Vibronic coupling in \( C_{60}^- \) anion revisited: Precise derivations from photoelectron spectra and DFT calculations

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The vibronic coupling constants of \( C_{60}^- \) are derived from the photoelectron spectrum measured by Wang et al. [X. B. Wang, H. K. Woo, and L. S. Wang, J. Chem. Phys., 123, 051106 (2005)] at low temperature with high-resolutions. We find that the couplings of the Jahn–Teller modes of \( C_{60}^- \) are weaker than the couplings reported by Gunnarsson et al. [O. Gunnarsson, H. Handschu, P. S. Bechthold, B. Kessler, G. Ganteför, and W. Eberhardt, Phys. Rev. Lett., 74, 1875 (1995)]. The total stabilization energy after \( h_g \) and \( a_g \) modes is reduced with respect to the previous derivation of Gunnarsson et al. by 30%. The computed vibronic coupling constants using DFT with B3LYP functional agree well with the new experimental constants, so the discrepancy between theory and experiment persistent in the previous studies is basically solved.

I. INTRODUCTION

Much attention has been paid to the Jahn–Teller effect of fullerene \( (C_{60}) \) in various electronic states not only because the Jahn–Teller effect is an interesting problem in molecular physics[3] but also because it is expected to play an important role in the mechanism of the superconductivity in alkali-doped fullerenes. Thus, the strength of the electron-vibration coupling (vibronic coupling) of \( C_{60} \) which characterizes the Jahn–Teller effect has been one of the important topics. The vibronic coupling constants (VCCs) have been estimated experimentally[3,11,12] and theoretically[60,61,62].

In the experimental studies of vibronic coupling in fullerene, a landmark is the photoelectron spectroscopy (PES) of \( C_{60}^- \) in gas phase by Gunnarsson et al. As \( C_{60}^- \) is one of the most studied systems, in addition to this experimental work, computational works have been performed by many authors. However, discrepancy between the coupling constants of the experimental and theoretical works have been reported[61,11,12]. The theoretical stabilization energies as estimated by density functional theory (DFT) calculation were always obtained smaller than that estimated by density functional theory (DFT).

Recently, Wang et al. remeasured photoelectron spectra of \( C_{60}^- \)[13]. In their experiment, the vibrational temperature of \( C_{60}^- \) is between 70 K and 90 K and the resolution is about 16 meV, i.e., much smaller than the resolution of 40 meV in the experiment of Gunnarsson et al. Accordingly, the spectrum of Wang et al. is narrower and has more structures, therefore, it is expected to yield more reliable coupling constants.

In this work, we simulate the photoelectron spectra of Wang et al.[13] and Gunnarsson et al.[3] and give new derivations of the VCCs of \( C_{60}^- \). We also compute the VCCs of \( C_{60}^- \) using the DFT method and compare them with the experimental values.

II. THE SOLUTION OF THE JAHN–TELLER PROBLEM OF \( C_{60}^- \)

The equilibrium geometry of neutral fullerene is taken as the reference nuclear configuration. At this reference structure, the ground electronic state of \( C_{60}^- \) is \( T_{1u} \). According to the selection rule, the \( T_{1u} \) electronic state couples with two \( a_g \) and eight \( h_g \) vibrational modes:

\[
[T_{1u}^2] = a_g \oplus h_g. \tag{1}
\]

We consider the linear \( T_{1u} \otimes (2a_g \oplus 8h_g) \) Jahn–Teller Hamiltonian. The Hamiltonian is written as follows:

\[
H = \sum_{i=1}^{2} \left[ \frac{1}{2} \left( P_{a_g(i)}^2 + \omega_{a_g(i)}^2 Q_{a_g(i)}^2 + V_{a_g(i)} Q_{a_g(i)} \right) \right] \hat{I} + \sum_{\mu=1}^{8} \sum_{m=-2}^{2} \left[ \frac{1}{2} \left( P_{h_g(\mu)m}^2 + \omega_{h_g(\mu)m}^2 Q_{h_g(\mu)m}^2 \right) \right] \hat{I} + \sqrt{\frac{3}{8}} (-1)^m V_{h_g(\mu)m} Q_{h_g(\mu)m} \hat{C}_m, \tag{2}
\]

where \( Q_{\Gamma(\mu)m} \) is the mass-weighted normal coordinate of \( m \) element of the \( \Gamma(\mu) \) mode (\( \Gamma = a_g, h_g \)), \( P_{\Gamma(\mu)m} \) is the conjugate momentum of the normal coordinate \( Q_{\Gamma(\mu)m} \), \( \omega_{\Gamma(\mu)} \) is the frequency of the \( \Gamma(\mu) \) mode, \( V_{\Gamma(\mu)m} \) is the VCC of the \( \Gamma(\mu) \) mode, and \( \hat{I} \) and \( \hat{C}_m \) are the \( 3 \times 3 \) unit matrix and a matrix whose elements...
are Clebsch–Gordan coefficients, respectively. The normal modes and frequencies of $C_{60}$ are used for $C_{70}$, so the higher vibronic terms which mix the normal modes of fullerene are neglected. As a $T_{1u}$ electronic basis set $\{|m_{el}\}; m_{el} = -1, 0, 1\}$ and normal coordinates of the $h_g$ modes $\{Q_{h_g(m)}; m = -2, -1, 0, 1, 2\}$, we use complex basis which transform as spherical harmonics $\{Y_{1m_{el}}; m_{el} = -1, 0, 1\}$ and $\{Y_{2m}; m = -2, -1, 0, 1, 2\}$, respectively, under the rotations. Then $\hat{I}$ and $\hat{C}_{-m}$ are written as $\hat{I} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, $\hat{C}_{-2} = \begin{pmatrix} 0 & 0 & \sqrt{\frac{3}{5}} \\ 0 & 0 & 0 \\ \sqrt{\frac{3}{5}} & 0 & 0 \end{pmatrix}$, $\hat{C}_{-1} = \begin{pmatrix} 0 & -\sqrt{\frac{3}{10}} & 0 \\ 0 & 0 & \sqrt{\frac{3}{10}} \\ 0 & 0 & 0 \end{pmatrix}$, $\hat{C}_0 = \begin{pmatrix} \frac{1}{\sqrt{10}} & 0 & 0 \\ 0 & \frac{1}{\sqrt{10}} & 0 \\ 0 & 0 & \frac{1}{\sqrt{10}} \end{pmatrix}$, $\hat{C}_1 = \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{\frac{3}{10}} & 0 & 0 \\ 0 & \sqrt{\frac{3}{10}} & 0 \end{pmatrix}$, $\hat{C}_2 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \sqrt{\frac{3}{5}} & 0 & 0 \end{pmatrix}$.

