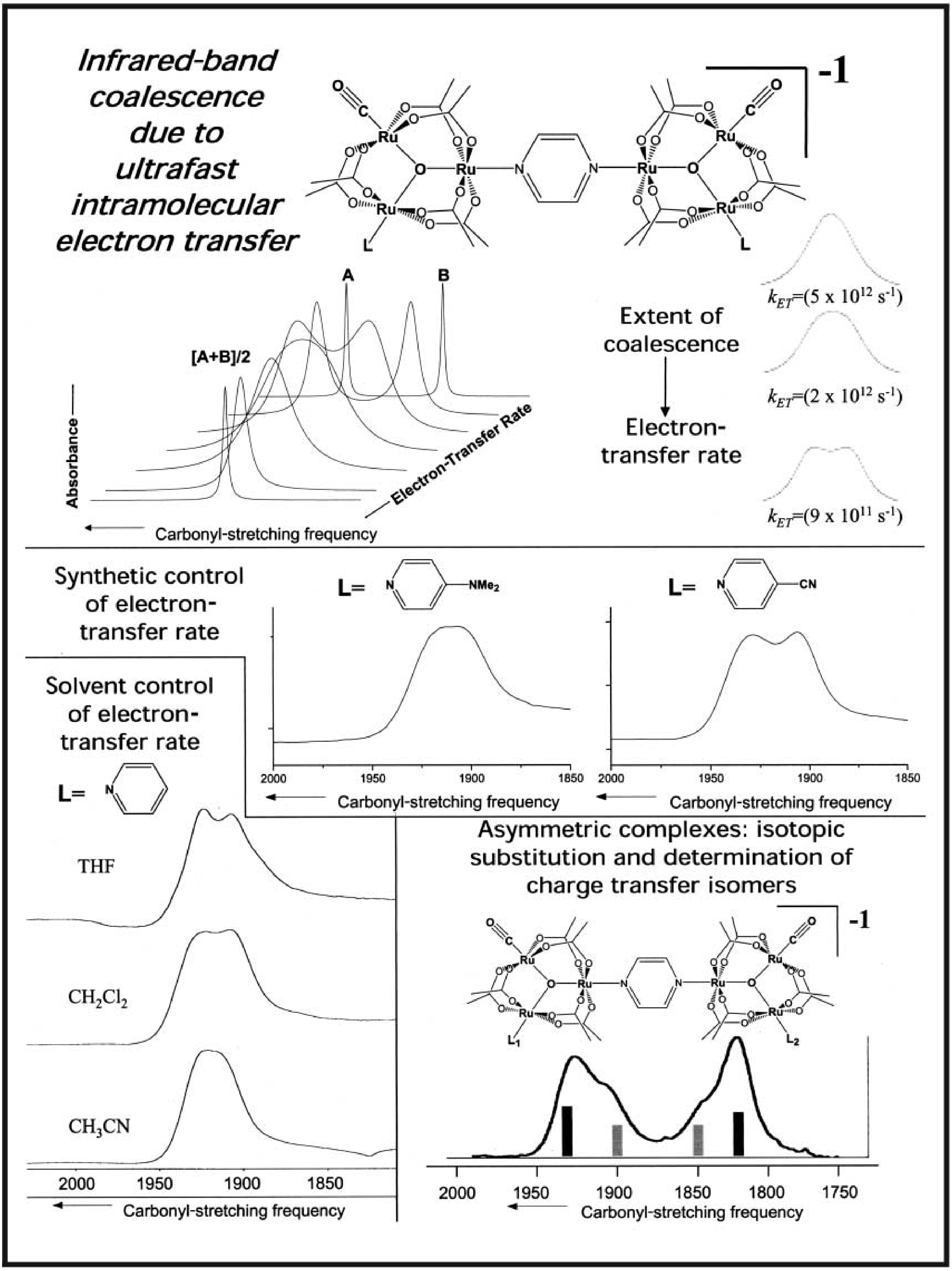

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DOI: 10.1002/chem.200305028

Chem. Eur. J. **2003**, *9*, 5962 – 5969

Electron Transfer and Dynamic Infrared-Band Coalescence: It Looks Like Dynamic NMR Spectroscopy, but a Billion Times Faster

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Abstract: Broadening and coalescence of infrared bands can occur due to chemical exchange processes occurring on very fast, femtosecond-to-picosecond timescales. One such fast process of recent investigation is intramolecular electron transfer in transition-metal complexes with strong communication between electron-donor and -acceptor sites. The observation of partial coalescence of metal–carbonyl stretching bands in hexanuclear ruthenium mixed-valence complexes due to electron-transfer rates on the order of 10^{11}–10^{12} s^{-1} is chronicled here. Several important advances have been made with the aid of dynamic infrared-band coalescence in these complexes, including the observation of dynamic solvent relaxation effects on electron-transfer rates, the determination of the equilibrium constant between charge-transfer isomers, and a reconsideration of the theory of electron transfer and delocalization in bridged, near-delocalized electron-transfer systems.

