Vibronic couplings in cycloadditions to fullerenes

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Abstract.
It is known to be difficult to predict the regioselectivity of cycloadditions to fullerenes based on the frontier orbital theory. To discuss the chemical reactivity of C\textsubscript{60}, vibronic coupling constants for localized stretching vibrational modes of C\textsubscript{60} anion which are the hypothetical reaction modes of cycloadditions are calculated. Furthermore, the product ratio of C\textsubscript{60} bisadduct (C\textsubscript{60}X\textsubscript{2}) is evaluated in the same way by considering the electronic state of C\textsubscript{60} monoadduct anion (C\textsubscript{60}X anion). It is found that there is a good correlation between vibronic coupling constants for the localized modes and experimental regioselectivity.

1. Introduction
Chemical reaction involves the formation and breaking of chemical bonds which connect atoms in molecules. Bond formation and breaking are caused by nuclear motions (molecular vibrations) with the rearrangement of electrons. The frontier orbital theory\cite{1, 2}, which is the most successful theory on the chemical reactivity, discusses molecular/bimolecular stabilization by considering only the rearrangement of electrons, that is, electron delocalization (charge-transfer) interactions via frontier orbitals. In addition to the frontier orbital interactions, vibronic (electron-vibration) couplings\cite{3, 4} can give rise to stabilization via molecular distortion in the early stage of a reaction. The vibronic coupling can be therefore a key concept to understand chemical reactions beyond the frontier orbital theory.

The frontier orbital theory has difficulty in predicting the chemical reactivity in some cases. For example, large molecules with delocalized frontier orbitals and molecules with degenerate frontier orbitals are such a case. The delocalization or degeneracy tends to smear a reactive site. The typical example with these problems is the cycloadditions to C\textsubscript{60} fullerene (Figure 1). Nucleophilic cycloadditions to C\textsubscript{60} have been studied widely in material chemistry\cite{5, 6}. The C\textsubscript{60} cage has two types of bonds. One is the bond between adjacent hexagon rings (6:6 bonds), and another is the bond between a hexagon ring and a pentagon ring (6:5 bonds). Cycloadditions are experimentally known to occur on 6:6 bonds\cite{5, 6}. According to the frontier orbital theory, the regioselectivity of nucleophilic cycloadditions is indicated by the distributions of $t_{1u}$ LUMOs of C\textsubscript{60}. However, since the averaged LUMO density has the totally symmetric distribution which is equivalent at each carbon atom, the regioselectivity cannot be predicted by the frontier orbital theory.

Recently, we have proposed that the concept of vibronic coupling density is effective to predict the chemical reactivity\cite{7, 8, 9}. The vibronic coupling density gives a local picture of the strength of linear vibronic interaction. The vibronic coupling density for the effective vibrational mode of C\textsubscript{60} anion is calculated and it is found that there is a good correlation between vibronic coupling constants for the localized modes and experimental regioselectivity.
Figure 1. C\textsubscript{60} fullerene and the labels of its atoms.

C\textsubscript{60} anion illustrates the reactive bonds of C\textsubscript{60} clearly\cite{9}. We have found that the C\textsubscript{60} cage has ethylene moieties as a functional group by comparing the distribution of the vibronic coupling density of C\textsubscript{60} anion with ethylene anion.

Furthermore, we have recently calculated vibronic coupling constants for localized stretching vibrational modes of C\textsubscript{70} anion which reproduce the experimental reactivity of each bond of C\textsubscript{70}\cite{10}. The localized stretching vibrational modes are the hypothetical reaction modes of cycloadditions.

In this study, in order to estimate the quantitative chemical reactivity of each bond of C\textsubscript{60}, we calculate vibronic coupling constants for localized modes of its anion. In addition, we evaluate the product ratio of C\textsubscript{60} bisadduct (C\textsubscript{60}X\textsubscript{2}, Figure 2) in the same way by considering the electronic state of C\textsubscript{60} monoadduct anion (C\textsubscript{60}X anion) based on that of C\textsubscript{60} anion.

