

Contrasting electroabsorbance behavior of two borderline class II/class III mixed-valence systems

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Abstract

Intervalence Stark effect spectroscopy of a symmetrically substituted and an asymmetrically substituted derivative of the Creutz–Taube ion, $(\text{NH}_3)_5\text{Ru-pyrazine-Ru}(\text{NH}_3)_5^{5+}$, is reported. Like the formally mixed-valent parent ion, both appear to lie near the boundary between valence delocalization and valence localization. Remarkably, despite the close structural similarities of the two compounds investigated, the corresponding electroabsorbance spectra are grossly different. Furthermore, neither spectrum is well fit by a classic Liptay approach. An alternative, qualitative approach that allows for the possibility that the externally applied electric field itself affects the degree of valence delocalization and, therefore, the electroabsorbance spectrum, was employed. The alternative approach relies upon the availability of compounds closely analogous to the investigated compounds, but differing slightly in degree of redox asymmetry. A subtle method for creating such compounds is to partially encapsulate a parent compound with a crown ether, such that a lower symmetry assembly is obtained. Using this approach the unusual Stark responses, including the disparate responses for symmetric vs. asymmetric structures, are reasonably well reproduced. Intervalence-enhanced resonance Raman spectra provide additional support for the proposed interpretation.

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1. Introduction

The Creutz–Taube ion, $(\text{NH}_3)_5\text{Ru-pyrazine-Ru}(\text{NH}_3)_5^{5+}$ (**1**), was one of the first intentionally prepared mixed-valence complexes. It was initially intended to serve as a model system for evaluating key intramolecular electron transfer reaction parameters – specifically, reorganization energies and electronic coupling energies – from intervalence absorption band energies and intensities [1,2]. The complex was found to display the hoped-for intervalence absorption, but the properties of the absorption band differed from those anticipated from the classical theory of Hush [3] for Robin–Day class II

(valence localized) systems [4]. The band is lower in energy and much narrower than had been anticipated. Additionally, it is characterized by substantial oscillator strength and an asymmetric rather than Gaussian lineshape. It is now largely accepted that the unanticipated spectral properties are consequences of intrinsic valence delocalization – likely via a mechanism entailing direct three-site (metal–bridge–metal) mixing rather than superexchange type bridging ligand (pyrazine) participation [5–7]. Indeed, from intervalence-enhanced Raman spectroscopy [8,9], a reasonably good limiting description of the transition appears to be electron promotion from a three-center bonding orbital (metal–bridge–metal) to two-center non-bonding orbital (metal–metal), as opposed to a simple metal-to-metal charge transfer; see Fig. 1 [10]. Perhaps the most compelling experimental evidence for intrinsic valence delocalization, i.e.,

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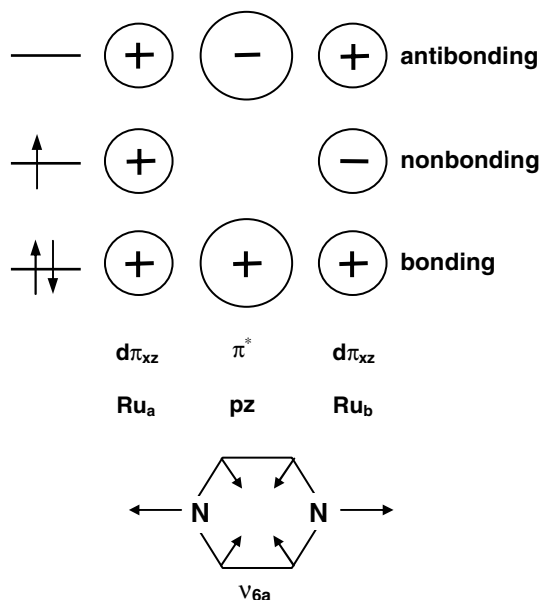
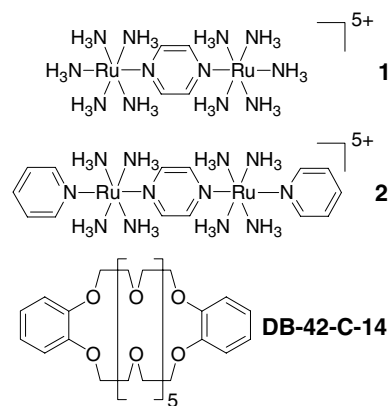


Fig. 1. Qualitative three-state orbital diagram for the Creutz–Taube ion. The combination of two $d\pi_{xz}$ (Ru) orbitals and one π^* (pyrazine) orbital yields three-center bonding and antibonding molecular orbitals, and a two-center non-bonding orbital. In this model, the intervalence transition corresponds to promotion of an electron from the bonding orbital to the antibonding orbital. Raman measurements show that the v_{6a} mode of pyrazine is strongly coupled to the intervalence transition.

Robin–Day class III behavior, comes from electroabsorbance or Stark spectroscopy. According to Liptay, an electronic transition that involves a change in dipole moment will display a second-derivative Stark spectral component whose magnitude is proportional to the dipole moment change or net charge-transfer distance [11]. Consistent with the scheme in Fig. 1 or other charge-delocalized descriptions, the experimental Stark spectrum of **1** has essentially no second-derivative character [12,13].

Despite the delocalized electronic description, the Creutz–Taube ion appears to fall close to the class III/class II boundary, perhaps even comprising a “class III–II” system in the language of Demadis et al. [14]. Evidence for borderline behavior comes, in part, from studies of chemical perturbations. Seemingly small perturbations, either of the external environment or the primary coordination sphere, can induce substantial spectral changes – changes that appear to signal the onset of charge localization [15]. This is especially true when the perturbations introduce a degree of redox asymmetry into the system. (“Redox asymmetry” is defined as the energy difference between vibrationally relaxed final and initial states in the hypothetical limit of no electronic coupling. For completely symmetrical mixed-valence systems, the redox asymmetry is zero.) For example, selective encapsulation of one end of the Creutz–

Taube ion by a large crown ether causes significant intervalence spectral broadening, intensity loss, and blue shifting. Similar but larger crown-derived effects are found with a closely related complex, *trans,trans*-(pyridine)(NH₃)₄Ru-pyrazine-Ru(NH₃)₄(pyridine)⁵⁺ (**2**) [16]. Electrochemical measurements with a model monomeric compound show that single-site encapsulation with dibenzo-42-crown-14 (**DB-42-C-14**) introduces a zeroth-order redox asymmetry of about 30 kJ mol^{−1} or 300 mV [17]. (The redox potentials of ammine complexes are highly solvent dependent because of hydrogen bonding between the ligated amines and solvent molecules. The neutral crown ether comprises a local solvent environment. By encapsulating only one of the two available redox sites, the sites are differentially solvated, resulting in redox asymmetry.) Additionally, as discussed further below, intervalence-enhanced Raman scattering measurements show that the symmetry reduction is accompanied by substantial quantitative changes in the nature of the vibrations coupled to the intervalence excitation. Notably, elimination of the asymmetry by addition of a second crown ether, such that both ends of the complex are encapsulated, reverses almost completely the vibrational and electronic spectral changes [18,19].



