$ of the corresponding z-axis top.

L	K	Wave function $\Phi_{\mathrm{rot}}^{(L,M,K)}$	Algebraic form
1	0	$\Phi_2^{(1,M,1)}$	1
2	2	$\Phi_1^{(2,M,1)}$	1
3	0	$-\sqrt{3/8}\Phi_2^{(3,M,1)}+\sqrt{5/8}\Phi_2^{(3,M,3)}$	$3-5\cos^2\gamma\sin^2\theta$
3	2	$\sqrt{5/8}\Phi_2^{(3,M,1)}+\sqrt{3/8}\Phi_2^{(3,M,3)}$	$\cos 2\theta+\cos^2\gamma\sin^2\theta$
4	2	$-\sqrt{1/8}\Phi_1^{(4,M,1)}+\sqrt{7/8}\Phi_1^{(4,M,3)}$	$1-7\cos^2\gamma\sin^2\theta$
4	4	$\sqrt{7/8}\Phi_1^{(4,M,1)}+\sqrt{1/8}\Phi_1^{(4,M,3)}$	$\cos 2\theta+\cos^2\gamma\sin^2\theta$
5	0	$1/8\sqrt{2}[\sqrt{30}\Phi_2^{(5,M,1)}-\sqrt{35}\Phi_2^{(5,M,3)}+3\sqrt{7}\Phi_2^{(5,M,5)}]$	$15-70\cos^2\gamma\sin^2\theta+63\cos^4\gamma\sin^4\theta$
5	2	$1/4\sqrt{2}[-\sqrt{14}\Phi_2^{(5,M,1)}+\sqrt{3}\Phi_2^{(5,M,3)}+\sqrt{15}\Phi_2^{(5,M,5)}]$	$\cos 2\theta-\cos^2\gamma\sin^2\theta(2+3(\cos^2\gamma-2)\sin^2\theta$
5	4	$1/8\sqrt{2}[\sqrt{42}\Phi_2^{(5,M,1)}+9\Phi_2^{(5,M,3)}+\sqrt{5}\Phi_2^{(5,M,5)}]$	$1+\sin^2\theta(3\cos 2\gamma-5)+\sin^4\theta(\cos^4\gamma+8\sin^2\gamma)$
6	2	$1/16[\sqrt{10}\Phi_1^{(6,M,1)}-9\Phi_1^{(6,M,3)}+\sqrt{165}\Phi_1^{(6,M,5)}]$	$1-18\cos^2\gamma\sin^2\theta+33\cos^4\gamma\sin^4\theta$
6	4	$1/4\sqrt{2}[-\sqrt{6}\Phi_1^{(6,M,1)}+\sqrt{15}\Phi_1^{(6,M,3)}+\sqrt{11}\Phi_1^{(6,M,5)}]$	$1-\sin^2\theta(7+5\cos 2\gamma)-11\cos^2\gamma\sin^4\theta(\cos^2\gamma-2)$
6	6	$1/16[3\sqrt{22}\Phi_1^{(6,M,1)}+\sqrt{55}\Phi_1^{(6,M,3)}+\sqrt{3}\Phi_1^{(6,M,5)}]$	$3+\sin^2\theta(5\cos 2\gamma-11)+\sin^4\theta(3\cos^4\gamma+16\sin^2\gamma)$

must be even and the required eigenstates are $\Phi_1^{(L,M,K)}$ for L odd and $\Phi_2^{(L,M,K)}$ for L even, where

$$\Phi_1^{(L,M,K)}=\begin{cases}\Phi^{(L,M,0)} & \text{for } K=0\\ \dfrac{1}{\sqrt{2}}(\Phi^{(L,M,K)}+\Phi^{(L,M,-K)}) & \text{otherwise}\end{cases}$$

$$\Phi_2^{(L,M,K)}=\frac{1}{\sqrt{2}}(\Phi^{(L,M,K)}-\Phi^{(L,M,-K)}). \tag{11}$$

This means that the states for $K=0$ only exist for odd L. The rotational energy of these states [i.e., of the final term in Eq. (9)] is[17,18]

