

## Exploring the Localized-to-Delocalized Boundary in Mixed-Valence Systems Using Infrared Spectroelectrochemistry

Reginaldo C. Rocha and Andrew P. Shreve\*

Bioscience Division, Mail Stop G755, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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Infrared spectroelectrochemistry has been used to explore the vibrational properties of a pyrazine-bridged osmium-polypyridine dimer as a function of its formally metal-centered oxidation states (i.e., Os<sup>II</sup>Os<sup>II</sup>, Os<sup>II</sup>Os<sup>III</sup>, and Os<sup>III</sup>Os<sup>III</sup>). The infrared spectrum of the "mixed-valent" species is particularly interesting and exhibits features consistent with both electronic localization and delocalization on the vibrational time scale, as revealed by the presence of both (i) a highly active totally symmetric mode from the bridging pyrazine ligand ( $\nu_{8a}$ ), and (ii) total coalescence of at least four modes from peripheral bipyridine ligands. The nature and origin of the observed peaks were confirmed by analysis of the shifts in vibrational frequencies accompanying deuteration of pyrazine and also by comparison of the data for the dimeric complexes with those for the parent monomers.

Mixed-valence charge-transfer molecular systems near the boundary of localized-to-delocalized behavior are of interest,<sup>1,2</sup> in part because of their importance in the context of vibrationally coupled fast electron-transfer dynamics.

It has been demonstrated that vibrational spectroscopies (see, for instance, refs 3 and 4) are useful and efficient probes in exploring such systems at the borderline of the Robin-Day<sup>5</sup> classes II and III, which reflects both the inherent time scale of these techniques (ca. 10<sup>-12</sup> s) and their ability to provide structural information. Steady-state infrared (IR) spectroscopy has particularly been used as a diagnostic tool for the study of localized versus delocalized behavior in mixed-valence complexes on the basis of either (i) the presence of totally symmetric vibrational modes involving the bridge, favoring a localized (i.e., symmetry-broken) description, or (ii) the observation of coalescence or broad-

ening of vibrational lines due to rapid electron transfer, supporting the (nearly) delocalized picture on the vibrational spectroscopic time scale.<sup>1</sup>

The problem, however, may be more challenging when features consistent with both electronic localization and delocalization are displayed in the very same IR spectrum. This is, indeed, the situation observed in the complex *cis-cis*-[(bpy)<sub>2</sub>(Cl)Os(pz)Os(Cl)(bpy)<sub>2</sub>]<sup>3+</sup> (**11**<sup>3+</sup>; where bpy = 2,2'-bipyridine, pz = pyrazine), for which there is previous experimental evidence for both valence trapping (presence of interconfigurational dπ–dπ transitions) and averaging (presence of narrow and solvent-independent intervalence charge-transfer bands) in the near-IR region.<sup>1,6</sup> IR activity in a totally symmetric vibrational mode of the bridging pyrazine near 1600 cm<sup>-1</sup> ( $\nu_{8a}$ ) and spectral coalescence for ancillary bipyridine vibrational peaks in the 1400–1500-cm<sup>-1</sup> range were also observed to exist as simultaneous markers for localization and delocalization, respectively.<sup>1,6</sup>

Motivated by the puzzling behavior displayed by this system, we performed and report here complementary IR investigations using spectroelectrochemistry (SEC). This approach has allowed us to monitor the continuous evolution of the vibrational spectra in the 1300–1700-cm<sup>-1</sup> region as a function of the molecular oxidation states (i.e., fully reduced [Os<sup>II</sup>Os<sup>II</sup>] – **11**<sup>2+</sup>, fully oxidized [Os<sup>III</sup>Os<sup>III</sup>] – **11**<sup>4+</sup>, and formally mixed-valent [Os<sup>II</sup>Os<sup>III</sup>] – **11**<sup>3+</sup> – species). The experiments were accomplished by modulation of the redox potentials, in situ, in a SEC cell suitable for thin-layer reflectance IR spectroscopy.<sup>7,8</sup> To provide further support to our assignments and interpretations, the monomers *cis*-