This type of the Jahn–Teller problem was investigated by O’Brien[15] and the vibronic coupling constants defined by her are often used. Thus we introduce the coefficient $\sqrt{5/2}$ in front of the vibronic term to make $V_h$ the same as O’Brien’s coupling constants.

Since the linear $T_{1u} \otimes (2a_g \otimes 8h_g)$ Jahn–Teller Hamiltonian[2] commutes with squared vibronic angular momentum $J$ and the $z$ component of $J$[25] the eigenstate of the Hamiltonian[22] is the simultaneous eigenstate of the vibronic angular momentum $J$, the $z$ component of the vibronic angular momentum $M$. Here, the vibronic angular momentum $J$ is the sum of the vibrational angular momentum $L$ and the “energy spin” $S$ describing the threefold orbital degeneracy ($S = 1$)[25]. In the case of linear vibronic coupling, the eigenstate of $H$ is the product of the $T_{1u} \otimes (8h_g)$ Jahn–Teller part and the $a_g$ vibrational part. As a vibronic basis a set of the products of electronic states and vibrational states of the $a_g$ and $h_g$ modes is used:

$$\{|m_{el}\}_i \cdots |n_{\mu}\}_v |v_1 v_2\rangle a_g.$$  (4)

Here, $|n_{\mu}\rangle$ means a set of vibrational quantum numbers of the $h_g(\mu)$ mode, $|v_1 v_2\rangle$ are vibrational quantum numbers of the $a_g(1)$ mode and the $a_g(2)$ mode respectively. Then the eigenstate $|\Psi_{v_1 v_2, kJM}\rangle$ of the Hamiltonian[25] which belongs to the eigenvalue $\sum_{i=1}^{2} (\hbar \omega_{a_g(1)} v_1 - V_{a_g(1)}^2 / (2 \omega_{a_g(2)}^2)) + E_{k,J}$ is represented as a linear combination of the vibronic basis with constants $C^{|m_{el}\rangle \cdots |n_{\mu}\rangle; kJM}$:

$$|\Psi_{v_1 v_2, kJM}\rangle = \sum_{m_{el} = -1}^{1} \sum_{n_1} \cdots \sum_{n_s} |m_{el}\rangle |n_{\mu}\rangle ... |v_1 v_2\rangle a_g.$$  (5)

where $E_{k,J}$ is an eigenvalue of the $T_{1u} \otimes (8h_g)$ Jahn–Teller Hamiltonian, $k$ distinguishes energy levels with the same $J$ and $M$, the dimensionless VCC of the $\Gamma(\mu)$ mode $g_{\Gamma(\mu)}$ ($\Gamma = a_g, h_g$) is defined as

$$g_{\Gamma(\mu)} = \frac{V_{\Gamma(\mu)}}{\hbar \omega_{\Gamma(\mu)}},$$  (6)

the Franck–Condon factor of the $a_g$ mode $S_{\nu', \nu}(g)$ is written as

$$S_{\nu', \nu}(g) = \sqrt{\frac{\nu'!}{\nu!} e^{-\frac{1}{2} g^2 v \nu' \nu}} \sum_{l=0}^{\nu'} \left( -\frac{1}{2} \right)^l \frac{g^{2l+\nu' - \nu}}{l!(\nu' - l)!((\nu' - \nu) + l)!},$$  \label{eq:FC}

$l_{min} = 0$ for $v \leq \nu'$, and $l_{min} = \nu' - \nu$ for $\nu > \nu'$. The origin of the energy is the lowest energy of $C_{60}^-$ without vibronic couplings.

To obtain the vibronic states, we diagonalize the linear $T_{1u} \otimes (8h_g)$ Jahn–Teller Hamiltonian numerically using Lanczos method. We use a truncated vibronic basis set,

$$\{|m_{el}\}_i \cdots |n_{\mu}\rangle; 8 \sum_{\mu=1}^{2} \sum_{m_{el}=-1}^{1} n_{\mu m} \leq N \}.$$  (8)

Here, $N$ is the maximum number of the vibrational excitations in the vibronic basis set[5]. We treat the vibronic states which $J_S$ are from 0 to 7. Frequencies $\omega_{a_g(1)}, \omega_{h_g(\mu)}$ are taken from the experimental frequencies of Raman scattering in solid state $C_{60}^-$ [21].

Lastly, we introduce stabilization energies which we use to show our results. The stabilization energy of each mode is defined as

$$E_{s, i} = \frac{V^2_{a_g(i)}}{2 \omega_{a_g(i)}},$$  (9)

$$E_{J_T, \mu} = \frac{V^2_{h_g(\mu)}}{2 \omega_{h_g(\mu)}},$$  (10)

and the total stabilization energies of the $a_g$ modes and $h_g$ modes are

$$E_s = \sum_{i=1}^{2} E_{s, i},$$  (11)

$$E_{J_T} = \sum_{\mu=1}^{8} E_{J_T, \mu}.$$  (12)

They represent the depth of the potential energy surface from the energy of undistorted fullerene monomoin.
III. SIMULATION OF THE PHOTOELECTRON SPECTRUM

