

## Absorption and Emission in Tris(2,2'-bipyridyl)ruthenium(II); Effects of Excited-state Asymmetry

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The absorption and emission spectra of  $[\text{Ru}(\text{bipy})_3]^{2+}$  (**1**) (bipy = 2,2'-bipyridyl), while assignable to a first approximation in  $D_3$  symmetry, are more properly discussed using a model that allows for direct Franck–Condon overlap between the trigonal ground state and each of three equivalent asymmetric excited states. This singlet excited state distortion is inherited by  $(\mathbf{1})^*$ , the emitting triplet, and can be semiquantitatively modelled on the asymmetry of  $[\text{Ru}^{\text{II}}(\text{bipy}^0)_2(\text{bipy}^-)]^+$  ( $\mathbf{1}^-$ ) and  $[\text{Ir}^{\text{III}}(\text{bipy}^0)_2(\text{bipy}^-)]^{2+}$ . The known polarisations of absorption and emission (including the thermally activated z-axis emission), the behaviour of the emission at low temperature in complex (**1**) and related mixed-ligand complexes, and the apparently anomalous photoselection behaviour of (**1**) are all natural consequences of such a model. The balance between electron trapping and delocalisation is briefly discussed. The classical theory of photoselection must be modified to cover the case of absorption-induced anisotropy, and changes in photoselection at very low temperatures are predicted.

Some of the controversies in the long and detailed study of the visible (metal to ligand charge transfer, m.l.c.t.) absorption and emission spectrum of the tris(2,2'-bipyridyl)ruthenium(II) cation  $[\text{Ru}(\text{bipy})_3]^{2+}$  (**1**) have recently been resolved.<sup>1</sup> The observed complexity of the m.l.c.t. absorption in some low-temperature spectra<sup>2</sup> had suggested contributions from both  $d \rightarrow \pi(7)$  and  $d \rightarrow \pi(8)$  processes, where  $\pi(7)$  and  $\pi(8)$  are the two lowest unoccupied orbitals on the bipy ligands, of type  $\psi$  and  $\chi$  respectively in Orgel's<sup>3</sup> notation. However, arguments based on relative energies<sup>4</sup> predict,<sup>5</sup> and experiment confirms,<sup>6</sup> that only  $d \rightarrow \pi(7)$  is relevant here, while  $d \rightarrow \pi(8)$  actually contributes to the band envelope in the intraligand  $[\pi(6) \rightarrow \pi(7)]$  absorption region of complex (**1**). The reported complexity in the absorption band<sup>2</sup> is now acknowledged<sup>7</sup> to have arisen from lattice effects in a biaxial crystalline host. The validity of the singlet–triplet distinction for the excited states of complex (**1**) had been questioned by Crosby and co-workers.<sup>8</sup> However, comparative studies of the species  $[\text{M}(\text{bipy})_3]^{2+}$  (M = Fe, Ru, or Os) provide strong experimental evidence for an incomplete spin–orbit coupling, which increases down the series,<sup>9</sup> and Crosby's own group now accept the use of spin labels, at least for closely related  $[\text{Ru}(\text{terpy})_2]^{2+}$  species (terpy = 2,2':6',2''-terpyridyl).<sup>10</sup> Trigonal splitting, and metal–ligand  $\pi$  bonding, give rise to a generally accepted orbital-energy ordering  $d(e) < d(a_1) < \pi(7)(a_2) < \pi(7)(e)$  in  $D_3$  symmetry, consistent with e.s.r. data for  $[\text{Ru}(\text{bipy})_3]^{3+}$ ,<sup>11</sup> and with the occurrence and energy ordering of one weak z- and two strong x,y-polarised absorptions.<sup>5</sup> (Here Oz is the three-fold molecular axis, while Ox links the metal to the midpoint of one particular ligand, and Oy is perpendicular to the other two axes, as in Figure 1. The relationship to the conventional axis labels of octahedral coordination, and choice of d orbitals, is given in ref. 12.) Most authors place  $\pi(7)(a_2)$  below  $\pi(7)(e)$ , but one recent discussion,<sup>12</sup> influenced perhaps unnecessarily<sup>7</sup> by the complexity<sup>2</sup> of reported crystal spectra, reverses this order. However, our aim is not to enter into controversy as to the best assignment within the  $D_3$  point group but rather to argue that such a use of this point group is misleading.

There remain major problems with the emitting state. As Crosby pointed out,<sup>8</sup> a configuration  $^3[d(e^4 a_1^1)\pi(7)(a_2)]$  generates only two levels ( $A_1 + E$  from  $^3A_2$ ) in  $D_3$ , but the

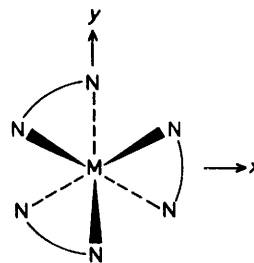


Figure 1. The chosen axis system; Oz is towards the reader. If OX, OY, and OZ are the conventional axes for an octahedron, then  $z = (X + Y + Z)/\sqrt{3}$  and  $x = (X - Y)/\sqrt{2}$

experimental data require *three* closely spaced levels in  $(\mathbf{1})^*$ , the emitting state of complex (**1**). The photoselection spectrum for emission from  $(\mathbf{1})^*$  is abnormal, with the emission polarisation as expected for an E-absorber E-emitter when excitation is at the frequency of strongest visible absorption, but increasing anomalously at lower exciting frequencies.<sup>13–16</sup> Finally, it is known from resonance-Raman<sup>17–19</sup> and electronic<sup>6</sup> spectroscopy that in  $(\mathbf{1})^*$  the promoted electron is trapped on a single ligand. If such asymmetric states show appreciable Franck–Condon overlap with the ground state (as we show below they do), then this asymmetry must somehow be incorporated into the description of the excitation even though the ground state is itself symmetric.

