

Electroabsorption Studies of Metal-to-Ligand Charge Transfer in Ru(phenanthroline)₃²⁺: Evidence for Intrinsic Charge Localization in the Initially Formed Excited State

Laba Karki and Joseph T. Hupp*

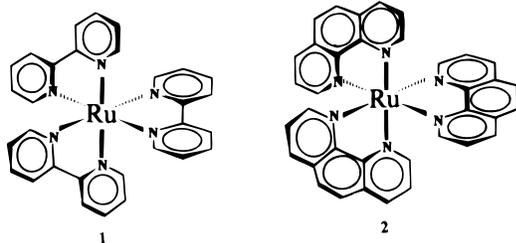
Department of Chemistry, Northwestern University, Evanston, Illinois 60093

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Electroabsorption studies of ruthenium(II) tris(phenanthroline) show that a substantial change in dipole moment ($|\Delta\mu| = 6.7 \pm 1$ D) accompanies ground state to “singlet” metal-to-ligand charge transfer (MLCT) excited-state formation. The change is nearly identical to that reported for the 2,2'-bipyridine analogue (Oh; et al. *J. Am. Chem. Soc.* **1989**, *111*, 1130). Since both species lack ground-state dipole moments, the finite values for $\Delta\mu$ are diagnostic of intrinsic charge localization in the excited states. The nominally triplet transition for the phenanthroline complex also involves the formation of a charge localized state. The combined results are inconsistent, therefore, with an alternative “delocalized” charge transfer excited-state interpretation suggested by time-resolved resonance Raman studies of the tris(phenanthroline) complex.

Introduction

The tris(diimine) complexes of ruthenium have played an enormous role in the development of our understanding of the basic photochemistry (photosubstitution, photooxidation, photoreduction, intermolecular energy transfer, etc.) and photophysics (radiative and nonradiative decay, intersystem crossing, energy gap law behavior, etc.) of transition metal based systems.¹ Among the fundamental questions that have been examined for these high-symmetry systems is the degree of spatial localization of transferred charge in the photo excited state(s). Two limiting possibilities are electron localization on a single ligand and electron delocalization among the three equivalent, but nominally orthogonal, ligands. For Ru(bpy)₃²⁺ (**1**), a variety of experiments now indicate that the transferred electron is essentially fully confined (transiently) to a single ligand² but that ligand-to-ligand charge hopping occurs on a time scale of ca. 1 ns.³



In view of the findings for the bipyridine complex we were surprised by a report by Turró et al. that suggested that the analogous 1,10-phenanthroline complex (**2**) might display *delocalized* excited-state behavior.⁴ The primary evidence was negative evidence from time-resolved resonance Raman (TR³)

spectroscopy: These measurements failed to show the formation of the expected phenanthroline radical anion in the photo excited state. On the other hand, solvatochromic results have been interpreted in terms of localized charge transfer.⁵ These results were suggestive of a significant excited-state/ground-state dipole moment difference ($\Delta\mu$), a conclusion inconsistent with charge transfer (CT) to a delocalized (charge symmetric) excited state. Further circumstantial evidence is provided by comparative analyses of nonradiative decay rates.^{6,7} These imply that similar (albeit, not identical) Franck–Condon factors exist for nonradiative decay from the lowest excited state of **1** versus **2**⁷—a result that would be surprising if the excited states were fundamentally different.

Given the apparent disagreement between the transient resonance Raman studies and the solvatochromic and Franck–Condon studies, we felt that further experimental investigation could prove instructive. Following Oh and Boxer,^{2c} who previously examined the bipyridine complex, we implemented an electronic Stark effect (or electroabsorption) study of the phenanthroline complex. The electroabsorption method is particularly appropriate for this problem because it yields a direct, quantitative measure of the dipole moment change accompanying excitation to a specific molecular excited state. For these high-symmetry systems, which lack a ground-state dipole moment, the presence or absence of a dipole moment change is, therefore, unambiguously diagnostic of localized versus delocalized excited-state charge distribution.