The photoelectron spectrum is simulated within the sudden approximation. We assume that each $C_{60}$ is in a thermal equilibrium state, hence we use a Boltzmann’s distribution to calculate the statistical weight. With these assumptions, the intensity of the transition which appears at the binding energy $\hbar \Omega$ is written as follows:

$$ I(\Omega) \propto \sum_{k,J} \sum_{v_1,v_2} p_{v_1} p_{v_2} k_j \sum_{m=1}^{1} \left| \frac{C_{JT}^{\prime}}{m_1 \cdots n_1 k_0} \psi_{v_1 v_2} (g_{a_g(1)}) \psi_{v_1 v_2} (g_{a_g(2)})^2 \right|^2 \times \delta \left[ \frac{E_0 + E_k - E_{kJ}}{\hbar} + \sum_{\mu=1}^{8} \sum_{m=2}^{2} \omega_{h_{\mu} (\rho \delta)} + \sum_{i=1}^{2} \omega_{a_g (i)} (v_i - v_0^i) - \Omega \right], \quad (13) $$

where, $p_{v_1}$ and $p_{k_j}$ are the statistical weights of the $a_g(i)$ mode and the Jahn-Teller part, respectively,

$$ p_{v_1} = \frac{1}{Z_{a_g}} \exp \left( \frac{-\hbar \omega_{a_g (i)} v_1 \beta}{\hbar} \right), \quad (14) $$

$$ p_{k_j} = \frac{2J + 1}{Z_{JT}} \exp \left( \frac{-E_{kJ} \beta}{\hbar} \right), \quad (15) $$

$Z_{a_g}$ and $Z_{JT}$ are corresponding statistical sums, and $E_0$ is the gap between the ground electronic energies of $C_{60}$ and $C_{60}^\circ$. The envelope function is represented by using the Gaussian function with the standard deviation $\sigma$:

$$ F(\Omega) = \int_{-\infty}^{\infty} I(\Omega') \exp \left[ -\frac{(\Omega - \Omega')^2}{2\sigma^2} \right] d\Omega'. \quad (16) $$

For a decent simulation of experimental PES one should include in Eq. (16), in principle, also the contributions from the rotational spectrum of $C_{60}$. However, due to a large momentum of inertia of fullerene and restrictive selection rules for the transitions between different rotational levels, our estimations gave an expected enlargement of the transition band of only several wave numbers. This is negligible compared the full width at half maximum (FWHM) given by the envelope function.

To evaluate the agreement between the simulated spectrum and the experimental spectrum, we calculate the residual of theoretical spectrum $F_{calc}(\Omega)$ and the experimental spectrum $F_{exp}(\Omega)$. The residual $R$ is defined by the equation:

$$ R = \min_{f,\Omega_{shift}} \left\{ \sum_{i=0}^{M} \left| F_{calc}(\Omega_i) - f F_{exp}(\Omega_i - \Omega_{shift}) \right|^2 \right\}, \quad (17) $$

Here, $f$ is the parameter to vary the height, $\Omega_{shift}$ is the parameter to shift the experimental spectrum, $\Omega_i$ is a sampling point. The minimum and maximum of $\Omega_i$ is $\Omega_{min}$ and $\Omega_{max}$, and the gap between adjacent sampling points $\Delta \Omega$ is constant. Then $M$ is represented as $M = (\Omega_{max} - \Omega_{min})/\Delta \Omega$ and $\Omega_i = \Omega_{min} + i \Delta \Omega$. In the calculation of the residual $R$, $\Omega_{min}$, $\Omega_{max}$, and $\Delta \Omega$ are $-200$ cm$^{-1}$, 1600 cm$^{-1}$, and 0.5 cm$^{-1}$ respectively. We avoid the truncation of the zero phonon line of Gunnarsson et al. VCCs are varied in order to make $R$ as small as possible within the accuracy of the experiment. The accuracy is determined from the range of the vibrational temperature of $C_{60}$ in the experiment of Wang et al. In their experiment, the vibrational temperature is between 70 K and 90 K. Although the shapes of the simulated spectra at 70 K and 90 K are different from each other, we cannot distinguish them from the experiment of Wang et al. In terms of the residual $R$, the difference between $R$ at 70 K and $R$ at 90 K is practically indistinguishable.

IV. DFT CALCULATION OF VIBRONIC COUPLING CONSTANTS

The linear vibronic coupling constant of the $a_g(i)$ mode is a diagonal matrix element of the first derivative of the electronic Hamiltonian with respect to the normal coordinate at the reference geometry.

$$ V_{a_g(i)} = \langle \psi | \left( \frac{\partial H_{el}(R)}{\partial Q_{a_g(i)}} \right) | \psi \rangle, \quad (18) $$

where $\psi$ is the ground electronic state. By applying the Hellmann–Feynman theorem to Eq. (15) and then transforming it into the formula with the vibrational vector, we obtain

$$ V_{a_g(i)} = \left( \frac{\partial E(R)}{\partial Q_{a_g(i)}} \right)_{R_0} \cdot \frac{u_{a_g(i)}^{\prime}}{\sqrt{M}}, \quad (19) $$

Here, $A$ indicates a carbon atom in $C_{60}$, $R_A$ is the Cartesian coordinate of $A$, $R$ is the set of all $R_A$, $H_{el}(R)$ is the electronic Hamiltonian at the structure $R$, $R_0$ is the reference nuclear configuration, $E(R)$ is the ground electronic energy $\langle \psi | H_{el}(R) | \psi \rangle$, $M$ is the mass of carbon atom, $u_{a_g(i)}^{\prime}$ is the vibrational vector of the $a_g(i)$ mode. Similarly, absolute value of the coupling constant of the
$h_g(\mu)$ mode is written as

$$V_{h_g(\mu)} = \sqrt{\sum_{m=-2}^{2} \left( \frac{\partial E(R)}{\partial Q_{h_g(\mu)m}} \right)^2_{R_0} \text{ (21)}}$$

The equilibrium geometry $R_0$, the vibrational vectors $u^{a_g(i)}$, $u^{h_g(\mu)m}$, and the gradient of the electronic energy $\left( \partial E(R) / \partial R_A \right)_{R_0}$, entering the Eqs. (21) and (22), are obtained from ab initio calculations. Note that the vibronic coupling constants (19), (21) are not equal to the gradients of the frontier levels (see Appendix).