### Results and Discussion

*Form of the Excited State.*—The emitting state  $(\mathbf{1})^*$  is formally derivable from  $(\mathbf{1})^-$  by the removal of a single  $d(a_1)$  electron. Thus, when we discovered that  $(\mathbf{1})^-$  has the electronic structure  $[\text{Ru}^{\text{II}}(\text{bipy}^0)_2(\text{bipy}^-)]^+$ , with electronically and hence geometrically distinct  $\text{bipy}^0$  and  $\text{bipy}^-$  ligands, we were led to suggest that  $(\mathbf{1})^*$  would likewise lack trigonal symmetry, being best formulated as  $[\text{Ru}^{\text{II}}(\text{bipy}^0)_2(\text{bipy}^-)]^{2+}$ .<sup>20</sup> It is this same model, which we have successfully applied<sup>6</sup> to the absorption spectrum of  $(\mathbf{1})^*$ , that we use here.

Spin-allowed absorption will generate a singlet excited state

of complex (1), while the emitting state (1)\* is a triplet. However, the energy difference between the singlet and triplet depends on factors such as electron-electron repulsion which are relatively independent of the detailed geometry. Thus we shall assume that the potential-energy surfaces for the singlet and triplet m.l.c.t. states of complex (1) lie parallel to each other, and can both be at least semiquantitatively modelled by the corresponding surfaces for (1)<sup>-</sup>. The molecular symmetry of (1)\* [and (1)<sup>-</sup>] is at most C<sub>2</sub>, but it is convenient for the moment to continue to describe the metal-based orbitals as in D<sub>3</sub>. (The more detailed effects on *d*-orbital splitting are discussed in a later section.) We follow Ferguson's group<sup>2,7</sup> in ascribing singlet-triplet mixing, in *d*→*π*\* configurations of complex (1), to coupling of states <sup>2</sup>[*d*(*e*<sup>4</sup>*a*<sub>1</sub><sup>1</sup>); M<sub>L</sub> = 0, M<sub>S</sub> = ±½] with states <sup>2</sup>[*d*(*e*<sup>3</sup>*a*<sub>1</sub><sup>2</sup>); M<sub>L</sub> = 1, M<sub>S</sub> = ∓½] within the *d*<sup>5</sup> moiety. It can be shown that, to first order, splitting of *d*(*e*) (D<sub>3</sub>) into *d*(*a*) and *d*(*b*) (C<sub>2</sub>) does not affect this coupling.

Our treatment places the series (1)<sup>-n</sup> in Vlček's class (a) of ligand-based redox series, in which each added electron is localised on one ligand.<sup>21</sup> By what he would accordingly describe as a Jahn-Teller distortion, (1)<sup>-</sup> and (1)\* adopt an equilibrium geometry in which the added or promoted electron resides on one only of the three ligands, which changes shape accordingly. Migration of this electron can take place as the result of the absorption of light, and is responsible for the broad ligand-ligand intervalence charge transfer (i.v.c.t.) band which we have reported for (1)<sup>-</sup> and other (bipy<sup>0</sup>)(bipy<sup>-</sup>) complexes.<sup>22</sup> The ligand-ligand interaction is weak, as shown by the low intensity of this band. Migration can also take place as a thermally activated process, through vibrational distortion of donor and acceptor ligands, and such thermally activated transfer has been observed through e.s.r. line broadening in this family of compounds.<sup>23,24</sup> We can think of the three separate trapping possibilities as three degenerate valence isomers. The optical transitions between these can be considered either as an electronic or a vibrational process; an electron is optically promoted to the 'wrong' π(7) orbital (in the sense of being geometrically inappropriate), but the energy required may be seen as vibrational activation of an isomer of equal electronic energy.

The excitation of a trigonal ground state to an excited manifold containing three asymmetric energy minima has been discussed in a different context by Ballhausen,<sup>25</sup> while the interaction of three degenerate valence isomers has more recently been considered (in connection with trinuclear complexes) by Borshch *et al.*<sup>26</sup> The range of possible behaviour is of some complexity, but where (as here) the interactions are weak, the treatment of Borshch tends towards that given by Ballhausen, which is adequate for our purposes and which we now apply to complex (1).

Vertical excitation of complex (1) from its equilibrium geometry, combined with an appropriate distortion of all three ligands, generates a hypothetical species [Ru<sup>III</sup>(bipy<sup>-1/3</sup>)<sub>3</sub>]<sup>2+</sup>, in which all ligands have the same geometry, displaced one third of the way along the co-ordinate that leads from the equilibrium geometry of (co-ordinated) bipy<sup>0</sup> towards that of bipy<sup>-</sup>. Two further symmetry co-ordinates (belonging to *E* in D<sub>3</sub>) then suffice to represent the differences in the degree of displacement between the individual ligands. As Ballhausen makes clear, the resultant potential-energy surfaces for motion in these two co-ordinates are generated by the intersection of three paraboloids. In the present case, the minimum of each paraboloid corresponds physically to trapping of the promoted electron on one of the ligands, while the other two revert to the geometry appropriate to co-ordinated bipy<sup>0</sup> (Figure 2). Even a weak interaction<sup>26</sup> splits these intersecting paraboloids into three non-crossing surfaces (Figure 3). Vertical excitation from the

