

### Summary of Recent Work:

Since 1997, I have been working in nonlinear optical materials research at the University of Alabama Birmingham, under the direction of Dr. Chris Lawson, where it soon became a goal of mine to improve upon the tools available for the characterization of nonlinear optical materials. After an introductory period in which I assisted in the measurement of the nonlinear optical response of a number of compounds using the standard characterization techniques (degenerate four-wave mixing, z-scan, and nonlinear absorption), I began to write programs to simulate the nonlinear optical response of compounds as measured by each of the aforementioned techniques. Through the use of dynamic modeling, I can track the change in population of the excited states of a molecule and the corresponding change in transmission of the applied laser pulse as it moves through the material, and thus gain unparalleled insight into which processes dictate the nonlinear optical response. During the past two years, I have also had the benefit of working with Dr. Sergey Mirov, and under his guidance I have designed and built a powerful ultrabroadband tunable laser that can be used to perform the above measurements at a wide range of wavelengths. Further, over the past year I have been working toward establishing a model to allow for the quantum chemical prediction of the molecular susceptibilities of a series of transition metal-center metallotexaphyrins.

While employed by JPL in 1998, under the guidance of Dr. Pantazis Mouroulis, I helped build and test a miniature Offner spectrometer and wrote computer code to track the spectral response through any given optical system.

### Publications (with abstracts):

P. Mouroulis, M. McKerns, "Pushbroom imaging spectrometer with high spectroscopic data fidelity: experimental demonstration", *Optical Engineering* **39**, 808 (2000).

Experimental results are described from a pushbroom imaging spectrometer module demonstrating very low spectral and spatial distortion (a few percent of a pixel) and similarly small variation in spectral response function with field position. These spectrometer properties significantly facilitate the extraction of accurate spectroscopic information. The spectrometer can achieve high performance despite relaxed tolerances in fabrication and alignment. A quick and effective alignment method is described that permits the spectrometer to approximate its design performance. The implications of the results for the calibration techniques of pushbroom imaging spectrometers are also discussed.

W. Sun, C. Byeon, M. McKerns, C. Lawson, G. Gray, D. Wang, "Optical limiting performances of asymmetric pentaazadentate porphyrin-like cadmium complexes", *Applied Physics Letters* **73**(9), 1167 (1998).

The optical limiting performances of seven asymmetric pentaazadentate porphyrin-like cadmium complexes have been measured at 532nm with nanosecond pulses. In a  $f/38$  geometry, with sample transmission of 0.51 ~ 0.80 in a 2 mm cell, the limiting thresholds for these complexes were 1.4 ~ 3.0 mJ/cm<sup>2</sup>. The throughputs of these complexes were limited to 0.31 ~ 1.13 J/cm<sup>2</sup> for incident fluences as high as 3.5 J/cm<sup>2</sup>. The limiting throughput was strongly influenced by the nature of the ligand. Lower bounds for the ratio of triplet excited-state to ground-state absorption cross sections have been estimated at 3.4 ~ 5.7. The lower limiting thresholds, lower limiting throughputs, as well as the ease of modification of the ligands, make these complexes promising candidates for optical power limiters.

W. Sun, C. Byeon, M. McKerns, C. Lawson, J. Dunn, M. Hariharasarma, G. Gray, "Oxidative enhancement of the  $\chi^{(3)}$  values of solutions of *cis*-Mo(CO)<sub>4</sub>L<sub>2</sub> (L = PPh<sub>3</sub>, AsPh<sub>3</sub>, PPh<sub>2</sub>Np) complexes as measured by DFWM", *Optical Materials* **11**, 87 (1998).

Detailed degenerate four wave mixing studies of four molybdenum complexes, *cis*-Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>, *cis*-Mo(CO)<sub>4</sub>(AsPh<sub>3</sub>)<sub>2</sub>, *cis*-Mo(CO)<sub>4</sub>(PPh<sub>2</sub>Np)<sub>2</sub> and *cis*-Mo(CO)<sub>4</sub>(P(OPh)<sub>3</sub>)<sub>2</sub> are reported in this paper. Upon exposure to air/oxygen, the  $\chi^{(3)}$  values of solutions of the first three complexes increase dramatically with time. However, when excess free ligand is added to any of the solutions, no additional increase in the  $\chi^{(3)}$  value is observed. Hence, it is possible to obtain solutions with high  $\chi^{(3)}$  values by first oxidizing the solution and then adding excess ligand to stabilize the solution. Further, the increase in the  $\chi^{(3)}$  values of the solutions parallels the increase in the linear absorption, but it is unclear whether the increased linear absorption plays any role in the increase in the  $\chi^{(3)}$  values of the solutions. This study also shows how degenerate four wave mixing can be used as a very sensitive technique to detect the chemical change in a solution when the third order optical nonlinearities of the reactant and product are very different.

