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ABSORPTION OF A CHARGED C_{60}^- MOLECULE

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ABSTRACT

The observable consequences of the dynamic Jahn-Teller effect due to quantum-fluctuations between the six degenerate D_{5d} polaronic configurations on a singly charged C_{60}^- molecule are considered. The multi-phonon infrared absorption spectrum is calculated taking into account the dynamic symmetry breaking. Some of the Jahn-Teller active (also Raman-active) modes are predicted to be observable as multi-phonon overtones in the infrared absorption.

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The synthesis of Buckminsterfullerene, C_{60} [1], has allowed the realization of a wide range of novel phenomena with promising applications [2]. One of the salient features of this carbon isomer is the possession of the highest point group symmetry (icosahedral group), which is readily subject to a Jahn-Teller effect (JTE), due to the electron-phonon (e -ph) coupling inherited in the high electronic degeneracy [3]. Many important aspects of the physical and chemical properties of C_{60} and its various derivatives are strongly influenced by this effect. Motivated by the discovery of the high- T_c superconducting alkali-metal-doped compounds A_xC_{60} [4], various e -ph coupling models have been proposed to provide the superconductivity mechanism [5]. Optical observations of phonon progressions and vibronic peak broadening in solution, matrix and solid-state neutral C_{60} and its charged species, clearly show the effect of the JT distorted buckyball [6,7]. Also, vibronic analysis has been performed using different theoretical approaches [8,9] to describe the lattice dynamics under the JTE.

There are two aspects of the JTE to be considered [10]. *First*, according to the JT theorem [3], nonlinear, highly symmetric molecules with a degenerate electronic state are subject to distorting forces, acting through certain non-totally-symmetric vibration modes (JT-active modes), and these vibrations will carry the molecule into distorted configurations, corresponding to subgroup symmetries of the parent molecular point group. For the case of singly charged buckyball C_{60}^- , the triply degenerate HOMO state, T_{1u} , vibronically couples to the eight JT-active h_g modes, distorting the system from I_h to D_{5d} or D_{3d} , as suggested by various theoretical approaches [11-13] and quantum chemical calculations [14]. *Second*, the dynamics of the JT distortions should be considered [10]. Quantum tunneling between a certain number of equivalent JT distorted configurations due to quantum fluctuations results in pseudorotations between these minima on the adiabatic potential surface, leading to the restoration of the parent symmetry [15,16]. In fact, the binding energies of D_{5d} or D_{3d} polarons are rather small (of the order of 40-70 meV) [14], which is comparable with the zero point energy for some JT-active h_g phonons. Therefore, it is *insufficient* to consider only the static JT distorted state. The true ground state of C_{60}^- should be an irreducible representation of the full I_h group due to the dynamic JT effect (DJTE), and this will play

a crucial role in interpreting related physical and chemical processes.

In a previous study [16], Wang *et al.* have solved the linear multi-mode $T_{1u} \otimes 8h_g$ dynamic JT problem for the C_{60}^- molecule in the framework of the self-consistent Bogoliubov-de Gennes formalism. The quantum tunneling among the six equivalent stationary D_{5d} polaronic minima results in a ${}^2T_{1u}$ vibronic ground state, accompanied by the low-lying ${}^2T_{3u}$ vibronic states. The splitting of ${}^2T_{1u}$ and ${}^2T_{3u}$ was estimated to be about 0.1 eV, and there is 0.016 eV energy reduction of the ${}^2T_{1u}$ ground state relative to the symmetry broken D_{5d} state.

