

ferentiate between terminal and bridging metal hydride sites and quantify the relative populations of  $M-H$  and  $M-H-M$  sites. Before assignment of bridging metal hydride resonances involving a transition metal can be attempted, an approximate value of the deuterium quadrupole coupling constant for a simple, terminal metal hydride of that metal is required. In the absence of the deuterium NMR spectrum for a terminal metal hydride site, an estimate of the deuterium quadrupole coupling constant can be made from the vibrational  $M-H$  stretching force constant.

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## Delocalization As Evidenced by Absorption, Luminescence, and Excitation Spectra of $Ru(bpy)_3^{2+}$ in $Zn(bpy)_3(PF_6)_2$ and Ethanol/Methanol Glasses

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The metal-ligand excited states of the  $Ru(bpy)_3^{2+}$  chromophore in  $Zn(bpy)_3(PF_6)_2$  can only be effectively described by a delocalized  $D_3$  model. This is in spite of the fact that the chromophore is at a low-symmetry site with only approximate  $C_2$  symmetry. Polarized spectra are completely inconsistent with a localized  $C_2$  model. Luminescence excitation polarization spectra detected at different energies within the emission profile are presented for 4:1 ethanol/methanol glasses at 110 K, and a resolution of the conflict among interpretations of luminescence polarization ratios, excited-state Raman spectra, and a larger body of spectroscopic evidence is given.

### Introduction

A large number of spectral techniques have been brought to bear on the  $Ru(bpy)_3^{2+}$  chromophore, but there appears to be a continued controversy about the nature of the excited states of this complex ion.<sup>1-3</sup> Although it is uniformly agreed that the visible absorption bands involve transfer of an electron from the metal ion to the ligands, two types of spectral evidence have been used to support arguments for the inequivalent involvement of the ligands in both absorption and emission processes, i.e., a localized rather than a delocalized description. The purpose of this paper is to report new data, which establish beyond reasonable doubt that localization arguments are flawed and all of the charge-transfer states are intrinsically delocalized, even in crystals where strict  $D_3$  symmetry is not maintained between the ligands.

The strongest argument for localization comes from excited-state resonance Raman (ERR) spectra observed in fluid solutions.<sup>4,5</sup> The evidence seems unequivocal in its support of localization of charge in the luminescent states. ERR spectra resemble free-radical  $bpy^-$  Raman spectra and are *not* dependent on substitution of one or two  $bpy$ s with completely different electrophobic ligands. However, this localization process has been shown<sup>6</sup> to be the result of a fast environmental relaxation that traps the electron on a single ligand which is inhibited in solid phases. Time-resolved luminescence (TRL) spectra can be observed and change markedly upon formation of a glass.<sup>6</sup> ERR spectra taken of  $Ru(bpy)_3^{2+}$  in solid phases are completely different from those observed in solution<sup>7</sup> and in fact show a quasi-continuum scattering.

The second argument is older and stems from a number of observations of the luminescence polarization ratio in glycol/water and other glass-forming mixtures. They were originally reported by Fujita and Kobayashi,<sup>8</sup> confirmed by Felix et al.,<sup>9</sup> and further

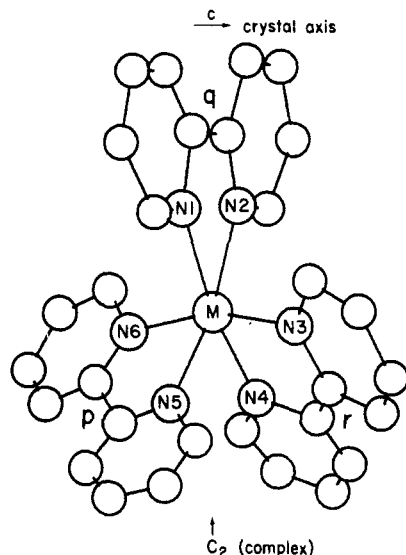
extensively investigated by DeArmond et al.<sup>1,2</sup> These results consistently show a region of anomalously high polarization ratio at about  $21\,000\text{ cm}^{-1}$ , too high for a planar oscillator in both absorption and emission ( $>1/7$ ). The fact that the polarization is greater than  $1/7$  suggests that the symmetry of the chromophore is not  $D_3$  but lower, so as to involve linear rather than planar oscillators.