Figure 2. The names of C\textsubscript{60} bisadduct isomers. X is diene or diene-like reactant. The red bonds with arrows indicate the bonds added by another reactant.

2. Theory

We discuss vibronic couplings in chemical reactions based on the Parr and Yang’s conceptual density functional theory\cite{11}. The ground electronic energy $E$ of an isolated reactant is the functional of the number of electrons $N$ and the potential $u(r)$ attracting a single electron: $E = E[N,u]$. They have introduced an electronic chemical potential $\mu$ as $\left(\partial E/\partial N\right)_{u}$. Since $\mu$
is also the functional of \(N\) and \(u(\mathbf{r})\): \(\mu = \mu[N, u]\), its differential is given by

\[
d\mu = 2\eta dN + \int f(\mathbf{r})du(\mathbf{r})d^3\mathbf{r},
\]

where an absolute hardness \(\eta\) is

\[
\eta := \frac{1}{2} \left( \frac{\partial \mu}{\partial N} \right)_u = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right)_u,
\]

and a Fukui function \(f(\mathbf{r})\) is

\[
f(\mathbf{r}) := \left( \frac{\delta \mu}{\delta u} \right)_N = \left( \frac{\partial \rho}{\partial N} \right)_u.
\]

\(\rho(\mathbf{r})\) is a total electron density. Based on equation (1), Parr and Yang have proposed the principle of chemical reactions that a chemical reaction occurs such that the initial \(|d\mu|\) is the maximum. Since \(f(\mathbf{r})\) is approximately the frontier orbital density, their principle in their opinion leads to the frontier orbital theory.

Our theory is also based on equation (1). We consider the case of an electron acceptor such as \(C_{60}\). We assume that \(f(\mathbf{r})\) can be approximated by the electron density difference \(\Delta \rho(\mathbf{r})\) between its neutral state and its anionic state. We also assume that \(du(\mathbf{r})\) can be expressed by a reaction coordinate \(s\):

\[
du(\mathbf{r}) = v_s(\mathbf{r})ds,
\]

where a potential derivative \(v_s(\mathbf{r})\) is defined as

\[
v_s(\mathbf{r}) := \left( \frac{\partial u}{\partial s} \right)_{R_0}.
\]

\(R_0\) is molecular reference geometry. As a result, equation (1) can be rewritten as

\[
d\mu = 2\eta dN + \int \Delta \rho(\mathbf{r})v_s(\mathbf{r})d^3\mathbf{r}ds = 2\eta dN + \int \eta_s(\mathbf{r})d^3\mathbf{r}ds,
\]

where vibronic coupling density \(\eta_s(\mathbf{r})\) for the reaction mode \(s\)[7, 8] is defined as

\[
\eta_s(\mathbf{r}) := \Delta \rho(\mathbf{r}) \times v_s(\mathbf{r}).
\]

The integration of the vibronic coupling density \(\eta_s(\mathbf{r})\) is known to be exactly equal to a linear vibronic coupling constant \(V_s\) for the reaction mode \(s\):

\[
V_s := \left\langle \Psi^- \left| \left( \frac{\partial \hat{H}}{\partial s} \right)_{R_0} \right| \Psi^- \right\rangle = \int \eta_s(\mathbf{r})d^3\mathbf{r},
\]

where \(\hat{H}\) denotes a molecular Hamiltonian and \(\Psi^-\) denotes an anionic state. In general, the reaction mode \(s\) is a mixture of totally symmetric modes, Jahn–Teller active modes and the other modes. Note that the vibronic coupling constant defined here is different from the Jahn–Teller coupling constant in the \(T \otimes h\) Jahn–Teller Hamiltonian[12] by the Clebsch–Gordan coefficients even if mode \(s\) coincides with some Jahn-Teller modes in \(C_{60}\).