$$E(L,K)=\frac{1}{2Q^2}\left[L(L+1)-\frac{3}{4}K^2\right]. \tag{12}$$

The above formula gives the results when $\alpha=\pi/2$. However, we have already stated that strain does not affect this solution so we should instead consider the case when $\alpha=\pi/6$. Using the parametrization of the Q'_λ and after some algebra, it is found that the kinetic energy can still be written in a form equivalent to Eq. (9) but with $(\lambda_x^2+4\lambda_y^2+4\lambda_z^2)$ instead of $(4\lambda_x^2+4\lambda_y^2+\lambda_z^2)$. This is still the Hamiltonian for a symmetric top but with the axis of quantization along the x axis instead of the z axis. The energies of the eigenstates are $E(L,K)$ as for the z-axis top, but the states are linear combinations of states (11) for the z-axis top involving different values of K. This is analogous to the more familiar three-dimensional angular momentum operators, where eigenfunctions of l_x are linear combinations of those of l_z but the energies of the eigenstates remain the same. The invariance and inversion relationships in this case require that the required combinations involve odd (rather than even) values of K. The resulting eigenstates will be labeled $\Phi_{\mathrm{rot}}^{(L,M,K)}(\Omega)$, where K is even as for the z-axis top, even though the states involve linear combinations of states $\Phi_i^{(L,M,K)}$ with K odd. The required linear combinations can be easily found by simple matrix diagonalization. The states up to $L=6$ are given in Table I, with the corresponding rotational energies being given by Eq. (12). The algebraic form of the states in terms of θ and γ is also given omitting the common factors $e^{iM\phi}\cos\gamma\sin\theta$ for L odd and $e^{iM\phi}\sin\gamma\sin 2\theta$ for L even.

V. THE WAVE FUNCTION

The wave function at point Ω on the trough of minimum-energy points consists of a vibronic part to take account of the coupling between the electrons and the vibrations, and the rotational part $\Phi_{\mathrm{rot}}^{(L,M,K)}$ discussed above. To apply to both the ground and excited states, the vibronic part must take account of excitations in the vibrational directions Q'_θ and Q'_ϵ (noting that the excitations only have meaning in the rotating coordinate system). If we suppose that there are r excitations in Q'_θ and s excitations in Q'_ϵ, we can write the vibronic wave function in the form $|\psi_{\mathrm{vib}}(\Omega);\theta'^r\epsilon'^s\rangle$. As all points on the trough are equivalent, the total wave function must, therefore, take account of all points equally. Thus, it will be written in the form

$$\Psi(L,M,K,r,s)=\int|\psi_{\mathrm{vib}}(\Omega);\theta'^r,\epsilon'^s\rangle\Phi_{\mathrm{rot}}^{(L,M,K)}(\Omega)d\Omega. \tag{13}$$

As the trough can be mapped onto the surface of a sphere in which θ and ϕ take their usual polar definitions, the volume element $d\Omega=\sin\theta d\theta d\phi d\gamma$. However, for this wave function to be of use, it is necessary to derive a more explicit form for the vibronic wave function. This can be achieved using a unitary transformation $U(\Omega)$ to displace the origin of the phonon coordinates to the bottom of the trough.[27] In the rotating coordinates, only the θ' mode is shifted. The required form of the transformation at a point Ω on the trough is thus[19]

$$U(\Omega) = \exp[\alpha'_\theta(b'^{\dagger}_\theta - b'_\theta)], \tag{14}$$

where α'_θ is a variational parameter, and $b'^{\dagger}_\theta$ and b'_θ are phonon creation and annihilation operators, respectively, for the mode θ'. These can be defined in terms of operators in the nonrotating coordinates in the same manner as Eq. (10) for the Qs. Fixing the value of α'_θ to displace the origin of coordinates to the bottom of the trough gives the result $\alpha'_\theta = -\rho$. The vibronic wave function is thus

$$|\psi_{\text{vib}}(\Omega);\theta'^r,\epsilon'^s\rangle = \psi_g(\Omega)U(\Omega)|\theta'^r,\epsilon'^s\rangle, \tag{15}$$

where the r and s in $|\theta'^r,\epsilon'^s\rangle$ again signify the number of θ' and ϵ' excitations, respectively.

VI. EVALUATION OF THE ENERGY

We will now use the wave function given in the previous section to determine the energies of this JT system. This involves the evaluation of matrix elements and overlaps between a point $\Omega_l \equiv (\theta_l, \phi_l, \gamma_l)$ with phonon excitation numbers $\{p,q\}$ and a point $\Omega_r \equiv (\theta_r, \phi_r, \gamma_r)$ with excitation numbers $\{r,s\}$. Care must be taken in evaluating these factors since the meaning of excitations in the rotating coordinates is different at different points on the trough. It is possible to carry out the calculation by converting all quantities (in U and in the phonon excitations) back to the fixed coordinate system. However, the result is very complicated. A simpler result can be obtained by evaluating the overlap in the rotating coordinates using appropriate commutation relations between phonon operators at different points on the trough.[19] The resulting overlap between the phonon parts of the wave function at two points on the trough can be obtained from Eqs. (19) and (21) of Ref. 19 (obtained for the $p^2 \otimes h$ system) putting $f=t=0$, giving

$$O(p,q,r,s) = \langle\theta'^p,\epsilon'^q|U(\Omega_l)^\dagger U(\Omega_r)|\theta'^r,\epsilon'^s\rangle, \tag{16}$$

