Temperature Effects for Localized versus Delocalized Optical Intervalence Transitions

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Recently we have begun to explore the role of temperature in optical intervalence charge-transfer (IVCT) processes.[1] For symmetrical mixed-valence complexes, we find that the energetics of IVCT are essentially unaffected by changes in temperature.[1] For asymmetric complexes, on the other hand, substantial energetic effects can exist, at least for valence localized systems.[1] We have shown experimentally that the latter effects are related to the temperature dependence of the redox asymmetry component (ΔE) of the overall intervalence absorption energy, E^{IVCT}.[1-3] We now report that valence-localized and valence-delocalized asymmetric systems respond differently to temperature perturbations, the latter exhibiting essentially no dependence of E^{IVCT} on temperature.[4] We also offer a primitive interpretation of the contrasting behavior and show that it is consistent with an elementary theoretical picture of the overall IVCT process.

Two closely related mixed-valence complexes were examined: (2,2′-bpy)$_2$ClRu-pyrazine-Ru(NH$_3$)$_5^{4+}$ (**1**) and (4,4′-CH$_3$-2,2′-bpy)$_2$ClRu-pyrazine-Ru(NH$_3$)$_4$(4-methylpyridine)$^{4+}$ (**2**).[5] In CD$_3$NO$_2$ as solvent, **1** displays a broad Gaussian IVCT absorption band ($\Delta\bar{\nu}_{1/2}$ = 4900 cm^{-1}, $\lambda_{\max}$ = 1350 nm) typical of valence-localized systems.[6-8] In contrast, **2** exhibits a significantly narrower ($\Delta\bar{\nu}_{1/2}$ = 2540 cm^{-1}), somewhat asymmetric, and substantially red-shifted absorption spectrum ($\lambda_{\max}$ = 1643 nm), strongly reminiscent of the Creutz–Taube ion and other valence-delocalized systems.[6,7a,8] We ascribe the differences between **1** and **2** primarily to differences in redox asymmetry. Recall that systems become delocalized when $2H_{\mathrm{if}}$ (i.e., twice the initial-state/final-state coupling energy) exceeds the sum of χ (the reorganization energy) and ΔE.[7] For **2**, the presence of several methyl substituents on bipyridine and replacement of a trans NH$_3$ ligand by 4-methylpyridine renders the trapping sites nearly equivalent energetically ($\Delta E \approx 0$).[9]

Examination of the temperature dependencies of the two spectra (Figure 1) yields $\mathrm{d}E^{\mathrm{IVCT}}/\mathrm{d}T = -18$ cm^{-1} deg^{-1} for **1** and $+2 \pm 1$ cm^{-1} deg^{-1} for **2**. The differences are striking, both quantitatively and qualitatively. Some insight can be gained, however, by considering a generalized (two-site) expression for IVCT energies:[7]

$$E^{\mathrm{IVCT}} = \sqrt{(\chi + \Delta E)^2 + 4H_{\mathrm{if}}^{\,2}} \tag{1}$$

If both χ and H_{if} are viewed as temperature independent,[10,11] and if the sum of χ and ΔE appreciably exceeds $2H_{\mathrm{if}}$ (i.e., strong valence localization), then the temperature coefficient for E^{IVCT} is expected to be simply $\mathrm{d}\Delta E/\mathrm{d}T$ where ΔE is most precisely defined as the zeroth-order redox asymmetry, i.e., the asymmetry when electronic coupling is absent. On the other hand, when $2H_{\mathrm{if}}$ is much larger than $\chi + \Delta E$ (i.e., strong delocalization), $\mathrm{d}E^{\mathrm{IVCT}}/\mathrm{d}T$ should approach zero, regardless of the magnitude of $\mathrm{d}\Delta E/\mathrm{d}T$.

