Dynamic Jahn-Teller effect in C_{60}: Self-trapped excitons and resonant Raman scattering

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The dynamic Jahn-Teller problem is solved for the lowest triplet and singlet self-trapped excitons of C_{60}. The resultant tunnel-split $^3T_{3g}\oplus^3T_{1g}$ states provide a good explanation for the available experimental data on the lowest triplet states. The observable consequences of this dynamical symmetry breaking in the photoinduced multiphonon resonant Raman scattering are explored in detail. The tunneling splitting itself should show up in the Raman spectrum, and the depolarization ratio (which can be normal or unusual, depending on exciting frequencies) is calculated explicitly.

The discovery and synthesis of fullerene[1] C_{60} has triggered an explosion of research into its physical and chemical properties,[2] including a wide range of novel phenomena [such as superconductivity in alkali-metal-doped C_{60} (Ref. 3) and various potential applications (e.g., nonlinear optics,[4] optical limiter,[5] and charge transfer in composites with polymers[6]). One of the salient features of this third allotropic form of carbon is the presence of the highest point group symmetry, I_h, which, however, is readily subject to a Jahn-Teller effect (JTE) due to the electron-phonon (e-ph) coupling.[7] Under various JTE environments, both static Jahn-Teller (SJT) distortions and a dynamic Jahn-Teller effect (DJTE) can be observed. The coherent states (in the sense of coherent superpositions) formed in the DJTE, which dynamically restore the higher symmetry due to quantum fluctuations among a number of degenerate SJT distorted configurations,[8,9] strongly influence many intrinsic physical and chemical properties of C_{60}.

A series of experimental and theoretical studies has been devoted to understanding the nature of the JTE in various nonlinear excitations of C_{60} and its charged species.[10–23] For $C_{60}{}^-$, optical observations of phonon progressions clearly show the JT distortions, while the electron spin resonance (ESR) line shape demonstrates their dynamic nature.[10] The SJT problem of $C_{60}{}^-$ has been considered in different theoretical approaches,[11,12] and results in a D_{5d} symmetry-broken configuration. Quantum fluctuations among the six degenerate D_{5d} configurations have also been taken into account, to predict $^2T_{1u}\oplus^2T_{3u}$ tunnel-split states[13] and observable effects in the infrared (ir) absorption.[14] For the lowest parity-forbidden singlet self-trapped exciton (STE) of C_{60}, the solution of the SJT problem[12] yields good agreement with experiment.[15] Recently, due to its importance in photophysics and its relevance to the optical performance of C_{60},[5] much attention has been given to the long-lived lowest triplet STE originating from the highly efficient intersystem crossing out of the lowest singlet STE.[16–19] This triplet STE possesses an energy of 1.55–1.70 eV, a nearly unit quantum yield of formation, and a relatively long lifetime on the order of 1.0 ms (40 μs–2.5 ms) (compared with the $\sim$1.0 ns lifetime of the singlet STE).[16,17] As indicated by the nonvanishing zero-field-splitting (ZFS) and spin-polarized ESR signals in ESR and absorption-detected magnetic resonance (ADMR), the symmetry of C_{60} in this excited state must be lower than I_h.[16–19] Meanwhile, a partial dynamic averaging of the dipolar splitting due to a fast pseudorotation has been suggested to explain the ESR and ADMR patterns.[17–19] Furthermore, the temperature dependence of the magnetic resonances in ESR and ADMR reveals two different triplet states with about 10 meV energy splitting and different ZFS's.[17–19] To date, no quantitative theoretical study has been carried out to solve either the SJT or the DJT problem for the triplet STE to our knowledge.

In this paper, using the solutions of the SJT and DJT problems, we describe a framework for interpreting the existing experimental results on the lowest STE's in C_{60}, and predict some intrinsic observable consequences of the JTE, especially for resonant Raman spectra (RRS). Our discussions are mainly focused on the triplet STE in view of its long lifetime. First, using the Bogoliubov–de Gennes (BdG) formalism,[20] we solve the $T_{1u} \otimes 8h_g$ SJT problem for the triplet STE within a Peierls-Hubbard model.[12] Then the coherent states under the DJTE are obtained for both triplet and singlet STE's using a standard perturbation approach,[9] and are used in turn to interpret the observed tunneling splitting and ZFS. Finally, the observable consequences of this dynamic symmetry breaking of the triplet STE are manifested in the calculated multiphonon RRS, where the tunnel splitting shows up as the satellite separation and the depolarization ratio (which can be either normal or unusual, depending on the excitation frequencies) is calculated explicitly. Rigorous symmetry considerations are used to make these predictions.