where

$$O(p,q,r,s) = e^{-\rho^2/2}\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\sum_{l=0}^{p}\sum_{m=0}^{r}\frac{(-1)^{i+j}\left(\dfrac{\rho}{\sqrt{2}}\right)^{i+j+l+m}\sqrt{r!p!(r-m+j)!(p-l+i)!}}{i!j!l!m!(r-m)!(p-l)!}\langle\theta'^{p-l+i},\epsilon'^q|\theta'^{r-m+j},\epsilon'^s\rangle \tag{17}$$

with

$$\langle\theta'^p,\epsilon'^q|\theta'^r,\epsilon'^s\rangle = \sum_{j=0}^{\min(q,r)}\sum_{m=0}^{\min(s,q-j)}\sqrt{p!q!r!s!}A^{r-j}_{\theta\theta}A^{s-m}_{\theta\epsilon} \times A^{p-r+j-s+m}_{\theta 6}A^{j}_{\epsilon\theta}A^{m}_{\epsilon\epsilon}A^{q-j-m}_{\epsilon 6}\delta(p+q,r+s), \tag{18}$$

where δ is the Kronecker δ function and $A^i_{mn} = (X_{mn})^i/i!$, with

$$X_{mn} = \sum_\lambda D_{m\lambda}(\Omega_l)D_{n\lambda}(\Omega_r). \tag{19}$$

The overlap between the electronic states at points Ω_l and Ω_r can be written as

$$\psi_g(\Omega_l)^*\psi_g(\Omega_r) \equiv Z = (2-\delta')Z_1 + (2+\delta')Z_2 \tag{20}$$

where Z_1 and Z_2 are functions of the angular variables (but not δ') and relate to the T and H parts of the electronic states, respectively. The total overlap integral involving the state in Eq. (13) with itself is thus

$$O^{\text{tot}}_{L,M,K}(r,s) = (2-\delta')O_{L,M,K}(Z_1,r,s,r,s) + (2+\delta')O_{L,M,K}(Z_2,r,s,r,s), \tag{21}$$

where

$$O_{L,M,K}(G,p,q,r,s) = \int G\Phi^{(L,M,K)*}_{\text{rot}}(\Omega_l)\Phi^{(L,M,K)}_{\text{rot}}(\Omega_r) \times O(p,q,r,s)d\Omega_l d\Omega_r. \tag{22}$$

The matrix elements of $\mathcal{H}$ are somewhat more complicated to calculate. When evaluating the terms in the rotating coordinate system it is necessary to include "excitations" in Q'_4, Q'_5, and Q'_6 for the purposes of the calculation, even though these modes correspond to rotations. After some algebra, it is found that the matrix elements of $\mathcal{H}_{\text{int}}$ are

$$\begin{aligned}M_{\text{int}} = \frac{k}{\sqrt{2}}\sqrt{4-\delta'^2}\Big[&\sqrt{r}O_{L,M,K}(Z_{12},r,s,r-1,s)\\ &+\sqrt{r+1}O_{L,M,K}(Z_{12},r,s,r+1,s) + \sqrt{p}O_{L,M,K}((1-X_{\theta\theta})\\ &\times Z_{12},r-1,s,r,s) - \sqrt{q}O_{L,M,K}(X_{\epsilon\theta}Z_{12},r,s-1,r,s)\\ &-\frac{\rho}{\sqrt{2}}O_{L,M,K}((3-X_{\theta\theta})Z_{12},r,s,r,s)\Big],\end{aligned} \tag{23}$$

where $Z_{12}=Z_1+Z_2$, the matrix element of $\mathcal{H}_{\text{vib}}$ is

$$\begin{aligned}M_{\text{vib}} = &\left(\frac{5}{2}+r+s+\frac{\rho^2}{2}\right)O_{L,M,K}(Z,r,s,r,s)\\ &-\frac{\rho}{\sqrt{2}}[\sqrt{r}O_{L,M,K}(Z,r,s,r-1,s)\\ &+\sqrt{r+1}O_{L,M,K}(Z,r,s,r+1,s)],\end{aligned} \tag{24}$$

and the matrix element of $\mathcal{H}_{\text{term}}$ is

$$M_{\text{term}} = \delta(2-\delta')O_{L,M,K}(Z_1,r,s,r,s). \tag{25}$$

The energies of the states are thus

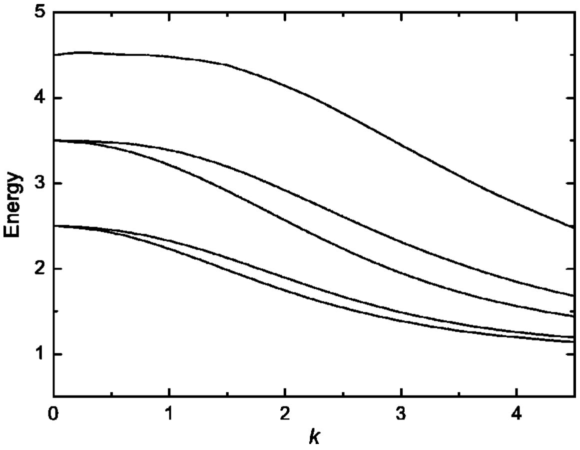

FIG. 1. Relative energies for some states with vibrational quantum numbers $\{r,s\}=\{0,0\}$ plotted as a function of the coupling strength k and in units of $\hbar\omega$. The results shown are for the rotational quantum number L from 1 to 5, in ascending order according to the values of energy in strong coupling, and with the lowest possible value of K in each case (namely $K_{\min}=0$ for L odd and 2 for L even).

