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

Tohru Sato
Fukui Institute for Fundamental Chemistry, Kyoto University, Takano-Nishihiraki-cho 34-4, Sakyo-ku, Kyoto 606-8103, Japan and Department of Molecular Engineering, School of Engineering, Kyoto University, Kyoto 615-8510, Japan

Ken Tokunaga
Department of Molecular Engineering, School of Engineering, Kyoto University, Kyoto 615-8510, Japan

Kazuyoshi Tanaka
Department of Molecular Engineering, School of Engineering, Kyoto University, Kyoto 615-8510, Japan and Core Research for Evolutional Science and Technology, Japan Science and Technology Agency (JST-CREST)

(Received 24 October 2005; accepted 17 November 2005; published online 11 January 2006)

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\(_5\)H\(_5\), 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 \( E_g'' \) state can be deduced as

\[
[E_g''^2] = a_{1}^e + e_2^x,
\]

where \( [\Gamma^2] \) denotes the symmetric product of an irreducible representation \( \Gamma \). Therefore, the radical should give rise to a JT distortion with \( e_2^x \) symmetry, and the resulting structure is \( C_{2v} \). The molecule has \( 3N-6=24 \) vibrational modes,

\[
\Gamma_{\text{vib}} = 2a_1^e + 3e_1^x + 4e_2^x + a_2^e + e_1^a + 2e_2^a.
\]

Thus the two \( a_1^e \) modes and four \( e_2^x \) 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 \( \tilde{A}^2A_2^e \rightarrow \tilde{X}^2E_g'' \) transition of the radical in detail and calculated observable spectroscopic constants by ab initio method. They estimated the vibronic coupling constants for the four \( e_2^x \) modes from their experiment and calculation. Since their assignment is...
FIG. 1. Cross section of the Jahn-Teller potential. Jahn-Teller crossing $R_0$ is the nuclear configuration of the molecule without Jahn-Teller distortion, and energy minimum $R_{\text{min}}$ is the molecular structure with the lowest energy. The $D_{3h}$ symmetry at $R_0$ is lowered into the $C_{2v}$ at $R_{\text{min}}$ because of the Jahn-Teller effect. For the structure $R'$ which is obtained after the optimization for the conical intersection, the energy difference $E_e(R') - E_e(R_{\text{min}}) = 1/2D^2$ is called Jahn-Teller stabilization energy $\Delta E$, where $D$ is dimensionless vibronic coupling constant.

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 view of the electronic and vibrational structures. To find a way to control the coupling is another purpose of this study.

The paper is organized as follows. In Sec. II, the model Hamiltonian of the problem is presented. The method of the calculation is presented in Sec. III. The calculations using the gradient of a Born-Oppenheimer potential at the JT crossing point is not appropriate, since the wave function gives rise to the symmetry breaking at the point. In addition the application of the Hellmann-Feynman theorem that the coupling is equal to the gradient is not valid. We discuss these points in Secs. IV and V, respectively. In Sec. VI, the results of calculations are shown and we discuss the constants in terms of the vibronic coupling density. Finally, we conclude this work in Sec. VII.

II. VIBRONIC HAMILTIONIAN

A molecular Hamiltonian is given by

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

where

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

$R$ denotes a set of nuclear coordinates, $r$ that of electronic coordinates, $\mathcal{T}$ a kinetic-energy operator, and $\mathcal{U}$ a sum of an electron-electron, electron-nuclear, and nuclear-nuclear potential operator. $\mathcal{H}_e$ is an electronic Hamiltonian which gives a potential surface $E_e(R)$ within the Born-Oppenheimer approximation,

$$\mathcal{H}_e(r,R) \phi(r,R) = E_e(R) \phi(r,R).$$

Starting from a reference nuclear configuration $R_0$, which is the JT crossing point in the JT problem, the electronic Hamiltonian for a deformed molecule whose nuclear coordinates are expressed by $R$ 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

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

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

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

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

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

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

$$+ \frac{1}{2} \sum_i \frac{1}{\omega_i^2} Q_i^2,$$

where $\omega_i$ is the frequency of the mode. The index $i$ runs over $2a_1^2 + 4e_1^2$ modes. The first term in Eq. (9) corresponds to the nuclear kinetic energy. The operator involved in the third term,
where the orbital level of HOMO is doubly degenerate \( e_1^0 \), one of them is denoted as \( e \), and the other as \( \theta \). The \( \theta \) is transformed as \( y \), and \( e \) is \( x \). Irreducible representations in the parentheses are those lowered into the subgroup \( C_{2v} \): \( E' \) and the electronic \( E'' \) state can be reduced using Wigner-Eckart theorem,

\[
\langle E''|V_{e,j}|E'\rangle = \frac{1}{\sqrt{2}} \left( \frac{1}{2} 0 \right),
\]

and

\[
\langle E''|V_{e,j}|E'\rangle = \frac{1}{\sqrt{2}} \left( 0 \frac{1}{2} 0 \right).
\]

