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Luminescence Polarization of the Tris(2,2'-bipyridine)ruthenium(II) Complex

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Polarization of the spin-forbidden luminescence of tris(2,2'-bipyridine)ruthenium(II) in EPA rigid glass at 77°K was measured. The luminescence polarization observed in the visible absorption band was close to +1/7. This implies that the predominant absorption and emission oscillators are in the same plane. However, a contribution of the collinear component of the emission and absorption oscillators should be noted since the polarization observed at 21,000 cm⁻¹ in the lowest wave number component of the visible band is higher than +1/7.

Introduction

The tris(2,2'-bipyridine)ruthenium(II) complex emits a fairly strong luminescence. The luminescence has been assigned to one of the lowest triplet-singlet "ligand to metal" charge-transfer transitions but not of the lowest triplet-singlet "ligand field" (d,d*) transitions.¹⁻³

A remarkable dichroism of the lowest charge-transfer bands has been observed in polarization studies of the absorption spectrum of tris(2,2'-bipyridine)ruthenium(II) doped in a crystal of tris(2,2'-bipyridine)zinc(II) sulfate.⁴ The visible absorption perpendicular to the C₃ axis of the tris(bidentate) chelate complex of D₃ symmetry is more than ten times as intense as that parallel to the C₃ axis. Exactly the same character has been observed in the iron(II) analog.

Hanazaki and Nagakura assigned the intense absorption bands of tris(2,2'-bipyridine)iron(II) in the visible region to "metal to ligand" charge-transfer transitions based on their molecular orbital calculations using a π approximation.⁵ The theory seems to be applicable to the isoelectronic ruthenium(II) complex as well, since the absorption spectra of these complexes show a good correspondence. The lowest spin-allowed excited states are of A₂ and E symmetry. The lowest linear oscillator ¹A₂ ← ¹A₁ polarized parallel to the C₃ axis is sparingly allowed, whereas one of the lowest degenerate planar oscillators ¹E ← ¹A₁ polarized perpendicular to the axis is allowed. The conclusion of the theory is consistent with the observed polarization of absorption spectra of the doped crystals.

The luminescence of tris(2,2'-bipyridine)ruthenium(II) arises from a spin-forbidden transition ³A₂ → ¹A₁ or ³E → ¹A₁. The spin-forbidden transition ³A₂ → ¹A₁ can borrow the intensity through spin-orbit coupling only from the planar oscillator ¹E → ¹A₁, whereas the transition ³E → ¹A₁ can borrow the intensity from both the planar oscillator ¹E → ¹A₁ and the linear oscillator ¹A₂ → ¹A₁. In other words, ³A₂ → ¹A₁ is a planar oscillator and ³E → ¹A₁ is a three-dimensional oscillator consisting of an intense component of polarization in the plane and only a weak component perpendicular to it. When the complex is excited by

linearly polarized light, the polarization of the luminescence should depend upon the relative polarizations of the absorption and emission oscillators.⁶ The polarization of three-dimensional oscillators was theoretically discussed by Jablonski many years ago.⁷ Their characteristics were never studied experimentally for lack of an appropriate example. In this paper, we present a polarization study of the luminescence of tris(2,2'-bipyridine)ruthenium(II).

Experimental Section

Emission and excitation spectra in glycerol solutions were recorded on a Hitachi EPA-2A fluorescence spectrophotometer which contains a 150-W xenon lamp for excitation, a grating monochromator (600 grooves/mm, blazed at 300 nm) for exciting light, and a grating monochromator (600 grooves/mm, blazed at 500 nm) for luminescence spectroscopy. The luminescence from the sample solution in a rectangular cell of 1-cm path length was detected by a Hamamatsu TV photomultiplier R-136 placed at right angles to the exciting beam. A Toshiba filter UV-D25 was used to eliminate the stray visible light in the ultraviolet exciting beam. Another Toshiba filter V-Y43 was placed at the entrance of the emission monochromator to cut the second-order light. The sample cell was thermostated. The luminescence spectra were corrected by the method described in the literature.⁸ The excitation spectrum was monitored at 605 nm, an emission maximum, employing a slit corresponding to a bandwidth of 10 nm. It was corrected by means of a photoquantum counter consisting of a concentrated ethylene glycol solution of rhodamin B (3 g/l.).⁹

