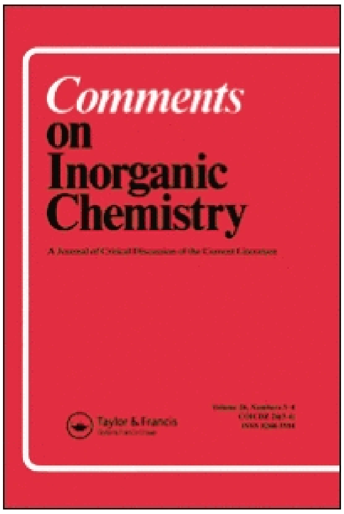

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Spectroscopic Evidence for the Nature of the Excited States of the $Ru(bpy)_3^{2+}$ System

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An overview of the recent developments in the spectroscopy of the $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) system is given. Particular interest lies in the nature of the charge transfer excited states, and an appraisal of various excited state properties, as determined by experiment, is put forward. The validity of the interpretations of some of these experiments is discussed and is related to prevailing current ideas such as "exciton hopping," "spatially isolated orbitals" and the concept of "localization" in general. On balance, it is suggested that the best initial description of the excited states involves the ligands equivalently, the excitation being fundamentally delocalized. Suggestions are made towards definitive experiments in this area.

Key Words: *charge transfer, localization, excited state, polarization, spectra*

INTRODUCTION

The continuing interest shown by a number of groups in the spectroscopy and photophysics of the $Ru(bpy)_3^{2+}$ (RBY) system and its analogues may seem rather surprising, particularly as the flurry of interest in RBY's seductive excited state photochemical poten-

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tial (the photoreduction of water by visible light) in the late 1970's has long past, without realizing its goal of harnessing solar energy photochemically. Also, in the minds of many chemists, the nature of the luminescent excited state was clearly established as one in which an electron is transferred to a single bpy ligand. This idea found relevance in regard to spectroscopic features of electrochemically generated reduction products of RBY and related compounds and to the idea of a "spatially isolated" redox orbital.

The idea that only one of three (equivalent) ligands was involved in a charge transfer absorption or luminescence process was very difficult to come to terms with when considering the detailed polarized spectroscopy of the RBY system, especially in work carried out in single crystal environments. Unfortunately the techniques and theoretical base for many of these more direct probes of the excited states are not accessible to some workers in the field and thus many of the constraints placed by these results have tended to be ignored or brushed aside. This in turn has led to some tension. The term "spectrologist" has been coined to describe an (inorganic) chemist, taking spectra, who has only a rudimentary understanding of spectroscopy and its classical and/or quantum mechanical basis. To a spectrologist, talk of experiments "done in single crystals at 4 K," "picosecond timescales" and "polarizations" have little relevance compared to more important chemical principles, which have to do with orbitals (the proposed identity of an electron in a system) and what it (the postulated identity) would like or not like to do.

Of course this is unfair, each approach has its own practical, empirical validity. The purpose of this Comment is to help establish a coherent base from which to consider the RBY system, based on all the types of experimental spectroscopic information that are now available, to briefly review the efficacy of each technique, and to suggest new experiments that may prove incisive and convincing to all.

Readers may consult any of a number of reviews that have been published in recent years.[1] A very extensive compendium of the photochemistry and photophysics of the myriad of substituted and RBY related materials has been provided by Balzani and his group,[2] and a more complete analysis and review of the rather complex spectroscopy of the RBY system is given by Ferguson and Krausz.[3]

A great number of papers have been published, and continue to be published, probably making RBY the most studied material in inorganic spectroscopy. There seems to be two main reasons for this sustained interest. First and foremost, it keeps showing fascinating new and experimentally easily accessible phenomena, a few of which still require an adequate explanation. The stunning example is of course that the very first (vibrational) excited state Raman spectrum was recorded with this material.[4] Second, studies on this system serve, through a number of perhaps merely pragmatic factors, to model optical charge transfer processes in general. This latter purpose has much wider implications in photochemistry and photobiology.

THEORETICAL BASIS AND TIMESCALES

There is little argument about the metal to ligand charge transfer (MLCT) nature of the observable excited states of RBY in the visible region. Paris and Brant[5] suggested a charge transfer assignment as early as 1959; Lytle and Hercules[6] proposed an (incorrect) energy level pattern some ten years later. The basic process involves transference of a *d* electron from the filled t_2^6 shell of Ru^{2+} and placing it in a low lying π^* state orbital configuration of the bipyridine ligands.

