

Analysis of Intramolecular Electron Transfer in A Mixed-Valence Cu(I)-Cu(II) Complex Using the PKS Model

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The transition probabilities for the thermal intramolecular electron transfer and the optical intervalence transfer band for a symmetric mixed-valence Cu(I)-Cu(II) compound were used to extract the PKS parameters $\epsilon = -1.15$, $\lambda = 2.839$, and $\nu = 923 \text{ cm}^{-1}$. These parameters determine the potential energy surfaces and vibronic energy levels. Three pairs of vibrational levels are below the top of the energy barrier in the lower potential surface. The contribution of each vibrational state to the intramolecular electron transfer was calculated. It is shown that the three pairs of vibrational states below the top of the barrier are responsible for most of the electron transfer at 261-306 K. So the intramolecular electron transfer in this system is a tunneling process. The transition probability exhibits the usual high-temperature Arrhenius behavior, but at lower temperature falls off to a temperature-independent value as tunneling from the lowest levels becomes the limiting process.

Introduction

Electron transfer is a critical elementary step underlying many important processes in physics, chemistry, and biology.^{1,2} Although numerous experimental and theoretical studies have been carried out, a detailed description of the electron transfer process in complicated systems is still not so easy. Mixed-valence compounds provide simple systems in which electron transfer between two metal ions can be detected clearly by electron paramagnetic resonance (EPR) spectroscopy.^{3,4} We have shown that transition probabilities for the intramolecular electron transfer in such compounds can be determined by simulating the EPR spectra.⁵

A theoretical model which can describe the electron transfer in mixed-valence compounds in detail is also available.⁶ This model was developed by Piepho, Krausz, and Schatz (PKS), who solved the full vibronic problem for a two-site one electron model in 1978.^{6,7} According to the PKS model, a mixed-valence system is characterized by three or four parameters: (1) the vibronic (or electronic-phonon) coupling parameter λ , (2) the electronic coupling parameter ϵ , (3) the frequency of the single effective vibrational mode ν , and in the unsymmetric case (4) the difference in zero-point energy between the two coupled states of the mixed-valence dimer W . The vibrational potential surfaces for a symmetric binuclear mixed-valence system are shown in Figure 1. When there is no electronic coupling between the two subunits ($\epsilon = 0$), the potential surfaces can be represented by two parabolas on a vibrational coordinate. When $\epsilon \neq 0$, the potential surfaces split into a lower surface with double minima and an upper one. (When ϵ is very large, the energy barrier in the lower potential surface vanishes.) Another effect of $\epsilon \neq 0$ is splitting of each vibronic level into two, from which the transition probability for the intramolecular electron transfer can be calculated.¹¹ The intervalence transfer (IT) band can be calculated from the transitions from populated vibronic levels to all higher vibronic levels. Thus both the IT band and the transition probability for the intramolecular electron transfer can be determined from the PKS parameters, and vice versa.

Previously the PKS model was applied to the Creutz-

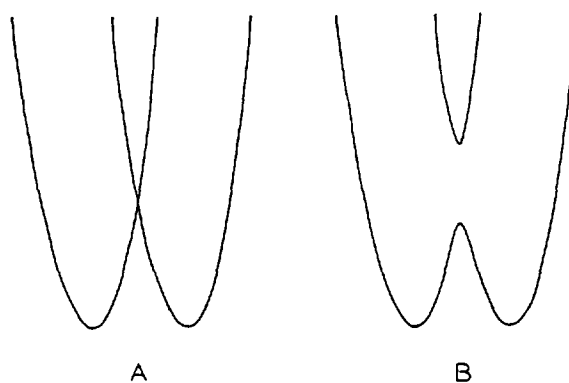


Figure 1. Potential energy surfaces of a symmetrical binuclear mixed-valence compound in terms of a vibrational coordinate. (A) When there is no electronic coupling and (B) there is electronic coupling between the two subunits.

Taube ion $[(\text{NH}_3)_5\text{Ru}(\text{NC}_4\text{H}_4\text{N})\text{Ru}(\text{NH}_3)_5]^{5+}$ and related complexes, and the PKS parameters were determined by simulating the IT bands.^{7,8} These parameters can also be extracted from fitting the temperature-dependent transition probabilities for the thermal electron transfer. However, reliable transition probability data are few and only one such analysis for $[\text{W}_6\text{O}_{19}]^{3-}$ has been published.⁹ However, this compound is not an ideal system for applying the PKS model, for each tungsten atom is connected to four tungsten atoms *via* bridging oxygen atoms. In addition, the transition probabilities, which were determined by analyzing the EPR line width,¹⁰ may not be very reliable. Complex III in Figure 2 is a symmetric binuclear mixed-valence compound well-suited for a PKS analysis. The transition probabilities for this compound were determined by simulating the EPR spectra.⁵ Using these values and the IT band position, we have determined the ground vibronic manifold of this system, and analyzed the contributions of the vibronic levels to the electron transfer.

