Probing the localized-to-delocalized transition

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Detailed understanding of the transition between localized and delocalized behaviour in mixed valence compounds has been elusive as evidenced by many interpretations of the Creutz–Taube ion, \((\text{NH}_3)_5\text{Ru(pz)Ru(NH}_3)_5\)^{5+}. In a review in 2001, experimental protocols and a systematic model to probe this region were proposed and applied to examples in the literature. The model included: (i) multiple orbital interactions in ligand-bridged transition metal complexes, (ii) inclusion of spin-orbit coupling which, for \(d_{\pi}^5-d_{\pi}^6\) complexes, leads to five low-energy bands, two from interconfigurational \((d_{\pi}\rightarrow d_{\pi})\) transitions at the \(d_{\pi}^5\) site and three from intervalence transfer transitions, (iii) differences in time scale between coupled vibrations and solvent modes which can result in solvent averaging with continued electronic asymmetry defining ‘class II–III’, an addition to the Robin–Day classification scheme, and (iv) delineation of coupled vibrations into barrier vibrations and ‘spectator’ vibrations. The latter provide direct insight into localization or delocalization and time scales for electron transfer. In this paper, the earlier model is applied to a series of mixed-valence molecules.

Keywords: intervalence transitions; Creutz–Taube ion; classification of mixed-valence compounds; vibrational coupling; localized-to-delocalized transition

1. Introduction

As illustrated in the series of \(d_{\pi}^5-d_{\pi}^6\) complexes \(\text{cis,cis-[(bpy)_2ClRu(pz)RuCl(bpy)_2]^3+}\) (1), \(\text{[(NH}_3)_5\text{Ru(pz)Ru(NH}_3)_5]^{5+}\) (2) and \(\text{[(NH}_3)_5\text{Os(NN)Os(NH}_3)_5]^{5+}\) (3) relatively subtle changes in ligands and metal can significantly change the extent of electronic delocalization of the odd electron (Brown 1980; Prassides 1991). In the Robin–Day classification scheme (Robin & Day 1967), the odd electron in (1) is localized and the complex is in class II. It is delocalized in (3) which is in class III and it is ‘intermediate’ in (2). Both limiting descriptions have been suggested to apply depending on the observation made or the assumptions used in a theoretical analysis (Führholz et al. 1984; Demadis et al. 2001).

The underlying theoretical principles describing the localized-to-delocalized transition between class II and III were developed by Hush in a semiclassical treatment with further elaboration by Sutin and co-workers (Hush 1967, 1968;
Creutz et al. 1994; Brunschwig & Sutin 1999; Brunschwig et al. 2002). Piepho, Krausz and Schatz (PKS) developed a quantum treatment with coupled electron and nuclear coordinates resulting in energies and wave functions dependent on both (Piepho et al. 1978; Schatz 1980; Wong & Schatz 1981). The quantum treatment has been extended by Piepho et al. and by Hush & Reimers (Neuenschwander et al. 1985; Piepho 1990; Reimers & Hush 1996).

Density functional theory (DFT) has been applied to the electronic and molecular structure of \((\text{NH}_3)_5\text{Ru(pz)}\text{Ru(NH}_3)_5\)^{5+} assuming delocalization (Bencini et al. 1999). Energy minimization based on INDO/1 calculations predicts an unsymmetrical structure (Broo & Lincoln 1997). Van Voorhis et al. have used constrained DFT to overcome forced delocalization in unconstrained DFT and applied their method to the tetrathiafulvalene–diquinone radical anion (Wu & Van Voorhis 2006a,b). A treatment of the solvent has been presented that includes specific interactions between individual solvent molecules and coordinated ligands (Reimers & Hush 1996).

Theory provides a useful framework for discussing the class II–III transition but care must be taken in its application to transition metal complexes. There are multiple electronic interactions involving both bridge and metal-based orbitals. Molecular vibrations and solvent modes are coupled which have different time scales and coupling mechanisms. Different measurements can appear to give different results (Brown 1980; Prassides 1991; Demadis et al. 2001; Brunschwig et al. 2002; Crutchley 2005; D’Alessandro & Keene 2006a,b).