Keywords: cluster compounds · electron transfer · IR spectroscopy · mixed-valent compounds · solvent effects

Introduction: A Brief History of Infrared-Band Coalescence

The use of line broadening and coalescence in NMR to determine rates of dynamic chemical-exchange processes is well established.[1] An illustration typical of dynamic NMR spectroscopy is given in Figure 1. The characteristic timescale for dynamically broadened and coalesced resonances in NMR spectroscopy is typically on the timescale of microseconds to milliseconds, depending on the separation in field between exchanging features. The use of vibrational-band broadening to interrogate dynamic processes has been much less widespread and has been controversial at times. The characteristic timescale for the coalescence of infrared absorption bands or Raman shifts is approximately femtoseconds to picoseconds, again depending on the spectral separation between exchange partners: this faster timescale means that vibrational-band broadening can probe a very different class of dynamics (which are typically only accessible using "ultrafast" techniques). The processes which can occur on this timescale and potentially lead to vibrational-band broadening and coalescence include environmental relaxation (in liquid or solid media),[2] fast (and often minor) intramolecular structural changes,[3,4] dephasing of high-frequency vibrational modes due to thermally excited coupled low-frequency modes,[5–7] very rapid self-exchange proton transfer,[8] and intramolecular electron transfer (next section).

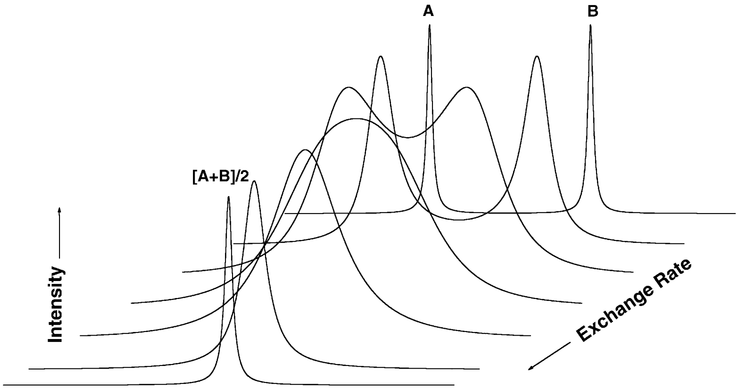

Figure 1. Increasing rates of chemical exchange lead to dynamic coalescence of spectral features. Right: "stopped exchange" with exchange rates slower than the measurement's intrinsic timescale. Left: "fast exchange" with exchanging features completely coalesced.

The case of [Fe(CO)$_3$(η^4-2,5-norbornadiene)]: Dynamic exchange on the timescale for IR-band coalescence has been invoked to explain several cases involving postulated fast, low-barrier structural changes. The most-discussed of these is [Fe(CO)$_3$(η^4-2,5-norbornadiene)] (**1**), whose temperature-dependent carbonyl-stretching spectrum in liquid and

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DOI: 10.1002/chem.200305028 © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

matrix-isolated samples exhibits a pattern typical of dynamic exchange (Figure 2).[9–13] The original proposed structural basis for a fast dynamic process leading to IR coalescence in **1** was a "turnstile" rotation of the three carbonyl ligands in relation to the diene ligand. A challenge to this mechanism for band broadening was offered by Strauss,[14] who argued that the temperature-dependent spectrum could be explained by an "intrawell" mechanism without invoking full "turnstile" rotation of the carbonyls.

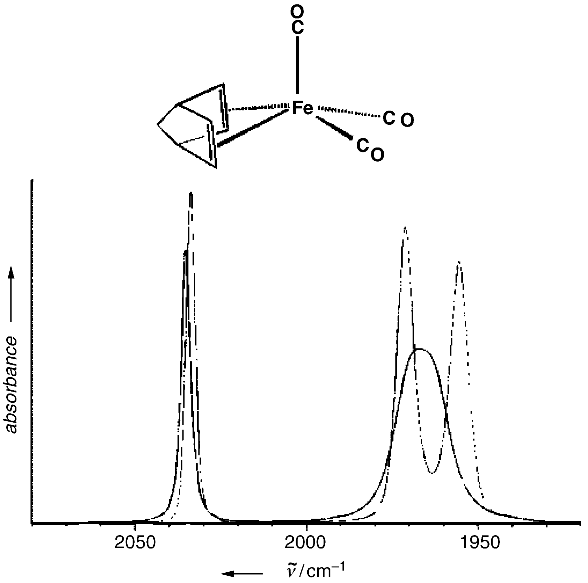

Figure 2. CO-stretching bands in the IR spectrum of $[Fe(CO)_3(\eta^4\text{-}2,5\text{-norbornadiene})]$ recorded in 2-methylpentane solution at 293 K (bold line) and 133 K (dotted line). Reproduced with permission from reference [13]. Copyright 1998, American Chemical Society.