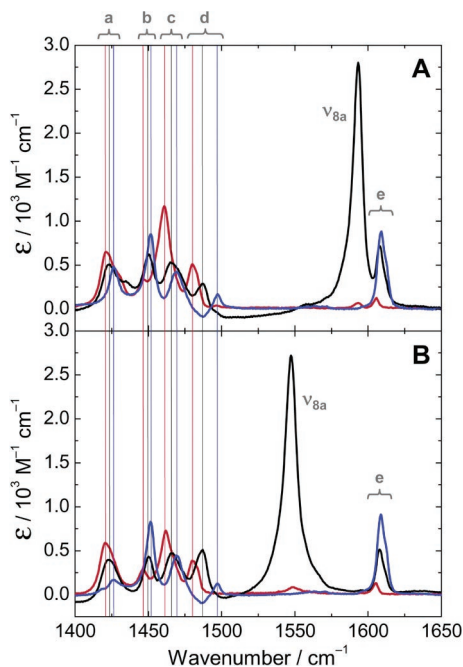
\* Corresponding author. E-mail: shreve@lanl.gov.

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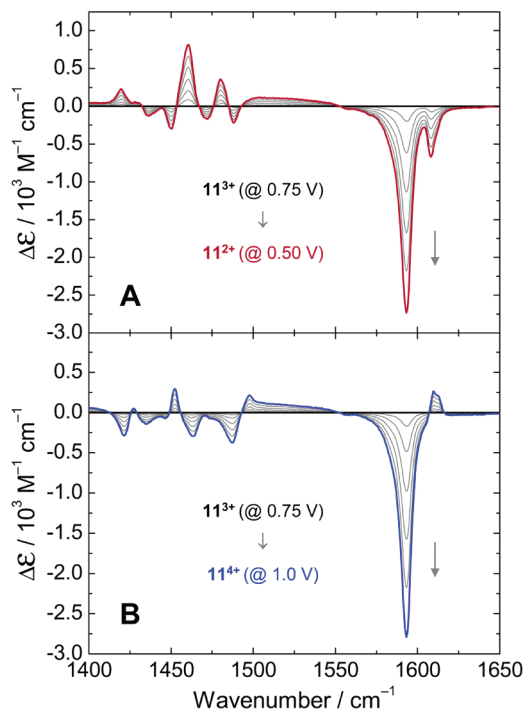
(8) Solution IR spectra were recorded on a Fourier transform instrument at 1 cm<sup>-1</sup> resolution (each spectrum was an average of 32 scans), by using dry CD<sub>3</sub>CN solvent and CaF<sub>2</sub> optical window with a 100-μm Teflon spacer in the spectroelectrochemical cell (~4-mm-diameter Pt working electrode, operating at room temperature). All solutions were ca. 5 mM sample and 0.1 M (*n*-Bu<sub>4</sub>N)PF<sub>6</sub> (TBAH) supporting electrolyte. A conventional three-electrode arrangement was used for cyclic voltammetric experiments (working electrode: 1-mm Pt disk; auxiliary electrode: coil of Pt wire; reference electrode: Ag/AgNO<sub>3</sub> 0.01 M). The sample solutions were all thoroughly deoxygenated with an Ar stream prior to each measurement.



**Figure 1.** IR spectra of the dimers  $11^{n+}$  (A) and  $22^{n+}$  (B) in acetonitrile- $d_3$  ( $CD_3CN$ ) solutions;  $n = 2$  (red), 3 (black), and 4 (blue).