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

\[
\langle E''|V_{e,j}|E'\rangle = 2\langle E''|V_{e,j}|E''\rangle = -(E''|V_{e,j}|E'').
\]

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

\[
\hat{V}_{e, j} = \frac{1}{2} \left( \frac{E''}{E'\rangle} \right) \left( \begin{array}{c}
0 \\
1
\end{array} \right) = \hat{V}_{e, j} \left( \begin{array}{c}
0 \\
1
\end{array} \right),
\]

and

\[
\hat{V}_{e, j} = \frac{1}{2} \left( \frac{E''}{E'\rangle} \right) \left( \begin{array}{c}
0 \\
1
\end{array} \right) = \hat{V}_{e, j} \left( \begin{array}{c}
0 \\
1
\end{array} \right).
\]
is a VCC for a totally symmetric $a'_{i}$ 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 $R_{0}$.

We introduce here some dimensionless quantities. For a vibrational mode $i$, the normal coordinate $Q_{i}$ is measured by

$$Q_{i} = \sqrt{\frac{h}{\omega_{i}}} q_{i},$$

where $q_{i}$ is a dimensionless normal coordinate. Dimensionless coupling constant $D_{i}$ can be defined as

$$D_{i} = \frac{V_{i}}{\sqrt{h/\omega_{i}}}.$$

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

$$\hat{H}_{JT} = E_{0}\hat{\sigma}_{0} + \sum_{k=1}^{2} \left\{ -\frac{h^{2}}{2} \left( -\frac{\partial^{2}}{\partial Q_{a_{i}(k)}^{2}} \right) \hat{\sigma}_{0} + \frac{1}{2} \omega_{a_{i}(k)}^{2} Q_{a_{i}(k)}^{2} \hat{\sigma}_{0} \\
+ Q_{a_{i}(k)} V_{a_{i}(k)}^{c} \hat{\sigma}_{0} + \frac{4}{3} \left\{ -\frac{h^{2}}{2} \left( -\frac{\partial^{2}}{\partial Q_{\epsilon_{0}(j)}^{2}} \right) \hat{\sigma}_{0} + \frac{2}{2} \frac{\partial^{2}}{\partial Q_{\epsilon_{0}(j)}^{2}} Q_{\epsilon_{0}(j)}^{2} \hat{\sigma}_{0} \\
- \frac{h^{2}}{2} \left( -\frac{\partial^{2}}{\partial Q_{\epsilon_{0}(j)}^{2}} \right) \hat{\sigma}_{0} + \frac{2}{2} \frac{\partial^{2}}{\partial Q_{\epsilon_{0}(j)}^{2}} Q_{\epsilon_{0}(j)}^{2} \hat{\sigma}_{0} + \frac{1}{2} \omega_{\epsilon_{0}(j)}^{2} Q_{\epsilon_{0}(j)}^{2} \hat{\sigma}_{0} \\
+ \frac{1}{2} \omega_{\epsilon_{0}(j)}^{2} Q_{\epsilon_{0}(j)}^{2} \hat{\sigma}_{0} + V_{\epsilon_{0}(j)}^{c} \left( Q_{\epsilon_{0}(j)}^{c} \hat{\sigma}_{0} + Q_{\epsilon_{0}(j)}^{c} \hat{\sigma}_{0} \right) \right\} \right\}$$

$$= E_{0}\hat{\sigma}_{0} + \sum_{k=1}^{2} \hbar \omega_{a_{i}(k)} \left\{ -\frac{1}{2} \left( -\frac{\partial^{2}}{\partial Q_{a_{i}(k)}^{2}} \right) \hat{\sigma}_{0} + \frac{1}{2} \omega_{a_{i}(k)}^{2} \hat{\sigma}_{0} \\
+ q_{a_{i}(k)} D_{a_{i}(k)} \hat{\sigma}_{0} + \sum_{j=1}^{4} \hbar \omega_{\epsilon_{0}(j)} \left\{ -\frac{1}{2} \left( -\frac{\partial^{2}}{\partial Q_{\epsilon_{0}(j)}^{2}} \right) \hat{\sigma}_{0} \\
- \frac{1}{2} \left( -\frac{\partial^{2}}{\partial Q_{\epsilon_{0}(j)}^{2}} \right) \hat{\sigma}_{0} + \frac{1}{2} \omega_{\epsilon_{0}(j)}^{2} \hat{\sigma}_{0} + D_{\epsilon_{0}(j)} \right\} \right\},$$

