

First principles study of the vibronic coupling in positively charged C_{60}^+

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Orbital vibronic coupling parameters for C_{60}^+ were derived by using frozen-phonon approach via density functional theory calculations with hybrid B3LYP and CAM-B3LYP functional. Based on these derived vibronic coupling parameters, the static Jahn-Teller effect of C_{60}^+ were analyzed. At the global minima of adiabatic potential energy surface (APES), the Jahn-Teller deformation shows a D_{5d} structure with stabilization energies of 110 and 129 meV with B3LYP and CAM-B3LYP respectively. These stabilization energies are two times larger than that in C_{60}^- , suggesting the crucial role of the dynamical Jahn-Teller effect in C_{60}^+ . Present coupling parameters enable us to assess the actual situation of dynamical Jahn-Teller effect in C_{60}^+ and also that of excited C_{60} in combination with the established coupling parameters for C_{60}^- .

KEYWORDS

Jahn-Teller Effect, C_{60}^+ , CAM-B3LYP, B3LYP.

1 | INTRODUCTION

Recent experimental confirmation of the presence of C_{60}^+ as interstellar materials [1, 2] renewed the interests in C_{60} cations, and burst various spectroscopic and theoretical investigations on C_{60}^+ and related systems [3, 4, 5, 6, 7, 8]. It is known that C_{60} in its charged and excited states exhibits complex Jahn-Teller (JT) effect due to its high symmetry (I_h) [9, 10]. In particular, JT effect in C_{60}^+ is one of the most involved cases because of the five-fold degenerate highest occupied molecular orbitals (HOMOs) of C_{60} . Toward understanding JT effect in C_{60}^{n+} cations, spectroscopic [11, 12, 13] and theoretical [14, 15, 16, 17, 18, 19, 20, 21, 22] investigations have been piled up.

Realistic description of JT effect in positively charged C_{60} relies on the combination of an adequate model and accurate enough vibronic coupling parameters. Derivations of vibronic coupling parameters have been addressed [23, 24, 25], and comprehensive sets of parameters have been estimated by density functional theory (DFT) calculations at local density approximation (LDA) level [23, 25]. Nevertheless, in studies about C_{60}^- , it has been shown that LDA tends to underestimate the coupling parameters [26], while hybrid B3LYP functional is found to give closer parameters to the experimental data. Furthermore, a good agreement between B3LYP and GW approximation calculations [27] supports the accuracy of hybrid functional in studies of C_{60} . Besides, one recent study showed that B3LYP with long-range interaction correction, CAM-B3LYP, could improve the accuracy of vibronic parameters in C_{60}^- with respect to experimental data, indicating CAM-B3LYP could give vibronic parameters much closer to the real situation [28]. Therefore, it is desired to derive the coupling parameters at a better level than LDA for accurate description of C_{60} cations.

In this work, we derived orbital vibronic coupling parameters for C_{60}^+ via DFT calculations with both B3LYP and CAM-B3LYP hybrid functionals. These obtained vibronic coupling parameters were compared with the previous data obtained by LDA calculations. Based on these parameters, the adiabatic potential energy surface (APES) was analyzed, and the symmetry of JT deformed C_{60}^+ as well as static JT energies were established.

2 | VIBRONIC HAMILTONIAN

The highest occupied molecular orbitals (HOMOs) of C_{60} with I_h symmetry [29] are characterized by five-fold degenerate h_u irreducible representation. According to selection rule, these orbitals linearly couple to mass-weighted normal vibrational modes involved in the symmetric product of h_u representation [30]:

$$[h_u \otimes h_u] = a_g \oplus g_g \oplus 2h_g. \quad (1)$$

Among them, g_g and h_g modes are JT active, while a_g is not because it does not change the symmetry of molecules. Thus, taking the equilibrium structure of neutral C_{60} as the reference, $H \otimes (a \oplus g \oplus 2h)$ JT Hamiltonian for C_{60}^+ is expressed as [14, 9, 10]

$$H = H_0 + H_{JT}, \quad (2)$$

$$H_0 = \frac{1}{2} (p_a^2 + \omega_a^2 q_a^2) + V_a q_a + \sum_{\gamma=a,x,y,z} \frac{1}{2} (p_{g\gamma}^2 + \omega_{g\gamma}^2 q_{g\gamma}^2) + \sum_{\gamma=\theta,\epsilon,\xi,\eta,\zeta} \frac{1}{2} (p_{h\gamma}^2 + \omega_{h\gamma}^2 q_{h\gamma}^2), \quad (3)$$