Isotopic substitution and extensive spectral simulation[13] showed that use of modified Bloch equations (analogous to dynamic NMR spectroscopy) could replicate the observed band shapes.[15] In addition, a density functional study[16] showed that the carbonyl-stretching spectrum does not change significantly with torsional angle, thus refuting a key supposition of the "intrawell" mechanism of broadening proposed by Strauss. The DFT study predicted a very low torsional barrier on the order of 1 kcal mol^{-1}.

The conclusion of much study and discussion is that IR-band coalescence in **1** is due to a structural, dynamic rearrangement for which the thermal barrier is very low (largely due to symmetry considerations: the transition state for turnstile rotation in **1** is only rotated 60° from the minimum-energy conformation). At low temperatures, only the lowest-energy torsional conformations are populated, and the carbonyl spectrum for a low-symmetry C_s structure is observed. At high temperatures, there is significant thermal population *above* the torsional barrier, the intramolecular rotation occurs quickly, and the IR spectrum is more characteristic of a higher-symmetry C_{3v} structure.

Investigation of **1** and its radical anion in liquid solution by spectroelectrochemistry[17] showed similar IR-coalescence behavior for the carbonyl stretches of the radical anion, with notable differences in C–O frequencies (due to increased π-backbonding) and the degree of coalescence (due to either a difference in spectral separation between the coalescing bands or a slower rotation rate). The establishment of **1** as a system that clearly exhibits dynamic IR-band coalescence due to a fast structural change opened the door to quantitative examination of another fast chemical process occurring on the vibrational timescale: electron transfer (ET).

The contribution of the current authors to the general study of IR-band coalescence is completely in the context of intramolecular electron transfer. The pioneering work by Turner, Grevels et al. cited above and the observations of Cannon (in the following section) formed the conceptual basis for spectral interpretation in the work of the research groups of Ito and Kubiak; this body of work displays the most remarkable instance of infrared band coalescence to date.

A Probe of Intramolecular Electron-Transfer Rates

The first report of IR-band broadening to estimate intramolecular ET rates was in the case of trinuclear iron clusters of the type $[Fe_3(\mu_3\text{-}O)(OAc)_6L_3]$ (formally $Fe_3^{II,III,III}$) in the solid state.[18] Broadening of the asymmetric μ_3-O deformation mode was used to estimate Fe-to-Fe ET rates in these clusters, which appear to be partially valence localized on the vibrational timescale.

A more quantitative analysis of the effects of intramolecular ET on IR-band shapes was first presented in 1997.[19] Ligand-bridged "dimers" of carbonyl-substituted trinuclear ruthenium clusters, $[\{Ru_3\mu_3\text{-}O(CO)(OAc)_6(L)\}_2(\mu\text{-pyrazine})]^-$ (formally $Ru_3^{II,II,III}$–$Ru_3^{II,III,III}$; $\mathbf{2}^-$; Figure 3), exhibit a partial coalescence of carbonyl stretching bands (Figure 4).

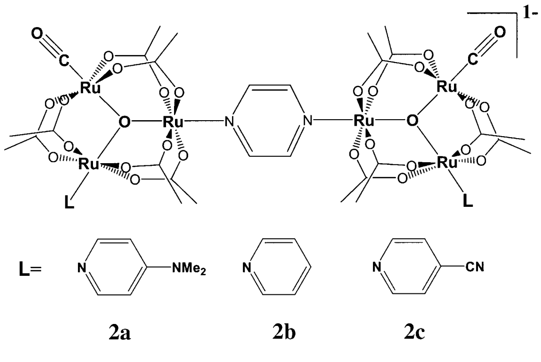

Figure 3. Pyrazine-bridged "dimers" of carbonyl-substituted trinuclear ruthenium clusters.

The Ru-bound carbonyl ligands of **2** are sensitive probes of the effective oxidation states of the clusters to which they are bound. Following normal π-backbonding arguments, more negative cluster oxidation states give lower C–O stretching frequencies. If an electron moves from one cluster to the other, both carbonyl ligand stretches are expected to shift in frequency: the carbonyl ligand bound to the donor cluster shifts to higher frequency, and the carbonyl ligand

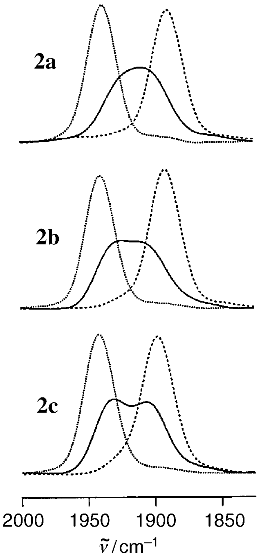

Figure 4. Carbonyl-stretching IR spectra for **2a**, **2b**, and **2c** in methylene chloride: reproduced with permission from reference [20]. Dotted lines: 0 oxidation states. Solid lines: −1 mixed-valence oxidation states. Dashed lines: −2 oxidation states. Copyright 1999, American Chemical Society.