The RBY complex has crystallographic D_3 symmetry in the hexagonal $Ru(bpy)_3(PF_6)_2$ (RPF) crystal system[7] (Fig. 1). The trigonal potential associated with the ligands in tris-immine complexes is quite strong[8] and this splits the t_2 (octahedral based) orbital into a_1 and ϵ metal orbitals, by the order of 0.2 eV. The back bonding nature of the (cf. Ref. 19) Ru-Nπ link in these systems naturally places the (trigonal) ϵ orbital below the a_1 (Fig. 2). The ground state configuration has no net orbital degeneracy, as it arises from the filled metal a_1, ϵ and ligand π configurations, and is thus *not* susceptible to a Jahn–Teller distortion. The excited states with orbital degeneracy could be particularly Jahn–Teller susceptible in this system. In addition one could also expect a strong interaction with the environment due to the accessible and polarizable electron density associated with the partly filled π^* bipyridine orbitals.

The simplest description of the *lowest energy* orbital jumps in-

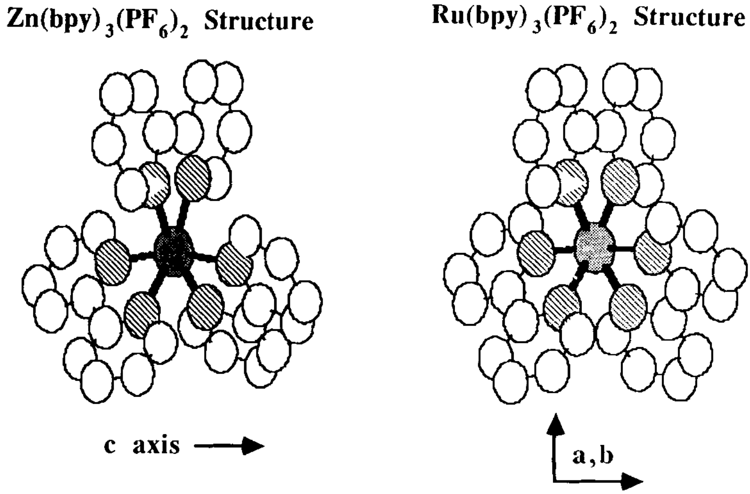


FIGURE 1 Structures in "dilute" $Zn(bpy)_3(PF_6)_2$ (ZPF) and "neat" $Ru(bpy)_3(PF_6)_2$ (RPF) lattices from data in Refs. 7 and 34. Both have hexagonal lattices; bpy nitrogens are shaded.

volves (one electron) jumps from the (filled) metal a_1 and ϵ metal d electron orbitals to the lowest energy (empty) orbitals of the ligand system. The ligand orbitals must transform as an irreducible representation of the point group of RBY (D_3). The usual approach is to first consider the two pyridine components of the bpy. The LUMO's on the pyridines combine in either a symmetric χ^* or antisymmetric ψ^* combinations (with respect to the C_2 axis of the ligand). The separation of these orbitals is around 1 eV with the ψ^* lying lowest.[9] Following Day and Sanders,[10] it is then possible to generate D_3 ligand orbitals from the ψ orbitals on the three ligands and they transform as a_2 and ϵ. The four orbital jumps in Fig. 2 then give rise to six orbital singlets and six doublets. Once the strong spin-orbit coupling on the metal core is considered (0.2 eV) 24 states evolve from the four orbital jumps. Further states originating from jumps to χ^* ligand orbitals may also overlap these, as the χ^*, ψ^* separation is comparable to electron repulsions and spin-orbit coupling.

The number of states observed optically is limited by the transition dipole intensity mechanism. If transfer term intensity is considered to be dominant,

$$\langle t_2 | \mathrm{qr} | \psi \rangle \neq 0,$$

this requirement for direct metal ligand overlap allows only $\epsilon \rightarrow a_2$ and $\epsilon \rightarrow \epsilon$ orbital jumps. This in turn gives rise to two singlet E's and three triplet E's having substantial intensity.[11]

A very important feature of this discussion is that it applies to electronic interactions within a fixed nuclear framework. By the Born–Oppenheimer separability, electronic rearrangements can occur very much more quickly than nuclear motions. Thus all excited states must have the same fixed nuclear geometry as the ground state, and the parameters extracted from such an analysis apply to these vertical processes. One may choose the electronic

