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Magnetically Induced Circular Polarization Of Emission: Application To Inorganic Complexes

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MAGNETICALLY INDUCED CIRCULAR POLARIZATION OF EMISSION:
APPLICATION TO INORGANIC COMPLEXES*

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Abstract

A sensitive spectrometer for the measurement of circular polarization of emission, utilizing a photoelastic modulator, is presented. This spectrometer, when augmented by a superconducting magnet and dewar assembly, provides an excellent system for studying magnetically induced circular polarization of emission (MICE). In order to exemplify both the system and the usefulness of MICE, a partial analysis of the MICE observed from Ru(4,7-diphenyl-1,10-phenanthroline)$_3$Cl$_2$ dispersed in a polymethylmethacrylate (PMM) matrix in the 2 to 100°K temperature range is reported. Also presented is a discussion of the effects of photoselection on the observed MICE for these D$_3$ symmetry complexes. It is found that MICE is more sensitive to the detailed nature of the levels involved in emission than a combination of **zero field techniques**. MICE should prove to be **an** exceptionally useful tool for probing excited states of inorganic complexes.

Introduction

The invention of the photoelastic modulator (PEM) in the late 1960's[1] was concurrent with, and stimulated, a rebirth of interest in the interaction of polarized light with matter. The photoelastic modulator has been used in studies of elipsometry, linear dichroism, circular dichroism, vibronic circular dichroism, circularly polarized emission, and magnetically induced circular polarization of emission (MICE).[2] This device may be used as the basis for almost any polarization spectrometer. It is characterized by a large angular aperature, a large spectral range, and a very modest voltage (∿ 20 V) requirement. The PEM is strongly competitive with the Pockels cell and is replacing it in many cases. The present study describes the details of a MICE spectrometer utilizing a PEM and its application in inorganic spectroscopy.

Although circular polarization of emission from systems in zero magnetic field is relatively rare, the magnetically induced analog is a property of all luminescent materials.[3] The external field induces a "handedness" to the states of molecules and atoms that is reflected in the momentum distribution (polarization) of the emitted light. This induced handedness is a consequence of the splitting and mixing of states by the magnetic field. MICE is therefore a sensitive probe of the magnetic properties of the electronic states of the system. To first order in magnetic field strength, these effects can be quantified in terms of three parameters: A', B', and C'. The A' parameters are non-zero when there is degeneracy present in either the ground or excited state. They are a direct consequence of the frequency shifts that occur as the zero field degeneracy is removed. A pure type A' spectrum is a scaled derivative with respect to energy of the zero field line shape. Idealized B' and C' type bands have the same frequency dependence as the zero field emission, with the exception of a signed constant. C' type spectra are intrinsically temperature dependent and arise because of variations in populations of states degenerate in zero field. B' terms are due to the mixing of states not degenerate in zero field. In reality, the detailed frequency dependence is a strong function of the vibronic as well as the electronic nature of the states involved, and it is frequently preferable to discuss the moments of the band. These moments are defined by

$$[\underline{I}]_a^n = \int_{band} \underline{I}(\omega) \frac{(\omega-a)^n}{\omega^3} d\omega \tag{1}$$

$$[\Delta\underline{I}]_a^n = \int_{band} \Delta\underline{I}(\omega) \frac{(\omega-a)^n}{\omega^3} d\omega \tag{2}$$

where I is the photon quantum yield per unit energy interval, ω is the energy (or frequency), and ΔI is the difference between left and right circularly polarized photon yields.

In order to extract optical properties independent of the radiationless problem,[3] we report the percent net circular polarization of emission defined by

$$\%NCP = 100[\Delta I]^0 / [I]^0 \tag{3}$$

where the %NCP is positive if the emitted light is preferentially left circularly polarized. The %NCP is easily parameterized via first-order perturbation theory to give

$$\%NCP = \frac{-100H \sum\limits_{i \to f} [B'(f\leftarrow i) + C'(f\leftarrow i)/\kappa T]N_i}{\sum\limits_{i \to f} N_i D'(f\leftarrow i)} \tag{4}$$

where D' is proportional to the zero field intensity, i and f label the initial and final states in zero field, and N_i is the population of state i. At temperatures above 50°K in the absence of isolated states of high degeneracy, the net circular polarization induced by a 50-kG field is expected to be a fraction of a percent. Thus we may measure the MICE from virtually any luminescent material, provided we have an instrument capable of measuring a %NCP of approximately 0.1 to 0.01. The spectrometer presented here is such an instrument.

