Application of the PKS Vibronic Coupling Model to Mixed-Valence Ferrocene Derivatives Biferrocene and Bis(fulvalene)diiron

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The PKS vibronic coupling model is applied to mixed-valence ions of biferrocene $(FcFc)^+$ and bis(fulvalene)diiron $(BFD)^+$. The model predicts a higher degree of interaction in $(BFD)^+$ than in $(FcFc)^+$ in agreement with experimental evidence. $(FcFc)^+$, however, is predicted to have a strong interaction approaching the Robin and Day class II–III borderline. The results are compared to those predicted by the Hush model.

Introduction

The study of binuclear, mixed-valence complexes, like the biferrocene derivatives[1-5] and the family of compounds related to the Creutz–Taube ion,[6,7] has been facilitated by the development of theoretical models that describe and classify mixed-valence systems. Robin and Day[8] introduced a classification scheme based upon the degree of ground-state interaction between the complex subunits: class I compounds have little or no interaction and have localized valence states; class III compounds have a high degree of interaction and are completely valence delocalized; class II have intermediate degrees of interaction but definable valence states.

A new physical property attributed to mixed-valence interaction is the intervalence transfer (IT) electronic transition from one valence description to the other (i.e., $Fe^{II}Fe^{III} \rightarrow Fe^{III}Fe^{II}$). A model proposed by Hush[9] predicts the characteristics of this IT band in localized systems by treating the IT band as the totality of Franck–Condon transitions between two coupled potential surfaces. The Hush formulas result. For the symmetrical case, the Hush formulas are

$$E_{op}/E_{th} = 4 \tag{1}$$

$$(h\Delta\nu_{1/2})^2/h\nu_{max} = 16kT \ln 2 \tag{2}$$

$$\alpha^2 = (4.24 \times 10^{-4})\epsilon_{max}\Delta\nu_{1/2}/\nu_{max}R^2 \tag{3}$$

where E_{op} is the energy of the optical transition resulting from vertical excitation from the minimum of the lower potential well to the upper and E_{th} is the thermal energy corresponding to the barrier between the potential surfaces. The interaction parameter (α^2) is the degree of interaction between the subunits in the ground state, $\Delta\nu_{1/2}$ is the bandwidth at half maximum, ν_{max} is the frequency of the band maximum, ϵ is the molar extinction coefficient, and R is the distance (in Å) between the subunit centers.

A new vibronic coupling model for mixed-valence systems has recently been developed by Peipho, Krausz, and Schatz—the PKS model.[10-13] Earlier models can only be usefully applied to localized systems—the further the deviation from class I, the less applicable the models become. These models do not treat the effect of vibronic coupling and are, therefore, only valid when applied to systems whose nuclear motion can be treated as if confined to a single potential surface—the localized limit. The PKS model, however, includes vibronic interaction. When solved, the PKS model yields a complete set of vibronic energies and eigenfunctions that enables one to calculate observables within the ground vibronic manifold—among which are the properties of the IT band. The inclusion of vibronic coupling, then, allows not only treatment of localized systems but application to the entire realm of mixed-valence cases including class II and class III.

The PKS model has been used to treat the Creutz–Taube ion[12] as well as other mixed-valence diruthenium complexes[14] and also Wolffram's red salt,[13] a $Pt^{II}Pt^{IV}$ mixed-valence system. The model predicts the CT complex to be delocalized and the Pt complex to be localized—both in agreement with previous experimental studies.

The model has not, however, been applied to mixed-valence ferrocene derivatives. As our studies of mixed-valence chemistry have centered on ferrocene systems, we were interested to examine the utility of the PKS model when applied to our systems by comparing the PKS treatment to experimental data. It would also be interesting to apply the PKS model to a pair of compounds made up of the same subunits but with different degrees of delocalization. By keeping a number of factors consistent, this would serve as a good test of the models' ability to predict mixed-valence related properties. In pursuit of these goals, we have applied the PKS model to biferrocene (FcFc) and bis(fulvalene)diirion (BFD) (Figure 1).

