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LUMINESCENCE IN APPLIED MAGNETIC FIELDS(U) WASHINGTON  
STATE UNIV PULLMAN DEPT OF CHEMISTRY G A CROSSBY  
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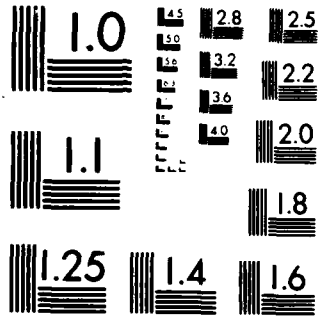
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MICROCOPY RESOLUTION TEST CHART  
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# AD-A173 805 DOCUMENTATION PAGE

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Crosby, Glenn A.

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

External fields (0-6 kG) applied to inorganic complexes of (nd)<sup>8</sup> configurations were shown to produce macroscopic changes in luminescence frequencies and lifetimes. Frequency shifts of ~400/cm<sup>-1</sup> were observed. A theoretical study of the octaphosphitoplatinum(II) ion was completed that relates the changes in optical properties to the degree of spin-orbit coupling in the anion. A search for complexes of iridium(I) and rhodium(I) possessing energy level schemes propitious for observing large perturbations of optical properties by relatively small external fields was completed and revealed several promising candidates. The technique of thermal modulation spectroscopy was developed and applied to several types of complexes to evaluate them for future magnetic perturbation measurements.

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OFFICE OF NAVAL RESEARCH

FINAL REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

Contract N00014-83-K-0609

R & T Code N63374  
Replaces Old  
Task #NR 051-848

**Luminescence in Applied Magnetic Fields**

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FINAL REPORT FOR THE PERIOD: 1 July 1983 - 30 September 1986

For Contract N00014-83-K-0609, R & T Code N63374 (Old Task No. NR 051-848)

Summary of Accomplishments

The fundamental goal of the project was to induce macroscopic changes in the optical properties of transition metal complexes by the application of external magnetic fields. We succeeded.

Proof of the feasibility of the original concept was supplied by experiments on the complex  $[\text{Ir}(\text{2-phos})_2]\text{ClO}_4$  [2-phos is cis-1,2-bis-diphenylphosphino-ethylene]. We obtained a large ( $\sim 400 \text{ cm}^{-1}$ ) shift in the frequency of the emission in an external field. These results are contained in ONR-TR-1. [See literature reference (1) below.] Since this molecule is a prototype molecule, the result is very significant.

During the investigations we also discovered a novel low-level excited state(s) in closed shell complexes. This discovery was reported in ONR-TR-2 and in the open literature (2). We also showed that these excited states were not in thermal equilibrium with the  $\pi-\pi$  states of the systems and that the barrier to energy migration could be measured. The first such measurement on any complex was included in ONR-TR-3 and reference (3).

We also investigated the effect of external magnetic fields on the emission of the barium salt of the octaphosphitoplatinum(II) ion. The changes in properties induced by the field were unusually large. Moreover, we observed large effects both in the crystals and in glasses containing this ion. The results will be submitted for publication.

We have also completed a theoretical calculation on the effect of a magnetic field on the octaphosphitoplatinum(II) ion. We repeated the energy calculation of Azumi et al. [J. Phys. Chem. 88, 2423-2425 (1983)], but the published wave functions are not suitable for applying the magnetic perturbation. We are now investigating the effect of external magnetic fields on both the frequencies and the lifetimes using our set of bases. These are properly symmetry adapted to the problem. The theoretical results look very promising for guiding us to new systems that may show even larger spectroscopic effects when subjected to external fields. The important feature of the theoretical study is to find which are the major terms in the field perturbations.

During the tenure of the contract we also refined the technique of Thermal Modulation Spectroscopy for the study of low-lying excited states of transition metal complexes whose splittings are not amenable to measurement by standard techniques such as direct infrared spectroscopic observation or indirect measurement by microwave-optical double resonance methods. The application of TME to transition-metal complexes will be discussed in detail in a forthcoming publication [G. A. Crosby and K. J. Jordan, "Application of Thermal Modulation in Luminescence Spectroscopy"; Manuscript in preparation (2)].



