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Kyoto University
Vibronic coupling in cyclopentadienyl radical: A method for calculation of vibronic coupling constant and vibronic coupling density analysis

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A method of calculation of vibronic or electron-phonon coupling constant is presented for a Jahn-Teller molecule, cyclopentadienyl radical. It is pointed out that symmetry breaking at degenerate point and violation of Hellmann-Feynman theorem occur in the calculations based on a single Slater determinant. In order to overcome these difficulties, the electronic wave functions are calculated using generalized restricted Hartree-Fock and complete active space self-consistent-field method and the couplings are computed as matrix elements of the electronic operator of the vibronic coupling. Our result agrees well with the experimental and theoretical values. A concept of vibronic coupling density is proposed in order to explain the order of magnitude of the coupling constant from view of the electronic and vibrational structures. It illustrates the local properties of the coupling and enables us to control the interaction. It could open a way to the engineering of vibronic interactions. © 2006 American Institute of Physics. [DOI: 10.1063/1.2150816]

I. INTRODUCTION

Vibronic interaction or electron-vibration (phonon) interaction is one of the most investigated problems in molecular physics. It plays an important role not only in solid-state physics but also in chemical reaction theory, for instance, Jahn-Teller (JT) effect, superconductivity, electron transfer reaction, and so on. These phenomena are ruled by the magnitude of the vibronic coupling or electron-phonon coupling constant.

Some authors have calculated the vibronic coupling constant from vibronic coupling integrals over hydrogenlike atomic orbitals, and others have evaluated them from the calculation of a conical intersection of Born-Oppenheimer potentials. Recently, on the other hand, Kato and Hirao have calculated a vibronic coupling constant of some JT molecules from the gradient of a Born-Oppenheimer potential near the JT crossing point \( R_0 \) (see Fig. 1) using density-functional method. However, as we will discuss in this article, their calculations involve some serious problems: (1) symmetry breaking of the wave function and (2) violation of Hellmann-Feynman theorem. One of the purposes of this article is to overcome these problems.

Among many JT molecules, cyclopentadienyl radical \((C_5H_5, \text{Fig. 2})\) is one of the most investigated molecule, since it has been not only an important species in organic chemistry but also a target of spectroscopy and quantum chemistry. The electronic state of the radical with \( D_{5h} \) symmetry is \( ^2E_g \), as shown in Fig. 3.

Throughout this article, we consider linear vibronic coupling and neglect higher-order couplings. The JT-active vibrational mode which couples to the electronic \( E' \) state can be deduced as

\[
\Gamma_{\text{vib}}^2 = 2a'_1 + a'_2 + 3e'_1 + 4e'_2 + a''_1 + a''_2 + e''_1 + 2e''_2.
\]

Thus the two \( a'_1 \) modes and four \( e'_2 \) can couple to the electronic state as long as the linear JT effect is considered.

The JT distortion of the radical has been first observed using electron-spin resonance (ESR) in condensed phase. After the ESR observations in condensed phase, the spectroscopy of the isolated radical has been reported. After pioneering work by Liehr, theoretical calculations have been piled up.

Recently Applegate et al. have observed \( \Delta^2A_1 \rightarrow \Delta^2E' \) transition of the radical in detail and calculated observable spectroscopic constants by \textit{ab initio} method. They estimated the vibronic coupling constants for the four \( e'_2 \) modes from their experiment and calculation. Since their assignment is
quite excellent, cyclopentadienyl radical is a good target for our calculation of the vibronic coupling.

In this paper, we will present a new method of the calculation of the vibronic coupling integrals as matrix elements of an electronic operator of the vibronic coupling and compare them with those by Applegate et al. Furthermore, we will propose a concept of vibronic coupling density in order to explain the order of magnitude of the coupling constant from them with those by Applegate et al.

Since the deformation is expressed in terms of a set of normal coordinates \( Q_i \) at \( R_0 \),

\[
\Delta \mathcal{U} = \sum_i \left( \frac{\partial \mathcal{U}}{\partial Q_i} \right)_0 Q_i + \frac{1}{2} \sum_i \left( \frac{\partial^2 \mathcal{U}}{\partial Q_i^2} \right)_0 Q_i^2 + \cdots
\]

\((i = 1, 2, \ldots, 3N - 6)\). \hfill (8)

Here we ignored intermode couplings so that the vibrations are considered as isolated. This expansion originates from Herzberg-Teller expansion around the JT crossing \( R_0 \) up to the second order in \( Q_i \). Therefore, the model Hamiltonian describing the coupling between harmonic vibration and electronic motion can be written as

\[
\mathcal{H} = \sum_i -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_i^2} + \mathcal{H}_e(R_0) + \sum_i \left( \frac{\partial \mathcal{U}}{\partial Q_i} \right)_0 Q_i + \frac{1}{2} \omega_i^2 Q_i^2,
\]

\hfill (9)

where \( \omega_i \) is the frequency of the mode. The index \( i \) runs over \( 2a'_1 \oplus 4e'_2 \) modes. The first term in Eq. (9) corresponds to the nuclear kinetic energy. The operator involved in the third term,

\[
\mathcal{H}(r, R) = \mathcal{T}(R) + \mathcal{U}(r, R) = \mathcal{T}(R) + \mathcal{H}_e(r, R),
\]

where

\[
\mathcal{H}_e(r, R) = \mathcal{T}(r) + \mathcal{U}(r, R),
\]

\( \mathbf{R} \) denotes a set of nuclear coordinates, \( \mathbf{r} \) that of electronic coordinates, \( \mathcal{T} \) a kinetic-energy operator, and \( \mathcal{U} \) a sum of an electron-electron, electronic-nuclear, and nuclear-nuclear potential operator. \( \mathcal{H}_e \) is an electronic Hamiltonian for a deformed molecule whose nuclear coordinates are expressed by \( \mathbf{R} \) is written as

\[
\mathcal{H}_e(r, R) = \mathcal{H}_e(r, R_0) + \mathcal{U}(r, R) - \mathcal{U}(r, R_0) = \mathcal{H}_e(r, R_0) + \Delta \mathcal{U}(r, R).
\]

Thus the molecular Hamiltonian is rewritten using the electronic Hamiltonian at \( R_0 \) as

\[
\mathcal{H}(r, R) = \mathcal{T}(R) + \mathcal{H}_e(r, R_0) + \Delta \mathcal{U}(r, R).
\]

II. VIBRONIC HAMILTONIAN

A molecular Hamiltonian is given by

\[
\frac{1}{2} m \dot{R}_0^2 + U_e(R) + \sum_{i=1}^{3N-6} \frac{1}{2} \omega_i^2 Q_i^2 + \mathcal{H}_e(R_0)
\]
The integrals $H_{9266}$ are replaced by vibronic coupling $\tilde{V}_i$, which are the matrix elements of the electronic operator $V_i$.