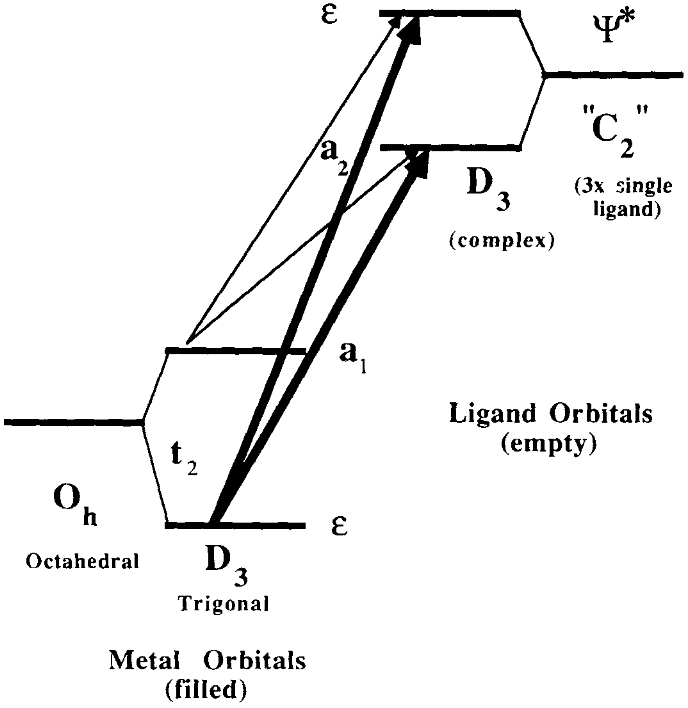
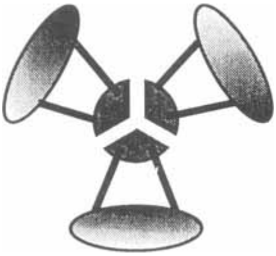


FIGURE 2 Orbital configurations in RBY and their parentage. Heavy arrows show allowed transfer term orbital jumps.

bases for RBY in various ways; by first combining ligand orbitals, or by concentrating on metal single-ligand fragments an equivalent representation is achieved if one uses an adequate basis. There is an analogy in MO and VB approaches to bonding. Which approach used is only a matter of choice and ultimately becomes insignificant when adequate basis sets are provided.

Within this purely electronic framework, the concept of MLCT excitation localization only has a meaning in a physically unrealistic extreme case. The total RBY system would need to be considered as three (almost) independent chromophoric $[(Ru^{2+})_{1/3}(bpy)]$ units.



The Divided Atom, Believe it or not!

An individual *d* electron on the metal would have to interact so weakly with others that, when singled out for transfer to a particular ligand (a ligand-localized excitation), other metal electrons would not be influenced. Given that all *d* electrons are on the one atom and electron interaction (repulsion) parameters of the *d* electrons are large and comparable to other interaction energies, this approach makes little physical sense. Direct interaction between ligands is possible through the usual virtual photon exchange dipole–dipole process; but the interaction between metal and ligand is strong, of the order of 2–3 eV and should dominate. As each ligand shares the same pool of interacting *d* electrons, it is very difficult to imagine an excitation involving the metal and just one ligand.

A retort often used in the arguments concerning localization is one of the timescale of the experimental measurement. A slow measurement of a fast process will reveal a spread or (apparent delocalization) whereas a faster measurement gives a true snapshot picture. By these qualitative arguments, a process localized on the optical timescale can be delocalized on (say) the EPR timescale. Any such discussion actually requires precise consideration.

A somewhat related dilemma arose when considering the classic mixed valence dimer $[(NH_3)_5Ru\text{-pyr-}Ru(NH_3)_5]^{5+}$ known as the Creutz–Taube complex. Every type of experimental measurement was at one time or another used as evidence for both localization or delocalization (type II or III mixed valence behavior) in this system.[12] The simple minded question was, basically: Is the charge on the metal atoms (2 and 3) or 2½? After careful analysis,[13] it became clear that the *balance* between nuclear displacements in a specific antisymmetric breathing mode of the complex, and the interaction between the metal centers, concomitant with a breakdown of the Born–Oppenheimer approximation, was critical to the discussion. Even inspection of the potential surfaces was *not* sufficient to decide the issue in marginal cases, the results being sometimes counter-intuitive. The useful criterion was found to be: Does the expectation value of the nuclear displacement have one maximum or two? Are the nitrogens sitting at one average position or are most likely found at two distinct distances? This distribution is easily calculated from the eigenfunctions of the vibronic Hamiltonian (calculating the eigenfunctions may not be easy) and provides a qualitative and quantitative answer to the question; but asking the timescale of the "delocalization process" had little practical meaning. In critical situations it had no unique meaning.