Most recently, Braterman et al.<sup>3</sup> have used the observations of solution ERR, anomalous polarization ratios, and evidence from excited-state absorption spectra in fluid solutions<sup>10</sup> to propose a localized description for the triplet states and "part" of the singlet states. In their view the spin-allowed transitions are considered to be either "trapped" at lower energies or "untrapped" at higher energies, thus explaining the anomalously high polarization ratio observed around  $21\,000\text{ cm}^{-1}$  where a changeover from "trapped" to "untrapped" absorption is considered to occur. The bulk of the spin-allowed band is considered "untrapped". It was further speculated<sup>3,10</sup> that transitions in the "trapped" region are followed by radiationless decay to a luminescent state in which the electron resides on the same ligand; i.e., the complex retains a memory of the initial absorption process. On the other hand, absorption to higher energies leads to a loss of memory by the excited ion and there is a random selection of the luminescent states.

This proposal by Braterman et al.<sup>3</sup> attempts to interpret the polarization result in glassy media without giving sufficient consideration to a larger body of spectroscopic data. In particular, the measurement of CD in the same spectral region in single crystals<sup>11</sup> of  $Zn(bpy)_3(BF_4)_2 \cdot Ru$  is quite inconsistent with their proposal. The absence of detailed structural information for the  $Zn(bpy)_3(BF_4)_2$  host crystal tends to weaken the case, and a similar lack of crystal structure information for the host  $Zn(bpy)_3(PF_6)_2$  could perhaps be used to dismiss some of the conclusions reached from a study of the spectroscopy in this host as well.<sup>12,13</sup> Fortunately, the crystal structure of  $Zn(bpy)_3(PF_6)_2$  has now been solved,<sup>14</sup> and the basic structural features predicted from the previous spectroscopic analysis have in fact been confirmed. We are therefore in a strong position to use the crystallographically

(1) Carlin, C. M.; DeArmond, M. K. *Chem. Phys. Lett.* **1982**, *89*, 297.  
 (2) Carlin, C. M.; DeArmond, M. K. *J. Am. Chem. Soc.* **1985**, *107*, 53.  
 (3) Braterman, P. S.; Heath, G. A.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1081.  
 (4) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391.  
 (5) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441.  
 (6) Ferguson, J.; Krausz, E. R.; Maeder, M. *J. Phys. Chem.* **1985**, *89*, 1852.  
 (7) Krausz, E. *Chem. Phys. Lett.* **1985**, *116*, 501.  
 (8) Fujita, I.; Kobayashi, H. *Inorg. Chem.* **1973**, *12*, 2758.  
 (9) Felix, F.; Ferguson, J.; Guedel, H. U.; Ludi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4096.

(10) Braterman, P. S.; Harriman, A.; Heath, G. A.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1801.  
 (11) Ferguson, J.; Herren, F.; McLaughlin, G. M. *Chem. Phys. Lett.* **1982**, *89*, 376.  
 (12) Ferguson, J.; Herren, F. *Chem. Phys. Lett.* **1982**, *89*, 371.  
 (13) Ferguson, J.; Herren, F. *Chem. Phys.* **1983**, *76*, 45.  
 (14) Bernal, I.; Palmer, R. A., unpublished results.



**Figure 1.** Projection of one  $\text{Zn}(\text{bpy})_3$  complex ion onto a plane perpendicular to its approximate threefold axis. The other two ions in the unit cell are obtained by rotations of  $120^\circ$  and  $240^\circ$  about the crystal  $c$  axis. Polarized absorption and emission spectra were measured with the electric vector either parallel ( $\pi$ ) or perpendicular ( $\sigma$ ) to the  $c$  axis of the crystal.

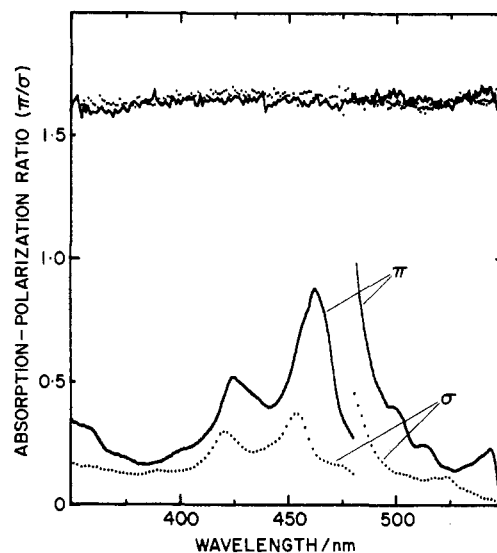
determined structure to carry out a more definitive analysis of the spectroscopic properties of  $\text{Ru}^{2+}$  in this host, and, in particular, we can consider the predictions of Braterman et al.<sup>3</sup> in detail.