For **1** and **2**, $\mathrm{d}\Delta E/\mathrm{d}T$ can be estimated from the known variable-temperature electrochemistry of either (bpy)$_2$Cl Ru-pz-Ru(NH$_3$)$_4$py$^{5+/4+/3+}$ or the less strongly coupled analog, (bpy)$_2$Cl Ru-4,4′bpy-Ru(NH$_3$)$_4$py$^{5+/4+/3+}$ (py is pyridine).[12] On this basis, $\mathrm{d}\Delta E/\mathrm{d}T \approx -8$ cm^{-1} deg^{-1}. Notably, this estimate differs from the observed $\mathrm{d}E^{\mathrm{IVCT}}/\mathrm{d}T$ for **1** by more than a factor of 2. Apparently an additional factor contributes. One possibility (admittedly speculative) is that as the temperature decreases (and ΔE increases) **1** becomes more strongly valence localized,[13] more charge is transferred upon IVCT absorption, and the difference between ground- and excited-state dipoles is enhanced. This, in turn, would lead to an increase in the solvent polarization component of χ with decreasing T. Presumably this additional factor would become important only when electronic coupling is fairly strong and valencies are only moderately well localized (as with **1**). Consistent with this hypothesis, replacement of pz by 4,4′-bpy (i.e., diminution of coupling) changes $\mathrm{d}E^{\mathrm{IVCT}}/\mathrm{d}T$ to -8 cm^{-1} deg^{-1}.

For **2**, the magnitude of $\mathrm{d}E^{\mathrm{IVCT}}/\mathrm{d}T$ (i.e., near zero) is consistent with our expectation for a simple delocalized system; the sign, however, is something of a surprise. It may be that the assumption that $\mathrm{d}H_{\mathrm{if}}/\mathrm{d}T$ is zero is not rigorously satisfied here.[11] Alternatively, it may be that the appropriate zeroth-order ground-state description of **2** is one in which the bipyridylruthenium, rather than ammineruthenium site, is oxidized.[14] If so, then the sign of $\mathrm{d}\Delta E/\mathrm{d}T$ would be reversed, and $\mathrm{d}E^{\mathrm{IVCT}}/\mathrm{d}T$ should be near zero but positive.

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(1) (a) Dong, Y.; Hupp, J. T. *Inorg. Chem.* **1992,** *31,* 3322. (b) Hupp, J. T.; Kober, E. M.; Neyhart, G. A.; Meyer, T. J. *Proceedings of the NATO Advanced Research Workshop on Mixed Valency Systems*; Kluwer Academic Publishers: Dordrecht, Netherlands, 1991; pp 51–66.

(2) See, also: Marcus, R. A.; Sutin, N. *Comments Inorg. Chem.* **1986,** *5,* 119.

(3) In the limit of weak electronic and electrostatic interaction, the temperature dependence of ΔE, of course, is related directly to the difference in temperature dependence of the formal potentials for the individual electron donor and acceptor sites; these differences in turn reflect the solvational consequences of size and charge differences for the two trapping sites (see: Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1984,** *23,* 3639).

(4) To avoid cumbersome descriptions, we apply the notation "IVCT" to transitions involving both localized and delocalized complexes, despite the lack of charge transfer character for the latter.

(5) The synthesis of **1** has been described previously.[6] **2** was prepared analogously. The mixed-valence (4+) forms of both ions were obtained by using Fe(bpy)$_3^{3+}$ as oxidant. Elem. Anal. Calcd for **2** (in reduced form): C, 31.85; H, 3.69; N, 12.02. Found (1st sample): C, 31.26; H, 3.89; N, 10.35; (2nd sample): C, 28.43; H, 3.49; N, 11.56. Despite the less than ideal elemental analysis results, proton NMR experiments confirmed the presence of 4,4′-CH$_3$-2,2′-bpy, pyrazine, and 4-methylpyridine ligands in the correct proportions. The NMR measurements, however, also revealed the presence of small amounts (variable from sample to sample) of an unidentified, but evidently electroinactive, impurity.

(6) See, also: Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986,** *25,* 4233.

(7) For reviews, see: (a) Creutz, C. *Prog. Inorg. Chem.* **1983,** *30,* 1. (b) Sutin, N. *Prog. Inorg. Chem.* **1983,** *30,* 441. (c) Hush, N. S. *Prog. Inorg. Chem.* **1967,** *8,* 391.

(8) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969,** *91,* 3988; **1973,** *95,* 1086.