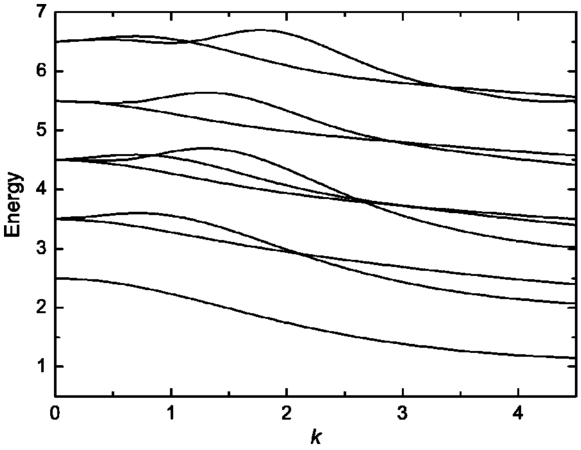

FIG. 2. Relative energies for states with rotational quantum numbers $L=1$ and $K=0$ plotted as a function of the coupling strength k and in units of $\hbar\omega$. The smooth curves are for the vibrational quantum numbers $\{r,s\}=\{0,0\}$, {1,0}, {0,1}, {2,0}, {1,1}, {0,2}, {2,1}, {0,3}, and {1,3} in ascending order in strong coupling.

$$E_{L,M,K}(r,s)=\frac{M^{\text{int}}_{L,M,K}(r,s)+M^{\text{vib}}_{L,M,K}(r,s)+M^{\text{term}}_{L,M,K}(r,s)}{O^{\text{tot}}_{L,M,K}(r,s)}. \tag{26}$$

We now have analytical expressions for the energies of the rotational-vibronic states in terms of integrals over $\Omega_l \equiv\{\theta_l,\phi_l,\gamma_l\}$ and $\Omega_r\equiv\{\theta_r,\phi_r,\gamma_r\}$. In fact, the integrals all involve $(\phi_l-\phi_r)$ and not $(\phi_l+\phi_r)$. This leaves five-dimensional integrals which must be evaluated numerically. The integrals depend upon the trough radius ρ, which in turn depends upon both the coupling strength k and the term splitting δ. Hence the integrals must be evaluated separately for different values of k and δ. We evaluate the integrals using standard (NAG) numerical library routines implementing an adaptive quadrature method. Most of the integrals can be evaluated to an accuracy of 0.001 without any difficulties. However, the integrals required for some of the higher excited states contain high order trigonometric functions of the angular parameters and are thus highly oscillating, especially for states with higher quantum numbers. This means that the results are rather unstable for certain values of k, resulting in very different answers when the requested accuracy is changed or when the value of k is varied slightly. This is clearly not physical. Fortunately, it is clear from the results where such instabilities cause difficulties.

VII. RESULTS

In order to understand the complicated results for this JT system, we will first look at the case of zero term splitting. We will present results for a range of lower-lying excited states, although it should be noted that energies have been obtained for many more excited states than those shown in the figures in this paper. Figure 1 shows the energies as a function of the coupling constant k for states with no vibrational excitations ($\{r,s\}=\{0,0\}$). The results plotted are for the lowest possible value of the rotational quantum number K for a given L, namely $K_{\min}=0$ for L odd and 2 for L even. The results are calculated for $M=0$, although the energies do not depend on the value of M. Results for L from 1 to 5 are plotted relative to the energy at the bottom of the trough given in Eq. (5) in units $\hbar\omega=1$. It should be noted that the shift transformation method upon which the results are based is targeted for solving strongly coupled JT problems, and the states do not all tend to appropriate limits in weak coupling. Similar behavior has been seen previously in other JT systems analyzed using the shift transformation method.[19,27] However, it can be seen that the ground state starts at a relative energy of $\frac{5}{2}\hbar\omega$ in weak coupling and progresses to a relative energy of $\hbar\omega$ in strong coupling. These are the expected zero-point energies for the two limits, which correspond to five vibrations and two vibrations plus three rotations, respectively. The excited rotational states also all converge towards the limit of $\hbar\omega$ in strong coupling. This is expected as these states are vibrational ground states ($\{r,s\}=\{0,0\}$) in this limit. As the coupling strength weakens but before the model breaks down, it can be seen that the excited states are tending towards limits which are integral numbers of $\hbar\omega$ above the ground state. This is because the states are excited vibrational states in weak coupling, where there is no JT effect and simply a five-dimensional potential well centered on the origin. Figure 2 shows equivalent results to Fig. 1 for states with $L=1$, $K=0$ and up to four phonon excitations in strong coupling. It can be seen that the curves with phonon excitations roughly follow that of the $\{1,M,K_{\min}\}$ state with no excitations, again consistent with the rotation-vibration interpretation.