Results and Discussion

The transition probabilities for Complex III in acetone de-

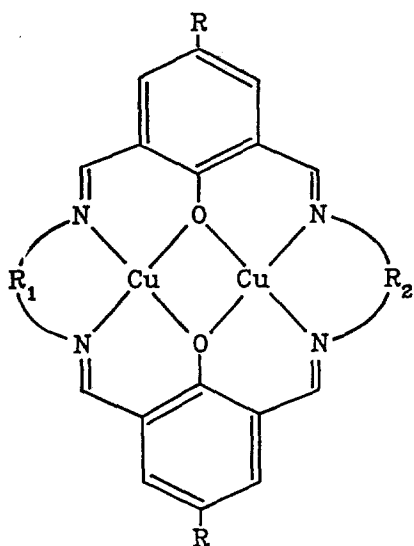


Figure 2. The structure of mixed-valence Cu(I)-Cu(II) complexes. Complex III: R = *tert*-butyl, R₁=R₂=butylene; Complex G: R = methyl, R₁=R₂=propylene.

Table 1. Transition Probabilities for Complex III in Acetone

Temp.(K)	\bar{P} (10 ⁹ s ⁻¹) from EPR simulation	\bar{P} (10 ⁹ s ⁻¹) from PKS calculation*
261	0.72	0.73
275	0.92	0.91
306	1.51	1.51

*Parameters used are $\epsilon = -1.15$, $\lambda = 2.839$, and $\nu_- = 923$ cm⁻¹.

terminated by simulating the EPR spectra are listed in Table 1.⁵ The visible spectrum of this compound exhibits a shoulder at 13.5 kK, which was assigned to the IT band.⁴ Since the IT band overlaps with a tail of a strong absorption occurring at a higher frequency, the band intensity was not used to determine the PKS parameters; see below.

To extract the parameters ϵ , λ and ν_- from the transition probabilities and the IT band, one proceeds by a trial and error fitting procedure, guessing values of ϵ , λ , and ν_- and diagonalizing the energy matrix.^{6,7} Although the matrix is infinite, drastic truncation is possible without significant loss of accuracy. A 35×35 matrix was found to be entirely satisfactory.

Having the vibronic energy levels and wave functions, one can calculate the position and intensity of the IT band.^{6,7} One can also calculate the transition probability for the intramolecular electron transfer. Suppose that there is no interaction between the two subunits. Then the electron is trapped on one subunit, and the probability of the electron transfer to the other subunit is zero. If interaction is turned on at $t=0$, electron transfer between the subunits will occur as t increases. It has been shown that the transition probability per second P'_v for the level v can be expressed *approximately* in terms of the splitting of the vibronic level.¹¹

$$P'_v = \nu_- \pi^2 \left(\frac{E_v^+ - E_v^-}{h\nu_-} \right)^2 \quad (1)$$

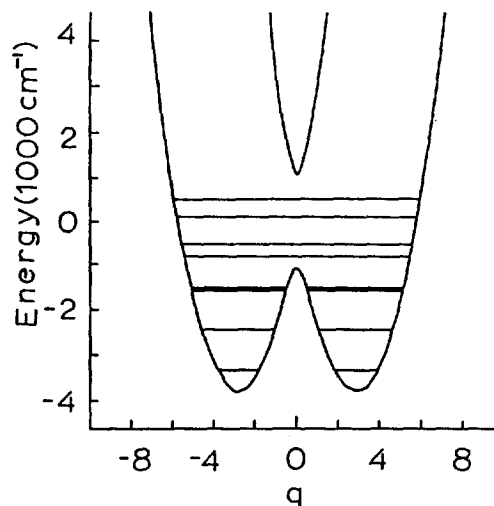


Figure 3. The potential energy surfaces and the vibronic energy levels of Complex III. The potential energy surfaces are given by $W = q^2/2 \pm (\epsilon^2 + \lambda^2 q^2)^{1/2}$; see ref. 6.

When the energy levels are below the top of the energy barrier, the splitting of the pair is small and P'_v is less than ν_- . However, for some levels above the top of the energy barrier the splitting of the pair is so large that Eq. (1) produces $P'_v > \nu_-$. Since the transition probability should not exceed ν_- , Zener's expression may be used.¹²

$$P_v = \nu_- \{1 - \exp(-P'_v/\nu_-)\} \quad (2)$$

It is noted that P'_v is equal to P_v when it is small. The thermally averaged transition probability per second is

$$\bar{P} = \frac{\sum_{v=0}^{\infty} P_v \{ \exp(-\Delta E_v^+/kT) + \exp(-\Delta E_v^-/kT) \}}{\sum_{v=0}^{\infty} \{ \exp(-\Delta E_v^+/kT) + \exp(-\Delta E_v^-/kT) \}} \quad (3)$$

Originally Zener's expression was applied to the thermally averaged transition probability,⁷ but our procedure of applying it to the transition probability for each pair of energy levels should be more reasonable.