We compute the VCCs of $C_{60}$ using the DFT method. As exchange-correlation functional, the hybrid functional of Becke (B3LYP) is used. To find VCCs which are close to the experimental results the fraction of the Hartree–Fock exchange energy are varied from the original fraction 20% to 30% by 5%. We use the triple zeta basis sets, 6-311G(d), 6-311+G(d), and cc-pVTZ.

The structure optimization and the calculation of the vibrational modes are performed for the neutral fullerene. The electronic wavefunction of $C_{60}$ is broken and the degeneracy of the singly occupied determinants is used, the spatial symmetry of the wavefunction is tiny and the symmetry of the electronic state may not be broken significantly. Thus we treat the wavefunction as a $T_{1u}$ wavefunction. We calculate the energy gradient $\left( \partial E(R) / \partial R_A \right)_{R=R_0}$ with the coupled perturbed Kohn–Sham method. In the calculation of the dimensionless VCCs (6) and the stabilization energies (10), we use the experimental frequencies (21) to compute electronic structures we use the Gaussian 03 program.

V. DERIVATION OF THE VIBRONIC COUPLING CONSTANTS OF $a_g$ MODES FROM THE STRUCTURES OF $C_{60}$ AND $C_{70}$

We also derive the stabilization energies of the $a_g$ modes from the experimental bond lengths of $C_{60}$ and $C_{70}$. The structures of $C_{60}$ and $C_{70}$ with $I_h$ symmetry are determined by the C-C bond lengths of the edges between two hexagons (6:6) and a hexagon and pentagon (6:5). We use average 6:6 and 6:5 C-C bond lengths of TDAE-$C_{60}$ for $C_{50}$ and fullerite for $C_{60}$. The data of TDAE-$C_{60}$ are obtained from the results of X-ray diffraction at 7K by Narymbetov et al. (22) and at 25K and 90K by Fujiwara et al. (30). The average bond lengths of fullerite are taken from the results of neutron diffraction at 5K by David et al. (31) and X-ray diffraction at 110K by Bürgi et al. (32). To remove the thermal expansion of the C-C bond lengths, we use sets of bond lengths of $C_{60}$ and $C_{70}$, which are measured at close temperature. That is, the bond lengths of $C_{60}$ measured at 5K is used with the bond lengths of $C_{60}$ measured at 7K and 25K, and the bond lengths of $C_{60}$ at 110K is used with the bond lengths of $C_{60}$ at 90K. The vibronic coupling constants of the $a_g$ modes $V_{a_g(i)}(i=1,2)$ are obtained from the equation

$$V_{a_g(i)} = - \sum_{A=1}^{M} \left( R_A - R_{0,A} \right) \cdot \frac{u_A^{a_g(i)}}{\sqrt{M}}. \text{ (23)}$$

To perform the calculation, we use the vibrational vector defined in the calculations with the B3LYP method and the cc-pVTZ basis.

VI. RESULTS AND DISCUSSIONS

A. Simulation of the PES of Wang et al.

We simulate the photoelectron spectrum measured by Wang et al. (15) at 70 K. The basis set in Eq. (5) includes up to 6 vibrational excitations ($N = 6$). The experimental and simulated spectra are shown in Fig. 1. The transition between the ground states of $C_{60}$ and $C_{60}$ (the 0–0 line) is chosen as the origin of these spectra. From the spectrum of Wang et al., we obtain several sets of VCCs listed as (1), (2), and (3) in Tables I and II. We extracted $\sigma = 80 \text{ cm}^{-1}$ by fitting the FWHM of the 0–0 line (188 cm$^{-1}$). The increase or decrease of the $\sigma$ makes the agreement between the simulated and experimental spectra worse.
### TABLE I. Absolute values of dimensionless vibronic coupling constants obtained in the present work.

| Frequency (cm\(^{-1}\)) | PES | Wang\(^a\) | Gunnarsson\(^b\) | 6-311G(d) | 6-311+G(d) | cc-pVTZ |
|--------------------------|-----|------------|----------------|----------|----------|---------|
|                          |     | (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) | (10) | (11) |
| \(a_g(1)\)              | 496 | 0.505 | 0.505 | 0.500 | 0.141 | 0.505 | 0.287 | 0.272 | 0.269 | 0.346 | 0.289 | 0.286 |
| \(a_g(2)\)              | 1470 | 0.100 | 0.200 | 0.300 | 0.424 | 0.200 | 0.415 | 0.445 | 0.460 | 0.455 | 0.430 | 0.450 |
| \(h_g(1)\)              | 273 | 0.500 | 0.500 | 0.490 | 0.740 | 0.820 | 0.436 | 0.437 | 0.444 | 0.426 | 0.442 | 0.452 |
| \(h_g(2)\)              | 437 | 0.525 | 0.520 | 0.515 | 0.860 | 0.690 | 0.498 | 0.504 | 0.508 | 0.479 | 0.498 | 0.494 |
| \(h_g(3)\)              | 710 | 0.465 | 0.460 | 0.455 | 0.390 | 0.350 | 0.418 | 0.464 | 0.476 | 0.412 | 0.403 | 0.414 |
| \(h_g(4)\)              | 774 | 0.310 | 0.310 | 0.300 | 0.490 | 0.490 | 0.259 | 0.241 | 0.243 | 0.252 | 0.273 | 0.283 |
| \(h_g(5)\)              | 1099 | 0.285 | 0.280 | 0.280 | 0.320 | 0.320 | 0.211 | 0.233 | 0.241 | 0.211 | 0.212 | 0.217 |
| \(h_g(6)\)              | 1250 | 0.220 | 0.230 | 0.230 | 0.190 | 0.160 | 0.126 | 0.169 | 0.178 | 0.126 | 0.125 | 0.124 |
| \(h_g(7)\)              | 1428 | 0.490 | 0.470 | 0.435 | 0.320 | 0.430 | 0.398 | 0.414 | 0.433 | 0.392 | 0.398 | 0.415 |
| \(h_g(8)\)              | 1575 | 0.295 | 0.285 | 0.260 | 0.350 | 0.225 | 0.338 | 0.335 | 0.345 | 0.330 | 0.333 | 0.343 |

\(^a\) (1),(2), and (3) are derived from the PES of Wang et al. (Ref. [15])

\(^b\) (4),(5) are derived from the PES of Gunnarsson et al. (Ref. [3])

\(^c\) The percentage 20 %, 25 %, and 30 % indicate fractions of the Hartree–Fock exact exchange taken in the exchange-correlation functional.