With these observations in mind, we reasoned that additional studies of borderline class II/class III systems – especially electroabsorbance studies – might prove instructive, particularly if these systems approached the class II/class III boundary even more closely than does **1**. We also reasoned that given the extraordinary sensitivity of such systems to the introduction or modulation of redox asymmetry, the Stark field itself might engender partial localization (or at least polarization) and, therefore, non-classical electroabsorbance responses. A similar point has recently been made in a more general way by Treynor and Boxer [20]. As shown below, we indeed do find evidence for non-classical (non-Liptay) behavior that

may well reflect incipient electric-field-induced charge localization and/or delocalization. Curiously, however, the putative field-induced effects are manifest in distinctly different ways for symmetrical vs. moderately asymmetrical mixed-valence systems.

2. Experimental

2.1. Materials

Di-ruthenium complexes **1**, **2**, **3**, and **4** were synthesized, as 4+ ions (hexafluorophosphate salts), according to the literature methods [15]. Butyronitrile was purchased from Aldrich and stored over molecular sieves. NOPF₆, employed as an oxidant, was purchased from Strem and used as received.

2.2. Stark spectroscopy

Samples were prepared by dissolving ≈ 1 –5 mg of the 4+ ions in 1–2 mL of butyronitrile in a quartz cuvette with a Teflon screw top cap. Small aliquots (a few microliters) of a saturated NOPF₆-butyronitrile solution were added to the cell, the mixture was agitated for ≈ 2 min, and the NIR absorption spectrum was recorded. Further, oxidant was added until the absorption intensity reached a maximum. The sample was then filtered through a 0.22 μm Teflon filter and used immediately. Stark measurements were performed using the same experimental setup as previously described [21]. Ni coated (~ 7 nm) glass slides, prepared by thermal evaporation, were used as semi-transparent electrodes. The cell pathlength was typically 50 μm . Typical field strengths were 6 – 8×10^7 V/m and typical oscillation frequencies were 220 Hz. Signals were detected by lock-in amplification at twice the modulation frequency.

2.3. Stark absorption analysis

Analysis of the data was initially performed using the Liptay method [11] as described in detail elsewhere [22]. Briefly, each Stark spectrum was fit to a linear combination of the zeroth, first, and second derivatives of the low-temperature absorption spectrum $A(v)$

$$\Delta A(v) = \left\{ A_z v + \frac{B_z v}{15hc} \frac{d[A(v)/v]}{dv} + \frac{C_z v}{30h^2 c^2} \frac{d^2[A(v)/v]}{dv^2} \right\} \mathbf{F}_{\text{int}}^2 \quad (1)$$

In Eq. (1), $\Delta A(v)$ is the frequency-dependent absorption change resulting from electric-field modulation, h is Planck's constant, c is the speed of light in vacuum, and v is the frequency of the absorbed light. $\mathbf{F}_{\text{int}}$ is the internal electric field experienced by the chromophore and can be written as

$$\mathbf{F}_{\text{int}} = f \cdot \mathbf{F}_{\text{ext}}, \quad (2)$$

where $\mathbf{F}_{\text{ext}}$ is the externally applied electric field and f is the local-field correction. $f = 1.3$, a value typically assumed for organic solvents [12,13], was used. It should be noted, however, that uncertainties of perhaps 20% exist for f . The coefficients A_z , B_z , and C_z provide information about electric-field-induced changes in the transition dipole moment, and about excited-state/ground-state polarizability and dipole moment differences, respectively. The molecular parameters are determined as follows:

$$A_z = \frac{\langle \alpha_m \rangle}{3} + \frac{1}{30} (3\cos^2 \chi - 1) [3\langle \beta_m \rangle - 2\langle \alpha_m \rangle], \quad (3)$$

$$B_z = \frac{5}{2} \text{Tr} \Delta \alpha + (3\cos^2 \chi - 1) \left(\frac{3}{2} \hat{\mathbf{g}} \cdot \Delta \alpha \cdot \hat{\mathbf{g}} - \frac{1}{2} \text{Tr} \Delta \alpha \right), \quad (4)$$

$$C_z = |\Delta \mu_v|^2 [5 + (3\cos^2 \xi - 1)(3\cos^2 \chi - 1)]. \quad (5)$$

In these equations, $\langle \alpha_m \rangle$ and $\langle \beta_m \rangle$ are the scalar portions of the transition moment polarizability and hyperpolarizability tensors, $\text{Tr} \Delta \alpha$ is the trace of the polarizability difference between the excited and ground electronic states, $\hat{\mathbf{g}} \cdot \Delta \alpha \cdot \hat{\mathbf{g}}$ is the polarizability change along the transition moment ($\hat{\mathbf{g}}$ is the unit vector), $\Delta \mu_v$ is the vector change in dipole moment, χ is the angle between the light and electric-field vectors, and ξ is the angle between transition dipole moment and $\Delta \mu_v$ vectors.

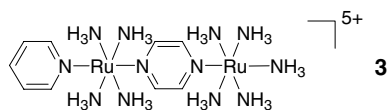
3. Results

3.1. Choice of systems

Delocalization in the Creutz–Taube ion arises primarily from strong π back-bonding by the Ru $d\pi_{xz}$ orbitals into the π^* orbitals of pyrazine (the z -direction coincides with the metal–metal axis; the x -direction is perpendicular to the pyrazine plane). One way of diminishing the electronic coupling responsible for delocalization is to replace the purely σ bonding ammine ligands trans to the bridge with π^* -orbital-containing ligands capable of competing with pyrazine for Ru $d\pi_{xz}$ electron density [2,15]. **2** is a good example and was chosen for further investigation.

As noted above, another way of influencing the extent or depth of delocalization is to introduce redox asymmetry. For a simple two-state system lacking appreciable vibronic coupling, the comparison of interest is twice the electronic coupling energy, H_{ab} , vs. the sum of the reorganization energy, λ , and the redox asymmetry, ΔE . While the Creutz–Taube ion likely satisfies neither the two-state criterion nor the negligible vibronic coupling criterion, redox asymmetry will nevertheless influence electronic localization/delocalization. Attractive examples of asymmetry introduction, because they leave unchanged other effects such as back-bonding, are crown-ether adducts of otherwise symmetrical

systems. Unfortunately, our attempts to examine such systems by Stark spectroscopy were inhibited by an inability to find a solvent that permitted both stoichiometric adduct formation and low-temperature glass formation. Consequently, asymmetry was engendered by ligand alteration and *trans*-(pyridine)(NH₃)₄-Ru-pyrazine-Ru(NH₃)₅⁵⁺ (**3**) was examined.