The coupling matrix between the $j$th vibrational degenerate $e_j'$ mode and the electronic $E_1'$ state can be reduced using Wigner-Eckart theorem,

$$\left( \begin{array}{c} \langle E_1' | V_{e,j} | E_1' \rangle \\ \langle E_1' | V_{e,j} | E_1' \rangle \end{array} \right) = \frac{1}{\sqrt{2}} \left( \begin{array}{cc} 0 & 1 \\ 0 & -\frac{1}{\sqrt{2}} \end{array} \right) \left( \begin{array}{cc} 1 & 0 \\ \frac{1}{\sqrt{2}} & 0 \end{array} \right),$$

and

$$\left( \begin{array}{c} \langle E_1' | V_{e,j} | E_1' \rangle \\ \langle E_1' | V_{e,j} | E_1' \rangle \end{array} \right) = \frac{1}{\sqrt{2}} \left( \begin{array}{cc} 0 & 1 \\ 0 & -\frac{1}{\sqrt{2}} \end{array} \right).$$

Therefore, the reduced matrix element $\langle E_1'|V_{e,j}|E_1'\rangle$ can be calculated from the following relations:

$$\langle E_1'|V_{e,j}|E_1'\rangle = 2\langle E_1'|V_{e,j}|E_1'\rangle = -2\langle E_1'|V_{e,j}|E_1'\rangle = 2\langle E_1'|V_{e,j}|E_1'\rangle.$$

Thus, for a single degenerate vibrational mode, the vibronic coupling matrix is obtained as

$$\tilde{V}_{e,j} = \frac{1}{2} \left( \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right)$$

and

$$\tilde{V}_{e,j} = \frac{1}{2} \left( \begin{array}{cc} 1 & 0 \\ 1 & 0 \end{array} \right)$$

where

$$V_{e,j} = \frac{1}{2} \left( \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \right)$$

is the vibronic coupling constant (VCC), which is the quantity we will calculate in this article.

On the other hand, the interaction matrix between vibrational $a_1'$ mode $k$ is written as

$$\tilde{V}_{a_1'|k} = \left( \begin{array}{cc} \langle E_1'|V_{a_1'|k}|E_1'\rangle & \langle E_1'|V_{a_1'|k}|E_1'\rangle \\ \langle E_1'|V_{a_1'|k}|E_1'\rangle & \langle E_1'|V_{a_1'|k}|E_1'\rangle \end{array} \right),$$

where

$$\langle E_1'|V_{a_1'|k}|E_1'\rangle = \frac{1}{\sqrt{2}} \left( \begin{array}{cc} 0 & 1 \\ 0 & 1 \end{array} \right)$$

The last term in Eq. (13) describes the vibronic coupling. The integrals $\langle E_1'|V_{e,j}|E_1'\rangle$ and so on are called vibronic coupling integrals (VCIs), which are the matrix elements of the electronic operator $V_i$. 

The graph shows the molecular orbitals of cyclopentadienyl radical. Because of the fivefold symmetry, the orbitals of HOMO is doubly degenerate $e_1'$, one of them is denoted as $\epsilon$, and the other as $\theta$. $\theta$ is transformed as $\gamma_2$, and $\epsilon$ is $\epsilon_x$. Irreducible representations in the parentheses are those lowered into the subgroup $C_2\eta$: $E_1'|C_2\eta=a_2\oplus b_1$. $\epsilon$ is $a_2$ and $\theta$ is $b_1$. 

$$V_i = \left( \frac{\partial U}{\partial Q_i} \right)_{0}$$

is called the electronic operator of the mode $i$, and $V_i Q_i$ describes the vibronic coupling.

The vibronic wave function is expanded in terms of the eigenfunctions of $\mathcal{H}_e(R_0)$,

$$\Psi(r, Q) = \sum_n \chi_n(Q) \phi_n(r, R_0),$$

where $\phi_n(r, R_0)$ is an eigenfunction belonging to the eigenenergy $E_0$ of $\mathcal{H}_e(R_0)$ in the electronic eigenequation (5), $\chi_n(Q)$ is an expansion coefficient which depends on the normal coordinates, and $n$ runs over the electronic configurations. To obtain a JT Hamiltonian, the domain of $n$ is restricted to the degenerate electronic state $|E_1'|\langle \theta|0\rangle, |E_1'|\langle \epsilon|0\rangle, |E_1'|\langle \epsilon|0\rangle$. $\theta$ and $\epsilon$ denote one of the irreducible representation of doubly degenerate one that decomposes into $b_1$ and $a_2$, when the symmetry is lowered from $D_{5h}$ into $C_{2v}$, respectively. We treat the model Hamiltonian with the model space spanned by $|E_1'|\langle \epsilon|0\rangle$ and $|E_1'|\langle \theta|0\rangle$. Thus we can write the JT Hamiltonian matrix as follows:

$$\mathcal{H}_{JT} = E_0 \delta_0 + \sum_i \left( \begin{array}{c} \frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial \epsilon_i^2} \delta_0 \right) + \frac{1}{2} \alpha_i^2 \epsilon_i^2 \delta_0 \\ \frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial \theta_i^2} \delta_0 \right) + \frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial \gamma_i^2} \delta_0 \right) \end{array} \right)$$

$$= \left( \begin{array}{cc} E_0 + \frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial \epsilon_i^2} \delta_0 \right) + \frac{1}{2} \alpha_i^2 \epsilon_i^2 \delta_0 \\ E_0 + \frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial \theta_i^2} \delta_0 \right) + \frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial \gamma_i^2} \delta_0 \right) \end{array} \right)$$

$$= \left( \begin{array}{cc} 0 & 1 \\ 0 & -1 \end{array} \right) \left( \begin{array}{cc} 1 & 0 \\ \frac{1}{\sqrt{2}} & 0 \end{array} \right),$$

where

$$\delta_0 = \left( \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \right).$$
is a VCC for a totally symmetric $\alpha'_i$ mode. Therefore, using Eqs. (20) and (22), the VCC can be obtained from a numerical calculation of the VCI. Furthermore Eqs. (20) and (22) involve conditions among the VCI due to the symmetry of the wave function which should be satisfied in the JT system. In Sec. IV, we will discuss the symmetry of wave functions at the degenerate point $R_o$.

