

SYMPOSIUM PP
Materials for Optical Limiting III

November 30 – December 3, 1999

Chairs

Keith Lewis

Defence Evaluation and Research Agency
Malvern Worcs, WR14 3PS UK
44-1684-895062

Ruth Pachter

AFRL/MLPJ
Air Force Research Lab
3005 P St Ste 1
WPAFB, OH 45433-7707
937-255-3808 x3177

Joseph Perry

Dept of Chemistry
Univ of Arizona
PO Box 210041
Tucson, AZ 85721-0041
520-626-9331

Richard Sutherland

Science Applications Intl Corp
Dayton, OH 45431
937-255-3808 x3157

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* Invited paper

SESSION PP1: RSA AND MULTICHROMOPHORE
MATERIALS

Chair: Keith L. Lewis
Tuesday Afternoon, November 30, 1999
Room 205 (H)

1:30 PM *PP1.1
SPATIAL, TEMPORAL, AND BIO-OPTICAL ISSUES FOR
OPTICAL LIMITERS. R.C. Hollins, Defence Evaluation and
Research Agency, Malvern, Worcester, UNITED KINGDOM.

The protective properties of all limiters (including those normally considered to be nonlinear absorbers) depend heavily on their ability to redistribute laser energy across the sensor surface. The paper will assess the retinal images produced by a variety of limiter types. The relationship between the sensor damage threshold and the size and shape of the retinal image will be examined; new data and physical models describing laser-retina interactions have been produced which may resolve long-standing anomalies in bio-optics and may have important implications for eye protection using optical limiting.

2:00 PM PP1.2
FEMTOSECOND TO NANOSECOND CHARACTERIZATION OF
OPTICAL LIMITING MECHANISMS IN POWER LIMITING
LIQUIDS AND SOLIDS. Laura Smilowitz, Anton Malko, Su Xu,
Hsing-Lin Wang, Victor I. Klimov and Duncan W. McBranch Los
Alamos National Laboratory, Los Alamos, NM; Steven R. Flom,
Richard G.S. Pong and James S. Shirk Naval Research Laboratory,
Washington, DC; Bill Moreshead and Jean-Luc Nogués GELTECH,
Inc., Orlando, FL; David Hagan and Eric W. Van Stryland CREOL,
University of Central Florida, Orlando, FL.

Metal-substituted porphyrins (Ph's) and phthalocyanines (Pc's) represent two classes of molecules with the best known performance for reverse saturable absorption of nanosecond pulses in the visible spectral region. General models of the limiter performance in the nanosecond regime have been developed for isolated molecules that can form a triplet state. However a detailed understanding of the temporal evolution of the excited states under conditions present in real limiters has not been achieved. This understanding is necessary to realize the potential of these compounds for use in power limiting devices (liquid or solid-state). In this work, we detail the evolution of the excited-state absorption spectrum from femtosecond (fs) to ns timescales, in several members of this class. We have examined dilute liquid solutions of several Zn- and Pb-substituted Ph's and Pc's, highly concentrated substituted Pb-Pc which is a liquid in its neat state, and solid-state composites in sol-gel glass hosts. We examine the connection between fs spectroscopic results and ns power limiting results for a range of compounds.

2:15 PM *PP1.3
OPTICAL PROPERTIES OF NANO-STRUCTURED PHTHALO-
CYANINES. James S. Shirk, Richard G.S. Pong, Steven R. Flom,
E.A. Bolden, Dawn D. Dominguez and Arthur W. Snow, Naval
Research Lab, Washington, DC.

Nonlinear materials are critical components in an optical limiter. Advances in limiters have come with the development of materials with larger nonlinearities, i.e. materials whose optical properties are more easily altered by intense light. At the molecular level, the current NRL phthalocyanine materials exhibit low thresholds for limiting and a long dynamic range. We describe the effect of two levels of order on the optical limiting properties of these phthalocyanine materials. First the phthalocyanines can form ordered, stacked supramolecular structures. The extent of this order is controlled by the concentration and the nature of the substituents. The size and structure of these supramolecular structures determines the magnitude of the intermolecular couplings and hence the electronic states and their relaxation dynamics. By this mechanism, the supramolecular structure can have a substantial influence on the nonlinear optical properties of these materials. Recently, we have also fabricated composite materials with the order on a larger scale. Specifically, the morphology was made to vary on about the same length scale as the wavelength of light. The optical properties of such nanostructured materials often differ from the properties of the component materials because of the presence of coherent optical effects. Nonlinear photonic crystals that possess periodic variations in their nonlinear absorption and nonlinear refraction coefficients were fabricated and their nonlinear optical properties measured. These crystals are promising optical limiters.

3:15 PM *PP1.4
SYNTHESIS AND OPTICAL LIMITING CHARACTERIZATION
OF A SERIES OF PORPHYRIN-BUCKMINSTERFULLERENE
DYADS. Leng-Leng Chng, How-Ghee Ang, Zhi-Heng Loh, Yiew-Wang
Lee, Guo-Ying Yang; DSO National Laboratories, SINGAPORE.
Kenneth J. McEwan and Keith L. Lewis, Defence Evaluation and
Research Agency, Malvern, UNITED KINGDOM.

We report on the synthesis of a series of porphyrin-C60 dyads in which the porphyrin and C60 moieties are held within close proximity of one another via a covalent bridge. The close inter-chromophore approach in these dyads is achieved via the introduction of an o-phenylene bridge linking the porphyrin and the fullerene moieties. The physical proximity of the two chromophores is expected to enhance the nonlinear optical responses of the resultant dyads relative to the individual components. This could be achieved either by means of photo-induced electron transfer to form the fullerene anion, or perturbation of the electronic structure of the dyads by inter-chromophore interaction. The electron-donating ability of the porphyrin moiety is systematically varied through chemical modification. This allows us to control the ease of electron transfer from the porphyrin to the C60 moiety. Investigations of the effect of electron transfer on the optical limiting properties of the dyads are reported. To qualify the effect of through-space interaction, we synthesize a dyad with the porphyrin and fullerene moieties separated by a p-phenylene bridge. Through-space interactions are not possible in this dyad due to the large inter-chromophore through-space separation. This will enable us to distinguish any contribution to the optical limiting or nonlinearity enhancement due to through-space interactions from those due to through-bond interactions. Results from optical limiting measurements, steady-state fluorescence experiments, UV-Vis spectroscopy, NMR spectroscopy and electrochemical experiments will be discussed.

3:45 PM PP1.5
PHOTO-INDUCED EFFECTS IN Mn4+:YAG. OBSERVATION OF
UNUSUALLY EFFICIENT EXCITED STATE ABSORPTION AND
A LONG LIVED METASTABLE STATE. Yanong Han and Lee H.
Spangler The Optical Technology Center (OpTeC) and The
Department of Chemistry, Montana State University, Bozeman, MT;
Ralph Hutcheson and Randy Equall, Scientific Materials Corp.,
Boxeman, MT.