$$H_{JT} = V_g \sum_{\gamma=a,x,y,z} \hat{C}_{g\gamma} q_{g\gamma} + \frac{\sqrt{5}V_{1h}}{2} \sum_{\gamma=\theta,\epsilon,\xi,\eta,\zeta} \hat{C}_{1h\gamma} q_{1h\gamma} + \frac{\sqrt{5}V_{2h}}{2} \sum_{\gamma=\theta,\epsilon,\xi,\eta,\zeta} \hat{C}_{2h\gamma} q_{2h\gamma} \quad (4)$$

where ω_Γ ($\Gamma = a_g, g_g, h_g$) are vibration frequencies, q_Γ are mass-weighted normal coordinates [31], V_Γ is vibronic coupling parameter for Γ mode, and $\hat{C}_{\Gamma\gamma}$ ($\gamma = a, x, y, z, \theta, \epsilon, \xi, \eta, \zeta$) are the Clebsch-Gordan coefficients, which are taken from Ref. [32] and listed in Appendix A. A coefficient $\sqrt{5}/2$ is multiplied to vibronic couplings terms of h_g modes

so that JT energy becomes:

$$E_g^{\text{JT}} = -\frac{V_g^2}{2\omega_g^2}, \quad E_{nh}^{\text{JT}} = -\frac{V_{nh}^2}{2\omega_h^2}, \quad (n = 1, 2). \quad (5)$$

There are two vibronic couplings to one h_g mode because h_g representation appears twice in selection rule, Eq. (1). The basis of vibronic Hamiltonian matrices are H_u electronic states of C_{60}^+ in the order of $|H_u\theta\rangle$, $|H_u\epsilon\rangle$, $|H_u\xi\rangle$, $|H_u\eta\rangle$, $|H_u\zeta\rangle$. For h_g and h_u representations, d orbital type basis are used, and hence, $\theta, \epsilon, \xi, \eta, \zeta$ transform as $(2z^2 - x^2 - y^2)/\sqrt{6}$, $(x^2 - y^2)/\sqrt{2}$, $\sqrt{2}yz$, $\sqrt{2}zx$, $\sqrt{2}xy$, respectively, under rotation. Although C_{60} has two a_g , six and eight sets of g_g and h_g modes, respectively, and indices distinguishing them are not explicitly written in Eq. (3) for simplicity. Phase factors of mass-weighted normal modes are the same as those in the Supplemental Materials of Ref. [32]. Since the equilibrium geometry of C_{60} is chosen as the reference structure of C_{60}^+ , vibronic coupling parameters of totally symmetric modes are also nonzero. JT energy by totally symmetric deformation is

$$E_a = -\frac{V_a^2}{2\omega_a^2}. \quad (6)$$

In many other literatures, like the work of [14], linear combinations of real d -type functions, d_{z^2} , $d_{x^2-y^2}$, are used, which could be transformed into irreducible representation in this work by

$$q_\theta = \sqrt{\frac{5}{8}}Q_\theta + \sqrt{\frac{3}{8}}Q_\epsilon, \quad q_\epsilon = \sqrt{\frac{3}{8}}Q_\theta - \sqrt{\frac{5}{8}}Q_\epsilon, \quad (7)$$

where Q_θ and Q_ϵ are normal coordinates in Ref. [14], while q_θ and q_ϵ are normal coordinates in this work, resulting in the relation between coupling parameters V_{1h} and V_{2h} in this work and F_{Hb} and F_{Ha} defined in Ref. [14]:

$$V_{1h} = \frac{F_{Hb}}{4\sqrt{5}}, \quad V_{2h} = \frac{F_{Ha}}{12\sqrt{5}}. \quad (8)$$

The modification introduced here is to treat the JT Hamiltonian in a framework consistent to the standard one in C_{60}^- [9].

3 | RESULTS

3.1 | Orbital vibronic coupling parameters

Vibronic coupling constants of C_{60} have been most intensively investigated in the case of C_{60}^- , and coupling constants have been derived by various methods. By definition, vibronic coupling parameters for JT active h_g modes, $V_{h_g}^-$, can be derived by [26]

$$V_{h_g}^- = -\left. \frac{\partial E_z^-(\mathbf{q}_{h_g})}{\partial q_{h_g\theta}} \right|_{\mathbf{q}_{h_g}=\mathbf{0}}, \quad (9)$$

where $E_z^-(\mathbf{q}_{h_g}) = \langle T_{1uz} | \hat{H}^- | T_{1uz} \rangle$, $|T_{1uz}\rangle$ is t_{1uz} electronic state of C_{60}^- , \hat{H}^- is Hamiltonian for C_{60}^- , and $\mathbf{q}_{h_g} = \mathbf{0}$ indicates equilibrium structure of C_{60} . Because of symmetry, contributions from occupied orbitals are zero, and only

partially filled t_{1u} orbital level contribute to vibronic couplings. In the case of C_{60}^- , the nature of t_{1u} orbitals do not differ from that of neutral C_{60} : although t_{1u} orbitals are mixed with the other t_{1u} orbitals, the mixing is very small due to high symmetry, and orbitals are separated each other by large orbital energy gaps. Consequently, gradients of total energy can be approximated by those of orbital energy levels with respect to normal modes of neutral C_{60} . Indeed, in the case of C_{60}^- , these two approaches give very close results [33, 26, 27, 32].

