Jahn-Teller effect in C_{60} monoanion and monocation

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Introduction

Highly symmetric C_{60} exhibits complex Jahn-Teller (JT) dynamics characterized by orbital-vibration entanglement in various charged and excited states, thus thorough understanding of the JT effect of C_{60} anions is crucial. Negatively charged C_{60} has been one of the most investigated cases because it forms various molecular crystals. Although JT effect, including dynamic one, of C_{60} anions has been intensively investigated, it is only past few years that the actual situation of the ground electronic states of C_{60}^{n-} molecule (n = 1-5) has been established with accurate vibronic coupling parameters, while in C_{60}^+, JT effect is one of the most involved cases because of the five-fold degenerate highest occupied molecular orbitals (HOMOs) of C_{60}, and has not been studied before.

Figure 1: Structure (a)., energy level (e). of C_{60}, the Fermi level is set between LOMOs and HUMOs. The molecular orbitals corresponding to T_{1g}, T_{1u} and H_u states are shown in (b). (c). and (d)., respectively.

On the other hand, to completely understand the real situation of JT effect on C_{60} anion, the LOMOs and HUMOs (even higher exited states) should be considered concomitantly, for which the studies of monocation C_{60}^+ and monoanion in its first excited state C_{60}^-, within a same framework, are necessary.

Objective: Investigation of Jahn-Teller effect in C_{60} monocation C_{60}^+ and monoanion in its firt extied state C_{60}^-.

Jahn-Teller effect analysis

Jahn-Teller Hamiltonian

C_{60}^+: The highest occupied molecular orbitals (HOMOs) of C_{60} with I_h symmetry are characterized by five-fold degenerate h_u irreducible representation (as shown in Figure. 1). According to the selection rule, these orbitals linearly couple to the mass-weighted normal vibrational modes involved in the symmetric product of the h_u representation: $[h_u \otimes h_u] = a_g \oplus g_g \oplus 2h_g$. The $H \otimes (a \oplus g \oplus 2h)$ JT Hamiltonian for C_{60}^+ is expressed as

$$H = H_0 + H_{JT}, \tag{1}$$
$$H_0 = \frac{1}{2}\left(p_a^2 + \omega_a^2 q_a^2\right) + V_a q_a + \sum_{\gamma=a,x,y,z} \frac{1}{2}\left(p_{g\gamma}^2 + \omega_g^2 q_{g\gamma}^2\right) + \sum_{\gamma=\theta,\epsilon,\xi,\eta,\zeta} \frac{1}{2}\left(p_{h\gamma}^2 + \omega_h^2 q_{h\gamma}^2\right),$$
$$H_{JT} = V_g \sum_{\gamma=a,x,y,z} \hat{C}_{g\gamma} q_{g\gamma} + \frac{\sqrt{5}V_{1h}}{2} \sum_{\gamma=\theta,\epsilon,\xi,\eta,\zeta} \hat{C}_{1h\gamma} q_{1h\gamma} + \frac{\sqrt{5}V_{2h}}{2} \sum_{\gamma=\theta,\epsilon,\xi,\eta,\zeta} \hat{C}_{2h\gamma} q_{2h\gamma}$$

where ω_Γ ($\Gamma = a_g, g_g, h_g$) are vibration frequencies, q_Γ are mass-weighted normal coordinates, V_Γ is vibronic coupling parameter for Γ mode, and $\hat{C}_{\Gamma\gamma}$ (γ = a, x, y, z, $\theta, \epsilon, \xi, \eta, \zeta$) are the Clebsch-Gordan coefficients, which are taken from Ref. [1].