#### Crystal Structure and Polarization Behavior

There are three  $\text{Zn}(\text{bpy})_3^{2+}$  chromophores in the hexagonal unit cell, and Figure 1 shows a projection of one ion onto a plane orthogonal to the chromophore's approximate threefold axis. The other two ions are obtained by  $120^\circ$  and  $240^\circ$  rotations about the crystal  $c$  axis. Each ion has an approximate  $C_2$  axis with ligands  $p$  and  $r$  being similar but different from  $q$ , and the axis is nearly orthogonal to the crystal  $c$  axis (Figure 1).

Braterman et al.<sup>3</sup> maintain that excitation to the triplet states is intrinsically localized and the transferred electron remains trapped on the same ligand until luminescence occurs. We note from Figure 1 that absorption (emission) to (from) ligand  $q$  is polarized perpendicular to the crystal  $c$  axis ( $\sigma$ ), while that involving ligands  $p$  and  $r$  occurs for both polarizations with a ratio  $\pi/\sigma = 6/1$  (averaged over the three ions in the cell). Following this hypothesis, excitation with  $\sigma$ -polarized light will lead to emission from ions in which the transferred electron resides on all three ligands (but unequally), whereas excitation with  $\pi$ -polarized light will lead to emission from ions in which the transferred electron resides only on ligands  $p$  and  $r$ . Orientation factors in the first case lead to the emission being nearly unpolarized ( $\pi \approx \sigma$ ) and in the second case to strong polarization ( $\pi/\sigma = 6/1$ ). Furthermore, in the spin-allowed region, following the same hypothesis, we would expect "loss of memory" at some threshold energy in the absorption process and the polarization of the luminescence would change on scanning across this part of the absorption band.

On the other hand, if the charge-transfer states are intrinsically delocalized in  $D_3$  symmetry and the  $C_2$  (and lower) symmetry is only a (minor) perturbation, we would expect polarization behavior quite different from that outlined above. The absorption in both singlet and triplet spectral regions leads to radiationless decay to the same set of luminescent states in each case, for both polarizations in absorption. The polarization ratio of the luminescence will be characteristic of this set of emitting states, for a given temperature, which may or may not be localized by some subsequent environmental relaxation. So far, the evidence from MCPL at 2 K in  $\text{Zn}(\text{bpy})_3(\text{BF}_4)_2:\text{Ru}$  shows at least one degenerate emitting state, indicating delocalization.<sup>15</sup> Thus the emission will



**Figure 2.** Polarized absorption spectra of  $\text{Zn}(\text{bpy})_3(\text{PF}_6)_2:\text{Ru}$ , measured at 10 K (bottom curves,  $\sigma$  and  $\pi$ ) and luminescence polarization ratios ( $\pi/\sigma$ ) (top curves) for  $\sigma$  (dots) and  $\pi$  (full lines) polarization in absorption. Two crystals of different absorbances are used to cover the singlet and triplet regions.

have the same polarization ratio, that characteristic of the emitting state, regardless of the excitation energy or polarization.

The question of localization is therefore answered by measurements analogous to those carried out in glassy media, but using a single crystal of  $\text{Zn}(\text{bpy})_3(\text{PF}_6)_2:\text{Ru}$ .

#### Experimental Section

Crystals (as hexagonal needles) were grown by slow evaporation of ethanol/acetonitrile (1:1) solutions of  $\text{Zn}(\text{bpy})_3(\text{PF}_6)_2$  and contained about  $10^{-3}$  mole ratio of the Ru replacing the Zn. Absorption spectra were measured on a Cary 17 spectrophotometer by using a cryogenic flow tube technique. Data were logged on a Camac microprocessor and transferred to a VAX 11/750 for further analysis and display. Excitation spectra were recorded on an apparatus previously<sup>16</sup> described and corrected for variations in excitation quantal output with rhodamine B used as a quantum counter.

