

OPTICAL ELECTRON TRANSFER PROCESSES. THE DEPENDENCE OF INTERVALENCE LINE SHAPE AND TRANSITION ENERGY ON CHROMOPHORE CONCENTRATION

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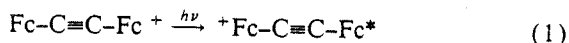
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Received 17 March 1988; in final form 9 June 1988

Optical electron transfer in the mixed-valence cation of biferrocenylacetylene (BF^+) has been examined in CD_2Cl_2 solvent. The intervalence absorption line shape is relatively narrow at both low and high chromophore concentrations, but broader at intermediate concentrations. The transition energy for metal-to-metal charge transfer increases from $\approx 4440 \text{ cm}^{-1}$ at infinite dilution to 5995 cm^{-1} for 3.8 mM BF^+ . Related effects exist due to added electrolyte. Neither the electrolyte nor chromophore concentration effects are expected from a simple reading of electron transfer theories. Nevertheless, both phenomena can be understood and within the context of theory upon careful consideration of the effects of ion-pairing (and tripling) equilibria upon electron-transfer energetics.

1. Introduction

In studies of optical electron transfer, cf.



(Fc = bis(cyclopentadienyl)iron) or ferrocene) the three most important experimental parameters are the energy, line shape and integrated intensity of the so-called intervalence (or metal-to-metal) charge-transfer transition [1]. From these parameters and available theories [2-5] one can, in principle, derive a variety of fundamentally significant quantities including: (1) inner-shell and solvent reorganization, or trapping, energies, (2) activation barriers for corresponding thermal electron transfer (ET) reactions, (3) resonance interaction energies, (4) vibrational anharmonicity constants, (5) fractional valencies, and (6) localization/delocalization parameters. Experimentally the intervalence-band properties are found to depend on a number of factors [1] including temperature, identity of the metal centers [6-8], nature of the bridging ligand (length, orbital symmetry, degree of conjugation, etc.) [9], identity of ancillary ligands [1,10,11], and identity of the solvent or other external environment [1,12].

For the most part these effects are expected from the existing theory, and for transition energies and intensities, in particular, the observed trends can generally be rationalized theoretically in a qualitative, or even semiquantitative, fashion. On the other hand, for line shapes (especially solvent effects on band widths) there is often a relatively poor correlation between experiment and theory [1,12].

In this Letter we report that intervalence line shapes as well as transition energies can exhibit a profound dependence upon chromophore concentration. We also report that both parameters are strongly dependent on the concentration of added electrolyte. Neither the electrolyte nor chromophore concentration effects would appear to be expected from the simplest reading of current electron transfer theories. Nevertheless, both phenomena can be understood in a detailed way (and within the context of current theories) from a careful consideration of the likely effects of ion-pairing equilibria upon ET energetics. The resulting understanding may provide a rationale for the failure in many previous studies to find agreement between experimental and calculated line shapes.

2. Experimental

The neutral acetylene-bridged ferrocene dimer was obtained from Dr. B. Patrick Sullivan. (A synthesis has been given by Rosenblum et al. [13].) The mixed-valence monocation (BF^+) was obtained as a solid hexafluorophosphate salt by oxidation in toluene with *p*-benzoquinone, following the method of Dong, Kamabara and Hendrickson [14]. In our hands the oxidation was incomplete, so that all samples were contaminated ($\approx 25\%$) by the neutral form. Tetrabutylammonium hexafluorophosphate (TBAH) was prepared and purified as outlined by Sawyer and Roberts [15]. Deuterated methylene chloride (99.6% D) was purchased from Aldrich. The deuterated form was required in order to obtain sufficient solvent transparency in the near-infrared spectrum.