The model Hamiltonian and its parameter set which we adopt are the same as described in our earlier publications.[12,21] They yield correct geometrical, electronic, and vibrational structures for the I_h ground state of C_{60}. The ten Raman-active modes ($2a_g + 8h_g$) are illustrated in Fig. 1(a), and are consistent with previous studies,[22,23] while the four ir-active modes ($4t_{1u}$) are given in Fig. 1(a) of Ref. 14. Within the self-consistent BdG formalism, as an outcome of the $T_{1u}\otimes 8h_g$ SJT problem, the symmetry of the SJT distorted C_{60} is identified to be D_{5d} for both singlet[12] and triplet STE's derived from the electronic $H_u \rightarrow T_{1u}$ transition. The energies of the singlet and triplet STE's are 1.93 and 1.73 eV with 0.09 and 0.31 eV as binding energies, respectively, and are consistent with experimental observations.[15–17] Considering the correlation relations between I_h and D_{5d} groups (i.e., $T_1 = A_2 + E_1, H = A_1 + E_1 + E_2$, etc.), the highest occupied molecular orbital (HOMO) H_u electronic level in I_h is split to $A_{1u} + E_{1u} + E_{2u}$, while lowest unoccupied molecular orbital (LUMO) T_{1u} is split to $A_{2u} + E_{1u}$ with 0.13 and 0.27 eV SJT energy splitting between A_{1u} and E_{1u}, A_{2u} and E_{1u}, respectively. Meanwhile, the I_h phonon structure, $2a_g + 3t_{1g} + 4t_{3g} + 6g_g + 8h_g + a_u + 4t_{1u} + 5t_{3u} + 6g_u + 7h_u$ is changed to $10a_{1g} + 7a_{2g} + 17e_{1g} + 18e_{2g} + 8a_{1u} + 9a_{2u} + 17e_{1u} + 18e_{2u}$ in the D_{5d} SJT distorted C_{60}, where a_{1g}, e_{1g}, and e_{2g} become Raman active, while a_{2u} and e_{1u} are ir active. The calculated single-phonon resonant Raman spectra of the triplet STE are shown in Figs. 1(b) and 1(c) for two different exciting frequencies in resonance.

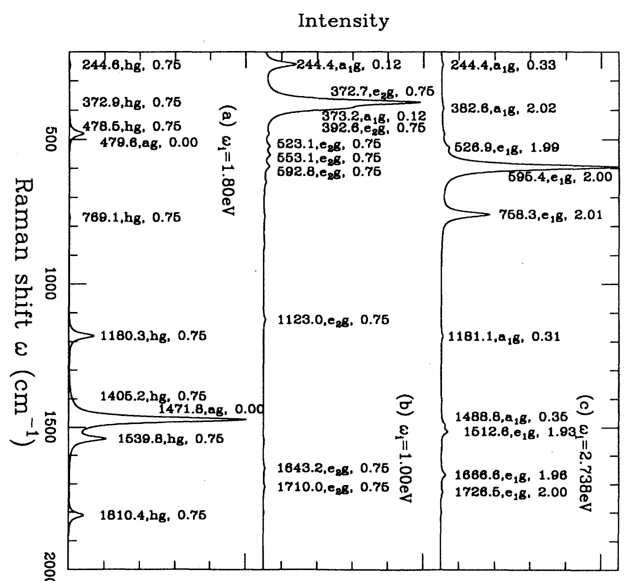

FIG. 1. Predicted single-phonon Raman spectrum of the ground state (a) and the SJT distorted STE state (b) and (c). The frequency, irreducible representation, and depolarization ratio ρ are indicated for each peak. The strengths are normalized to the highest peaks, and the Lorentzian broadening is 10 cm^{-1}.