We introduce here some dimensionless quantities. For a vibrational mode $i$, the normal coordinate $Q_i$ is measured by \( \sqrt{\hbar/\omega_i} \),

\[
Q_i = \sqrt{\frac{\hbar}{\omega_i}} q_i,
\]

where $q_i$ is a dimensionless normal coordinate. Dimensionless coupling constant $D_i$ can be defined as

\[
D_i = \frac{V_i}{\sqrt{\hbar \omega_i}}.
\]

Therefore, the JT Hamiltonian is written in terms of these dimensionless quantities:

\[
\hat{H}_{JT} = E_0 \hat{\sigma}_0 + \sum_{k=1}^{2} \left\{ -\frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial Q_{\alpha'_i}^2} \right) \hat{\sigma}_0 + \frac{1}{2} \omega_{\alpha'_i}^2 Q_{\alpha'_i}^2 \hat{\sigma}_0 
+ Q_{\alpha'_i} V_{\alpha'_i} \hat{\sigma}_0 \right\} + \sum_{j=1}^{4} \left\{ -\frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial Q_{\epsilon'_j}^2} \right) \hat{\sigma}_0 
+ \frac{1}{2} \omega_{\epsilon'_j}^2 Q_{\epsilon'_j}^2 \hat{\sigma}_0 
+ \frac{1}{2} \omega_{\epsilon'_j}^2 Q_{\epsilon'_j}^2 \hat{\sigma}_0 \right\} 
\]

\[
= E_0 \hat{\sigma}_0 + \sum_{k=1}^{2} \hbar \omega_{\alpha'_i} \left\{ -\frac{1}{2} \left( \frac{\partial^2}{\partial Q_{\alpha'_i}^2} \right) \hat{\sigma}_0 + \frac{1}{2} \omega_{\alpha'_i}^2 Q_{\alpha'_i}^2 \hat{\sigma}_0 
+ Q_{\alpha'_i} D_{\alpha'_i} \hat{\sigma}_0 \right\} + \sum_{j=1}^{4} \hbar \omega_{\epsilon'_j} \left\{ -\frac{1}{2} \left( \frac{\partial^2}{\partial Q_{\epsilon'_j}^2} \right) \hat{\sigma}_0 
+ \frac{1}{2} \omega_{\epsilon'_j}^2 Q_{\epsilon'_j}^2 \hat{\sigma}_0 + \frac{1}{2} \omega_{\epsilon'_j}^2 Q_{\epsilon'_j}^2 \hat{\sigma}_0 
+ \frac{1}{2} \omega_{\epsilon'_j}^2 Q_{\epsilon'_j}^2 \hat{\sigma}_0 \right\} 
\]

\[
\times (q_{\epsilon'_j} \hat{\sigma}_0 + q_{\epsilon'_j} \hat{\sigma}_0),
\]

where

\[
\hat{\sigma}_0 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.
\]

III. METHOD OF CALCULATION

As the reference structure $R_0$ of the JT system, we take the structure of cyclopentadienyl anion, which is called parent system throughout this article. Since the parent system does not give rise to any JT distortion, its geometry has $D_{3h}$ geometry.

The electronic operator $V_i$ is a sum of one-electron operators $v_i(a)$ and the derivative of the nuclear-nuclear repulsion potential $U_m$ with respect to $Q_i$,

\[
V_i = -\sum_a \sum_a \left[ \frac{\partial}{\partial Q_i} \left( \frac{Z_a e^2}{|r_a - r_a|} \right) \right]_0 + \frac{\partial U_m}{\partial Q_i}
\]

\[
= \sum_a v_i(a) + \frac{\partial U_m}{\partial Q_i},
\]

where

\[
v_i(a) = -\sum_a \left[ \frac{\partial}{\partial Q_i} \left( \frac{Z_a e^2}{|r_a - r_a|} \right) \right]_0 = \left( \frac{\partial u(a)}{\partial Q_i} \right)_0,
\]

indices $a$ and $a'$ denote nucleus and electron, respectively, $Z_a$ charge of the nucleus $\alpha$, and

\[
u(a) = -\sum_a \frac{Z_a e^2}{|r_a - r_a|}.
\]

It should be noted that $\partial U_m/\partial Q_i$ is zero except for the $\alpha'_i$ modes.

The normal coordinate $Q_i$ ($i=1,2,\ldots,3N-6$) is related to $3N$ Cartesian coordinates $R_a=(X_a,Y_a,Z_a) = (R_{3a-2},R_{3a-1},R_{3a})$ ($a=1,2,\ldots,N$) by

\[
R_\beta = \frac{1}{\sqrt{M_a}} \sum_{i=1}^{3N-6} l_{\beta i} Q_i \quad (\beta = 1,2,\ldots,3N),
\]

where $l_{\beta i}$ can be determined from a vibrational analysis, and $M_a$ denotes the mass of a nucleus $\alpha$. The one-electron electronic operator $v_i(a)$ is written as

\[
v_i(a) = \left( \frac{\partial u(a)}{\partial Q_i} \right)_0 = \sum_{\beta=1}^{3N} \left( \frac{\partial u(a)}{\partial R_\beta} \right)_0 \left( \frac{\partial R_\beta}{\partial Q_i} \right)_0
\]

\[
= \sum_{\beta=1}^{3N} \left( \frac{\partial u(a)}{\partial R_\beta} \right)_0 \frac{1}{\sqrt{M_a}} \sum_{\beta=1}^{3N} v_\beta(a) l_{\beta i},
\]

where

\[
v_\beta(a) = \frac{1}{\sqrt{M_a}} \left( \frac{\partial u(a)}{\partial R_\beta} \right)_0.
\]

For the Hartree-Fock (HF) methods, the $E_\alpha^\pi$ wave functions are written as a single Slater determinant,

\[
|E_\alpha^\pi(\theta(HF))\rangle = |\psi_\alpha \psi_{\pi_m} \psi_{\pi_{m+1}} \cdots \psi_0 \psi_{\pi_1} \psi_{\pi_2} \psi_{\pi_3} \rangle = |\theta \rangle,
\]

and

\[
|E_\alpha^\pi(\phi(HF))\rangle = |\psi_\theta \psi_{\phi_m} \psi_{\phi_{m+1}} \cdots \psi_0 \psi_{\phi_1} \psi_{\phi_2} \psi_{\phi_3} \rangle = |\phi \rangle,
\]

where $\psi_\theta$ and $\psi_\phi$ denote the degenerate highest occupied molecular orbital (HOMO) (see Fig. 3), and $\alpha, \beta$ are spin functions. The complete active space self-consistent-field (CASSCF) wave functions are written as
\[ |E'_n(\text{CASSCF})| = \sum_i C_{i|\theta}\phi_i, \]

\[ |E''_n(\text{CASSCF})| = \sum_i C_{i|\theta}\phi_i, \]

where \( \phi_i \) is a ground or excited electronic configuration within the active space, and \( C_i \) is a coefficient.