The Mn4+ ion has the same d3 electron configuration as Cr3+, but is less stable and can transform to other valence states. Both ions are known to occupy several sites in garnet hosts, giving rise to rather complicated optical spectra and photo-induced phenomena. Here, the systemic spectra of the transient photo-induced absorption and the emission of Mn4+:YAG are analyzed over a broad wavelength region (from 450 to 1200nm) and over widely different time scales (from ns to minutes). Very large amplitude and extremely broadband excited state absorption are observed. Additionally, a long life-time photo-induced species was detected that is likely formed via charge transfer. The demonstrated behavior of this material shows it has potential applications for optical limiting and optical storage.

4:00 PM PP1.6
OPTICAL LIMITING WITH NEUTRAL NICKEL DITHIOLENE
COMPLEXES. Wei Lian Tan and Wei Ji, Department of Physics,
National University of Singapore, SINGAPORE; Jun Feng Bai, Jing
Lin Zuo and Xiao Zeng You, Coordination Chemistry Institute, State
Key Laboratory of Coordination Chemistry, Nanjing University, P.R.
CHINA; Jin Hong Lim, Sidney S. Yang, David J. Hagan and Eric W.
Van Stryland, School of Optics/CREOL, University of Central
Florida, Orlando, FL.

Nickel dithiolene complexes have been used as Q-switch dyes for near infrared lasers since the early seventies[1] and have also been proposed as optical switching materials for optical communications[2]. Recently, in our search for optical limiting materials, we have found that such complexes also possess optical limiting behavior. Here, we report the investigation of optical-limiting behavior in two neutral nickel complexes with multi-sulfur 1,2 dithiolene ligands, [Ni(medt)₂] 1 (medt = 5,6-dihydro-6-methyl-1,4-dithiin-2,3-dithiolate) and [Ni(phdt)₂] 2 (phdt = 5,6-dihydro-5-phenyl-1,4-dithiin-2,3-dithiolate) in benzene solution. We measured the fluence-dependent transmission of the two complexes with picosecond laser pulses at 532 nm. With an aperture placed in front of the transmission detector, the limiting threshold was ~0.3 J/cm² for both complexes, which was about 8 times better than the results obtained without the aperture. This shows that the complexes have large nonlinear refraction, which enhances limiting action. Similar behavior was also observed with nanosecond laser pulses. To study the mechanism leading to the observed limiting effects, we carried out Z-scan measurements and picosecond time-resolved pump-probe experiments. The results can be fitted by a five-level model for input fluences of less than 0.5 J/cm². The excited state absorption cross-sections for both the complexes are comparable to those of silicon naphthalocyanine (SiNc) and chloro-aluminum phthalocyanine (CAP)[3], while the excited state refraction cross-sections in the complexes are ~7 times superior than those of SiNc. Also, we have noticed that the transparency range between the B and Q bands of the complexes is from 400 nm to 900 nm, which is about 2.5 times broader than phthalocyanine complexes. Based on these results, we believe that neutral nickel dithiolenes are

promising candidates for broad-band, optical-limiting applications. [1]K. H. Drexhage and U. T. Muller-Westerhoff, IEEE J. Quantum Electron., QE-8,(1972). [2]C. S. Winter, C. A. S. Hill, and A. E. Underhill, Appl. Phys. Lett. 58, 107 (1991). [3]T. H. Wei, D. J. Hagan, M. J. Sence, E. W. Van Stryland, J. W. Perry, and D. R. Coulter, Appl. Phys. B54, 46 (1992)

4:15 PM **PP1.7**

EFFECTS OF PURIFICATION AND ADDITION OF ELECTRON ACCEPTOR DYES TO SOLUTIONS OF MACROCYCLIC DYES. Warrick Allen, Gurmit Bahra, William Healy, DERA, UNITED KINGDOM.

This paper will deal with the electronic and physical effects of purification on the optical limiting performance of the macrocyclic dye SiNC (silicon 2,3-naphthalocyanine bis(trihexylsilyloxy)). The cause of the differences in performance between the pure and impure dye solutions are also discussed. The changes in optical limiting performance of SiNC and several porphyrin solutions produced by the addition of an electron acceptor material, methyl viologen dichloride hydrate, will also be shown and the results discussed.

4:30 PM ***PP1.8**

PORPHYRIN DYE MEDIA FOR OPTICAL LIMITING. Kenneth J. McEwan and John M. Robertson, Defence and Evaluation Research Agency, Great Malvern, UNITED KINGDOM; Harry L Anderson, The Dyson Perrins Laboratory, Oxford, UNITED KINGDOM.

Porphyrin dyes are strong candidates for optical limiting applications in the visible waveband by virtue of their large excited state absorption properties. In this paper recent progress on the synthesis and characterisation of porphyrin dye media will be reviewed. The characteristic linear and nonlinear absorption properties will be summarised and the optical limiting performance will be compared with that of other macrocyclics such as phthalocyanines and naphthalocyanines. A range of standard and novel porphyrin media will be introduced and broadband measurements of their excited state absorption properties will be described. Finally, experimental results on a new class of porphyrins designed to exploit energy transfer to other macrocyclics will be discussed.

SESSION PP2: POSTER SESSION:
MATERIALS FOR OPTICAL LIMITING
Tuesday Evening, November 30, 1999
8:00 P.M.
Exhibition Hall D (H)

PP2.1

OPTICAL LIMITING PROPERTIES OF DENDRONS AND DENDRIMERS INCORPORATING DITHIENYLPOLYENE MOIETIES. Berrak Ozer, Bong-Soo Kang, Charles Spangler, Montana State University, Dept of Chemistry and Biochemistry, Optical Technology Center, Bozeman, MT.

Dithienylpolyenes have been shown to form exceptionally stable and highly absorbing polaronic radical-cations and bipolaronic dicationic upon chemical oxidation. These charge states also are among the most nonlinear of small organic molecules, exhibiting dramatic red-shifts in oscillator strength in going from the neutral to polaron or bipolaron states. Recent studies have also shown that optical pumping of similar donor molecules in the presence of strong acceptors such as C60 result in photogenerated charge states capable of optical power limiting (OPL) via reverse saturable absorption (RSA). These chromophores are also good two-photon absorbers on the ps and ns time scales, and thus may be considered as potential bimechanistic OPLs. We will focus on the incorporation of these chromophores into dendrons, followed by dendrimer formation to yield processible monodisperse macromolecules for potential device fabrication.

PP2.2

Abstract Withdrawn.

PP2.3

PHOSPHORESCENCE STUDIES OF REVERSE SATURABLE ABSORPTION MATERIALS FOR OPTICAL LIMITING APPLICATIONS. Eric Pooler, Southwestern Ohio Council for Higher Education, Dayton, OH; Sean M. Kirkpatrick, Science Applications International Corporation, Dayton, OH; Casey Clark, University of Dayton, Dayton, OH.