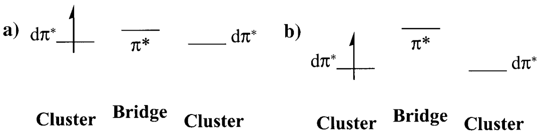

Figure 5. ET and electronic communication are influenced by orbital overlap between specific cluster and bridging ligand orbitals. Cluster orbitals can be tuned in energy by varying the donor character of the ancillary ligands L. a) A better donor ligand (the case of **2a**) pushes the cluster orbitals closer in energy to the bridging ligand LUMO, leading to more electronic communication between clusters. b) A weaker donor ligand (the case of **2c**) leads to less overlap between orbitals and less electronic communication between clusters.

bound to the acceptor cluster shifts to lower frequency upon ET from donor to acceptor.

If both carbonyl frequencies were the same and the odd electron were completely delocalized over both clusters, the −1 state would be averaged-valence, or formally $\mathrm{Ru_3^{II,II\frac{1}{2},III}Ru_3^{II,II\frac{1}{2},III}}$, and the −1 IR spectrum would exhibit a single C–O stretching peak close to the average of the 0 and −2 oxidation states. The fact that the −1 spectra display two partially coalesced peaks indicates that there is at least partial localization of the −1 charge on one of the two clusters. The degree of IR coalescence in $\mathbf{2}^-$ is dependent on the degree of electronic communication between clusters as varied by the ancillary ligands L.

Cyclic voltammetry and electronic spectroscopy measurements confirm this picture of increased IR-band coalescence with increased electronic communication between clusters.[19,20] The IR spectra of $\mathbf{2a}^-$–$\mathbf{2c}^-$ were simulated with a program based on modified Bloch equations (the same used by McClung[13] to simulate the IR spectra of **1**), with estimated ET rate constants on the order of 1×10^{11}–$2\times10^{12}\,\mathrm{s^{-1}}$. The direct observation of such fast, zero driving-force ET rates in mixed-valence or other systems is unprecedented and is only made possible here by the partial coalescence of IR bands.

The fine control (through ancillary ligands L) of electronic communication and ET rates in $\mathbf{2}^-$ is unique. The simple orbital picture invoked to rationalize this control is presented in Figure 5. Recent results[21] have shown the same degree of synthetic control of ET rates through substituents on the pyrazine bridge rather than ancillary cluster ligands. In addition, drastic reduction of the electronic communication between clusters by substitution of 4,4′-bipyridine as bridging ligand halts the IR-band coalescence, presumably by slowing the intramolecular ET rate to the "stopped exchange" limit for dynamic IR spectrosocopy (which could still be very fast, i.e., $>10^{10}\,\mathrm{s^{-1}}$).[20]

Solvent Effects on ET and Infrared-Band Coalescence

As noted above, IR-band broadening can be a sensitive probe of local dynamics of a molecule's (or a particular vibrator's) environment. In specific cases of exchange between occupation sites in solid media,[2] coalescence of bands corresponding to occupation in different sites was observed. Much progress has been made in the understanding of dynamic dipolar relaxation processes in liquids through ultrafast optical spectroscopy, particulary through time-resolved emission experiments, in which characteristic relaxation times have been calculated by fitting the time-dependent emission Stokes shift of dyes like Coumarin 153[22] in different solvents.

Observation of the strong solvent-dependence of IR-band coalescence in $\mathbf{2}^-$ was documented recently (see Figure 6).[23] Correlation between calculated ET lifetimes ($1/k_{\mathrm{ET}}$) and the solvent parameter t_{1e} from time-resolved emission red-shift experiments shows that ET in $\mathbf{2}^-$ is strongly

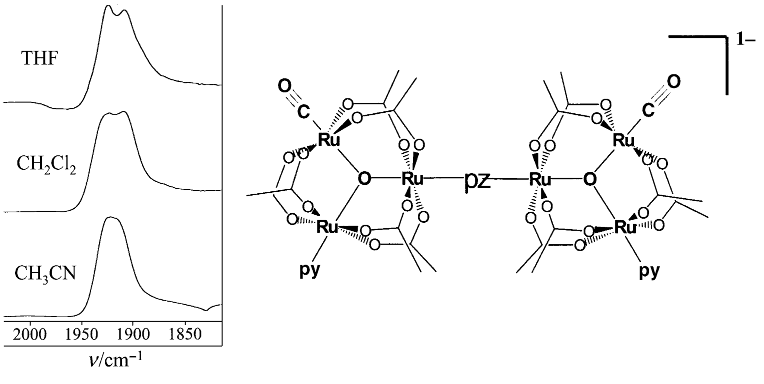

Figure 6. Solvent-dependence of IR-band coalescence in **2b**. In different solvents, a clear difference in the extent of coalescence is observed.

coupled to, and largely controlled by, dynamic solvent reorganization. The partial coalescence of carbonyl IR bands in **2**$^-$ indicates the ability of IR coalescence to probe a specific type of relaxation in liquids given the right probe molecule. It also emphasizes the specific importance of the solvent in a full theoretical description of intramolecular ET.