The vibronic coupling matrices of the HF and CASSCF wave functions are given by

\[ \hat{V}^{\text{HF}}_i = \left( \begin{array}{cc} \langle \theta|\theta|\theta \rangle & \langle \theta|\theta|e \rangle \\ \langle e|\theta|\theta \rangle & \langle e|\theta|e \rangle \end{array} \right), \]

\[ \hat{V}^{\text{CAS}}_i = \left( \begin{array}{cc} \sum_{LL'} C_{iL}^* C_{L'e}(\phi_i|\theta|\phi_{L'}) & \sum_{LL'} C_{iL}^* C_{L'e}(\phi_i|e|\phi_{L'}) \\ \sum_{LL'} C_{iL}^* C_{L'e}(\phi_i|e|\phi_{L'}) & \sum_{LL'} C_{iL}^* C_{L'e}(\phi_i|e|\phi_{L'}) \end{array} \right), \]

respectively. All matrix elements are constructed from the integrals over Slater determinants. In general the integrals of a one-electron operator \( O_i = \sum_j j(i) \) over Slater determinants are expressed as

\[ \langle \cdots mn \cdots |O_i| \cdots mn \cdots \rangle = \sum_m \langle m|h|m \rangle, \]

\[ \langle \cdots mn \cdots |O_i| \cdots pn \cdots \rangle = \langle m|h|p \rangle, \]

\[ \langle \cdots mn \cdots |O_i| \cdots pq \cdots \rangle = 0, \]

where \( m, n, p, \) and \( q \) denote spin-orbitals. Since \( \theta \) is a sum of the one-electron operator \( v_i \), the integrals in Eq. (38) can be decomposed as

\[ \langle \theta|\theta|\theta \rangle = \sum_m n_m \langle \psi_m|\psi_m|\psi_m \rangle, \]

\[ \langle \theta|\theta|e \rangle = \langle \psi_m|\psi_m|\psi_m \rangle, \]

\[ \langle e|\theta|\theta \rangle = \langle \psi_m|\psi_m|\psi_m \rangle, \]

\[ \langle e|\theta|e \rangle = \sum_m n_m \langle \psi_m|\psi_m|\psi_m \rangle, \]

where \( m \) runs over the occupied spatial orbitals, and \( n_m \) is an occupation number of the orbital \( m \). On the other hand, evaluation of those in Eq. (39) is slightly complicated. The integral \( \langle \phi_i|\theta|\phi_{L'} \rangle \) is finite if the two configurations differ by less than one spin-orbital, otherwise zero. For instance, for the case that both \( \phi_i \) and \( \phi_{L'} \) are single-electron excited configurations, the integral is decomposed as follows:

\[ \langle \theta|\theta|\theta \rangle = \sum_m \langle \psi_m|\psi_m|\psi_m \rangle \]

\[ \langle \theta|\theta|e \rangle = \langle \psi_m|\psi_m|\psi_m \rangle \]

\[ \langle e|\theta|\theta \rangle = \langle \psi_m|\psi_m|\psi_m \rangle \]

\[ \langle e|\theta|e \rangle = \sum_m n_m \langle \psi_m|\psi_m|\psi_m \rangle, \]

where \( m \) runs over the occupied molecular orbitals with

\[ \langle \theta|\theta|\theta \rangle = \sum_m \langle \psi_m|\psi_m|\psi_m \rangle \]

\[ \langle \theta|\theta|e \rangle = \sum_m \langle \psi_m|\psi_m|\psi_m \rangle \]

\[ \langle e|\theta|\theta \rangle = \sum_m \langle \psi_m|\psi_m|\psi_m \rangle \]

\[ \langle e|\theta|e \rangle = \sum_m n_m \langle \psi_m|\psi_m|\psi_m \rangle, \]

where \( m \) runs over the occupied spin-orbitals. For example, for the \( e_1 \) mode, the largest displacement locates on the carbon atoms for \( e_1(1) \) and \( e_1(3) \), and on hydrogen atoms for \( e_1(2) \) and \( e_1(4) \). The displacements of the bold arrows greatly contribute to the VCC. Inserted values are the magnitude of bold arrows. \( C_{2a}, E_{1a} \) for the \( e_1(1) \) mode over molecular orbitals, and \( C_{2b}, E_{1b} \) for the \( e_1(3) \) mode over molecular orbitals.
bital $E_1'$ and $E_2'$ symmetry, and $\psi_{e(m)}$ and $\psi_{e(m)}$ denote the degenerate pair of the $E_1'$ or $E_2'$ spatial orbitals. $n_{e(m)}$ and $n_{e(m)}$ are occupation numbers of $\psi_{e(m)}$ and $\psi_{e(m)}$. Note that all the orbitals with the $E_1'$ symmetry can also couple to the $E_2'$ mode since $[E_1'^2]=A_1' \oplus E_2'$. Furthermore, it should be noted here that

$$\langle \psi_{\theta(m)}|\psi_{\theta(m)}\rangle + \langle \psi_{e(m)}|\psi_{e(m)}\rangle = 0,$$

(49)
because of the symmetry of the matrix elements as appeared in Eq. (17). Therefore, contributions from a pair of $\psi_{\theta(m)}$ and $\psi_{e(m)}$ are canceled and the vibronic coupling integrals can be reduced into OVCI over the doubly occupied frontier orbitals $\psi_{\theta}$ or $\psi_{e}$,

$$\langle \theta|V_{\theta(k)}|\theta\rangle = \langle \psi_{\theta}|V_{\theta(k)}|\psi_{\theta}\rangle,$$

$$\langle \varepsilon|V_{\varepsilon(k)}|\varepsilon\rangle = \langle \psi_{\varepsilon}|V_{\varepsilon(k)}|\psi_{\varepsilon}\rangle.$$

(50)

On the other hand, the VCI for the $\epsilon$ mode is written as

$$\langle \theta|V_{\theta(k)}|\epsilon\rangle = \langle \psi_{\theta}|V_{\theta(k)}|\psi_{\epsilon}\rangle,$$

$$\langle \epsilon|V_{\epsilon(k)}|\theta\rangle = \langle \psi_{\varepsilon}|V_{\epsilon(k)}|\psi_{\theta}\rangle.$$

(51)

Therefore, the vibronic coupling matrix in the HF methods is equal to the OVCI matrix,

FIG. 5. Totally symmetric $a_1'$ vibrational modes. The largest displacement locates on the carbon atoms for $a_1'(1)$, and on hydrogen atoms for $a_1'(2)$.