Experimental Section

The hexafluorophosphate salt of ruthenium(II) tris(phenanthroline) was synthesized and purified according to a literature method.⁷ Absorption measurements were performed at 77 K in a 1:1 (v:v) butyronitrile:2-methyl tetrahydrofuran glass by using a retrofitted Cary-14 spectrophotometer featuring OLIS control software. This matrix

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- (1) For reviews, see: (a) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: New York, 1992. (b) Juris, A.; Belsler, P.; von Zelewsky, A.; Barigelletti, P.; Balzani, V. *Coord. Chem. Rev.* **1988**, *84*, 85. (c) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94. (d) Benasson, R.; Salet, C.; Balzani, V. *J. Am. Chem. Soc.* **1977**, *98*, 3722.
- (2) See, for example: (a) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391. (b) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441. (c) Oh, D. H.; Boxer, S. G. *J. Am. Chem. Soc.* **1989**, *111*, 1130.
- (3) Malone, R. A.; Kelley, D. F. *J. Chem. Phys.* **1991**, *95*, 8970.

- (4) Turró, C.; Young, Y. C.; Leventis, N.; Kuchenmeister, M. E.; Wagner, P. J.; Leroi, G. E. *Inorg. Chem.* **1996**, *35*, 5104.
- (5) Kober, Sullivan and Meyer (*Inorg. Chem.* **1984**, *23*, 2098) (See also: Brunschwig; et al. *J. Phys. Chem.* **1987**, *91*, 4714) conclude from solvatochromic studies that $\Delta\mu$ for MLCT excitation of **1** is 14 ± 6 D. From related studies of **2** (see Supporting Information) we obtain an estimated $\Delta\mu$ of 13 ± 5 D.
- (6) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 107.
- (7) (a) Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630. (b) Ellis, C. D.; Margerum, L. D.; Murray, R. W.; Meyer, T. J. *Inorg. Chem.* **1989**, *22*, 1283.

forms an excellent quality glass at 77 K and is suitable for glassing nonpolar hexafluorophosphate salts. Electroabsorption measurements were performed in a single-beam mode with polarized light using a Glan–Taylor polarizing prism (Melles Griot, Irvine, CA), immediately following dual beam absorption measurements. An important experimental consideration here is to avoid changes in alignment of the optical cell between absorption and electroabsorption measurements. Fogging of the liquid-nitrogen dewar containing the electroabsorption cell was circumvented by blowing dry nitrogen gas over the dewar windows. Scattering effects from nitrogen bubble formation within the dewar were eliminated by bubbling with helium gas and creating a nucleation point just above the electroabsorption cell. The monochromator was scanned at 30 nm/min from low to high energy. Slits were adjusted to provide a spectral resolution of ~4 nm. There is a trade off between resolution and signal to noise ratio, since a higher resolution demands narrower monochromator slits which leads to diminished photon fluxes. The path length of the electroabsorption cell (indium tin oxide coated quartz plates, Delta Technologies Ltd., Stillwater, MN; Kapton tape spacers, Saunders Corp., Los Angeles, CA) was ca. 50 μm as determined interferometrically in the near IR region with an empty cell via the following equation:⁸

$$d = i \frac{\lambda_{n-i}}{[\lambda_{n-i} - \lambda_n]} \lambda_n \quad (1)$$

In eq 1, d is the thickness of the cell in nanometers and i is the number of interference peaks (typically we used 10) between the lower wavelength (λ_{n-i}) and the upper wavelength (λ_n) in nanometers. The applied sinusoidal oscillating field was 3.6×10^7 V/m (peak to peak) provided by an ac power supply constructed by Joseph Rolfe Associates of Palo Alto, CA.