The Shape of Low-Barrier Potential-Energy Surfaces

ET in mixed-valence complexes has most frequently been described by using the semiclassical model of Hush,[24] which is convenient in that it includes the Marcus[25] reorganization energy for ET (λ) and provides a link between the energy and shape of the intervalence transfer (IT) electronic absorption band and the electronic-coupling parameter H_{AB} (Figure 7). Two effects of H_{AB} in the Hush model are to mix the two diabatic basis states (cluster$^-$–cluster and cluster–cluster$^-$ in Figure 7) and to lower the thermal barrier to ET across the two-minimum ground-state potential surface. The Hush model is essentially a perturbative treatment of electron transfer between two distinct sites and is expected to best describe systems in which ET sites are weakly communicating.

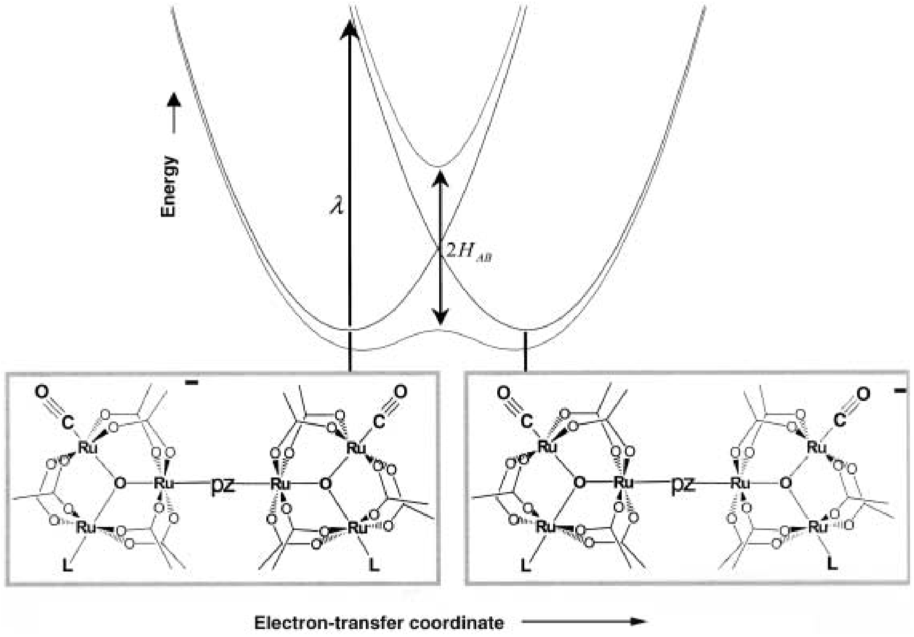

Figure 7. Potential-energy surfaces in the Hush model[25] for ET in symmetric mixed-valence complexes.

Thermal ET rates in mixed-valence complexes have been estimated by interpolating the shape of the ground-state surface from the shape of the observed IT band. A unique feature of **2**$^-$ is that the thermal rate of ET can be directly determined from IR spectroscopy. In the limit of strong electronic communication between clusters (large H_{AB} in the Hush model), the link between solution-sample IT bands and thermal ET is expected to be tenuous at best: a simple estimate of the thermal ET rates in **2**$^-$ based on IT band parameters predicts thermal ET rates two orders of magnitude slower than simulation of the IR spectrum. If a smooth, semi-classical potential-energy surface for ET is assumed, IR-band coalescence in **2**$^-$ appears to be a very sensitive probe of the thermal barrier to ET. From the same point of view, IR-band coalescence has also been shown to be a sensitive probe of the thermal barrier to torsional motion in **1**. In both low-barrier processes at relatively high temperatures,[26] there is significant thermal population above the thermal barrier and the processes occur fast enough for significant coalescence of IR bands.

Indeed, in the case of **2**$^-$, it is possible to simulate the partially coalesced IR C–O bands by using the thermal population along a low-barrier Hush surface, Figure 8 (making specific assumptions about the variation in carbonyl-stretching frequencies with position on the reaction coordinate). This alternative simulation method does not make any dynamic conclusions and does not use Bloch equations, but re-emphasizes two central points: 1) thermal population above a low thermal barrier leads to IR-band coalescence in the case of **2**$^-$, and 2) a two-minimum potential surface (implying partial charge localization) with a low but finite barrier is needed to reproduce the carbonyl IR spectra of **2**$^-$.