Emission and excitation spectra in spectrograde EPA (a 2:5:5 mixture of ethanol, isopentane, and diethyl ether) rigid solution at 77°K were detected through a JASCO 100-cm monochromator CT-100 with a 1200 grooves/mm grating blazed at 750 nm using a Hamamatsu TV photomultiplier of S-20 response, R-374.¹⁰ The slit was set 5 mm in width which corresponds to a resolution of 4-nm half-width. The sample solution in a rectangular cell (1 × 1 cm) was immersed in liquid nitrogen in a transparent Dewar. Monochromatic exciting light was obtained from a 500-W xenon arc source Ushio Model UXL-500DS and then through a Bausch and Lomb high-intensity grating monochromator. The exciting light was incident perpendicular to the optical axis of detection. The emitted light from the sample was passed through a Toshiba filter VO-55 which blocked wavelengths shorter than 550 nm and then a quartz depolarizer before it was focused onto the entrance slit of the 100-cm monochromator. The emission was chopped by a 270-cps rotating sector to permit ac amplification. The response current was amplified on a lock-in amplifier of NF Circuit Design Block Co. Model LI-572A and then recorded on a Yokogawa Electric Works Model 3047 chart recorder. The spectra were corrected for the sensitivity of the photomultiplier and the transmittance of the monochromator using a standard tungsten lamp.

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The absorption spectrum was taken on a Beckman spectrophotometer Model DU.

Tris(2,2'-bipyridine)ruthenium(II) chloride hexahydrate was prepared by the method given in the literature and was repeatedly recrystallized from water.^{4,10}

Polarization ratio of luminescence spectra was detected using two sheet polarizers. The exciting light was polarized by a sheet polarizer and the emitted light was passed through a second sheet polarizer. Both polarizers could be positioned with axes at any angle between 0 and 90°.

The polarization P is defined as

$$P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$$

where I_{\parallel} and I_{\perp} are the intensities of the component of emission resolved parallel and perpendicular, respectively, to the direction of the oscillating electric vector of the exciting light. The oscillation of the exciting light was polarized vertically unless otherwise stated. To obtain the exact values of I_{\parallel} and I_{\perp} , it is necessary to know the relative transmittance T of the second monochromator for vertically and horizontally polarized lights as a function of wavelength.¹¹ The polarization is then expressed in terms of the observed photomultiplier readings and the relative transmittance T

$$P = (R_{\parallel} - TR_{\perp}) / (R_{\parallel} + TR_{\perp})$$

where R_{\parallel} and R_{\perp} are the observed readings of the vertical and horizontal components of emission, respectively. The value of T was obtained by the method proposed by Azumi and McGlynn.¹² Upon horizontally polarized excitation, the emission observed in a direction at right angles to the incident light must be unpolarized and the photomultiplier readings of the vertical and horizontal components of emission R_{\parallel}' and R_{\perp}' for the horizontally polarized exciting light are caused only by instrumental factors. Thus, the relative transmittance T is equal to $R_{\parallel}'/R_{\perp}'$. The polarization of emission is corrected by

$$P = \frac{R_{\parallel} - R_{\perp}(R_{\parallel}'/R_{\perp}')}{R_{\parallel} + R_{\perp}(R_{\parallel}'/R_{\perp}')}$$

The probable error of our measurements of P is estimated to be less than ± 0.02 .

Reabsorption and reemission were wholly neglected because of the dilute concentration of the solution used in the present work.

Results and Discussion

The absorption and emission spectra of $[\text{Ru}(2,2'\text{-bipy})_3]^{2+}$ are shown in Figure 1. The excitation spectrum of the complex was in good agreement with the absorption spectrum as shown in Figure 2. This reveals that the emission arises from the complex but not from some possible impurity included. A positive polarization of the luminescence close to $+1/7$ was observed for the complex in EPA rigid glass at 77°K by monitoring an emission maximum at 570 nm ($17,400 \text{ cm}^{-1}$) as shown in Figure 2.