FIG. 6. Incorrect symmetry breaking of the frontier orbitals in cyclopentadienyl radical with $D_{5h}$ symmetry. The left two diagrams are those of cyclopentadienyl anion, and the remaining ones are those of cyclopentadienyl radical. The HOMO should be degenerate because of the high symmetry. However, the HOMO calculated by the methods based on a single determinant, ROHF, ROB3LYP, UHF, and UB3LYP exhibit symmetry breaking.

FIG. 7. Calculated electronic state of cyclopentadienyl radical $^2E_1'$ state. Though the results using GRHF and state-averaged CASSCF give correct degeneracy, the calculations using ROHF, ROB3LYP, UHF, and UB3LYP exhibit an incorrect energy splitting.

$$V_{\theta}^{HF} = \begin{pmatrix} 0 & \langle \psi_{\theta}|v_{\theta}\rangle \\ \langle \psi_{\theta}|v_{\theta}\rangle & 0 \end{pmatrix}.$$

(52)

and

$$V_{\varepsilon}^{HF} = \begin{pmatrix} 0 & \langle \psi_{\varepsilon}|v_{\varepsilon}\rangle \\ \langle \psi_{\varepsilon}|v_{\varepsilon}\rangle & 0 \end{pmatrix}.$$

(53)

As for the $a_1'$ modes, there is no such cancellation;

$$V_{a_1'(k)} = \langle \theta|V_{a_1'(k)}|\theta\rangle = \langle \epsilon|V_{a_1'(k)}|\epsilon\rangle = \sum_m \langle \chi_m|v_{a_1'(k)}|\chi_m\rangle + \sum_{m'} \langle \chi_{m'}|v_{a_1'(k)}|\chi_{m'}\rangle = \frac{\partial U_m}{\partial Q_{a_1'(k)}},$$

(54)

where $m$ and $m'$ run over the occupied spin-orbitals of $|\theta\rangle$ and $|\epsilon\rangle$, respectively.

Using $I_{\beta\varepsilon}$ in Eq. (31), the VCC for the $e_2'$ mode can be written as

FIG. 8. Energy curves of the $A_2$ and $B_1$ states along the $e_2'(3)$ mode (UHF/6–31G(d,p)). The Jahn-Teller crossing is disappeared at $Q=0$ where the two energy curves should cross.
Vj = ⟨E′1|θ|vβ⟩|E′′1|θ⟩ \tag{55}

= \sum_{β=1}^{3N} l_{βR(j)}⟨E′1|θ|vβ⟩|E′′1|θ⟩ \tag{56}

= \sum_{β=1}^{3N} uβl_{βR(j)} \tag{57}

= K \sum_{β=1}^{3N} x_dβl_{βR(j)} \tag{58}

= Kk_j \tag{59}

where

uβ = ⟨E′1|θ|vβ⟩|E′′1|θ⟩. \tag{60}

FIG. 9. Symmetry breaking in the lowest π orbital of cyclopentadienyl radical and the anion (framed). The calculations were performed for the D3h structure. The symmetric π orbital u(1) becomes asymmetric when a single-determinant-based calculation is applied. This gives rise to the vibronic coupling matrix with a wrong symmetry (see text). The calculations were performed using STO-3G basis set.

FIG. 10. Energy gradient δE/δR and ⟨δH/δR⟩ (VCI in the figure) using ROBF towards the minimum of the potential on the 2A1 manifold. The unity of the displacement corresponds to that between the minimum of the potential and the origin, the Jahn-Teller crossing. The absolute value of ⟨δH/δR⟩ at the Jahn-Teller crossing is larger than that of the energy gradient.

\[ V_j = \langle E'_1|\theta|v_β\rangle|E''_1|\theta\rangle \]

\[ = \sum_{β=1}^{3N} l_{βR(j)}\langle E'_1|\theta|v_β\rangle|E''_1|\theta\rangle \]

\[ = \sum_{β=1}^{3N} u_βl_{βR(j)} \]

\[ = K\sum_{β=1}^{3N} x_dβl_{βR(j)} \]

\[ = Kk_j, \]

where

\[ u_β = \langle E'_1|\theta|v_β\rangle|E''_1|\theta\rangle. \]

\[ \text{distortion vector } x_d \text{ is the unit vector in the direction of } u = (u_β); \]

\[ k_j = \sum_{β=1}^{3N} x_dβl_{βR(j)}, \]

\[ K \]

and \( K \) is a constant. The value of \( x_d \) is obtainable from the OVCI. Vibrational analysis yields the value of \( l_{βR(j)} \) and \( k_j \) can be calculated from these quantities. The value of \( K \) is calculated from a JT stabilization energy, i.e., reorganization energy \( ΔE \).

\[ ΔE = \sum_{j=1}^{4} \frac{V_j^2}{2ω_j} = K^2\sum_{j=1}^{4} \frac{k_j^2}{2ω_j^2}. \]

Therefore,

\[ K^2 = ΔE \left( \sum_{j=1}^{4} \frac{k_j^2}{2ω_j^2} \right)^{-1}, \]

where \( ΔE \) is the difference between the minimum energy of the radical optimized within \( C_{2v} \) symmetry and that of conical intersection optimized within \( D_{3h} \) symmetry.7

In order to obtain the optimized geometry \( R_0 \) and vibronic structure of the parent system, restricted Hartree-Fock (RHF) method is employed for cyclopentadienyl anion. At the geometry \( R_0 \), we employed state-averaged CASSCF method using GAUSSIAN 98 (Ref. 32) and generalized restricted Hartree-Fock (GRHF) method using CADPAC (Ref. 33) to determine the wave function of cyclopentadienyl radical. All calculations were performed using the 6-31G(d,p) basis set. The VCI was evaluated using these wave functions.

From the results of the electronic structure calculation for the radical at \( R_0 \) and the vibrational analysis for the anion, we calculated \( u \) and \( x_d \) using Eq. (60). \( l_{βR} \) is obtained from the vibrational analysis, and \( k_j \) was calculated from Eq. (61). \( K \) was obtained using Eq. (63) from the results of the
calculation of the JT stabilization energy. Scaled $V_i$ was calculated from Eq. (59) using $K$, and unscaled $V_i$ from Eq. (56).