In this overview we revisit an earlier analysis which presented a model for analysing the localized-to-delocalized transition with an emphasis on transition metal complexes (Demadis et al. 2001). It provides a comprehensive and systematic basis for understanding this transition and for accounting for experimental observations.

2. Background

(a) Theory

The influence of electronic coupling on the barrier to intramolecular electron transfer, e.g. \([(\text{bpy})_2\text{ClRu}^{III}(\text{pz})\text{Ru}^{II}\text{Cl(bpy)}_2]\)^{3+} → \([(\text{bpy})_2\text{ClRu}^{III}(\text{pz})\text{Ru}^{II}\text{Cl(bpy)}_2]\)^{3+}, was initially treated by using the semiclassical approach of Hush (1967, 1968) with extensions by Sutin and co-workers (Creutz et al. 1994; Brunschwig & Sutin 1999; Brunschwig et al. 2002). For symmetrical electron transfer, with \(\Delta G=0\), the barrier was parametrized in terms of a reorganization energy, \(\lambda\), and a resonance energy, \(H_{ab}\). The reorganization energy assumed a single, coupled harmonic oscillator and \(H_{ab}\) arose from mixing initial and final diabatic electronic wave functions. Mixing of the diabatic states results in two new adiabatic states, \(E_1\) and \(E_2\), separated by \(E_2 - E_1 = \left\{ [\lambda (2X - 1)]^2 + 4H_{ab}^2 \right\}^{1/2}\). \(X\) is the reduced coordinate \(x/a\) with \(a\) or \(\Delta Q_{eq}\) the difference in equilibrium displacement for the harmonic oscillator in the adiabatic state. The absorption maximum for intervalence transfer is given by \(E_2 - E_1 = \tilde{\nu}_{\text{max}} = \lambda = \lambda' + 4H_{ab}^2/\lambda\), where \(\lambda'\) is the adiabatic reorganization energy including the effects of electronic coupling. As electronic coupling and \(H_{ab}\) are increased, \(\lambda'\) and \(\Delta Q_{eq}\) are
decreased. In the limit that $2H_{ab} \geq \lambda$, both are zero, there is no barrier to electron transfer, and the system is delocalized.

In the quantum PKS treatment, the Schrödinger equation is solved with the nuclear kinetic energy operator included giving expressions for energies and wave functions that depend on both electron and nuclear coordinates. The energy-coordinate curves that result are functions of $H_{ab}$, the quantum spacing for the coupled vibration and the reorganization energy (Piepho et al. 1978; Neuenschwander et al. 1985; Piepho 1990; Reimers & Hush 1996).

The single-mode approximation breaks down in failing to delineate between solvent and coupled vibrations. They are coupled differently to electron transfer and on different time scales. In order to explain the appearance of narrow solvent-independent IT bands with structural and IR evidence for localization, an intermediate class between class II and III has been proposed, class II–III. In this class, electron transfer is rapid on the solvent time scale. The solvent is averaged and no longer contributes to $\lambda$, $\nu_{\text{max}}$ or $\nu_{1/2}$ (Demadis et al. 2001).

(b) Experimental criteria

The semiclassical theory predicts a gradual transition from class II to III as molecules are modified and $H_{ab}$ increased relative to $\lambda$. In class II, a low-energy absorption band is predicted to appear at energy $\lambda$, which is strongly coupled to the solvent and to vibrations coupled to the change in structure with $\Delta Q_{eq} \neq 0$. In the delocalized limit, a band is predicted to appear having a 0–0 energy difference of $2H_{ab}$ which is coupled to symmetric vibrations and only weakly coupled to solvent (Ko & Ondrechen 1985; Ferretti et al. 1995).

Experimental criteria that have been applied to the class II–III transition have been summarized in a recent review by D’Alessandro & Keene (2006a). They include evaluation of $H_{ab}$ by IT absorption band measurements (Hush 1967, 1968; Creutz et al. 1994; Brunschwig & Sutin 1999; Brunschwig et al. 2002), analysis of metal-to-ligand and ligand-to-metal charge transfer absorption bands (Creutz et al. 1994; Brunschwig & Sutin 1999; Brunschwig et al. 2002), IT bandshape analysis (Creutz et al. 1994; Brunschwig & Sutin 1999; Nelsen 2000), electroabsorption (Stark effect) measurements (Bublitz & Boxer 1997; Walters 2004) and electrochemical measurement of the difference in redox potentials between adjacent one-electron couples (Creutz 1983; Richardson & Taube 1984; Ward 1995).