### TABLE II. Stabilization energies (meV) obtained in the present work.

| Frequency (cm\(^{-1}\)) | PES | Wang\(^a\) | Gunnarsson\(^b\) | 6-311G(d) | 6-311+G(d) | cc-pVTZ |
|--------------------------|-----|------------|----------------|----------|----------|---------|
|                          |     | (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) | (10) | (11) |
| \(a_g(1)\)              | 496 | 7.8 | 7.8 | 7.7 | 0.6 | 7.8 | 2.5 | 2.3 | 2.2 | 3.7 | 2.6 | 2.5 |
| \(a_g(2)\)              | 1470 | 0.9 | 3.6 | 8.2 | 16.4 | 3.6 | 15.7 | 18.0 | 19.3 | 18.9 | 16.9 | 18.5 |
| \(h_g(1)\)              | 273 | 4.2 | 4.2 | 4.1 | 9.3 | 11.4 | 3.2 | 3.2 | 3.3 | 3.1 | 3.3 | 3.5 |
| \(h_g(2)\)              | 437 | 7.5 | 7.3 | 7.2 | 20.0 | 12.9 | 6.7 | 6.9 | 7.0 | 6.2 | 6.7 | 6.6 |
| \(h_g(3)\)              | 710 | 9.5 | 9.3 | 9.1 | 6.7 | 5.4 | 7.7 | 9.5 | 10.0 | 7.5 | 7.2 | 7.6 |
| \(h_g(4)\)              | 774 | 4.6 | 4.6 | 4.3 | 11.5 | 11.5 | 3.2 | 2.8 | 2.8 | 3.1 | 3.6 | 3.8 |
| \(h_g(5)\)              | 1099 | 5.5 | 5.3 | 5.3 | 7.0 | 6.1 | 3.0 | 3.7 | 4.0 | 3.0 | 3.0 | 3.2 |
| \(h_g(6)\)              | 1250 | 3.9 | 4.1 | 4.3 | 2.8 | 2.0 | 1.2 | 2.2 | 2.5 | 1.2 | 1.2 | 1.2 |
| \(h_g(7)\)              | 1428 | 2.13 | 19.6 | 16.8 | 9.1 | 16.4 | 14.0 | 15.2 | 16.6 | 13.6 | 14.0 | 15.2 |
| \(h_g(8)\)              | 1575 | 8.5 | 7.9 | 6.6 | 12.0 | 16.4 | 11.2 | 11.0 | 11.6 | 10.7 | 10.9 | 11.5 |

\(^a\) (1),(2), and (3) are derived from the PES of Wang et al. (Ref. [15])

\(^b\) (4),(5) are derived from the PES of Gunnarsson et al. (Ref. [3])

\(^c\) The percentage 20 %, 25 %, and 30 % indicate fractions of the Hartree–Fock exact exchange taken in the exchange-correlation functional.

To assess the thermal population of the excited vibronic states, we calculate statistical weights of the excited Jahn–Teller levels \(p_{J\&T}\) at 70 K and 90 K. The vibronic levels are obtained using the set of VCCs (1). In the calculation of the distribution function \(Z_{JT}\), we include all excited vibronic levels whose weights are larger than \(10^{-7}\). The computed weights are shown in Table III. Although these statistical weights are computed using the set (1), rest of the sets of VCCs (2), (3) give similar results. The statistical weights of the ground vibronic level at 70 K and 90 K are more than 90 %. This indicates that the transition from the ground vibronic level is dominant in the PES of Wang et al. We focus, therefore, on the ground vibronic level to discuss the effect of the size of the basis \(8\) on the calculated vibronic states. The ground vibronic level is \(-962.65\) cm\(^{-1}\) when...
Jahn–Teller coupling is weaker than previously expected.

of a cannot be distinguished from the experiment of Wang almost within the ambiguity of the vibrational temper-
ences of the residuals of the different sets of VCCs are 90 K. The values are shown in Table IV. The differ-
the simulated spectra for all sets of VCCs at 70 K and
ergy of Gunnarsson et al.

we use the basis set with \( N = 5 \). Compared with the
gap between the ground and first excited vibronic levels with
\( J = 1 \), the change of the ground vibronic level due to the increase of the size of the vibronic basis set is only
about 0.07 \%. Therefore, we regard our basis set as large
enough to simulate the spectrum of Wang et al.

The differences between several sets of VCCs are in
the constants of \( a_g(2), h_g(7), \) and \( h_g(8) \) modes. If we in-
crease the dimensionless VCC (the stabilization energy)
of the \( a_g(2) \) mode from 0.1 to 0.3 (0.9 to 8.2 meV) and
at the same time decrease the dimensionless VCCs of
\( h_g(7), h_g(8) \) modes, the shape of the PES does not vary significantly (see Fig. 2). This is due to a poor reso-
lation of the peaks of \( a_g(2), h_g(7), \) and \( h_g(8) \) modes and
essentially the same problem arose in the analysis of Gunnarsson et al.\(^3\) In the latter case, the stabilization energy
of \( a_g(2) \) is varied from 0 to 45 meV, i.e., in a range larger
than ours. Owing to the narrow peaks of the spectrum of
Wang et al., we can derive the VCCs with less ambiguity.

We compute the residuals \(^{17}\) of the experimental and
the simulated spectra for all sets of VCCs at 70 K and
90 K. The values are shown in Table \( \text{V} \). The differ-
ces of the residuals of the different sets of VCCs are
almost within the ambiguity of the vibrational tempera-
ture. Therefore, we conclude that these sets of VCCs
cannot be distinguished from the experiment of Wang et al.