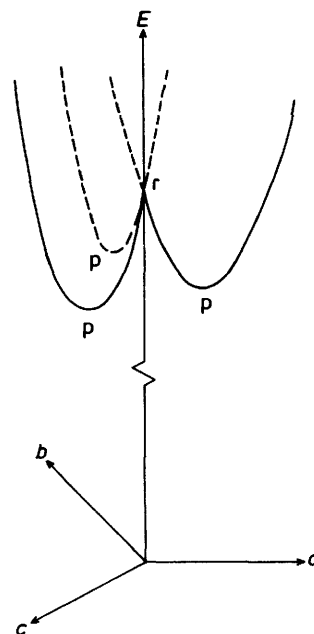


Figure 2. Potential surfaces for three non-interacting degenerate valence isomers

ground-state equilibrium geometry is to the triple cusp *r* of the lowest surface. This surface, however, has three minima *p*, corresponding to the three valence isomers. Passage from one paraboloid to another (at the saddle-points *q*) corresponds to thermal intervalence hopping, while the second surface has local minima at *q*, connected by a triple saddle-point at *r*, and the third surface has a single minimum at *r*. In the limit of zero interaction, the first and second surfaces touch along the directions *rq*, the second and third touch along *rp*, and the three surfaces touch at *r*. Simple trigonometry shows that in the limit of negligible interaction, if the height from the first surface to the second (and third) at *p* is *H*, then the elevation from the minimum *p* to the saddle-points *q* is *H*/4, from *p* to *r*, *H*/3; and from *q* to *r*, *H*/12. In our case, as we shall see, *H*/12 < *hν*(vib)/2 < *H*/4 where *v*(vib) is the vibrational frequency in the distortion co-ordinate, and *hν*(vib)/2 the appropriate zero-point energy. This means that a static (rather than dynamic) deviation from trigonal symmetry is possible only for the lowest surface. Should the system be promoted to the lowest excited surface, it will become localised at one of the three minima; but if it is raised to either of the two upper surfaces, thermal relaxation will bring it to the lowest surface at any of the three minima indifferently. In the limit of zero interaction between ligands the three paraboloids could intersect but not interact. However, experiment shows (see below) that within the time required for decay to the lowest surface the suggested randomisation of configuration does in fact occur. The upper surfaces are then real but (on the emission time-scale) short lived.

*Quantification of the Model.*—The above model can be quantified given *H* and *v*(vib). If *v*(vib) is known then *H* can be found by observation of an i.v.c.t. band, at *H* - ½*hν*(vib). [The correction ½*hν*(vib), for zero-point energy, is commonly neglected,<sup>27</sup> since *v*(vib) is usually small compared with *H*. This is not so here.] As we have pointed out,<sup>6</sup> (1)\* should have an i.v.c.t. transition but there is little prospect of observing it with present near-i.r. detectors. We can, however, use (1)<sup>-</sup> and [Ir<sup>III</sup>(bipy<sup>0</sup>)<sub>2</sub>(bipy<sup>-</sup>)]<sup>2+</sup> (ref. 28) as model systems. {The best model would be the hypothetical [Rh<sup>III</sup>(bipy<sup>0</sup>)<sub>2</sub>(bipy<sup>-</sup>)]<sup>2+</sup>, but

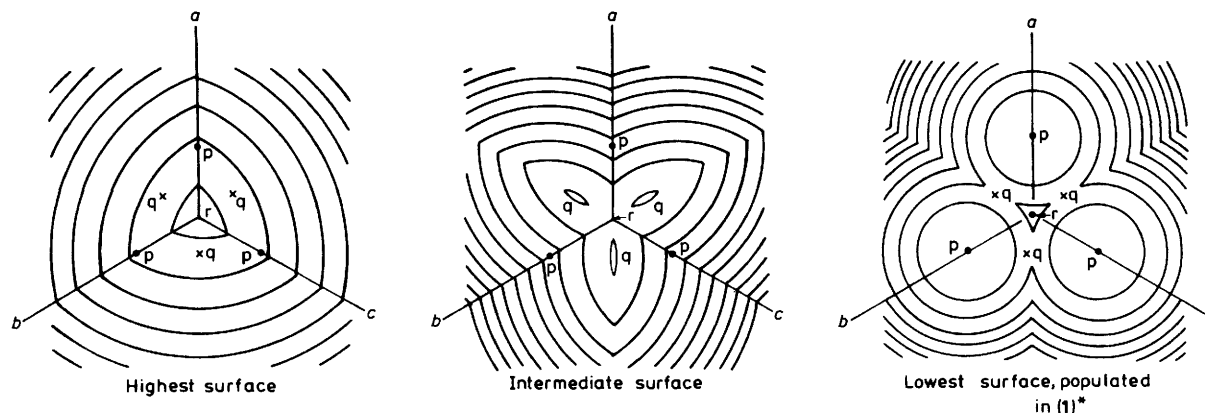


Figure 3. Surfaces generated by minimum interaction between the paraboloids of Figure 2

the electrochemistry of  $[\text{Rh}(\text{bipy})_3]^{3+}$  is complicated by ligand loss and metal-centred reductions.<sup>29</sup> The i.v.c.t. bands are weak and broad, but according to our observations on the various model systems<sup>22,28,30</sup> they lie in the range 4 500–6 500  $\text{cm}^{-1}$ .