Intervalence absorption bands were obtained using 0.2, 1.0 and 10.0 cm matched cells in a Perkin-Elmer 330 UV-vis-NIR spectrophotometer. The measurements were ultimately limited by the onset of solvent absorption at $E < 4700 \text{ cm}^{-1}$ and by insufficient signal-to-noise for peak absorbances of less than ≈ 0.1 . Values of E_{op} (the apparent energy of the intervalence transition) could be determined reproducibly to within $\pm 40 \text{ cm}^{-1}$ under most conditions and $\pm 65 \text{ cm}^{-1}$ for chromophore concentrations of less than 0.1 mM.

3. Results

Fig. 1 shows intervalence absorption bands for 0.008, 0.076 and 3.8 mM BF^+ solutions without added electrolyte and for 0.076 mM BF^+ with 3.1 mM TBAH. Note that the band maximum changes significantly with either chromophore or electrolyte addition. Fig. 2 shows a plot of the apparent transition energy or band maximum (E_{op}) for a range of BF^+ concentrations. Also shown (as open circles) are E_{op} values versus total PF_6^- concentration for a series of solutions containing 0.076 mM BF^+ and varying amounts of TBAH.

Besides the energy effects there are also substantial line-shape effects. The intervalence absorption band is relatively narrow (by mixed-valence standards) at both low and high concentrations (chromophore or chromophore+electrolyte), but somewhat broader

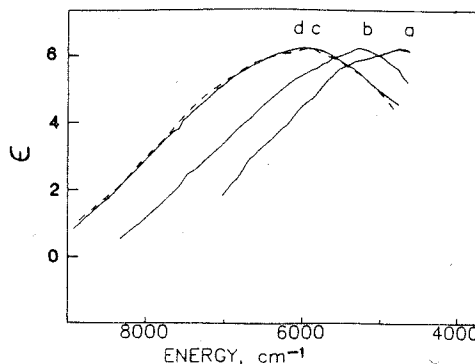


Fig. 1. Intervalence absorption bands for (a) 0.008 mM BF^+ , (b) 0.076 mM BF^+ , (c) 3.8 mM BF^+ , and (d) 0.076 mM BF^+ + 3.1 mM TBAH (dashed line); each in CD_2Cl_2 as solvent.

at intermediate concentrations. Table 1 gives a quantitative listing, where full widths at half height ($\Delta\nu_{1/2}$) have been obtained by doubling half the width at half height, measured on the high-energy side. Uncertainties, assuming symmetrical line shapes, are essentially twice the uncertainty in E_{op} .

4. Discussion

The striking dependence of E_{op} as well as $\Delta\nu_{1/2}$ on both chromophore and electrolyte concentration is unexpected in the sense that neither effect has been addressed (or predicted) in an explicit way by existing theories of optical electron transfer. The results are also surprising in view of earlier experimental observations [12]. Nevertheless, there are a few reports of similar phenomena for other mixed-valence systems. For example, Curtis et al. have noted that E_{op} for intervalence transfer in $[(2,2'\text{-bipyridine})_2(\text{Cl})\text{Ru}^{\text{II}}(\text{pyrazine})\text{Ru}^{\text{III}}(\text{NH}_3)_4(\text{pyridine})]^{4+}$ can depend on the nature of the counter ion (PF_6^- versus Br^-) [16]. Also, a dependence of both line shape and transition energy on chromophore concentration has been observed by Hammack, Drickamer, Lowery and Hendrickson for biferrocene monocation in nitrobenzene as solvent [17]. It should be noted, however, that the latter system may differ importantly from ours in that it exhibits substantial valence delocalization [18]. Finally, we note the appearance, during the prepa-