Now consider the DJTE due to quantum fluctuations between the six degenerate D_{5d} SJT distorted configurations.[9,13] The quantum tunneling between the six minima involves the self-consistent lattice plus π-electron state, and the resultant coherent excitonic state should belong to a certain irreducible representation of the parent I_h group. The coherent state wave function can be written as

$$|\Psi_k\rangle = \sum_\alpha B_k^\alpha \; |e^\alpha\rangle \otimes |n^\alpha\rangle \quad , \tag{1}$$

where $\alpha = 1, 2, ..., 6$ is the index of the D_{5d} SJT states, and $|e^\alpha\rangle$ and $|n^\alpha\rangle$ are the electronic and phonon wave functions at the αth minimum, respectively. The states with different α are related through proper fivefold rotations. The coefficients B_k^α are determined through

$$\| \langle \Phi_{\beta'} \, |H| \, \Phi_\beta \rangle - E \, \langle \Phi_{\beta'} \, | \Phi_\beta \rangle \| = 0 \quad , \tag{2}$$

with $|\Phi_\beta\rangle = |e^\alpha\rangle \otimes |n^\alpha\rangle$, and H the full Hamiltonian of the system including quantum fluctuations.[13] Note that both the electronic and vibrational wave functions for any pair of D_{5d} STE configurations are nonorthogonal. This nonorthogonality breaks the degeneracy in the SJTE with a tunneling splitting $\delta_{t(s)}$ for the triplet and singlet STE's, and gives rise to multiphonon characteristics. There exist two types of symmetries for the tunnel-split coherent states, i.e., $T_3 \oplus T_1$ and $A \oplus H$.[13] It can be proved that the singly charged anion or the lowest exciton state belongs to the type $T_1 \oplus T_3$. The resulting coherent excitonic states are $^3T_{3g} \oplus ^3T_{1g}$ and $^1T_{3g} \oplus ^1T_{1g}$ for the triplet and singlet STE's with tunneling splittings $\delta_t = 0.010$ eV and δ_s=0.012 eV between lower T_{3g} and higher T_{1g} states. The B_k^α coefficients are listed in Table I of Ref. 13 with the total overlap integrals $S = -0.012$ and -0.013 for triplet and singlet STE, respectively. Now we present our physical interpretation of the experiments on the triplet STE.

First, it is clear that neither the mechanism without including the JTE nor that including only the SJTE can explain the existence of thermally activated tunnel splitting and nonvanishing ZFS. On the contrary, the 0.010 eV tunneling splitting δ_t, predicted in the above DJTE study, can provide not only a *qualitative* but also a *quantitative* interpretation for the observed 9–17 meV thermal activation energy for the second triplet signal in

ESR and ADMR.[17–19] We notice that the lowest triplet $^3T_{3g}$ and its tunnel-split excited $^3T_{1g}$ states cannot be linked through any direct dipole-allowed vibronic transition. Meanwhile, the dynamics of the triplets, i.e., the fast pseudorotation of the D_{5d} configurations in $^3T_{3g}$ and $^3T_{1g}$ states (not a single D_{5d} state) can explain the thermodynamics of magnetic resonance spectra.[17–19] In addition, the observed nearly unit quantum transition rate from singlet to triplet STE's ($^1T_{3g} \rightarrow ^3 T_{3g}$) can also be explained as a consequence of the DJTE, since including spin-orbit (SO) coupling and spin dipole interaction the nonradiative intersystem crossing can easily be achieved without further invoking symmetry breaking and large lattice relaxation.

Second, let us consider the spin distribution and spin dipole interaction in the triplet STE $^3T_{3g}$ and $^3T_{1g}$ states to estimate the observed nonzero ZFS. The spin density distribution in $^3T_{3g}$ and $^3T_{1g}$ can be derived under the DJTE as $\sigma_i^z(^3T_{3g};^3T_{1g}) = \sum_{k,k' \in ^3T_{3g};^3T_{1g}} \langle \Psi_{k'} | \hat{\sigma_i^z} | \Psi_k \rangle$. It is found that the symmetry of spin density distributions in both the $^3T_{3g}$ and $^3T_{1g}$ states is almost C_{2h}. In contrast, for the SJTE, the symmetry is D_{5d} and 95% of the exciton spins reside at the equator perpendicular to the fivefold axis. Then we can estimate the ZFS within the usual approximations adopted in two-dimensional molecular systems.[24] The results are $|D| = 0.0090$ cm^{-1}, $|E| = 0.0$ cm^{-1} for the SJT case; $|D(^3T_{3g})| = 0.0221$ cm^{-1}, $|E(^3T_{3g})| = 0.0021$ cm^{-1}; $|D(^3T_{1g})| = 0.0201$ cm^{-1}, $|E(^3T_{1g})| = 0.0021$ cm^{-1}. Thus $|D|$ is larger for the DJTE and $|E|$ does not vanish, when compared with the static case. However, the observed relations $|D_1| > |D_2|$ and $|E_1| < |E_2|$ (Refs. 17, 19) cannot be explained quantitatively even by considering the DJTE, since we do not see any qualitative symmetry difference of spin distribution between the two triplets. Another intrinsic factor, the SO coupling (which is absent in the present model), might differentiate the two triplets, since $^3T_{1g}$ belongs to the rotation symmetry species of I_h, which are necessarily subject to SO coupling,[24] whereas $^3T_{3g}$ does not belong to the rotation symmetry species and may not be subject to SO coupling. As suggested by Wei and Vardeny,[17] another extrinsic effect, random strains in the matrices used to isolate C_{60} molecules, should also be taken into account in the explanation of the magnetic spectra since it can further split the tunnel-split states.[9]