Returning to the RBY system, consider for a moment that the excited state is built from a $[Ru^{3+}_{1/3}(bpy)^-]$ and two $[Ru^{3+}_{1/3}(bpy)]$ units. The (weak) interaction between these imaginary fragments allows an excitation transfer rate ν related to the interaction energy in the usual way.

$$\nu = \Delta E/h; \quad \Delta E = |E_a - E_\epsilon|$$

E_a and E_ϵ being the energies of the electronic configurations evolving from this basis.[14] The existence of this rate of course assumes we can create the system in a preselected (localized) configuration. Consider a measurement of the Raman spectrum of this system; if the interaction vanishes and $\nu = 0$, independent Raman modes associated with the two types of units (say bpy and bpy$^-$) will be observed in the scattering process. When the transfer rate is increased, the Raman lines will be modulated (broadened in frequency space) giving a linewidth of $\sim\nu$ to each mode. If the separation *between* the frequencies of the Raman modes is *less than* ν, the distinction between the two is lost and one mode frequency at the average of bpy and bpy$^-$ will be seen. As the shift in ring mode frequencies for bpy and bpy$^-$ are only a few cm^{-1},[4] the "timescale" of this experiment appears as 10^{-11} s and not the "optical timescale" of 10^{-15} s. The timescale of the experiment is not necessarily that of the interrogating radiation; it is related to the frequency shifts observed. A Mössbauer experiment uses gamma ray photons but gives information only on the MHz timescale.

Once a Jahn–Teller effect in the excited states is considered, some significant degree of breakdown of the Born–Oppenheimer separability occurs. The electronic part becomes a function of the nuclear component. This, in general, allows coupling to non-totally symmetric modes, changes in potential surfaces, polarizations and selection rules. Collins and Krausz[14] have established a framework and algebraic solutions for some simple cases and much more work needs to be done in this area. However it should be noted that the interaction with the environment for Jahn–Teller systems can be particularly critical.[15]

EXCITED STATE MEASUREMENTS

(a) Polarized Absorption, CD and MCD and Excited State Absorption

Absorption spectra of RBY in solutions and glasses are broad and relatively featureless. Spectra taken in dilute single crystals have somewhat more structure (see Fig. 7), but only spectra taken of concentrated materials such as RPF show sharp fine structure. Although doubts have been expressed as to the nature of this structure, and puzzling transverse Zeeman behavior of the origins has been noted,[16] the large body of carefully obtained data from Yersin's group[17] provide mounting evidence that the fine structure may in fact be due to an intrinsic RBY chromophore, although the relatively low intensity of the structured components and the lack of structure in dilute crystals is puzzling. Historically,[18] most structure and intrinsic details in electronic spectra are obtained for both inorganic and organic systems *diluted* in a transparent host!

Unfortunately, spectra in the main singlet absorption region cannot be recorded for neat materials in σ polarization, due to the difficulty in obtaining sufficiently thin (<1 μ) crystals. However it is clear in all cases that the dominant intensity for RBY in both singlet and triplet regions is in the XY plane. This is consistent with the basic transfer term intensity process giving rise to planar (E) oscillators. A number of electronic states have been identified in polarized spectra, and an analysis based on ideas presented in the previous section are reasonably successful.[19] Work on the related $Os(bpy)_3^{2+}$ system where spectral structure in ZPF was better developed and the spin-orbit coupling stronger is important in understanding the overall trends in these complex spectra. Absolute configuration CD measurements indicate[20] the need for including contact term intensity[11] as simple transfer term intensity does not give rise to CD.

MCD measurements of RBY in glasses, crystals and plastics are remarkably consistent.[21,22] Two A terms, of opposite sign, are seen indicating two electronic E states in the main singlet region with opposite signs of their magnetic moments. The work of Thompson *et al.*[23] is incorrect in associating one A term with the main absorption peak. It is clearly associated with a distinct electronic state, seen as a shoulder near 21,500 cm^{-1} in (glass or crystal) absorption spectra of sufficient resolution. This electronic state also gives rise to the dominant CD activity.[21] The fact that the main absorption peak has neither MCD *nor* CD poses rather fundamental difficulties in the theory of the intensity process itself. The question arises whether to consider a *trigonal* or *octahedral* basis in the intensity process. That is, how well defined are the trigonal orbitals a_1 and ϵ of Fig. 2? Can we indeed consider the various one electron jumps to be sufficiently distinct. When transforming from one basis to the other, there is an embarrassing lack of nitrogen *p* orbital basis functions which may lie at the heart of the dilemma.

The existence of a/D ratios[24] with the correct magnitude confirms the planar (XY) polarization and a substantial magnetic moment of two different degenerate (E) states. Any localized excitation to one ligand would naturally be linearly polarized, and could not be degenerate and thus could *not* give rise to an A term. Convincing MCD studies of substituted RBY complexes where one ligand is substantially more electrophilic than bpy, and localization of the lowest energy MLCT is expected, show (Fig. 3) a strongly reduced MCD and no distinctive A terms.[22]

A number of studies of the absorption spectrum of the excited state have now been made, though most report uncalibrated changes of absorption upon partial excitation and there are quite inexplicable discrepancies between some reported spectra. The most recent work[25] was carefully calibrated and covered the entire range from 220 nm to 2400 nm. It failed to detect any evidence for an excited state intervalence transition, as seen in the electrochemically generated $[Ru^{2+}(bpy)_2(bpy)^-]$ species,[26] but detected a low energy transition, evidently arising from the $\psi^* \rightarrow \chi^*$ process on