Even this extensive array of experimental probes is insufficient to delineate the localized-to-delocalized transition. There are others that give more insight.

3. Experimental model

(a) Near-IR/IR spectra

Existing theoretical descriptions are inadequate to explain the full range of experimental mixed-valence phenomena. Typically, they fail to include the multiple orbital interactions that lead to multiple transitions, assume delocalization or fail to account for time-scale differences among the vibrational and solvent modes that are coupled to electron transfer.
Multiple transitions and the variety of near-IR–IR spectral observations that have been observed are illustrated by the near-IR spectra of \((\text{bpy})_2\text{ClRu}(\text{pz})\text{RuCl}(\text{bpy})_2\)\(^{3+}\) in figure 1 and \((\text{bpy})_2\text{ClOs}(\text{BL})\text{OsCl}(\text{bpy})_2\)\(^{3+}\) (BL = pz, 4,4'-bipyridine) in figure 2 (Powers & Meyer 1980; Demadis et al. 1999a,b).

Figure 1. Near-IR spectrum of cis,cis-\((\text{bpy})_2\text{ClRu}^\text{II}(\text{pz})\text{Ru}^\text{III}\text{Cl}(\text{bpy})_2\)\(^{3+}\) in CD\(_3\)CN, including the results of bandshape analysis indicating three possible overlapping IT bands. The energies of the IC bands labelled with (?) are tentative, see text.

Figure 2. IR/near-IR spectra of (a) cis,cis-\((\text{bpy})_2\text{ClOs}(\text{pz})\text{OsCl}(\text{bpy})_2\)\(^{3+}\), (b) cis,cis-\((\text{bpy})_2\text{ClOs}(4,4'-\text{bpy})\text{OsCl}(\text{bpy})_2\)\(^{3+}\) in CD\(_3\)CN. Band assignments are provided in the text.

Multiple transitions and the variety of near-IR–IR spectral observations that have been observed are illustrated by the near-IR spectra of \(((\text{bpy})_2\text{ClRu}(\text{pz})\text{RuCl}(\text{bpy})_2\)\(^{3+}\) in figure 1 and \(((\text{bpy})_2\text{ClOs}(\text{BL})\text{OsCl}(\text{bpy})_2\)\(^{3+}\) (BL = pz, 4,4'-bipyridine) in figure 2 (Powers & Meyer 1980; Demadis et al. 1999a,b).
In this comparison, the exchange of Os for Ru in \[(\text{bpy})_2\text{ClM(pz)MCl(bpy)}_2\]_3 (M=Ru or Os) has a profound impact on the near-IR spectrum. The broad featureless absorption that appears at 1580 nm in CD$_3$CN for M=Ru is solvent dependent with $\tilde{\nu}_{\text{max}}$ varying with the solvent dielectric function $1/D_{\text{op}} - 1/D_{S}$. $D_{\text{op}}$ and $D_{S}$ are the optical and static dielectric constants of the solvent, respectively. The band width is greater than predicted by the Hush band width equation, $(\tilde{\nu}_{1/2})^2 = 16k_B T \ln 2$, by factors of 1.1–1.4 for this and related complexes (Powers & Meyer 1980).

Five near-IR/IR bands appear for the Os analogue, labelled I–V in figure 2a. They are narrow with $\Delta \tilde{\nu}_{1/2} = 500–1000 \text{ cm}^{-1}$ and solvent independent. The same five-band pattern is observed for $\mu$-N$_2$ complexes such as \[(\text{bpy})_2\text{ClOs(NN)OsCl(bpy)}_2\]$_3$ and \[(\text{tpy})(\text{Cl})_2\text{Os(NN)Os(Cl)}_2(\text{tpy})\] (Demadis et al. 1998a, b, 1999a, b). X-ray diffraction (XRD) data on the latter show that the structure is asymmetrical with $D_{r}(\text{OsII–Cl})/D_{r}(\text{OsIII–Cl}) \approx 0.04 \text{ Å}$. An intense $\nu(\text{NN})$ stretch also appears at 2011 cm$^{-1}$ in CD$_3$CN consistent with a local electronic asymmetry on the IR time scale (see below).