To manifest the DJTE of STE's in C_{60}, the nonorthogonality between the components of the coherent states should also be considered. Due to the relatively small overlap and large lattice relaxation between any pair of D_{5d} states, compared with C_{60}^-,[13] the multiphonon effects arising from this nonorthogonality are unlikely to be observable in nonresonant single-photon measurements (uv or ir absorption).[25] However, as shown below, several characteristic features of the DJTE will appear in the resonant two-photon measurement, i.e., photoinduced resonant Raman scattering. The first feature of the DJTE for the triplet STE is the appearance of an unusual depolarization ratio and its dispersion with the incident photon energy ω_i, as illustrated in Figs. 1(b) and 1(c) even for the SJTE. For the ω_i=2.738 eV resonance, which corresponds to the electronic transitions between E_{1g}, A_{1g} (split from H_g, HOMO+2 in I_h) and A_{2u} (split from T_{1u} of I_h), the depolarization ratio, defined as $\rho = (3G^s + 5G^a)/(10G^0 + 4G^s)$, where G^0, G^s, and G^a are the three Placzek constants,[26] is much larger than the usual nonresonant case [$\rho \leq 0.75$ (Ref. 26)] for e_{1g} phonon modes at 595.4 and 758.3 cm^{-1}. This behavior can be seen from the antisymmetric Raman tensor:

$$\alpha_{zx} = \frac{\langle f \, | r_s^z | \, m_2 \rangle \langle m_2 \, | F_{e_{1g}} | \, m_1 \rangle \langle m_1 \, | r_i^x | \, i \rangle}{(\mathcal{E}_{A_{1g}} - \mathcal{E}_{A_{2u}} - \hbar\omega_s)(\mathcal{E}_{E_{1g}} - \mathcal{E}_{A_{2u}} - \hbar\omega_i)} > 0,$$

$$\alpha_{xz} = \frac{\langle f \, | r_s^x | \, m_1 \rangle \langle m_1 \, | F_{e_{1g}} | \, m_2 \rangle \langle m_2 \, | r_i^z | \, i \rangle}{(\mathcal{E}_{E_{1g}} - \mathcal{E}_{A_{2u}} - \hbar\omega_s)(\mathcal{E}_{A_{1g}} - \mathcal{E}_{A_{2u}} - \hbar\omega_i)} < 0. \quad (3)$$

Here $i = f = A_{2u}$, $m_1 = E_{1g}$, $m_2 = A_{1g}$, $r_{i(s)}^\sigma$ is the σ component of the dipole moment coupled with the incident (scattering) photon ($\sigma = x, y, z$), and F_Γ is the e-ph coupling operator for mode Γ. Note that the appearance of this unusual ρ depends on the SJT splittings of $T_{1u} \rightarrow A_{2u} + E_{1u}$ and $H_g \rightarrow A_{1g} + E_{1g} + E_{2g}$, and the condition $\hbar\omega_i > \mathcal{E}_{A_{1g}} - \mathcal{E}_{A_{2u}} > \hbar\omega_s$, since the SJT energy splitting of H_g is comparable with the phonon energy of some e_{1g} modes. In contrast, the ω_i=1.0 eV resonance does not show unusual ρ for the resonance-enhanced a_{1g} and e_{2g} modes since it corresponds to electronic transition between A_{1u} and E_{1g} states. The second observable feature is the appearance of multiphonon lines and the possibility of directly observing δ_t in the RRS. Taking into account the two types of cross sections originating from the selection of initial and final states ($^3T_{3g}$ or $^3T_{1g}$) in the scattering, and the four kinds of resonant state configurations arising from the nonorthogonal components of $^3T_{3g}$ or $^3T_{1g}$ states, the total multiphonon Raman cross section for the coherent states formed in the DJTE at low temperatures can be obtained as