From the form of  $\pi(7)$  we expect the effect of the added electron on  $\text{bipy}^-$  to be greatest in the  $\text{C}_{10}\text{N}_2$  skeleton, where CN bond orders within the rings will be decreased but the bond between the rings will be strengthened. {It is relevant that the central carbon-carbon bond is only 141.7 pm in  $[\text{Fe}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)(\text{bipy})]^{31}$  and 142.5 pm in  $[\text{Mo}(\text{OPr}^i)_2(\text{bipy})_2]^{32}$  as opposed to 149.0 pm in free  $\text{bipy}$ .<sup>32</sup>} Comparison of the Raman spectra of  $\text{bipy}^0$  and  $\text{bipy}^-$  in  $(1)^*$  shows changes principally in the 1 300–1 400  $\text{cm}^{-1}$  region,<sup>17-19</sup> and so, ignoring small differences, we adopt 1 400  $\text{cm}^{-1}$  as our value for  $\nu(\text{vib})$  in both ground and excited states. {Our assumption here that frequency changes are diagnostic of bond-length changes is confirmed by the data<sup>32</sup> for  $[\text{Mo}(\text{OPr}^i)_2(\text{bipy})_2]$ .} The activation energy for hopping, calculated classically, is  $H/4 - h\nu/2 + kT$ , or 700–1 200  $\text{cm}^{-1}$  at 300 K for  $H = 4 500\text{--}6 500 \text{ cm}^{-1}$ . This agrees remarkably well with the experimental value<sup>23</sup> of  $960 \pm 50 \text{ cm}^{-1}$  for  $(1)^-$ .

**Calculation of Franck-Condon Factors.**—As Ballhausen points out,<sup>25</sup> the series of Franck-Condon overlap factors for a direct transition between a trigonal ground state and any one of three asymmetric minima are in the same ratio as the corresponding overlaps for transitions between two electronic states with single minima offset along a single co-ordinate. After some manipulation (Appendix 1) the normal harmonic oscillation treatment can be written in terms of  $H$  and  $\tilde{\nu}(\text{vib})$  (both measured in  $\text{cm}^{-1}$ ) to give equation (1). For  $\tilde{\nu} = 1 400 \text{ cm}^{-1}$

$$I(0 \rightarrow v)/I(0 \rightarrow 0) = (H/3\tilde{\nu})^v/v! \quad (1)$$

this gives, for the relative integrated intensities of the  $0 \rightarrow 0$ ,  $0 \rightarrow 1$ , and  $0 \rightarrow 2$  emission components, values in the range 1:1.24:0.77 to 1:1.71:1.47 corresponding to the range 4 500–6 500  $\text{cm}^{-1}$  for the i.v.c.t. transition. The total intensity is of course independent of the individual Franck-Condon factors, whose sum rapidly converges to unity. Comparison with the range of published emission spectra shows that our treatment tends to overestimate the weight of the higher  $v$  components. There are many possible reasons for this:  $H$  may in fact be slightly less in  $(1)^*$  (which is  $d^5$ ) than in the  $d^6$  model systems; anharmonicity may well cause the vibrational wavefunction of  $(1)^*$  to skew inwards; and we are clearly oversimplifying when we identify the displacement co-ordinate with a single normal mode. Despite all this our value for  $H$  is clearly of the right order and our treatment correctly predicts the spacing in the emission

envelope and explains, as a delocalised model could not (Appendix 2), the observed<sup>16,33</sup> similarity of m.l.c.t. emission envelopes for mono-, bis-, and tris-bipyridyl complexes of  $\text{Ru}^{\text{II}}$ .

For absorption, the only meaningful harmonic Franck-Condon factor is that for the  $0 \rightarrow 0$  transition, since an extra 'vibrational' quantum would suffice to raise the excited molecule above the parabolic region, or even to one of its upper surfaces. This  $0 \rightarrow 0$  factor represents the probability of a transition occurring directly from the  $D_3$  ground state to the lowest vibrational level around any of the three minima in the lowest excited-state surface, at which (since the zero-point energy is less than the saddle-point energy) the molecule will remain trapped. Thus the  $0 \rightarrow 0$  excitation directly transforms the  $D_3$  ground state to a less symmetric ( $C_2$ ) excited state. It may seem paradoxical that the act of absorption should itself select among equiprobable minima, but this is merely an instance of the general paradox<sup>34</sup> by which time passing transforms a quantum-mechanically indeterminate future state into a historically determined present.

**Selection Rules in Absorption and Emission: Comparison with  $D_3$  Model.**—Consider the promotion of an electron from the  $d$  orbitals into  $\pi(7)$  of one particular ligand, by the  $0 \rightarrow 0$  process discussed above. The point group of the  $\text{Ru}^{\text{II}}(\text{bipy})$  chromophore in the molecule is  $C_2$ , in which  $\pi(7)$  spans  $b$  and  $d(a_1) + d(e)$  span  $2a + b, d(b)$  of  $C_2$  deriving directly from a member of  $d(e)$  in  $D_3$ . For a charge-transfer transition moment to contain a transfer term<sup>35</sup> it is necessary for the donor and acceptor orbitals to belong to the same irreducible representation of the chromophore point group, since a transfer term requires mixing. Thus if, as Day and Saunders<sup>35</sup> assert, the transfer term dominates, the strongest transitions in the lowest m.l.c.t. region will be of type  $d(e;b) \rightarrow \pi(7)$  and polarised along the metal-ligand axis in the  $x, y$  plane. Thus the strongest absorption will come from the transition  $[d(e) \rightarrow \pi(7)]$ , and will be  $x, y$ -polarised. Ceulemans and Vanquickenborne<sup>5</sup> reached this same conclusion, but went on to express their results in language appropriate to  $D_3$ . The two treatments are equivalent; in  $D_3$ ,  $a_1$  and  $a_2$  are distinguished by being even and odd respectively under the two-fold rotations, while in  $C_2$ ,  $a$  and  $b$  are even and odd under  $C_2$ . The three  $C_2$  axes of the  $\text{Ru}(\text{bipy})$  chromophores are of course identical with  $3U_2$ .