Although we obtain several sets of VCCs, the stabiliza-
tion energies \( E_s + E_{JT} \) are similar to each other (see \( 1 \),
\( 2 \), and \( 3 \) in Table \( \text{II} \)). On the other hand, present sta-
bilization energies are smaller than the stabilization energy
of Gunnarsson et al.\(^3\) by 30 \% (see Table \( \text{V} \)), i.e., the
Jahn–Teller coupling is weaker than previously expected.

**TABLE III.** The lowest vibronic levels (cm\(^{-1}\)) and the statistical weights \( p_{\mu J} \) (%) at 70 K and 90 K. \( J \) is the magnitude of the vibronic angular momentum. To calculate the vibronic levels, the set of VCCs (1) in Table \( \text{I} \) is used.

| Level | \( J \) | Energy | Weight |
|-------|------|--------|--------|
|       |      | 70 K   | 90 K   |
| 1     | 1    | -962.85| 97.75  | 92.48  |
| 2     | 3    | -713.97| 1.37   | 4.04   |
| 3     | 2    | -683.40| 0.52   | 1.77   |
| 4     | 1    | -672.75| 0.25   | 0.90   |
| Sum   |      |        | 99.89  | 99.19  |

**TABLE IV.** Residuals of the experimental and simulated spec-
tra. The calculation of the residual is performed for all sets
of VCCs in Table \( \text{II} \) at 70 K and 90 K.

| Set (1) | Set (2) | Set (3) |
|---------|---------|---------|
| 70 K    | 90 K    | 70 K    | 90 K    | 70 K    | 90 K    |
| \( R \times 10^{-4} \) | 8.35 | 8.07 | 8.41 | 8.16 | 8.76 | 8.41 |

**FIG. 2.** The peak of the photoelectron spectra due to \( a_g(2), h_g(7), \) and \( h_g(8) \) modes. The black line indicates the experimental spectrum of Wang et al.\(^3\) the red line indicates the simulated spectrum, and the blue line indicates the difference between the experimental and simulated spectra. The top of the two spectra is simulated using the VCCs (1) and the bottom one is simulated using the VCCs (3) from Table \( \text{I} \). The simulation is performed at 70 K with \( N = 6 \) and \( \sigma = 80 \) cm\(^{-1}\).

We find that the distributions of \( E_s \) and \( E_{JT,\mu} \) also differ from each other (Tables \( \text{II} \) \( \text{IV} \)). In Ref. \( \text{III} \) the stabilization
energy of \( h_g(2) \) was found the strongest, while our results show that the strongest is the stabilization energy
of \( h_g(7) \).

Hands et al. estimated the Jahn–Teller stabilization
energy \( E_{JT} \) of 57.94 meV within the single-mode \( T_{1u} \otimes
h_g \) Jahn–Teller model from the visible and near-infrared
spectrum.\(^2\) The present Jahn–Teller stabilization energy
agrees well with their value.

**B. Simulation of the PES of Gunnarsson et al.**

As a preliminary calculation, we compute the vibronic
levels using the data from Ref. \( \text{III} \) that is, the same VCCs
and the same size of the vibronic basis (\( N = 5 \)). The
statistical weight of the ground state at 200 K is obtained
ca. 39 \%. This result indicates that not only the ground level but also excited levels must be considered in order
to simulate the spectrum of Gunnarsson et al.\(^3\)

We simulate this spectrum at 200 K with the FWHM
of 283 cm\(^{-1}\) (\( \sigma = 120 \) cm\(^{-1}\)). The size of the vibronic
basis set is \( N = 7 \). The experimental and the simulated
spectra are shown in Fig. \( \text{III} \). As was mentioned also by
Gunnarsson et al.\(^3\) we obtain several sets of VCCs that
give close stabilization energies. These sets of dimension-
less VCCs and stabilization energies are (4), (5) in Table
TABLE V. Comparison between the obtained stabilization energies of C\textsubscript{60} with previous results (meV).

|   | Freq. (cm\textsuperscript{-1}) | PES \[3\] | LDA | GGA | MNDO | B3LYP |
|---|-------------------------------|---------|-----|-----|------|-------|
| \(a\textsubscript{g}(1)\) | 496 | 7.7 | 0.6 | 0.2 | 1.5 | 1.5 |
| \(a\textsubscript{g}(2)\) | 1470 | 8.2 | 16.4 | 2.7 | 9.0 | 11.0 |
| \(b\textsubscript{g}(1)\) | 273 | 4.1 | 11.4 | 2.7 | 6.0 | 2.8 |
| \(b\textsubscript{g}(2)\) | 437 | 7.2 | 24.0 | 6.3 | 15.6 | 7.0 |
| \(b\textsubscript{g}(3)\) | 710 | 9.1 | 7.8 | 5.5 | 6.6 | 6.1 |
| \(b\textsubscript{g}(4)\) | 774 | 4.3 | 10.8 | 2.4 | 3.0 | 2.4 |
| \(b\textsubscript{g}(5)\) | 1099 | 5.3 | 7.2 | 2.6 | 3.6 | 2.6 |
| \(b\textsubscript{g}(6)\) | 1250 | 4.3 | 3.0 | 1.5 | 1.8 | 1.9 |
| \(b\textsubscript{g}(7)\) | 1428 | 16.8 | 10.2 | 9.0 | 9.6 | 9.0 |
| \(b\textsubscript{g}(8)\) | 1575 | 6.6 | 13.8 | 8.2 | 4.8 | 8.8 |

\(E\textsubscript{s}\) | 15.9 | 17.0 | 2.9 | 10.5 | 12.5 | - |
\(E\textsubscript{JT}\) | 57.7 | 88.2 | 38.2 | 51.0 | 40.6 | 33.6 |
\(E\textsubscript{s} + E\textsubscript{JT}\) | 73.6 | 105.2 | 41.1 | 61.5 | 53.1 | - |

\textsuperscript{a} Results given in Tables \[1\].
\textsuperscript{b} The stabilization energies of the \(a\textsubscript{g}\) modes are not reported.