$[Os(Cl)(bpy)_2(pz)]^{n+}$  ( $1^{n+}$ ) and the deuterated ( $pz-d_4$ ) version of both dimeric ( $22^{n+}$ ) and monomeric ( $2^{n+}$ ) species were also prepared and investigated in this study.<sup>9</sup>

The IR spectra for the three redox states of **11** are shown in Figure 1A. The most evident feature is the highly intense peak at  $1593\text{ cm}^{-1}$  ( $\epsilon = 2.8 \times 10^3\text{ M}^{-1}\text{ cm}^{-1}$ ), which appears only for the molecule in the “mixed-valent” ( $11^{3+}$ ) state. The association of this peak to the  $11^{3+}$  species is best illustrated in the differential spectroelectrochemical (SEC) progression shown in Figure 2, where the bleach evolving at  $1593\text{ cm}^{-1}$  is quite evident as  $11^{3+}$  (whose absorption spectrum is taken as background) is electrochemically converted into either  $11^{2+}$  (Figure 2A) or  $11^{4+}$  (Figure 2B) by reversible, mono-electronic reduction/oxidation.<sup>10</sup> This peak was definitively assigned to the totally symmetric  $\nu_{8a}$  mode<sup>11</sup> of the  $pz$  bridge on the basis of deuteration of the  $pz$  ligand. As can be seen in Figure 1B (see also Supporting Information), where the spectra for the  $pz-d_4$  modified complex are presented, the only change in frequencies upon deuteration of pyrazine is



**Figure 2.** Differential IR SEC reduction (A) and oxidation (B) of  $11^{3+}$  (reference species; black line) in  $CD_3CN/TBAH$ . [Potentials versus SHE; red and blue traces refer to the formation of  $11^{2+}$  and  $11^{4+}$ , respectively.]

**Table 1.** Summary of Infrared Vibrational Frequencies ( $\text{cm}^{-1}$ )

	a (bpy)	b (bpy)	c (bpy)	d (bpy)	e (bpy)	8a (pz)
$11^{2+}$	1421	1447	1461	1480	1606	1593
$11^{3+}$	1423	1450	1465	1488	1608	1593
$11^{4+}$	1426	1452	1469	1497	1609	
$1^+$	1420	1446	1462	1479	1606	1585
$1^{2+}$	1421	1451	1470	1496	1609	1596
$22^{2+}$	1421	1447	1462	1480	1605	1547
$22^{3+}$	1424	1450	1466	1487	1607	1547
$22^{4+}$	1427	1452	1469	1497	1609	
$2^+$	1421	1446	1462	1479	1605	1544
$2^{2+}$	1426	1451	1468	1496	1609	1557

the downshift of the peak assigned as  $pz[\nu_{8a}]$  from  $1593\text{ cm}^{-1}$  ( $pz-h_4$ ) to  $1547\text{ cm}^{-1}$  ( $pz-d_4$ ). This shift of  $46\text{ cm}^{-1}$  is consistent with that observed ( $42\text{ cm}^{-1}$ ) for free (uncoordinated) pyrazine.<sup>11b</sup> Except for this particular  $pz$  mode, all other spectral features (peak sets labeled a–e in Figure 1) have frequencies unchanged with deuteration and were all assigned to modes involving the peripheral  $bpy$  ligands. These five sets of vibrational frequencies were also observed in  $[Ru(bpy)_3]^{2+}$  and have been previously assigned by normal-coordinate analysis.<sup>12</sup>

Examination of Figures 1 and 2 indicates that the  $bpy$  modes in  $11^{3+}$  are seen as single peaks with frequencies intermediate between those of  $11^{2+}$  and  $11^{4+}$  (see Table 1). Thus, these features are assigned as coalesced lines rather than a sum of oxidized ( $Os^{III}$ ) and reduced ( $Os^{II}$ ) moieties. Such coalescence is typical for strongly coupled mixed-valence systems and has normally been attributed to fast electron-transfer dynamics compared to the vibrational time scale, indicating substantial electron delocalization.