Depolarization of the luminescence arises from the molecular rotation during the Brownian motion of the excited species in solution. In fact, the polarization of the complex in glycerol almost vanished at 30°. Temperature dependences of the luminescence polarization in glycerol upon excitation at 460 nm ($21,700 \text{ cm}^{-1}$) are shown in Table I. When the temperature of the solution was lowered, a positive polarization was detectable. Methyl substitutions in 2,2'-bipyridine decrease molecular rotation. In fact, the polarization of $[\text{Ru}(4,4'\text{-Me}_2\text{-2,2'\text{-bipy})_3]^{2+}$ is a sizable value at a temperature near 0°; however, the rotational depolarization is not completely inhibited even at 0°. In a rigid solution, the rotational depolarization is eliminated. The polarization observed in EPA rigid glass for $[\text{Ru}(2,2'\text{-bipy})_3]^{2+}$ at 77°K as shown in Figure 2 was very close to $+1/7$ in the

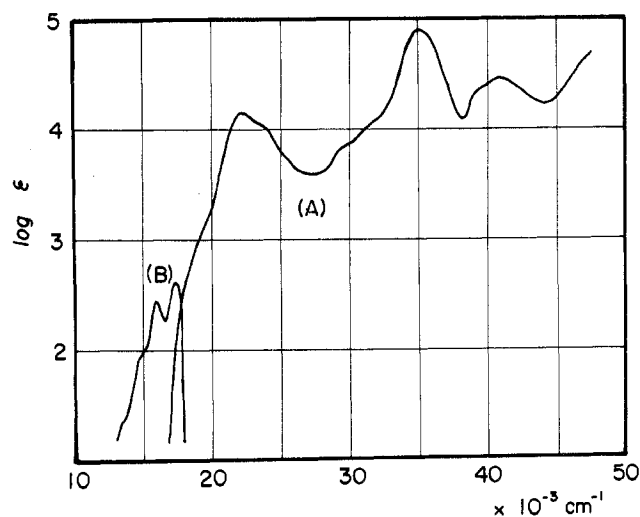


Figure 1. Absorption spectrum in aqueous solution and luminescence spectrum in EPA at 77°K of $[\text{Ru}(2,2'\text{-bipy})_3]^{2+}$: (A) absorption spectrum; (B) luminescence spectrum.

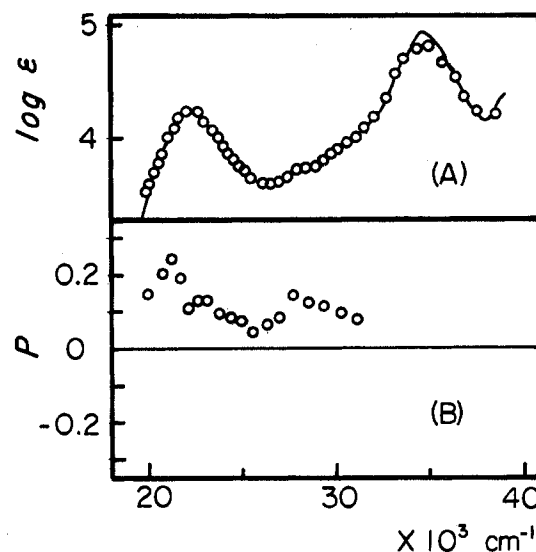


Figure 2. Excitation and absorption spectra of $[\text{Ru}(2,2'\text{-bipy})_3]^{2+}$ in glycerol and polarization of the luminescence in EPA at 77°K: (A) excitation and absorption spectra, full line, absorption spectrum; circles, excitation spectrum; (B) polarization of the luminescence measured by monitoring at 570 nm ($17,400 \text{ cm}^{-1}$).