In the  $D_3$  model the absorption spectrum contains two electronically distinct components with transfer terms, namely  $d(e) \rightarrow \pi(7)(a_1)$  and  $d(e) \rightarrow \pi(7)(e)$ , which determine its general form.<sup>5</sup> In our model, however, the strong vibronic coupling blurs the distinction between electronic and vibrational structure in the absorption band. The  $0 \rightarrow 1$  component of  $[d(e;b) \rightarrow \pi(7)]$  has enough energy to reach the upper surfaces;

or, alternatively, to surmount the barriers within the lowest surface, with concomitant orbital following. Thus it is almost a question of words whether the splitting in the strong absorption band is described as vibrational or electronic. The exact form of the absorption band must, however, be sensitive to whatever small degree of coupling may exist between the surfaces.

The lowest-energy transition,  $d(a) \rightarrow \pi(7)$ , can borrow intensity from the ligand transition  $\pi(6) \rightarrow \pi(7)$ , since this  $d$  orbital overlaps  $\pi(6)$ . Thus it should be polarised, at right angles to the metal–ligand axis ( $a \rightarrow b$  in  $C_2$ ), along the ligand long axis. This will give components along both  $y$  and  $z$  axes. It follows that the transition should be of mixed polarisation, and hence that the  $z$ -polarised absorptions resolved at low temperature should also appear in the  $(x,y)$ -polarised spectrum, albeit against the background of the far stronger  $\parallel C_2$  absorptions. Close inspection of published spectra [e.g. Figure 3 of ref. 2(b)] confirms this prediction. The effect must be genuine, not instrumental, as the weak  $z$ -polarised absorption is not contaminated by the far stronger  $(x,y)$ -polarised bands; thus  $d(a_1) \rightarrow \pi(7)$  is of mixed polarisation in  $D_3$ , as our model demands. Such mixed polarisation is no novel or *ad hoc* suggestion. The phrase was applied many years ago by Albrecht<sup>36</sup> in his general discussion of the effects of vibronic coupling on selection rules, of which our model provides an extreme case.

Within the  $D_3$  model, emission is assigned as  ${}^3A_2[d(e^4a_1^1)\pi(7)(a_2)](A_1 + E) \rightarrow {}^1A_1$ . The observed  $E$  polarisation of emission follows at once, but only two levels are predicted. In our model,  ${}^3[d(e^4a_1^1)\pi(7)]$  is of type  ${}^3B$  in  $C_2$ , with components  $2A + B$ . This provides the three levels required by Crosby's data, both for  $[\text{Ru}(\text{bipy})_3]^{2+}$  itself<sup>8</sup> and also for mixed complexes containing the  $\text{Ru}^{\text{II}}(\text{bipy})$  chromophore.<sup>37</sup> Spin-orbit coupling mixes the triplet term with  ${}^1[d(e^3a_1^2)\pi(7)]$ , which spans  ${}^1A + {}^1B$  in  $C_2$ . The greatest emission will come from the mixing in of the strongly allowed  ${}^1A \rightarrow$  ground state component, giving  $x,y$  polarisation as in the strongest absorption.

*The Thermally (650 cm<sup>-1</sup>) Activated z-Polarised Emission.*—Recently, a thermally activated  $z$ -polarised emission from  $(\mathbf{1})^*$  has been reported, but no electronic assignment proposed.<sup>38</sup> We ascribe it, in our model, to an expected consequence of the electronic structure of the emitting state (whether the deviation from  $D_3$  is considered or neglected). Let thermal activation promote an electron in  $(\mathbf{1})^*$  from  $d(e)$  to  $d(a_1)$ . This will give an emitting state  ${}^3[d(e^3a_1^2)\pi(7)]$ , mixed by spin-orbit coupling with  ${}^1[d(e^4a_1^1)\pi(7)]$ . The emission will thus gain a component polarised along the  $z$  axis, in agreement with the data. The possible mixing of  $d(a_1;a)$  with  $d(e;a)$  on going from classification in  $D_3$  to  $C_2$  does not affect this conclusion.

*Photoselection Re-examined.*—A long-standing problem<sup>13–16</sup> with the  $D_3$  assignment system is the strange emission photoselection spectrum of complex  $(\mathbf{1})$ . The classical theory<sup>36,39</sup> of emission photoselection is expressed in terms of independent absorption and emission probabilities  $r_x, r_y, r_z$  and  $q_x, q_y, q_z$  respectively. For an  $E$ -absorber  $E$ -emitter,  $r_x = r_y = \frac{1}{2}$  and  $q_x = q_y = \frac{1}{2}$ . It is explicitly assumed in this treatment, and admitted<sup>36</sup> as a restriction on its validity, that the emitting molecule retains no memory of whether the initial excitation was by  $x$ - or  $y$ -polarised light; in other words, that the act of absorption does not itself induce anisotropy in the  $x,y$  plane.