The strong solvent-dependence of the partially coalesced IR bands in **2**$^-$ shows that the coalescence is due to a dynamic process: that process is largely controlled by dynamic reorganization of the solvent. This is consistent with an ET reaction coordinate that includes not just intramolecular normal modes but also outer-sphere adjustments.

The modeling of ET rates across a one-dimensional Hush surface with solvent friction applied by means of a generalized Langevin equation approach[27]

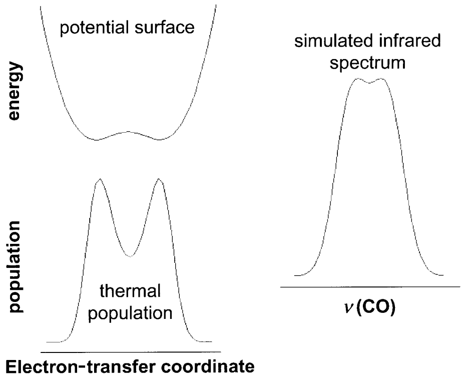

Figure 8. Simulation of IR coalescence in **2**$^-$ by using thermal population along the ET reaction coordinate.

does *not* result in rates similar to those calculated from the partially coalesced band shapes.[28] A more complex, multidimensional approach to the respective dynamic contributions of inner- and outer-sphere reorganization and the general problem of electronic delocalization may provide a better model for ET in **2**$^-$.

Dynamic Exchange of Two Unequal Populations: Determination of Charge-Transfer Isomers

Dynamic exchange between two unequal populations (in the simplest case, exchange between two distinguishable structures related by an equilibrium constant) is well-understood in dynamic NMR spectroscopy. Complexes of the type $[\{Ru_3O(CO)(OAc)_6(L_1)\}(\mu\text{-pyrazine})\{Ru_3O(CO)(OAc)_6(L_2)\}]^{1-}$, **3**$^-$, whereby $L_1 \neq L_2$,[29] present a more complicated challenge to the estimation of ET rates by IR-band coalescence. Compound **3**$^-$ has two distinguishable isomers related by ET between clusters, or "charge-transfer isomers", whereby one isomer is thermodynamically favored over the other. Figure 9 shows the Hush potential surfaces corresponding to this situation.

In examining the surfaces relating the two "charge-transfer isomers", two effects are notably in opposition. The electronic coupling (H_{AB}) tends to mix the ET basis states and delocalize the charge. The driving force (ΔG_0) tends to localize the charge on the thermodynamically favored cluster. The competition between these two effects leads to a decreased driving force (ΔG_1) in the presence of strong electronic communication between clusters, and thus a decreased equilibrium constant between isomers.

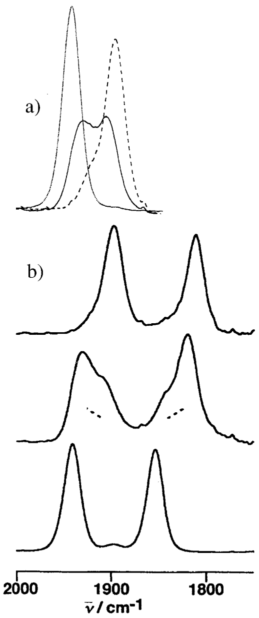

Figure 10. Infrared spectra of **3** with L_1 = 4-dimethylaminopyridine and L_2 = pyridine. a) Dotted line: 0 oxidation state. Solid line: −1 mixed-valence oxidation state. Dashed line: −2 oxidation state. b) Bottom: 0 oxidation state, exhibiting two C–O bands (high ν: $^{12}C^{16}O$, low ν: $^{13}C^{18}O$. Center: −1 mixed-valence oxidation state, exhibiting two unequal exchange pairs. Top: −2 oxidation state, again exhibiting two C–O bands.

The Ru–carbonyl IR spectra of a specific **3**$^-$ are shown in Figure 10. Four overlapping C–O stretching bands with a complex intensity pattern are expected, and the effects on the partially coalesced spectrum of equilibrium constant and ET rate are not separable. In NMR spectroscopy, one way to resolve overlapping resonances is to increase the field strength. In IR spectroscopy, isotopic substitution can have the same resolving effect. In **3**$^-$, a single substitution of $^{13}C^{18}O$ separates the four unresolved bands into two pairs of unequal exchange partners, allowing estimates of both the relative populations (equilibrium constants between isomers) and the exchange rate (ET rate).