Table I. Temperature Dependence of the Luminescence Polarization of the Tris(bipyridine)ruthenium(II) Complex in Glycerol upon Excitation at 460 nm ($21,700 \text{ cm}^{-1}$)

Polarization ^a	30°	20°	10°	0°
P (bipy)	0.000	0.015	0.036	0.047
P (4-Me ₂ bipy)	0.000	0.026	0.047	0.087
Viscosity, ^b cP	624	1,429	3,950	12,000

^a 2,2'-Bipyridine is abbreviated to bipy and 4,4'-dimethyl-2,2'-bipyridine, 4-Me₂bipy. ^b Reference 16.

23,000 and $28,000\text{-cm}^{-1}$ bands. The viscosity of EPA at -180° has been obtained as $9 \times 10^3 \text{ P}$.¹³

The magnitude of the depolarization due to energy transfer is proportional to a product of the concentration and the excitation lifetime.^{14,15} The lifetime of the excited ruthenium

(11) See, for example, C. A. Parker, "Photoluminescence of Solutions," Elsevier, Amsterdam, 1968, Chapter 3.

(12) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **37**, 2413 (1962).

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(15) G. Weber, *Trans. Faraday Soc.*, **50**, 552 (1954).

complex has been determined as an order of 10^{-6} sec.^{2b,3b} The rate of decreasing the excited complex is given by

$$-\frac{d[\text{Ru}^*]}{dt} = (k_0 + k_d[\text{Ru}])[\text{Ru}^*]$$

where $[\text{Ru}]$ and $[\text{Ru}^*]$ are the concentrations of the ruthenium complex in the ground state and the lowest triplet state, respectively, k_0 is the rate of the intramolecular process which is the reciprocal of the lifetime, and k_d is the rate constant of diffusion-controlled intermolecular energy transfer. Since the diffusion-controlled bimolecular rate constant in glycerol at 0° has been estimated to be 5×10^5 l. mol⁻¹ sec⁻¹¹⁶ and the concentration of the complex employed in the present work was less than 10^{-4} mol l.⁻¹, $k_d[\text{Ru}]$ is much smaller than k_0 . Thus, concentration depolarization can be excluded. Another factor, an electrostatic repulsion between the positively charged complex ions, also prevents their encounter. In fact, no appreciable change in the polarization was observed when the concentration of the complex in glycerol was varied from 10^{-3} to 10^{-6} mol l.⁻¹.

The angle between the absorption oscillator and the emission oscillator is denoted by θ . In any given experiment, the polarization is given by

$$P = \frac{3\langle \cos^2 \theta \rangle - 1}{\langle \cos^2 \theta \rangle + 3}$$

where $\langle \cos^2 \theta \rangle$ is the ensemble average of $\cos^2 \theta$. In the absence of perturbations by intramolecular vibrations and environmental interactions, the dipole linear oscillator remains fixed. In such a case $\langle \cos^2 \theta \rangle = 1$ and $P = +1/2$. When the emission arises from a state different from the original excited state, the perturbation has certainly intervened. In such a case $P < 1/2$. In the special case where the emission oscillator is perpendicular to the absorption oscillator, $\langle \cos^2 \theta \rangle = 0$ and $P = -1/3$. For the degenerate excited state of E symmetry, any small perturbation can rotate the oscillator. Thus the emission oscillator is randomized in the plane and $\langle \cos^2 \theta \rangle = 1/2$, $P = +1/7$. It is a planar oscillator. Similarly, the degenerate excited state of T symmetry will lose any memory of the polarized excitation. In such a case, the emission oscillator is randomized in three-dimensional space and $\langle \cos^2 \theta \rangle = 1/3$, $P = 0$. When the absorption oscillator is planar and the emission oscillator is linearly polarized perpendicular to the absorption planar oscillator, or the absorption oscillator is linear and the emission oscillator is plane-polarized perpendicular to the absorption linear oscillator, $\langle \cos^2 \theta \rangle = 0$ and $P = -1/3$. Another possibility is that both the absorption and emission oscillators are polarized in the same plane. In such a case $\langle \cos^2 \theta \rangle = 1/2$ and $P = +1/7$. The values of possible polarizations are summarized in Table II.