The second-order Stark signal ($\Delta I_{2\omega}$) was measured with a Hamamatsu R928 photomultiplier tube (PMT) featuring five dynode stages with an accelerating potential of 200 V. The current (I) was converted to voltage (V) by passage through a current to voltage converter and finally detected by a lock-in amplifier (Stanford Research Systems, Model SR 850) at twice the field modulation frequency, ω (typically 225 Hz). Since the field-independent and the field-dependent transmittance signals were detected by the same PMT, the following relationship holds:⁸

$$\frac{\Delta I_{ac}}{I_t} = \frac{V_{ac}}{V_{dc}} \quad (2)$$

Here ΔI_{ac} is the *small* oscillating second-order transmittance current and I_t is the total transmittance current, which is a function of the chromophore concentration, monochromator grating efficiency, band pass, photomultiplier sensitivity, and excitation lamp intensity. Finally, the change in absorbance in the presence of the applied field is given by the following expression:⁹

$$\Delta A = -\log \left[\frac{2\sqrt{2}(V_{ac} \pm k)}{V_{dc}} + 1 \right] \quad (3)$$

In eq 3, k represents the background lock-in amplifier voltage (typically 1–5 mV). The factor of $2\sqrt{2}$ corrects for (a) differences between rms voltages (detected by the lock-in) and peak voltages and (b) the fact that the oscillating signal at 2ω carries only *half* the total signal amplitude. After accounting for finite bandpass effects, and correcting for lock-in amplifier time constant effects the electroabsorption spectra obtained at any two angles, χ , were fit to a linear combination of zero, first, and second derivatives of the energy-weighted absorption band. (χ is the angle between the electric polarization vector of the light beam and the applied electric field.) According to Liptay, the energy-dependent change in chromophore absorbance in the presence of an

applied external field can be quantitatively represented as^{10,11}

$$\Delta A(\nu) = \left\{ A_x A(\nu) + \frac{B_x}{15hc} \frac{\nu d[A(\nu)\nu]}{d\nu} + \frac{C_x}{30h^2c^2} \frac{\nu d^2[A(\nu)/\nu]}{d\nu^2} \right\} \mathbf{F}_{int}^2 \quad (4)$$

\mathbf{F}_{int} is the internal electric field¹² (i.e. the field actually experienced by the chromophore), ν is the frequency of the absorbed light, h is Planck's constant, and c is the speed of light. C_x provides information regarding $\Delta\mu$. Formally,¹¹

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

where ξ is the angle between the transition dipole moment and the change in dipole moment. B_x provides information regarding the change in the polarizability of the molecule and is given by¹³

$$B_x = {}^5/2 \text{Tr}\Delta\alpha + (3 \cos^2 \chi - 1)({}^3/2 \hat{\mathbf{g}} \cdot \Delta\alpha \cdot \hat{\mathbf{g}} - {}^1/2 \text{Tr}\Delta\alpha) \quad (6)$$

where $\text{Tr}\Delta\alpha$ is the trace of the polarizability change between the two states (diagonal components) and $\hat{\mathbf{g}} \cdot \Delta\alpha \cdot \hat{\mathbf{g}}$ is the component of the polarizability change along the transition moment, where $\hat{\mathbf{g}}$ is the unit vector. A_x provides information about the transition moment polarizability and hyperpolarizability and is given by the following expression:¹⁴

$$A_x = S^{(1)}/3 + {}^1/30(3 \cos^2 \chi - 1)[3S^{(2)} - 2S^{(1)}] \quad (7)$$

In eq 7, $S^{(1)}$ and $S^{(2)}$ are scalar functions of the transition moment polarizability and hyperpolarizability tensors. Typically, for charge transfer transitions, the contribution of the A_x term is negligible in comparison to the B_x and C_x terms.