In the present work, we will quantify the observable consequences of the DJTE for the optical response in the infrared (ir) region. We find that, as a direct consequence of the dynamic symmetry breaking, the ir absorption shows a multi-phonon structure, and the JT-active (and also Raman-active) h_g modes are predicted to be observable in the ir spectrum. (Note that the JT-active modes do not include the dipole-active modes (t_{1u}) for C_{60}). As pointed out on general grounds by Berzaker [10], all the JT-active vibrations will appear in the ir spectrum since all the above-mentioned modes are interdependent under the DJTE. The vibronically induced absorption of forbidden ir transitions was considered by Thorson [17]. Considering a nondegenerate configuration, he has shown that the usual selection rules governing the ir fundamental frequencies in absorption, based on the degenerate ground state, are broken in the case of a strong JTE [17]. However, neither the tunnel-split state nor the non-orthogonality of the electronic and phonon wave functions between the equivalent polaronic minima have been accounted for. As will be shown below, it is this non-orthogonality which results in the appearance of Raman-active modes in the ir absorption as multi-phonon lines (not as fundamental frequencies). This effect was not captured by the theory of Thorson. The type of selection rule break-down proposed there can not be applied to the case of C_{60} since all the JT-active modes of C_{60} are gerade [17]. On the other hand, the modification of the usual absorption selection rule proposed in this study is in a sense similar to the false origin of UV absorption for a self-trapped-exciton in neutral C_{60} [9].

In accordance with Ref. [16], our Hamiltonian for describing the linear $T_{1u} \otimes 8h_g$ JT problem for C_{60}^- is written as

$$H = - \sum_{\langle i,j \rangle \sigma} t_0 (c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.}) + \sum_{\mu} \hbar \omega_{\mu} (\hat{b}_{\mu}^\dagger \hat{b}_{\mu} + \frac{1}{2}) + \sum_{\mu} \kappa F^{\mu} (\hat{b}_{\mu} + \hat{b}_{\mu}^\dagger), \quad (1)$$

where

$$F^{\mu} = \sqrt{\frac{\hbar}{2M\omega_{\mu}}} \sum_{\langle i,j \rangle \sigma} (\xi_i^{\mu} - \xi_j^{\mu}) \cdot \mathbf{e}_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.}). \quad (2)$$

Here $c_{i\sigma}$ ($c_{i\sigma}^\dagger$) and $\hat{b}_{\mu}$ ($\hat{b}_{\mu}^\dagger$) are annihilation (creation) operators of π -electrons and phonons, respectively; κ is the linear mode-independent vibronic coupling constant; ξ_i^{μ} is the unit vector of the normal mode μ at site i ; $\mathbf{e}_{ij}$ is the unit vector along the carbon bond $< i,j >$. The parameter set adopted in this study is the same as that of previous publications, which yields satisfactory geometric, electronic and vibrational structures for C_{60} [18,16]. The system under DJTE is described by the wave function obtained in the Born-Oppenheimer approximation [16]:

$$|\Psi_k\rangle = \sum_{\alpha} B_k^{\alpha} |e^{\alpha}\rangle \otimes |n^{\alpha}\rangle, \quad (3)$$

where $\alpha = 1, 2, \dots, 6$ is the index of the static JT distorted D_{5d} polaronic states, and k is the quantum number for the eigen-states of the system's total Hamiltonian under DJTE. $|e^{\alpha}\rangle$ and $|n^{\alpha}\rangle$ are the electronic and phonon wave-functions at the α th minima, respectively. The coefficients B_k^{α} are presented in Table 1 of Ref. [16]. Note that both the electronic and vibrational wave-functions for any pair of D_{5d} polaronic configurations are non-orthogonal. This leads to the following dipole ir transition moment in the low temperature limit ($n_{e_i}^{\alpha} = 0$):

$$\begin{aligned} \langle f | D_k | i \rangle &= \sum_{\alpha, \beta} B_k^{\alpha*} B_k^{\beta} \sum_{\nu} \sum_j \left\langle e^{\alpha} \left| \sum_{\sigma} (c_{j\sigma}^\dagger c_{j\sigma} - Z_{j\sigma}) \right| e^{\beta} \right\rangle \xi_{j,\beta}^{\nu} \prod_{\mu \neq \nu} \langle n_{\mu}^{\alpha} | 0_{\mu}^{\beta} \rangle \\ &\times \left[\frac{Q_{\nu}^{\alpha} + Q_{\nu}^{\beta}}{2} \langle n_{\nu f}^{\alpha} | 0_{\nu}^{\beta} \rangle + \sqrt{\frac{\hbar}{2M\omega_{\mu}}} \sqrt{n_{\nu f}^{\alpha}} \langle n_{\nu f}^{\alpha} - 1 | 0_{\nu}^{\beta} \rangle \right], \end{aligned} \quad (4)$$