where

$$\hat{\sigma}_{x} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_{z} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$
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

$$
\hat{V}^{HF}_i = \begin{pmatrix}
\langle \theta | V | \theta \rangle & \langle \theta | V | e \rangle \\
\langle e | V | \theta \rangle & \langle e | V | e \rangle
\end{pmatrix},
$$

and

$$
\hat{V}^{CAS}_i = \begin{pmatrix}
\sum_{LL'} C^*_i C_{i',L'} \langle \phi_i | V | \phi_{i',L'} \rangle & \sum_{LL'} C^*_i C_{i',L'} \langle \phi_i | V | \phi_{i',L'} \rangle \\
\sum_{LL'} C^*_i C_{i',L'} \langle \phi_i | V | \phi_{i',L'} \rangle & \sum_{LL'} C^*_i C_{i',L'} \langle \phi_i | V | \phi_{i',L'} \rangle
\end{pmatrix},
$$

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

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

$$
\langle \cdots mn \cdots | O_i | \cdots np \cdots \rangle = \langle m | h | p \rangle,
$$

$$
\langle \cdots mn \cdots | O_i | \cdots pq \cdots \rangle = 0,
$$

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

$$
\langle \theta | V | \theta \rangle = \sum_m n_m \langle \psi_m | v | \psi_m \rangle,
$$

$$
\langle \theta | V | e \rangle = \langle \psi_e | v | \psi_e \rangle,
$$

$$
\langle e | V | \theta \rangle = \langle \psi_e | v | \psi_e \rangle,
$$

$$
\langle e | V | e \rangle = \sum_m n_m \langle \psi_m | v | \psi_m \rangle,
$$

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 $\langle \phi_i | V | \phi_{i'} \rangle$ 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 $\phi_{i'}$ are single-electron excited configurations, the integral is decomposed as follows:

$$
\langle \theta | V | \theta \rangle = \sum_m \langle \chi_m | v | \chi_m \rangle \text{ if } a = b, \ r = s
$$

$$
- \langle \chi_a | v | \chi_b \rangle \text{ if } a = b, \ r \neq s
$$

$$
0 \text{ if } a \neq b, \ r \neq s,
$$

where $\chi_a$ and $\chi_b$ denote occupied spin-orbitals, and $\chi_r$ and $\chi_t$ unoccupied spin-orbitals. $m$ runs over the occupied spin-orbitals.

The VCI over Slater determinants $| \theta \rangle$ and $| e \rangle$ can be decomposed into orbital vibronic integrals (OVCIs) for the $\theta$ mode over molecular orbitals,

$$
\langle \theta | V | \theta \rangle = - \langle \theta | V | e \rangle = \sum_{\alpha \beta} \{ n_{\alpha(m)} \langle \psi_{\alpha(m)} | v | \psi_{\alpha(m)} \rangle
$$

$$
+ n_{e(m)} \langle \psi_{e(m)} | v | \psi_{e(m)} \rangle \text{ if } a = b, \ r = s
$$

$$
0 \text{ if } a \neq b, \ r \neq s,
$$

where $m$ runs over the occupied molecular orbitals with or-
equal to the OVCI matrix, therefore, the vibronic coupling matrix in the HF methods is

\[ \langle \psi_{\theta(m)} | V_{\theta} | \psi_{\theta(m)} \rangle + \langle \psi_{\epsilon(m)} | V_{\epsilon} | \psi_{\epsilon(m)} \rangle = 0, \]  

(49)

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

\[ \langle \theta | V_{\theta} | \theta \rangle = \langle \psi_\theta | V_{\theta} | \psi_\theta \rangle, \]

\[ \langle \epsilon | V_{\epsilon} | \epsilon \rangle = \langle \psi_\epsilon | V_{\epsilon} | \psi_\epsilon \rangle. \]

(50)

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

\[ \langle \theta | V_{\epsilon} | \theta \rangle = \langle \psi_\theta | V_{\epsilon} | \psi_\theta \rangle, \]

(51)

\[ \langle \epsilon | V_{\epsilon} | \theta \rangle = \langle \psi_\epsilon | V_{\epsilon} | \psi_\theta \rangle. \]

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

![Diagram of totally symmetric \( a'_1 \) vibrational modes. The largest displacement locates on the carbon atoms for \( a'_1(1) \), and on hydrogen atoms for \( a'_1(2) \).](image)

![Diagram of energy curves of the A1 and B1 states along the e1(3) mode.](image)

