Dynamical Cooperativity in Electron Delocalization of Mixed-Valence Biferrocenium Complexes

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DYNAMICAL COOPERATIVITY IN ELECTRON DELOCALIZATION OF MIXED-VALENCE BIFERROCENIUM COMPLEXES

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Abstract Intramolecular electron transfer in the mixed-valence biferrocenium complexes in crystals shows qualitatively different behavior from that in the complexes in solutions. The "extra" electron in a mixed-valence complex in the crystal may be localized at low temperature and delocalized at higher temperature. The electron localization-delocalization transition induced thermally corresponds to a kind of order-disorder phase transition. In order to clarify the mechanism of the transition, a statistical mechanical model has been proposed (T. Kambara, D.N. Hendrickson, T.-Y. Dong, and M. J. Cohn, <u>J. Chem. Phys.</u>, <u>86</u>, 2362 (1987)). The temperature dependences of the physical quantities relevant to the cooperative electron localization-delocalization transition are calculated base on the model. In the calculation a more elaborate treatment is adopted for the intermolecular interactions. Those calculated values are compared with the observed ones for various kinds of mixed-valence biferrocenium trihalide crystals and reasonable agreements are obtained.

INTRODUCTION

The electron transfer process between metal ions in binuclear mixed-valence complexes has been studied mainly in dilute solutions[1]. However, recently it has been found from the study of the process in the solid state[2-5] that a new type of intramolecular electron transfer occurs due to the cooperative interaction between the mixed-valence complexes. At very low temperature the "extra" electron in each complex locates on one specified metal ion. When the temperature increases, the electron transfers to the other

metal ion in some complexes. At a definite temperature the electron in all of the complexes begins transfering between the two metal ions. This electron localization-delocalization transition corresponds to a kind of order-disorder phase transition[5,6].

We have proposed a statistical mechanical model[5] for binuclear mixed-valence trihalides, which may clarify the mechanism of various types of electron localization-delocalization phase transitions. The basic idea of the model is as follows : A binuclear mixed-valence biferrocenium cation has the two vibronic states $[Fe_A^{II}Fe_B^{III}]$ and $[Fe_A^{III}Fe_B^{II}]$, corresponding to the electronic states in which the "extra" electron locates on Fe_A and Fe_B ions, respectively. The electrons in the states are coupled to an out-of-phase combination of symmetric ligand-metal stretching modes. Each trihalide counteranion $X_A Y X_B$ also has the two vibronic states, $[X_A^- ---Y-X_B]$ and $[X_A-Y---X_B^-]$. The intra-molecular vibronic interaction induces the electron transfer between the two states in these ions. The cation-cation and cation-anion intermolecular interactions may induce cooperatively the electronic localization in the mixed-valence cation, that is, only one state(say $[Fe_A^{II}Fe_B^{III}]$) is occupied. The localized state ($[Fe_A^{II}Fe_B^{III}]$) becomes more unstable with increasing temperature, that is, the "extra" electron transfers more and more rapidly between the two iron ions, Fe_A and Fe_B, and the mixed-valence cation becomes delocalized at temperatures above a critical temperature T_C. The model has consistently explained the various observed data from Mössbauer spectra, heat capacity measurements, X-ray crystallography, and infrared spectroscopy[5].

In the model[5] the intermolecular interactions were treated by the molecular field approximation. Specifically, the molecular field was assumed to keep one crystallographic direction of the compounds. What this assumption suggests a degeneration of the two vibronic states in the cation for $T > T_C$.

However, recently Sorai et al[6] indicated based on the results of heat capacity measurements that the ground state of the cation is not degenerate even at temperatures above T_C. Therefore, in the present paper we reconsider the problem by taking into account a variation of the direction of the molecular field. We calculate the temperature dependences of the localization rate, the heat capacity, and the energy separation between the two vibronic states in the cation for various kinds of biferrocenium trihalide crystals. These calculated results are in a reasonable agreement with the observed ones[2-4,6].

MODEL

Since a detailed explanation of the model has been given in reference[5], we describe here only an essential part of the model for later convenience. The two vibronic states in the cation and in the anion are denoted by the Pauli spin operators, σ_{cz} and σ_{Az}, respectively: $[Fe_A{}^{II}Fe_B{}^{III}]$ and $[Fe_A{}^{III}Fe_B{}^{II}]$ are assigned to $\sigma_{cz} = 1$ and -1, respectively. $[X_A{}^- ---Y-X_B]$ and $[X_A-Y---X_B{}^-]$ are assigned to $\sigma_{Az} = 1$ and -1, respectively. The two states in each ion couple with each other through the intramolecular interaction which is denoted by α for the cation and β for the anion; α and β are both positive. We consider the two types of arrangements of mixed-valence cations and trihalide anions in the solid state, where one arrangement shown in Figure 5 of reference 5 corresponds to biferrocenium trihalide and dialkylbiferrocenium trihalide crystals, and the other shown in Figure 6 of reference 5 corresponds to dihalobiferrocenium trihalide crystals.