where Q_{ν}^{α} is the ν -mode lattice distortion at polaron α , $\xi_{j,\beta}^{\nu}$ is the normal mode belonging to the β D_{5d} configuration, $\langle n_{\nu f}^{\alpha} | 0_{\nu}^{\beta} \rangle$ is the Frank-Condon overlap integral. $Z_{j\sigma}$ is the charge

at site j with spin σ which is not explicitly included in the present π -electron model (it is assumed to be 0.5). Therefore, the contribution from the phonon polarizability to the ir absorption can be expressed as

$$^1I(\omega) = \sum_k \sum_{\nu} \left| \sum_{\alpha} |B_k^{\alpha}|^2 D_{\nu}^{\alpha\alpha} \right|^2 \delta(\omega - \omega_{\nu}^{\text{ir}}) + \sum_k \sum_{\nu} \sum_{\{\mu_f\}} \left| \sum_{\alpha \neq \beta} B_k^{\alpha*} B_k^{\beta} D_{\nu}^{\alpha\beta} \right|^2 \delta\left(\omega - \omega_{\nu}^{\text{ir}} - \sum_{\mu}^R n_{\mu f}^{\alpha} \omega_{\mu}\right), \quad (5)$$

where

$$D_{\nu}^{\alpha\beta} = \sqrt{\frac{\hbar}{2M\omega_{\nu}}} \left\langle e^{i\alpha} \sum_{j,\sigma} (c_{j\sigma}^{\dagger} c_{j\sigma} - Z_{j\sigma}) e^{\beta} \right\rangle \prod_{\mu \neq \nu}^R \left\langle n_{\mu f}^{\alpha} | 0_{\mu}^{\beta} \right\rangle \boldsymbol{\xi}_{j,\beta}^{\nu}. \quad (6)$$

Here we have used symmetry considerations to derive Eq. (5) from Eq. (4), and superscripts “ir” and “R” indicate ir- or Raman-active modes, respectively. Only the ir-active modes a_{2u} and e_{1u} (split from t_{1u} of C_{60}) can contribute to the fundamental single phonon ir absorption term, i.e. the first term in Eq. (5). Only certain of the Raman- and JT-active modes (a_{1g} , e_{1g} and e_{2g} split from h_g) can contribute to ir absorption (coming from $\prod_{\mu \neq \nu} n_{\mu f}^{\alpha} | 0_{\mu}^{\beta} \rangle$), since only these modes participate in the lattice relaxation between different D_{3d} configurations, giving rise to the multi-phonon lines in the ir absorption (second term in Eq. (5)). Another contribution to the ir response comes from the electron polarizability. Using the Kramers-Heisenberg formula [19], the transition moment due to the electron polarization can be expressed as

$$M_k = \sum_{\alpha\beta} B_k^{\alpha*} B_k^{\beta} \sum_{\nu} \left({}^1P_{\alpha\beta}^{\nu} + {}^2P_{\alpha\beta}^{\nu} \right) \delta_{\alpha\nu, 1^{\beta}} \prod_{\nu' \neq \nu}^{\text{ir}} \delta_{n_{\nu' f}^{\alpha}, 0^{\beta}} \prod_{\mu \neq \nu, \nu'}^R \left\langle n_{\mu f}^{\alpha} | 0_{\mu}^{\beta} \right\rangle, \quad (7)$$

where

$$^1P_{\alpha\beta}^{\nu} = \sum_{\lambda_1 > F > \lambda_2} \frac{\left\langle e_{\lambda_2}^{\alpha} \left| \sum_{j,\sigma} \mathbf{r}_j (c_{j\sigma}^{\dagger} c_{j\sigma} - Z_{j\sigma}) \right| e_{\lambda_1}^{\alpha} \right\rangle \left\langle e_{\lambda_1}^{\beta} \left| F^{\nu} \right| e_{\lambda_2}^{\beta} \right\rangle}{\mathcal{E}_{\lambda_2} - \mathcal{E}_{\lambda_1} - \hbar\omega_{\nu}}, \quad (8)$$