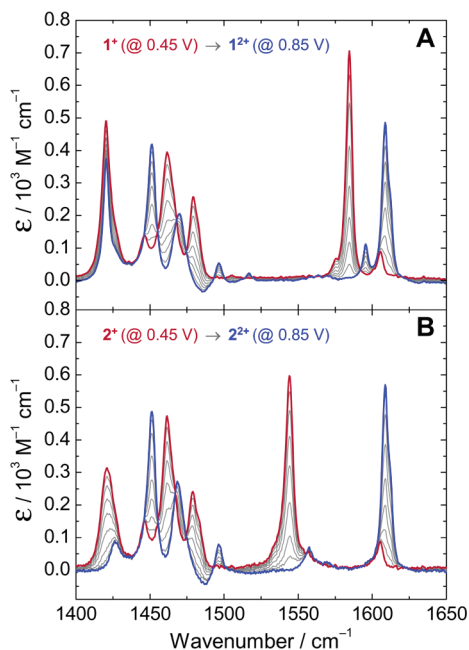
This idea, on the other hand, contrasts with the fact that IR activity of a totally symmetric mode centered on the

(9) *cis,cis*- $[(bpy)_2(Cl)Os^{II}(L)Os^{III}(Cl)(bpy)_2](PF_6)_2$  ( $L = pz-h_4$ ; **11**) and *cis*- $[Os^{II}(Cl)(bpy)_2(L)]PF_6$  ( $L = pz-h_4$ ; **1**) were prepared as described previously.<sup>6</sup> Similar procedures were adopted in the syntheses of the pyrazine-deuterated analogues **22** and **2**, respectively, except that pyrazine- $d_4$  (Aldrich) was used as  $L$ . The purity of products was assessed by comparison of their electrochemical and spectroscopic features with reported data.<sup>6</sup> Species resulting from  $Os(II)/Os(III)$  oxidation were generated by controlled-potential electrolysis of the isolated, reduced species at suitable potential (based on cyclic voltammetry). Measured half-wave potentials ( $E_{1/2}$  vs SHE) are 0.65 and 0.85 V for dimers ( $\Delta E_{1/2} = 200\text{ mV}$ ) and 0.66 V for monomers.

(10) Chemical/electrochemical reversibility was verified via complete recovery of the spectra in the reversed oxidative/reductive steps (e.g.,  $11^{2+} \rightarrow 11^{3+} \rightarrow 11^{4+} \rightarrow 11^{3+} \rightarrow 11^{2+}$ ); the application of potentials was based on the redox potentials ( $E_{1/2}$ ) determined by cyclic voltammetry. The potential separation ( $\Delta E_{1/2}$ ) between  $11^{3+}/11^{2+}$  and  $11^{4+}/11^{3+}$  provides a sufficiently large potential window<sup>9</sup> in which the “mixed-valent” species  $11^{3+}$  can be (electro)generated.

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**Figure 3.** IR SEC of the monomers  $1^{n+}$  (A) and  $2^{n+}$  (B) in  $\text{CD}_3\text{CN}/\text{TBAH}$  solutions (potentials versus SHE). Red and blue traces correspond to the reduced ( $n = 1$ ) and oxidized ( $n = 2$ ) species, respectively.

bridge ( $\text{pz}[\nu_{8a}]$ ) is observed. Such activity is often used as a signature for electron localization in symmetric dimers. In the case of electron localization, the nonequivalent oxidation states and charge distribution on each metal moiety introduces symmetry breaking and, consequently, a mechanism through which the nominally “fully symmetric” bridging modes can gain intensity in the IR absorption. [Note from Figure 1 that the reduced  $11^{2+}$  and oxidized  $11^{4+}$  isovalent species and their  $\text{pz}$ -deuterated analogues ( $22^{2+}$  and  $22^{4+}$ ) do not exhibit any significant absorption for  $\nu_{8a}$ .]