A typical planar oscillator has been revealed in the lowest (π, π^*) transitions of porphyrin by magnetic optical rotatory dispersion and magnetic circular dichroism measurements¹⁷⁻¹⁹ and fluorescence polarization studies.^{20,21} The planar os-

Table II. Luminescence Polarization

Absorption oscillator	Emission oscillator	Polarization, P
Linear (z)	Linear (z)	$+1/2$
Linear (z)	Linear (x)	$-1/3$
Linear (z)	Planar (z, x)	$+1/7$
Linear (z)	Planar (x, y)	$-1/3$
Planar (x, y)	Linear (z)	$-1/3$
Planar (x, y)	Planar (x, y)	$+1/7$

cillator character has been also observed for polarization of the phosphorescence of metal porphyrin.²² The phosphorescence polarization shows a low positive value very close to $+1/7$ which does not depend on the wave number of the exciting light. However, the (π, π^*) phosphorescence polarization in a large number of aromatic and N-heterocyclic compounds is negative, which indicates that the phosphorescence oscillator is polarized vertical to the molecular plane.²³ The phosphorescence borrows the intensity through spin-orbit coupling from the singlet (σ, π^*) transitions which are polarized vertical to the molecular plane. In the case of metal porphyrin, however, the allowed (π, π^*) transition, a planar oscillator in the molecular plane, directly grants the intensity to the triplet-singlet emission through a spin-orbit coupling in the central heavy metal or a paramagnetic perturbation by the open shell of the central transition metal.

In the case of tris(2,2'-bipyridine)ruthenium(II), a strong spin-orbit coupling at the central metal ion [$\zeta = 990$ cm⁻¹ for Ru(II)]²⁴ through the "metal to ligand" charge transfer in the ground and excited states gives a spectral intensity to the spin-forbidden emission oscillator directly from the oscillators of the spin-allowed charge-transfer transitions. In fact, a rather short lifetime for the lowest triplet-singlet transition has been measured.^{2b,3b} The absorption oscillator in the lowest wave number region has been assigned to a "metal to ligand" charge-transfer transition. By polarization studies on the absorption spectra of the doped crystals⁴ and also molecular orbital calculations by Hanazaki and Nagakura,⁵ the predominant absorption oscillator in the lowest wave number region is concluded to be a planar oscillator (Figures 3 and 4). The linear oscillator participates less in the absorption. As far as the absorption oscillators are concerned, the oscillators in the complex are anisotropic rather than isotropic as expected from a coordination sphere of O_h symmetry. In the absence of perturbations by intramolecular vibrations and environmental interactions, the extreme of luminescence polarization is expected to be $+1/7$ and $-1/3$ for planar and linear emission oscillators, respectively.

As shown in Table III, the excited triplet 3A_2 can emit by borrowing the spectral intensity only from the singlet-singlet transition $^1E \rightarrow ^1A_1$ through a spin-orbit coupling of E symmetry. Therefore, the emission oscillator of 3A_2 should be planar. However, the excited triplet 3E emits by alternative borrowings of the intensity from the transition $^1E \rightarrow ^1A_1$ by a spin-orbit coupling of A_2 symmetry or from the transitions $^1A_2 \rightarrow ^1A_1$ and $^1E \rightarrow ^1A_1$ by a spin-orbit coupling of E symmetry.

The polarization of $+1/7$ observed at 23,000 and 28,000 cm⁻¹ reveals that a planar oscillator emits a spin-forbidden luminescence upon excitation of a planar oscillator of the

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(23) See, for example, S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, Chapter 6.