Glasses were made by rapid cooling of degassed solutions of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  dissolved ( $10^{-5}$  M) in 4:1 ethanol/methanol mixtures.

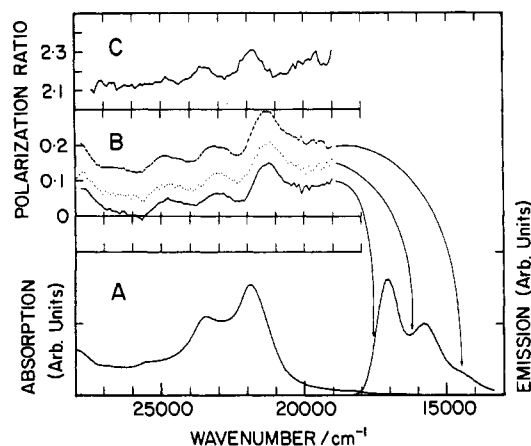
#### Results

Figure 2 shows the polarized excitation spectral polarization ratios, at 10 K (for  $90^\circ$  geometry), detected for total emitted light polarized parallel and perpendicular to the crystal  $c$  axis of  $\text{Zn}(\text{bpy})_3(\text{PF}_6)_2:\text{Ru}$ . Analogous experiments were carried out at 1.4 and 100 K, with similar results. The only difference is the values of the polarization ratio, which are temperature dependent. These ratios were obtained by measuring two excitation spectra (detected parallel and perpendicular to the  $c$  crystal axis, respectively) for each of the two polarizations of the incident light (parallel and perpendicular to the crystal  $c$  axis, respectively). Two crystals of threefold differing Ru absorbance were used to cover the spin-allowed and spin-forbidden regions. Figure 2 also displays the polarized absorption spectra of the two crystals at the same temperature (10 K). It is abundantly clear that the polarization ratio of the emitted light is independent of both the polarization and the energy of the incident light. This is consistent with delocalization of the excited states, both triplet and singlet, but completely inconsistent with the predictions of Braterman et al.<sup>3</sup> as outlined in the Introduction.

The anomalous polarization ratio observed in glassy media that occurs near  $21\,000\text{ cm}^{-1}$  needs to be understood in relation to the results shown above. Felix et al.<sup>9</sup> ascribed this anomaly to a distribution of molecular geometries inherent in a glassy matrix, but this explanation was rejected by Carlin and DeArmond<sup>1,2</sup> who argued in favour of a single emitting species in which the excitation

(15) Ferguson, J.; Krausz, E. *Chem. Phys. Lett.* **1982**, *93*, 21.

(16) Ferguson, J. *SPEX Speaker* **1976**, *21*(1).



**Figure 3.** (A) Absorption (left) and luminescence (right) spectra of Ru(bpy)<sub>3</sub><sup>2+</sup> in ethanol/methanol (4:1) at 110 K. (B) Luminescence polarization ratios detected at the points in the luminescence spectrum shown by the arrows. (C) Ratio of unpolarized excitation spectra (incident and detection electric vectors horizontal) detected at 17330 and 14480 cm<sup>-1</sup>.

is localized on a single ligand. Carlin and DeArmond<sup>1,2</sup> provided no explanation for the excitation-dependent luminescence reported by Felix et al.<sup>9</sup> Our recent work<sup>6,7</sup> shows that localization onto a single ligand only occurs in fluid media. It is important to reexamine the luminescence polarization data in glassy media in order to account for the polarization ratio anomaly without resorting to a localized model. We therefore measured the luminescence polarization ratio ( $P$ ) detected at *different* energies using the simple expedient of interference filters in front of the photomultiplier detector. If emission is due to a single species in the ordinary way there should be no difference in the measured values of  $P$  when detected at different emission energies. Significant differences were however found. The modulation of  $P$  across the absorption region at the three detected energies are similar, but there is an overall increase of  $P$  as detection is moved to lower energy (Figure 3B). Although Carlin and DeArmond<sup>1</sup> did not explicitly report this phenomenon, it is implicit in their reported emission photoselection spectra for different wavelengths of excitation (see Figure 1d-f in ref 1). Further studies of the excitation polarization ratio in glasses and PVA polymer films do not exhibit any significant change down to about 20 K.

Figure 3C displays the ratio of the unpolarized excitation spectra (measured with incident polarization vector horizontal, detection polarization horizontal) detected at 17330 and 14480 cm<sup>-1</sup>. This curve reproduces the work of Carlin and DeArmond<sup>1</sup> (their Figure 1g).