Time resolved phosphorescence experiments are used to determine the relative energy and radiative lifetime of the first triplet state of reverse saturable absorption materials (RSA). Halogenated free-base and zinc porphyrins are investigated. Spectra are collected from 700 nm to 5 μ m. Results are compared to calculations performed by Nguyen *et. al.* and experiments performed by Bhyrappa *et. al.*

PP2.4

LIQUID VERSUS SOLID HOST EFFECTS ON EXCITED STATES OF SOME OPTICAL LIMITER MATERIALS. S. Chandra¹, D.G. McLean¹, P.A. Fleitz, W. Su², H. Jiang³, AFRL/MLPJ, Wright-Patterson AFB, OH; R.V. Goedert, TARDEC, Warren, MI; ¹SAIC, Beaver Creek, OH, ²TMC, Beaver Creek, OH, ³Anteon Corp., Dayton, OH.

A study is made to compare liquid host vs. solid state host effects on the excited state properties of silicon naphthalocyanine (SiNc), fullerene (C60) and zinc octobromoporphyrin (ZnOBP) using laser flash photolysis. Polymer hosts included epoxy, PMMA and others. Samples were excited at 355 nm and 532 nm wavelengths and the excited state characteristics such as the lifetime and differential excited state absorbance spectra were measured. Observed spectral shifts and dramatic changes in lifetimes between the hosts will be discussed.

SESSION PP3/BB7: JOINT SESSION:
TWO-PHOTON ABSORPTION AND
APPLICATIONS

Chair: Joseph W. Perry
Wednesday Morning, December 1, 1999
Salon G (M)

8:30 AM ***PP3.1/BB7.1**

MULTIPHOTON EXCITATION (MPE) OF ORGANIC MOLECULES IN BIOLOGICAL MATERIALS. Watt W. Webb, Applied and Engineering Physics, Cornell University, Ithaca, NY.

Molecular excitation by simultaneous absorption of two or more infrared (low energy) photons by an individual molecule provides a powerful tool for excitation of visible or ultraviolet fluorescence for biological and photophysical research at molecular and microscopic scales. Simultaneous at a Heisenberg uncertainty time of $\sim 10^{-16}$ s in a typical molecular cross section of 10^{-16} cm² requires very bright illumination by femtosecond pulses from a mode locked laser. The quantum photophysics of multiphoton excitation and the features that enable convenient application in biological and organic materials will be introduced. Excitation by a strongly focused pulse train provides laser intensity enhancement by $\sim 10^{14}$ in a submicron focal point which can be scanned in a video roster for 3-dimensionally resolved multiphoton fluorescence microscopy (MPM). Images in living cells and tissues of the autofluorescence of intrinsic biomolecules such as adenine dinucleotide (NADH), elastin, collagens, serotonin, melatonin and indolamine oxidation products, chitin, and numerous still unknown structures characterize biological structures and processes and provide means for diagnosing disease states. Many common drugs and pathologists stains are conveniently two photon excited in living tissues, providing a convenient means of imaging functional responses. The most important advance of recent years in technology for study of dynamics of molecular process in living animals and tissues is Green Fluorescent Protein (GFP) gene constructs, which can be inserted in the genome of living organisms to label particular proteins and to provide an intrinsic pH indicator. GFP in living materials is best imaged with MPM.

In materials applications of MPM and sometimes in biological preparations extrinsic organic fluorescent marker molecules are needed. Organic fluorophores are notoriously photolabile and of course never bright enough. Unfortunately, the non-organic nanoparticle substitutes have been found to be just as pathological. Nevertheless, the complexity of the photophysics of multiphoton excitation offers new opportunities. The spectra for two photon excitation tend to be blue shifted and broadened relative to twice the one photon excitation wavelengths because the dipole excitation quantum parity is even instead of odd. Progress in design of fluorescent molecules specifically for two photon excitation has only recent begun and progress will be reported in the following lectures. Our data showing the success of early progress in creating fluorophores of large two photon cross sections by electric quadrupole moment enhancement will be illustrated.

9:00 AM ***PP3.2/BB7.2**

APPLICATIONS OF MOLECULES WITH LARGE TWO-PHOTON ABSORPTION CROSS SECTIONS. K. Cammack, S. Kuebler, S. Marder, J. Perry, University of Arizona, Dept. of Chemistry, Tucson, AZ; B. Cumpston, D. Dyer, California Institute of Technology, Beckman Institute, Pasadena, CA; E. Hendrickx, B. Kippelen, M. Lipson, N. Peyghambarian, University of Arizona, Dept. of Optical Science, Tucson, AZ.

Molecules with large two photon cross sections have been recently reported. It has been shown that such molecules can be used to initiate the polymerization of acrylate monomers. In this presentation

the applications of these highly sensitive two-photon absorbing molecules to excited state charge transfer mediated processes will be discussed.

9:30 AM *PP3.3/BB7.3

THEORETICAL DESIGN OF ORGANIC MOLECULES WITH LARGE TWO-PHOTON ABSORPTION CROSS SECTIONS.

J.L. Bredas, Department of Chemistry, University of Arizona, Tucson, AZ and Center for Research in Molecular Electronics and Photonics, University of Mons-Hainaut, Mons, BELGIUM.

Previous theoretical work on the design of novel compounds with large two-photon absorption cross-sections, δ , focused on quasi-one-dimensional molecules [1-2] such as oligophenylene vinylenes or diphenylpolyenes. Such compounds can act as efficient optical limiters. Substitutions that promote charge transfer between the ends and the central part of the molecules were found to be very effective in boosting the δ value. This is done e.g. via substitution with amino donor groups at the ends and cyano acceptor groups in the middle of the oligomer. Such substitutions, by inducing a quadrupolar-type charge transfer in the relevant excited states, result in an increase by over a factor of 3 in the transition dipole moment, M12, between the lowest one-photon excited state (S1) and the lowest two-photon excited state (S2); for instance, M12 is on the order of 3.1 D in unsubstituted stilbene and reaches nearly 10 D upon donor/acceptor/donor substitution [1]. Since δ depends on M12 squared, this factor alone enhances the two-photon absorptivity by over one order of magnitude[1].

In this contribution, we discuss other types of compounds, that also provide for major charge transfer between the ends or periphery of the molecule and the center upon excitation, thus potentially opening similar in-out polarization mechanisms for high two-photon absorption response. We focus namely on macrocyclic compounds (phthalocyanines, porphyrins) substituted by a metal in their center.

[1] M. Albota et al. Science, 281, 1653-1656 (1998).

[2] T. Kogej et al. Chem. Phys. Lett., 298, 1-6 (1998).

10:30 AM *PP3.4/BB7.4

TWO PHOTON PROCESSES FOR OPTICAL LIMITING AND 3D MICROFABRICATION. P.N. Prasad, G.S. He, J. Swiatkiewicz, H. Pudavar, Y.H. Min, S.J. Chung, K.S. Kim and T.Z. Lin.