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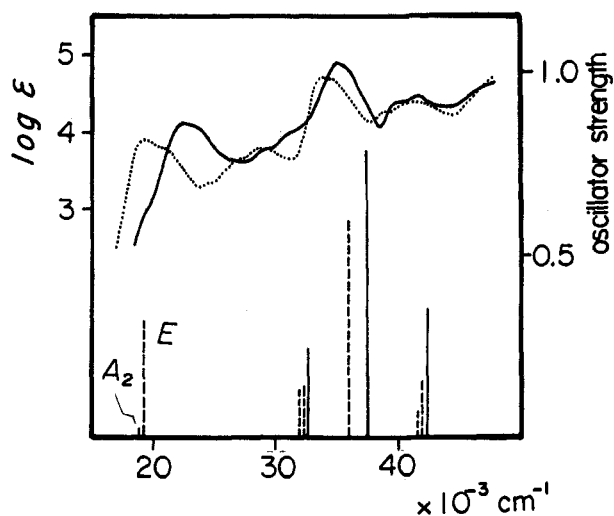


Figure 3. Absorption spectra of $[\text{Fe}(2,2'\text{-bipy})_3]^{2+}$ and $[\text{Ru}(2,2'\text{-bipy})_3]^{2+}$: (—), $[\text{Ru}(2,2'\text{-bipy})_3]^{2+}$; (·····), $[\text{Fe}(2,2'\text{-bipy})_3]^{2+}$. The assignments of the excited states of $[\text{Fe}(2,2'\text{-bipy})_3]^{2+}$ are those given by Hanazaki and Nagakura:⁵ (—), A_2 oscillator; (-----), E oscillator.

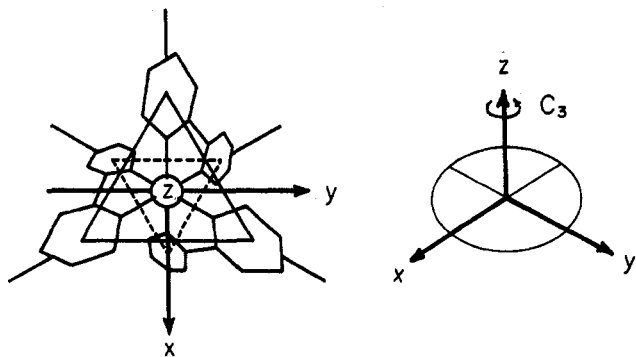


Figure 4. Geometry of the linear and planar oscillators in tris(bidentate)metal chelate.

Table III. Spin-Orbit Coupling Selection Rules, D_3

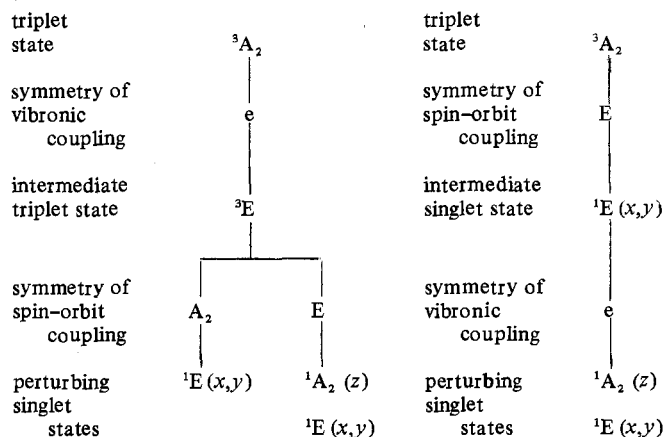
Triplet state spatial symmetry	Symmetry of spin-orbit coupling	Perturbing singlets
3A_2	A_2	1A_1 (forbidden)
	E	$^1E(x,y)$
3E	A_2	$^1E(x,y)$
	E	1A_1 (forbidden) + $^1A_2(z)$ + $^1E(x,y)$