Similar situation is expected in C_{60}^+ : the nature of the h_u orbital does not change by adding one hole to the same molecular structure. Thus, orbital vibronic coupling parameters of neutral C_{60} can be used to express vibronic coupling parameters of C_{60}^+ . Since C_{60}^+ has one hole in h_u HOMOs, it is convenient to perform particle-hole transformation [34], under which, the sign of orbital vibronic coupling parameter for one electron in HOMOs of C_{60} should be inverted for that in the case of one hole in HOMOs. Therefore,

$$V_{\Gamma} = -v_{\Gamma}, \quad (10)$$

where v_{Γ} is one orbital vibronic coupling parameter for C_{60} and V_{Γ} is the parameter for C_{60}^+ .

Orbital vibronic coupling parameters were calculated using frozen-phonon approach. Orbital energy levels of distorted C_{60} are fitted to the eigenvalues of JT Hamiltonian matrix (Eq. (4)). In the present case, $h_g(\mu)\epsilon$ and $g_g(\mu)a$ deformations are used because diagonalizing the model Hamiltonian is easier. For DFT calculations, a triple-zeta basis set [6-311G(d)] was employed for both B3LYP and CAM-B3LYP functionals within Gaussian [35]. Some fittings are shown in Fig. 1 (see Supplemental Materials for other fittings). Black points indicate DFT levels originating from HOMOs, with gray lines for energy level calculated from model Hamiltonian. Derived orbital vibronic coupling parameters are shown in Table 1. From this table, JT stabilization energies for different JT active modes are improved about 30 % with CAM-B3LYP compared with these with B3LYP. One should note that there is almost no nonlinear splitting due to vibronic effect in HOMO levels, indicating weak quadratic or higher vibronic couplings as in the case of C_{60}^- [32]. This guarantees the validity of linear vibronic model (Eq. (3)) for the description of JT effect of C_{60} cations.

3.2 | Static Jahn-Teller effect

Vibronic coupling lifts degeneracy with the deformation keeping one of the highest subgroup symmetries [36], resulting in six D_{5d} and ten D_{3d} minima [14], as there are six C_5 and ten C_3 axes in C_{60} . Thus, based on present basis, using symmetry adapted deformations [20], deformations for D_{5d} and D_{3d} minima are expressed by

$$\begin{aligned} \mathbf{q}_{h_g}^{D_{5d}} &= q_{h_g} \left(\frac{\phi^2}{2\sqrt{5}}, \frac{\phi^{-1}}{2} \sqrt{\frac{3}{5}}, 0, \sqrt{\frac{3}{5}}, 0 \right), \\ \mathbf{q}_{g_g}^{D_{5d}} &= q_{g_g} (0, 0, 0, 0), \end{aligned} \quad (11)$$

and

$$\begin{aligned} \mathbf{q}_{h_g}^{D_{3d}} &= q_{h_g} \left(-\frac{\phi^{-1}}{2}, \frac{\phi^2}{2\sqrt{3}}, 0, \frac{1}{\sqrt{3}}, 0 \right), \\ \mathbf{q}_{g_g}^{D_{3d}} &= q_{g_g} \left(\frac{1}{\sqrt{6}}, 0, -\sqrt{\frac{5}{6}}, 0 \right), \end{aligned} \quad (12)$$

respectively[32]. Substituting these symmetrized deformations, Eqs. (11) and (12), into potential terms of model Hamiltonian (kinetic energy term is ignored), and then diagonalizing model Hamiltonian, we obtain the lowest adiabatic