3.2. Low-temperature electronic absorption

Fig. 2 shows the relative intensities of the intervalence absorption spectra of **1**, **2**, and **3** at 77 K in a butyronitrile glass as solvent. The band maxima for **1** and **2** are slightly red shifted compared to their room temperature values in CH₃CN (6240 vs. 6270 cm⁻¹ for **1** and 5860 vs. 5940 cm⁻¹ for **2**). The absorption band for **2** is marginally wider than for **1**, but both are slightly narrower than the corresponding room temperature absorption bands. Like the room temperature spectra, the low-temperature spectra are highly asymmetric, with diminished absorbance on the low-energy side of the band maximum. In contrast, the intervalence band for **3** is nearly Gaussian. At low temperatures, however, this band is also clearly asymmetric, with diminished intensity on the low energy side. Unlike **1** and **2**, the absorption band for **3** is significantly blue shifted (7400 vs. 6270 cm⁻¹) and broader (2540 vs. 2420 cm⁻¹) than the room temperature absorption in CH₃CN. Despite the lineshape differences, the transition dipole moments at 77 K for the three complexes are similar: $\mu_t \approx 0.75$ e Å.

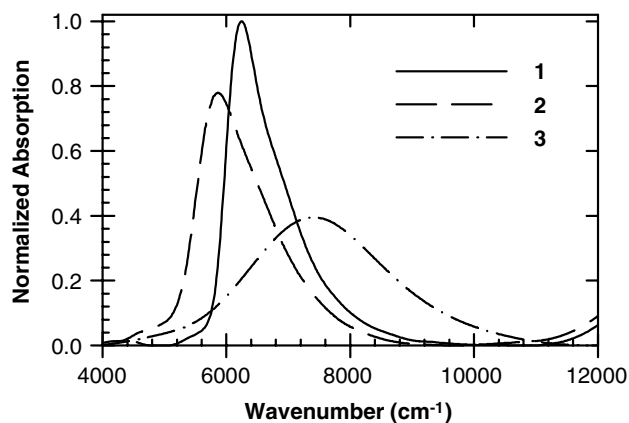


Fig. 2. Normalized IT absorption bands for **1** (solid line), **2** (long dashed line), and **3** (dashed-dotted line) butyronitrile at 77 K.

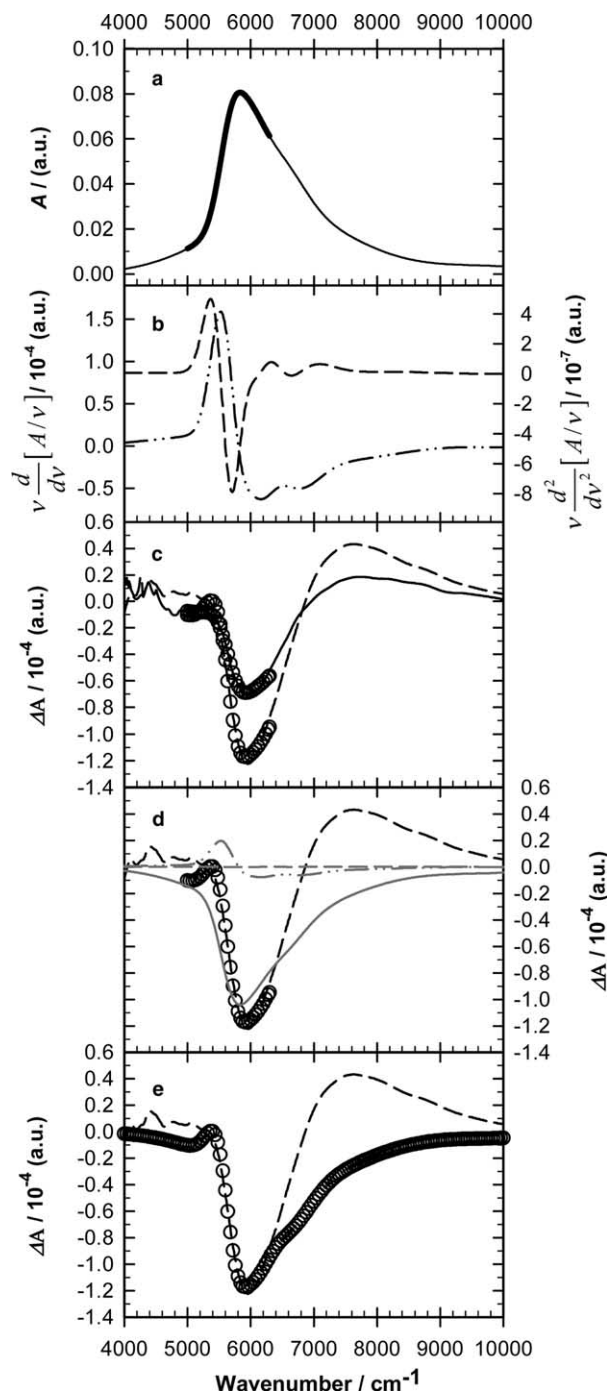


Fig. 3. Liptay analysis of Stark spectra for **2**. Panel (a) shows the unperturbed absorption spectrum at 77 K in butyronitrile (solid line) and panel (b) shows the energy weighted first and second derivatives (solid and dashed line, respectively). Panel (c) shows the measured Stark signals at $\chi = 90^\circ$ and 55° (solid and dashed lines, respectively) and fits (open circles). The wavelength region over which the Stark signal was fit is signified by the bold black line of the absorption spectra in panel (a). Panel (d) shows the measured Stark signal at $\chi = 55^\circ$ with the corresponding contributions from the zeroth-, first- and second-derivative components (grey lines) of the fit (open circles). Panel (e) shows the measured Stark signal at $\chi = 55^\circ$ with the fit parameters from panel (c) used to generate a spectrum covering the full wavelength range.