The integration of \(\eta_s(\mathbf{r})\) is also equal to the gradient of the anionic potential surface due to the Hellmann-Feynman theorem[13, 14]:

\[
V_s = \int \eta_s(\mathbf{r})d^3\mathbf{r} = \left( \frac{\partial (E^- + U_{nn})}{\partial s} \right)_{R_0},
\]
where $E^-$ denotes an electronic energy of the anionic state, and $U_{nn}$ the sum of nuclear-nuclear repulsive potentials. The anionic state is stabilized in the direction such that $V_a$ is negative. Therefore, we have proposed that chemical reaction occurs such that $V_a$ is a minimum, and its local picture is given by $\eta_a(r)[10]$.

In our previous work, we have regarded an effective vibrational mode as a reaction mode $s[7, 8, 9]$. The effective vibrational mode is the steepest descent of the anionic state, that is constructed by only totally symmetric modes and Jahn–Teller active modes. As for cycloadditions, some localized stretching vibrational modes can be regarded as a reaction mode rather than the effective mode[10]. Each localized mode is a linear combination of some intramolecular vibrational modes including totally symmetric modes, Jahn–Teller active modes and the others. All the localized modes construct the effective mode. The localized stretching vibrational vector $\mathbf{v}_{\text{loc}(A,B)}$ of the bond between atom $A$ and atom $B$ is defined as

$$\mathbf{v}_{\text{loc}(A,B)} := \sum_{\xi=x,y,z} \frac{M_B}{M_A^2 + M_B^2} \frac{R_{A\xi} - R_{B\xi}}{\|\mathbf{R}_A - \mathbf{R}_B\|} \mathbf{e}_{A\xi} - \sum_{\xi=x,y,z} \frac{M_A}{M_A^2 + M_B^2} \frac{R_{A\xi} - R_{B\xi}}{\|\mathbf{R}_A - \mathbf{R}_B\|} \mathbf{e}_{B\xi},$$

where $M_A$ denotes the mass of nucleus $A$, $R_{A\xi}$ is the $\xi^{th}$-component of the molecular geometry $\mathbf{R}$ constructed with $N$ atoms represented by the $3N$-dimensional orthonormal vectors $\{\mathbf{e}_{A\xi}\}$:

$$\mathbf{R} = \sum_A \sum_{\xi=x,y,z} R_{A\xi} \mathbf{e}_{A\xi},$$

and $\mathbf{R}_A$ is defined as

$$\mathbf{R}_A := \sum_{\xi=x,y,z} R_{A\xi} \mathbf{e}_{A\xi}.$$
the anionic state is stabilized by molecular distortion along the corresponding bond-elongated modes. On the other hand, the positive values indicate the destabilization. Table 1 shows that the elongation of $8 - 8'$ bond gives the maximum stabilization, and the elongation of $3 - 3'$ bond gives the maximum destabilization. Since a reactive bond will be longer in cycloadditions to C$_{60}$, $8 - 8'$ bond can be regarded as the most reactive bond, and $3 - 3'$ bond the most unreactive bond. Vibronic coupling densities for localized modes at $8 - 8'$ and $3 - 3'$ bonds are shown in Figure 4. Since vibronic coupling density for the localized mode at $8 - 8'$ bond has the similar distribution to ethylene anion, $8 - 8'$ bond can be regarded as the functional group of ethylene moiety. It should be noted that $8 - 8'$ bond is a reactive bond between adjacent hexagon rings (6:6 bond) and $3 - 3'$ bond is an unreactive bond between a hexagon ring and a pentagon ring (6:5 bond).

In addition, in order to consider the degeneracy of anionic states, we averaged the vibronic coupling constants for localized modes over the $T_{1u}$ three-fold degenerate states:

$$
\tilde{V}_{\text{loc}(A,B)} = \frac{1}{3} \left( V_{\text{loc}(A,B)} [T_{1u}(x)] + V_{\text{loc}(A,B)} [T_{1u}(y)] + V_{\text{loc}(A,B)} [T_{1u}(z)] \right),
$$