To evaluate the electroabsorption spectra, the structured absorption spectrum obtained at 77 K was first fit to a series of overlapping, idealized component transitions by using a commercially available fitting program (Spectra Calc: version A2.23, Galactic Industries Corp., Salem, NH). The absorption spectrum for the current experiment was fit as the sum of three transitions where each contained about 25% lorentzian and 75% gaussian character. Zeroth, first, and second derivative representations of the component transitions were then generated. To obtain changes in dipole moment and molecular polarizability, electroabsorption spectra were evaluated via least-squares fitting procedures that utilize the model in eq 4. In its simplest form the fitting expression is

$$y(x) = a_1 \cdot \mathbf{f}_1(x) + a_2 \cdot \mathbf{f}_2(x) + a_3 \cdot \mathbf{f}_3(x) \quad (8)$$

where a_1 , a_2 , and a_3 are the coefficients of the fitting parameters for a particular Stark spectrum, $y(x)$, and x is the absorption energy in wavenumbers. The modeling parameters or basis functions are $\mathbf{f}_1(x)$, $\mathbf{f}_2(x)$ and $\mathbf{f}_3(x)$, which are the zeroth, first, and second derivatives of the energy-weighted absorption band. The fitting procedure here entailed a Gauss–Jordan reduction of the modeling parameters via a χ^2 minimization routine to yield optimal values for the coefficients a_1 , a_2 , and a_3 .¹⁵ From values of the coefficients at two angles, χ , and from the magnitude of the applied field, the absolute dipole moment change and the molecular polarizability change are readily obtained. Among the virtues of this analysis protocol is the possibility of fitting

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(11) Boxer, S. G. In *The Photosynthetic Reaction Center*; Academic Press: New York, 1993; Vol II, pp 179–220.

(12) $\mathbf{F}_{int} = f \mathbf{F}_{external}$, where f is a local field correction factor. For a spherical cavity, f can be approximated as $3D_s/(2D_s + 1)$ where D_s is the static dielectric constant of the glass or solvent. From glass dielectric data reported by Karki and Hupp (*J. Am. Chem. Soc.*, in press) f is ~1.3.

(13) Mathies, R. A. Ph.D. Thesis, Cornell University, 1974.

(14) (a) Liptay, W. *Ber. Bunsen-Ges. Phys. Chem.* **1976**, *80*, 207–217. (b) Oh, D. H.; Sano, M.; Boxer, S. G. *J. Am. Chem. Soc.* **1991**, *113*, 6880.

(15) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. In *Numerical Recipes: The Art of Scientific Computing*; Cambridge University Press: Cambridge, U.K., 1989.

(8) Shin, Y. K.; Brunschwig, B. S.; Creutz, C.; Sutin, N. *J. Phys. Chem.* **1996**, *100*, 8157.

(9) Colvin, V. L.; Cunningham, K. L.; Alivisatos, A. P. *J. Chem. Phys.* **1994**, *101*, 7122.