W. Sun, M. McKerns, C. Lawson, G. Gray, C. Zhan, D. Wang, "Solvent Effect on the Third-Order Nonlinearity and Optical Limiting Ability of a Stilbazolium-like Dye", *Proceedings of SPIE* Vol. **4106**, 280 (2000).

Stilbazolium-like dyes, which contain different heterocyclic groups as electron donors and an *N*-methylpyridinium iodide group as an electron acceptor, are very interesting optical limiting materials. These materials exhibit low linear absorption, but potentially very strong nonlinear absorption at high intensities. In this paper, the results from investigations of the third-order susceptibilities and nonlinear refractive indices of a stilbazolium-like dye, *trans*-4-[2-(pyrryl)vinyl]-1-methylpyridinium iodide (PVPI), in different solvents using degenerate four wave mixing and Z-scan techniques with 6.8 ns laser pulses at 532 nm are reported. The molecular second-order hyperpolarizability of PVPI increases from  $1.6 \times 10^{-31}$  esu in methanol to  $3.4 \times 10^{-29}$  esu in chloroform, a factor of 212. The third-order nonlinearity of this compound is dominated by nonlinear absorption, which leads to strong optical limiting of nanosecond laser pulses. The strength of the optical limiting is dramatically influenced by the solvent used, with limiting decreasing in the order chloroform > dichloromethane, 1,2-dichloroethane > methanol, acetonitrile. While both nonlinear absorption and nonlinear scattering contribute to the optical limiting, nonlinear absorption is the dominant mechanism.

W. Sun, C. Byeon, M. McKerns, C. Lawson, S. Dong, D. Wang, G. Gray, "Characterization of third-order nonlinearity of [(CH<sub>3</sub>-TXP)Cd]Cl", *Proceedings of SPIE* Vol. **3798**, 107 (1999).

The third-order nonlinear optical properties of a methyl substituted Texaphyrin, [(CH<sub>3</sub>-TXP)Cd]Cl, were studied by degenerate four wave mixing and Z-scan techniques using 40 ps laser pulses at 532 nm. The molecular second-order hyperpolarizability ( $\gamma$ ), the excited-state absorption cross section, the nonlinear refractive cross section, and the optical limiting performances at both nanosecond and picosecond time scales have been determined. The  $\gamma$  value for [(CH<sub>3</sub>-TXP)Cd]Cl is  $6.9 \times 10^{-31}$  esu, which is 4 times as larger as that of SiNc. The nonlinearity of [(CH<sub>3</sub>-TXP)Cd]Cl is predominantly electronic in origin with picosecond laser pulses. The excited-state absorption cross section and the nonlinear refractive cross section obtained from the theoretical simulation and calculation of Z-scan results are  $7.0 \times 10^{-17}$  cm<sup>2</sup> and  $1.7 \times 10^{-17}$  cm<sup>2</sup>, respectively. The complex shows strong optical limiting performance via reverse saturable absorption for 5 ns laser pulses. The nonlinear absorption of this molecule for 40 ps laser pulses exhibits a transition from reverse saturable absorption to saturable absorption when the fluence is higher than 0.3 J/cm<sup>2</sup>. These data suggest that this complex and related complexes are a promising class of nonlinear optical materials.

W. Sun, C. Byeon, M. McKerns, C. Lawson, G. Gray, D. Wang, "Investigation of relationship between chemical structure and optical limiting properties of asymmetric pentaazadentate porphyrin-like metal complexes", *Proceedings of SPIE* Vol. **3472**, 127 (1998).

The optical limiting performances of nine asymmetric pentaazadentate porphyrin-like metal complexes ( $[(R-APPC)M]Cl_n$ ) have been measured at 532nm with nanosecond pulses. In a  $f/38$  geometry, with sample transmission of 0.51 ~ 0.80 in a 2 mm cell, the limiting thresholds for these complexes were 1.4 ~ 150.0 mJ/cm<sup>2</sup>. The throughputs of these complexes were limited to 0.31 ~ 1.42 J/cm<sup>2</sup> for incident fluences as high as 3.5 J/cm<sup>2</sup>. The limiting throughput was strongly influenced by the nature of the ligand and metal ions. Lower bounds for the ratio of triplet excited-state to ground state absorption cross sections have been estimated at 2.3 ~ 5.7. The lower limiting thresholds, lower limiting throughputs, as well as the ease of modification of the ligands and variation of the metal ions, make these complexes promising candidates for optical power limiters.