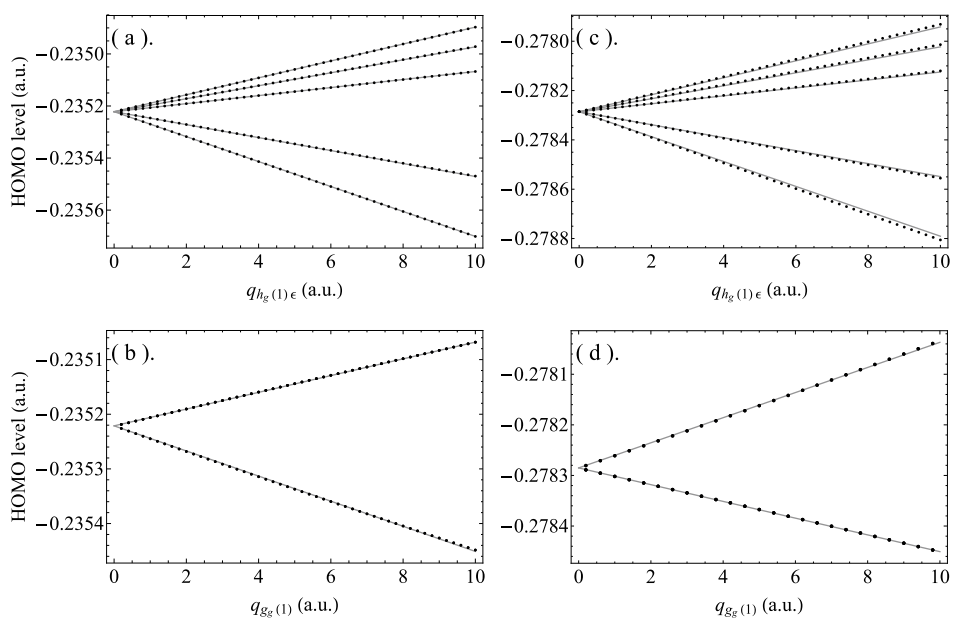


FIGURE 1 The JT splitting of the HOMO levels with respect to $q_{hg(1)\epsilon}$ ((a) and (c)) and $q_{gg(1)a}$ ((b) and (d)) deformations (in atomic unit). (a) and (b) are calculated with B3LYP functional, while (c) and (d) are with CAM-B3LYP functional. The black points and gray lines indicate the DFT values and model energy, respectively.

TABLE 1 The frequencies ω_Γ (cm^{-1}), orbital vibronic coupling parameters v_Γ (10^{-4} a.u.), and stabilization energies E_Γ (meV) for the a_g , g_g , and h_g modes. The data calculated with B3LYP for LUMOs are taken from Ref. [32].

$g_\Gamma = V_\Gamma / \sqrt{\hbar\omega_\Gamma^3}$ is dimensionless vibronic coupling parameter.

B3LYP								CAM-B3LYP						
μ	ω_Γ	ν_Γ		g_Γ		E_Γ		ω_Γ	ν_Γ		g_Γ		E_Γ	
	1	2	1	2	1	2		1	2	1	2	1	2	
HOMO														
a_{g1}	497	−0.121		−0.112		0.389		506	−0.118		−0.106		0.355	
a_{g2}	1498	1.040		0.184		3.159		1527	1.369		0.236		5.268	
g_{g1}	481	−0.375		−0.366		3.984		502	−0.405		−0.370		4.265	
g_{g2}	584	−0.101		−0.074		0.196		586	−0.207		−0.150		0.815	
g_{g3}	768	0.923		0.446		9.466		787	1.083		0.504		12.400	
g_{g4}	1092	−1.281		−0.365		9.019		1092	−1.583		−0.451		13.781	
g_{g5}	1335	0.541		0.114		1.076		1356	0.739		0.152		1.947	
g_{g6}	1540	1.477		0.251		6.029		1576	1.571		0.258		6.509	
h_{g1}	266	0.690	−0.080	1.635	−0.190	44.099	0.593	271	0.727	−0.090	1.674	−0.206	47.120	0.714
h_{g2}	439	−0.508	−0.290	−0.568	−0.324	8.776	2.860	450	−0.558	−0.363	−0.601	−0.391	10.063	4.269
h_{g3}	726	−0.043	0.977	−0.023	0.514	0.023	11.869	745	−0.061	1.053	−0.031	0.532	0.043	13.086
h_{g4}	786	0.923	−0.059	0.431	−0.027	9.038	0.037	802	0.930	−0.139	0.421	−0.063	8.821	0.198
h_{g5}	1125	−0.101	−0.495	−0.028	−0.135	0.053	1.269	1148	−0.074	−0.565	−0.020	−0.150	0.028	1.591
h_{g6}	1269	0.965	0.272	0.220	0.062	3.790	0.301	1300	0.986	0.025	0.216	0.005	3.768	0.002
h_{g7}	1443	2.860	1.487	0.537	0.279	25.745	6.960	1480	3.425	2.010	0.618	0.363	35.072	12.081
h_{g8}	1607	2.721	−1.542	0.434	−0.246	18.790	6.034	1663	3.217	−1.701	0.488	−0.258	24.523	6.854
LUMO														
a_{g1}	497	−0.264		−0.245		1.849		506	−0.253		−0.228		1.629	
a_{g2}	1498	−2.380		−0.422		16.543		1527	−2.921		−0.503		23.971	
h_{g1}	266	0.192		0.455		3.415		271	0.209		0.481		3.884	
h_{g2}	439	0.450		0.503		6.886		450	0.456		0.491		6.735	
h_{g3}	726	0.754		0.396		7.069		745	0.849		0.429		8.512	
h_{g4}	786	0.554		0.259		3.256		802	0.575		0.260		3.367	
h_{g5}	1125	0.766		0.209		3.038		1148	0.827		0.219		3.402	
h_{g6}	1269	0.578		0.132		1.360		1300	0.513		0.113		1.019	
h_{g7}	1443	2.099		0.394		13.867		1480	2.553		0.461		19.492	
h_{g8}	1607	2.043		0.326		10.592		1663	2.325		0.352		12.808	