As shown in scheme 1, a five-band pattern is predicted, given the internal electronic structure of $d^5$ Os(III). Low symmetry and spin-orbit coupling at Os(III) ($\zeta(\text{OsIII})$, approx. 3000 cm$^{-1}$) split the $d\pi^5$ core into three levels giving rise to two interconfigurational (IC), $d\pi \rightarrow d\pi$, transitions, IC(1) and IC(2) (Kober 1982; Demadis et al. 2007). They gain intensity by spin-orbit coupling which mixes the $d\pi$ orbitals. Further, IT transitions create a $d^5$ core at initial Os(II) resulting in three IT transitions (scheme 1). The lowest energy transition, IT(1), is $[d\pi^2_{1,a}d\pi^2_{2,a}d\pi^2_{3,a}]d\pi^1_{3,b} \rightarrow [d\pi^2_{1,a}d\pi^2_{2,a}d\pi^2_{3,a}]d\pi^2_{3,b}$, with the metal sites labelled a and b.

IT and IC band energies are related by $E_{\text{IT}}(1) = \lambda$, $E_{\text{IT}}(2) \sim E_{\text{IT}}(1) + E_{\text{IC}}(1)$ and $E_{\text{IT}}(3) \sim E_{\text{IT}}(1) + E_{\text{IC}}(2)$. This neglects the reorganization energies of the IC transitions, which are expected to be negligible.

In this model, only IT(1) arises from ‘pure’ electron transfer. The others are of mixed IT–IC character. The IT bands in the spectrum of \[(\text{bpy})_2\text{ClOs(pz)OsCl(bpy)}_2\]$_3$ in figure 2 are labelled I, IV and V and the IC bands II and III.

This electronic structural model applies to all $d\pi^5$–$d\pi^6$ mixed-valence complexes. In $d\pi^5$–$d\pi^6$ mixed-valence complexes of Fe and Ru, the lower spin-orbit coupling constants ($\zeta(\text{RuIII})$, approx. 1000 cm$^{-1}$, $\zeta(\text{FeIII})$, approx. 400–500 cm$^{-1}$) result in smaller splittings between IT bands. The absorptivities of the IC bands depend on the
square of the spin-orbit coupling constant. They are greatly decreased in absorptivity and shifted into the IR making them difficult to observe.

In general, multiple electronic interactions and multiple IT bands are predicted for all mixed-valence transition metal complexes. Of the three IT bands, only the energies and widths of IT(1) are relevant to intramolecular electron transfer in the groundstate. IT(2) and IT(3) arise from mixed IT–IC transitions and result in IC excited states. These states are mixed into the groundstate and contribute to the overall resonance energy, $H_{ab}$. In applying the delocalization criterion, $2H_{ab}/\lambda \geq 1$, the total resonance energy, $H_{ab}$, and unperturbed, diabatic reorganization energy, $\lambda$, are the quantities to be evaluated. IT band measurements on a single band consisting of overlapping contributors, as in figure 1, overestimate $H_{ab}$. Measurements on only one of the three components underestimate $H_{ab}$.

The spectra of [(bpy)$_2$ClOs(pz)OsCl(bpy)$_2$]$^{3+}$ and [(bpy)$_2$ClOs(4,4′-bpy)OsCl(bpy)$_2$]$^{3+}$ are also dramatically different but the same five-state analysis applies to both. For the latter, IC bands appear at 4200 and 6000 cm$^{-1}$ and a broad, solvent-dependent band with overlapping IT components at approximately 7700, 11 900 and 13 700 cm$^{-1}$ with $\Delta\tilde{v}_{1/2} \sim 4000–5000$ cm$^{-1}$. The key difference between these two spectra is the decrease in band energy and width for the IT bands for BL=pz. As discussed below, this is a consequence of solvent averaging with the pz-bridged complex in class II–III and the 4,4′-bpy complex in class II.