Experimental

Instrumental

Figure 1 is a schematic diagram of the spectrometer used in this study. Collimated light from a 1000-W Hg-Xe lamp is filtered by 20 cm of aqueous $CuSO_4$ and a series of glass filters to remove all visible and uv radiation excepting a narrow band at $\sim$ 17 kK, which corresponds to the x-y polarized absorption band of the complex studied. This carefully depolarized light is then focused onto the sample, which is mounted in the bore of a 50-kG horizontal access superconducting magnet system. Since the bore area is evacuated, special precautions are necessary to adjust and determine the sample temperature accurately. The sample is sealed into a small capsule under a few psi of He gas. This capsule is then screwed into a copper heat exchanger whose temperature is varied via a dynamic balance of He vapor flow rate and resistive heating.
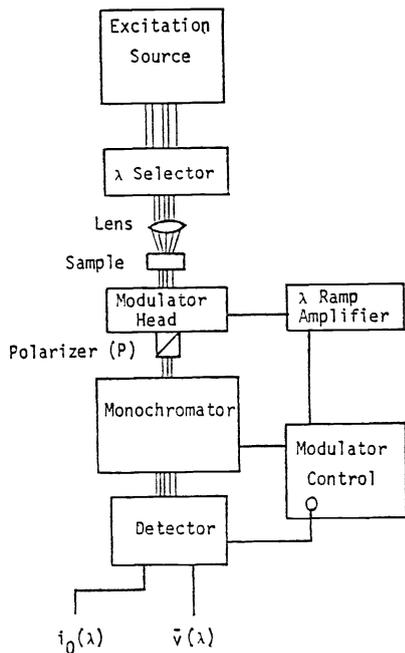
Light emitted from the sample falls on the modulator and then passes through a polarizer. If the emitted light consists of circular polarized light plus unpolarized light, the intensity entering the monochromator (I_m) is given by

$$I_m = \frac{I_0}{2} + \Delta I \; J_1(\phi_0)\cos(2\omega_m t) \tag{5}$$

where J_1 is a Bessel function of first order, ω_m is the resonance frequency of the PEM (50 kHz), and t is the time. This beam is therefore composed of a dc portion that represents the total emission and an ac component that is related to the differential circular polarization. In the above equation, ϕ_0 is the maximum phase shift experienced by the beam during one oscillation of the PEM.

Fig. 1. Schematic diagram of a MICE spectrometer.

Its magnitude is proportional to the driving voltage and inversely proportional to wavelength. By coupling the modulator drive voltage to the monochromator, as shown, we may keep ϕ_0, and therefore J_1, constant. J_1 maximizes at $\phi_0 \simeq \pi/2$ with a value of ~ 0.6; therefore ϕ_0 is kept fixed at $\pi/2$ by the monochromator coupling.

This time dependent radiation is then frequency analyzed by a Spex 1/4-m monochromator and detected by an EMI 9558 photomultiplier. The signal from the photomultiplier is then Fourier analyzed by a lock-in, electrometer combination. The lock-in output is proportional to ΔI, while the electrometer output is proportional to I. These outputs are recorded on a strip chart recorder and may be later corrected for detector frequency dependent sensitivity. Alternately, they may be fed directly to a microprocessor and corrected before plotting. The data presented here were corrected by the former method.