The PKS Model. As detailed presentation of the PKS model have appeared elsewhere,[10-12] only a brief working

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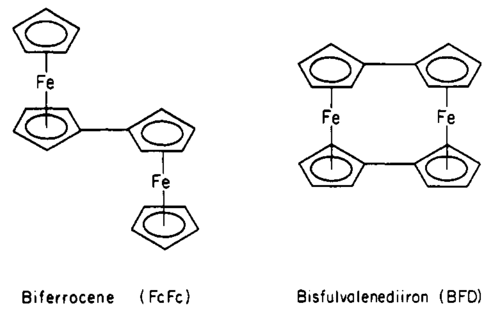

Figure 1. Biferrocene (FcFc) and bis(fulvalene)diirion (BFD).

description of the model will be given here for the symmetrical case. There are two equivalent zero-order electronic wave functions that describe a mixed-valence system composed of monomeric subunits A and B with attainable oxidation states M and N:

$$\psi_a = \psi_A{}^M\psi_B{}^N \qquad \psi_b = \psi_A{}^N\psi_B{}^M$$

With the assumption that the subunits have the same point-group symmetry in both oxidation states, the vibrational coordinate (q) that is significant to the mixed-valence problem is the antisymmetric combination of the totally symmetric modes of the subunits (Q_A, Q_B) and is represented by

$$q = 2\pi(\nu_-/h)^{1/2}Q_- \qquad (4)$$

where $Q_- = 1/(2)^{1/2}(Q_A - Q_B)$ and ν_- is the energy of the totally symmetric metal–ligand stretch of the subunits.

Two parameters of the model that define the mixed-valence system are the vibronic coupling parameter, λ, which measures the difference in equilibrium displacements along the coordinate q or the difference in bond lengths of the subunits in different oxidation states and the electronic coupling parameter, ϵ, which is the resonance integral of the two electronic basis functions.

Employing an electronic basis of $\psi_\pm = 1/(2)^{1/2}(\psi_a \pm \psi_b)$ and using the above definitions, the model describes potential energy surfaces

$$W_{1,2} = q^2/2 \pm \sqrt{\epsilon^2 + \lambda^2 q^2} \qquad (5)$$

The Robin and Day classification scheme can be quantitifed in terms of the PKS parameters ϵ and λ based on the above potential surfaces. Class I corresponds to cases where $\lambda^2 >> |\epsilon|$, class II to cases where $\lambda^2 \geqslant |\epsilon|$, and class III to cases where $\lambda^2 < |\epsilon|$.

With a vibrational basis of harmonic oscillator functions in coordinate q, $\chi_n(q)$, vibronic solutions are of the form

$$\Phi_\nu{}^+ = \psi_+ \sum_{n=0,2,4...}^{\infty} r_{\nu n}\chi_n + \psi_- \sum_{n=1,3,5...}^{\infty} r_{\nu n}\chi_n \qquad (6a)$$

$$\Phi_\nu{}^- = \psi_+ \sum_{n=1,3,5...}^{\infty} s_{\nu n}\chi_n + \psi_- \sum_{n=0,2,4...}^{\infty} s_{\nu n}\chi_n \qquad (6b)$$

where Φ_ν are divided according to behavior under interchange of A and B. The $r_{\nu n}$ satisfy the secular equations

$$\sum_{n=0}^{\infty} r_{\nu n}\,(H_{mn} - \delta_{mn}E_\nu{}^+) = 0$$
$$m = 0, 1, 2 \ldots \qquad n = 0, 1, 2 \ldots \qquad (7)$$

where

$$H_{mn} = [(m/2)^{1/2}\delta_{m,n+1} + ((m+1)/2)^{1/2}\delta_{m,n-1}] + (m + 1/2 + (-1)^m\epsilon)\delta_{m,n} \qquad (8)$$

which is tridiagonal. The corresponding secular determinant yields $E_\nu{}^+$. By analogy, the set $E_\nu{}^-$ and $s_{\nu n}$ can be obtained by substituting $-\epsilon$ for ϵ, $s_{\nu n}$ for $r_{\nu n}$, and $E_\nu{}^-$ for $E_\nu{}^+$. The energies are in units of $h\nu_-$. The dipole strength of a vibronic line $\Phi_\nu{}^\pm \to \Phi_\nu{}^\mp$ is

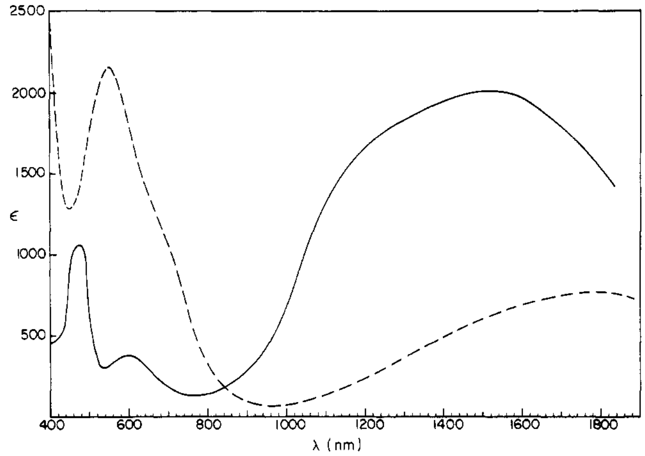

Figure 2. Near-IR spectra of (biferrocene)$^+$ (broken line) and (BFD)$^+$ (solid line).