Recent development has produced novel materials with significantly enhanced two-photon absorption cross-sections and highly efficient up-converted emission. This achievement has opened up doors for many new technological applications. This talk will present our rational approach to design molecules and bulk forms with enhanced two-photon properties. Then the various techniques including ultrashort laser pulses being utilized in our laboratory to study the dynamics of two-photon process will be discussed. Although many applications of the photon technology are being pursued in our laboratory, this talk will focus only on two. Optical limiting and 3D microfabrication. A useful approach for optical limit is to use cooperative manifestations of two effects to broaden the coverage against laser sources of varying spectral and temporal conditions. Examples of 3-D microfabrications will involve 3-D complex optical circuitry in a preformed plastic block and 3-D MEMS type structures.

11:00 AM *PP3.5/BB7.5

DESIGN, SYNTHESIS AND CHARACTERIZATION OF NEW BI-MECHANISTIC OPTICAL POWER LIMITERS BASED ON REVERSE SATURABLE AND TWO-PHOTON ABSORPTION.

Charles Spangler, El Hadj Elandaloussi, Berrak Ozer, Kimba Ashworth, Luis Madrigal, Benjamin Reeves, Montana State Univ, Dept of Chemistry and Biochemistry, Optical Technology Center, Bozeman, MT.

During the past few years there has been considerable progress in the design, synthesis and characterization of new organic optical power limiting (OPL) materials. The common dominating mechanisms in organic chromophores are reverse saturable absorption (RSA) and more recently, two-photon absorption (TPA). There have been a number of recent reviews of the structure-property relationships inherent in the design of new materials for either RSA and TPA, but it has only been most recently that our group has proposed that careful design of the chromophore will allow both mechanisms to operate efficiently, albeit at different irradiation frequencies. In this presentation we will review the design and synthesis criteria for new bi-mechanistic chromophores, such as the bis-(diphenylamino)diphenylpolyene series, and illustrate how these new materials can be used as effective optical power limiters. We will particularly focus on the incorporation of these photonic-active moieties into dendrimer structures, and explore the advantages of dendritic architecture in optical power limiting and other nonlinear absorption processes.

11:30 AM *PP3.6/BB7.6

DIRECT FABRICATION OF THREE-DIMENSIONAL STRUCTURES BY TWO-PHOTON LITHOGRAPHY.

Benjamin J. Schwartz, Vinh Doan, UCLA, Dept of Chemistry and Biochemistry, Los Angeles, CA; Bruce Dunn, Pu-Wei Wu, UCLA, Dept of Materials Science and Engineering, Los Angeles, CA; Eli Yablonovitch, George Witzgall, Rutger Vrijen, UCLA, Dept of Electrical Engineering, Los Angeles, CA.

Photolithography is a well-known technique for converting patterns of light into physical structures. Absorption of light initiates a photochemical reaction which changes the solubility of the photoresist, allowing selective etching of the exposed material. Because the absorption of light proceeds from the surface down to the substrate, photolithographic techniques are inherently limited to the production of 2-D structures: etching of the resist must be uniform in the direction normal to the substrate. Modern applications, however, require the ability to produce fully 3-D structures. Multilayer techniques can produce limited 3-D structures by stacking of a few conventional 2-D layers, but at the expense of difficult layer-to-layer alignment. This talk describes a new photolithographic technique which is inherently capable of fabricating 3-D structures: photolithography by two-photon absorption (2PA). The method uses ultrashort light pulses with high peak-powers whose wavelength is too red to expose the resist by conventional one-photon absorption. When focused with a high numerical aperture objective, however, the peak intensity in a small volume near the focal region is sufficient to expose the resist via 2PA, even though the intensity is insufficient to expose the resist at its surface. By scanning the focal volume in all three dimensions, truly 3-D structures can be fabricated in a single step. We can use this technique to produce 3-D structures in commercial photoresists, including a lincoln log lattice where one layer consists of 2 micron thick logs laid horizontally, while in the next layer the logs are laid vertically. We are also working to use 2PA to write 3-D images in silver-doped sol-gel glasses. The hope is that this form of 3-D photography will allow the direct fabrication of 3-D metal wire networks.

SESSION PP4: TWO-PHOTON ABSORBERS AND SPECTROSCOPY OF OPTICAL LIMITING

Chair: Richard L. Sutherland

Wednesday Afternoon, December 1, 1999

Room 205 (H)

1:30 PM PP4.1

TWO-PHOTON ABSORBING HETEROCYCLIC AROMATIC DYES: STRUCTURE-PROPERTY RELATIONSHIPS. Jeffery W. Baur, Max D. Alexander Jr. and Lisa R. Denny, Air Force Research Laboratory, Wright-Patterson AFB, OH; Ramamurthi Kannan, Sysran Corporation, Dayton, OH; Sean M. Kirkpatrick, SAIC, Dayton, OH.

Due to the recent development of organic chromophores with large two-photon cross-section values, there has been intense interest in optimizing the nonlinear absorption response for a variety of applications including optical limiters, nondestructive inspection of coatings, 3D microfabrication, and photocuring of thick laminates. Asymmetric chromophores consisting of pi-electron donating and pi-electron accepting heterocyclic moieties separated by aromatic core(s) have been shown to give large nonlinear absorptions. However, the effective two-photon cross-section is observed to vary with incident pulse duration by several orders of magnitude. This sensitivity must be considered in the establishment of structure-property relationships. We will discuss the origins of this sensitivity to the effective two-photon cross-section and variations of the effect with chemical structure.

1:45 PM PP4.2

EXCITED STATE ABSORPTION IN DENDRIMER MODELS INCORPORATING DIPHENYLAMINODIPHENYLPOLYENE MOIETIES VIA PHOTO-INDUCED ELECTRON TRANSFER.

Wendi Sonnenberg, Amy Hyfield, Kurt Short, Lee Spangler, Charles Spangler, Montana State Univ, Dept of Chemistry and Biochemistry, Optical Technology Center, Bozeman, MT.

During the past few years there has been a resurgence of not only efforts to design new organic chromophores, but also to explore the detailed mechanisms involved in reverse saturable absorption (RSA), and two-photon absorption (TPA) optical power limiting (OPL). There has been recognition that OPL design must take into account time domains spanning many orders of magnitude, and that one may need more than one simple component in the device, and perhaps more than one operative mechanism in the chromophore. In this presentation we will examine dendrimers based on bis-(diphenylamino)stilbene repeat units and capable of both RSA and TPA

optical limiting. We will also describe a new spectroscopic technique for characterizing OPL materials with full time and frequency resolution capable of tracking the both the formation and decay of the transient species.

2:00 PM **PP4.3**

WAVELENGTH DISPERSION OF OPTICAL POWER LIMITING IN TPA AND RSA ORGANIC MOLECULES. Pierre-Alain Chollet, Vianney Hully, Aurelie Sornin, Francois Kajzar, Jean-Michel Nunzi, CEA-LETI, Saclay, FRANCE; Patrice Baldeck, Dept of Spectrometry, CNRS St Martin d'Herès, FRANCE; Michele Maggini, Gianfranco Scorrano, Alberto Bianco, Dipartimento di Chimica Organica, Università di Padova, ITALY; Maurizio Prato, Tatiana Da Ros, Università di Trieste, ITALY.