In the vibrational analysis, positive directions of the normal coordinates are defined in Figs. 4 and 5. All quantities that the geometrical structure employed throughout this work is that of the radical with the $D_{5h}$ symmetry. The lowest $\pi$ orbital, which should be $d_{xz}^2$ symmetry within the $D_{5h}$ geometry, becomes asymmetric when a single-determinant-based calculation, such as ROHF, ROB3LYP, UHF, and UB3LYP, is applied for the radical.

This gives rise to the vibronic coupling matrix with a wrong symmetry. From Eq. (17), $\langle E_i|V_\phi|E_j\rangle$ has the same absolute value as $\langle E_i|V_\phi|E_j\rangle$. However, the calculation of the coupling for the $e_2^x(3)$ mode using the ROHF wave function yields $\langle E_i|V_\phi|E_j\rangle=0.000 976 415 9$ and the ROB3LYP calculation gives $\langle E_i|V_\phi|E_j\rangle=0.000 803 151 2$. Therefore, the symmetry broken orbitals give rise to a symmetry broken interaction matrix. In other words, as for the wave function obtained by ROHF and ROB3LYP, the Wigner-Eckart theorem is not satisfied.

V. HELLMANN-FEYNMAN THEOREM AND ENERGY GRADIENT

The Hellmann-Feynman theorem\textsuperscript{10,11} states that, when a Hamiltonian depends on a parameter $\lambda$, the derivative of the energy with respect to the parameter is equal to the expectation value of the derivative of the Hamiltonian with respect to $\lambda$,

$$\frac{\partial E(\lambda)}{\partial \lambda} = \left\langle \frac{\partial H(\lambda)}{\partial \lambda} \right\rangle. \tag{64}$$

If the normal coordinate $Q$ is taken for the parameter $\lambda$,

$$\frac{\partial E(Q)}{\partial Q} = \left\langle \frac{\partial H(Q)}{\partial Q} \right\rangle = \left\langle \frac{\partial H(Q)}{\partial Q} \right\rangle. \tag{65}$$

Therefore, if we had applied the theorem for the problem, the VCC could be calculated as the derivative of energy with respect to $Q$. However, we cannot resort to the Hellmann-Feynman theorem for the calculation of the VCC, because the Hellmann-Feynman theorem is not valid in present calculations.

Figures 10 and 11 demonstrate that the energy gradient $\partial E/\partial R$ is not equal to the Hellmann-Feynman force $\langle \partial H/\partial R \rangle$ along the path towards the minimum of the potential on the $A_2$ manifold in $C_{2v}$ ($2E_u \subset C_{2v} \cong A_2 \oplus B_1, C_{2v} \subset D_{5h}$), where the calculations were performed using ROHF and ROB3LYP, respectively. The unity of the displacement corresponds to that between the minimum of the potential and the origin, the JT crossing. In both calculations, the absolute value of the Hellmann-Feynman force at the JT crossing is larger than that of the energy gradient. Therefore, we cannot calculate the vibronic coupling from the energy gradient.

### Table I. Bond length ($\lambda$) of cyclopentadienyl anion $\text{C}_{5}\text{H}_{4}$ calculated using RHF/6-31G(d,p) and the neutral radical using GRHF/6-31G(d,p). Note that the geometrical structure employed throughout this work is that of the anion.

<table>
<thead>
<tr>
<th>Species</th>
<th>Method</th>
<th>C–C</th>
<th>C–H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anion</td>
<td>RHF/6-31G(d,p)</td>
<td>1.4021</td>
<td>1.0800</td>
</tr>
<tr>
<td>Neutral</td>
<td>GRHF/6-31G(d,p)</td>
<td>1.4037</td>
<td>1.0725</td>
</tr>
</tbody>
</table>

### Table II. Wave number (cm$^{-1}$) of cyclopentadienyl anion calculated using RHF/6-31G(d,p) and the neutral radical calculated using GRHF/6-31G(d,p). Experimental values are taken from Ref. 8.

<table>
<thead>
<tr>
<th>Species</th>
<th>Method</th>
<th>$a_i^1(1)$</th>
<th>$a_i^1(2)$</th>
<th>$e_i^1(1)$</th>
<th>$e_i^1(2)$</th>
<th>$e_i^1(3)$</th>
<th>$e_i^1(4)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anion</td>
<td>RHF</td>
<td>1233</td>
<td>3321</td>
<td>914</td>
<td>1144</td>
<td>1497</td>
<td>3263</td>
</tr>
<tr>
<td>Neutral</td>
<td>GRHF</td>
<td>1236</td>
<td>3349</td>
<td>918</td>
<td>1198</td>
<td>1596</td>
<td>3313</td>
</tr>
<tr>
<td>Expt.</td>
<td></td>
<td>1071</td>
<td>872</td>
<td>1041</td>
<td>1320</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE III. Total energy and unscaled vibronic coupling constant $V$ ($10^{-4}$ a.u.) of C$_5$H$_5$ anion. The vibrational vectors are obtained by RHF/6-31G(d,p) for the anion.

<table>
<thead>
<tr>
<th>C$_5$H$_5$</th>
<th>RHF</th>
<th>GRHF</th>
<th>CAS(3,4)</th>
<th>CAS(5,5)</th>
<th>CAS(5,6)</th>
<th>CAS(5,8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>−192.1430$^a$</td>
<td>−192.1719</td>
<td>−192.1952</td>
<td>−192.2357</td>
<td>−192.2379</td>
<td>−192.2433</td>
</tr>
<tr>
<td>$a_1^1(1)$</td>
<td>−31.26</td>
<td>3.49</td>
<td>2.82</td>
<td>1.13</td>
<td>1.17</td>
<td>1.39</td>
</tr>
<tr>
<td>$a_1^2(2)$</td>
<td>22.63</td>
<td>2.67</td>
<td>2.45</td>
<td>1.87</td>
<td>1.89</td>
<td>1.99</td>
</tr>
<tr>
<td>$e_2^1(1)$</td>
<td>9.00</td>
<td>8.76</td>
<td>6.50</td>
<td>4.78</td>
<td>4.83</td>
<td>5.09</td>
</tr>
<tr>
<td>$e_2^2(2)$</td>
<td>13.53</td>
<td>13.60</td>
<td>13.27</td>
<td>11.63</td>
<td>11.58</td>
<td>11.62</td>
</tr>
<tr>
<td>$e_2^3(3)$</td>
<td>−14.16</td>
<td>−14.61</td>
<td>−15.38</td>
<td>−14.58</td>
<td>−14.50</td>
<td>−14.18</td>
</tr>
<tr>
<td>$e_2^4(4)$</td>
<td>−7.85</td>
<td>−7.83</td>
<td>−4.95</td>
<td>−3.20</td>
<td>−3.34</td>
<td>−3.34</td>
</tr>
</tbody>
</table>

$^a$The energy is estimated using Koopmans’ theorem. The energy of the anion is −192.1903 a.u., and HOMO energy is −0.0473.