First excited states of C_{60}^-: The t_{1g} NLUMOs of neutral C_{60} with I_h symmetry are triply degenerate and separated from other orbitals. According to selection rule, these t_{1g} orbitals couple to totally symmetric a_g and five-fold degenerate h_g normal modes as in the case of t_{1u} LUMOs $[t_{1g} \otimes t_{1g}] = a_g \oplus h_g$. Therefore, the linear vibronic Hamiltonian of C_{60}^- for first excited t_{1g}^1 electronic configuration is given as in the case of t_{1u}^1:

$$H = H_0 + H_{JT} \quad H_0 = \frac{1}{2}\left(p_a^2 + \omega_a^2 q_a^2\right) + V_a q_a, \tag{2}$$

$$H_{JT} = \sum_{\gamma=\theta,\epsilon,\xi,\eta,\zeta} \frac{1}{2}\left(p_{h\gamma}^2 + \omega_h^2 q_{h\gamma}^2\right) + V_h \begin{pmatrix} \frac{1}{2}q_{h\theta} - \frac{\sqrt{3}}{2}q_{h\epsilon} & \frac{\sqrt{3}}{2}q_{h\zeta} & \frac{\sqrt{3}}{2}q_{h\eta} \\ \frac{\sqrt{3}}{2}q_{h\zeta} & \frac{1}{2}q_{h\theta} + \frac{\sqrt{3}}{2}q_{h\epsilon} & \frac{\sqrt{3}}{2}q_{h\xi} \\ \frac{\sqrt{3}}{2}q_{h\eta} & \frac{\sqrt{3}}{2}q_{h\xi} & -q_{h\theta} \end{pmatrix}. \tag{3}$$

Here, $q_{\Gamma\gamma}$ and $p_{\Gamma\gamma}$ ($\gamma = \theta, \epsilon, \xi, \eta, \zeta$ for $\Gamma = h$) are mass-weighted normal coordinates and conjugate momenta, respectively, ω_Γ is frequency, and V_Γ vibronic coupling parameters.

JT energy and the lowest adiabatic potential energy surface (APES)

JT energy: The JT energy is defined as $E_{n\Gamma}^{JT} = -\frac{V_{n\Gamma}^2}{2\omega_{n\Gamma}^2}$. To make the analysis of both C_{60}^+ and C_{60}^- consistent, a coefficient $\sqrt{5}/2$ is multiplied to vibronic couplings terms of h_g modes so that JT energy becomes: $E_g^{JT} = -\frac{V_g^2}{2\omega_g^2}$ and $E_{nh}^{JT} = -\frac{V_{nh}^2}{2\omega_h^2}$, $(n = 1, 2)$, while for C_{60}^-, the JT energy express as: $\frac{V_a^2}{2\omega_a^2}$, and $\frac{V_h^2}{2\omega_h^2}$.

APES of C_{60}^+: Vibronic coupling lifts degeneracy with the deformation keeping one of the highest subgroup symmetries, resulting in six D_{5d} and ten D_{3d} minima, as there are six C_5 and ten C_3 axes in C_{60}. The deformations for D_{5d} and D_{3d} minima are expressed by $\mathbf{q}_{h_g}^{D_{5d}} = q_{h_g}\left(\frac{\phi^2}{2\sqrt{5}}, \frac{\phi^{-1}}{2}\sqrt{\frac{3}{5}}, 0, \sqrt{\frac{3}{5}}, 0\right)$, $\mathbf{q}_{g_g}^{D_{5d}} = q_{g_g}(0,0,0,0)$, and $\mathbf{q}_{h_g}^{D_{3d}} = q_{h_g}\left(-\frac{\phi^{-1}}{2}, \frac{\phi^2}{2\sqrt{3}}, 0, \frac{1}{\sqrt{3}}, 0\right)$, $\mathbf{q}_{g_g}^{D_{3d}} = q_{g_g}\left(\frac{1}{\sqrt{6}}, 0, -\sqrt{\frac{5}{6}}, 0\right)$. respectively[1]. The lowest potential energy are

$$U^{D_{5d}} = \frac{1}{2}\omega_h^2 q_h^2 + V_{1h}q_h, \quad U^{D_{3d}} = \frac{1}{2}\omega_g^2 q_g^2 + \frac{1}{2}\omega_h^2 q_h^2 + \frac{1}{3}\left(2V_g q_g + \sqrt{5}V_{2h}q_h\right), \tag{4}$$

for D_{5d} and D_{3d} deformations, respectively. These minima energies could be expressed in terms of JT stabilization energies as $E_{JT}^{D_{5d}} = -E_{1h}^{JT}$, $E_{JT}^{D_{3d}} = -\frac{1}{9}\left(4E_g^{JT} + 5E_{2h}^{JT}\right)$.