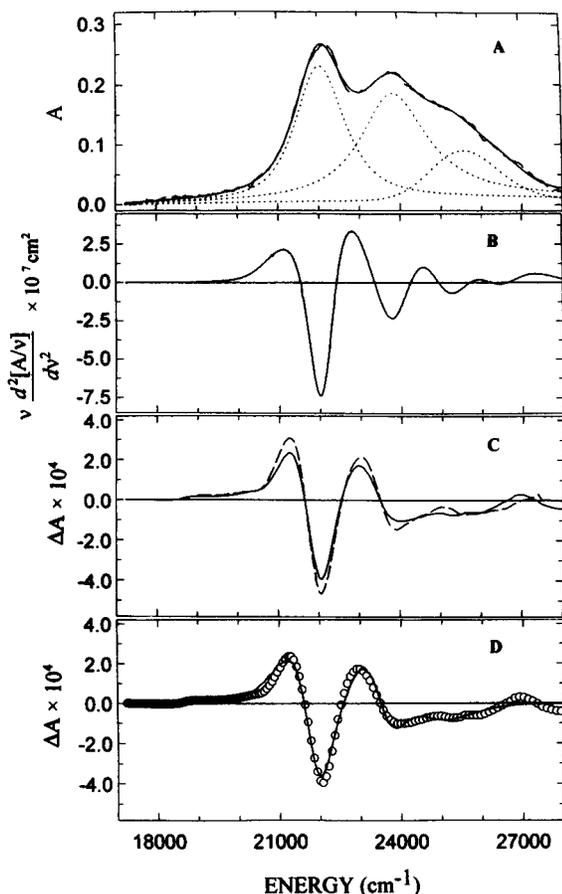


Figure 1. Panel A: Absorption spectrum of ruthenium tris(phenanthroline) in a 1:1 (v:v) 2-MeTHF:butyronitrile glass at 77 K. The dotted lines illustrate a deconvolution of the overall absorption band into three transitions. Panel B: Numerical second derivative of the energy normalized absorption spectrum. Panel C: Electroabsorption signals at $\chi = 90^\circ$ (solid line) and 55° (dashed line). Panel D: Comparison of experimental electroabsorption signal (open circles) and with a fit to eq 4 based on three electronic transitions (solid line).

electroabsorption signals for multicomponent spectra to an expanded collection of basis functions (for example, 6, 9, or 12 basis functions (eq 8) for a spectrum containing 2, 3, or 4 electronic transitions).

Results and Discussion

Panel A of Figure 1 shows a low-temperature visible-region absorption spectrum for **2** in a 2-methyltetrahydrofuran:butyronitrile glass. The dominant feature is a strongly allowed metal-to-ligand charge transfer (MLCT) transition at 22 000 cm^{-1} corresponding to formation of a nominally singlet excited state. The higher energy components evidently also are charge transfer transitions.¹⁶ Panel B shows the numerical second derivative of the overall absorption band. Panel C shows the Stark spectra obtained at angles, χ , of 55 and 90° . Note the similarity to the numerical second derivative spectrum in panel B, implying that large changes in dipole moment accompany the excitation. Panel D compares the 90° spectrum with a nine-parameter (three transition) fit to eq 3.¹⁷ From the fit, the absolute value of $\Delta\mu$ is 6.7 ± 1 D for the lowest MLCT transition.¹⁸ This value is in fair agreement with the estimate from solvatochromic measurements⁵ and is very close to the value reported by Oh and Boxer^{2c} for MLCT excitation of **1**. It

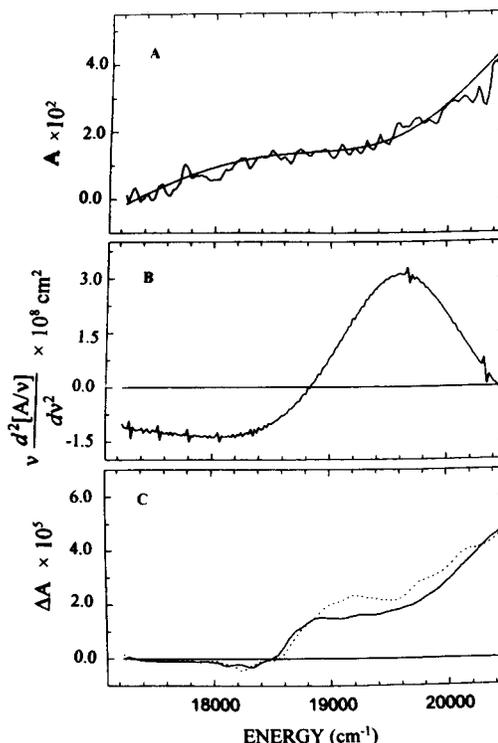


Figure 2. Panel A: Low-Temperature absorption spectrum of **2** in the triplet MLCT region. Also shown is the apparent spectral response after application of a smoothing function. Panel B: Numerical second derivative of the smoothed spectrum in panel A. Panel C: Experimental electroabsorption spectra at $\chi = 90^\circ$ (solid line) and 55° (dashed line).