We will now look at results for a finite value of the electronic term splitting δ. An interesting feature of a nonzero term splitting is that, as stated in Sec. III, the minimum position of the APES is at the origin in Q space for $\delta'>2$, and hence for the weakly coupled region in which $k^2<\delta/2$. This means that the JT effect is totally quenched by the presence

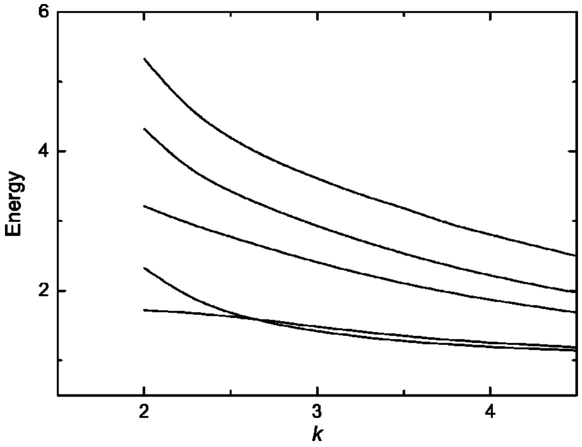

FIG. 3. Relative energies for states with vibrational quantum numbers $\{r,s\}=\{0,0\}$ calculated with the inclusion of term splitting $\delta=5.9$ plotted with respect to coupling strength k and in units of $\hbar\omega$. The rotational quantum numbers for these states are $\{L,M,K\}\equiv\{L,M,K_{\min}\}$ with L from 1 to 5, in ascending order according to the values of energy in strong coupling.

of the electronic splitting term until the vibronic coupling is sufficiently large to overcome it. For this reason, the energy curves can only be calculated for $k>\sqrt{\delta/2}$ (in units where $\hbar\omega=1$). We will choose $\delta=0.191$ eV by reference to Table 9 (model 3) of Nikolaev *et al.*,[25] which corresponds to $\delta\approx 5.9\hbar\omega$ in terms of the accepted value of 260 cm^{-1} for the vibrational frequency of the strongest coupled JT-active h_g mode. This means that the curves can be plotted for $k>1.7$. However, the energies cannot be calculated reliably for values of k close to $\sqrt{\delta/2}$ so the curves are plotted for $k>2$ in most cases, and $k>2.5$ for two of the higher-excited states. Figure 3 shows results for the states with no vibrations (vibrational quantum numbers $\{r,s\}=\{0,0\}$) but rotational excitations, and Fig. 4 shows results for the states with the lowest rotational quantum numbers $L=1$ and $K=0$, and different vibrational excitations.

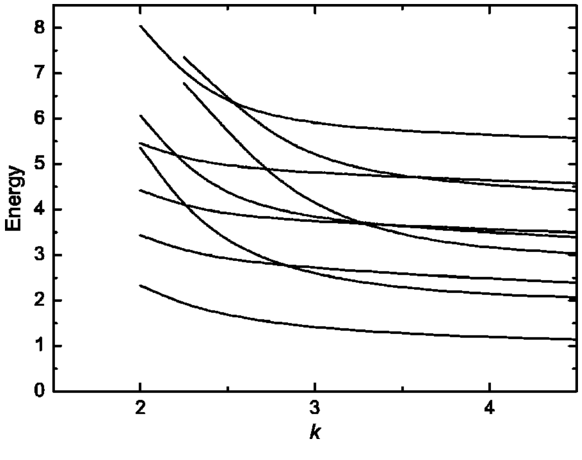

FIG. 4. Relative energies for states with rotational quantum numbers $L=1$ and $K=0$ calculated with the inclusion of term splitting $\delta=5.9$ plotted with respect to coupling strength k and in units of $\hbar\omega$. The vibrational quantum numbers for these states are $\{r,s\}=\{0,0\}$, {1,0}, {0,1}, {2,0}, {1,1}, {0,2}, {2,1}, {0,3}, and {1,3} in ascending order in strong coupling.

The general behavior of the energy curves in strong coupling is similar to that found in the absence of any term splitting. This is because the JT coupling dominates over the term splitting in this limit. However, the energies of those states that have a significant component coming from the P states increase quite substantially in weak coupling compared to the case of no term splitting. This is where the JT effect no longer dominates over the term splitting. In weak coupling, the {2,0,2} state is higher in energy than the {1,0,0} state. This is to be expected because δ has been taken to be positive, and so the P state is higher in energy than the D state with no JT coupling.