To further explore the mechanisms for  $\text{pz}[\nu_{8a}]$  IR activity in these osmium dimer systems, we compared the “mixed-valent” dimers  $11^{3+}$  or  $22^{3+}$  to monomers in either redox state. The motivation is that mononuclear complexes represent the extreme symmetry-broken situation, both structurally and electronically. As shown in Figure 3 and Table 1 (see also Supporting Information), even for  $1^+$ —which displays the highest IR activity for pyrazine among such monomers—the absorptivity of  $\text{pz}[\nu_{8a}]$  is only about one-fourth that of the dimer  $11^{3+}$ . The comparatively very large IR intensity in the dimer would be unexpected, even if it were fully electronically localized, since it would still present improved structural symmetry relative to the monomer. Hence, this direct comparison indicates that there is indeed a significant unexpected enhancement of IR activity for the totally symmetric mode  $\nu_{8a}$  of pyrazine in the “mixed-valent” dimer, even though the line coalescence of the bpy peaks simultaneously indicates a high degree of electronic coupling and charge delocalization.

Similar behavior has been observed by Kubiak et al.<sup>3,13</sup> in cluster dimers of the type  $[(\text{Ru}_3\text{O})(\text{OAc})_6(\text{CO})(\text{L})_2(\text{pz})]$ , where both (partial) coalescence of the peripheral carbonyl

groups and absorption in the totally symmetric  $\nu_{8a}$  mode of the bridging pyrazine are manifest in IR spectroscopy. In this case, it was suggested that the IR activity of  $\text{pz}[\nu_{8a}]$  is promoted by a vibronic coupling mechanism, rather than purely electronic asymmetry or localization.<sup>13</sup> The idea of electron transfer (exchange) dynamics strongly coupled to the vibrational motions of the intervening ligand on these cluster dimers has recently been reinforced via resonance Raman spectroscopy,<sup>4</sup> which revealed enhancement of only totally symmetric modes of the  $\text{pz}$  bridge accompanying excitation resonant with the “intervalence” charge-transfer bands. That result is in qualitative agreement with the proposition of a three-site vibronic coupling model<sup>14</sup> for the Creutz-Taube dimer,<sup>1,15</sup> and almost-delocalized analogues, in which both electronic and vibrational states for the two terminal metal centers plus the intermediate organic center (bridge) have to be explicitly taken into consideration.

Successful quantitative modeling of the results reported here requires at least three elements. First, incorporation of ligand ( $\text{pz}$ ) orbitals into the description of the electronic states of  $11^{3+}/22^{3+}$  is necessary to provide the possibility for strong vibronic coupling involving  $\text{pz}$  vibrations and low-lying electronic transitions. Second, significant electronic delocalization on the metal centers is needed to account for the peripheral bpy vibrations appearing at the intermediate, coalesced line positions between those of fully reduced and those of fully oxidized species. Finally, some degree of symmetry breaking on the vibrational time scale is required for the totally symmetric ( $\nu_{8a}$ ) vibration of  $\text{pz}$  to gain IR intensity. However, since electronic delocalization is also required, the symmetry breaking must not be a full one-electron metal-based charge asymmetric situation. As argued above, symmetry breaking alone is insufficient to produce the observed IR intensity in  $\text{pz}[\nu_{8a}]$  for the dimers. Thus, IR absorption enhancement due to mixing of electronic and vibrational states (i.e., vibronic coupling) in  $11^{3+}$  (or  $22^{3+}$ ) must also be invoked. Overall, it is increasingly clear that straightforward interpretation of vibrational spectroscopic observables for mixed-valence systems near the localized-to-delocalized boundary is difficult, and further experimental and theoretical investigation of vibrationally coupled electron transfer in such systems is still required.

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**Supporting Information Available:** Total and differential spectra (i.e., spectroelectrochemistry) for all (**11**, **22**, **1**, **2**) species reported herein. Full version of Table 1, including molar absorptivities for all vibrational modes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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