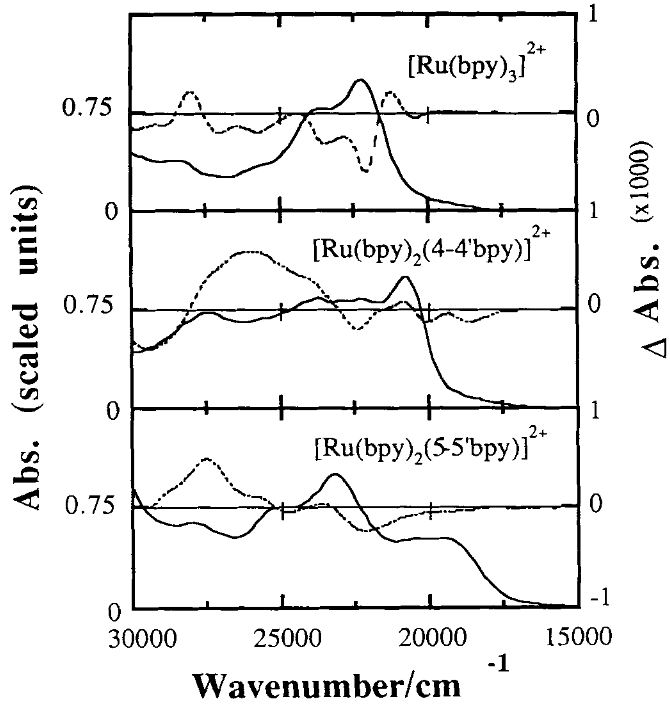


FIGURE 3 Absorption (scaled to unit peak height) ---, and MCD at 4T ——, of RBY and dicarboethoxy substituted complexes. Adapted from Ref. 22.

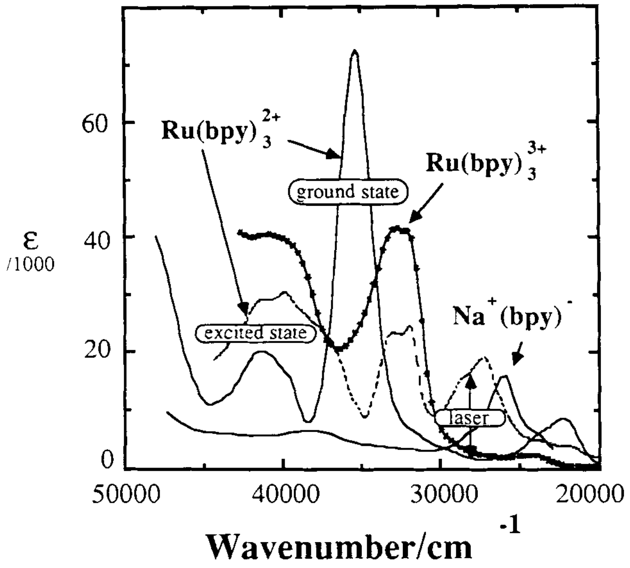


FIGURE 4 Molar extinction spectra of RBY in ground and excited states, along with "component" bpy$^-$ and Ru(bpy)$_3^{3+}$ spectra. Also shown is the location of the ERR laser excitation. Adapted from Ref. 25.

bpy$^-$ near 10,000 cm^{-1} (1.2 eV). In fact the excited state absorption looks remarkably like (Fig. 4) a combination of separately measured bpy$^-$ and Ru(bpy)$_3^{3+}$ absorption spectra. Furthermore, spectra taken in solution and plastic films differ significantly *only* in the $\psi^* \rightarrow \chi^*$ region; thus any relaxation occurring in solution has little overall effect. This qualitative similarity immediately suggests that the excited state is in fact best described as a combination of a single bpy$^-$ and a Ru(bpy)$_2^{3+}$ component, but one could also imagine that in a delocalized excited state little would happen to change the energetics of such processes, i.e., [Ru^{3+}(bpy)$_3^-$] would absorb at around the same energies as [Ru^{3+}(bpy)$_2$(bpy)$^-$].