Optical limiting has been measured in the visible range (450-700 nm) in solutions of a laser dye (stilbene3, 200 g/L) and a functionalized fullerene (20 g/L). The former is transparent over the whole range, while the latter has an absorption which increases with decreasing wavelength. Optical limiting was observed in the whole range for the dye, but only in the absorption range for the fullerene which suggests that it originates from two photon absorption (TPA) and reverse saturable absorption (RSA) respectively. The laser pulses delivered by an OPO had a 2.6 ns FWHM duration and the beam was collimated inside the samples, whose thickness was 1 or 2 mm. The time dependence and spatial shape of the pulses were carefully measured and had both a gaussian shape (the waist was close to 200 micrometers). In the experiments, the transmitted energy was measured versus incident energy (0-3 mJ). The transmission dependence was fitted using a five level model for the fullerene (two excited singlets and two excited triplets) and a three level model (two excited singlets) for the dye. This model has enabled the determination of the wavelength dependence of the cross sections of the various transitions. In the fullerene, the optical limiting chromatic dispersion is mainly governed by the linear absorption of the ground state and the cross sections between the excited singlets and between triplets ($\sim 20 \cdot 10^{-18} \text{cm}^2$) remain rather constant. On the other hand, a resonance of optical limiting was observed in stilbene3, which is connected with a resonance of the one-photon absorption cross section between the first and second excited singlet state ($\sigma_{max} \sim 30 \cdot 10^{-18} \text{cm}^2$), while the two-photon cross section between the ground and first excited state is rather constant ($\sim 3 \cdot 10^{-19} \text{cm}^4/\text{GW}$). This work was partially supported by the French Defense DGA (contract number 98 364) and the Brite Euram program (Project BE-4408).

2:15 PM **PP4.4**

SPECTROSCOPIC INVESTIGATIONS OF DITHIENYL POLYENES. Thomas M. Cooper, Laura Sowards, Materials And Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH; Lalgudi V. Natarajan, Suresh Chandra, Sean Kirkpatrick, Daniel McLean, Science Applications International Corporation, Dayton, OH; Charles W. Spangler, Dept. of Chemistry, Montana State University, Bozeman, MT.

In order to design efficient nonlinear absorbers, we are investigating the structure-optical property relationships of dithienyl polyenes. Dithienyl polyenes are potential two photon absorbers and charge transfer donors. We will present photophysical data, including fluorescence, solvatochromism, flash photolysis and two photon absorption coefficient measurements on these compounds. Based on these results, the feasibility of using these dyes as optical limiters will be discussed.

3:00 PM ***PP4.5**

MEASUREMENT OF GROUND AND EXCITED PROPERTIES OF SUBSTITUTED PORPHYRIN MATERIALS. P.A. Fleitz, W. Su¹, K.T. Nguyen¹, T.J. Marrinan², S. Chandra³, and D.G. McLean³, Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH. ¹Technical Management Concepts, Inc., Beaver Creek, OH, ²Carroll High School, Dayton, OH, ³Science Applications International Corporation, Dayton, OH.

The ground and excited state properties of a variety of porphyrin materials have been characterized in an attempt to establish structure-property relationships. Measurements of the ground state include absorption and fluorescence spectra. Excited state measurements include absorption spectra, cross-sections and lifetimes. Through our previous investigations, we have shown that Zinc Octabromotetraphenylporphyrin (ZnOBP) exhibits strong nonlinear absorption at 532nm. Using the laser flash photolysis experiment, we have studied the influence of bromine substitution on the excited state absorption spectra and lifetimes of this material. In this paper we present the results of these investigations.

3:30 PM **PP4.6**

FOURIER TRANSFORM TECHNIQUES FOR MEASURING ABSORPTION OF TRANSIENT SPECIES IN OPTICAL LIMITING

MATERIALS. Yanong Han, Wendi Sonnenberg, Kurt W. Short, Amy Hyfield and Lee H. Spangler, The Optical Technology Center (OpTeC) and The Department of Chemistry, Montana State University, Bozeman, MT.

We have developed methods of measuring absorption of transient species utilizing both rapid scan and stepped-scan Fourier transform interferometry that allows a combination of broad spectral coverage (10,000 - 15,000 cm^{-1} per spectrum), good spectral resolution, and the ability to cover temporal ranges from minutes to nanoseconds. A wide range of pump sources are used including continuous, modulated, ns pulsed, and ultrafast lasers. The probe is provided by a broadband, incoherent source providing large spectral information in each experiment. This capability enables investigation of phenomena such as excited state absorption, charge transfer, formation of metastable species, and others. Extension of the technique to the ps realm is underway and will be discussed.

3:45 PM **PP4.7**

OPTICAL POWER LIMITERS FOR NANOSECOND PULSES: NEW DENDRITIC CHROMOPHORES WITH EXCEPTIONALLY LARGE TWO-PHOTON ABSORPTION CROSS-SECTIONS. E.H. Elandaloussi, C. Spangler, Montana State Univ, Dept of Chemistry and Biochemistry, Optical Technology Center, Bozeman, MT; M. Casstevens, D. Kumar, J. Weibel, R. Burzynski, Laser Photonics Technology, Amherst, NY; G.-S. He and P. Prasad, Dept of Chemistry, SUNY-Buffalo, Buffalo, NY.

Organic chromophores with extended conjugation have been of interest as two-photon absorbers (TPA) for a number of years, but practical applications were minimal due to the relatively small cross-sections. Recently, interest has been rekindled in their design due to structure-property studies that have resulted in TPA design paradigms. Large two-photon cross-sections have been observed for bis-(diphenylamino) substituted polyenes, PPV oligomers, and most recently, dendrimers based on bis-(diphenylamino)stilbene repeat units. In this presentation we will present evidence to explain why these chromophores have extremely large effective two-photon cross-sections, and how they may be designed to solve optical power limiting problems for specific laser frequencies in the nanosecond time domain.

4:00 PM **PP4.8**

SINGLET STATE ABSORPTION SPECTRA OF NOVEL MATERIALS FOR OPTICAL LIMITING. Sean M. Kirkpatrick, Science Applications International Corporation, Dayton, OH; Paul A. Fleitz, Air Force Research Laboratory, Wright Patterson Air Force Base, OH; Richard L. Sutherland, Science Applications International Corporation, Dayton, OH.

During the absorption of a laser pulse of moderate length, the leading edge can experience excited state absorption out of the first singlet state. These excited state absorption spectra can only be accurately probed using short pulse pump-probe techniques. Specifically, we examine several excited state spectra of ZnOBP in several hosts using ultrafast transient white light absorption spectroscopy. By exciting these materials with a femtosecond laser, the absorption spectra can be probed transiently using a supercontinuum pulse. The resulting excited states can exhibit coherence for time scales that can affect further singlet state absorption. We examine these polarization and dephasing effects and discuss the possible implications with regards to optical limiting.