Similarly, IT spectra for [(bpy)$_2$ClM(pz)MCl(bpy)$_2$]$^{3+}$ (M=Ru or Os) can be accounted for by assuming a common electronic origin. IT and IC bands are shifted to higher energy for M=Os due to the higher spin-orbit coupling constant. Based on a Gaussian deconvolution analysis of the [(bpy)$_2$ClRu(pz)RuCl(bpy)$_2$]$^{3+}$ spectrum, it has been estimated that IT bands appear at 5800, 7600 and 8500 cm$^{-1}$ with $\Delta\tilde{v}_{1/2} \sim 4000$ cm$^{-1}$. IC bands are predicted to appear at approximately 1600 and 2700 cm$^{-1}$ (figure 1). In this comparison, M=Ru is in class II and M=Os in...
class II–III. Once again, loss of a solvent contribution to $\lambda$ for M=Os explains the shift of IT bands to higher energy for M=Ru.

Multiple IT bands can also be observed for Ru complexes in class II–III. This is illustrated for [(Cl)$_3$Ru(tppz)Ru(Cl)$_3$]$^-$ in figure 3. There is also evidence for IC bands in the IR spectrum of this complex, but of very low absorptivity. The structure is asymmetrical with $\Delta$(Ru–N(pz))=0.03 Å and $\Delta$(Ru–Cl)=0.01–0.04 Å. A $\nu$(pz) band appears at 1596 cm$^{-1}$.

Although interpretation of the Creutz–Taube ion, [(NH$_3$)$_5$Ru(pz)Ru(NH$_3$)$_5$]$^{5+}$, has remained controversial, its properties are analogous to those of [(Cl)$_3$Ru(tppz)Ru(Cl)$_3$]$^-$ and it is also in class II–III (Führholz et al. 1984; Demadis et al. 2001). Coordination geometries are asymmetrical. Averaged IR band wave numbers are observed for spectator vibrations but symmetrical $\nu$(pz) stretches appear in the IR and Ru-N stretches at 324 and 262 cm$^{-1}$ act as barrier vibrations from resonance Raman measurements (Lu et al. 1995). Most near-IR measurements on this complex have been made on an intense, narrow (D//C$_{2h}$=2) band at 6410 cm$^{-1}$. It has been assigned to overlapping IT(2) and IT(3) transitions (Demadis et al. 2001). Additional IR near-IR bands are observed at 2000 cm$^{-1}$ (IC(1)), 3200 cm$^{-1}$ (IC(2)) and 4500–5000 cm$^{-1}$ (IT(1)), although in different media.

By contrast, in the delocalized complex [(NH$_3$)$_5$Os(NN)Os(NH$_3$)$_5$]$^{5+}$, no $\nu$(NN) stretch is detected. A five-band pattern appears at 4700, 5500, 5700, 8200 and 14 300 cm$^{-1}$ in poly-vinyl alcohol at 8 K. The bands arise from delocalized transitions from spin-orbit split $\pi$, $d_x$ and $\pi^*$ levels to a lowest, slightly antibonding $\pi^*$(d$\pi$) hole all within a delocalized d$\pi$ manifold (Rocha et al. in press; Dubicki et al. 1985).

(b) Time scales, solvent averaging and class II–III

As noted in §2, greatly decreased IT band energies and widths for [(bpy)$_2$ClM(pz)MCl(bpy)$_2$]$^{3+}$ with M=Os compared with M=Ru, provide evidence for solvent averaging (Demadis et al. 2001). This is a consequence of time-scale differences in the coupling mechanisms for vibrations and solvent. Solvent is coupled by changes in local electric fields that accompany electron transfer (Ulstrup 1979; Dogonadze et al. 1985; Reichardt 1988; Chen & Meyer 1998). Dynamics of solvent coupling have been measured by observing absorption band shifts following ultrafast laser excitation of charge transfer transitions (Kahlow et al. 1987; Horng et al. 1995; Fleming & Cho 1996).