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**FIG. 3.** The experimental photoelectron spectrum measured by Gunnarsson \textit{et al.} \[3\] (black line) and the simulated spectrum (red line). The simulation is performed at 200 K with \(\sigma = 120\) cm\textsuperscript{-1}.

\[\text{hv} = 4.025\text{ eV EXP.} \quad \text{CALC.} \quad \]

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C. DFT calculations of the vibronic coupling constants

We compute the vibronic coupling constants of C\textsubscript{60} using the DFT method described in Sec. \[IV\]. For DFT calculations with pure functionals, it is well known that in the high-symmetry geometry the occupied level belonging to one degenerate representation moves upwards in energy relative to the empty levels belonging to the same degenerate manifold. However, in our case the situation is opposite (the occupied level is the lowest one) because of the Hartree–Fock exchange contribution contained in the B3LYP functional. The splitting between hence, we must consider many excited vibronic states. To represent the excited vibronic states with enough accuracy, we expect that the vibronic basis must be larger than the present one. Furthermore, as the vibrational temperature is further increased, the weight of each vibronic level and the shape of the spectrum varies easily. Although the range of the vibrational temperature is not reported, we increased the temperature by 20 K which is the uncertainty range of vibrational temperature in the case of Wang \textit{et al.} \[15\]. The statistical weights of the ground vibronic level decreased from ca. 37 % to ca. 31 % with this increase of the temperature. This change of the weight affects the shape of the spectrum. Therefore it is difficult to perform an accurate simulation and to estimate VCCs from the spectrum of Gunnarsson \textit{et al.}.

Given better the experimental conditions of Wang \textit{et al.} \[15\] allowing for more accurate simulations, we may conclude that the VCCs extracted from these experiments should be considered more reliable than those obtained by Gunnarsson \textit{et al.}
On the contrary, the theoretical stabilization energy of the \( a_g(1) \) mode is too small and that of the \( a_g(2) \) mode is too large compared to \( E_{s,i} \) derived from experiment (Tables 11 and 15). To find the correct order of the corresponding VCCs, we derive the coupling constants of the \( a_g \) modes from the experimental bond lengths as described in Sect. V. The obtained stabilization energies \( E_{s,i} \) are shown in Table VIII. Unfortunately, as we can see, \( E_{s,i} \) depend very strongly on the set of the C-C bond lengths,

The statistical weights are calculated at 200K.

| Level | Set (4) | Energy | Weight | Set (5) | Energy | Weight |
|-------|---------|--------|--------|---------|--------|--------|
|       | J       | 200 K  | J       | 200 K  |
| 1     | 5       | -1067.6| 36.56  | 1       | -1134.4| 37.00  |
| 2     | 3       | -845.2 | 17.22  | 2       | -850.2 | 7.98   |
| 3     | 2       | -785.9 | 8.03   | 3       | -829.9 | 4.14   |
| 4     | 1       | -771.3 | 4.34   | 4       | -771.3 | 4.34   |
| 5     | 3       | -679.7 | 5.95   | 5       | -742.5 | 5.15   |
| 6     | 2       | -616.0 | 2.37   | 6       | -687.8 | 2.48   |
| 7     | 5       | -613.1 | 5.10   | 7       | -685.5 | 5.37   |
| 8     | 1       | -590.0 | 1.18   | 8       | -667.0 | 1.28   |
| 9     | 3       | -580.3 | 2.56   | 9       | -650.1 | 2.65   |
| 10    | 2       | -535.1 | 1.32   | 10      | -590.5 | 1.27   |
| 11    | 4       | -531.4 | 2.06   | 11      | -594.0 | 2.02   |
| 12    | 1       | -525.4 | 0.74   | 12      | -590.6 | 0.74   |
| 13    | 3       | -485.2 | 1.29   | 13      | -543.5 | 1.23   |
| 14    | 5       | -464.8 | 1.75   | 14      | -515.2 | 1.58   |
| 15    | 4       | -445.7 | 1.11   | 15      | -495.6 | 1.00   |
| 16    | 2       | -404.6 | 0.52   | 16      | -456.7 | 0.47   |
| 17    | 7       | -371.4 | 1.22   | 17      | -446.6 | 1.31   |
| 18    | 4       | -362.7 | 0.61   | 18      | -436.7 | 0.57   |
| 19    | 3       | -362.1 | 0.53   | 19      | -432.7 | 0.63   |
| 20    | 5       | -339.6 | 0.71   | 20      | -414.8 | 0.77   |
| 21    | 0       | -330.5 | 0.06   | 21      | -400.2 | 0.06   |
| 22    | 2       | -317.4 | 0.28   | 22      | -388.3 | 0.46   |
| 23    | 4       | -316.8 | 0.44   | 23      | -387.9 | 0.29   |
| 24    | 1       | -291.3 | 0.14   | 24      | -357.6 | 0.14   |
| 25    | 6       | -275.4 | 0.53   | 25      | -336.5 | 0.52   |
| Sum   | 96.62   | 96.88  |

| Energy | Weight |
|--------|--------|
| 6-311G(d) | 6-311+G(d) | cc-pVTZ |
| 20 %    | 25 %    | 30 %    | 20 %    | 25 %    |
| \( \Delta \varepsilon \) | 691  | 874  | 1059 | 686  | 693  | 876  |

The \( t_{1u} \) Kohn–Sham levels are about 1 eV (see Table VII) and the variations of the total electronic energies for different occupation schemes of \( t_{1u} \) orbitals are less than 0.2 meV. Moreover, the vibronic coupling constants do not depend on the choice of the electronic states significantly. The variation of the total stabilization energy is about 1 meV. The dimensionless VCCs and the stabilization energies are shown in Table 11 and 11. Although we use several basis sets, the VCCs do not depend on the basis set significantly. On the other hand, the VCCs vary with the increase of the fraction of the Hartree–Fock exchange energy in the exchange-correlation functional. Increasing this fraction leads to larger VCCs and stabilization energies. We find that the stabilization energies of high frequency modes, \( a_g(2), h_g(7), \) and \( h_g(8) \) are the strongest. Compared with other DFT calculations, we may conclude that the stabilization energies of \( a_g \) modes agree well with the previous calculations, while the present stabilization energy \( E_s + E_{JT} \) is larger than the previous results.