Calculating transition probabilities and the IT band for various combinations of ϵ , λ and ν_- , we have found a unique set of parameters ($\epsilon = -1.15$, $\lambda = 2.839$, $\nu_- = 923$ cm⁻¹) that produce the experimental values; see Table 1.

The vibronic energy levels determined by these parameters are shown along with the potential energy surfaces in Figure 3. The height of the barrier on the lower potential surface is given by⁷

$$E_d/h\nu_- = \lambda^2/2 - |\epsilon| + \epsilon^2/2\lambda^2; \quad |\epsilon| \leq \lambda^2 \quad (4)$$

The height of the barrier for this system is 2734 cm⁻¹. It is seen that three pairs of levels are below the top of the barrier.

Relative populations and transition probabilities for several vibronic levels at 261 and 306 K are listed in Tables 2 and 3. The product of these two quantities represent the contribution of the vibrational state to the intramolecular electron transfer.

The transition probability for the $v=0$ levels is 2.5×10^8 s⁻¹, and it increases rapidly with increasing v . Although over

Table 2. Transition Probabilities and Populations at 261 K

ν	P_ν (s^{-1})	Relative population	$P_\nu \times \text{Rel. Pop.}$ ($10^9 s^{-1}$)
0	2.458×10^8	0.99327	0.244
1	5.593×10^{10}	0.00668	0.374
2	2.101×10^{12}	0.00004	0.104
3	1.390×10^{13}	0.00000	0.006
			total 0.729

Table 3. Transition Probabilities and Populations at 306 K

ν	P_ν (s^{-1})	Relative population	$P_\nu \times \text{Rel. Pop.}$ ($10^9 s^{-1}$)
0	2.458×10^8	0.99595	0.242
1	5.593×10^{10}	0.01384	0.774
2	2.101×10^{12}	0.00021	0.443
3	1.390×10^{14}	0.000004	0.052
			total 1.513

98% of the molecules are in the $\nu=0$ levels even at 306 K, the levels corresponding to $\nu=1$ and 2 contribute more than the $\nu=0$ level to the electron transfer. Since these three pairs of levels below the top of the barrier are responsible for most of the transition probability, the transition from one well to the other (or the intramolecular electron transfer) is a tunneling process.

Temperature dependence of the transition probabilities calculated using the PKS parameters is shown in Figure 4. The transition probability exhibits the usual high-temperature Arrhenius behavior, but at lower temperature falls off to a temperature-independent value as tunneling from the lowest vibrational levels becomes the limiting process. Previously we determined the activation energy for this system by fitting the transition probabilities to the Arrhenius equation.⁵ The activation energy 910 cm^{-1} thus obtained does not represent the height of the barrier, but agrees approximately with ν_- or the separation of vibronic levels.

The frequency $\nu_- = 923 \text{ cm}^{-1}$ provides a clue to the nature of the vibrational mode coupled with the electron transfer. The molecular structure of Complex G¹³ (see Figure 2), a compound closely related to Complex III, shows that the Cu^{2+} ion is in a square planar environment. The Cu^+ ion is found in two different configurations, a distorted square planar and a square pyramidal one. The axial position in the square pyramidal configuration is occupied by an aromatic carbon atom of an adjacent molecule in the crystal. The geometry about Cu^+ is not the tetrahedron favored for four coordinate cuprous complexes, indicating that such distortion is prevented by the rigid near-planar nature of the macrocyclic ligand. Complex III can have similar configurations. However, absence of solvent effects for the IT band (see below) suggests that a square pyramidal configuration about the Cu^+ ion with solvent coordination does not form in acetone. So we will consider only the distorted square planar configuration about the Cu^+ ion. Now the environments of both metal sites should be equalized prior to thermal electron transfer. So a vibrational mode which deforms the geo-

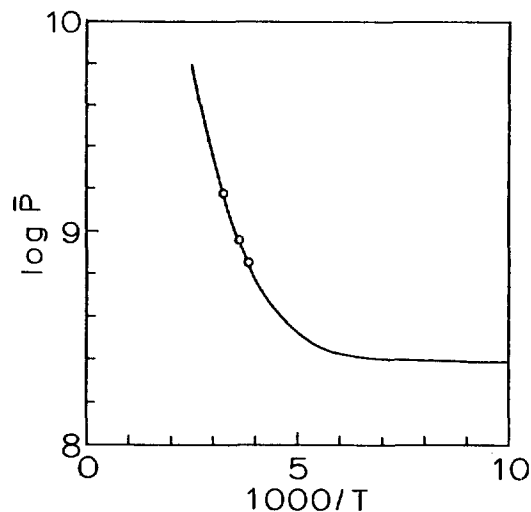


Figure 4. Temperature dependence of the transition probability for the intramolecular electron transfer in Complex III. The line represents the calculated values using the PKS parameters, and the circles represent the values determined by simulation of the EPR spectra.