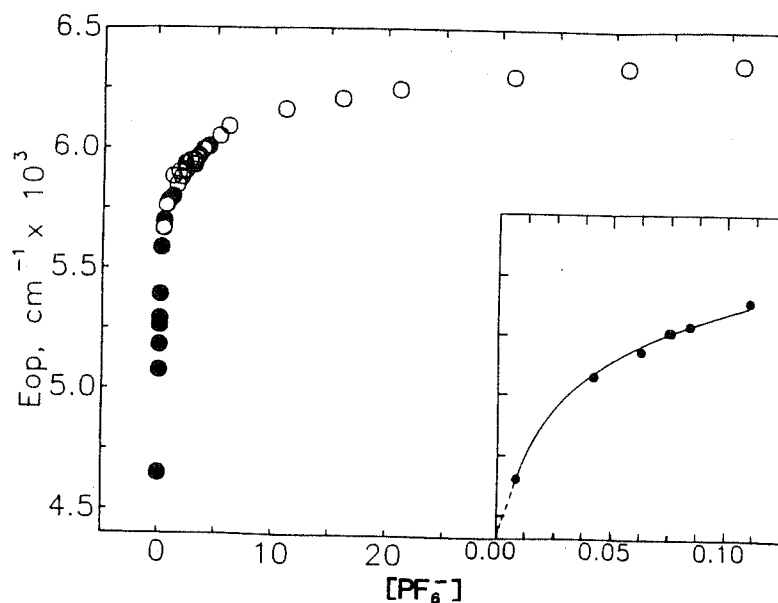
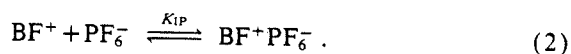


Fig. 2. Intervalence absorption band maximum (E_{op}) as a function of total PF_6^- concentration. Filled circles: various chromophore concentrations without added electrolyte. Open circles: 0.076 mM (or 3.0 mM) BF^+PF_6^- with added TBAH (see table 1).

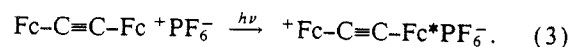
ration of this report, of a follow-up paper on the ferrocene system [19].

To understand the basis for the concentration effects in the present system, it is useful to reexamine the plot of E_{op} versus $[\text{BF}^+]$ in fig. 2. The shape is typical of that seen for so-called binding curves, and suggests the occurrence of a simple chromophore-based equilibrium [20]. A likely candidate for that equilibrium would be ion pairing:



To test that hypothesis, we performed a second series of experiments, in which excess hexafluorophosphate ions were introduced, in the form of TBAH, into a dilute chromophore solution. The results are recorded in fig. 2 as open circles, and within experimental error, they are *identical* to those for the first experiment (see also table 1 and fig. 1). Since the changes in E_{op} are independent of the source of PF_6^- , the clear implication is that eq. (2) indeed is the process responsible for the energy effects.

To understand why ion pairing might lead to intervalence energy shifts, it is useful to rewrite the optical reaction in ion-paired form:



Since the mixed-valence ion exists in a valence-localized form, there is a clear opportunity in eq. (3) for electrostatic stabilization in the ground state at the oxidized end. For the optically generated excited state, however, the positive charge is (to a first approximation) too far removed to interact significantly with the counter ion. Assuming no other effects intervene, E_{op} should shift upon ion pairing to a value that is larger than in the unpaired state by $\Delta E_{op} = RT \ln K_{IP}/K_{IP}^*$, where K_{IP} and K_{IP}^* are the equilibrium constants for the formation of the vibrationally equilibrated, ion-paired species on the left- and right-hand sides, respectively, of eq. (3). In fig. 3 we show that, in terms of potential energy surfaces, the effect is simply a net downward displacement of the reactant surface relative to the product.

To gain a more quantitative understanding of the ion-pairing induced energetic effects it would be desirable to determine K_{IP} . For sufficiently small energy shifts, it can be shown that the energy at the absorption maximum (E_{op}) for any degree of ion pairing will be given by [21]

Table 1
Dependence of intervalence transition energy and line shape on chromophore and electrolyte concentration in CD_2Cl_2 as solvent