We confirmed that the Hellmann-Feynman theorem is also violated as well as the Wigner-Eckart theorem. This is the reason why we compute the VCC from the VCI employing the wave function based on the GRHF and state-averaged CASCF calculation.

VI. RESULTS AND DISCUSSION

A. Geometrical and vibrational structures

The optimized symmetry of the parent system C$_5$H$_5$ and that of the conical intersection for the neutral radical C$_5$H$_5$ are $D_3h$. In Table I, the bond lengths of the anion and the neutral radical are tabulated. It is found that the optimized geometries of the energy minimum for the anion and the conical intersection for the radical are almost the same. The bond lengths differ within 0.002 Å for C–C and 0.01 Å for the C–H bond. Thus we take the geometry of the anion as that of the JT crossing point in order to reduce computational resources.

The calculated and experimental$^8$ vibrational frequencies are summarized in Table II. The calculated vibrational structures are also the same. Therefore, we took the geometrical and vibrational structures of the anion as those of the JT crossing of the radical throughout this study.

B. Vibronic interaction matrix and Wigner-Eckart theorem

The vibronic coupling matrix for the $e_2^3(3)$ vibrational mode calculated by RHF is obtained as

\[
\begin{pmatrix}
  \langle E_{a}|V_{e_{a}}|E_{e}\rangle & \langle E_{a}|V_{e_{e}}|E_{e}\rangle \\
  \langle E_{e}|V_{e_{a}}|E_{a}\rangle & \langle E_{e}|V_{e_{e}}|E_{e}\rangle
\end{pmatrix} =
\begin{pmatrix}
  0.001 416 302 4 & 0.000 000 000 0 \\
  0.000 000 000 0 & -0.001 416 302 4
\end{pmatrix},
\]

and

\[
\begin{pmatrix}
  \langle E_{a}|V_{e_{a}}|E_{e}\rangle & \langle E_{a}|V_{e_{e}}|E_{e}\rangle \\
  \langle E_{e}|V_{e_{a}}|E_{a}\rangle & \langle E_{e}|V_{e_{e}}|E_{e}\rangle
\end{pmatrix} =
\begin{pmatrix}
  0.000 000 000 0 & 0.001 416 302 4 \\
  0.001 416 302 4 & 0.000 000 000 0
\end{pmatrix}.
\]

TABLE IV. Unscaled dimensionless vibronic coupling constant $D$ of C$_5$H$_5$ calculated using 6-31G(d,p) basis set. The vibrational vectors employed in these calculations were obtained with RHF/6-31G(d,p) for the anion. The values outside the parentheses were calculated using the vibrational frequencies of the anion obtained by RHF/6-31G(d,p), and the values in the parentheses using the vibrational frequencies of the radical evaluated by GRHF/6-31G(d,p). Negative signs are neglected.

<table>
<thead>
<tr>
<th>C$_5$H$_5$</th>
<th>RHF</th>
<th>GRHF</th>
<th>CAS(3,4)</th>
<th>CAS(5,5)</th>
<th>CAS(5,6)</th>
<th>CAS(5,8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1^1(1)$</td>
<td>7.42(7.40)</td>
<td>0.83(0.83)</td>
<td>0.67(0.67)</td>
<td>0.27(0.27)</td>
<td>0.28(0.28)</td>
<td>0.33(0.33)</td>
</tr>
<tr>
<td>$a_1^2(2)$</td>
<td>1.22(1.20)</td>
<td>0.14(0.14)</td>
<td>0.13(0.13)</td>
<td>0.10(0.10)</td>
<td>0.10(0.10)</td>
<td>0.11(0.11)</td>
</tr>
<tr>
<td>$e_2^1(1)$</td>
<td>3.35(3.33)</td>
<td>3.26(3.24)</td>
<td>2.42(2.40)</td>
<td>1.78(1.77)</td>
<td>1.80(1.79)</td>
<td>1.89(1.88)</td>
</tr>
<tr>
<td>$e_2^2(2)$</td>
<td>3.59(3.35)</td>
<td>3.61(3.37)</td>
<td>3.53(3.29)</td>
<td>3.09(2.88)</td>
<td>3.08(2.87)</td>
<td>3.09(2.88)</td>
</tr>
<tr>
<td>$e_2^3(3)$</td>
<td>2.51(2.28)</td>
<td>2.59(2.36)</td>
<td>2.73(2.48)</td>
<td>2.59(2.35)</td>
<td>2.57(2.34)</td>
<td>2.52(2.29)</td>
</tr>
<tr>
<td>$e_2^4(4)$</td>
<td>0.43(0.42)</td>
<td>0.43(0.42)</td>
<td>0.27(0.27)</td>
<td>0.18(0.17)</td>
<td>0.18(0.18)</td>
<td>0.18(0.18)</td>
</tr>
</tbody>
</table>
TABLE V. Dimensionless scaled vibronic coupling constants for the degenerate \( e_2' \) modes calculated by CASSCF(5,8)/6-31G(d,p). Negative signs are neglected. The calculations 1–3 and experimental values are taken from Ref. 8.

<table>
<thead>
<tr>
<th>Method</th>
<th>( D_{e_2'(1)} )</th>
<th>( D_{e_2'(2)} )</th>
<th>( D_{e_2'(3)} )</th>
<th>( D_{e_2'(4)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>0.79</td>
<td>1.30</td>
<td>1.06</td>
<td>0.08</td>
</tr>
<tr>
<td>Calculation 1</td>
<td>0.77</td>
<td>0.98</td>
<td>1.40</td>
<td>&lt;0.14</td>
</tr>
<tr>
<td>Calculation 2</td>
<td>0.66</td>
<td>0.82</td>
<td>1.17</td>
<td>&lt;0.14</td>
</tr>
<tr>
<td>Calculation 3</td>
<td>0.85</td>
<td>0.82</td>
<td>1.14</td>
<td>&lt;0.14</td>
</tr>
<tr>
<td>Experimental</td>
<td>0.62</td>
<td>1.07</td>
<td>0.85</td>
<td>0</td>
</tr>
</tbody>
</table>

Since it has the correct symmetry which is expected from the Wigner-Eckart theorem, we can obtain the vibronic coupling constant \( 1/2\langle E|V|E\rangle = 0.001416 \). Furthermore, we confirmed that the GRHF and CASSCF wave functions satisfy the Wigner-Eckart theorem as well as the RHF wave function.