### Luminescence Photoselection Model

The fact that the excitation polarization ratios are sensitive to the detected wavelength of emission argues against a single emitting species as proposed by Carlin and DeArmond.<sup>1,2</sup> We feel, in view of the clear cut interpretation of the results from the single-crystal polarization work given in Figure 2, that the interpretation of the glassy media results requires at least two sets of emitting species. In the simplest model, one species is a planar emitter and the other is a (distorted) linear emitter. In frozen glasses a continuum could be expected between these two extremes, but for simplicity, we can consider there are just two species present. The luminescence spectra of the two species nearly overlap but they have somewhat different intensity distributions. Selecting one energy of detection over another will give a small change in the bias of one species over the other. The polarization ratio of the luminescence itself varies across its excitation profile, being lowest on the high-energy side.

A comparison of the various quantities displayed in Figure 3 is instructive. In particular, considering the absorption in Figure 3A and the excitation polarization ratios in Figure 3B, the three distinct maxima of polarization ratio do *not* correspond in position to the (two) maxima in the absorption spectra. The polarization

ratio features, perhaps, correspond to weaker features in absorption due particularly to the distorted (linear) species, appearing at lower energies. The ratio of (unpolarized) excitation spectra ( $R$ ) detected at two different energies (Figure 3C) does, however, show peaks at the same positions as occur in absorption (Figure 3A) with comparable relative intensities. This variation in  $R$  is only small, being at most 5% of the average (constant) ratio around 2.3.  $R$  is composed of a number of factors. If one defines  $c_p$  as the fraction of light absorbed by the first species at wavenumber  $\bar{\nu}$  and  $q_1$  and  $q_2$  and  $I_1(\bar{\nu})$  and  $I_2(\bar{\nu})$  as the quantum efficiencies and normalized intensity profiles for the first and second species, respectively,  $R$  is expressed as

$$R(\bar{\nu}, \bar{\nu}_1, \bar{\nu}_2) = \frac{q_1[I_1(\bar{\nu}_1)]c_p + q_2[I_2(\bar{\nu}_1)](1 - c_p)}{q_1[I_1(\bar{\nu}_2)]c_p + q_2[I_2(\bar{\nu}_2)](1 - c_p)} \quad (1)$$

where  $\bar{\nu}$  is the excitation energy and  $\bar{\nu}_1$  and  $\bar{\nu}_2$  are the two detecting energies.

$$\int I_i(\bar{\nu}) d\bar{\nu} = 1 \quad (2)$$

If the two intensity profiles  $I_1$  and  $I_2$  and the quantum efficiencies are identical,  $R$  is independent of the fraction absorbed as a function of exciting energy  $c_p$ , and reduces to the constant ratio  $I(\bar{\nu}_1)/I(\bar{\nu}_2)$ . Only a small variation is seen in  $R$  (Figure 3C), which confirms that the two species have only slightly differing emission intensity profiles. As the maxima seen in Figure 3C occur at the absorption maxima, it is reasonable to assume that they are associated with the majority species. This follows the variation of  $c$  with  $\bar{\nu}$ . The majority species has a luminescence spectrum that lies slightly to higher energy with respect to the minority species. The minority species has a luminescence spectrum that is more strongly polarized as evident in Figure 3B.

One difficulty in quantifying the description at this point is that there is no good reason to expect that the quantum efficiencies of the two emitters are equal. If the relative concentration of the components could be estimated and the individual absorption spectra thus deconvoluted, the individual emission and quantum efficiencies could be established.