(b) Polarized Luminescence, MCPL and Excitation Polarization Ratios

Luminescence spectra suffer the same fate as absorption spectra, in that little structure is seen, except again in neat single crystals where very weak but sharp structure is seen below ~10 K in PF$_6$

and ClO_4 anions. Several electronic transitions contribute to the luminescence, as evidenced by changing lifetimes, quantum efficiencies and polarizations. The classic temperature and field dependence analysis of RBY luminescence properties, particularly those measured in poly(methyl-methacrylate) by Crosby and his group,[27] established three electronic levels in RBY, spaced by 10.1 and 62.1 cm^{-1}. The experiments were performed using flash lamp excitation. Ferguson and Krausz later reported a lack of thermal equilibrium on short timescales using N_2 laser excitation, questioning the Crosby analysis.[28]

The studies of Yersin's group[17] on magnetic field and temperature dependence of luminescence spectra in neat materials is consistent with a ~7 cm^{-1} gap between two E states, as seen in the fine structure, but the null axial Zeeman effect and anisotropy of the transverse Zeeman seem inconsistent with a simple E assignment for the states.[16,29,30]

Short pulse (5 ns) and high energy (337 nm) N_2 laser excitation leads to the enhancement of weak transient processes in the RBY system and it becomes very difficult to work at low enough excitation powers to make meaningful experiments. Krausz and Moran,[30] by using a long pulse acousto-optically chopped Ar^+ laser at 515 nm to excite luminescence, and a high speed digital scope to accumulate good decay profile statistics, were able to show that most of the low temperature non-exponential luminescence effects reported[29,30] using short pulse excitation were due to transients and heating. An analysis of this more accurate lifetime data using a modified Crosby three level model gives levels at 8.0 ± 0.2 and 68 ± 3 cm^{-1} for RBY in a number of crystalline and solid solution host systems. This substantially improves the correspondence to the gap seen by Yersin of 7 ± 0.5 cm^{-1}.

Even at the lowest powers, some irregularities remain. The component of luminescence of RBY doped in ZPF appearing at *higher* energy on cooling below 10 K reported[28] earlier does indeed show a shorter lifetime to that of the main luminescence band. Transient processes occur in glassy materials even at the lowest excitation energies and powers attainable on the 0–500 ns timescale, most probably due to the low thermal conductivity of amorphous materials at low temperatures. Extreme caution needs to be taken to avoid the possibility of artifacts in these studies.[30]

Measurements of the excitation polarization ratio $P = (I_{\parallel} - I_{\perp})/$

$(I_{\parallel} + I_{\perp})$ in glassy solutions were perhaps the first indication that all was not well with the simple XY model of RBY.[31,32] The value of P cannot exceed 1/7 (0.14) for an XY absorber/emitter, but near 21,500 cm^{-1} a value of ~0.2 is consistently observed in a number of solvents. DeArmond has made a great number of measurements of P as a function of solvent and temperature, but most recently has made the stunning observation that P is *time dependent* in the ~10–20 ns range.[33a] Higher values of P are observed at short times, close to the maximum value of P for a linear absorber emitter of 0.5. This result is then taken as evidence for an initial linear polarization. "Exciton hopping" occurs, reducing P by a diffusional averaging process after just a few nanoseconds, and P is then reduced to close to the XY value of 1/7.

Krausz[33b] has repeated some of these measurements (Fig. 5) using advantageous data accumulation equipment and very low

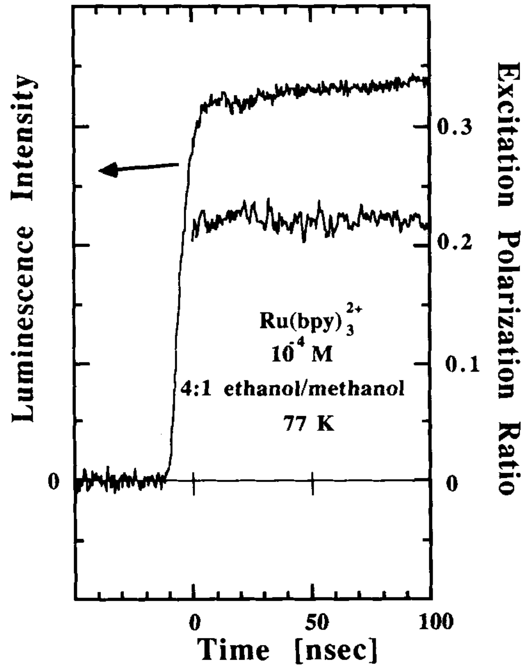


FIGURE 5 Luminescence excited at 468 nm and its polarization ratio *P* as a function of time in the first 100 ns for 2 × 10^{-4} M RBY in 4:1 ethanol/methanol at 77 K. Adapted from Ref. 33b. Overall lifetime of the luminescence is 5.31 ± 0.01 μs.