$$D(\nu' \to \nu) = \sum_{\gamma=x,y,z} \left(\frac{N_{\nu'} - N_\nu}{N}\right) |\langle \Phi_{\nu'}{}^+ | m_\gamma | \Phi_\nu{}^- \rangle|^2 \qquad (9)$$

where $N_{\nu'} = e^{-E_{\nu'}/kT}$ and $N = \sum_{\nu'} N_{\nu'}$.

Within the context of the model equation (9) simplifies to

$$D(\nu' \to \nu) = \left(\frac{N_{\nu'} - N_\nu}{N}\right) \delta_{\nu'\nu}{}^2 (Re/2)^2 \qquad (10)$$

where $\delta_{\nu'\nu} = \sum_n r_{\nu' n} s_{\nu n}$.

The IT absorbtion profile then is obtained by calculating the dipole strength of transitions from populated vibronic levels to all higher vibronic levels. By varying ϵ and λ to obtain a "best fit" with the observed IT band, values of ϵ and λ can be assigned to a system and characteristics such as degree of delocalization can be predicted.

Results

Biferrocene (FcFc) and bis(fulvalene)diirion (BFD) are ferrocene dimers that when singly oxidized form mixed-valence species that have been the subject of many studies. Biferrocene cation has been assigned to class II of the Robin and Day classification scheme. Mössbauer,[2,5] PES,[15,16] infrared,[2] and electronic spectroscopy[2,5] indicate distinct Fe^{II} and Fe^{III}, ferrocene–ferrocenium sites. Electronic absorption spectroscopy shows a near-IR transition (λ_{max} 1800 nm (ϵ 740)) (Figure 2), which is attributed to the IT band. Applying the Hush treatment to (FcFc)$^+$, the interaction parameter α^2 can be estimated as 0.9×10^{-2}.[1]

Bis(fulvalene)diirion monocation, however, is valence delocalized according to Mössbauer,[3,5] magnetic susceptibility,[3,5] and PES[3,16] measurements. (BFD)$^+$, therefore, is fractionally valent and has been assigned as a Robin and Day class III species. The IT band (Figure 1) (λ_{max} 1550 (ϵ 2000)) is somewhat sharper and more intense than that of (FcFc)$^+$.

To obtain a calculated intervalence band contour for biferrocene and BFD, eq 7 was used with a basis set of 40 vibrational quanta. The resulting energies and coefficients

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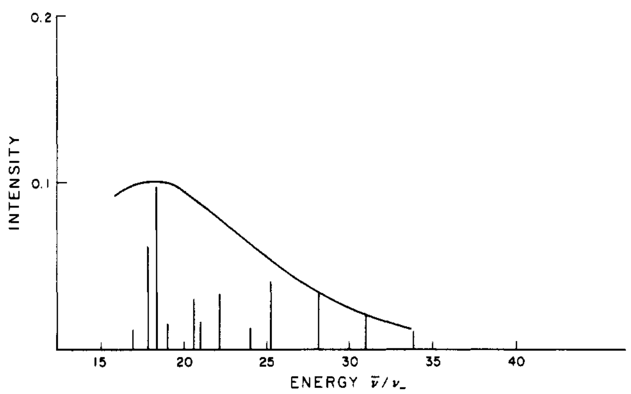

Figure 3. Observed IT band of $(FcFc)^+$ superimposed on PKS stick spectrum for $\lambda = 3.8$ and $\epsilon = -8.7$. Intensities are scaled to correspond to the $(BFD)^+$ spectrum[18] (Figure 4).

for each set of ϵ and λ then enabled calculation (eq 10) of a stick spectrum corresponding to the IT band. The parameters ϵ and λ were then varied until a best fit set were obtained for each experimental band. All calculations were done for room-temperature spectra. The frequency of the totally symmetric metal–ring stretch of ferrocene is 300 cm^{-1},[17] and this is the value of ν_- used. Energies are in units of $\nu_- = 300$ cm^{-1}, and transition intensities are in units of $(Re/2)^2$.