3.3. Electroabsorbance spectroscopy

Fig. 3, panel (a), shows the intervalence absorption spectrum of **2** in butyronitrile at 77 K. Panel (b) shows the energy-weighted first and second derivatives of the absorption spectrum. Panel (c) shows the measured Stark responses at $\chi = 90^\circ$ and 55° (solid and dashed lines, respectively), along with fits to Eq. (1). The wavelength region over which the Stark responses are fit are indicated by the bold section of the absorption line in panel (a). Qualitatively, the measured Stark response is very similar to that reported previously for **1** in glycerol/water [12,13]. The electroabsorbance spectrum of **2** is characterized by a large negative peak near the maximum in the unperturbed absorbance spectrum and a smaller positive lobe on the high-energy side of the spectrum. Similar to the reports for **1**, we found that reasonable fits could be obtained only by restricting the fits to the low-energy portion of the spectrum. The magnitude of the problem is illustrated in panel (e) where the best-fit parameters for the peak region are used to generate a full Stark spectrum. Note the marked deviations from the experimental spectrum at energies above ca. 6500 cm^{-1} and especially the inability to replicate the positive region of the Stark spectrum between 7000 and $10,000\text{ cm}^{-1}$.

Panel (d) shows a breakdown of the fit spectrum into zeroth-, first-, and second-derivative components; the largest component clearly is a negatively signed zeroth-derivative component. Notably, the second-derivative component, ordinarily indicative of a dipole moment change, is nearly absent, implying essentially complete delocalization. A quantitative Liptay analysis indeed does yield a near zero change in dipole moment ($|\Delta\mu| = 0.14 \pm 0.01\text{ e Å}$), along with small apparent polarizability changes ($\text{Tr}\Delta\alpha = 21 \pm 1\text{ Å}^3$ and $\Delta\alpha = 24 \pm 2\text{ Å}^3$). A fit to measurements of **1** in butyronitrile (not shown) yields $|\Delta\mu| = 0.07 \pm 0.01\text{ e Å}$, $\text{Tr}\Delta\alpha = 8.2 \pm 0.2\text{ Å}^3$, and $\Delta\alpha = 10 \pm 1\text{ Å}^3$ in good agreement with earlier measurements [12,13].

Fig. 4 shows the near-infrared Stark response and fit for **3**. Qualitatively, it can be seen that the measured Stark signals differ tremendously from those of **1** and **2**. They now resemble the positive first-derivative of the absorption spectrum, although they also contain a non-negligible second-derivative component. Reasonable fits to the measured Stark signals could be obtained over a larger wavelength range than was possible for **1** and **2**, but were still problematic away from the absorption maximum. Notably, the fits greatly exaggerate the signal magnitude below 6000 cm^{-1} . A quantitative Liptay analysis yielded: $|\Delta\mu| = 1.4 \pm 0.1\text{ e Å}$, $\text{Tr}\Delta\alpha = 438 \pm 1\text{ Å}^3$, and $\Delta\alpha = 530 \pm 7\text{ Å}^3$. (The reported uncertainties are spectral fitting uncertainties and do not include the aforementioned uncertainties in f .)

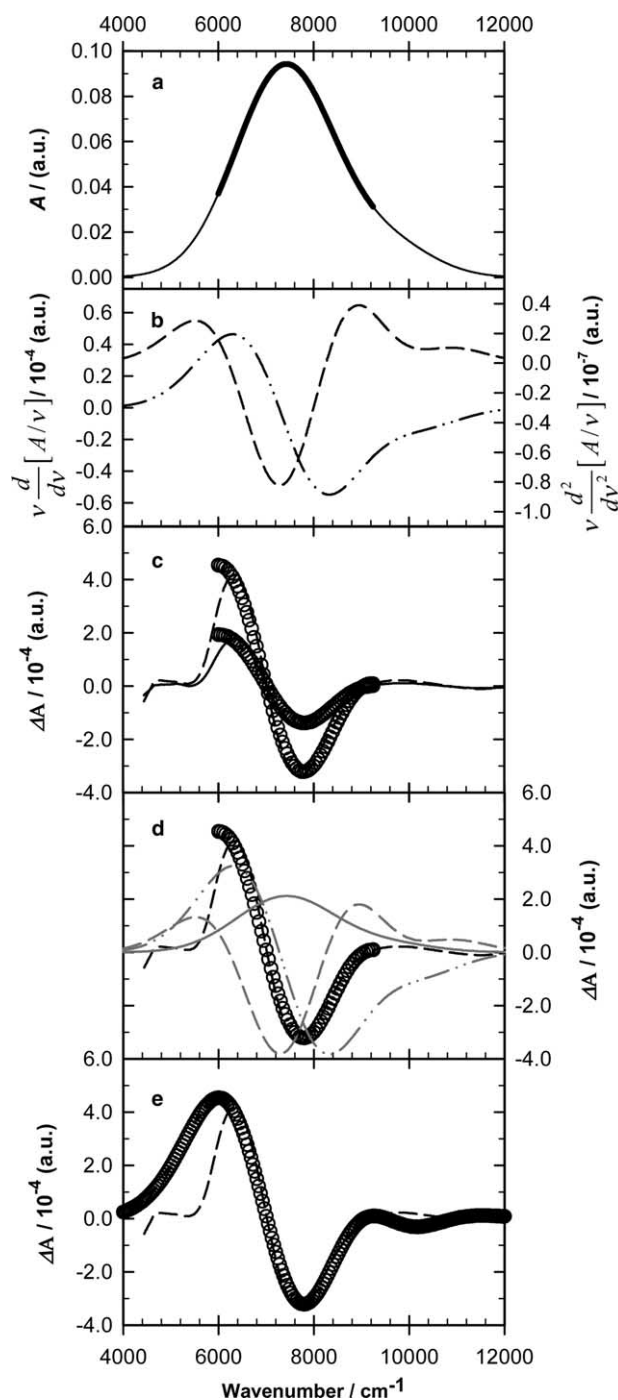


Fig. 4. Liptay analysis of the Stark spectra for **3**. Panel (a) shows the unperturbed absorption spectrum at 77 K in butyronitrile (solid line) and panel (b) shows the energy weighted first and second derivatives (solid and dashed line, respectively). Panel (c) shows the measured Stark signals at $\chi = 90^\circ$ and 55° (solid and dashed lines, respectively) and fits (open circles). The wavelength region over which the Stark signal was fit is signified by the bold black line of the absorption spectra in panel (a). Panel (d) shows the measured Stark signal at $\chi = 55^\circ$ with the corresponding contributions from the zeroth-, first- and second-derivative components (grey lines) of the fit (open circles). Panel (e) shows the measured Stark signal at $\chi = 55^\circ$ with the fit parameters from panel (c) used to generate a spectrum covering the full wavelength range.