$$^2P_{\alpha\beta}^{\nu} = \sum_{\lambda_1 > F > \lambda_2} \frac{\left\langle e_{\lambda_2}^{\alpha} \left| F^{\nu} \right| e_{\lambda_1}^{\alpha} \right\rangle \left\langle e_{\lambda_1}^{\beta} \left| \sum_{j,\sigma} \mathbf{r}_j (c_{j\sigma}^{\dagger} c_{j\sigma} - Z_{j\sigma}) \right| e_{\lambda_2}^{\beta} \right\rangle}{\mathcal{E}_{\lambda_2} - \mathcal{E}_{\lambda_1} + \hbar\omega}. \quad (9)$$

Here λ_1 and λ_2 stand for the electron-hole pair excitations over the Fermi level. Thus the contribution to the ir absorption is obtained as

$$^2I(\omega) = \sum_k \sum_{\nu} \left| \sum_{\alpha} |B_k^{\alpha}|^2 ({}^1P_{\alpha\alpha}^{\nu} + {}^2P_{\alpha\alpha}^{\nu}) \right|^2 \delta(\omega - \omega_{\nu}^{\text{ir}}) + \sum_k \sum_{\nu} \sum_{\{\mu_f\}} \left| \sum_{\alpha \neq \beta} B_k^{\alpha*} B_k^{\beta} ({}^1P_{\alpha\beta}^{\nu} + {}^2P_{\alpha\beta}^{\nu}) \prod_{\mu \neq \nu}^R \left\langle n_{\mu f}^{\alpha} | 0_{\mu}^{\beta} \right\rangle \right|^2 \delta\left(\omega - \omega_{\nu}^{\text{ir}} - \sum_{\mu}^R n_{\mu f}^{\alpha} \omega_{\mu}\right). \quad (10)$$

Here k denotes the degenerate component of the ${}^2T_{1u}$ ground state. The first and second terms contribute to single- and multi-phonon lines in the ir absorption, respectively. The electronic matrix elements between non-orthogonal polarons α and β in the above equations are calculated through the Slater determinant formalism [20]. The Frank-Condon overlap integrals $\left\langle n_{\mu f}^{\alpha} | 0_{\mu}^{\beta} \right\rangle$ are evaluated through Huang-Rhys (HR) factors, which are determined by the self-consistent Bogoliubov-de Gennes formalism [16]. The relaxed modes, i.e. the modes with non-vanishing HR factors, turn out to be the five JT-active h_g modes when the I_h phonon spectrum of the C_{60} ground state is applied to expand the D_{3d} distortions. The corresponding HR factors are 0.70, 0.02, 0.07, 0.07 and 0.23 for the modes observed experimentally at 273, 437, 774, 1428 and 1575 cm^{-1} , respectively.

The calculated ir absorption spectra are shown in Figs. 1 and 2, where the irreducible representation of each single-phonon line is labeled in the figure, and the origin of each multi-phonon line is also indicated. The ir absorption spectra of the neutral C_{60} and charged C_{60}^{-} are shown in Figs. 1(a) and (b), respectively. We note that the result for the pristine C_{60} is consistent with a previous study [21] using the same model and parameter values. The main deviations of these results from the experimental observations arise from the simplicity of the present modeling of the elastic interactions [18,21] — the four calculated t_{1u} frequencies of C_{60} are 425, 581, 1322 and 1493 cm^{-1} , correspond to modes 527, 577, 1183 and 1428 cm^{-1} , observed experimentally [22]. Another deviation from experiments is the calculated ir intensities, where the two low-frequency t_{1u} modes have relatively much lower strengths than the experimental values [22]. These shortcomings will also affect the results below for the charged buckyball (cf. Fig. 1(b) and Fig. 2). The ir spectrum of C_{60}^{-} calculated using the same parameter set. is shown in Fig. 1(b), when only one static D_{3d} JT distorted configuration is considered [21]. Comparing it with the pristine result, there is only one