$10^3[\text{BF}^+]$ (M)	$E_{\text{op}}(\text{cm}^{-1})$	$\Delta\nu_{1/2}(\text{cm}^{-1})$
3.75	5995	4676
3.38	5970	4690
3.00	5940	4788
2.63	5949	4838
2.25	5907	4852
1.88	5879	4882
1.50	5847	4936
1.13	5797	4968
0.75	5780	5064
0.38	5698	5128
0.19	5586	5154
0.11	5391	5130
0.084	5291	4882
0.076	5263	4682
0.075	5263	4976
0.063	5181	4680
0.042	5076	4668
0.0083	4651	4400
0.076+ 5.12 TBAH	6053	a)
0.076+ 4.14 TBAH	6010	
0.076+ 3.11 TBAH	5959	
0.076+ 2.07 TBAH	5935	
0.076+ 1.55 TBAH	5900	
0.076+ 1.04 TBAH	5882	
0.076+ 0.52 TBAH	5764	
0.076+ 0.26 TBAH	5900	
3.00 +48.00 TBAH	6365	
3.00 +38.00 TBAH	6349	
3.00 +28.00 TBAH	6309	
3.00 +18.00 TBAH	6250	
3.00 +13.00 TBAH	6211	
3.00 + 8.00 TBAH	6165	
3.00 + 3.00 TBAH	6094	

a) Due to spectral tailing from the visible region at high PF_6^- concentrations, bandwidths were unobtainable at $\Delta\nu_{1/2}$ in the presence of TBAH.

$$E_{\text{op}} = \frac{E_{\text{op}}(\text{initial}) + K_{\text{IP}}[\text{PF}_6^-] \Delta E_{\text{op}}(100\% \text{ IP})}{1 + K_{\text{IP}}[\text{PF}_6^-]}, \quad (4)$$

where $E_{\text{op}}(\text{initial})$ is the value in the absence of ion pairing. From eq. (4), a plot of $\{\Delta E_{\text{op}}(100\% \text{ IP})/[E_{\text{op}} - E_{\text{op}}(\text{initial})] - 1\}$ versus $1/[\text{PF}_6^-]$ will yield $1/K_{\text{IP}}$ as the slope. To construct such a plot we require values for E_{op} in the limits of complete ion pairing and no ion pairing. The former can be estimated with reasonable accuracy from fig. 2, yielding

$E_{\text{op}}(\text{final}) = 6410 \text{ cm}^{-1}$. The latter entails a significant extrapolation; with some uncertainty we obtain $E_{\text{op}}(\text{initial}) = 4440 \text{ cm}^{-1}$. Using these in the appropriate plot we obtain the somewhat surprising result shown in fig. 4. In the plot the expected linear correlation exists, but at the smallest values of $1/[\text{PF}_6^-]$ a second (steeper) linear (or nearly linear) region appears. Clearly at high PF_6^- concentrations a second ionic equilibrium intervenes. In terms of the analysis for K_{IP} , the occurrence of a second equilibrium is a point of concern since it leads to a falsely large value for $E_{\text{op}}(\text{final})$ and an incorrect estimate for $\Delta E_{\text{op}}(100\% \text{ IP})$. Nevertheless, an improved estimate is easily obtained by a very brief extrapolation (less than 25 cm^{-1}) of the "low-concentration" line to the y-intercept (5910 cm^{-1}). Discarding the points at higher concentrations and replotting, we obtain $K_{\text{IP}} = 20000 \text{ M}^{-1}$ (correlation coefficient $r = 0.998$). It should be noted that despite the high correlation coefficient, the uncertainty in K_{IP} is substantial. The largest potential source of error is in the value for E_{op} at the lowest BF^+ concentration (see fig. 4); considering only this ingredient we obtain, as alternative estimates, $K_{\text{IP}} = 12960 \text{ M}^{-1}$ ($r = 0.996$) and $K_{\text{IP}} = 29970 \text{ M}^{-1}$ ($r = 0.980$). (Or, if the lowest BF^+ concentration is arbitrarily omitted we obtain $K_{\text{IP}} = 17400 \text{ M}^{-1}$, with $r = 0.993$.) For comparison, Yang, Chan and Wahl obtained an ion-pairing constant of 25000 ± 10000 for cobalticinium hexafluorophosphate in dichloromethane [22].