Application of the model to biferrocene(II, III) results in a best fit corresponding to PKS parameters $\lambda = 3.8$ and $\epsilon = -8.7$ (Figure 3).[18] Variation of $\epsilon \pm 0.1$ results in unacceptable band maximums and of $\lambda \pm 0.1$ results in unacceptable band shape and intensity. These parameters place biferrocene into class II of the refined Robin and Day classification scheme with $|\epsilon|/\lambda^2 = 0.6$, surprisingly close to the class II–III border ($|\epsilon| \rightarrow \lambda^2$).

The IT band for BFD(II, III) is shown in Figure 2. Filling the band with a PKS stick spectrum of intensity compatible with that of the biferrocene spectrum proved unsuccessful. Parameters that produce spectra with proper intensity yield too narrow a band, and those that produce a spectrum of adequate bandwidth result in a band of low intensity. It has been suggested that the IT band of $(BFD)^+$ can be resolved into two bands[3,5,19] where the second transition is due to IT from a low-lying excited state perhaps the A_{1g} of ferrocenium.[5] By treating the band as two IT transitions, the band is nicely fit with two PKS stick spectra[18] (Figure 4). By treating the lower energy band, a fit is obtained with PKS parameters $\lambda = 3.5$ and $\epsilon = -10.5$. Again, changing $\epsilon \pm 0.1$ moves the band maximum away from the experimental maximum (ν_{max}), and changing $\lambda \pm 0.1$ gives intensities that do not fit the band. The PKS model, therefore, places mixed-valent BFD at the class II–III borderline with $|\epsilon|/\lambda^2 = 0.86$ and successfully predicts a higher degree of interaction between the ferrocene subunits than in biferrocene.

Discussion

The increased electronic interaction going from the singly bridged compound to the bis-bridged is manifested in the PKS treatment by an increase in $|\epsilon|$. In this range of interaction, it is ϵ which influences the intensity of the spectrum. The vibronic coupling parameter, λ, which regulates the energy of the band will reflect the changes in ϵ when comparing systems containing the same subunit. Increased electronic interaction will reduce the differences in subunit coordination geometries in different oxidation states. This is the case for $(BFD)^+$ where λ is smaller than in $(FcFc)^+$.

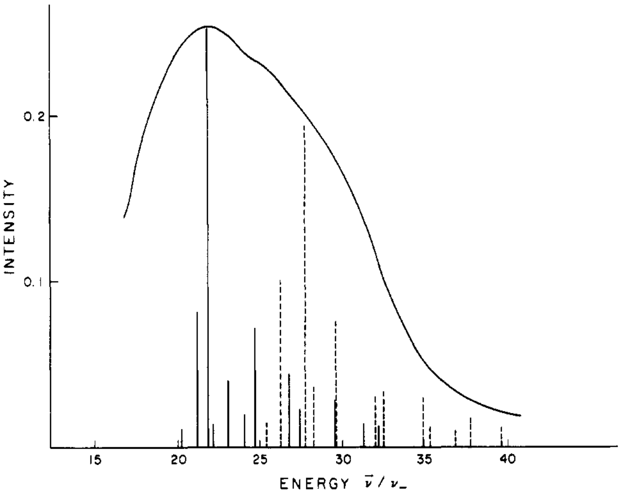

Figure 4. Observed IT band of $(BFD)^+$ superimposed on PKS stick spectra for $\lambda = 3.5$ and $\epsilon = -10.5$ (solid line) and $\lambda = 3.95$ and $\epsilon = -13.0$, (broken line).[18]

As was mentioned above, $(BFD)^+$ has been proposed to be a delocalized system by Mössbauer and ESCA measurements while biferrocene has been shown to be a localized or trapped-valence system. Within the PKS framework, a description for the degree of delocalization can be obtained by defining

$$P_\nu(\text{el}) = \int |\Phi_\nu|^2 \, dq \qquad (11)$$

where $P_\nu(\text{el})$ is the probability of finding the system in a given electronic configuration of vibronic state Φ_ν. By noting that $\langle \chi_n | \chi_{n'} \rangle = \delta_{nn'}$ and again taking advantage of the symmetry of the subunits, $P_\nu(\text{el})$ can be expressed as

$$P_\nu^+(\text{el}) = \tfrac{1}{2}(\psi_a^2 + \psi_b^2) + \psi_a\psi_b\Big(\sum_{n=\text{even}} r_{\nu n}^2 - \sum_{n=\text{odd}} r_{\nu n}^2\Big) \qquad (12)$$