The various states of the mixed-valence cations and the trihalide anions in a crystal are determined by the Hamiltonian H,

$$H = \alpha \sum_{i=1}^{N} \sigma_{cx,i} + \beta \sum_{k=1}^{N} \sigma_{Ax,k} - J_c \sum_{i>j}' \sigma_{cz,i} \sigma_{cz,j}$$
$$- \sum_{i,k}' J_{A,ik} \sigma_{cz,i} \sigma_{Az,k} \qquad (1)$$

where the first and second terms are the Hamiltonians for the N
free cations and the N free anions, respectively, the third and
fourth terms are the cation-cation and cation-anion interactions,
and the double summation of these terms is made only over nearest
neighbor pairs.   Here, $2J_c$ is the energy difference between the
parallel localized state($\sigma_{cz,i} = \sigma_{cz,j}$) and the antiparallel($\sigma_{cz,i} =$
$-\sigma_{cz,j}$) and is positive; $2J_{A,ik}$ corresponds to the energy
difference between the cation-anion pair with $\sigma_{cz,i} = \sigma_{Az,k}$ and the
pair with $\sigma_{cz,i} = -\sigma_{Az,k}$. The interaction strength $J_{A,ik}$ is common
for any anion and positive for dialkylbiferrocenium trihalides,
but $J_{A,ik}$ depends on the relative position of cation i and anion k
in dihalobiferrocenium trihalides.

In   order   to   calculate   analytically the thermal average of
relevant quantities of the system, we transform $\sigma_{Bz,i}$ and $\sigma_{Bx,i}$
(B = c, A) into the new spin operators, $S_{Bz,i}$ and $S_{Bx,i}$ such as

$$\sigma_{Bz,i} = S_{Bz,i}\cos\theta_B - S_{Bx,i}\sin\theta_B , \tag{2}$$

$$\sigma_{Bx,i} = S_{Bz,i}\sin\theta_B + S_{Bx,i}\cos\theta_B . \tag{3}$$

We introduce a model Hamiltonian H_0 which approximates reasonably
the real Hamiltonian H:

$$H_0 = -y_c\sum_{i=1}^{N} S_{cz,i} - y_A\sum_{k=1}^{N} S_{Az,k} . \tag{4}$$

The strength y_B and the direction θ_B of the molecular fields for
the cation(B=c) and anion(B=A) are determined so as to minimize
the free energy F of the system.   F is given as

$$F = -k_BT \ln Z_0 + \langle H - H_0\rangle , \tag{5}$$

where the partition function Z_0 of the model system is

$$Z_0 = Tr[\exp(-\frac{H_0}{k_BT})] , \tag{6}$$

and the thermal average of a quantity Q is given by

$$\langle Q \rangle = \frac{1}{Z_0} \mathrm{Tr}[Q \exp(-\frac{H_0}{k_B T})] . \tag{7}$$

The equations for y_C, y_A, θ_C, and θ_A are obtained as

$$\sin\theta_C = -\alpha/y_C , \quad \sin\theta_A = -\beta/y_A , \tag{8}$$

$$y_C \cos\theta_C - j_C Y_C \cos\theta_C - j_A Y_A \cos\theta_A = 0, \tag{9}$$

$$y_A \cos\theta_A - j_A Y_C \cos\theta_C = 0, \tag{10}$$

where $j_C = 2J_C$ and $j_A = 4J_A$ for dialkylbiferrocenium trihalide crystals, $j_C = 0$ and $j_A = -2J_{A1} + 4J_{A2}$ for dihalobiferrocenium trihalide crystals, J_{A1} and J_{A2} are the strengths of the intrastack and interstack cation-anion interactions, respectively, $Y_C = \tanh(y_C/k_B T)$ and $Y_A = \tanh(y_A/k_B T)$.

COOPERATIVE ELECTRON LOCALIZATION-DELOCALIZATION TRANSITION

Relevant Quantities

Although there exist various physical quantities relevant to the cooperative electron localization-delocalization transition, the quantities which have been measured experimentally are the electron localization rate of the mixed-valence cations, heat capacity, and the effective energy difference between the two vibronic states in the cation. These quantities also can be calculated based on the present model.