4. Discussion

4.1. Electronic absorption

The slight broadening of the low-temperature absorption spectrum of **2** in comparison to **1** is consistent with a slight diminution in electronic coupling and has been observed previously in ambient temperature spectra. For **3**, the considerably greater broadening and the line-shape change are strongly suggestive of less severe delocalization or perhaps the onset of localization. The roughly 1200–1500 cm^{-1} blue shift for **3** vs. **1** and **2** is consistent with the introduction of redox asymmetry, estimated from electrochemical measurements with monometallic complexes to be between 1500 and 2100 cm^{-1} , depending on the monometallic complexes chosen.

Not shown by the absorption measurements, but clearly evident from resonance Raman experiments, is a striking change in the nature of vibrational coupling to the intervalence transition for the redox symmetric vs. asymmetric case. These measurements, which were performed using 1320 and 1337 nm excitation, have been previously described in part, albeit in a relatively inaccessible venue [18,23]. The approach used to evaluate the spectra was a time-dependent (wavepacket propagation) analysis of scattering intensities that neglects complications from vibronic coupling [24–26]. The information obtained was the magnitude of the unitless displacement, $|\Delta|$ of each of the modes coupled to the intervalence transition, along with mode-specific contributions, χ'_k ($= 0.5\Delta^2\nu$), to the vibrational reorganization energy. Examined were **1**, **2**, and **3**, along with complex **4** and single- and double-crown adducts of **2**, where the crown used was dibenzo-36-crown-12. As illustrated below, **4** is another mono-substituted derivative of the Creutz–Taube ion, **1**. As such, it is a redox asymmetric complex like **2**. The asymmetry, however, is greater; ΔE is estimated to be ca. 2400–2800 cm^{-1} .

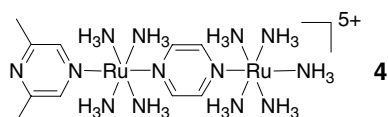


Table 1 summarizes the findings. The key ones are these: (a) The most intense scattering peak (although not the greatest contributor to the vibrational reorganization energy) for the three symmetrical species, **1**, **2**, and **crown · 2 · crown**, is a symmetrical pyrazine ring displacement, ν_{6a} . As has been noted previously [10], for a two-site valence-localized system this mode cannot couple to the intervalence transition. On the other hand, the three-site scheme in Fig. 1, which symmetrically redistributes charge from the bridging ligand to the metal

centers upon intervalence excitation, does allow displacement of ν_{6a} . (b) For all six systems, the dominant mode in terms of vibrational reorganization energy is a low-frequency metal–nitrogen(pyrazine) stretch. (c) Activity in the Ru–N(pyrazine) mode, as indicated by relative scattering intensities and, especially, contributions to the vibrational reorganization energy, is substantially greater for the three redox-asymmetric species (**2 · crown**, **3**, and **4**) than for the symmetric species. Particularly striking are the 5-fold increase in the reorganizational energy contribution from Ru–N(pyrazine) upon crown binding of **2** and symmetry reduction, and the reversal of the increase upon binding of a second crown.

From oxidation-state-dependent X-ray structural studies of a monomeric model compound, $\text{Ru}(\text{NH}_3)_5\text{-(pyrazine)}^{3+/2+}$ [27], any changes (or partial changes) of charge at the metal centers should incite substantial displacements of the Ru–N(pyrazine) stretching mode. Note that the three-site valence-delocalized electronic description of intervalence excitation (Fig. 1) does entail charge density changes at the metal centers and, indeed, the symmetrical assemblies do exhibit vibrational activity in Ru–N(pyrazine). However, the introduction of charge polarization or even incipient valence localization, such that charge is also transferred *between* metal centers upon intervalence excitation, should amplify the activity in Ru–N(pyrazine).

Combining the information from absorbance, electroabsorbance, and resonance Raman scattering measurements, we conclude that: (a) intervalence excitation in the three symmetrical assemblies examined is reasonably well described by a model that assumes a three-site ground electronic state and no metal-to-metal charge transfer, but (b) intervalence excitation in the redox-asymmetric assemblies does involve net metal-to-metal charge transfer and a change in dipole moment. At the same time, the persistence of activity in ν_{6a} for the redox-asymmetric assemblies implies that three-site mixing and simultaneous transfer of charge from the bridging ligand to both metal centers (i.e., a change in quadrupolar moment) remain important.

4.2. Liptay analysis

An underlying assumption of the Liptay electroabsorbance analysis (Eq. (1)) is that the applied electric field perturbs only the transition moment (μ_{12}) and the absorption maximum (ν_{max}) of an electronic transition. A corollary is that the absorption lineshape is *not* changed by the electric field. Under these conditions, a change in transition moment engenders a zeroth-derivative response to an applied electric field. A ground-state/excited-state polarizability change engenders a first-derivative response, i.e., a shift of the absorption of the entire population of chromophores to either the

Table 1
Parameters from wavepacket analysis

Compound	Frequency (cm ⁻¹)	Intensity (arb. units)	Δ	χ'_k (cm ⁻¹)	Assignment
<i>Symmetric ions</i>					
1	324	0.8	1.26	260	Ru–N(pyrazine)
	697	1.0	0.53	100	ν_{6a} (pyrazine)
	1316	0.4	0.01	10	δ_s (NH ₃)
2	320	0.7	1.36	300	Ru–N(pyrazine)
	676	1.0	0.64	140	ν_{6a} (pyrazine)
	1320	0.3	0.13	10	δ_s (NH ₃)
crown · 2 · crown	320	0.6	1.40	310	Ru–N(pyrazine)
	676	1.0	0.73	180	ν_{6a} (pyrazine)
	1320	0.6	0.23	30	δ_s (NH ₃)
<i>Asymmetric ions</i>					
2 · crown	320	2.3	3.20	1640	Ru–N(pyrazine)
	676	1.0	0.94	300	ν_{6a} (pyrazine)
	1320	2.0	0.63	260	δ_s (NH ₃)
3	320	2.0	2.24	800	Ru–N(pyrazine)
	696	1.0	0.64	140	ν_{6a} (pyrazine)
	1320	0.4	0.18	20	δ_s (NH ₃)
4	320	1.8	2.70	1170	Ru–N(pyrazine)
	660	1.0	0.93	290	ν_{6a} (pyrazine)
	1314	3.1	0.80	420	δ_s (NH ₃)

red or the blue, depending on whether the excited state or the ground state experiences the greater polarizability-based stabilization when subjected to an electric field. A change in dipole moment also leads to differential electric-field stabilization (or destabilization) of the excited state vs. the ground state. How this influences the Stark spectrum is strongly dependent upon the orientation of the individual molecular dipole with respect to the external field. A parallel orientation will yield a spectral shift opposite to that of an anti-parallel orientation, while an orthogonal orientation will result in no shift. For an isotropic sample, both red shifts and blue shifts will occur, producing an overall broadening of the spectrum. When subtracted from the parent spectrum (field-off spectrum) the resulting difference spectrum will closely approximate a second-derivative of the parent spectrum.