potential energies as

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

(13)

for D_{5d} and D_{3d} deformations, respectively. Furthermore, these global minima energies could be expressed in terms of stabilization energies (Eq. (5)), as[14]

$$E_{JT}^{D_{5d}} = -E_{1h}^{JT},$$
$$E_{JT}^{D_{3d}} = -\frac{1}{9}\left(4E_g^{JT} + 5E_{2h}^{JT}\right).$$

(14)

JT stabilization energies of C_{60}^+ are obtained using these equations and the calculated vibronic coupling parameters. When treating C_{60}^+ , we have to sum up contributions from all g_g and h_g modes. Manini *et al.* also have derived vibronic coupling parameters and JT stabilization energies in the same way with LDA. [23] Besides, there is always the stabilization due to the totally symmetric modes (Eq. (6)).

JT stabilization energies of C_{60}^+ have been calculated with different methods with various functionals. These methodologies to derive JT energies are classified into four. We denote the present method (I). In the second method, JT stabilization energy is directly obtained from the energy difference between high- and low-symmetric structures. This method was employed by Lykhin *et al.* [7] with B3LYP. The third and the fourth methods, (III) and (IV), are called interaction mode approach [37, 38] and intrinsic distortion path approach [39, 40, 41, 42], respectively. In both methods, vibronic coupling parameters or JT energies are extracted from optimized geometry with each subgroup of I_h . The interaction mode induces deformation along JT minima from high-symmetric coordinates and is expressed by a linear combination of normal modes of high-symmetric C_{60} . The coefficients of the linear combinations contain the information of the vibronic coupling. By expanding the difference of JT deformed and high-symmetry geometries, ΔR_{JT} , with the eigen modes of mass-weighted normal modes e_i [31] at high-symmetry structure as

$$\frac{V_i}{\omega_i^2} = c_i \sqrt{M} \Delta R_{JT} \cdot e_i, \quad (15)$$

the vibronic coupling parameters V_i could be obtained. The frequencies ω_i are obtained from first principles calculations and M is mass of carbon, and the coefficients c_i depend on the structure of the JT interaction matrix. This approach was used in Refs. [25, 43]. On the other hand, within the intrinsic distortion path analysis, the high-symmetric structure is expressed by the linear combination of the eigen vectors from low-symmetric structure. Combining the vibronic coupling parameters derived from the deformation, V'_i , and the frequencies at the low-symmetric structure, ω'_i , the JT energy could be written as $E_{JT} = \sum_i V_i'^2 / (2\omega_i'^2)$. The last method was applied to C_{60}^+ in Ref. [25].

JT stabilization energies in this work, as well as those from previous studies, are shown in Table 2, 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. In particular, data calculated with LDA from Manini *et al.* [23] is only about 60 % of the present data. The underestimation of JT energy by LDA method is consistent with the situation in C_{60}^- [26]. However, since with LDA methods (II) and (III) give similar data as the one by method (I), [23] the difference of these methods would not be the origin of discrepancies seen in B3LYP data. Thus, a possible reason is that the deformed geometry with B3LYP functional in Ref. [25] is the one at a local minima. For B3LYP, Ref. [7] and present work give much close results, whereas the former is larger than the latter by 11 meV. So such a difference is expected to come from that JT stabilization energies contributed by totally symmetric modes, Eq. (6), are included in Ref. [7]. However, JT stabilization energy contributed from a_g modes in this work is about 3.5 meV (Table 1), which is still smaller than 11 meV. The underestimation of vibronic coupling of totally symmetric modes may come from the lack of contributions from occupied orbitals and change of frequencies. In general, only the partially filled frontier orbitals contribute to the vibronic coupling to the JT modes due to the symmetry [44], whereas all occupied orbitals do contribute to vibronic coupling to the totally symmetric modes [45]. Indeed, in the case of a planar molecule, picene, orbital vibronic coupling parameters for totally symmetric modes differ by 10-20 % from those obtained by fitting the gradients of total system energy [46]. Frequencies can be changed due to the removal of electron by 5-15 % [47]. Another possible origin of this discrepancy is nonlinear vibronic coupling, however, such coupling is much weaker than linear vibronic coupling as in the case of C_{60} anions [32].