metry about the copper ion will be coupled with the electron transfer. The IR spectrum of Complex III has not been reported, but it should be very similar to that of the oxidized species.³ The IR spectrum of the latter¹⁴ exhibits a band near 923 cm^{-1} , which may be assigned to the $\text{C}=\text{N}-\text{C}$ deformation. Similar assignments were made for the 919 and 860 cm^{-1} bands of *N-p*-tolylsalicylaldehyde and its $\text{Cu}(\text{II})$ chelate.¹⁵ Such deformation in Complex III will bring about geometrical adjustments to equalize the environments of both metal sites.

Thus the PKS model provides a coherent picture for the intramolecular electron transfer and the IT band in this system. Now we will consider some problems related with this picture. The first problem is the solvent effect. The PKS model was criticized for its neglect of solvent reorganization,¹⁶ which can contribute to the energy barrier for the intramolecular electron transfer. Both theory and experiment have shown that the IT band position of a mixed-valence compound having a potential surface with double minima varies linearly with the solvent function $(1/n^2 - 1/D_s)$ where n and D_s represent the refractive index and static dielectric constant of the solvent respectively.^{17,18} However, the IT band of Complex III appears at the same frequency for two different solvents, acetone and dichloromethane, the solvent functions of which differ considerably (0.493 vs. 0.383). This seems to justify the application of the PKS model to Complex III. On the other hand, Complex G exhibits significant solvent effects both for the IT band and the electron transfer rate.^{3,5} Its IT bands appear at 5.8 and 8.5 kK in dichloromethane and at 10 kK in acetone.³ The transition probability for the intramolecular electron transfer is about 20 times larger in dichloromethane than in acetone.⁵ These results indicate that the energy barrier for this compound is higher in the more polar solvent, as expected from the solvent reorganization mechanism.¹⁴ The reason why then the solvent effect is not so important for Complex III, a compound closely related to Complex G, is not clearly understood.

The second problem is the intensity of the IT band. The IT band of Complex III in acetone appears at $\nu_{max}=13.5$ kK with $\epsilon_{max}=303$ M⁻¹ cm⁻¹ as a shoulder on a strong absorption occurring at a higher frequency.⁴ The IT band is the totality of transitions, $\nu'\rightarrow\nu$. But the major contribution originates in the transitions from the $\nu'=0$ vibrational levels, the relative population of which is over 98% even at 306 K. Associating a Gaussian lineshape (half width, 2000 cm⁻¹) with each transition $0\rightarrow\nu$, we get an IT band with $\nu_{max}=13.5$ kK and $\epsilon_{max}=526$ M⁻¹ cm⁻¹. The calculated ϵ_{max} is much larger than the measured value, considering the IT band overlaps with another absorption. This means that the PKS parameters determined from the IT band alone can be quite different from our values. The discrepancy may be attributed to Eq. (1), which is an approximation for the transition probability. In order to check how good this equation is, we need to study mixed-valence systems for which both the transition probabilities and the IT band contour can be measured accurately.

In summary, we have determined the ground vibronic manifold of Complex III using the PKS model, and have shown that the intramolecular electron transfer in this system at 261-306 K is a tunneling process occurring mostly at the lowest three pairs of vibrational levels below the top of the energy barrier. More work on related systems is needed to clarify the solvent effects and the validity of Eq. (1).

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Piperoctadecalidine, a New Piperidine Alkaloid from *Piper retrofractum* Fruits

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A chemical investigation of the fruits of *Piper retrofractum* (Piperaceae) has led to the isolation and characterization of a novel piperidine alkaloid, piperoctadecalidine together with three known alkaloids piperine, pipernonaline and guineensine. The structure of the new compound was determined to be (2E,4E,14Z)-N-(2,4,14-Octadecatrienoyl) piperidine by spectral and synthetic methods.

Introduction

The fruits of Piperaceae plants have been recently received much attention because they have many physiologically active principles, and a number of studies on the chemical constituents of the fruits have been conducted.^{1,2} Among these components, unsaturated amides constitute a major

group of secondary metabolites. In continuing our studies on the chemical components of Piper fruits, we have isolated a new piperidine named piperoctadecalidine (1) from *P. retrofractum*, together with three known alkaloids, piperine (2), pipernonaline (3) and guineensine (4). This paper describes the structural elucidation of the new compound.