A further assumption is that relative energetic populations (for example, the two populations present in a system featuring a double-welled ground potential-energy surface) do not change when an electric field is applied [11,28]. While not an issue here, Treynor and Boxer [20] have pointed out that the assumption could be difficult to satisfy with a symmetrical charge-localized mixed-valence system. The main effect anticipated is an extra first-derivative contribution. In any case, systems that do satisfy the above requirements have been termed “classic” Stark responsive systems [20]. The failure of the Liptay scheme to fit the full intervalence spectra of **1**, **2**, and **3** indicates that to greater or lesser degrees these are non-classic Stark systems. In view of the non-classic behavior, quantitative significance, espe-

cially for polarizability parameters, ought not to be attached to the parameters derived by restricting the analysis to the peak regions of the spectra. The main conclusions we draw from the analyses are simply that the dipole moment changes for intervalence excitation of both **1** and **2** are very likely small or zero, while for **3** $|\Delta\mu|$ is non-zero.

4.3. Non-Liptay evaluation

One cause for the observed non-classic Stark responses may be failure of the Born–Oppenheimer approximation, in the sense that vibronic coupling may be important. Borderline class II/class III mixed-valence systems are good candidates for strong vibronic coupling, although certain predictions of vibronic coupling models such as very low energy “tunneling” transitions [29] have yet to be observed experimentally. Notably, Treynor and Boxer [20] have recently presented a quantitative two-site treatment of Stark behavior for vibronically coupled mixed-valence systems. (Electric-field modulation of vibronic coupling has also been discussed by Matyushov and Newton [30].)

Rather than attempting to implement their methodology here, however, we present a qualitative and empirical discussion that enlists data from related experimental model systems to account in a phenomenological way for the non-classic Stark behavior of **2** and **3** as well as the striking differences between the pair. One concern in applying the Treynor–Boxer treatment here is the potential complicating effects of three-site mixing and of the evolution of the electronic structure toward a two-

site picture as redox asymmetry is introduced. Nonetheless, it would be interesting to discover at some point whether the Treynor–Boxer treatment is already sufficiently general to describe well the behavior of **2** and **3**.

Previous work from our laboratory showed that equimolar solutions of **1** or **2** and macrocyclic crown ethers (charge neutral species) such as dibenzo-30-crown-10, dibenzo-36-crown-12, and dibenzo-42-crown-14, display intervalence transitions that are considerably blue shifted and broadened in comparison to solutions containing only the metal complex (see top panel of Fig. 6) [16]. These spectral perturbations arise from complexation of one of the ruthenium ammine moieties by the crown ether through ether-oxygen/ammine-hydrogen bonding. As discussed above and in earlier reports, the spectroscopic perturbations indicate that binding of the crown ether induces charge redistribution in the ground state such that the encapsulated ruthenium site loses electron density to the non-encapsulated site and/or bridging ligand [23]. In other words, the ground electronic state is charge polarized or partially valence localized; see Fig. 5.

It is important to note that because crown binding is a *second*-sphere association effect, perturbations due to ancillary-ligand back-bonding are not an issue in the polarization or localization problem. Instead, the introduction of significant redox asymmetry is the factor responsible for inducing charge polarization. Indeed, when the supramolecular symmetry is restored by binding a second crown, the original intervalence lineshape is restored and Robin–Day class III behavior is recovered [16]. Returning to the asymmetric case, crown encapsulation is known (from monomer electrochemical studies and from optical studies with less strongly interacting mixed-valence systems [31]) to induce a zeroth-order redox asymmetry of ca. 0.3 eV [16,19,32]. Given the ~ 7 Å metal–metal separation distance in **2**, asymmetric encapsulation can be viewed as a chemical method for gener-

ating an effective internal field of ca. 4×10^8 V/m, i.e., a *chemically induced Stark effect*. In comparison, typical field strengths used for Stark absorption measurement are about an order of magnitude smaller ($6\text{--}8 \times 10^7$ V/m). (Note that the crown-induced polarization is not a consequence of net second-sphere ligand charge. The crowns are charge neutral.) The polarization arises, as discussed above and in earlier work, from differential solvation of the two ammine-ruthenium sites – one by the crown ether + nitromethane molecules, the other by only nitromethane molecules. The magnitude of the effective field created in this way is estimated as the electrochemically determined difference in redox potential for tetraammine ruthenium species in the two local solvent environments divided by the distance between metal centers in **2**.

The Stark spectrum is, by definition, the difference between “*field on*” and “*field off*” spectra. Note that for an initially symmetrical, charge-delocalized system, the sign of the field is unimportant. The system initially lacks a dipole moment, making distinctions between field-parallel and field-antiparallel molecular orientations meaningless. Similarly, distinctions between left- vs. right-side crown encapsulation of an initially symmetric, valence-delocalized system are obviously meaningless in terms of spectral perturbations. Fig. 6 shows the Stark-like spectrum obtained by taking the difference between spectra for **2** · crown (“*field on*”) and **2** (“*field off*”). Comparison to the electroabsorbance spectrum for **2** reveals remarkably similar lineshapes. Agreement between the two is not perfect, however. The crown-induced difference spectrum is shifted by $500\text{--}1000\text{ cm}^{-1}$ to the red of the true electroabsorbance spectrum. This may be due in part to solvatochromism and in part to differences in thermal broadening; the crown spectra were of necessity recorded in nitromethane rather than butyronitrile and at ambient temperature rather than 77 K.

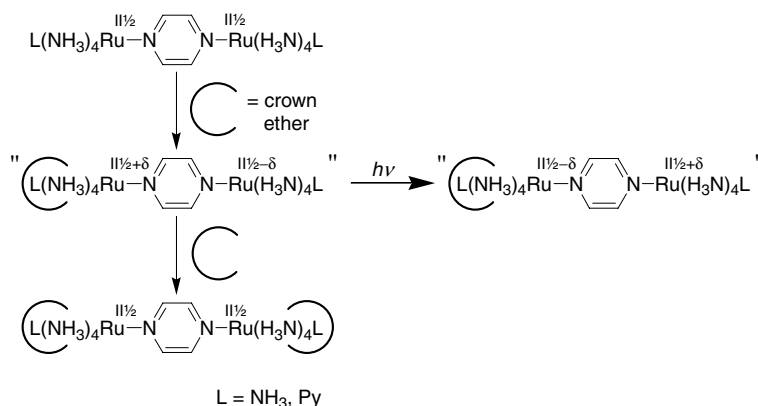


Fig. 5. Schematic representation of the stepwise binding of dibenzo crown ethers to **1** and **2**. The unencapsulated and the doubly encapsulated forms of the compounds are charge symmetrical. The singly encapsulated forms of **1** and **2**, on the other hand, are slightly charge polarized and their excitation results in net metal-to-metal charge transfer.