This is expected on our model to be true for excitation to the upper surfaces, since these lack real traps (see above). It will *not*, however, hold good for direct excitation to the lowest. Let us consider specifically the transfer of a  $d(e)$  electron to one of the ligands, consequent on absorption of a photon  $x$ -polarised in the molecular axis system. If the  $d(e)$  electron is promoted to  $\psi(1)$ , *i.e.* to the  $\pi(7)$  orbital localised on the  $x$ -axis ligand  $(1)$ , then the initial excited state will be  ${}^1[d(e^3a_1^2)\psi(1)]$  which will relax, by

some combination of radiationless transition and intersystem crossing, to  ${}^3[d(e^4a_1^1)\psi(1)]$ .

The excited-state lifetime at 77 K is 6  $\mu\text{s}$ ,<sup>8</sup> while the hopping time for  $(\mathbf{1})^-$  at the same temperature is 13 ms.<sup>23</sup> Thus the electron is unlikely to hop before emission occurs. The emission will therefore be dominated by the  $x$ -polarised term due to mixing with  ${}^1[d(e^3a_1^2)\psi(1)]$ , and all our criteria<sup>6</sup> for a memory effect in photoselection are met. The classical model still applies for excitation to an upper surface, followed by random selection of one of the three emitting state minima. In that case, absorption and emission are constrained to lie in the  $xy$  plane, but are not otherwise correlated. For direct excitation to an emitting minimum, the classical model fails. Although  $r_x, r_y, q_x$ , and  $q_y$  still all take the value  $\frac{1}{2}$ , this grossly underestimates the degree of correlation between the directions of absorption and emission. Each  $\text{Ru}^{\text{II}}(\text{bipy})$  chromophore acts as an independent linear parallel absorber–emitter, described by equation (2). The attempt to represent the molecule by a single set of principal absorption and emission axes has failed.

$$A = 3 \text{ and } B = C = 1; P = (A - B)/(A + B) = \frac{1}{2} \quad (2)$$

(To illustrate this point, consider an array of oriented molecules containing three independent linear parallel absorber–emitters at right angles. The classical treatment requires all  $q$  and all  $r$  to equal  $\frac{1}{3}$ , so that  $P$  is zero. Indeed, since all  $q$  equal  $\frac{1}{3}$ , emission should be depolarised and anisotropic, even for  $x$ -axis polarised incident light. In reality,  $x$ -axis excitation must lead exclusively to  $x$ -polarised emission. If the molecules are now arranged at all possible angles, as in a glass, the averaging of  $x$ -axis absorption and emission over all possible molecular orientations will proceed as for a linear parallel absorber–emitter, as will that for the two other such absorber–emitters in the same molecule; and  $P$  will ideally take the value  $\frac{1}{2}$ . As it happens, Albrecht's exposition was developed as much for selective photochemistry as for selective emission, and the above model may be relevant to the 'sudden' component in the photolysis of octahedral complexes in matrices.)

There is, however, one important geometrical difference between the behaviour of complex  $(\mathbf{1})$  and that open to linear oscillators such as  $[\text{Ru}(\text{bipy})(\text{py})_4]^{2+}$  ( $\mathbf{2}$ ) ( $\text{py} = \text{pyridine}$ ).<sup>16</sup> If  $(\mathbf{2})$  gives a salt in which the individual chromophores are parallel, then 100% polarisation of emission is in principle possible if the exciting light is correctly oriented and polarised. For  $(\mathbf{1})$ , however, as we shall show elsewhere, the maximum polarisation in the  $xy$  plane is  $\frac{1}{2}$  unless there is lattice site lowering of ground-state symmetry.

We can now account for the relative forms of the excitation photoselection spectra of  $\text{Ru}(\text{bipy})_3(\text{ClO}_4)_2$  and  $\text{Ru}(\text{bipy})(\text{py})_4(\text{ClO}_4)_2$  recently published in some detail by Carlin and DeArmond.<sup>16</sup> Complex  $(\mathbf{2})$  is a linear oscillator with an ideal polarisation ratio of 0.5. In fact it shows a sharp maximum of around 0.34, coinciding precisely with the maximum in the absorption band. We ascribe both these features to the  $d(b_1) \rightarrow \pi(7)(b_1)$  charge-transfer band (labels refer to  $C_{2v}$ ). The behaviour of the perchlorate of  $(\mathbf{1})$  is significantly different. The excitation photoselection spectrum gives some structure, but  $P$  remains  $< \frac{1}{2}$  throughout most of the strong absorption band, exactly as we would expect for excitation to an upper surface followed by random decay to any one of the three emitting state minima. At the low-energy edge, however,  $P$  increases, as predicted, reaching a maximum of 0.23 as opposed to an ideal value in the present theory of 0.5. Some shortfall is quite usual in photoselection emission studies. The larger shortfall for  $(\mathbf{1})$  may be due to imperfect resolution of transitions to upper and lower states, or to non-zero Franck–Condon overlaps with the 'wrong' chromophores within the lower state itself. For complex  $(\mathbf{1})$ ,  $P$  also shows an increase at the lowest energies for which

measurement is possible; this we would expect for triplet absorption-triplet emission.

There remains a wealth of fine detail in Carlin and DeArmond's spectra, and a significant dependence of emission spectrum on exciting wavelength, which we have not attempted to discuss. We have merely distinguished between the trapped minima of the lowest excited surface, whose existence had been established by other techniques, and all untrapped states, with no regard to the details of movement between surfaces, or to any motion other than in an idealised trapping co-ordinate. This has enabled us to explain the apparently anomalous polarisation peak at the red edge of the absorption band with no *ad hoc* assumptions whatsoever.