4:15 PM **PP4.9**

LASER FLASH PHOTOLYSIS CHARACTERIZATION OF REVERSE SATURABLE ABSORBER MATERIALS. Daniel G. McLean¹, Suresh Chandra¹, Weijie Su² and Paul A. Fleitz, Air Force Research Laboratory, MLPJ, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH; ¹Science Applications International Corporation, Beaver Creek, OH, ²Technical Management Concepts Incorporated, Beaver Creek, OH.

The Laser Flash Photolysis experiment and its use in characterizing Reverse Saturable Absorber (RSA) materials are described. The experiment is described and specifics of data acquisition, data analysis, and calibration of the experiment are given. The experiment can measure triplet state effects such as the triplet-triplet absorption cross section spectra, lifetimes, formation quantum efficiency. This is illustrated in several important RSA dyes, such as zinc octobromoporphyrin (ZnOBP) and silicon-naphthalocyanine (SiNc), and other tetrapyrroles. The chemical photodegradation of ZnOBP in dichloromethane is shown and the spectra of the intermediate species. The ability of the experiment to investigate energy transfer between species and identify the species is illustrated by an investigation of ZnOBP in several polysiloxanes. Hot electron effects are observed in several materials and reported for platinum-poly-yne. The multiplicity of bromine substitution in zinc-tetraphenylporphyrin is varied. It is

found that for substitution of zero to four bromines only a long triplet decay time, $\sim 10 \mu\text{s}$, is observed, but that as an increasing number of bromines is added a secondary process with a short decay time, ~ 200 nanoseconds, appears and completely dominates for seven or more bromines. All of these results illustrate the power of this experimental method to clarify the photophysical and photochemical processes critical to the development of new RSA materials.

SESSION PP5: THEORY AND MODELING

Chair: Ruth Pachter

Thursday Morning, December 2, 1999

Room 205 (H)

8:30 AM *PP5.1

OPTICAL LIMITER DESIGN, TESTING AND MODELING.

D. Hagan, S.S. Yang, D. Kovsh and E.W. Van Stryland, School of Optics/CREOL, University of Central Florida, Orlando, FL.

Ongoing efforts in designing, building, testing and modeling optical limiting devices will be discussed including tandem optical limiters using reverse saturable absorbing materials, e.g. phthalocyanine dyes in solid hosts and in liquid solvents. In liquids, both linear and nonlinear absorption generate significant acoustic waves that eventually lead to strong thermal refraction. On a nanosecond time scale, the refraction is in the transient regime, and modeling becomes difficult, since solutions to both the electromagnetic and acoustic wave equations are needed. We will report on numerical methods for solving this problem and when certain approximations that are often invoked are valid. Comparison with experiments will also be presented. These comparisons depend heavily on the many material parameters used as inputs to the numerical codes; therefore, careful characterization of the materials is required. Several methods for this characterization will also be discussed.

9:00 AM PP5.2

TOWARD FIRST PRINCIPLE DESIGNS OF MATERIALS FOR OPTICAL LIMITING APPLICATIONS.

Kiet A. Nguyen, Paul N. Day and Ruth Pachter, Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson Air Force Base, OH.

First principle electronic structure calculations are carried out to predict properties of reverse saturable absorption (RSA) materials that are important in optical limiting applications. The RSA dyes under investigation are free-base and zinc porphyrins with a combination of halogen and phenyl substituents. The computed data include structures and electronic spectra for the ground and triplet excited states as well as ionization potentials and binding energies. These properties are important in predicting the performance of optical limiting materials. Since comprehensive data are not available, we begin with the basic porphyrin unit, then systematically replace the peripheral hydrogens of porphyrin with halogen and phenyl groups to study the substituent effects. The results of halogenated porphyrins and halogenated tetraphenylporphyrins provide insightful accounts of effects of phenyl, fluoro, chloro, and bromo substituents on the spectra of these systems. The computed spectra are in excellent agreement with available experimental data.

9:15 AM PP5.3

POLARONIC AND BIPOLARONIC ENHANCEMENT OF HYPERPOLARIZABILITIES IN DITHIENYL POLYENES FROM AB INITIO QUANTUM METHODS.

Steven Trohalaki, Robert J. Zellmer, Ruth Pachter, Materials & Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH.

Spangler and He (*MRS Symp Proc.*, **479**, 59, 1997) have shown that dithienyl polyenes form extremely stable bipolaron-like cations when oxidatively doped in solution. Previous theoretical studies of polaronic and bipolaronic enhancement employed semi-empirical molecular orbital theory and predicted different power-law dependencies, albeit for different molecular systems. We employ density functional theory to optimize the molecular conformations of neutral, cationic, and dicationic forms of a series of dithienyl polyenes and subsequently calculate second hyperpolarizabilities, γ , using ab initio molecular orbital theory. Previously, we showed that the cations display an increase in γ but that the dications treated as closed shells do not. As expected, γ increases with the number of ethene repeat units for a given charge. We report γ values for dications calculated using open shells as well as results for larger polyenes.

9:30 AM PP5.4

AB INITIO DESIGN OF TWO-PHOTON ABSORBING MATERIALS. Paul N. Day, Kiet A. Nguyen, Ruth Pachter, Air Force Research Lab, Wright-Patterson AFB, OH.

Two-photon absorbing materials such as conjugated polyenes show

promise as optical limiting materials. Prediction of two-photon absorption frequencies and cross-sections has been limited by the high level of ab initio calculations that must be carried out in order to accurately calculate excited state energies and transition dipole moments, by the size of many of the compounds of interest, and by the difficulty of handling condensed phase effects in the calculations. We have carried out geometry optimizations at the multi-configurational self-consistent field (MCSCF) level of hexatriene, octatetraene, and several substituted analogs of these compounds both in the gas-phase and in solution, with the solvent effects being modeled by the effective fragment potential (EFP). The excited-state energies have been calculated by the multiconfiguration quasidegenerate perturbation theory (MCQDPT2). Transition dipole moment calculations have also been carried out, from which the two-photon absorption cross-section can be estimated. The calculated frequencies and cross-sections are compared to experimental results, when available. The results are applied to the design of new two-photon absorbing materials.

10:15 AM *PP5.5

NONLINEAR OPTICAL LASER BEAM PROPAGATION

THROUGH SEMICONDUCTOR MATERIALS.

Shekhar Guha, Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright Patterson Air Force Base, OH; Chris Reyerson, Anteon Corporation, Dayton, OH; David J. Hagan, Vladislav Dubikovskiy, Eric W. Van Stryland, CREOL, University of Central Florida, Orlando, FL; Srinivasan Krishnamurthy, SRI International, Menlo Park, CA.