where $V_{\text{loc}(A,B)} [T_{1u}(\xi)]$ denotes a vibronic coupling constant for a localized mode in the $T_{1u}(\xi)$ anionic state. We obtain two types of the averaged vibronic coupling constants since all the 6:6 bonds and all the 6:5 bonds become equivalent by this average, respectively. The averaged vibronic coupling constants at the 6:6 bonds are $-0.43 \times 10^{-4}$ a.u., and those at the 6:5 bonds are $0.22 \times 10^{-4}$ a.u. Since the number of 6:6 bonds and 6:5 bonds are 30 and 60 in the C$_{60}$ cage, we summed up these averaged vibronic coupling constants to be $-12.82 \times 10^{-4}$ a.u. and $13.44 \times 10^{-4}$ a.u., respectively. This result shows that 6:6 bonds are much more reactive than 6:5 bonds, that is consistent with experimental findings[5, 6].

Next, we discuss the chemical reactivity of a C$_{60}$ monoadduct in the same way. C$_{60}$ bisadduct isomers are named as shown in Figure 2. We calculated only the 6:6 bonds which is the reactive bonds of C$_{60}$. We calculated vibronic coupling constants for the localized modes, and averaged

Table 1. Vibronic coupling constants for the localized stretching vibrational modes in the $T_{1u}(z)$ state of C$_{60}$ anion. The bond notation is defined in Figure 1.

| bond | vibronic coupling constant in $10^{-4}$ a.u. |
|------|------------------------------------------|
| 1 − 1' | 0.14 |
| 1 − 2 | -0.06 |
| 2 − 3 | 0.22 |
| 2 − 4 | -0.06 |
| 3 − 3' | 0.80 |
| 3 − 5 | -0.86 |
| 4 − 4' | 0.24 |
| 4 − 6 | -0.24 |
| 5 − 7 | 0.69 |
| 5 − 9 | 0.04 |
| 6 − 7 | -0.38 |
| 6 − 8 | 0.69 |
| 7 − 7' | -0.35 |
| 8 − 8' | -1.33 |
| 9 − 9' | -0.09 |
Figure 4. Vibronic coupling densities for localized modes at (a) $8 - 8'$ and (b) $3 - 3'$ bonds of $C_{60}$ anion, and (c) vibronic coupling density for an effective mode of ethylene anion. The violet lines indicate positive and the cyan lines indicate negative.

the vibronic coupling constants for the localized modes over the $T_{1u}(x)$ and $T_{1u}(y)$ anionic states of $C_{60}$, which can be regarded as the anionic states of $C_{60}$ monoadduct:

$$\tilde{V}_{\text{loc}(A,B)} = \frac{1}{2} \left( V_{\text{loc}(A,B)} [T_{1u}(x)] + V_{\text{loc}(A,B)} [T_{1u}(y)] \right).$$

(14)

In addition, the averaged vibronic coupling constants for the localized modes which give the same $C_{60}$ bisadduct isomer are summed up (Figure 5). According to experimental findings[16],

Figure 5. Sum of the averaged vibronic coupling constants for the localized modes which give the same $C_{60}$ bisadduct isomer. In this figure, tr indicates trans. The notation of trans−1 to trans−4 and e is defined in Figure 2.

the order of the yields is $e > \text{trans}−3 > \text{trans}−2 > \text{trans}−4 > \text{trans}−1$ on the whole. The experimental facts are consistent with our results. Cis−products are also obtained experimentally much less than trans−products. However, the product ratio of cis−products are not reproduced by our method since we ignored steric effects so that the reactivities of cis−1, cis−2 and cis−3 are equal to trans−2, trans−3 and trans−4, respectively.
5. Conclusion
In terms of vibronic coupling, we discussed the chemical reactivity of C\textsubscript{60} and its monoadduct (C\textsubscript{60}X). We found that vibronic coupling constants for the localized stretching vibrational modes correlate with the experimental product ratios of cycloadditions to C\textsubscript{60} and its monoadduct. Our simple method used to evaluate the reactivity of C\textsubscript{60} monoadduct is also effective to investigate the reactivities of all multiadducts (C\textsubscript{60}X\textsubscript{n}) without much computational costs. We believe that our theory is helpful for the prediction of chemical reactivities of higher fullerenes, endohedral fullerenes and the other attractive reactants.

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