By defining the degree of delocalization (β_d^2) as the square of the coefficient of the term $\psi_a\psi_b$, then

$$\beta_d^2(\nu) = [\sum_n r_{\nu n}^2 - r_{\nu n'}^2]^2 \qquad (13)$$

Averaging over thermally populated states gives

$$\overline{\beta_d^2} = \frac{\sum_\nu \beta_d^2(\nu) e^{-E_\nu/kT}}{\sum_\nu e^{-E_\nu/kT}} \qquad (14)$$

For a completely localized system $\beta_d^2 = 0$, and the system can be described as $\psi_1 = \psi_a = \psi_A^M\psi_B^N$ and $\psi_2 = \psi_b = \psi_A^N\psi_B^M$. As the system approaches complete delocalization $\beta_d^2 \rightarrow 1$. For $(BFD)^+$ where $\lambda = 3.5$ and $\epsilon = -10.5$, $\overline{\beta_d^2}$ can be calculated to be 0.77, and for biferrocene where $\lambda = 3.8$ and $\epsilon = -8.7$, $\overline{\beta_d^2} = 0.49$. BFD cation is predicted to have a higher degree of delocalization than biferrocene(II, III) which is again in good agreement with experiment.

It is interesting to compare the results of the PKS treatment to those treatments that assume the localized limit. PKS parameters corresponding to the Hush treat-

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(17) (a) Lippincott, E. R.; Nelson, R. D. *Spectrochim. Acta* **1958**, *10*, 307–329; (b) Long, T. V., Jr.; Huege, F. R. *J. Chem. Soc., Chem. Commun.* **1968**, 1239–1241.

(18) The intensity of the most intense vibronic line of the stick spectrum corresponding to PKS parameters $\lambda = 3.4$ and $\epsilon = -10.5$ is adjusted to have the same height as the maximum molar absorbtivity of the IT band of $(BFD)^+$ (Figure 4). The intensity scales of Figures 3, 4, and 5 are based on this point of reference. That is the vibronic lines in Figures 3 and 5 are not adjusted to the absorbtion spectra in those figures.

(19) Mueller-Westerhoff, U. T.; Eilbracht, P. *J. Am. Chem. Soc.* **1972**, *94*, 9272–9274.

ment can be obtained from eq 15 and 16. Application to

$$\lambda_{\max} = 2\lambda^2\nu_- \qquad (15)$$

$$\alpha^2 = \epsilon^2/4\lambda^4 \qquad (16)$$

biferrocene(II, III) results in PKS parameters $\lambda = 3$ and $\epsilon = -3$. A stick spectrum corresponding to $\lambda = 3$ and $\epsilon = -3$ is shown in Figure 5. The band maximum appears at $\bar{\nu}_{\max} = 7.0\nu_-$ much lower than the experimental maximum, and the intensity of the band is about half of that obtained for our best fit of $\lambda = 3.8$ and $\epsilon = -8.7$. It is interesting, also, that a reasonably high value of β_d^2 is obtained for biferrocenium. In the localized limit, β_d^2 can be related to α^2, the Hush interaction parameter, by $\beta_d^2 = 4\alpha^2$. Comparison of the two measures of delocalization $4\alpha^2 = 3.6 \times 10^{-2}$ and $\beta_d^2 = 4.9 \times 10^{-1}$ reveals a significant difference. The PKS model predicts a much higher degree of delocalization for biferrocene than do treatments that assume the localized limit.

This discrepancy along with the poor fit of the stick spectrum predicted by the treatment in the localized limit suggests that one or both of the models does a poor job of describing the mixed-valence state of biferrocene. The Hush model has met with great success in treating the properties of other localized mixed-valence systems. However, if one is to believe the predictions of the PKS model FcFc(II, III) is not a rigorously localized system and is, then, ineffectively treated by the Hush model. A possible explanation for the discrepancies in the predictions of the two models lies therein. $(FcFc)^+$ is a too highly interacting system to be treated by any model assuming a high degree of localization.