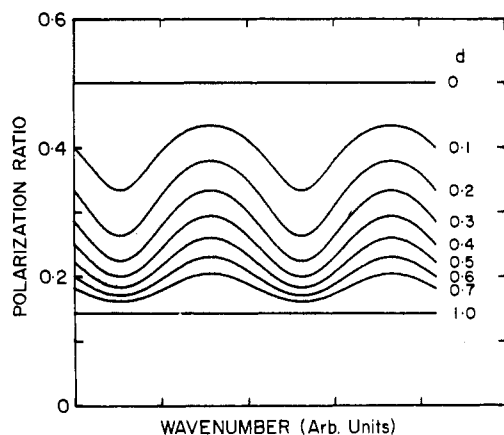
We assume that the majority species has essentially  $D_3$  symmetry, so its polarization ratio is that of a planar oscillator ( $1/7$ ). We then assume that the minority species has a distorted symmetry so that it is a linear oscillator and the charge transfer to one ligand is different (localized) from the charge transfer to the other two ligands (delocalized). This leads to a polarization ratio of  $1/2$ . As the absorption spectrum of the linear oscillator does *not* precisely follow that of the planar oscillator, the excitation photoselection spectrum will oscillate, approaching  $1/7$  for energies dominated by the planar oscillator absorption or  $1/2$  for energies dominated by the linear oscillator. This picture is simplified, as we are neglecting the possibility of absorption and emission oscillators being orthogonal. This of course is needed to account for polarization ratios  $< 1/7$ , but the model contains the essential features needed to understand the main features of excitation photoselection spectra in Figure 3B.

We again denote by  $c_p$  the fraction of light absorbed by the planar chromophores and  $(1 - c_p)$  is the fraction absorbed by the linear chromophores. The corresponding fractions of emitted light are  $d$  and  $(1 - d)$ , respectively. From Albrecht,<sup>17</sup> the polarization ratio  $P_p$  is given straightforwardly by the expression

$$P_p = [c_p d / 2 + 2(1 - c_p)(1 - d)] / [7c_p d / 2 + 4(1 - c_p)(1 - d)] \quad (3)$$

This simple formula allows us to examine the variation of  $P_p$  with  $d$ , which changes slightly with detected energy. This requires the variation of  $c$  with absorption energy  $\bar{\nu}$  to be known. The  $d$  parameter is smaller for detection at 14470 cm<sup>-1</sup> and the larger for detection at 17330 cm<sup>-1</sup> by arguments outlined above.

Figure 4 simulates the basic phenomenon, giving excitation polarization spectra calculated for different values of  $d$  from



**Figure 4.** Simulated dispersion of the polarization ratio (eq 3) for various fractions ( $d$ ) of light detected due to the majority species (planar oscillator), which absorbs the fraction of light  $c_p = 0.8 + 0.1 \sin \bar{\nu}$ .

expression 3. The fraction of light absorbed by the majority species is given by  $0.8 + 0.1 \sin \bar{\nu}$ . That is, a 80% constant fraction of absorption is modulated by  $\pm 10\%$  in a harmonic fashion with respect to the dependent variable  $\bar{\nu}$ . This expression is chosen to reveal the basic phenomenon rather than an attempt to fit the observed polarization ratio spectra. An attempted numerical fit to the data would need to include the out-of-phase oscillator component of the absorption spectrum of the (distorted) linear oscillator to reduce the overall ratio below  $1/7$  and would require many additional unknown parameters.

The limiting values of the polarization ratios are simply constants of  $1/2$  for  $d = 0$  (linear emitter only detected in emission) and  $1/7$  for  $d = 1$  (planar emitter only). The effect of varying the value of  $d$  slightly (10%) for intermediate values of  $d$  shifts the varying component of polarization excitation spectrum up or down as a whole without changing the amplitude of the variation greatly. Detecting the luminescence spectrum at various points across the luminescence profile corresponds to slightly different values of  $d$ . The correspondence of the data (Figure 3B) with the basic features in Figure 4 supports our interpretation.

### Discussion

The question of delocalization in crystalline environments seems beyond doubt. The uniformity and magnitude of the single-crystal polarization excitation spectrum in Figure 2 are consistent with and only with an absorption process involving the three bpy ligands in unison and not individually. The observation of temperature-dependent magnetic circular-polarized luminescence<sup>15</sup> (MCPL) of  $\text{Ru}(\text{bpy})_3^{2+}$  doped in  $\text{Zn}(\text{bpy})_3(\text{BF}_4)_2$  single crystals taken in the 10–50 K range can only be understood if the emitting state maintains an electronic degeneracy to the level of  $\sim kT$  and has a substantial magnetic moment. The  $\text{Ru}(\text{bpy})_3^{2+}$  system, being an (even electron)  $d^6$  configuration, has no degenerate states in any symmetry less than  $D_3$ , and the implication is that low symmetry potentials only split the degeneracy of the emitting state by less than  $\sim 10 \text{ cm}^{-1}$ . The MCPL indicates a symmetry close to  $D_3$  for the  $\text{BF}_4$  crystals. The  $\text{Zn}(\text{bpy})_3(\text{PF}_6)_2$  crystals, by virtue of the fact that  $g_{\text{perp}}$  of an even electron system is zero, have vanishing MCPL,<sup>17</sup> and this again is consistent with the fact that approximate molecular threefold axis of the crystal is perpendicular to the  $c$  axis of the crystal. MCPL measurements taken in plastic film of poly(vinyl alcohol) and 1:1 glycol/water glasses show<sup>18</sup> MCPL spectra in the same temperature range (10–50 K) similar to that seen in the  $\text{Zn}(\text{bpy})_3(\text{BF}_4)_2$  crystal, again demanding a uniform planar oscillator and *not* independent linear oscillators for each metal–bpy electron transfer.