C. Vibronic coupling constant

The calculated VCCs by RHF, GRHF, and CASSCF methods are tabulated in Table III. These methods yield the appropriate wave function with the correct symmetry. Note that the RHF wave function is not variationally optimized for the radical since the RHF calculation was performed for the parent system, cyclopentadienyl anion. For the \( a_1' \) modes, the RHF wave function yields quite large value, comparing with the variationally optimized wave function. This is because all the occupied orbitals contribute to the VCC of the \( a_1' \) modes, and the errors are accumulated, while only frontier \( e_1'' \) orbitals contribute to that of \( e_2' \) modes.

In each calculation, the VCC of the \( e_2'(3) \) mode has the largest value of all the \( e_2' \) modes. All calculations show the tendency, \( e_2'(3) > e_2'(2) > e_2'(1) > e_2'(4) \), and this agrees with the experimental result. In other words, as long as we are interested in a qualitative aspect of the \( e_2' \) modes, we can employ the RHF wave function for the VCC calculation.

Table IV shows the dimensionless vibronic coupling constant \( D \), which is calculated using the frequency. Though

\[ D \text{ calculated by the GRHF frequency is smaller than that calculated by the RHF frequency, the difference is rather small.} \]

The calculated \( D \) after the scaling using the constant \( K \) is tabulated in Table V. Table V demonstrates good agreement of the present results with the calculation and experiment reported by Applegate et al.\(^8\)

D. Vibronic coupling density analysis

Since we have the explicit expressions for the coupling integral, Eq. (52), as discussed in Sec. III, we can discuss VCC in terms of the electronic and vibrational structures. In particular, for the HF wave functions, we can define vibronic coupling density \( \eta_j(r) \) in a simple form to analyze the VCC.

**Vibronic coupling density** \( \eta_j(r) \) for the \( e_2'(j) \) mode is defined by

\[ \eta_j(r) = \psi_{\theta_j}(r)\psi_{\theta_j}(r)v_{\theta_j}(r) = \rho_{\theta_j}(r)v_{\theta_j}(r), \]

where \( \rho_{\theta_j}(r) \) is the frontier electron density of the molecular orbital \( \psi_{\theta_j} \) and \( v_{\theta_j}(r) \) the one-electron electronic operator defined in Eq. (32). The VCC is written as

\[ \langle E|V|E\rangle = \sum_{j} \int \eta_j(r)dr, \]

where \( \langle E|V|E\rangle \) is the vibronic coupling constant.
V_j = \int dr \eta_i(r).

The vibronic coupling density enables us to analyze the calculated VCC in terms of the electronic structure \( \rho_b(r) \) and the derivative of the potential with respect to the normal coordinate \( v_{\theta j}(r) \).

In Fig. 4, the JT-active \( \epsilon_j^4 \) modes are shown. It should be noted that the larger components of the vibrational modes lie on the carbon atoms for \( \epsilon_j^2(1) \) and \( \epsilon_j^2(3) \), while the hydrogens in \( \epsilon_j^2(2) \) or \( \epsilon_j^2(4) \) have large contribution.

Figure 12 shows the contour plot of the frontier electron density \( \rho_b(r) \) of \( \epsilon_j^2(3) \) orbital calculated from the GRHF wave function (see Fig. 3).

In Fig. 13(a), the derivative of the potential with respect to the \( \epsilon_j^2(1) \) mode is shown. It is found that the large values are distributed on the C1–H1, C2–H2, and C5–H5 bonds. However, there is little electron density on the C2–H2 and C5–H5 bonds. Consequently, the vibronic coupling density of this mode \( \eta_1 \) is small and negative, and localized on the C1–H1 bond, as shown in Fig. 13(b).

Figure 14(a) shows the derivative of the potential with respect to the \( \epsilon_j^2(2) \) mode. The derivative of the potential has a large value not just on the C–C bonds but near the C3–C4, C2–C3, and C4–C5 bonds. This is because the large displacement of this mode lies on the hydrogen atoms. Since the electron density is localized on the C3–C4 bond, the vibronic coupling density for this mode \( \eta_2 \) gives rather large near the C3–C4 bond as shown in Fig. 14(b).

The derivative of the potential with respect to the \( \epsilon_j^2(3) \) mode is shown in Fig. 15(a). This mode yields the largest VCC among the four. The derivative plot shows a distribution on the C3–C4, C2–C3, and C4–C5 bonds. Figure 14(b) shows the vibronic coupling density \( \eta_3 \). As the result of the electron and derivative potential distributions, \( \eta_3 \) is distributed in the region near the C3–C4 bond. The broad distribution makes the VCC of this mode large. The coincidence between the electron density distribution \( \rho_b \) and the distribution of the derivative potential is the reason why the VCC of the \( \epsilon_j^2(3) \) mode is the largest of the four.

In Fig. 16(a), the derivative potential with respect to the \( \epsilon_j^2(4) \) mode is shown. It is distributed on the C1–H1, C2–H2, and C5–H5 bonds where \( \rho_b \) gives small value. The vibronic coupling density of this mode [Fig. 16(b)] illustrates...
low density near the C1 atom. The distribution of the derivative potential does not coincide with the electron density distribution $\rho_\beta$. This is the reason why the VCC of this mode is the smallest.

It is interesting to note that it is not necessary for the VCC of the mode which has large component on the carbons to be large.

**VII. CONCLUSION**

We present a new method of calculation of vibronic coupling constant, taking a JT molecule, cyclopentadienyl radical, as an example. It is confirmed that symmetry breaking at degenerate point and violation of Hellmann-Feynman theorem occur in the calculations based on a single Slater determinant. In order to overcome these difficulties, the electronic wave functions are calculated using generalized restricted Hartree-Fock (GRHF) and CASSCF methods, and the couplings are computed as matrix elements of the electronic operator of the vibronic coupling. Our result agrees well with the experimental and theoretical values by Applegate et al. A concept of vibronic coupling density is proposed in order to explain the order of magnitude of the coupling constant from view of the electronic and vibrational structures. It is found that the vibronic coupling of the JT-active mode is large when the frontier electron density $\rho$ matches the one-electron electronic operator $v_i$. Furthermore it can illustrate the local properties of the coupling and enables us to control the interaction. This could open a way to the engineering of vibronic interactions. For instance, replacement by a heteroatom or introduction of a functional group for a molecule alters, the matching between the frontier electron density and the one-electron electronic operator.

**ACKNOWLEDGMENT**

Numerical calculation was partly performed in the Supercomputer Laboratory of Kyoto University.