peak, at 1764 cm^{-1} , higher than 1493 cm^{-1} . The other lines are all red-shifted. In Fig. 2, the ir spectrum of the ${}^2T_{1u}$ ground state C_{60}^- under the DJTE is depicted. The single-phonon contributions from the first terms of Eqs. (5) and (10) are given in Fig. 2(a), while the multi-phonon contributions from the second terms of Eqs. (5) and (10) are shown in Fig. 2(b), and the full ir spectrum is given in Fig. 2(c). Notice that according to the present theory, the strength of a multi-phonon line in the ir spectrum is determined not only by the electronic polarizabilities ${}^{(2)}P$ and their interference effect in Eq. (10), but also by the extent of lattice relaxation (HR factors). Therefore, no multi-phonon line from an a_g mode of C_{60} is predicted to appear in the ir absorption due to the DJTE since its HR factor is zero between any pair of D_{3d} polaronic states. We note that the contribution of Eq. (5) is negligible compared with that of Eq. (10) because the dipole moment due to the net charge in C_{60} is small. The multi-phonon lines show significant structures in the region beyond 1800 cm^{-1} mainly due to the multi-phonon contributions from the $1575\text{ }h_g$ mode. However, the multi-phonon lines in the $300 \sim 1000\text{ cm}^{-1}$ region are not strong enough to be distinguished since the low-frequency zero phonon lines cannot provide enough strengths due to the limitations of the model mentioned above. The low-frequency ir modes could be stronger in an improved model, and it is reasonable to expect the observation of multi-phonon lines in this region as well.

We have quantified the multi-phonon ir absorption of C_{60}^- so as to manifest the DJTE. The role of the DJTE in C_{60}^- has also been indicated by ESR observations [7,23], for which a detailed interpretation would require the inclusion of the spin-orbital coupling. Additional experiments are still needed to confirm the DJTE of C_{60}^- , such as strong temperature dependence of the vibronic ir spectrum, and phonon-related spectroscopy [10]. The same DJTE philosophy can also be applied to the photo-excited states of C_{60} [24], suggested by recent experiments [25]. A multi-phonon Raman spectrum can also be predicted in the same spirit as for ir absorption. However, no ir-active modes are expected to be observable in Raman scattering because the JT-active mode in C_{60} is itself Raman-active [26]. It should be emphasized that our predictions for the DJTE in C_{60}^- are based on considerations of an

isolated ball. These effects should also be observable in solution or matrix samples of C_{60} . For solid-state samples; additional solid-state effects such as intra-band e -ph coupling and orientational disorder should be included. For alkali-metal-doped C_{60} films, the classical Fano [27] and charged phonon effects with orientational disorder [28] have been suggested to explain the appearance of Raman modes as fundamental lines in the ir reflection spectrum [27].

In summary, we have proposed an observable consequence of the DJTE in a singly-charged buckyball, C_{60}^- . As a direct consequence of the dynamical symmetry breaking, a multi-phonon infrared absorption spectrum was evaluated with the prediction that some of the relaxed JT-active Raman modes should be observable as multi-phonon lines in the ir absorption. The apparent breakdown of ir parity selection rules (namely, the appearance of some Raman-active modes in the ir spectrum not as fundamental frequencies but as phonon overtones) is a generic property of the DJTE whenever the JT-active modes are not ungerade ir-active but gerade Raman-active. This phenomenon should be observable in other similar systems. And the effect will be missed if only the static JTE is considered.

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FIGURES

FIG. 1. The calculated low-temperature ir spectra of neutral C_{60} (a) and charged C_{60}^- (b) *without* inclusion of the DJTE. The strengths are normalized to the highest peak in (a), and the Lorentzian broadening is 8 cm^{-1} .

FIG. 2. The calculated ir absorption spectrum for charged C_{60}^- considering the DJTE in the low temperature limit: (a) Single-phonon contribution; (b) Multi-phonon contribution; (c) The spectrum combining (a) and (b). The strengths are normalized to the highest peak in (a), and the Lorentzian broadening is 8 cm^{-1} .