Carlin and DeArmond have argued strongly against environmental localization effects in their recent paper<sup>2</sup> devoted to solvent and temperature dependence of the polarization photoselection

spectrum of  $\text{Ru}(\text{bpy})_3^{2+}$ . A single (localized) emitting species is assumed. Felix et al.<sup>9</sup> previously reported a significant dependence of the emission spectrum *band shape* on excitation energy, and this was used by them to infer a range of species in the glass measured. We have further shown that the excitation polarization spectrum is dependent on the energy used in detection and neither of these phenomena seem compatible with a single emitting species.

Considering the 4:1 ethanol/methanol system in particular, it is easy to see how the data in Figure 3 of ref 2 could be misinterpreted. Over the range from 110–180 K, the emission spectrum undergoes a substantial shift to the blue.<sup>6</sup> TRL measurements<sup>6</sup> at 130 K have shown that the blue component emits at short times ( $< 100 \text{ ns}$ ) and a red component emits at longer times, indicating a fast environmental relaxation of the system at higher temperatures. Excitation polarization measurements were made at a fixed wavelength of 580 nm, favoring the red-shifted (long time or high temperature) emission. Steady-state ratios measured at *differing* temperatures but at this *fixed* wavelength could be difficult to understand.

We suggest that in low-temperature glasses, there is a range of sites present, some of which emit with polarizations greater than  $1/7$ . The differences in emission spectra among these species are *not great*, but the distorted species emit to slightly lower energy. As the temperature is increased to the softening point of the glass, an environmental relaxation process can occur in which *strongly* distorted species are created (the excitation localizes), and the emission evolves to the strongly red-shifted emission with a time scale depending on the medium viscosity. Rotational diffusion, also depending on medium viscosity, but not in an identical manner, occurs at similar temperatures, and there is a competition among shifting emissions, changing polarization ratios, and rotational averaging.

Time-resolved luminescence polarization ratio measurements may provide interesting data on the dynamics of the environmental relaxation process. The environmentally induced relaxation process gives rise to substantial shifts of the emission to low energy. We propose that the small distortions evidenced in the rigid glasses are due to ion pairing and solvent phenomena and may be usefully studied by varying the counterion, counterion concentration, and glass-counterion solvation properties.

### Conclusion

The very clear uniformity of excitation polarization ratio observed with the  $\text{Ru}(\text{bpy})_3^{2+}$  chromophore doped in  $\text{Zn}(\text{bpy})_3(\text{PF}_6)_2$  is compelling evidence for complete delocalization in all the excited states in this crystal system where, notably, substantial distortions are present. The proposals of Braterman et al.<sup>3</sup> must be discounted on the basis of this evidence.

A better understanding of the nature of the chromophore in glassy environments also evolves from this work, and the anomalies in photoselection polarization ratios, responsible for considerable discussion, can be understood as due to a range of different subspecies absorbing and emitting with slightly different energies but absorbing with substantially different polarizations.

A unified description of the spectroscopy of the  $\text{Ru}(\text{bpy})_3^{2+}$  system is possible once the difference between spectra measured in solution and those measured in the solid phase (either as glasses or as doped crystals) is taken into account. Emission, ERR, and excited-state absorption spectra, taken in solution, are measuring properties of an environmentally relaxed species that is strongly localized and quite different from the species initially created in absorption. Once environmental relaxation is inhibited (in rigid media), luminescence can only be effectively described as delocalized.

The dynamics of the localization process and the influence of the environment present an interesting theoretical and experimental challenge. An understanding of these may have bearing on the well-known photochemical potentialities of the system.

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