(9) Electrochemical data (SCE reference) in CH$_3$NO$_2$ (or acetone): for **1**, $E_{\mathrm{f}}(5+/4+) - E_{\mathrm{f}}(4+/3+)$ = 273 (485) mV; for **2**, $E_{\mathrm{f}}(5+/4+) - E_{\mathrm{f}}(4+/3+)$ = 237 (301) mV. Note that in all instances $E_{\mathrm{f}}(5+/4+) - E_{\mathrm{f}}(4+/3+)$ will exceed ΔE because of backbonding, electrostatic, and electronic coupling contributions to the stability of the 4+ form (Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981,** *20,* 3125). Indeed, data for related symmetrical systems (Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980,** *102,* 1289. De laRosa, R.; Chang, P. J.; Salaymeh, F.; Curtis, J. C. *Inorg. Chem.* **1985,** *24,* 423. Dong, Y., unpublished experiments) would suggest an E_{f} difference of ca. 240–270 mV for the asymmetric complexes when $\Delta E = 0$.

(10) Prior studies[1] with symmetrical class II systems (where ΔE is necessarily zero, and $E^{\mathrm{IVCT}} \approx \chi$) clearly show that χ (in the fully localized limit) is essentially T independent (i.e., $\mathrm{d}E^{\mathrm{IVCT}}/\mathrm{d}T \approx 0$).

(11) Unpublished studies with (NH$_3$)$_5$Ru-pz-Ru(NH$_3$)$_5$)$^{5+}$, a class III system for which ΔE is necessarily zero and $E^{\mathrm{IVCT}} \approx 2H_{\mathrm{if}}$, reveal no T dependence for the latter. On the other hand, modest increases in IVCT oscillator strength accompany cooling of both **1** and **2** in CD$_3$NO$_2$ as well as acetone. This suggests that H_{if}, under class II or weakly class III conditions, may possibly increase slightly with decreasing T (thereby yielding a slight negative contribution to $\mathrm{d}E^{\mathrm{IVCT}}/\mathrm{d}T$).

(12) Curtis, J. C.; Blackbourn, R. L.; Hu, S.; Ennix, K. S.; Roberts, J. A.; Hupp, J. T. *Inorg. Chem.* **1989,** *28,* 3791.

(13) Recall that the fraction of charge transferred during intervalence absorption is approximately $1 - 2(H_{\mathrm{if}}/E^{\mathrm{IVCT}})^2$, if a simple two-state (Hush–Mulliken) description is employed.[7]

(14) See, for example: (a) Curtis, J. C.; Roberts, J. A.; Blackbourn, R. L.; Dong, Y.; Massum, M.; Johnson, C. S.; Hupp, J. T. *Inorg. Chem.* **1991,** *30,* 3856. (b) Hupp, J. T.; Neyhart, G. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1986,** *108,* 5349.

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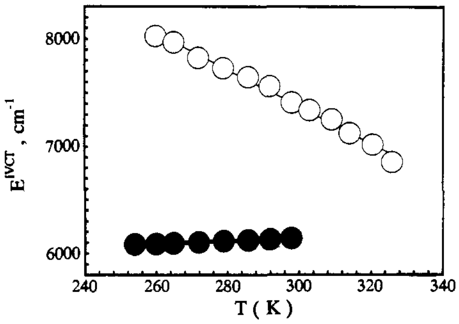

Figure 1. Temperature dependence of intervalence absorption for **1** (open circles) in nitromethane as solvent.

Finally, we have also examined **1** and **2** in acetone as solvent. Here the ΔEs are larger,[9] and both complexes appear to be valence localized. Consistent with this description, both display large negative absorption-energy temperature coefficients: $dE^{IVCT}(\mathbf{1})/dT = -8$ and $dE^{IVCT}(\mathbf{2})/dT = -12$ cm^{-1} deg^{-1}. Presumably, with appropriate modification of ancillary ligands and/or solvent, intermediate behavior could be seen. It might then be possible to use temperature changes to interconvert the complex between predominantly localized and predominantly delocalized forms. Work in progress with $(bpy)_2Cl$ Ru-pz-Ru$(NH_3)_4$(pyridine)$^{4+}$ supports this intriguing notion and will eventually be reported elsewhere.

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