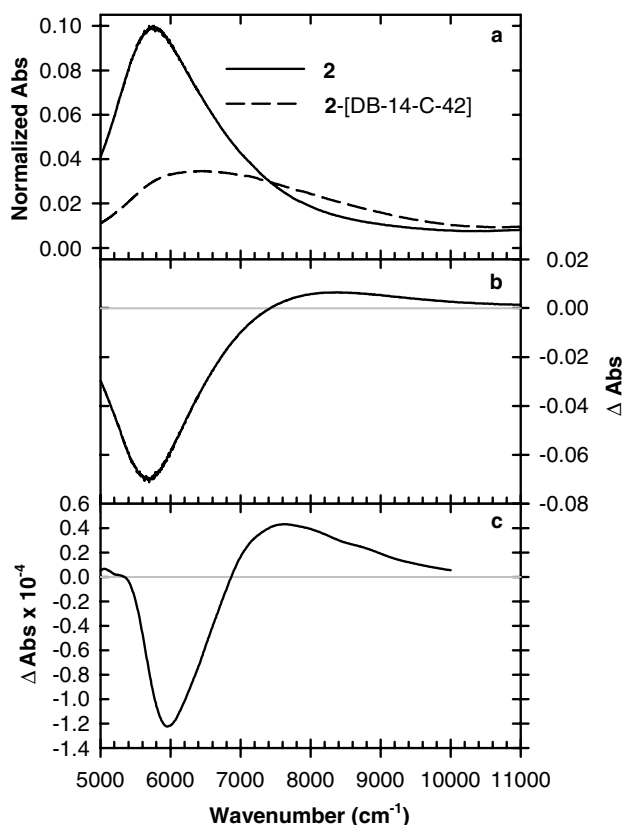


Fig. 6. Panel (a): Normalized intervalence absorption bands for **2** (solid line) and **2** in the presence of 1 equivalent of DB-14-C-42 (long dashed line). Panel (b): Difference spectrum of **2** from **2** · [DB-14-C-42], described in the text as “chemically induced Stark signal”. Panel (c): Measured Stark signal (77 K) at $\chi = 55^\circ$ for **2** in butyronitrile. (Note that the intervalence absorption for **2** at 77 K is narrower than the room temperature spectra shown in panel (a).)

Given the agreement in Fig. 6, we conclude that the electronic structural changes accompanying crown encapsulation also accompany the application of an electric field – but to a smaller extent, of course, because of the smaller magnitude of the externally applied field. In other words, we conclude that the non-classical Stark

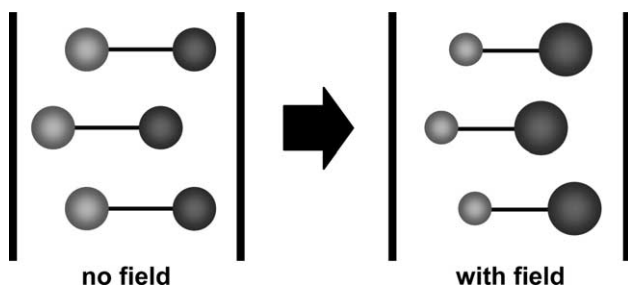


Fig. 7. Proposed external-electrode-field induced modulation of valence distribution for a symmetrical, weakly class III mixed-valence system. Medium-sized spheres correspond to sites of valence 2.5 (in a two-site description). Smaller spheres have a slightly higher valence; larger spheres have a slightly lower one.

behavior of **2** arises from: (a) electric-field induced ground-state charge polarization that, in the extreme (not achieved here), culminates in valence localization, and (b) the emergence of metal-to-metal charge-transfer character in the intervalence transition, again engendered by the applied electric field; see Fig. 7. Returning briefly to the differences in spectral intensity for the two types of experiments, recall that the magnitude of ΔA measured in a Stark experiment usually scales as F_{int}^2 , suggesting that intensities might differ by about two orders of magnitude.

Using the same approach with the Creutz–Taube itself yields the results shown in Fig. 8. Again the agreement between the electroabsorbance spectrum and the crown difference spectrum is striking, with the crown difference spectrum effectively capturing the features at the extremes of the electroabsorbance spectrum that are not reproduced by Liptay fits.

A similar but slightly more involved approach can be used with **3**. As illustrated in Fig. 9, an applied field can influence the properties of an individual molecule of **3** in either of two orientation-dependent ways. If aligned parallel to the field, the ligand-field-induced redox asym-

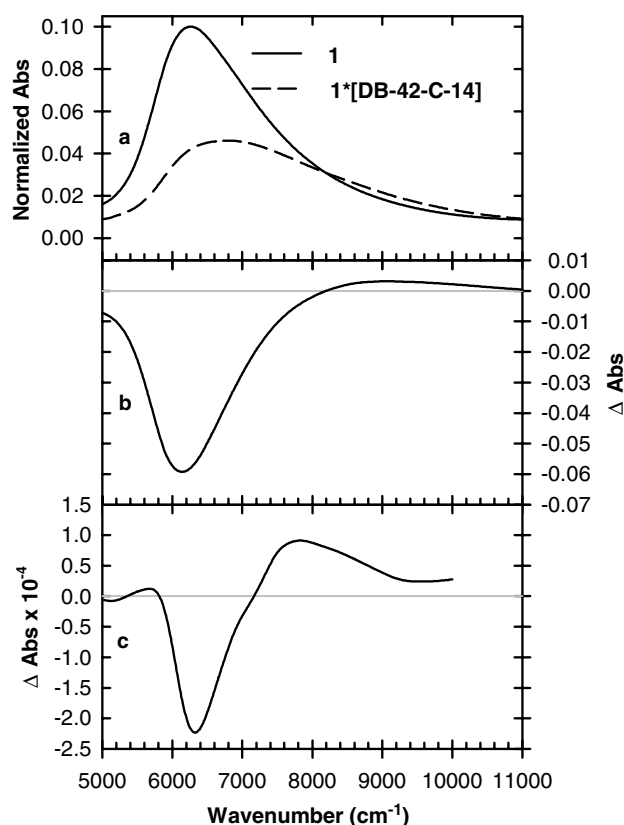


Fig. 8. Panel (a): Normalized intervalence absorption bands for **1** (solid line) and **1** in the presence of 1 equivalent of DB-14-C-42 (long dashed line). Panel (b): Difference spectrum of **1** from **1** · [DB-14-C-42]. Panel (c): Measured Stark signal (77 K) at $\chi = 55^\circ$ for **1** in butyronitrile. (Note that the intervalence absorption for **1** at 77 K is narrower than the room temperature spectra shown in panel (a).)