*Extensions and Predictions.*—Our argument uses ligand-based electrochemical reduction as a model for ligand reduction by m.l.c.t. If this is permissible, then localisation in m.l.c.t. states should correlate with localisation in reduced species. For instance,  $[\text{Ru}(\text{phen})_3]^{2+}$  (phen = 1,10-phenanthroline) shows excitation photoselection behaviour very similar to complex (1);<sup>16</sup> we therefore expect that  $[\text{Ru}(\text{phen})_3]^+$  would show trapping of the added electron on one particular ligand, in accord with recent e.s.r. data.<sup>24</sup> Ligand-based reduction of  $[\text{Ru}(\text{terpy})_2]^{2+}$  also occurs with trapping,<sup>24</sup> in accord with our interpretation<sup>40</sup> of low-temperature photoselection effects in related complexes.

Localisation in our theory does not depend on the spin state. Thus the lowest excited singlet of complex (1) will contain the same  $(\text{bipy}^0)_2(\text{bipy}^-)$  chromophore as the lowest triplet, and will presumably have a similar electronic and vibrational spectrum. For  $[\text{Os}(\text{bipy})_3]^{2+}$  (3), however, we are surprised by the absence in its excitation photoselection spectrum of the special features associated with excited-state localisation. The variation of emission with temperature<sup>41</sup> requires for complex (3) a three-level model similar to that for (1), once more indicating localisation. The absence of a polarisation anomaly then suggests ligand-ligand hopping in (3)\* within the time-scale of emission. This is at first sight surprising; (3)\* is shorter lived than (1)\*,<sup>8,41</sup> and since  $\text{Os}^{\text{III}}$  is presumably larger than  $\text{Ru}^{\text{II}}$  ( $\text{Os}^{4+}$  is certainly some 15 pm larger than  $\text{Ru}^{4+}$ )<sup>42</sup> we would expect poorer overlap between the ligands. We tentatively suggest a second-order effect, operating in (3)\* more efficiently than in (1)\* because of greater spin-orbit coupling, and involving mixing of the separately localised ligand excited states with a common singlet, possibly the ground state.

*Expected Temperature Effects on Photoselection.*—The emitting states of (1)\* are in our model the components of  ${}^3B$ , assigned as  $A + B + A$  in  $C_2$ , related to  ${}^3A_2(A_1 + E)$  in  $D_3$ . Thus to a first approximation we have  $A(A_1$  in  $D_3)$  forbidden,  $B(E)$  weak and  $x,y$ -polarised, and  $A(E)$  polarised along the initial excitation direction. The treatment of  $A(E)$  (which we identify with the highest of Crosby's levels, since that is the strongest emitter) is given in equation (2) above, correctly predicting the emission polarisation at  $T \gg 30$  K. If Crosby's second term is  $B(E)$ , then for that term we have an assemblage of linear perpendicular absorber-emitters, to which expression (3)

$$A = 1 \text{ and } B = C = 2; P = \frac{1}{3} \quad (3)$$

applies. Where Crosby's second and third terms are of equal weight, around 30 K, we have equal contributions from (2) and (3), giving  $P = \frac{1}{2}$  as in the classical case. Thus, if the second term is indeed  $B$ , the high-polarisation anomaly should disappear at 30 K, and be replaced by a low (ideally reversed) polarisation at lower temperature. However, if the second term is  $A(A_1)$ , borrowing intensity from any term  $A(E)$ , we would

expect no such anomaly except perhaps at the very lowest temperatures.†

For complex (2) we cannot hedge our bets. The analysis must proceed in  $C_{2v}$ , in which the filled  $d$  orbitals span  $b_1 + a_2 + b_2$  while  $\pi(7)$  belongs to  $b_1$  (we choose  $b_2$  in the metal-ligand plane). The strongest singlet absorption can be assigned as  $d(b_1) \rightarrow \pi(7)$ , which contains a transfer term. The emitting state is of type  ${}^3\Gamma$ , where  $\Gamma$  could be any of  $A_1, B_2$ , or  $A_2$  depending on which  $d$  orbital lies highest. Thus the emitting manifold of complex (2) could be either  ${}^3A_1(A_2 + B_1 + B_2)$ ,  ${}^3B_2(B_1 + A_1 + A_2)$ , or  ${}^3A_2(A_1 + B_2 + B_1)$ . We can exclude the first of these since (2) is a linear absorber-parallel emitter,<sup>16</sup> showing that  ${}^3\Gamma_n$  contains the same representation as the dominant absorption, in this case  $A_1$ . Thus the emitting state contains three components: one ( $A_1$ ) giving parallel emission, one ( $B_1$ ) perpendicular, and one ( $A_2$  or  $B_2$ ) forbidden or perpendicular;  $A_1$  dominates at the temperature studied,<sup>16</sup> but the emission polarisation should change at sufficiently low temperature. Such change has been reported<sup>10</sup> for complexes of type  $[\text{Ru}(\text{terpy})_2]^{2+}$ , to which we have applied arguments of the same form as these presented here.<sup>40</sup> Further data for complexes (1) and (2) below 30 K would evidently be of the greatest interest.