![Diagram of calculated electronic state of cyclopentadienyl radical \( ^2E' \) 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.](image)
at the Jahn-Teller crossing is larger than that of the energy gradient. The symmetric π orbital ω(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.

\[ V_j = \langle E_1^1 | \theta | \nu_{\beta(j)} | E_1^1 \theta \rangle \]

\[ = \sum_{\beta=1}^{3N} l_{\beta \beta(j)} \langle E_1^1 | \theta | \nu_{\beta} | E_1^1 \theta \rangle \]

\[ = \sum_{\beta=1}^{3N} u_{\beta j} \]

\[ = K \sum_{\beta=1}^{3N} x_{d \beta j} \]

\[ = K k_j, \]

where

\[ u_{\beta} = \langle E_1^1 | \theta | \nu_{\beta} | E_1^1 \theta \rangle. \]

**FIG. 9.** Symmetry breaking in the lowest π orbital of cyclopentadienyl radical and the anion (framed). The calculations were performed for the D_{3h} structure. The symmetric π orbital ω(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.

\[ \Delta E = \sum_{j=1}^{4} \frac{V_j^2}{2\omega_j} = K^2 \sum_{j=1}^{4} \frac{k_j^2}{2\omega_j}, \]

where \( \Delta E \) 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.\(^7\)

**FIG. 10.** Energy gradient \( \partial E/\partial R \) and \( \langle \partial H/\partial R \rangle \) (VCI in the figure) using ROH/F towards the minimum of the potential on the \( ^2A_1 \) 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 \( \langle \partial H/\partial R \rangle \) at the Jahn-Teller crossing is larger than that of the energy gradient.

Therefore,

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

**FIG. 11.** Energy gradient \( \partial E/\partial R \) and \( \langle \partial H/\partial R \rangle \) (VCI in the figure) using ROB3LYP towards the minimum of the potential on the \( ^2A_1 \) 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 \( \langle \partial H/\partial R \rangle \) at the Jahn-Teller crossing is larger than that of the energy gradient.
TABLE I. Bond length (Å) of cyclopentadienyl anion C5H5 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>

IV. SYMMETRY BREAKING AND WIGNER-ECKART THEOREM

Figure 6 shows the energy levels of the frontier orbitals calculated using RHF and ROB3LYP for the anion and ROHF, ROB3LYP, UHF, and UB3LYP for the neutral radical. As for the anion which has a closed shell, the calculations give a degenerate \( \epsilon^\sigma \) HOMO with the correct degeneracy. However, either in HF or in density-functional theory (DFT) calculations, the restricted open-shell and unrestricted calculations exhibit symmetry broken orbitals for the radical which should have the degenerate \( \epsilon^\sigma \) orbitals. The orbital symmetry cannot be assigned within the D5h point group. It is known that such an incorrect symmetry breaking of the orbitals sometimes occurs in the system involving a degenerate electronic state when a calculation is based on a single determinant. We confirmed the same situation in the present calculation.

Figure 7 shows the calculated total energy of the electronic \( 2\epsilon^\sigma \) state for the radical. Since the electronic \( 2\epsilon^\sigma \) is degenerate, the total energy of two electronic configurations, \( \langle \psi_0 | \epsilon^\sigma | \psi_0 \rangle \) and \( \langle \psi_1 | \epsilon^\sigma | \psi_1 \rangle \), should be equal. However, the calculations using ROHF, ROB3LYP, UHF, and UB3LYP exhibit incorrect energy splittings, while the results using GRHF and state-averaged CASCCF give correct degeneracy. Moreover, as shown in Fig. 8, the JT crossing point is disappeared at the point \( Q=0 \) where the two energy curves should cross.

Symmetry breaking is observed not only in the energy but also in the wave function. Figure 9 illustrates the examples of the symmetry broken orbital of cyclopentadienyl radical with the D5h symmetry. The lowest \( \pi \) orbital, which should be \( d^\pi \) symmetry within the D5h 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), \( \langle E_\lambda | V_{\phi \rho} | E_\lambda \rangle \) has the same absolute value as \( \langle E_\lambda | V_{\phi \rho} | E_\lambda \rangle \). However, the calculation of the coupling for the \( \epsilon^\sigma(3) \) mode using the ROHF wave function yields \( \langle E_\lambda | V_{\phi \rho} | E_\lambda \rangle = 0.000 \ 976 \ 415.9 \) and the ROB3LYP calculation gives \( \langle E_\lambda | V_{\phi \rho} | E_\lambda \rangle = 0.000 \ 803 \ 151.2 \). 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\(^{10,11} \) states that, when a Hamiltonian depend 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 \( \lambda \),

\[
\frac{\partial E(\lambda)}{\partial \lambda} = \left\langle \frac{\partial \mathcal{H}(\lambda)}{\partial \lambda} \right\rangle.
\]

(64)

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

\[
\frac{\partial E(Q)}{\partial Q} = \left\langle \frac{\partial \mathcal{H}(Q)}{\partial Q} \right\rangle = \left\langle \frac{\partial \mathcal{H}(Q)}{\partial Q} \right\rangle.
\]

(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 the present calculations.