A bimodal distribution of solvent relaxation times is observed with fast (inertial, 100–300 fs) and slow (frictional, greater than or equal to 1 ps) components. The time scales for coupled vibrations can be significantly shorter than those for the frictional component. A useful IR marker is the appearance or non-appearance of symmetrical bridging $\nu$(pz) and $\nu$(N$_2$) stretches. Appearance of symmetrical modes requires a local electronic asymmetry on the time scale of the vibration. The period of the $\nu$(pz) stretch for [(bpy)$_2$ClOs(pz)OsCl(bpy)$_2$]$^{3+}$ at 1599 cm$^{-1}$ is approximately 20 fs requiring a local electronic asymmetry on that time scale. This sets an approximate upper limit on $k_{ET}$ for intramolecular electron transfer of approximately $5 \times 10^{13}$ s$^{-1}$.

Rapid electron transfer and solvent averaging provide an explanation for decreased band energies and widths. In this regime, electron transfer is rapid on
the solvent time scale but slow on the vibrational time scale. A vibrational barrier remains but the solvent is averaged, which decreases $\lambda$, $\tilde{v}_{\text{max}}$, and $\Delta \tilde{v}_{1/2}$. As noted above, this has led to the addition of a class II–III to the Robin–Day classification scheme. In class II–III, the electronic distribution is asymmetrical but the surrounding solvent is averaged (Demadis et al. 2001).

Intermediate band widths have been observed as the time scale for electron transfer approaches and exceeds that for coupled solvent motions. This occurs in the series cis and trans-$[\{(NH_3)4(L)Ru(pz)Ru(L)(NH_3)4\}]^{5+}$ ($L=NH_3$, 3,5-Me$_2$py, py, 3-Fpy, 3-Clpy, 2,6-Me$_2$pz) in which variations in $L$ were used to vary the extent of electronic coupling across the bridge. This observation provides evidence for a transition between class II and class II–III and an explanation for intermediate band widths (Salaymeh et al. 1993).

\[ (c) \text{ Time scales, vibrational coupling} \]

Based on the analysis presented here, appearance of solvent-independent energies and narrow widths for IT bands is not a sufficient criterion for delocalization. A more direct probe comes from IR measurements on coupled vibrations. There are three types of coupling: (i) symmetrical bridging vibrations which require a local electronic asymmetry to be IR active, (ii) spectator vibrations for which $\Delta Q_e \sim 0$ but for which there is a change in frequency ($\omega \neq \omega'$; $\omega = 2\pi v$), and (iii) barrier vibrations, $\Delta Q_e \neq 0$, which are the origin of the vibrational barrier to electron transfer.

\[ (i) \text{ Symmetrical vibrations in the bridge} \]

The shortest vibrational time-scale markers are $\nu(pz)$ and $\nu(NN)$ symmetrical bridging vibrations in complexes such as $[(bpy)_2ClOs(pz)OsCl(bpy)_2]^3+$ and $[(NH_3)_5Os(NN)Os(NH_3)_5]^{5+}$. Their appearance depends on the existence of a local electronic asymmetry on the time scale of the vibrational period, 20–30 fs. In the former, $\nu_{sa}(pz)$ appears at approximately 1600 cm$^{-1}$ while there is no intensity for $\mu$-NN in $[(NH_3)_5Os(NN)Os(NH_3)_5]^{5+}$ (Dubicki et al. 1985).

An additional feature appears in the spectrum of $[(bpy)_2ClOs(pz)OsCl(bpy)_2]^3+$ in the enhanced absorptivity of $\nu_{sa}(pz)$ in figure 2. For this band, $\varepsilon = 2600$ M$^{-1}$ cm$^{-1}$ compared with $\varepsilon = 800$ M$^{-1}$ cm$^{-1}$ in cis-$[Os(bpy)_2(pz)Cl]^+$. This appears to be a non-Condon effect with coupling of the vibration to intervalence transfer across the bridge (Demadis et al. 1998a, b, 1999a, b; Rocha & Shreve 2004, 2006).

\[ (ii) \text{ Spectator vibrations} \]