Very few other calculations have been made of the energies of the $p^3\otimes h$ JT system with which our results can be compared. References 17 and 18 give results for the energies of the lowest ^2P and ^2D states. These correspond to our $\{r,s\}=0$ and $\{L,M,K\}=\{1,M,0\}$ and $\{2,M,2\}$ states, respectively. They calculate their results using a Lanczos numerical diagonalization procedure, and give energies as a function of the coupling constant both for zero term splitting and for a term splitting corresponding to $\delta=2\hbar\omega$. Unfortunately, it is unclear exactly what the energies have been plotted relative to in their figures, which makes a quantitative comparison difficult. However, it can be seen that when the term splitting is zero, the energies of their ^2P and ^2D states coincide at zero coupling and the difference in energy between these two states remains small at all couplings, with the ^2D state always above the ^2P state. This is the same behavior we observe in Fig. 1. Their results with a term splitting of $\delta=2\hbar\omega$ are also qualitatively similar to ours with $\delta=5.9\hbar\omega$; the ^2P term is significantly higher in energy than the ^2D term in weak coupling, but the energies cross as the coupling strength increases so that the ^2P state is slightly lower in energy than the ^2D state in strong coupling. One difference is that they plot their results down to a JT coupling strength of zero, which as we explain above is not appropriate with our method of calculation.

VIII. THE EFFECT OF STRAIN

We will now consider the effect of $\mathcal{H}_{\text{strain}}$ as a perturbation on the states in Eq. (13). The dynamical nature of the JT effect means that without any strains present, the average $\langle Q_\lambda\rangle$ of one (or more) of the collective displacements will be zero. Equivalently, the average $\langle\sigma_\lambda\rangle$ of the corresponding electronic operator σ_λ will be zero.[2,20,28] According to standard results, the thermal average of σ_λ at a temperature T can be given by the expression

$$\langle\sigma_\lambda\rangle=\frac{\sum_n\langle\psi_n|\sigma_\lambda|\psi_n\rangle e^{-E_n/k_BT}}{\sum_n e^{-E_n/k_BT}},\qquad(27)$$

where n is summed over all of the states ψ_n of the system (with energy E_n). Thus we expect to find $\langle\psi_n|\sigma_\lambda|\psi_n\rangle=0$. In our case, if strain is considered to zeroth order, the states $\psi_n\equiv\psi_n^{(0)}$ are the wave functions $\Psi(L,M,K,r,s)$. Mathematically it is found that the matrix elements

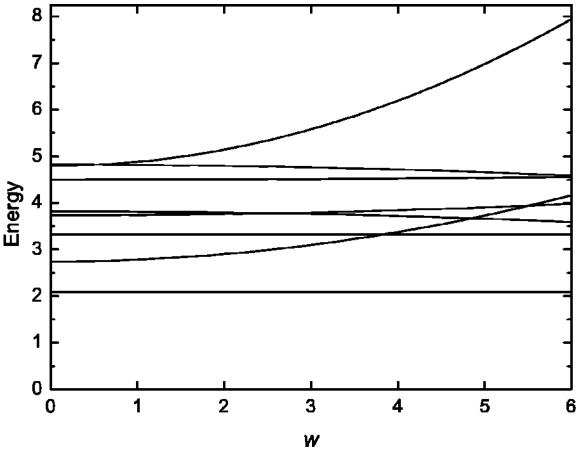

FIG. 5. Energy levels of states with rotational quantum numbers $\{L,M,K\}=\{3,M,K_{\min}\}$ to second order in perturbation theory as a function of positive strain w for a coupling constant $k=3.5$ and term splitting $\delta=5.9$ in units of $\hbar\omega$. The vibrational numbers $\{r,s\}$ are {0,0}, {0,1}, {1,0}, {1,1}, {0,2}, {2,0}, {0,3}, and {2,1}, respectively, for the curves in an ascending order when $w=0$.

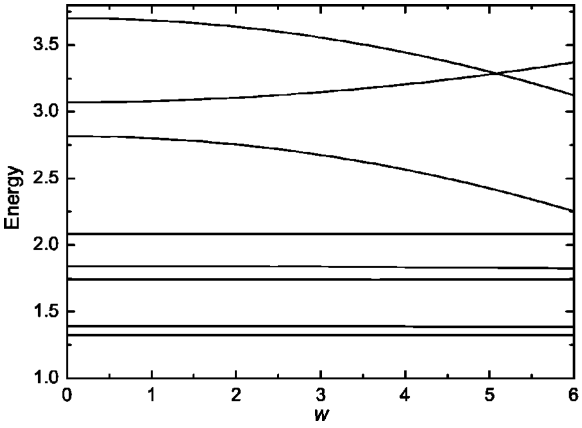

FIG. 6. Energy levels of states with vibrational quantum numbers $\{r,s\}=\{0,0\}$ to second order in perturbation theory as a function of positive strain w for a coupling constant $k=3.5$ and term splitting $\delta=5.9$ in units of $\hbar\omega$. The rotational numbers $\{L,M,K\}$ are $\{1,M,0\}$, $\{2,M,2\}$, $\{4,M,4\}$, $\{3,M,2\}$, $\{3,M,0\}$, $\{5,M,2\}$, $\{5,M,0\}$, and $\{6,M,2\}$, respectively, for the curves in an ascending order when $w=0$.