From the values for ΔE_{op} (1470 cm^{-1}) and K_{IP} (20000 M^{-1}), K_{IP}^* is 16 M^{-1} . This value is surprisingly large given that the counter ion is paired to the uncharged ferrocene fragment and that specific donor-acceptor interactions [23] are likely to be absent. Evidently in the electronic excited state ($^+ \text{Fc}-\text{C}\equiv\text{C}-\text{Fc}^+ \text{PF}_6^-$) the bound counter ion is still able to interact to a small extent with the remote ferricenium fragment and therefore to provide a finite degree of electrostatic stabilization. (On this basis one might expect ΔE_{op} to be even larger for a mixed-valence chromophore like $\text{Fc}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Fc}^+$, since in the ion-associated excited state Coulombic stabilization will be almost completely absent.)

Finally, returning to fig. 4, an explanation is still needed for the second equilibrium. One obvious possibility is an ion-tripling reaction [24,25]: $\text{BF}^+ \text{PF}_6^- + \text{PF}_6^- \rightleftharpoons \text{BF}^+ 2\text{PF}_6^-$. If the equilibrium is of

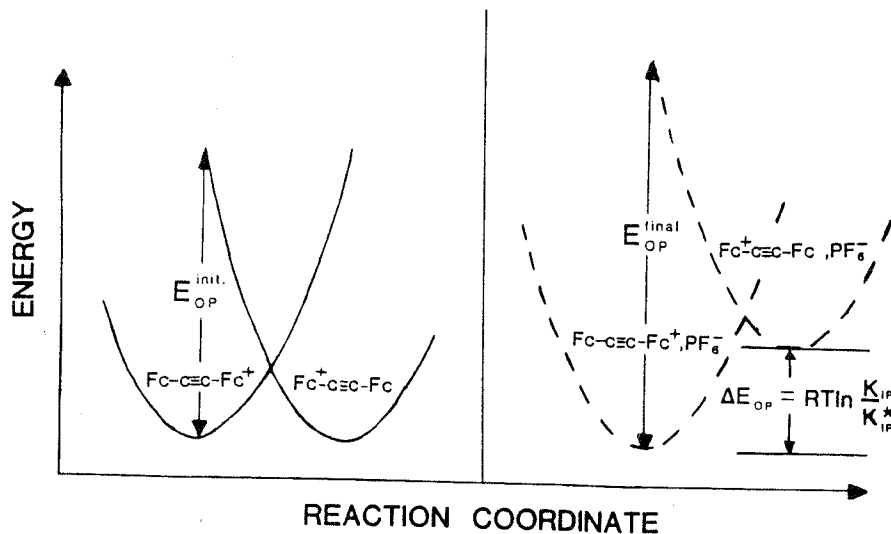


Fig. 3. Schematic representation of zero-order potential energy surfaces for various acetylene-bridged biferrocene mixed-valence species.

this form, an analysis similar to that for ion pairing yields a ground-state equilibrium constant of 90 and an excited-state equilibrium constant of 8. (Another possibility would be the creation of an asymmetric quartet. [24,25]: BF^+PF_6^- , $\text{TBA}^+\text{PF}_6^-$.)

The interpretation of energetic effects provides a basis for understanding the line shapes as well. In those cases where ion pairing (or tripling) is only partially complete, E_{op} corresponds not to a "true" transition energy but to a weighted average of ener-