Besides these works, we note that Kern *et al* [13] have optimized the structure to simulate infrared (IR) absorption

TABLE 2 Jahn-Teller 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	[23]
B3LYP	(II)	121	-	[7]
LDA	(III)	74	27	[25]
OPBE	(III)	74	28	[25]
B3LYP	(III)	80	32	[25]
PBE	(III)	74	28	[43]
LDA	(IV)	72	20	[25]
OPBE	(IV)	74	21	[25]
B3LYP	(IV)	94	25	[25]

spectrum with BP86 functional, but JT energy was not derived.

4 | DISCUSSION

To fully reveal the molecular nature of C_{60}^+ , non-adiabatic dynamical Jahn-Teller effect is crucial. The most straightforward way would be exact diagonalizing molecular Hamiltonian, which fully quantizes both nuclear and electronic coordinates, nevertheless, it is not practical. To partly overcome this difficulty, combining Jahn-Teller model Hamiltonian (3) with accurate enough vibronic coupling parameters is indispensable to derive low-energy states.

Vibronic coupling parameters of C_{60}^+ have been derived by using DFT calculations with LDA [23, 25] and B3LYP [24] functionals. As discussed in Sec. 2, model Hamiltonian is described by one vibronic coupling parameter for each a_g and g_g mode, and two parameters for each h_g mode. Both parameters for the h_g modes, V_{1h} and V_{2h} , have been derived only in Ref. [23] and Ref. [25], while they have not in Ref. [24]. Ramanantoanina *et al.* [25] shows that the magnitudes of derived coupling parameters obtained from the gradient of HOMO levels [23] and those from adiabatic potential energy surface agree well with each other, which has been also seen in C_{60}^- [26, 33, 32]. Thus, the present orbital vibronic coupling parameters derived from C_{60} must be close to the parameters for C_{60}^+ derived based on the definition.

The accuracy of LDA data have been discussed [25, 48] based on the comparison between experimental photoelectron spectra (PES) [12] and those from numerical simulation [17]. Indeed, PES is very useful to establish vibronic coupling parameters, whereas the simulation of PES requires high accuracy both in theoretical simulation and experiments. In the case of C_{60}^- , vibronic coupling parameters derived from broad PES at high-temperature [49] have been proved to be overestimated by the simulation of high-resolution PES spectra [26]. Furthermore, it was also found that the error bar of vibronic coupling parameters derived from broad PES is very large [26]. Thus, the derivation of accurate coupling parameters is only possible if we have high-resolution PES spectra measured at low-temperature [50, 51]. In the case of C_{60}^+ , as pointed out by Manini *et al.* [17], experimental PES is broad and fine structure of low-

energy region due to vibronic coupling is completely smeared out, which prevents the direct comparison between theory and experiment. Moreover, in the case of PES of C_{60}^+ , theoretical ratio of the second strongest peak to the strongest one is smaller than those of experimental data, implying the underestimation of vibronic coupling by LDA. From this point, the present data larger than the LDA data by 40 % would give better agreement.

The quality of B3LYP calculations has been checked in C_{60} anions by comparing theoretical and experimental data in previous studies. Besides the good agreement between coupling parameters from B3LYP calculations and high-resolution PES [26], the good quality of B3LYP calculations also has been confirmed from Néel temperature [52], spin gap [53], and the explanation for the origin of temperature evolution of infrared spectra [47] in Mott-insulating Cs_3C_{60} using the same vibronic coupling parameters. Furthermore, vibronic coupling parameters from B3LYP calculations tend to give good description of inelastic electron tunneling spectra of other organic molecule [54]. All these facts show that B3LYP values are closer to the reality in C_{60}^+ , but there still a mismatch when compared with experimental data. The application of CAM-B3LYP could eliminate such mismatch of vibronic parameters in fullerene system, as shown in recent study of C_{60}^- [28].