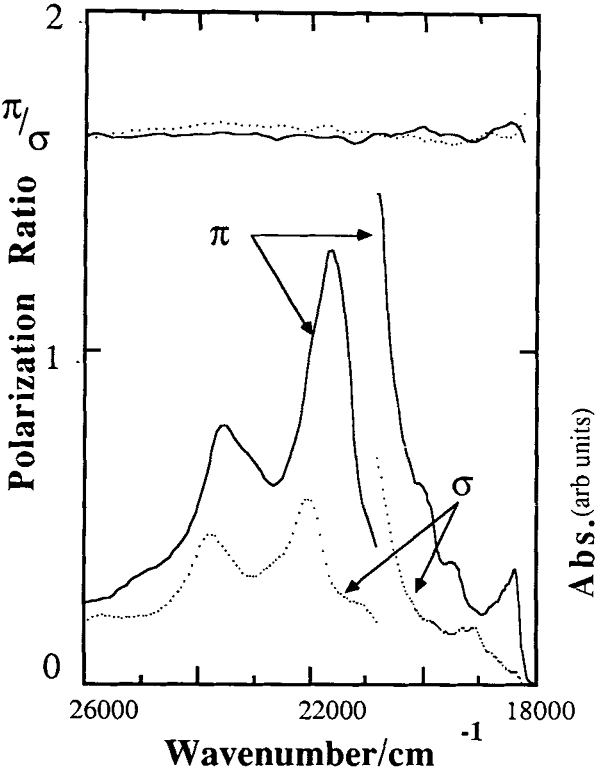


FIGURE 6 Absorption spectra (bottom) and the polarization ratio of detected luminescence (top), of RBY in ZPF (two crystals with differing concentrations) with light incident in π --- or σ —— polarization taken at 10 K. Adapted from Ref. 34.

power excitation, but found no such time variation of *P*. Again it seems that the use of high energy pulse lasers may be leading to artifacts.

Studies of excitation spectra of RBY in the ZPF single crystal system (see Fig. 1) are relevant. The crystal luminescence polarization ratios are entirely independent of energy excitation, detection and polarization[35] as one expects from a well defined system (Fig. 6). The lifetime is also utterly independent of excitation polarization or detected energy as is the case in the ZBF system as well.[36]

As previously stressed, the location of the solid solution P_{max} feature is precisely where MCD indicates a separate electronic state. Furthermore, consistent luminescence and MCPL variations

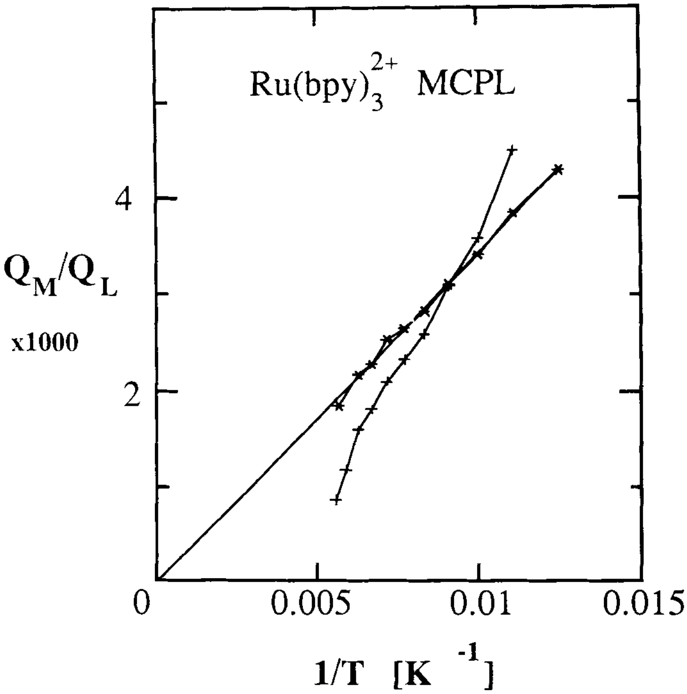


FIGURE 7 Integrated MCPL divided by integrated luminescence of RBY dissolved in poly-(vinyl alcohol) *** and 9M LiCl glass + + +. Adapted from Ref. 36.

are seen scanning this anomaly region.[35] Detected energy dependence of lifetimes and *P* has been observed for a number of glasses, the details of the effects depending considerably on the precise nature and history of the glasses.[36]

The inhomogeneities associated with frozen solutions are compounded by strain birefringence effects on polarized measurements. However it is abundantly clear that the MCPL of RBY in the 20–200 K region can only be explained by a predominantly XY luminophore, staying well below the glass freezing temperature.[35,36] The accurate 1/T (C term) dependence of the MCPL in a polymer film is most convincing (Fig. 7). Upon glass melting, a sharp drop in MCPL is seen, consistent with a lowering of the symmetry of the excited state.[37,38] Time resolved luminescence spectra measured during melting are largely attributable to solvent dielectric relaxation,[39] though some fundamental changes in the luminophore may also occur.[37]

(c) Excited State Raman and EPR

Excited state resonance Raman (ERR) spectrum of RBY is relatively easily measured with a pulsed laser operating at the 3rd harmonic of the Nd/YAG laser near 355 nm and solutions of RBY, replenishing the active volume. This near UV light falls close to the maximum of an excited state absorption, but near a minimum of the ground state absorption (see Fig. 4). Two photons of the exciting pulse are used, the first to create and the second to probe the excited state. Spectra are dominated by ring modes of the bipyridine which are strongly enhanced. Correlations can be made between excited state and free bpy^- scattering frequencies, but frequency shifts from the ground state are quite small. Overall one would expect mode frequencies to reduce via the antibonding nature of the excited state.