Sample Preparation

A 0.3-mm thick plastic containing about 10^{-4} M tris(4,7-diphenyl-1,10-phenanthroline)-ruthenium(II) chloride, Ru(4,7-diϕphen)$_3$Cl$_2$, was prepared in the following manner. A few milligrams of this compound were dissolved in chloroform and added to a solution of PMM in chloroform. The resulting solution was stirred until it was a thick syrup. The syrup was then poured onto flat glass plates and allowed to evaporate to dryness under reduced pressure. Plastics were carefully checked for strain and scratches under a polarizing microscope prior to use; the best of these was used. It should be noted that these plastics are relatively insensitive to radiation damage by the exciting light. No change in the observed emission or color of the sample was noted after several hours of continuous excitation. Also, samples may be stored for up to a year or more without measurable degradation, provided they are kept at subzero centigrade temperatures. We are not certain of their room temperature life, but it exceeds one month.

Results

Presented in Figure 2 are the MICE and total emission spectra obtained at 6°K. This figure contains direct tracings of the experimental spectra uncorrected for the wavelength response of the monochromator-photomultiplier combination. The intensity scale for the MICE spectrum is 0.05 times that of the total emission. The noise level obtained with a 3 sec time constant was within the width of the pen line. The MICE is clearly blue shifted with respect to the total emission. It is apparent from the difference in band shapes that the MICE spectrum contains information that is not extractable from the total emission.

Figure 3 displays the temperature dependence of the observed %NCP. The 2°K point is the least certain since it was obtained using an immersion dewar system with some strain in the windows. We expect, however, that the error should amount to no more than 20%. Despite the marked differences in band shapes of the MICE and total emission, it is interesting to note that the simple ratio of peak MICE to peak total emission was proportional to the %NCP within about 20%; the proportionality constant was 1.35. The %NCP was obtained by first correcting the MICE and total emission for detector and monochromator response and then numerically integrating the resultant corrected photon intensities according to eq (1) and (2) for use in eq (3).

At every temperature above 2°K, spectra were taken at three or four field strengths in order to ascertain whether a linear, or super-linear, effect was operative. In all these cases, the measured MICE was linear with respect to the field to within the experimental error of about 5% of the applied field. In the case of the 2°K data, we can only state that the effect was predominantly linear.
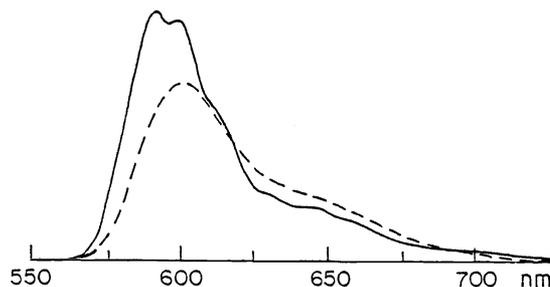

Fig. 2. The emission (---) and MICE (———) spectra of Ru(4,7-diϕphen)$_3$Cl$_2$ in PMM at 6°K. For illustration purposes, the MICE has been multiplied by a factor of about 20.
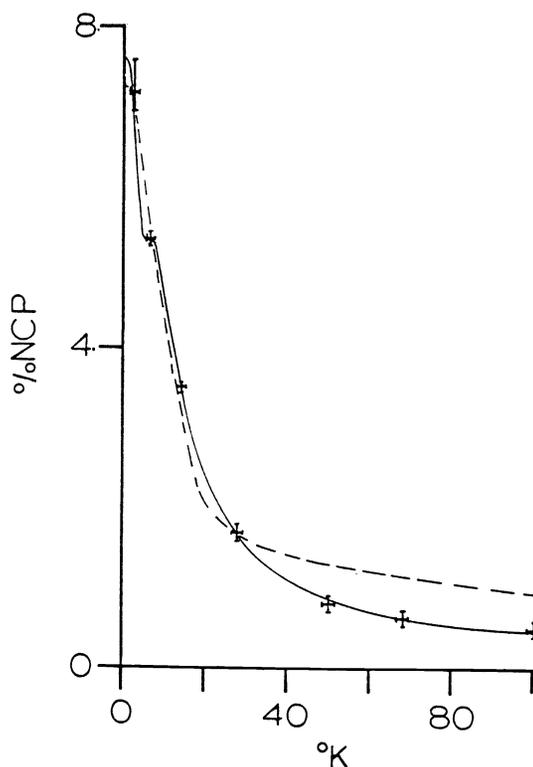
Fig. 3. %NCP as a function of temperature.
Experimental data (+++); least-squares fits
of EIP (———) and ^3E (- - - - -) models.