“metal to ligand” charge-transfer singlet-singlet transitions $^1E \leftarrow ^1A_1$. The linear oscillator $^1A_2 \leftarrow ^1A_1$ is less participating to the 23,000- and 28,000- cm^{-1} charge-transfer absorption bands; however, polarization studies on the absorption spectra of the doped crystals and molecular orbital calculations give evidence of a weak $^1A_2 \leftarrow ^1A_1$ component participating to the lowest wave number band at 21,000 cm^{-1} . In fact, a polarization ratio greater than $+1/7$ was observed in good reproducibility at 21,000 cm^{-1} . This cannot be attributed to some instrumental artifacts and systematic errors. Corrections to be carried out for experimental errors in the luminescence detection and for polarization characters of the monochromators and the photomultiplier employed were almost constant and showed only a continuous change in the entire wave number region used in the present polarization study. Thus, a striking jump of the error in measurement is not expected to occur in a

particular wave number at 21,000 cm^{-1} . Even if the uncorrected systematic error is assumed as large as $+0.05$, the polarization ratio at 21,000 cm^{-1} is still larger than $+1/7$. The instrument can reproduce the established polarization ratios within ± 0.02 in the wave number region. The polarization higher than $+1/7$ observed at 21,000 cm^{-1} shows a certain participation of the linear emission oscillator upon excitation of the oscillator $^1A_2 \leftarrow ^1A_1$. A positive value higher than $+1/7$ is possible only by a contribution of the emission arising from a linear oscillator upon excitation of a linear absorption oscillator polarized in the same direction. Since the spin-forbidden transition $^3A_2 \rightarrow ^1A_1$ borrows the intensity only from the planar oscillator $^1E \rightarrow ^1A_1$ whereas the spin-forbidden transition $^3E \rightarrow ^1A_1$ borrows the intensity from both the linear oscillator $^1A_2 \rightarrow ^1A_1$ and the planar oscillator $^1E \rightarrow ^1A_1$, the polarization higher than $+1/7$ observed at 21,000 cm^{-1} indicates, at least, that the lowest emitting triplet state is 3E rather than 3A_2 .

As was discussed by Albrecht,²⁵ spin-vibronic coupling, spin-orbit coupling with vibronic coupling in the singlet manifold, and vibronic coupling in the triplet manifold with spin-orbit coupling should be taken into account for the intensity borrowing of phosphorescence in the low spin-orbit coupling systems. In this particular complex, a vibronic coupling between the triplet states 3A_2 and 3E or between the singlet states 1A_2 and 1E through a degenerate vibrational mode e can grant an intensity of the spin-allowed linear oscillator $^1A_2 \rightarrow ^1A_1$ to the spin-forbidden transition $^3A_2 \rightarrow ^1A_1$. The coupling paths are shown in Chart I.

Chart I



A static distortion, which corresponds to the degenerate vibrational mode e , among those caused by terms of symmetry lower than D_3 also gives rise to the similar coupling. If such a coupling occurs sufficiently, the emitting state could be 3A_2 rather than 3E . In the “metal to ligand” ($d\pi, \pi^*$) charge-transfer excited states such as the lowest triplet and singlet excited states in $[\text{Ru}(2,2'\text{-bipy})_3]^{2+}$, the distortions or vibrations of the metal-ligand coordination framework of the complex cannot give rise to an appreciable mixing between the states. The vibronic coupling between the triplet states 3A_2 and 3E or between the singlet states 1A_2 and 1E is group theoretically allowed; however, the actual coupling is not so crucial. Thus, such a weak vibronic coupling through a degenerate vibrational mode e can actually not grant the intensity of the weak linear oscillator $^1A_2 \rightarrow ^1A_1$ to the spin-forbidden transition $^3A_2 \rightarrow ^1A_1$. Since this complex consists of ruthenium(II) ion with high spin-orbit cou-

pling, the direct spin-orbit coupling grants an intensity to the spin-forbidden transition ${}^3A_2 \rightarrow {}^1A_1$ only from the spin-allowed planar oscillator ${}^1E \rightarrow {}^1A_1$. The transition ${}^3A_2 \rightarrow {}^1A_1$ is actually a planar oscillator. However, the transition ${}^3E \rightarrow {}^1A_1$ is a three-dimensional oscillator consisting of an intense component of polarization in a plane and only a weak component perpendicular to it. In the region of $21,000\text{ cm}^{-1}$, a weak linearly polarized transition ${}^1A_2 \leftarrow {}^1A_1$ is superposing on an intense plane-polarized transition ${}^1E \leftarrow {}^1A_1$. The polarization ratio must be $+1/7$ when the planar component of the transition ${}^3E \rightarrow {}^1A_1$ emits upon excitation of the plane-polarized transition ${}^1E \leftarrow {}^1A_1$, while it is $-1/3$ when the planar component of the transition ${}^3E \rightarrow {}^1A_1$ emits upon excitation of the linearly polarized transition ${}^1A_2 \leftarrow {}^1A_1$ or the linear component of the transition ${}^3E \rightarrow {}^1A_1$ emits upon excitation of the plane-polarized transition ${}^1E \leftarrow {}^1A_1$. Only in the case of the emission of the linear component of the transition ${}^3E \rightarrow {}^1A_1$ upon excitation of the linearly polarized transition ${}^1A_2 \leftarrow {}^1A_1$, the