W. Sun, C. Byeon, M. McKerns, C. Lawson, J. Dunn, M. Hariharasarma, G. Gray, "Enhancement of the third-order susceptibilities of *cis*-Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> solution by oxygen in different solvents", *Proceedings of SPIE* Vol. **3472**, 108 (1998).

Detailed degenerate four wave mixing studies of one molybdenum complex, *cis*-Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and tetrahydrofuran (THF) are reported in this paper. Upon exposure to air/oxygen, the  $\chi^{(3)}$  values of CH<sub>2</sub>Cl<sub>2</sub> and THF solutions of this complex increase dramatically with time. However, when excess free ligand is added to CH<sub>2</sub>Cl<sub>2</sub> solution of the complex, the increase in  $\chi^{(3)}$  values is stopped. Hence, it is possible to obtain a CH<sub>2</sub>Cl<sub>2</sub> solution with high  $\chi^{(3)}$  value by first oxidizing the solution and then adding excess ligand to stabilize the solution. For THF solution, due to the different mechanism causing the increase of  $\chi^{(3)}$  values, the increase in  $\chi^{(3)}$  values doesn't stop even though excess free ligand is added. Further, the increase in the  $\chi^{(3)}$  values of both the CH<sub>2</sub>Cl<sub>2</sub> and THF solutions parallels the increase in the linear absorption but it is unclear whether the increased linear absorption plays any role in the increase in the  $\chi^{(3)}$  value of the solution.

M. McKerns, I. Moskalev, C. Lawson, S. Mirov, "Utilization of a new powerful LiF:F<sub>2</sub><sup>\*\*\*</sup> tunable laser as a source for nonlinear absorption measurements on (CH<sub>3</sub>-CdTXP)Cl", *In Preparation* (2002).

Material parameters such as absorption cross-section are wavelength-dependant, so in order to fully understand the role of these parameters in the excited-state absorption and nonlinear optical (NLO) response of metallotetraphyrin (MTXP) complexes, nonlinear absorption measurements at a wide range of wavelengths have been performed. To obtain a fluence strong enough to sufficiently characterize the NLO response of solutions of MTEXP, a relatively strong laser such as a Nd:YAG must be used as a light source. However, the use of a Nd:YAG constrains the available wavelengths to 1064 nm, 532 nm, and harmonics thereof, and thus only provides for a very slight set from which to draw conclusions. In order to allow for a more complete study of the NLO response of MTEXP, a new, powerful, continuously tunable (over 0.8 – 1.2  $\mu$ m, and harmonics thereof) laser system has been constructed utilizing LiF:F<sub>2</sub><sup>\*\*\*</sup> color centers as the active medium. The design and construction of this new laser, and its utilization in a few preliminary measurements of the wavelength-dependant NLO response of CdTXP are discussed below.

M. McKerns, J. Harrison, C. Lawson, G. Gray, "Quantum chemical calculation of molecular nonlinear optical properties of a series of pentaazadentate metalloporphyrins", *In Preparation* (2002).

In order to obtain a more solid understanding of the molecular origins of the nonlinear optical response of metallotexaphyrins (MTXP), molecular dynamic calculations of molecular structure and susceptibility were performed. In the following preliminary study of a short series of MTXP complexes, the vibrational ground states are calculated, and an attempt is made to form a structure-property relationship through calculation of static hyperpolarizability, analysis of ground-state structure, and the reaction to an external electric field defined by point charges (Sparkles). The correspondence of measured and calculated hyperpolarizability, as well as the contributions from molecular structure (i.e. bond angle, bond length) and molecular composition (i.e. the variation of substituents), is discussed.

M. McKerns, W. Sun, C. Lawson, G. Gray, "Nonlinear absorption and population dynamics in a series of pentaazadentate metalloporphyrin complexes", *In Preparation* (2002).

As evidenced by Z-scan, optical limiting, and spectral studies, the excited state population dynamics of metallotexaphyrins (MTXP) dominate the nonlinear optical (NLO) response of this important class of reverse saturable absorbing materials. These measurements however can only provide information about the ground- and first excited-states of the molecular system. In order to more fully characterize the NLO response of MTXP, the excited state absorption and population dynamics of these complexes are modeled by the use of a semiempirical fit of transmission versus fluence data. In the following preliminary study, the excited state population dynamics, absorption cross-sections, and upper excited state lifetimes have been calculated for a short series of MTXP. The significance of the contribution of each energy level to the NLO response of the medium, and the trends in bridging group substitution effects are also discussed.