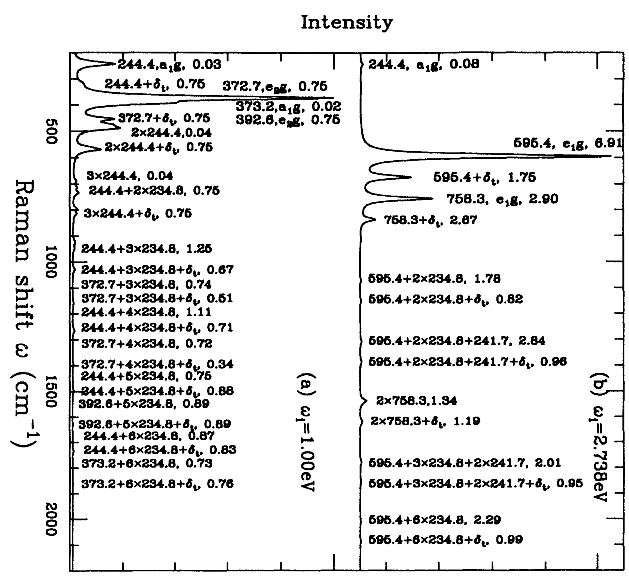

FIG. 2. Predicted multiphonon resonant Raman spectra of the DJT distorted triplet STE for two different excitation frequencies.

$$I(\omega_i,\omega_s) \propto \omega_i\omega_s^3 \sum_{\rho,\sigma}\sum_{\{n_f\}} |\mathcal{A}_{\rho\sigma}(\omega_i,\omega_s,\{n_f\})|^2 \times\delta\left(\omega_i-\omega_s-\sum_{\mu} n_f^{\mu}\hbar\omega_{\mu}\right) + \omega_i\omega_s^3 \sum_{\rho,\sigma}\sum_{\{n_f\}} |\mathcal{C}_{\rho\sigma}(\omega_i,\omega_s,\{n_f\})|^2 \times\delta\left(\omega_i-\omega_s-\delta_t-\sum_{\mu} n_f^{\mu}\hbar\omega_{\mu}\right) , \quad (4)$$

where $\mathcal{A}_{\rho\sigma}$ and $\mathcal{C}_{\rho\sigma}$ are the full multiphonon Raman tensors corresponding to ${}^3T_{3g} \to {}^3T_{3g}$ and ${}^3T_{3g} \to {}^3T_{1g}$ scatterings, respectively, which consist of six time-ordered scattering diagrams[27] comprised of nonorthogonal electronic transition matrix elements and multimode Frank-Condon overlaps. The outcome of Eq. (4) for two ω_i's is illustrated in Fig. 2. Here the multiphonon overtones are seen (at the scale of the graph) for the resonance-enhanced and relaxed modes (e.g., the 244.4 cm^{-1} mode at ω_i=1.00 eV and the 758.3 cm^{-1} mode at ω_i=2.738 eV) and for other relaxed modes, while the tunneling splitting δ_t shows up as the separation between the main peaks (coming from the $\mathcal{A}$ term) and their satellites (coming from the $\mathcal{C}$ term). Note that the unusual depolarization ratio ρ and its dispersion with ω_i still persist in the multiphonon spectrum under the DJTE (for ω_i=2.738 eV), although they are modified by fluctuations. The details of this calculation will be presented elsewhere.[28]

In conclusion, the DJT problem has been solved for the lowest triplet and singlet STE's of C_{60}. The experimental observations of the lowest triplet STE can be explained in terms of the tunnel-split ${}^3T_{3g} \oplus {}^3T_{1g}$ coherent states in a DJTE. Within the formulation of multiphonon resonant Raman scattering for these coherent states, the tunnel splitting, multiphonon effects, and unusual depolarization ratio are exhibited. These constitute predictions observable for photoinduced resonant Raman experiments.

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