For many peripheral ligand vibrations, $\Delta Q_e \sim 0$ but there is a frequency change between initial and final states. Their contribution to the barrier is minimal with $e^{-S} \sim 1$. There is also a small contribution from the frequency change, $1/2\hbar \Omega \coth(h\omega/2k_B T)$ with $\Omega = (\omega^2 - \omega'^2)/2\omega$ (coth $x = (e^x + e^{-x})/(e^x - e^{-x})$) (Hupp et al. 1992). Frequency changes can provide useful markers for localization and a probe for intramolecular electron transfer dynamics. An example is shown in figure 4 in the $\nu(bpy)$ ring-stretching region for $[(bpy)_2ClOs(BL)OsCl(bpy)_2]^{2+}$ and $[(bpy)_2ClOs(4,4'-bpy)OsCl(bpy)_2]^{3+}$ (BL = pz and 4,4'-bpy). The spectrum of $[(bpy)_2ClOs(4,4'-bpy)OsCl(bpy)_2]^{3+}$ is the sum of spectra for Os(III) and Os(II) with shifts of 5–7 cm$^{-1}$ providing direct evidence for
an asymmetric electronic distribution and localized oxidation states (Demadis et al. 1998a, b, 1999a, b; Rocha & Shreve 2004, 2006).

By contrast, the ν(bpy) spectrum of \([(\text{bpy})_2\text{ClOs(pz)OsCl(bpy)}_2]^{3+}\) is the average of those of Os(III) and Os(II) with bands appearing at 1316, 1423, 1450, 1465 and 1487 cm\(^{-1}\). These observations demonstrate localization in BL\(_{4,4}\)-bpy. In BL\(_{\text{pz}}\), the appearance of ν\(_{8a}\)(pz) at 1599 cm\(^{-1}\) also demonstrates localization even though the bpy bands are averaged. The two observations are not contradictory. The coalescence time scale for ν(bpy) (approx. 10 ps) is considerably longer than the ν\(_{8a}\)(pz) vibrational period (approx. 20 fs) allowing the intramolecular electron transfer rate constant to be bracketed in the range, 5\(\times\)10\(^{13}\) s\(^{-1}\)\(<k_{ET}<10^{11}\) s\(^{-1}\). IR line broadening and coalescence occur if there is chemical site exchange during the lifetime of the vibrational excited state. The use of IR band broadening to measure electron transfer chemical site exchange has been explored extensively by Kubiak and co-workers in measurements on ligand-bridged \(\mu\)-oxo ruthenium clusters (Ito et al. 1997; Londergan & Kubiak 2003; Salsman et al. 2005).

(iii) Barrier vibrations

From XRD data, bond length changes between Os(III) and Os(II) in \([(\text{tpy})(\text{Cl})_2\text{Os(NN)Os(Cl)}_2(\text{tpy})]\) are Δr = r(Os\(^{\text{II}}\)-Cl) − r(Os\(^{\text{III}}\)-Cl) = 0.04 Å. This points to a contribution to the electron transfer barrier by low wave number (less than 500 cm\(^{-1}\)) Os–Cl vibrations. The contribution to the reorganization energy by mode \(j\) is \(\lambda_{i,j} = S_j \omega_j\) with \(S_j\), the electron–vibrational coupling constant. It is related to the reduced mass, \(M_j\), and equilibrium displacement difference, Δ\(Q_{\text{e},j}\), by \(S_j = 1/2(M_j\omega_j/\hbar)(\Delta Q_{\text{e},j})^2\). For harmonic oscillator vibrational wave functions, the contribution to the barrier through the \(v = 0 \rightarrow v = 0\) channel is \(\exp(-S)(S^v/v!)\).