Although the derivation of vibronic coupling parameters is the first step toward full description of the molecular states of C_{60}^+ , we believe this is a crucial step. Once calculations of accurate enough vibronic states become possible, it is possible to interpret various spectra such as scanning tunneling measurements of C_{60} [55], inverse PES [56] and angle resolved PES [57] to mention a few. Furthermore, present coupling parameters are derived based on the well-defined phase factor of normal modes which has been also used for orbital coupling parameters of LUMO [32] and next LUMO [28]. Therefore, by combining present coupling parameters with them, it is also possible to address complex vibronic problems of excited C_{60} [58], and also to analyze e.g. luminescence spectra [59] and relaxation process and thermally activated delayed luminescence [60].

5 | CONCLUSIONS

In this work, orbital vibronic coupling parameters for h_u HOMO level of C_{60} are derived using both B3LYP and CAM-B3LYP hybrid functional. We believe that these vibronic coupling parameters are high accurate and close to the real situation. With these obtained coupling parameters, JT stabilization energies of C_{60}^+ are calculated, and JT structure at the minima of APES is confirmed to be D_{5d} , with the stabilization energy 110 meV and 129 meV calculated with B3LYP and CAM-B3LYP, respectively. JT stabilization energies in C_{60}^+ are about two times larger than that in C_{60}^- , suggesting the crucial role of the dynamical JT effect to reveal the actual situation of C_{60}^+ .

Present coupling parameters have been derived within the same framework used for our studies on ground and excited C_{60}^- . Thus, combining present data with that from other works, it is also possible to analyze the vibronic problems of excited C_{60} .

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conflict of interest

There are no conflicts to declare.

6 | APPENDIX

6.1 | Clebsch-Gordan coefficients: $\hat{C}_{\Gamma\gamma}$

For the derivation of the vibronic Hamiltonian, the Clebsch-Gordan coefficients, $\hat{C}_{\Gamma\gamma}$ are taken from Ref. [32], and listed below, in which $\phi = (1 + \sqrt{5})/2$, $\Gamma = g, 1h, 2h$, and $\gamma = a, x, y, z, \theta, \epsilon, \xi, \eta, \zeta$.

$$\hat{C}_{ga} = \begin{pmatrix} \frac{1}{2}\sqrt{\frac{3}{2}} & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2}\sqrt{\frac{3}{2}} & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{\sqrt{6}} & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{\sqrt{6}} & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{\sqrt{6}} \end{pmatrix} \quad (16)$$

$$\hat{C}_{gx} = \begin{pmatrix} 0 & 0 & -\frac{\phi}{4}\sqrt{\frac{5}{2}} & 0 & 0 \\ 0 & 0 & \frac{\phi^{-2}}{4}\sqrt{\frac{5}{6}} & 0 & 0 \\ -\frac{\phi}{4}\sqrt{\frac{5}{2}} & \frac{\phi^{-2}}{4}\sqrt{\frac{5}{6}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2}\sqrt{\frac{5}{6}} \\ 0 & 0 & 0 & \frac{1}{2}\sqrt{\frac{5}{6}} & 0 \end{pmatrix} \quad (17)$$

$$\hat{C}_{gy} = \begin{pmatrix} 0 & 0 & 0 & \frac{\phi^{-1}}{4}\sqrt{\frac{5}{2}} & 0 \\ 0 & 0 & 0 & -\frac{\phi^2}{4}\sqrt{\frac{5}{6}} & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2}\sqrt{\frac{5}{6}} \\ \frac{\phi^{-1}}{4}\sqrt{\frac{5}{2}} & -\frac{\phi^2}{4}\sqrt{\frac{5}{6}} & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2}\sqrt{\frac{5}{6}} & 0 & 0 \end{pmatrix} \quad (18)$$

$$\hat{C}_{gz} = \begin{pmatrix} 0 & 0 & 0 & 0 & \frac{1}{4}\sqrt{\frac{5}{2}} \\ 0 & 0 & 0 & 0 & \frac{5}{4\sqrt{6}} \\ 0 & 0 & 0 & \frac{1}{2}\sqrt{\frac{5}{6}} & 0 \\ 0 & 0 & \frac{1}{2}\sqrt{\frac{5}{6}} & 0 & 0 \\ \frac{1}{4}\sqrt{\frac{5}{2}} & \frac{5}{4\sqrt{6}} & 0 & 0 & 0 \end{pmatrix} \quad (19)$$