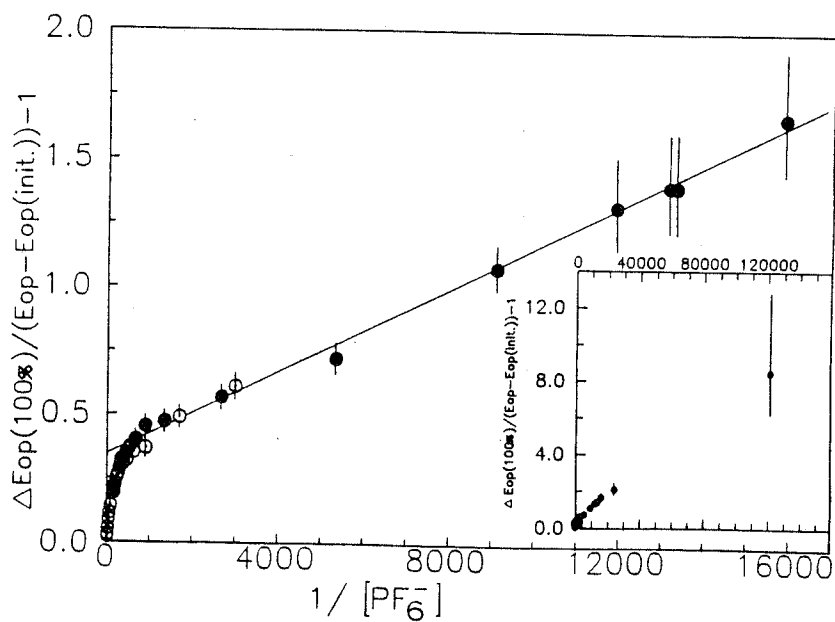


Fig. 4. Plot of $\{\Delta E_{\text{op}}(100\% \text{ IP}) / [E_{\text{op}} - E_{\text{op}}(\text{initial})] - 1\}$ versus $1/[\text{PF}_6^-]$ (see text). Filled and open circles designated as in fig. 2.

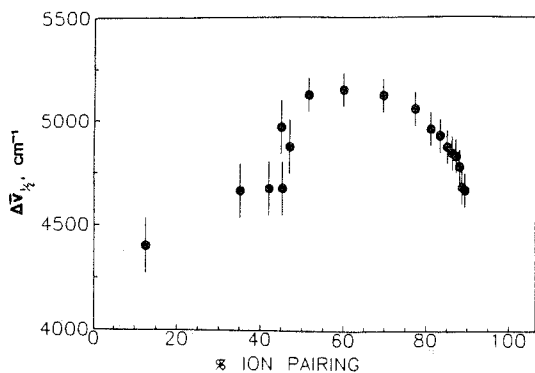


Fig. 5. Intervalence band width versus extent of ion pairing, based on $K_{IP} = 20000 \text{ M}^{-1}$.

gies for the paired and unpaired forms. The overall line shape likewise contains contributions from both forms, and the line shapes corresponding to the component transitions evidently are those at limiting high and low concentrations. On this basis, the experimentally observed intervalence absorption band is anticipated to be relatively narrow at the concentration extremes and widest in the vicinity of 50% ion pairing. Fig. 5 shows a plot of $\Delta\bar{\nu}_{1/2}$ versus the percent of ion pairing, based on $K_{IP} = 20000 \text{ M}^{-1}$. The plot shows that there indeed is a systematic distribution of line widths as a function of ion pairing (IP), with the distribution centered at about 60% IP. It should be noted that the calculated percent IP is sensitive to the choice of K_{IP} ; if a K_{IP} value of 12960 M^{-1} is chosen (vide supra), the maximum in $\Delta\bar{\nu}_{1/2}$ is at 53% IP. One further point concerns the implication from fig. 5 that the band width in the limit of complete ion pairing is little different than in the complete absence of ion pairing. This indicates that the intrinsic reorganization energy is unchanged by ionic association and therefore validates the claim that ΔE_{op} is due exclusively to $RT \ln K_{IP}/K_{IP}^*$.