polarization ratio is a higher positive value $+1/2$. Thus, a weighed mean value of the polarization of the luminescence arising from the transition ${}^3E \rightarrow {}^1A_1$ upon excitation at $21,000\text{ cm}^{-1}$ can exceed $+1/7$, although the value depends upon the contribution of the components. The corresponding value expected for the transition ${}^3A_2 \rightarrow {}^1A_1$ upon the same excitation is $+1/7$ or less than $+1/7$. Therefore, it is concluded that the lowest emitting triplet state is 3E rather than 3A_2 .

The polarization was also measured by monitoring at $16,100\text{ cm}^{-1}$ (620 nm) in the second emission maximum. The results were in good agreement with that measured by monitoring at $17,400\text{ cm}^{-1}$ (575 nm).

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X-Ray Photoelectron Spectroscopy of Nickel Compounds

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X-Ray photoelectron spectra (XPS) of the Ni($2p_{3/2,1/2}$) levels for about 70 compounds containing nickel in all of its known oxidation states have been studied. The binding energies have been correlated with ligand electronegativities, delocalization of charge on the ligands, and stereochemistry. Shake-up satellites associated with the Ni(2p) photoelectron lines have been investigated in detail, and a definitive relationship between the shake-up transition and paramagnetism has been established. In the case of octahedral compounds of nickel(II), the separation between the shake-up satellite and main line is found to correlate with the nephelauxetic series of the ligands attached to the metal. The investigation of several carefully chosen isomeric pairs has proven that XPS can be used to differentiate the magnetic behavior between them. The Ni(2p) binding energies are observed to increase in the order square planar < tetrahedral < octahedral, as expected on the basis of known metal-ligand bond lengths.

Introduction

The transition metals as a group show such interesting properties as variable valence, paramagnetism, and a highly diverse stereochemistry. Hence, they are ideally suited for study by X-ray photoelectron spectroscopy (XPS), with which one probes directly the electronic environment of the transition metal atom or ion. Recent studies of this kind have uncovered such phenomena as shake-up satellites in the XPS of 2p orbitals²⁻⁴ and multiplet splitting in the 3s spectra arising from the exchange interaction between the partially filled 3s and 3d orbitals.⁵⁻⁷ The latter phenomenon has been investigated in depth by Carver, *et al.*,^{6,7} from

the spectra of some 40 Cr, Mn, Fe, and Co compounds. Most recently Frost, *et al.*,⁸ reported the first systematic XPS measurements on the copper ion in 46 copper compounds and attempted to correlate the characteristics of the shake-up satellites and the binding energies of the copper core levels with its electronegativity and oxidation states, as well as the kind and the number of ligand atoms surrounding the copper.

The diversity of structures possible for nickel offers yet another possibility for the detailed XPS study of the variation of binding energies and shake-up satellites as a function of stereochemistry, magnetic properties, and ligand surroundings. Hitherto, such information concerning nickel compounds has been scant and desultory.⁹ In general, the results of our XPS investigations on 70 nickel compounds tend to confirm the trends and interpretations reported by Frost, *et al.*,⁸ for copper compounds. In addition, we have studied in detail and established the definitive relationship between shake-up satellites and paramagnetism. In some instances, existing ambiguities in electronic structure have also been clarified by XPS through the examination of both

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