is important to note that if the electron were symmetrically delocalized in the excited state, the state would possess no dipole moment and the net dipole moment change would be zero (since the ground state has a negligible dipole moment). In contrast, from the Stark-derived changes in dipole moment, we conclude that *optical excitation of 2, like 1, yields an intrinsically localized ¹MLCT excited state*:



We are unable to explain the contrary finding of Turró and co-workers.⁴ We note, however, that the TR³ experiment almost certainly interrogates primarily the long-lived triplet MLCT state (accessed by intersystem crossing), whereas the electroabsorption experiment reports on the short-lived singlet state. It is conceivable, albeit unlikely, that the charge distribution fundamentally differs in the two excited states. To check this possibility, however, we also examined the Stark behavior of

(17) If the Stark spectrum is instead fit to only 3 parameters (i.e., if the absorption spectrum is treated as a single electronic transition), then an overall $|\Delta\mu|$ value of 7.1 ± 1 D is obtained (see Supporting Information). The result perhaps should not be too surprising given the similarities of the values determined for each of the three component transitions.¹⁸ Nevertheless, the approximate agreement between the dipole parameters derived from the one-component versus three-component fit suggests that the numerical findings are robust with respect to the details of spectral deconvolution.

(18) Also accompanying the excitation is a polarizability change of $+570 \pm 100 \text{ \AA}^3$, where the sign of the change indicates that the CT excited state is more polarizable than the ground electronic state. The angle, ξ , between $\Delta\mu$ and the transition dipole moment vector was found to be 38° , rather than the expected 0° . Nearly identical behavior has been observed by Oh (Ph.D. Thesis, Dept. of Chemistry, Stanford University, 1991) for **1**. He has suggested that the deviation might arise from incomplete deconvolution of overlapping electronic transitions. From the fit in Figure 1, the absolute dipole moment changes for the higher energy transitions ($E = 23\,700$ and $26\,000 \text{ cm}^{-1}$) are both ca. 5.5 ± 2 D.

the formally forbidden triplet MLCT transition.¹⁹ As highlighted in Figure 2A, this transition is observable as a weak feature lying somewhat to the red of the nominally singlet transition. Panel B illustrates the second derivative of the fit of panel A. Panel C shows Stark spectra at $\chi = 90$ and 55° . The dipole moment change for the singlet to triplet charge transfer was estimated to be 11 ± 4 D where the larger uncertainty reflects an interference (i.e. partial spectral overlap) by the singlet transition. The uncertainty also reflects the low oscillator strength and high signal-to-noise ratio for the triplet transition. Despite the uncertainty, the dipole moment change again is apparently large²⁰ and is clearly suggestive of excited-state charge localization.

Conclusions

Electronic Stark effect measurements reveal that the initially formed “singlet” MLCT excited state of Ru(phenanthroline)₃²⁺

(19) For related examples, see: Coe, B. J.; Thompson, D. W.; Culertson, C. T.; Schoonover, J. R.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 3385.

(20) We have no explanation for the apparently greater dipole moment change for the triplet versus singlet MLCT transition. We note, however, that comparative electroabsorption and electroemission experiments for **1** reveal a similar dependence on nominal spin of the excited state.^{2c,18}

exists in a charge localized form that both qualitatively and quantitatively resembles the initially formed MLCT state of the well-known bipyridine analogue. The nominally “triplet” transition also involves the formation of a charge-localized state. The Stark findings are inconsistent, therefore, with a “delocalized” interpretation suggested in a recently reported time-resolved resonance Raman investigation of the phenanthroline complex.

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Supporting Information Available: Figure S1, illustrating the dependence of the absorption energy maximum for **2** upon solvent composition, and Figure S2, showing a global three-parameter fit to the 90° Stark spectrum of **2** in the singlet MLCT region (2 pages). Ordering information is given on any current masthead page.

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