*Localisation or Delocalisation.*—Localisation will place the promoted electron on a ligand with geometry appropriate to  $\text{bipy}^-$ , and delocalisation must be preceded by changes that make all ligands geometrically equivalent. This would require an energy input, related to the old notion of 'compression energy'.<sup>43</sup> Such localisation may be favoured by correlation effects.<sup>44</sup> In the present case, delocalisation would result in significant equilibrium changes in a bond (the central C-C bond) of high force constant. Ligand-ligand interaction, however, is rather small (we have treated it as zero), partly because the nitrogen atoms on different ligands are poorly oriented for overlap, and partly because the coefficients of  $\pi(7)$  on these interacting nitrogens are low. This last could be an important difference between polypyridyl complexes and those of simpler di-imines, which may account for the reported<sup>45</sup> delocalisation of the added electrons in  $[\text{Ru}(p\text{-MeOC}_6\text{H}_4\text{N}=\text{CHCH}=\text{NC}_6\text{H}_4\text{OMe-}p)_3]$  if, as we suspect, the reduction of the corresponding  $2+$  complex is ligand-based.

## Appendix 1

Ballhausen gives (ref. 25, p. 112) equation (A1) for  $v$  the same in

$$I(0 \rightarrow v)/I(0 \rightarrow 0) = [(\Delta x)^2 \alpha]^v / 2^v v! \quad (\text{A1})$$

the ground and excited states, where  $\alpha = M\omega/\hbar = (2\pi)^2 Mv/\hbar$ ,  $\Delta x$  is the displacement of the respective minima along a vibrational co-ordinate,  $v$  is the frequency in that co-ordinate,  $M$  the effective mass, and  $v$  the vibrational quantum number.

Let  $\Delta E$  be the potential energy of the ground state at the equilibrium dimensions of the excited state. Then we obtain expressions (A2) and (A3). On substituting and simplifying, equation (A4) is found where  $H$  and  $\tilde{\nu}$  are in  $\text{cm}^{-1}$ .

$$\Delta E = k(\Delta x)^2/2 \quad (\text{A2})$$

† Note added in proof: E. M. Kober and T. J. Meyer, in their most recent treatment (*Inorg. Chem.*, 1984, **23**, 3877), submitted shortly after this paper, agree with us in the present (and also our earlier<sup>20,6</sup>) work in relating the lowest manifold to a localised  $[d(e^4 a^1)\pi(7)]$  configuration, and likewise predict one singlet-derived and three triplet-derived levels, but do not themselves address the problem of apparently excessive population in the in-plane emission, and take no cognisance of nearby delocalised states.

$$2\pi\nu = \sqrt{k/M} \quad (\text{A3})$$

$$I(0 \rightarrow \nu)/I(0 \rightarrow 0) = \left(\frac{\Delta E}{\hbar\nu}\right)^{\nu} \cdot \frac{1}{\nu!}$$

$$= \left(\frac{H}{3\tilde{\nu}}\right)^{\nu} \cdot \frac{1}{\nu!} \quad (\text{A4})$$

### Appendix 2

In a localised model,  $\Delta x$ ,  $\Delta E$ ,  $\tilde{\nu}$ , and the band intensity ratios will be the same for complexes (1) and (2). In a hypothetical delocalised m.l.c.t. state of (1) each ligand will be displaced by an amount  $\Delta x(1) = \Delta x(2)/3$ , as befits a charge of  $-\frac{1}{3}$ , giving equation (A5) after summing over all three ligands. Thus a

$$\Delta E(1) = \frac{3}{2}k[\Delta x(1)]^2$$

$$= \frac{3}{2}k\left[\frac{1}{3}\Delta x(2)\right]^2$$

$$= \frac{1}{3}\Delta E(2) \quad (\text{A5})$$

delocalised model predicts a three-fold decrease in the  $0 \rightarrow 1$  band of (1)\*, relative to the  $0 \rightarrow 0$  band, compared to the corresponding intensities in complex (2).

### Appendix 3

It is usual to write expressions (A6)–(A8) where  $\psi(1)$ ,  $\psi(2)$ , and

$$\pi(7)(a_2) = [\psi(1) + \psi(2) + \psi(3)]/\sqrt{3} \quad (\text{A6})$$

$$\pi(7)(e_x) = [2\psi(1) - \psi(2) - \psi(3)]/\sqrt{6} \quad (\text{A7})$$

$$\pi(7)(e_y) = [\psi_2 - \psi_3]/\sqrt{2} \quad (\text{A8})$$

$\psi(3)$  are non-overlapping orbitals on the three separate ligands. We are free to invert this procedure, giving equations (A9)–(A11). Promotion of an electron from  $d(a_1)$  to any one of  $\psi(1)$ ,

$$\psi(1) = [\pi(7)(a_2)/\sqrt{3}] + \sqrt{\frac{2}{3}}\pi(7)(e_x) \quad (\text{A9})$$

$$\psi(2) = [\pi(7)(a_2)/\sqrt{3}] - [\pi(7)(e_x)/\sqrt{6}] + [\pi(7)(e_y)/\sqrt{2}] \quad (\text{A10})$$

$$\psi(3) = [\pi(7)(a_2)/\sqrt{3}] - [\pi(7)(e_x)/\sqrt{6}] - [\pi(7)(e_y)/\sqrt{2}] \quad (\text{A11})$$

$\psi(2)$ , or  $\psi(3)$  may then be formally assigned to mixed ( $a_2, e$ ) symmetry in  $D_3$ .

### Acknowledgements

We thank the S.E.R.C. for support and Gary Mitchell for computer-generated Figures.

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Received 4th April 1984; Paper 4/555