The consequences of the isotopic substitution study results for **3**$^-$ are far-reaching. This is the first known determination of coexisting charge transfer isomers. The very low calculated equilibrium con-

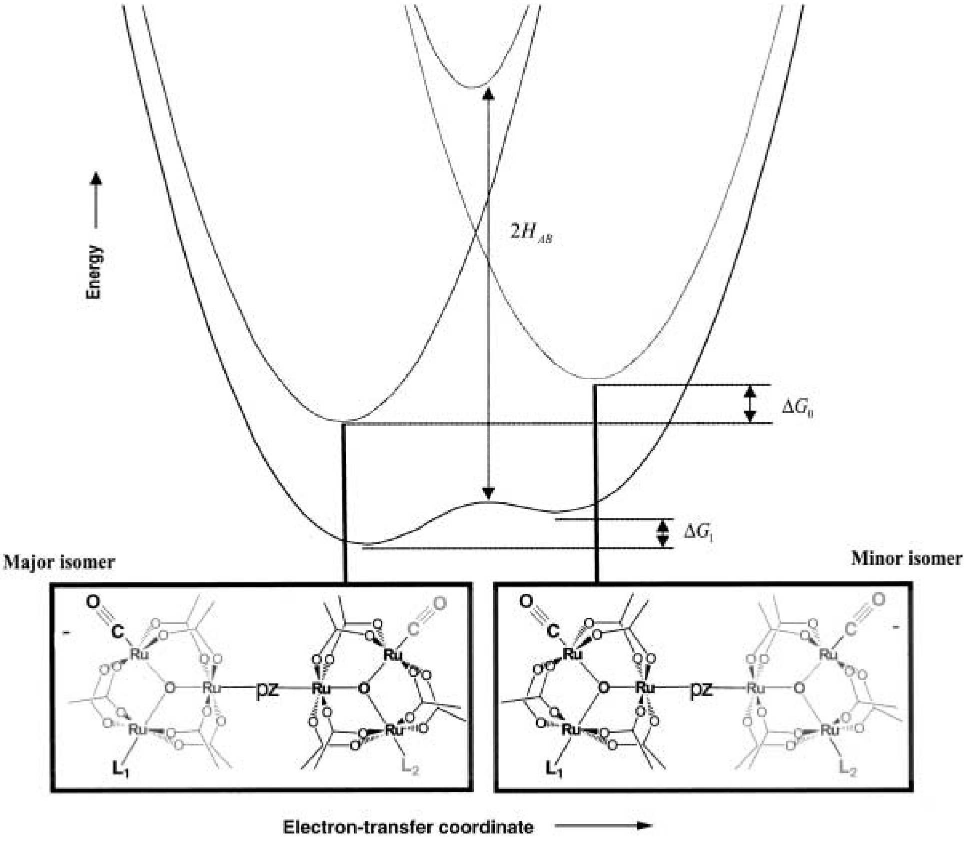

Figure 9. Hush potential surfaces for asymmetric mixed-valence complexes.

stants (between 1.6 and 3.4 for three variations of $\mathbf{3}^-$) suggest a dominant effect of electronic communication in these complexes. They also imply that, as suggested previously, the Hush semiclassical theory is not directly applicable in such a strongly coupled (yet still partially electronically localized) mixed-valence system. The relatively slow calculated ET rates (between $4\times10^{10}\,s^{-1}$ and $8\times10^{11}\,s^{-1}$) highlight the ability of IR-band coalescence to probe slightly slower dynamic processes in the case of unequal exchanging populations.

Vibronic Effects on Infrared Spectra

Observation of incomplete C–O band coalescence shows that pyrazine-bridged mixed-valence "dimers" of trinuclear ruthenium clusters like $\mathbf{2}^-$ and $\mathbf{3}^-$ are partially charge-localized on a timescale not typically accessible to other common spectroscopic techniques. This knowledge of partial localization can give unique insight into other spectroscopic properties of electronic systems in the poorly characterized regime between complexes exhibiting strongly communicating charge centers with dynamic, localized electronic structures and complexes with fully delocalized structures. Vibrational signatures of valence localization (separated bands corresponding to two charge sites) and delocalization ("averaged" bands) have been reported, but no partial coalescence due to ET has been documented save in Cannon's iron clusters (vide supra) and in $\mathbf{2}^-$ and $\mathbf{3}^-$.

The Creutz–Taube ion, $[(NH_3)_5Ru(\mu\text{-pz})Ru(NH_3)_5]^{5+}$ ($\mathbf{4}^{5+}$),[30] is a complex which evaded definitive characterization of its electronic structure for decades. A general consensus that $\mathbf{4}^{5+}$ is delocalized has emerged, although some features of its spectroscopy are still open to interpretation. The IR activity of symmetric modes of the bridging pyrazine ligand in $\mathbf{4}^{5+}$ and other, similar binuclear Os systems has been interpreted as evidence for electronic localization on the timescale of one period of these modes (~20 fs for ν_{8a} of pyrazine).[31–33] Isotopic substitution using [D$_4$]pyrazine in $\mathbf{2}^-$ showed IR activity in these same symmetric modes of pyrazine (Figure 11).[34] This observation appears to be consistent with the explanation that electronic asymmetry causes the IR activity in these otherwise forbidden modes, since $\mathbf{2}^-$ have already been classified as partially localized on a slower timescale by partial C–O band coalescence.