$\langle\Psi(L,M,K,r,s)|\sigma_\theta|\Psi(L,M,K,r,s)\rangle$ are indeed zero, as expected to preserve the zero values for the thermal averages in the absence of strain. One further consequence of this is that strain can have no effect on the energies of the states to first order in perturbation theory, as the perturbation corrections contain the same matrix elements $\langle\Psi(L,M,K,r,s)|\sigma_\theta|\Psi(L,M,K,r,s)\rangle$.

We will, therefore, calculate the energies $E_n=E_n^{(0)}+E_n^{(2)}$ to second-order perturbation theory, where $E_n^{(0)}$ is the energy without strain and

$$E_n^{(2)} = w^2\sum_{i\neq n}\frac{|\langle\psi_n^{(0)}|\sigma_\theta|\psi_i^{(0)}\rangle|^2}{E_n^{(0)}-E_i^{(0)}}, \tag{28}$$

where n is summed over all allowed values of L, M, j, r, and s. The results for $w>0$ are shown in Figs. 5 and 6. It can be seen that some of the energies increase with strain, some decrease, and some are almost independent of strain. This is because some points on the lowest APES increase their energy with strain, some decrease and some stay the same. It should be noted that the energies are plotted relative to the same energy zero as without strain. Results can also be obtained for $w<0$, which need not be the same as for $w>0$ as the matrix elements and energies in Eq. (28) can have different values.

IX. CONCLUSIONS

In this paper, we have analyzed the $p^3\otimes h$ JT system using a semianalytical method, whereby analytical expressions are obtained for the energy levels and eigenstates which are then evaluated numerically. The form of the wave functions allows the motion of the system to be understood in terms of a composition of vibrations and rotations. The method can be used to determine energies of a wide range of states with rotational and vibrational excitations over a range of coupling strengths. These will be of use in interpreting the results of any experiments that probe the vibronic spectrum of fullerene ions, such as various spectroscopic measurements. A precise value for the strength of the intermlecular JT coupling in fullerene anions is not yet known either experimentally or theoretically. Although our method fundamentally assumes strong coupling, reasonable results can be obtained in intermediate coupling, and for some states even in weak coupling. Hence our results can be expected to apply to these real problems as long as the JT coupling is not significantly smaller than the term splitting (when there is no JT distortion as shown in Sec. III). Also, they may apply to icosahedral molecules other than C_{60}. It will be interesting to compare our results with numerical ones (e.g., from a Lanczos diagonalization) if they become available in the future.

The formulas as presented in this paper, are for coupling to a single h_g mode only, whereas a real C_{60} molecule is coupled to eight different h_g modes of vibration. If the JT couplings are not too strong and the spread of frequencies is not too large, it is possible to view the vibronic coupling problem in terms of a single effective mode,[31,32] in which case our formalism is appropriate as it stands. However, in fullerenes the JT couplings are of intermediate strength with a wide spread of frequencies, and so it will be more appropriate to consider all eight modes explicitly.[17,33] Our results can easily be expanded to include all eight modes by introducing appropriate sums into the formulas. However, there will then be eight coupling constants and eight frequencies, which make the results much harder to interpret.

Our results considering the effect of strain are important because cooperative JT effects between C_{60}^{3-} anions can be modeled as an effective strain. Cooperative effects can be expected to result in a nonzero static distortion $\langle Q_\lambda\rangle$ and equivalently a nonzero value for $\langle\sigma_\lambda\rangle$. When the states ψ_n are taken to second order in perturbation theory (or higher), the $\langle\sigma_\lambda\rangle$ are still zero for $\lambda\neq\theta$ but $\langle\sigma_\theta\rangle$ is nonzero. In other (simpler) JT systems, such as the cubic $E\otimes e$ system, the thermal average increases with increasing strain until it saturates at a maximum value for large strains.[20] Furthermore, a larger strain is needed to produce the maximum thermal average at higher temperatures than at lower ones. Similar behavior can be expected in this system, although to do this it is necessary to consider the whole range of strains from very weak to very strong (compared to the strength of the JT coupling).