The localization rate η_C for the cation in the crystals is given by

$$\eta_C = \rho_{cA} - \rho_{cB} = \tanh(\frac{y_C}{k_B T}) \cos\theta_C , \tag{11}$$

where ρ_{cA} and ρ_{cB} are the thermally averaged population probabilities of the localized states, $[Fe_A^{II} Fe_B^{III}]$ and $[Fe_A^{III}$

Fe_B^{II}], respectively. When the "extra" electron locates only on the Fe_A ion, n_c becomes unity. When the electron transfers frequently between Fe_A and Fe_B, the populations of the two states becomes equivalent and n_c becomes zero. Therefore, the state of $n_c = 1$ corresponds to the completely localized state, while that of $n_c = 0$ corresponds to the completely delocalized state. In the case where the intermolecular interactions, j_c and j_A, are much larger than the intramolecular couplings, α and β, n_c becomes unity. However, in the case where α and β are much larger than j_c and j_A, n_c becomes zero.

The effective energy separation ΔE_c in the cation is given by

$$\Delta E_c = 2 |y_c| \quad . \tag{12}$$

The value of ΔE_c becomes $2(j_c + j_A)$ in the case of j_c, $j_A \gg \alpha$, β, while ΔE_c becomes 2α in the case of α, $\beta \gg j_c$, j_A.

The heat capacity C_p is generally obtained from the thermo-dynamic equation,

$$C_p = - T \left(\frac{\partial^2 F}{\partial T^2} \right)_p . \tag{13}$$

The expression of C_p in the present system is obtained by using the free energy F given in Eq.(5). If the transition between the electronically localized($n_c > 0$) and delocalized($n_c = 0$) states in cations is induced cooperatively by the intermolecular inter-actions, that is, the transition is a kind of phase transition, C_p should show an irregular temperature dependence around the transition temperature T_c.

Effect of Crystal Environments to Electron Localization-Delocalization Transition

The electron localization-delocalization transition in the mixed-valence complexes is affected in various ways by crystal environments. The effects of environments are represented in the present model through the cation-cation interaction j_c, the cation-anion interaction j_A and the coupling strength β in the anion. In order

to see how these factors affect the localization–delocalization transition, we have calculated the temperature dependences of η_c, ΔE_c, and C_p for various values of α, β, j_c and j_A.

We show the calculated temperature dependences of the electron delocalization rate η_c in Figure 1 for the three cases, (a), (b), and (c), where the values of α, β, j_c, and j_A are chosen so that η_c may reproduce the observed values for (a) biferrocenium I_3^-, (b) biferrocenium IBr_2^-, and (c) di-n-butylbiferrocenium I_3^-.
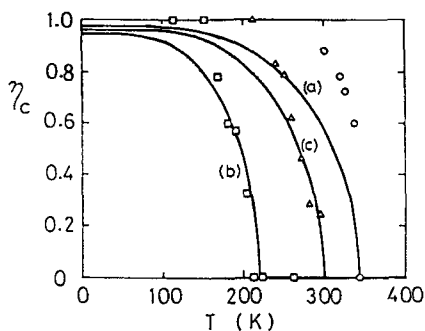

FIGURE 1   Temperature dependences of the localization rate η_c for the cases of (a), (b), and (c) whose meanings are explained in the text. The observed relevant values[2,3] are also plotted.

The adjusted values(in cm^{-1} unit) of α, β, j_c, and j_A are 50, 300, 150, 180 for (a), 50, 350, 150, 50 for (b), and 50, 300, 115, 180 for (c), respectively. The agreement of the calculated T-dependence of η_c with the observed one is quite reasonable. It is suggested from these calculations that the change of counteranion from I_3 to IBr_2 induces a drastic change in the cation-anion interaction strength j_A whereas the transition temperature T_c is rather insensitive to a change of β. The substitution of butyl into the cation induces a noticeable change in the cation-cation interaction j_c.

The calculated temperature dependences of ΔE_c and C_p are shown in Figures 2 and 3, respectively, where the observed values[6]
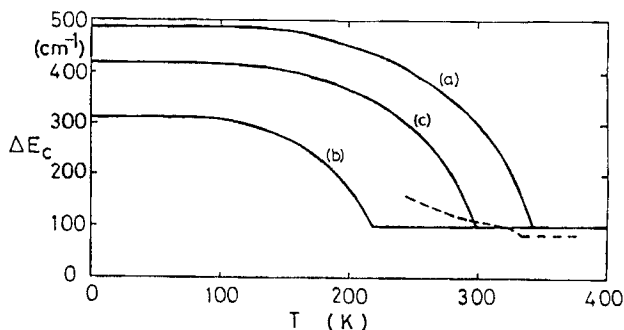