In comparison with present simulation of the experimental PES, the DFT calculations with the energy functionals including fractions of 20 % and 25 % of the Hartree–Fock exchange energy give close values. Although the stabilization energy \( E_s + E_{JT} \) obtained using the original B3LYP functional is slightly smaller than the experimental value, the result obtained with it is also close to the experimental one. The distribution of the computed stabilization energy of each \( h_g \) mode \( E_{JT,u} \) qualitatively agrees with the experimental results. The stabilization energy of the \( h_g(7) \) mode is obtained smaller and that of the \( h_g(8) \) mode is obtained larger than the experimental values. The slight difference between theoretical and experimental results should originate from still inaccurately computed vibrational vectors. Indeed, it was shown that a small mixing of the vibrational vectors in fullerene affects the values of VCCs significantly.

Besides the present computational results, the LDA calculation by Manini et al. and the GGA calculation by Frederiksen et al. give similar relative values for the coupling constants of \( h_g \) modes as the present simulations of PES of Wang et al. On the other hand, these calculations give smaller absolute values of the VCCs and of the total stabilization energies than the presently obtained. Contrary to these calculations, the B3LYP calculation by Saito and Lafamme Janse give close values of VCCs to the present results. However, despite of using the same B3LYP functional, our calculations of VCCs differ from the ones in Refs. 12 and 14 since we used here the derivative of the total energy, which does not coincide with the derivative of the Kohn–Sham orbital energy (see the appendix). The LDA calculation of Breda et al. gives the distribution of relative strengths of VCCs which is similar to the results of Gunnarsson et al. and do not agree with the values derived here from PES of Wang et al. Varma et al. computed VCCs using MNDO method, however, the distribution of the stabilization energies is different from the present simulations of experiment and the theoretical values obtained here.

The statistical weights are derived from the experimental spectrum of Gunnarsson et al. The statistical weights are calculated at 200K.
TABLE VIII. Stabilization energies (meV) derived from the experimental C-C bond lengths of C_{60} and C_{60}.

| Frequency (cm\(^{-1}\)) | Stabilization energies of \(a_g\) modes (meV) |
|-------------------------|-----------------------------------------|
|                         | (3) | (10) | Fujiwara | Fujiwara |
| a_g(1)                  | 496 | 7.7  | 2.6      |          |
| a_g(2)                  | 1470| 8.2  | 16.9     |          |

- The structure of C_{60} is taken from neutron diffraction at 5K (Ref. 31).
- The structure of C_{60} is taken from X-ray diffraction at 110K (Ref. 32).

VII. CONCLUSION

In this work, we simulated the PES of Wang et al. and derived the vibronic coupling constants of C_{60}. We obtain several sets of VCCs, because the frequencies of \(a_g(2)\), \(h_g(7)\), and \(h_y(8)\) modes are close to each other.

Considering the ambiguity of the vibrational temperature in the experiment, these sets of VCCs cannot be distinguished. Thus, to obtain more accurate coupling constants, it is desired to perform an observation of a PES of C_{60} in still better experimental conditions. Although we find several sets of VCCs from the spectrum, the stabilization energies are similar to each other. In comparison with the total stabilization energy derived by Gunnarsson et al., our value is smaller by 30%. We also calculated the VCCs using the DFT method. Even though the experimental and theoretical orders of \(E_{s,i}\) disagree with each other, the distribution of \(E_{JT,\mu}\) and the total stabilization energy \(E_s + E_{JT}\) agrees well with the experimental values. Thus we may conclude that the problem of the discrepancy between the experimental and calculated coupling constants, persistent in the previous studies, is basically solved in the present work. As an extension of the present work, we expect that the theoretical approach used here could be successfully applied for the calculation of VCC of C_{60} anions in \(A_n\)C_{60} fullerides as well as of their multiplet splitting parameters.

Appendix: Vibronic coupling constants and the gradient of Kohn–Sham levels

The total energy \(E(R)\) in the DFT is written as follows:

\[
E(R) = \sum_{\mu\Gamma} \epsilon_{\mu\Gamma} n(R) - \frac{1}{2} \int \frac{d\mu d\Gamma n(R)n'(R)}{|r - r'|}
+ E xc[n(R)] - \int d\mu d\Gamma \epsilon_{\mu\Gamma} n(R) + \frac{\partial V_{nn}(R)}{\partial \Gamma}\]  
(A.1)

Here, \(\Gamma\) is the irreducible representation of the Kohn–Sham orbital, \(\mu\) is the quantum number other than \(\Gamma\), \(\epsilon_{\mu\Gamma}\) is the Kohn–Sham level, \(\sum_{\mu\Gamma} n\) is taken over occupied levels, \(n(R)\) is the ground electronic density, \(E xc[n(R)]\) is the exchange-correlation energy functional, \(V_{xc}(r, R)\) is the exchange-correlation potential, and \(V_{nn}(R)\) is the Coulomb potential energy between nuclei. The vibronic coupling constant of \(\Gamma'\gamma'\) mode is

\[
V_{\Gamma'\gamma'} = \sum_{\mu\Gamma} \left\langle \frac{\partial \epsilon_{\mu\Gamma\gamma}}{\partial \Omega_{\Gamma'\gamma'}} \right\rangle_{R_0} - \int d\mu d\Gamma \frac{\partial n(R)}{\partial Q_{\Gamma'\gamma'}} \int d\mu d\Gamma \frac{\partial n'(R)}{\partial Q_{\Gamma'\gamma'}} \]  
(A.2)

For the totally symmetric modes, all the derivatives in the right-hand side of Eq. (A.2) are not zero. For the Jahn–Teller active modes, the sum of the gradient of the completely occupied Kohn–Sham levels belonging to the same \(\Gamma\) is zero due to the symmetry reasons, and the gradient of the Coulomb potential between the nuclei is zero also because of the symmetry. However, the second and third terms which include the derivative of...
$n(r; R)$ and $V_{xc}(r; R)$ with respect to $Q_1$, respectively, are nonzero because $n(r; R)$ is not a totally symmetric function. Therefore, in general, the vibronic coupling constant is not equal to the gradient of the frontier Kohn–Sham level.

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