The general problem of a strained environment in a JT system with a trough of minimum-energy points, as in C_{60}^{3-}, is difficult to solve accurately by theoretical means. The strain will lower some of the minimum-energy points below others. If the strain is strong, distinct wells will be produced and one or more of the pseudorotational modes in the absence of strain will be converted to a vibration. The system can then be analyzed using well-developed techniques, including taking into account the effects of anisotropy in the wells, and the results used to determine the thermal average $\langle \sigma_\theta \rangle$. However, for weaker strains the wells in the APES will be shallow and a description in terms of simple vibrations will not be appropriate. The pseudorotations then become hindered rotations in which there is a preference for the system to be localized near one of the wells but the overall motion is still a rotation. It is hoped that our results can later be combined with results for a strong strain to give a full description of the JT effects experienced by C_{60}^{3-} ions in a strained environment. This in turn will help explain some of the interesting features of, for example, the A_3C_{60} fullerides.

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[1] I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals* (Springer, Berlin, 1989).

[2] M. D. Kaplan and B. G. Vekhter, *Cooperative Phenomena in Jahn-Teller Crystals* (Plenum Press, New York, 1995).

[3] G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. **38**, 1 (1975).

[4] T. Kawamoto, M. Tokumoto, H. Sakamoto, and K. Mizoguchi, J. Phys. Soc. Jpn. **70**, 1892 (2001).

[5] O. Gunnarsson, Rev. Mod. Phys. **69**, 575 (1997).

[6] L. Forró and L. Mihály, Rep. Prog. Phys. **64**, 649 (2001).

[7] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, New York, 1996).

[8] C. M. Varma, J. Zaanen, and K. Raghavachari, Science **254**, 989 (1991).

[9] N. Breda, R. A. Broglia, G. Colò, H. E. Roman, F. Alasia, G. Onida, V. Ponomarev, and E. Vigezzi, Chem. Phys. Lett. **286**, 350 (1998).

[10] O. Gunnarsson, H. Handschuh, P. S. Bechthold, B. Kessler, G. Ganteför, and W. Eberhardt, Phys. Rev. Lett. **74**, 1875 (1995).

[11] A. S. Alexandrov and V. V. Kabanov, Pis'ma Zh. Eksp. Teor. Fiz. **62**, 920 (1995) [JETP Lett. **62**, 937 (1995)].

[12] I. D. Hands, J. L. Dunn, and C. A. Bates, Phys. Rev. B **63**, 245414 (2001).

[13] L. F. Chibotaru, A. Ceulemans, and S. P. Cojocaru, Phys. Rev. B **59**, R12728 (1999).

[14] Y. Iwasa and T. Kaneyasu, Phys. Rev. B **51**, 3678 (1995).

[15] P. W. Stephens, L. Mihaly, P. L. Lee, R. L. Whetten, S. M. Huang, R. Kaner, F. Deiderich, and K. Holczer, Nature (London) **351**, 632 (1991).

[16] A. Auerbach, N. Manini, and E. Tosatti, Phys. Rev. B **49**, 12998 (1994).

[17] C. C. Chancey and M. C. M. O'Brien, *The JT Effect in* C_{60} *and Other Icosahedral Complexes* (Princeton University Press, Princeton, NJ, 1997).

[18] M. C. M. O'Brien, Phys. Rev. B **53**, 3775 (1996).

[19] S. Sookhun, J. L. Dunn, and C. A. Bates, Phys. Rev. B **68**, 235403 (2003).

[20] L. F. Feiner, J. Phys. C **15**, 1495 (1982).

[21] D. R. Pooler, J. Phys. C **13**, 1029 (1980).

[22] J. L. Dunn, M. R. Eccles, Y. M. Liu, and C. A. Bates, Phys. Rev. B **65**, 115107 (2002).

[23] F. G. Anderson, F. S. Ham, and G. Grossman, Mater. Sci. Forum **83–87**, 475 (1984).

[24] A. Ceulemans, Top. Curr. Chem. **171**, 27 (1994).

[25] A. V. Nikolaev and K. H. Michel, J. Chem. Phys. **117**, 4761 (2002).

[26] S. A. Borshch and K. Prassides, J. Phys. Chem. **100**, 9348 (1996).

[27] J. L. Dunn and M. R. Eccles, Phys. Rev. B **64**, 195104 (2001).

[28] J. L. Dunn, Phys. Rev. B **69**, 064303 (2004).

[29] U. Öpik and M. H. L. Pryce, Proc. R. Soc. London **238**, 425 (1957).

[30] P. R. Bunker and P. Jensen, *Molecular Symmetry and Spectroscopy* (NRC Research Press, Ottawa, Ontario, Canada, 1998).

[31] M. C. M. O'Brien, J. Phys. C **16**, 6345 (1983).

[32] L. F. Chibotaru, J. Phys. A **27**, 6919 (1994).

[33] N. Manini and E. Tosatti, Phys. Rev. B **58**, 782 (1998).