Discussion

Instrumental

Although the spectra presented here attest to the quality of the spectrometer des-
cribed, several improvements would enhance its performance in the 0.01 to 0.001 %NCP
range. (1) The spectrometer could be interfaced with a computer so that the drive speed
could be controlled to provide a constant signal-to-noise ratio at all wavelengths. (2)
The exciting radiation could be chopped at low frequency to allow the total emission also
to be detected by lock-in amplification. (3) An RCA C31034 photomultiplier and cooled
housing would extend the usable spectral range. (4) The computer interface could be used
for calculation of moments, correction of spectra, base line correction, and in the
case of certain transient spectra, statistical averaging.

Theoretical

The emission from $Ru(4,7-di\phi phen)_3Cl_2$ and other complexes of its type has been
characterized as charge transfer in nature.[4] Whether that emission is more properly
called a phosphorescence or should be described by another model is still an open
question. We demonstrate here that the %NCP data, although of apparently simple form,
serve as a severe test for the two most reasonable available models, the ^3E[5] and electron
ion-parent (EIP)[6] models. In order to pursue this end, we extracted data on the total
decay time and quantum efficiency of this complex as a function of temperature from ref [4].
In that reference, the EIP model was used to fit the zero field data to within experimental
accuracy. In Figure 4 we present the radiative decay times, total decay times, and excited
state energy-level scheme determined by that fitting procedure. Also depicted in Figure 4
is an energy-level scheme that gives equally good reproduction of the lifetime and quantum
yield data and is consistent with the ^3E model after inclusion of strong to medium first-
order spin-orbit coupling and weak higher order effects.[7] Finally, the actual lifetime
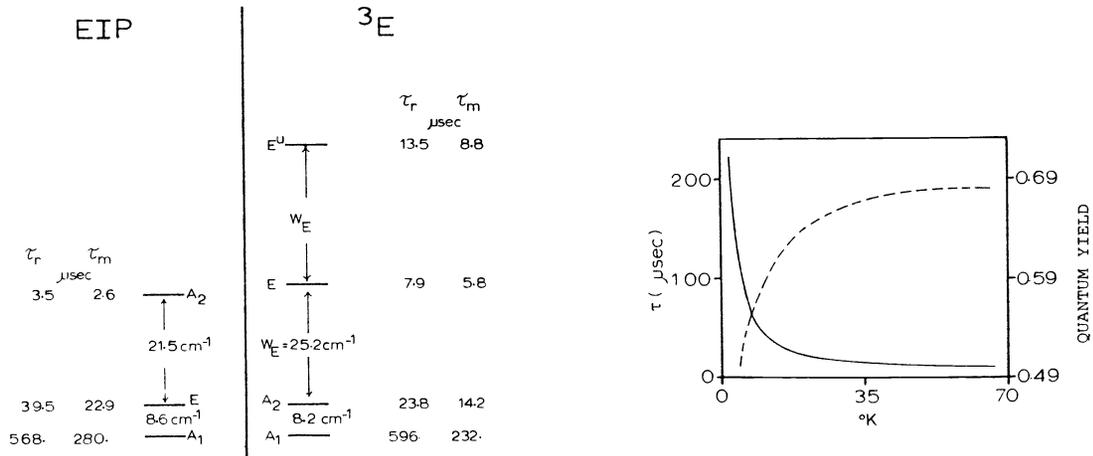and quantum yield curves are given.

Fig. 4. Parameters for the excited charge transfer states of Ru(4,7-diϕphen)$_3$Cl$_2$ in two models. Also shown are the experimental temperature dependent curves of the total decay time (————) and of the quantum yield (----) from which these parameters were derived.

These models predict qualitatively the same behavior for the MICE spectrum. We expect both C' and B' terms to play strong roles in the temperature dependence of the %NCP and the MICE observed at the lowest temperature either to be vibronic or higher than first order in field dependence (the ground state is A$_1$ in symmetry). Obviously, these are multiple level models. The %NCP data cannot be fit by a single level, or set of degenerate levels, scheme. Having agreed that the models are qualitatively similar, we must turn to a more quantitative test.