FIGURE 2   Thermal variations of the energy separation ΔE_c for the cases of (a), (b), and (c). The observed values[6] for (a) are also plotted by a broken line.
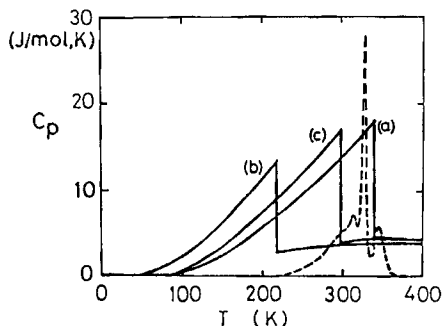

FIGURE 3   Thermal variations of the heat capacity C_p[6] for the cases of (a), (b), and (c). The observed values[6] for (a) are also plotted by a broken line.

for biferrocenium trihalide, (a), are also plotted.   The energy separation ΔE_c in the very low temperature region is induced by the intermolecular interactions, j_c and j_A, where the ground and excited states correspond to the two localized states, [Fe$_A^{II}$ Fe$_B^{III}$] and [Fe$_A^{III}$ Fe$_B^{II}$], respectively. On the other hand, in the higher temperature region ($T > T_c$) ΔE_c is induced by the intramolecular coupling α and is independent of T, where both the ground and excited states correspond to the delocalized electron-

tunneling states, that is, ΔE_C is the tunneling splitting. It is seen from Figures 1, 2, and 3 that the present model may reproduce the essential features of the observed temperature dependences. Therefore it is highly possible that the energy splitting for $T > T_C$ is due to the tunneling of "extra" electron.

We show the calculated temperature dependence of η_C with the observed values in Figure 4 for the three cases, (d), (e), and (f)
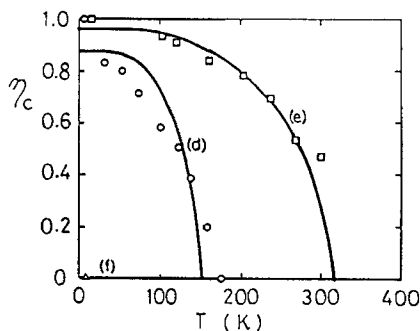

FIGURE 4   Temperature dependences of η_C for the cases of (d), (e), and (f) corresponding to dihalobiferrocenium trihalides. The observed values are also plotted[6].

with the dihalobiferrocenium(X_2-BiFc) trihalide crystal structure, where (d), (e), and (f) correspond to Cl_2-BiFc·IBr_2, Br_2-BiFc·IBr_2, and I_2-BiFc·I_3, respectively. The values of α, β, j_C, and j_A in cm^{-1} unit are 50, 350, 0, 200, respectively for (d), 50, 350, 0, 290, respectively for (e), and 50, 300, 0, <120, respectively for (f). The calculated curves reproduce well the observed temperature dependences.

The calculated temperature dependences of ΔE_C and C_p are shown for the cases of (d), (e), and (f) in Figures 5 and 6. Unfortunately, at the present time we have no experimental datum of ΔE_C and C_p for dihalobiferrocenium trihalide crystals.

It is clear from these considerations that the present model may reproduce well the essential features of observed electron localization-delocalization transitions in the crystals.
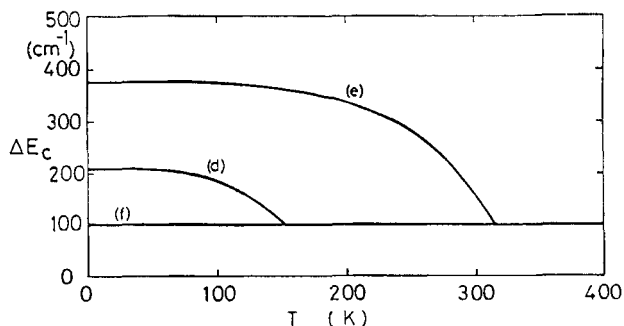
FIGURE 5   Thermal variations of ΔE_c for the cases of (d), (e), and (f).
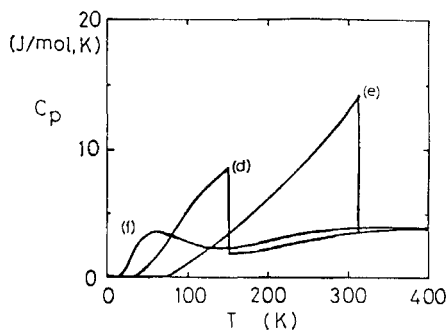
FIGURE 6   Thermal variations of C_p for the cases of (d), (e), and (f).

Therefore, it is reasonably concluded that the electron delocalization process observed in the various kinds of mixed-valence biferrocenium complexes is due to the cooperative intermolecular interactions which do not exist in solutions.

Acknowledgment

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