A corollary to the observation that intervalence parameters gathered at millimolar concentration levels, or in the presence of added electrolyte, are distorted by ion pairing, is that a comparison of these to calculated parameters will not provide a particularly useful evaluation of the underlying theory [2-5]. The most appropriate parameters, instead, are

likely to be those obtained at infinite dilution. For BF^+ in dichloromethane, these values are $E_{op} \approx 4440 \text{ cm}^{-1}$ and $\Delta\bar{\nu}_{1/2} \approx 4350 \text{ cm}^{-1}$. For comparison, from Hush's theory [2], E_{op} is given by

$$E_{op} = \lambda_i + \lambda_o, \quad (5)$$

where

$$\lambda_o = e^2(r^{-1} - d^{-1})(D_{op}^{-1} - D_s^{-1}). \quad (6)$$

In eqs. (5) and (6), λ_i and λ_o are the inner- and outer-shell reorganization energies, respectively; e is the unit electronic charge, r is the trapping radius ($\approx 3.8 \text{ \AA}$), d is the site-to-site separation distance ($\approx 7.3 \text{ \AA}$ for a trans configuration), and D_{op} and D_s are the so-called optical and static dielectric constants. Inserting appropriate values into the expressions (i.e. $D_{op} = 2.022$, $D_s = 8.93$, $\lambda_i \approx 500 \text{ cm}^{-1}$) [26], the value calculated for E_{op} is 6100 cm^{-1} . For the band width, Hush's prediction (see also Marcus [27]) is [2]

$$\Delta\bar{\nu}_{1/2} = [16(\ln 2)kTE_{op}]^{1/2}. \quad (7)$$

Using E_{op} from eq. (5), the calculated value is $\Delta\bar{\nu}_{1/2} = 3740 \text{ cm}^{-1}$. Alternatively, if the experimental value for E_{op} is used, eq. (7) gives $\Delta\bar{\nu}_{1/2} = 3190 \text{ cm}^{-1}$.

Both calculated parameters are in substantial disagreement with the infinite-dilution experiments. E_{op} is "too large" by $\approx 37\%$, while $\Delta\bar{\nu}_{1/2}$ is "too small" by 15 to 26% depending on the basis of comparison with experiment. In an earlier report, excellent agreement was found for the transition energy ($E_{op}(\text{experiment}) = 6180 \text{ cm}^{-1}$), but agreement was poor for the line shape ($\Delta\bar{\nu}_{1/2}(\text{experiment}) = 5200 \text{ cm}^{-1}$) [12]. From our studies it is now clear that the earlier agreement for E_{op} was partially fortuitous; the experimental data [12] appear to correspond to an ion triple. In a sense, the present results account for the surprisingly large band width in the earlier study: in the absence of partial ionic association the band is much narrower. Nevertheless, because the transition energy is also affected by association, there is ultimately, for this system, only a weak correspondence between experiment and theory. A reasonable conclusion for valence-localized systems may be that the Hush model is only partially accurate in describing the basis for intervalence transitions.

We believe that in many other instances, reported

discrepancies may lie more with experiment than theory. We have, in fact, observed ion-pairing "artifacts" in other systems and these will be described in part in a forthcoming report on the implications of these effects in thermal ET reactions [28].

5. Concluding comments

Profound chromophore and electrolyte concentration effects exist in optical electron transfer reactions and these are due to ion pairing, or higher-order ion-association reactions. Energy shifts of up to 2000 cm^{-1} exist for the acetylene-bridged biferrocene cation in dichloromethane as solvent. The effects are likely to be somewhat smaller in solvents of higher dielectric strength. Nevertheless, because the effects are apparently scaled, in part, by the log of the association constant, even modest association may lead to significant transition energy and line shape distortions (for example, for $K_{\text{IP}}/K_{\text{IP}}^* = 5$, $\Delta E_{\text{op}} = 330 \text{ cm}^{-1}$).

Because most previous investigations have been carried out without particular attention to the consequences of ionic association, any conclusions ought to be viewed with appropriate caution.

Acknowledgement

This work was supported by the US Department of Energy, Office of Energy Research under grant No. DE-FG02-87KR13808. RLB acknowledges support as a Shell Graduate Fellow. We also acknowledge helpful comments from a reviewer and from Professor Michael Weaver.

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