However, the anomalously large extinction coefficients of these bands arising from symmetric bridging ligand modes, especially as compared to their lack of intensity in $\mathbf{3}^0$, $\mathbf{3}^{2-}$, or in the "monomeric" trinuclear complexes $[Ru_3O(CO)(OAc)_6(L)(\eta^1\text{-pyrazine})]$, suggests that their IR intensity has another origin. A three-site Hückel-type vibronic model[35] has been proposed to explain the electronic spectroscopy of $\mathbf{4}^{5+}$ and other near-delocalized complexes; this model also tacitly predicts increased infrared absorption intensity in all of the modes vibronically coupled to the near-delocalized analogue of the "IT" electronic band mentioned above. Preliminary resonance Raman experiments[36] with excitation in this "IT" band show resonant enhancement of precisely the symmetric bridge modes that are observed in the infrared spectra of $\mathbf{2}^-$ and appear to support the argument of vibronic coupling (rather than electronic asymmetry) as the origin of infrared activity in symmetric bridging ligand bands.

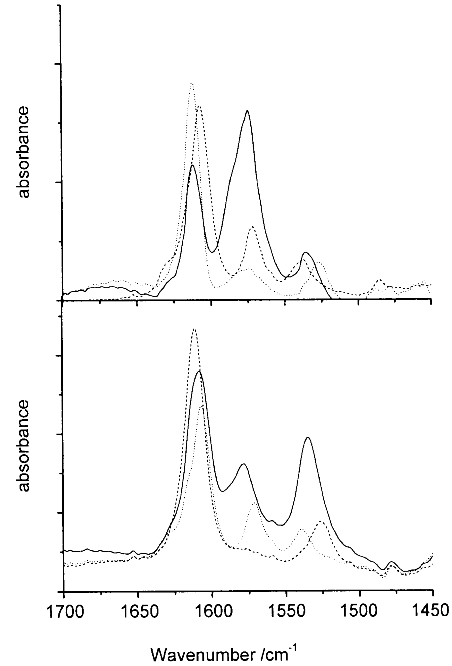

Figure 11. Infrared spectroelectrochemistry of **2a** with [H$_4$]pyrazine (top) and [D$_4$]pyrazine (bottom) as bridging ligand. Dashed line: 0 oxidation state. Solid line: −1 mixed-valence oxidation state. Dotted line: −2 oxidation state.

The three-site vibronic model explicitly includes the participation of the bridging ligand in electron transfer and communication, and it appears to overcome many of the deficiencies of the low-dimensional, semiclassical Hush model, which are highlighted by infrared results for $\mathbf{2}^-$ and $\mathbf{3}^-$. It is important to note here that without the partial coalescence of infrared C–O bands due to dynamics, none of this specific insight into the multidimensional, vibronic nature of these systems would have been possible.

Conclusion

Coalescence of infrared bands can be a very useful probe of *fast* dynamic processes with low thermal barriers. As such, it is a very different phenomenon from dynamic line broadening and coalescence in NMR spectroscopy and requires specific knowledge of the system exhibiting coalescence for correct interpretation of experimental results (the case of **1** is a much-debated example). It can uniquely probe low-barrier reactions and structural realignments in a quantitative fashion. In the specific instances of intramolecular electron transfer in $\mathbf{2}^-$ and $\mathbf{3}^-$, coalescence of oxidation-state-sensitive C–O bands yields quantitative information about rarely-observed *thermal* electron-transfer rates. By using $\mathbf{2}^-$ as a probe molecule, the C–O band shape is also a probe of the fast solvent-dipole relaxation process. Unequal exchange populations allow the determination of equilibrium constants between coexisting charge transfer isomers in **3**$^-$. The definitive assignment of **2**$^-$ as partially localized systems allows new interpretation of other aspects of the vibrational spectra of mixed-valence complexes, that is, the vibronically activated nature of symmetric bridging ligand modes. The specific and unique information from IR-band coalescence in **2**$^-$ and **3**$^-$ has led to a continued questioning and possibly conclusive revision of the paradigm used to explain strongly communicating mixed-valence complexes.

It is expected that similarly unique insight can be gained in other, as-yet-undiscovered molecular systems that display dynamic coalescence of infrared bands. We include the expectation that a good knowledge of any such system from other analytical techniques and appropriate calculations will be needed to accurately interpret the vibrational band coalescence.

Acknowledgments

We thank Professor J. J. Turner for helpful discussions in the early stages of work on **2**$^-$. Professor M. P. Maroncelli is acknowledged for extensive communication regarding simulations of solvent-dependent ET rates in **2**$^-$. NSF is acknowledged for continuing support of work on analogues of **2**$^-$: (CHE-0315593), and a JSPS-NSF travel grant is acknowledged for aid in transoceanic collaboration with the group of Professor T. Ito.

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