The B', C', and D' terms of eq 4 can be calculated if certain transition moments and matrix elements of the angular momentum are known. Formulas for these in the case of an isotropic sample are developed in ref 3. In our case, however, the anisotropy of the absorption (x-y) coupled with the anisotropy of the exciting light, leads to a modification of those parameters. For any system with a threefold axis of symmetry that, subsequent to excitation in an x-y polarized band, emits light without geometrical relaxation, the following hold.

$$D'(A_1 \leftarrow A_2) = (18/20)D_0'(A_1 \leftarrow A_2) \tag{6}$$

$$D'(A_1 \leftarrow E) = (21/20)D_0'(A_1 \leftarrow E) \tag{7}$$

$$C'(A_1 \leftarrow E) = (24/20)C_0'(A_1 \leftarrow E) \tag{8}$$

$$B'(A_1 \leftarrow A_2) = (18/20)B_0'(A_1 \leftarrow A_2) \tag{9}$$

where the D$_0'$, C$_0'$, and B$_0'$ are given on page 208 of reference 8, except that d$_A$ is replaced by d$_J$ and C$_0'$ is modified as indicated in ref 3. Using the above relations, the radiative lives depicted in Figure 4, and assuming the E and A$_2$ to A$_1$ transitions are dipole allowed, we may determine the D' and the transition moment portion of the B' and C' parameters for the A$_2$ and E levels. Since we lack detailed information about the transition mechanism for the A$_1$ to A$_1$ transition, we treat B'(A$_1$ ← A$_1$) as an adjustable parameter. In order to determine values for the B' and C', we must determine matrix elements of the angular momentum.

We make the approximation that the magnetic field effect on our excited manifold of A$_2$ and E states is predominantly within that manifold; i.e., we neglect mixing of A$_2$ and E manifold states with higher non-radiative excited states and the ground state. Within this approximation, the wavefunctions given in ref 6 completely determine the stated problem in the EIP model. In the case of the triplet E model, our assumption of a principally first-order spin-orbit interaction allows us to use group theory to determine the problem with one additional parameter: the expectation value of the z component of angular momentum for the E+ orbital component (a). We reasonably expect that a $\lesssim$ h.

Since neither theory is very rigorous, a least-squares fitting routine was used with three adjustable parameters in each case. One of these in both models was $B'(A_1 \leftarrow A_1)$, which was discussed previously. In both cases $B'(A_1 \leftarrow A_1)/D'(A_1 \leftarrow A_1) \sim 1.5 \times 10^{-3}$ kG^{-1}. The other two parameters and their calculated values are presented in Table 1. The resultant fits are shown in Figure 3.

Table 1. Parameters Used in Fitting %NCP

Model	Parameter	Least-Squares Value	Calculated Value
EIP	g	0.15	3.10
	$\lvert <A_2\lvert\mu_x - i\mu_y\lvert E+> \rvert$	$0.014 \ cm^{-1}/kG$	$0.024 \ cm^{-1}/kG$
^3E	$\underline{a} = <E+\lvert L_z \lvert E+>$	$0.11 \ \hbar$	$0 < \underline{a} \lesssim \hbar$
	$\lvert B'(A_1 \leftarrow A_2) \rvert$	$0.12\lvert B'_{calc}\rvert$	$\lvert B'_{calc}\rvert$

Perusal of Figure 3 and Table 1 suggests that the ^3E model is entirely unsatisfactory. The EIP model is capable of fitting the data, predicts within a factor of 2 the A_2,E matrix element, but gives an unreasonably low value for the g factor of the E state. This tremendous difference between the calculated and observed g's cannot be accounted for within the simple EIP model. The lack of quantitative agreement of the %NCP data with the predictions of both models points out the sensitivity of MICE to the detailed characteristics of the system state functions. One can conclude that MICE measurements will provide extreme tests for any theoretical model for excited states of inorganic complexes.

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