$$\hat{C}_{1h\theta} = \begin{pmatrix} \frac{\sqrt{5}}{16} & \frac{3\sqrt{3}}{16} & 0 & 0 & 0 \\ \frac{3\sqrt{3}}{16} & -\frac{\sqrt{5}}{16} & 0 & 0 & 0 \\ 0 & 0 & -\frac{\phi^{-2}}{4} & 0 & 0 \\ 0 & 0 & 0 & \frac{\phi^2}{4} & 0 \\ 0 & 0 & 0 & 0 & -\frac{\sqrt{5}}{4} \end{pmatrix} \quad (20)$$

$$\hat{C}_{1h\epsilon} = \begin{pmatrix} \frac{3\sqrt{3}}{16} & -\frac{\sqrt{5}}{16} & 0 & 0 & 0 \\ -\frac{\sqrt{5}}{16} & -\frac{3\sqrt{3}}{16} & 0 & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{3}\phi}{4} & 0 & 0 \\ 0 & 0 & 0 & \frac{\sqrt{3}\phi^{-1}}{4} & 0 \\ 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{4} \end{pmatrix} \quad (21)$$

$$\hat{C}_{1h\xi} = \begin{pmatrix} 0 & 0 & -\frac{\phi^{-2}}{4} & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{3}\phi}{4} & 0 & 0 \\ -\frac{\phi^{-2}}{4} & -\frac{\sqrt{3}\phi}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (22)$$

$$\hat{C}_{1h\eta} = \begin{pmatrix} 0 & 0 & 0 & \frac{\phi^2}{4} & 0 \\ 0 & 0 & 0 & \frac{\sqrt{3}\phi^{-1}}{4} & 0 \\ 0 & 0 & 0 & 0 & 0 \\ \frac{\phi^2}{4} & \frac{\sqrt{3}\phi^{-1}}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (23)$$

$$\hat{C}_{1h\zeta} = \begin{pmatrix} 0 & 0 & 0 & 0 & -\frac{\sqrt{5}}{4} \\ 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{4} \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ -\frac{\sqrt{5}}{4} & \frac{\sqrt{3}}{4} & 0 & 0 & 0 \end{pmatrix} \quad (24)$$

$$\hat{C}_{2h\theta} = \begin{pmatrix} \frac{9}{16} & -\frac{\sqrt{15}}{16} & 0 & 0 & 0 \\ -\frac{\sqrt{15}}{16} & -\frac{9}{16} & 0 & 0 & 0 \\ 0 & 0 & \frac{\phi}{4} & 0 & 0 \\ 0 & 0 & 0 & -\frac{\phi^{-1}}{4} & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{4} \end{pmatrix} \quad (25)$$

$$\hat{C}_{2h\epsilon} = \begin{pmatrix} -\frac{\sqrt{15}}{16} & -\frac{9}{16} & 0 & 0 & 0 \\ -\frac{9}{16} & \frac{\sqrt{15}}{16} & 0 & 0 & 0 \\ 0 & 0 & -\frac{\phi^{-2}}{4\sqrt{3}} & 0 & 0 \\ 0 & 0 & 0 & \frac{\phi^2}{4\sqrt{3}} & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{4}\sqrt{\frac{5}{3}} \end{pmatrix} \quad (26)$$

$$\hat{C}_{2h\xi} = \begin{pmatrix} 0 & 0 & \frac{\phi}{4} & 0 & 0 \\ 0 & 0 & -\frac{\phi^{-2}}{4\sqrt{3}} & 0 & 0 \\ \frac{\phi}{4} & -\frac{\phi^{-2}}{4\sqrt{3}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{\sqrt{3}} \\ 0 & 0 & 0 & \frac{1}{\sqrt{3}} & 0 \end{pmatrix} \quad (27)$$

$$\hat{C}_{2h\eta} = \begin{pmatrix} 0 & 0 & 0 & -\frac{\phi^{-1}}{4} & 0 \\ 0 & 0 & 0 & \frac{\phi^2}{4\sqrt{3}} & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{\sqrt{3}} \\ -\frac{\phi^{-1}}{4} & \frac{\phi^2}{4\sqrt{3}} & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{\sqrt{3}} & 0 & 0 \end{pmatrix} \quad (28)$$

$$\hat{C}_{2h\zeta} = \begin{pmatrix} 0 & 0 & 0 & 0 & -\frac{1}{4} \\ 0 & 0 & 0 & 0 & -\frac{1}{4}\sqrt{\frac{5}{3}} \\ 0 & 0 & 0 & \frac{1}{\sqrt{3}} & 0 \\ 0 & 0 & \frac{1}{\sqrt{3}} & 0 & 0 \\ -\frac{1}{4} & -\frac{1}{4}\sqrt{\frac{5}{3}} & 0 & 0 & 0 \end{pmatrix} \quad (29)$$

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