Study of the interaction of high intensity pulsed or continuous wave (cw) laser beams with semiconductor materials provides detailed information about nonlinear charge carrier dynamics in the materials as well as knowledge of two-photon and free-carrier absorption coefficients. An experimental study of the interaction of short pulse and long pulse infrared laser beams at different wavelengths in the mid-wave and the long-wave infrared spectra through a variety of semiconductor materials was undertaken. The spatial and temporal shapes of the laser beam transmitted through the materials contained interesting features such as multiple peak at high laser intensities. Modeling of nonlinear optical laser beam propagation through the media and a theoretical study of the charge carrier dynamics in narrow band gap semiconductors are being conducted to explain the observed features and to extract accurate values of materials parameters. The results of the experimental and theoretical work will be presented.

10:45 AM PP5.6

CALCULATIONS OF THE MACROSCOPIC LINEAR AND NONLINEAR OPTICAL PROPERTIES OF NEMATIC LIQUID CRYSTALS.

Steven M. Risser, Battelle Memorial Institute, Columbus, OH; Kim F. Ferris and Gregory J. Exarhos, Pacific Northwest National Laboratories, Richland, WA.

There have been many studies that have focused on the computation of the structural and electronic properties of liquid crystal molecules in a single static conformation. However, description of the evolution of NLO properties from the molecular level to the macroscopic level (as is measured experimentally) in liquid crystals is hindered by the anisotropy of the molecules, their partial ordering, and the dynamical fluctuations of the molecules. In this paper, we will examine the transition from molecular to bulk properties for the nematogen 5-alkyl-cyanobiphenyl (5CB), using both molecular dynamics and quantum mechanical calculations. We perform molecular dynamics simulations using periodic boundary conditions and a reparameterized version of the MM3 force field. We then sample the trajectory to create a representative collection of structures of individual molecules. Electronic structure calculations are performed on the structures sampled from the trajectory. Subsequently, we calculate the NLO properties of individual molecules from the trajectory. The local environment is included in the NLO calculations by introducing an anisotropic electric potential at each atom, determined from a point-charge representations of adjacent molecules. Comparisons will also be made to calculations on 5CB clusters, which include other neighbor-neighbor interactions not included in the point charge representation.

11:00 AM *PP5.7

MAXIMUM CROSS SECTIONS FOR EXCITED-STATE AND

TWO-PHOTON ABSORPTION. Roger Becker, Air Force Research Laboratory, Materials and Manufacturing Directorate, WPAFB, OH.

Maximum performance limits are presented for nonlinear absorption processes, with an emphasis on Reverse Saturable Absorber (RSA) and two-photon absorption (2PA) limiters. The expressions are based on a maximum polarizability associated with a single electron transition, which is 18 cubic angstroms at 500 nm. The limits can be derived in various ways from differing fundamental physical precepts. In the limit of strong absorption the induced nonlinear polarizability

can be expressed in term of the linear polarizability. Typically the matrix elements are dominated by a single transition. In all cases the peak absorption is an inverse function of the width of the absorption resonance, so that the only meaningful measure of the strength of a transition is the integrated line strength. Comparisons are made with experiment. It appears that the better materials studied to date operate near the theoretical performance limit. The consequences of the maximum values for the absorption response of a material are considered. It is fortunate that the absorption cross section cannot be increased beyond the maximum limit. Otherwise, several calamities would occur.

11:30 AM PP5.8

Abstract Withdrawn.

**SESSION PP6: LIQUID CRYSTALS, NANOTUBES
AND PHOTOREFRACTIVES**

Chair: Keith L. Lewis

Thursday Afternoon, December 2, 1999

Room 205 (H)

1:30 PM *PP6.1

SUPRA-NONLINEAR LIQUID AND LIQUID CRYSTALS FOR EXTREMELY LARGE DYNAMIC RANGE OPTICAL LIMITING APPLICATION. I.C. Khoo, Department of Electrical Engineering, Pennsylvania State University, University Park, PA.

We have discovered [1] an unusually nonlinear organic liquid suitable for fabricating nonlinear fiber array for optical limiting application against ps-ns laser pulses. Experimentally obtained results show that the effective nonlinear absorption coefficient in this liquid is on the order of 5 cm/GW in the ps regime, and can be as large as 300 cm/GW in the nanosecond regime. As a result, optical limiting with clamped transmission < 1 microJoule with ps-ns laser pulses have been observed. For microsecond and longer time scale, we have discovered an extremely nonlinear liquid crystalline material [2] that possesses an effective third order nonlinear susceptibility on the order of 600 esu, or equivalently a refractive index change coefficient of >20 cm²/Watt. The underlying mechanism is optically induced director axis reorientation.[3] Such nonlinearities enable the observation of nonlinear optical processes with laser power in the nanoWatt-microWatt range. We discuss the origins of these nonlinearities, and present the results of recent experimental studies of image conversion and optical limiting using these films in all-optical configurations. These processes are characterized by unprecedented low threshold laser power/intensity, and large dynamic range. Excellent performance against laser jamming with long-pulse or cw lasers are demonstrated. Such nematic liquid crystals thus present themselves as promising next generation image processing and optical switching/limiting material. References 1. I. C. Khoo et al, J. Chem Physics [In Press, 1999]; see also I. C. Khoo et al, J. Opt. Soc. B15, pp 1533-1540 (1998). 2. I. C. Khoo, S. Slussarenko, B. D. Guenther, Min-Yi Shih, P. H. Chen and M. V. Wood. Optics Letts. vol. 23 p. 253-255 (1998); I. C. Khoo, M. V. Wood, M. Y. Shih and P. H. Chen, Optics Express vol. 4, no. 11, pp 431-442 (1999). 3. I. C. Khoo [Liquid Crystals: Physical Properties and Nonlinear Optical Phenomena(Wiley Interscience, NY, 1994)].

2:00 PM PP6.2

MODELISATION AND EXPERIMENTAL STUDY OF NON LINEAR SCATTERING IN POLYMER DISPERSED LIQUID CRYSTAL. Michel Pacilli, Patrick Sebbah, Pierre Sixou, Christian Vanneste Laboratoire de Physique de la Matière Condensée, CNRS UMR 6622, Université de Nice-Sophia Antipolis, Nice, FRANCE.

We investigate the optical limiting capabilities of composite materials consisting of nematic liquid crystal inclusions contained in a polymer matrix in the millisecond and CW regime. By matching the polymer refractive index to the ordinary refractive index of the nematic, good optical transparency is achieved when for example an electric field is used to align the anisotropic molecules of the liquid crystal. Alternatively, a good choice of the crystal liquid and a careful chemical process allows us to make films which are transparent without electric field. At high optical power, optical reorientation of the nematic molecules modify the refractive index of the crystal liquid inclusions: the medium becomes opaque. Multiple scattering contributes itself to spread energy in the medium which is favorable to increase the non linear process. We present an experimental study of non-linear diffusion in polymer dispersed liquid crystal. Discrimination between optical reorientation effect and thermal effect is obtained from time response measurements. CW optical power limiting study of these films demonstrates promising limiting characteristics of such materials. Here, the role of numerical modelisation is essential to understand the linear and non-linear physical processes involved in these experiments. We present a numerical study of light propagating in (a) 2D heterogeneous isotropic

linear media, (b) 2D heterogeneous optically anisotropic linear media and (c) 2D heterogeneous non linear Kerr media. This study uses the wave automaton, a numerical model developed in our group, based on elementary rules of propagation and scattering on a network, which reproduces wave propagation in complex media. This work is currently supported by DGA contract 97-406, by CNRS and the GdR PRIMA.