The PKS model, therefore, successfully predicts that BFD cation has a larger degree of delocalization and stronger subunit interaction than biferrocene(II, III) in agreement with experimentation. The model also suggests that the amount of subunit interaction and degree of delocalization $(\overline{\beta_d^2})$ for FcFc is larger than that predicted by earlier treatments and that they are not that different than in BFD. There is some experimental evidence to corroborate this. The presence of a shoulder in the Mössbauer of $(FcFc)^+$ at ΔQs intermediate to that of Fc and Fc^+ has been attributed to the presence of some average valence species in $(FcFc)^+(TCA)^-\cdot 2TCAA$[5] ($(TCA)^-$ stands for trichloroacetate and TCAA for trichloroacetic acid) and $(FcFc)^+(picrate)^-$.[2]

Mössbauer studies on the mixed-valence salts of 1′,1‴-diethylbiferrocene and 1′,1‴-dipropylbiferrocene have shown an interesting temperature dependence of the valence states of these compounds in the temperature range 4.2–300 K.[20] At low temperature the systems are of the trapped-valence type while at high temperatures the salts are average valence, suggesting that these compounds lie at the Robin and Day class II–III borderline. Biferrocene monocation does not show such a dramatic temperature-dependent Mössbauer spectrum in this range[2,5] but, nevertheless, would be expected to have a similar degree of interaction.

Gleiter[16] has proposed that the existence of trapped or average valency is due to the Δt of exchange being greater or slower than vibrational motions (10^{-14} s). On the basis of the UV-PES, the Δt of exchange of $(FcFc)^+$ was estimated as $8 \times 10^{-15} \rightarrow 2 \times 10^{-14}$ s and of $(BFD)^+$ as $3.1 \times 10^{-15} \rightarrow 4.7 \times 10^{-15}$ s. For $(FcFc)^+$ then phonon coupling

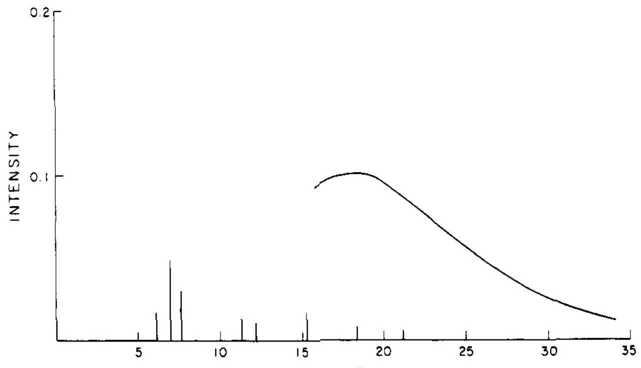

Figure 5. Observed IT band for $(FcFc)^+$ superimposed on PKS stick spectrum for $\lambda = 3.0$ and $\epsilon = -3.0$—the parameters predicted by assuming a localized limit for $(FcFc)^+$. Intensities are scaled to correspond to the $(BFD)^+$ spectrum[18] (Figure 4).

is possible, leading to trapped valences while Δt is $(BFD)^+$ is faster than vibrational motion and a delocalized system exists. It should be noted, however, that the rates of exchange are different by less than an order of magnitude and that differences in subunit interaction are not necessarily large—a result predicted by the PKS treatment.

As one of the goals of this work was to test the usefulness of the PKS vibronic coupling model's treatment of mixed-valence ferrocene derivatives, possible shortcoming of the model or, more appropriately, of its application to these systems should be mentioned. A fundamental premise of the model is that the subunits have the same point-group symmetry and that the mode coupling the subunits of different oxidation states is the totally symmetric mode. The model becomes increasingly inappropriate as other modes become more important in the coupling of the subunits. Ferrocenium ion distorts from rigorous D_5 symmetry as evidenced by EPR.[21] Bending of the subunits in mixed-valent BFD[22] has been shown crystallographically and used as evidence for direct Fe–Fe interaction in this system. It is possible then that the totally symmetric mode is not the only important mode coupling the ferrocene subunits and that the problem becomes much more complicated. The PKS model (as well as earlier models) correlates the energy of the IT band (E_{op}) with the displacement of the two subunits along a geometric coordinate—in this case coordinate q associated with the totally symmetric mode Q. It would be interesting to look for a relationship between the energy of the IT band and the degree of distortion from D_5 symmetry of the ferrocenium subunit in these mixed-valence systems.

Summary

In summary, the results of the PKS model suggest that $(BFD)^+$ is more strongly delocalized than $(FcFc)^+$—in agreement with our notion, however, *both* systems experience considerable delocalization. Further, it appears that the Hush treatment of these systems is an oversimplification even for trapped-valent species when there is some degree of interaction.

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Registry No. $(FcFc)^+$, 51263-10-6; $(BFD)^+$, 51140-52-4.

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