APES of C_{60}^-: The model Hamiltonian, and hence the formulae, for the ground electronic configuration and the first excited configuration have the same structure. The depth of the

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adiabatic potential energy surface (APES) with respect to the reference structure is given by

$$U_{min} = -E_a - E_{JT} = -\frac{V_a^2}{2\omega_a^2} - \frac{V_h^2}{2\omega_h^2}, \tag{5}$$

with $q_{a,0} = -\frac{V_a}{\omega_a^2}$, $|\mathbf{q}_{h,0}| = \frac{V_h}{\omega_h^2}$, where E_a and E_{JT} are the first and the second terms in the last expression in Eq. (5), respectively, and $\mathbf{q}_h$ is the list of $q_{h\gamma}$, and "0" in subscript indicates the deformation at the global minimum of APES. The APES has two-dimensional continuous trough, suggesting the presence of SO(3) symmetry.

Calculation details

The reference structures for both C_{60} monoanion and monocation are chosen as the equilibrium structure of C_{60}. For DFT calculations, a triple-zeta basis set [6-311G(d)] is employed in Gaussian 16. Hybrid functional, B3LYP is used while the non-local interaction correction is added by CAM-B3LYP functionals.

Influence of non-local interaction correction: The agreement between vibronic coupling constants calculated with CAM-B3LYP and that from experiments[2] is better than that with B3LYP.

Taking the largest vibronic coupling constant, corresponding to h_{g7} mode, as an example, the values calculated with B3LYP and CAM-B3LYP are 13.9 and 19.5 meV, while it is about 19.6 meV from experimental data. Besides, CAM-B3LYP improved the total static JT stabilization energy from 50.3 meV (with B3LYP) to 59.3 meV, with the value about 60.0 meV from experiment. All these facts indicate the success of CAM-B3LYP for prediction of fullerene properties.

Table 1: Contributions to ground vibronic energy (E_{total}) of NLUMOs and LUMOs of C_{60}^- with B3LYP and CAM-B3LYP, respectively. E_{static}, and $E_{dynamic}$ represent static JT and dynamic JT stabilization energies.

Orbital		E_{total}	E_{static}	$E_{dynamic}$
NLUMOs	B3LYP	-113.8	-65.6	-48.2
	CAM-B3LYP	-136.1	-81.7	-54.4
LUMOs	B3LYP	-96.5	-50.3	-46.2
	CAM-B3LYP	-111.8	-59.3	-52.5

Results

Contributions to total ground vibronic energy (E_{total}) from static JT stabilization energy (E_{static}) and dynamic one ($E_{dynamic}$) are summarized in Table 1 [7]. JT stabilization energies in this work, as well as those from previous studies, are shown in Table 2 [8], from which we could see that CAM-B3LYP could enhance JT stabilization energies for D_{5d} and D_{3d} minima by 17% and 30% respectively compared to that with B3LYP. And JT stabilization energies obtained with both B3LYP and CAM-B3LYP are larger than those from LDA or PBE-related functionals.

Table 2: Jahn-Teller stabilization energies of C_{60}^+ (meV) for D_{5d} and D_{3d} minima of the APES, respectively.

Functional	Method	D_{5d}	D_{3d}	Ref
B3LYP	(I)	110	30	Present
CAM-B3LYP	(I)	129	39	Present
LDA	(I)	69	22	[3]
B3LYP	(II)	121	-	[4]
LDA	(III)	74	27	[5]
OPBE	(III)	74	28	[5]
B3LYP	(III)	80	32	[5]
PBE	(III)	74	28	[6]
LDA	(IV)	72	20	[5]
OPBE	(IV)	74	21	[5]
B3LYP	(IV)	94	25	[5]

Conclusions

1. Non-local interaction correction is important for the calculation of vibronic coupling constant for C_{60};

2. In C_{60}^-, the results for t_{1g} configuration showed stronger dynamic JT stabilization than those for t_{1u} configuration by about 18% and 22% for B3LYP and CAM-B3LYP, respectively, indicating the importance of JT effect in excited states;

3. In C_{60}^+, JT structure at the minima of APES is confirmed to be D_{5d};

4. Static JT stabilization energies in C_{60}^+ are about two times larger than that in C_{60}^-.

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