Figures 10 and 11 demonstrate that the energy gradient \( \partial E/Q \) is not equal to the Hellmann-Feynman force \( \partial \mathcal{H}/\partial Q \) along the path towards the minimum of the potential on the \( 2A_2 \) manifold in \( C_{2v} \) (\( 2\epsilon^\sigma \) C2v=\( ^2A_2 \oplus ^2B_1 \), C2v⊂D5h), 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 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'_1(1) )</th>
<th>( a'_1(2) )</th>
<th>( e'_1(1) )</th>
<th>( e'_1(2) )</th>
<th>( e'_1(3) )</th>
<th>( e'_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></td>
<td>Expt.</td>
<td>1071</td>
<td>872</td>
<td>1041</td>
<td>1320</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 CASSCF calculation.

### VI. RESULTS AND DISCUSSION

#### A. Geometrical and vibrational structures

The optimized symmetry of the parent system C₅H₅ and that of the conical intersection for the neutral radical C₅H₅ are D₅h. 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 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 eₙ(3) vibrational mode calculated by RHF is obtained as

\[
\begin{pmatrix}
    \langle E_d | V_{e_d} | E_d \rangle & \langle E_d | V_{e_d} | E_c \rangle \\
    \langle E_c | V_{e_d} | E_d \rangle & \langle E_c | V_{e_d} | E_c \rangle
\end{pmatrix} = \begin{pmatrix}
    0.001 416 302 4 & 0.000 000 000 0 \\
    0.000 000 000 0 & -0.001 416 302 4
\end{pmatrix},
\]

and

\[
\begin{pmatrix}
    \langle E_d | V_{e_d} | E_d \rangle & \langle E_d | V_{e_d} | E_c \rangle \\
    \langle E_c | V_{e_d} | E_d \rangle & \langle E_c | V_{e_d} | E_c \rangle
\end{pmatrix} = \begin{pmatrix}
    0.000 000 000 0 & 0.001 416 302 4 \\
    0.001 416 302 4 & 0.000 000 000 0
\end{pmatrix}.
\]

### Table IV. Unscaled dimensionless vibronic coupling constant D of C₅H₅ calculated using 6-31G(d,p) basis set. The vibrational vectors employed in these calculations were obtained with 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>C₅H₅</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>a₁(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>a₁(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>e₁(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>e₁(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>e₁(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>e₁(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 $e'_1$ 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></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 $D$ 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.\textsuperscript{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

$$\eta_j(r) = \psi_d(r)\psi_d(r)v_{\alpha j}(r) = \rho_d(r)v_{\alpha j}(r),$$

where $\rho_d(r)$ is the frontier electron density of the molecular orbital $\psi_d$ and $v_{\alpha j}(r)$ the one-electron electronic operator defined in Eq. (32). The VCC is written as
The vibronic coupling density enables us to analyze the calculated VCC in terms of the electronic structure $\rho_\eta(r)$ and the derivative of the potential with respect to the normal coordinate $v_{\eta j}(r)$.

In Fig. 4, the JT-active $\epsilon_2^t$ modes are shown. It should be noted that the larger components of the vibrational modes lie on the carbon atoms for $\epsilon_2^t(1)$ and $\epsilon_2^t(3)$, while the hydrogens in $\epsilon_2^t(2)$ or $\epsilon_2^t(4)$ have large contribution.

Figure 12 shows the contour plot of the frontier electron density $\rho_\eta(r)$ of $\epsilon_2^t(1)$ orbital calculated from the GRHF wave function (see Fig. 3).

In Fig. 13(a), the derivative of the potential with respect to the $\epsilon_2^t(1)$ 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 $\epsilon_2^t(2)$ 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 $\epsilon_2^t(3)$ 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 15(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 $\rho_\eta$ and the distribution of the derivative potential is the reason why the VCC of the $\epsilon_2^t(3)$ mode is the largest of the four.

In Fig. 16(a), the derivative potential with respect to the $\epsilon_2^t(4)$ mode is shown. It is distributed on the C1–H1, C2–H2, and C5–H5 bonds where $\rho_\eta$ 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 \( \rho_e \). 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 \( v_\tau \). 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.