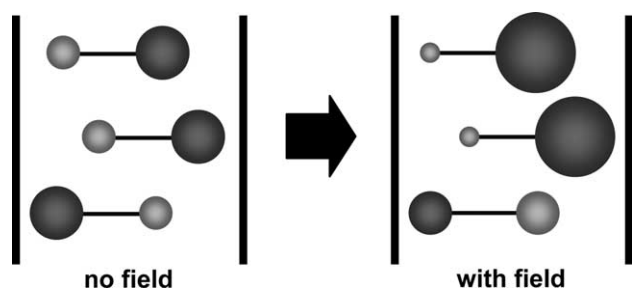


Fig. 9. Proposed external-electrode-field induced modulation of valence distribution for an initially redox-asymmetric, weakly class III mixed-valence system. Medium-sized spheres correspond to sites of valence 2.5 (in a two-site description). Smaller spheres have a slightly higher valence; larger spheres have a slightly lower one. Note that the effect of the external field upon the valence distribution varies depending on the orientation of the molecule with respect to the field (only completely parallel and completely anti-parallel cases shown).

metry of the molecule will be reinforced by the electric field. If aligned antiparallel, the inherent redox asymmetry will be opposed and partially cancelled by the electric field. We suggest that the putative cancellation effect can be mimicked chemically by replacing **3** with the symmetrical analogue **2**. The reinforcement effect can be mimicked by replacing **3** with a similar but more strongly redox-asymmetric assembly, **4**. (The difference in redox asymmetry for **4** vs. **3** is ca. +0.11 V; for **2** vs. **3** it is ca. −0.19 V.)

The top panel of Fig. 10 compares the normalized intervalence absorption spectra for **1**, **3**, and **4**. Our premise is that the spectrum of **4** corresponds crudely to the “field on” spectrum of a parallel-aligned subset of a sam-

ple of **3**, and that the spectrum of **2** corresponds crudely to the “field on” spectrum of a second subset aligned in an antiparallel fashion. (The “chemically induced Stark effect” field again, however, is roughly an order of magnitude greater than the field in the true electroabsorbance experiment.) Overlooked in the analogy are other chemical effects of ligand substitution upon the intervalence spectrum. In particular, the consequences of changes in back-bonding are ignored (cf. comparison in Fig. 2, above, of the redox-symmetric pair, **1** and **2**). Nevertheless, shown in the bottom panel of Fig. 10 is the “chemically induced Stark effect” spectrum obtained by subtracting the spectrum of **3** (“field off”) from half the sum of the spectra for **2** and **4**. The agreement with the true electroabsorbance spectrum, while less good than obtained for the symmetric systems above, is still remarkable. The “chemical Stark effect” spectrum does a good job of recreating the sharp drop off at $\approx 5500\text{ cm}^{-1}$ in the true electroabsorbance spectrum, while also capturing at least qualitatively, the differences in amplitude and width of positive vs. negative going lobes in the true electroabsorbance spectrum. More generally, the striking electroabsorbance lineshape differences for redox-asymmetric vs. redox-symmetric complexes are reproduced. We again interpret the agreement as evidence for electric-field-induced modulation of the degree of ground-state (de)localization and the amount of charge-transfer character in the intervalence transition.

5. Conclusions

Electroabsorbance measurements of the Creutz–Taube derivatives **2** and **3** in the intervalence region yield remarkably different responses. Neither set is well fit by a classic Liptay treatment. However, an alternative, qualitative approach that: (a) assumes that both are borderline class II/class III systems; (b) allows for the possibility that the externally applied electric field itself affects the degree of valence delocalization, does reproduce the key features of the disparate spectra. For the symmetrical complex, **2**, the applied field appears to function in the same way as internal redox asymmetry and to push the system toward localization. For the already redox-asymmetric system, **3**, the externally applied field can act either to reinforce and increase the asymmetry or oppose and diminish it, depending on molecular orientation with respect to the field. The resulting Stark spectrum appears to be a sum of spectra for two kinds of responses: slight increases in valence differences (incipient localization) and slight decreases in valence differences (greater delocalization). The proposed responses can be emulated chemically by introducing first- or second-sphere perturbations that either increase or decrease redox asymmetry.

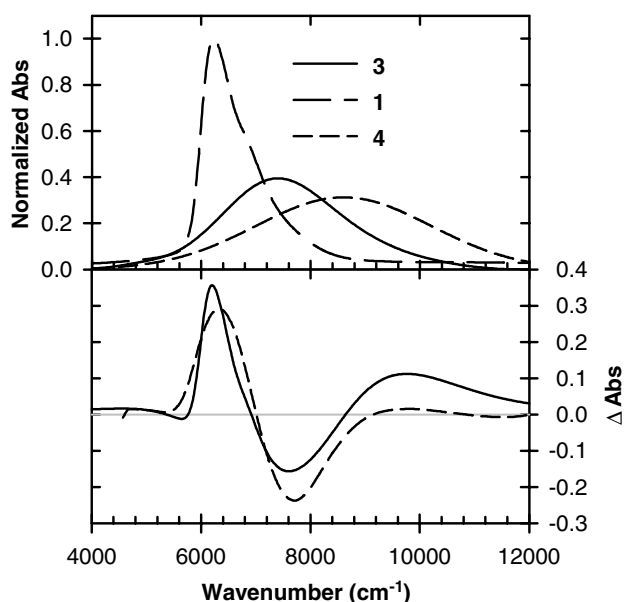


Fig. 10. Top panel: Normalized IT absorption bands, at 77 K for **3** (solid line), **1** (long dashed line) and **4** (short dashed line). Bottom panel: Difference spectrum of **3** from **1** and **4** (solid line) and the measured Stark spectra of **3** (dashed line).

Intervalence-enhanced resonance Raman spectroscopy measurements for a total of six mixed-valence systems support the contention that the symmetrical complex **2**, in unperturbed form, is a valence delocalized system with delocalization occurring via three-site mixing. The Raman measurements for the asymmetrical system, **3**, also indicate three-site mixing and suggest significant delocalization. Additionally, however, they provide evidence for some degree of metal-to-metal charge-transfer upon intervalence excitation and therefore, some degree of valence differentiation. When redox asymmetry is introduced into **2** by encapsulating one end with a crown ether, Raman spectroscopic evidence for the emergence of metal-to-metal charge-transfer behavior is similarly obtained – evidence that disappears when symmetry is restored by encapsulating both ends of the complex.

Acknowledgments

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