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Availability Codes	
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### Papers Published in Refereed Journals

ONR-  
TR-#

1. T. J. Johnson, S. D. Phillips, G. A. Crosby, "Magnetically-Induced Luminescence of  $[\text{Ir}(\text{2-phos})_2]\text{ClO}_4$ ", Chemical Physics Letters **114**, 388-392 (1985). (ONR)
2. K. A. Truesdell and G. A. Crosby, "Observation of a Novel Low-Lying Excited State in Zinc(II) Complexes", Journal of the American Chemical Society **107**, 1787-1788 (1985). (ONR/AFOSR)
3. R. G. Highland and G. A. Crosby, "Determination of the Activation Barrier to Energy Transfer from  $\pi-\pi$  to Charge-Transfer Levels Via Steady State and Transient Luminescence Measurements on Bis(4-chlorothiophenol)(1,10-phenanthroline)zinc(II)", Chemical Physics Letters **119**, 454-458 (1985). (ONR/NSF)

### Manuscripts in Preparation

1. K. J. Jordan and G. A. Crosby, "Application of Thermal Modulation in Luminescence Spectroscopy", SPIE (1987), Proceedings, Society of Photo-Optical Instrumentation Engineers, Symposium on Fluorescence Detection, Los Angeles, Jan 11-16, 1987.
2. C. A. Helms<sub>4</sub> and G. A. Crosby, "Perturbation of the Excited States of  $[\text{Pt}_2(\text{pop})_4]^{4-}$  Via External Magnetic Fields", to be submitted.

### Invited Presentations at Topical or Scientific/Technical Society Conferences

"Excited States of Bis(terpyridine)Complexes of Ruthenium(II)", Symposium Honoring Arthur Adamson, University of Southern California, Los Angeles, CA, Dec 84. (Current and previous support)

"Spectroscopic Properties of  $(\text{nd})^{10}$  Complexes", Symposium on the Photochemistry and Photophysics of Metal Complexes, 1984 Chemical Conference of Pacific Basin Societies, Honolulu, HI, Dec 84. (ONR/NSF)

"Excited States of Transition Metal Complexes: Properties of  $(\text{nd})^8$  Monomeric and Dimeric Systems", American Chemical Society Tour Speaker, Texas Circuit, Heart O' Texas Section, Feb 85. (ONR/NSF)

"Light As a Research Tool", Idaho Science Teachers Association Conference, Plenary Address, Boise, ID, Oct 84; American Chemical Society Tour Speaker, Texas Circuit, Feb 85; San Antonio Section, Texas A & M Section, Dallas-Ft. Worth Section; all 4 Institutes of Chemical Education, Jul 85; University of Maryland, University of Wisconsin, University of Arizona, University of California; MARC Conference on Graduate Studies, Plenary Address, Tougaloo College, Sep 85 (Current and previous support)

"Luminescence: A Key to Atomic and Molecular Structure", SUNOCO Lectures, National Science Teachers Association Convention, San Francisco, Mar 86 (Current and previous support)

Lecture Tour 12 Universities and 2 Research Establishments in Japan, sponsored by Yamada Foundation, Apr-Jun 1986: 17 presentations. (ONR/NSF)

Contributed Presentations at Topical or Scientific/Technical Society Conferences

9 presentations at national and regional meetings

Personnel

Principal Investigator: G. A. Crosby

Associate in Chemistry: J. L. Crosby

Graduates Students: R. Cummings, G. R. Gamble, C. A. Helms, R. G. Highland,  
T. J. Johnson, K. J. Jordan, T. R. Reynolds

Undergraduates: D. Casebier, M. Clawson, S. D. Phillips

Honors/Awards/Prizes

American Chemical Society Award in Chemical Education, 1985.

Invited Six-Week Research Lecture Tour in Japan, 17 presentations at 12 Universities and 2 Research Establishments sponsored by Yamada Foundation, 1986.

<u>Complete Funding History:</u>	7/1/83-6/30/84	\$55,828
	7/1/84-6/30/85	57,626
	7/1/85-6/30/86	<u>60,584</u>
		\$174,038

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