Figure 4. Mid-IR spectra of (a) cis,cis-\([(\text{bpy})_2(\text{Cl})\text{Os(pz)Os(Cl)}(\text{bpy})_2]^{3+}\) (thick line) and, for comparison, the average of the spectra of \([(\text{bpy})_2\text{ClOs(pz)OsCl(bpy)}_2]^{2+}\) and \([(\text{bpy})_2\text{ClOs(pz)OsCl(bpy)}_3]^{4+}\), thin line, (b) the same but for cis,cis-\([(\text{bpy})_2\text{Cl}Os(4,4'-\text{bpy})\text{Os(Cl)(bpy)}_2]^{3+}\) (Demadis et al. 1998a, b, 1999a, b; Rocha & Shreve 2004, 2006).
The barrier vibrations are the key to the localized-to-delocalized transition. There are limited experimental data from far-IR or Raman measurements. For $[(\text{NH}_3)\text{Ru(pz)Ru(NH}_3)\text{}_5]^{5+}$, Hupp et al. have reported resonance enhancements with excitation into the intense IT–IC band at 6410 cm$^{-1}$. Symmetric and asymmetric $v(\text{pz})$ vibrations are enhanced but the greatest enhancements are for Ru–N stretches at 324 and 262 cm$^{-1}$ (Lu et al. 1995).

(iv) Other time scales, other measurements

The appearance or non-appearance of symmetric bridging vibrations provides a reliable short time-scale probe for localization or delocalization. With its $10^{-17}$ s time scale, X-ray photoelectron spectroscopy (XPS) provides the ultimate short time-scale measurement and has been applied successfully to delocalized systems (Spreer et al. 1994). However, Hush has noted that the appearance of two XPS-binding energies is potentially ambiguous owing to the influence of the core hole produced by ionization on relaxation and localization (Citrin 1973; Hush 1975).

The appearance of well-defined, relatively unperturbed IC bands, such as those that appear in the spectra of $[(\text{bpy})\text{ClO(pz)OsCl(bpy)}]^{3+}$ and $[(\text{bpy})\text{ClO(NN)OsCl(bpy)}]^{3+}$, provide characteristic short time-scale markers for d$^{5}$ Os(III). However, interpretation of these spectra must be conducted with care since multiple bands are predicted and observed for delocalized complexes as shown, for example, by the appearance of five low-energy bands from 4700 to 14 300 cm$^{-1}$ for $[(\text{NH}_3)\text{Os(NN)Os(NH}_3)\text{}_5]^{5+}$ (Dubicki et al. 1985).

4. Conclusions and final comments

From the analysis and experimental data presented here, a clear picture emerges for describing the localized-to-delocalized transition in ligand-bridged transition metal complexes. The analysis is inherently complex. It involves multiple orbital interactions between metals using multiple orbital interactions on the bridge. Molecular vibrations and the solvent are coupled in different ways and with different time scales.

— Five low-energy bands are predicted in d$\pi^{5}$–d$\pi^{6}$ mixed-valence complexes. In class II and II–III, they arise from a combination of three interivalence transfer (IT) and two interconfigurational (IC) bands. In the delocalized limit, their origin is from a series of spin-orbit split, $\pi \rightarrow \pi^*$, d$_{5} \rightarrow \pi^*$ and $\pi^* \rightarrow \pi^*$ transitions within a delocalized d$\pi$ core.

— Only the lowest energy of the three possible IT bands arises from electron transfer within the groundstate. The other two bands are of mixed IT–IC character.

— There is an intermediate class between class II and III, class II–III. In class II–III, valences (oxidation states) are localized but solvent averaged. This occurs owing to the difference in time scales between coupled solvent and vibrational modes. In class II–III, IT band energies and widths are decreased relative to class II owing to the loss of a solvent contribution to $\lambda$.

— Intermediate IT band widths and partial solvent averaging are predicted as the time scales for electron transfer and solvent relaxation to become comparable and the transition from class II to class II–III occurs.
Localization versus delocalization is dictated by $2H_{ab}/\lambda$ but with $H_{ab}$ the total resonance energy from all three orbital interactions. $\lambda$ is the vibrational reorganization energy for the diabatic, unperturbed state.

IR line broadening and coalescence for spectator vibrations provide a basis for probing the dynamics of electron transfer. They are not a definitive probe for localization versus delocalization.

The IR appearance or non-appearance of symmetrical vibrations in the bridge provides the shortest time scale, most reliable means for deciding on localization versus delocalization. Measurement of barrier vibrations by far-IR or resonance Raman spectroscopy would be of great value.

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