More convincing is the chemically based argument where un-, mono- and bis-substituted RBY type materials show almost identical ERR spectra.[40] Thus the presence of more than one bpy in the complex is irrelevant to the spectra when the available orbitals of the substituted ligands are higher in energy. This independence of substitution is also apparent in luminescence spectra of some complexes.[41]

ERR spectra were reported to change markedly in the rigid phase,[42] but this result has been shown[43] to be caused by photochemical damage of RBY at the high pulse energies found necessary in the experiment. Recent more sensitive measurements of ERR spectra in glasses where RBY is more photochemically stable reveal small but specific changes in spectra in going from rigid to fluid phases.[44] Mabrouk and Wrighton[45] have measured the ERR spectra of a large range of substituted complexes and notably have discovered a number of cases in which mode frequencies do not correspond to those of the most reducible ligand.

Chang *et al.*[46] have reported the first time resolved ERR spectra of RBY. These were made in a specifically viscous medium, glycerol, in order to slow down solvent motions. Time resolution was achieved by using laser pulses of varying widths in the 30–150 ps range. Changes in the spectra were interpreted as due to an environmentally induced localization process, as first suggested by Ferguson and Krausz,[29] but may also be due to internal conversion from the singlet to triplet excited states.

One preliminary report of the excited state EPR of RBY has been given[46] and the spectrum was analyzed as arising from a (spin-only) triplet state with a very small zero field splitting (~0.1 cm^{-1}), reminiscent of the values obtained for the triplet state of a free (neutral) ligand. This result is again very surprising, given the enormous spin-orbit coupling on ruthenium ($\lambda = 1500\ cm^{-1}$) and needs confirmation. It was also necessary to perform the experiment at pumped helium temperatures, where it is known, from optical studies, that substantial transient heating is inevitable under the experimental conditions used. Any interpretation of the EPR should be made in the light of these studies as well.

LOOKING FORWARD

The results that have the most influence are often those most accessible to individual workers, and a balanced view may be hard to achieve. The MCD, MCPL and polarized single crystal data that have had the greatest influence on the author's perspective seem not as compelling to other workers. However, at a fundamental level it is difficult to consider that an excited state of RBY could be broken into metal–single ligand components that interact only at the 0.03 cm^{-1} level giving a ~ns excitation hopping rate between these pseudo-fragments. The onus then is clearly for any proponents to provide strong evidence for such a viewpoint that cannot be interpreted in any other way. If the time dependent luminescence polarization changes observed by DeArmond's group are truly intrinsic to the RBY system, time dependent luminescence polarization effects should be observable in a single crystal environment, where concerns of inhomogeneity, strain and microviscosity are largely absent. Obviously some type of hole-burning or other selective site spectroscopy of RBY would be of great value in glassy mixtures. Turning the problem around, RBY may prove to be a very valuable probe to the nature of micro-environments such as glasses, polymers and proteins.

The correspondence between excited state and "component" absorption spectra (Fig. 4), along with the similarity between luminescence spectra of variously substituted complexes,[41] have an immediate impact, and probably limit the level of interaction between ligands to below around 1000 cm^{-1}. Measurements of the MCD in the excited state and MCPL of the substituted complexes would be much more sensitive, more direct and informative in this respect.

ERR spectra still form the heart of the argument for localization in RBY. If the localization argument is correct, and the interaction between sub-units is less than ~1 cm^{-1}, then it is possible to experimentally verify this by observing excitation profiles of the ERR spectra. Resonance with bpy $\pi \rightarrow \pi^*$ band must then give Raman frequencies associated with bpy and not with bpy^-. ERR measurements, in particular, would be far more definitive when performed with doped single crystals as they undergo minimal photochemical damage and have a well defined and truly rigid environment.

Polarized single crystal spectroscopy, MCD and MCPL provide the strongest evidence for delocalized excited states in RBY. Below 10 K it is imperative to use the lowest power and longest wavelength excitation possible to avoid heating effects. This means that it will be difficult to make meaningful excited state measurements at these low temperatures, especially in glassy media that have poor conductivity. Local heating may be extreme. Significant progress could be made by finding a (UV) transparent single crystal host material for RBY that had high (D_3) site symmetry.

Acknowledgment

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