2:15 PM *PP6.3

OPTICAL LIMITING WITH LITHIUM NIOBATE. Gary Cook, David. C. Jones, Lesley L. Taylor, Tony W. Vere, Defence Evaluation and Research Agency, Malvern, Worcs., ENGLAND; Craig J. Finnan, Optical Materials Research Centre, Strathclyde University, Glasgow, SCOTLAND.

Photorefractives are attractive materials for optical limiting, and they can be used in a range of optical configurations for this application, although most are based on two-beam coupling. Unfortunately, the widespread use of photorefractives for optical limiting has been restricted by factors such as the complexity and bulk of the optical arrangements, sensitivity to ambient vibration and noise, slow response times, insufficient change in optical density and restricted operating temperature ranges. However, Fe:LiNbO₃ in a simple focal plane geometry has overcome many of these problems, demonstrating a change in optical density (ΔOD) of more than 3 with a 1/e switching speed of less than 2msec. The performance is largely independent of the total Fe concentration and the oxidation state of the Fe ions, providing the linear optical transmission of uncoated crystals is between 30% and 60%. Both the maximum ΔOD and the speed improve with increasing pumping intensity, and neither the ΔOD or the speed have shown any signs of saturation for local cw pumping intensities up to 10kW/cm². Optical limiting in Fe:LiNbO₃ has been shown to be very much greater than predicted by simple diffusion theory. The reason for this is a higher optical gain than expected. It is suggested that this may be due to an enhancement of the space-charge field from a combination of hot diffusion with the photovoltaic effect. The standard two-beam coupling equations have been modified to include the effects of the dark conductivity. This has produced a theoretical intensity dependence on the ΔOD which follows the general behaviour observed in the laboratory. A further modification to the theory has shown that the focusing lens f-number greatly affects the optical limiting characteristics of Fe:LiNbO₃. A lens f-number of approximately 20 gives the best results.

3:15 PM *PP6.4

LIQUID CRYSTAL DEVICES FOR LIGHT LIMITING APPLICATIONS. J.S. Patel, Zhizhong Zhuang, Young Jin Kim. Departments of Physics and Engineering, The Pennsylvania State University, University Park, PA.

Liquid crystals have been used in many different ways to make light limiters. A variety of device structures are possible because of the range of properties and structures of liquid crystals. The commonly encountered twisted nematic liquid crystal structure is an example of a simple but common device, which can be used to control the transmission of the light over a broad wavelength range using electric field. In the talk, we will discuss several device geometries made from simple nematic liquid crystals to more complex twisted smectic liquid crystal structures, and highlight the advantages and disadvantages of these devices.

3:45 PM PP6.5

PDLC-BASED DEVICE FOR OPTICAL LIMITING. Frédéric Genty, Patrick Fenevrou, Evelyne Chastaing, Pierre Le Barny, Véronique Dentan, Brigitte Loiseaux, Jean-Pierre Huignard, Thomson-CSF, Central Research Laboratory, Domaine de Corbeville, Orsay, FRANCE.

The light scattering properties of classical direct Polymer Dispersed Liquid Crystal (PDLC) composites have been investigated for optical limiting applications. Considering the orientation time of liquid crystal molecules, which has been measured in the range of 30 to 50 ms, these composites are identified as potential candidates for protection against Continuous Wave threat. We will report on the results of devices with thickness ranging from 10 to 50 μm , fabricated by photopolymerization of PDLC composite between two glass plates. Scanning Electron Microscopic observations have shown a network PDLC morphology with a characteristic size of 2 μm for liquid crystal domains. Electrical driving is obtained via Indium Tin Oxide electrode deposited at each interface between glass and composite. It will be shown that using an optimized mixture allows to obtain high contrast and low driving voltage (the resulting measured electric field is of about 1.4 V/ μm of thickness). The evolution of response times in function of the operating voltage has been evaluated. Experimental results involving PDLC scattering effect will be presented in terms of linear transmission in the transparent state, scattered light versus angle with incident beam, and optical limiting properties in a f/5 optical bench. Finally, the different solutions for scattering addressing

either electrically or optically will be discussed. This work was supported by Delegation Generale pour l'Armement, Service Technique des Technologies Communes.

4:00 PM PP6.6

NONLINEAR OPTICAL PROPERTIES OF CARBON NANOTUBES FOR OPTICAL LIMITING. Laurent Vivien, Didier Riehl, Marc Andrieux, Fernande Lafonta, DGA/DCE/CTA, Dept Laser, Optique et Thermo-optique, Arcueil, FRANCE; Eric Anglaret, Montpellier II Univ, Groupe de Dynamique des Phases Condensees, Montpellier, FRANCE; Francois Hache, Ecole Polytechnique, Groupe d'Optique Quantique, Palaiseau, FRANCE.

Since their discovery, carbon nanotubes have been the subject of numerous physical studies and are of great interest for optical limiting in view of their strong nonlinearity and broadband transmission. Optical limiting properties of single- and multi-walled carbon nanotubes suspended in water have been evaluated with 7 ns pulses at 532 and 1064 nm and compared with those of another materials (carbon black suspension in water and C60 in toluene solutions). In order to determinate the origin of optical limiting, we carried out a Z-scan experiment at 532 nm and 1064 nm at different input energies (open and closed aperture). We evidenced strong nonlinear scattering and white light emission in the focal zone, as for carbon black suspension, and a refractive effect with a positive nonlinear index. The kinetics of nonlinear transmission, from the nanosecond to millisecond time scale, were studied using a pump-probe set-up at 1064 nm, coupled with time-resolved measurements of light emission. We observed also strong refractive signals generated by an acoustic shock wave, and at high input fluence due to cavitation bubbles. The different nonlinear effects evidenced are discussed in terms of physical origin and in terms of broadband optical limiting efficiency.

4:15 PM PP6.7

INVESTIGATION OF OPTICAL-LIMITING MECHANISM IN MULTI-WALLED CARBON NANOTUBES. Xuan Sun, Yuenan Xiong, Ping Chen, Jianyi Lin, and Wei Ji, Department of Physics, National University of Singapore, Republic of Singapore; Jin Hong Lim, Sidney S. Yang, David J. Hagan and Eric W. Van Stryland, School of Optics/CREOL, University of Central Florida, Orlando, FL.

Recently we reported the observation of broadband optical limiting with multi-walled carbon nanotubes [1,2]. Here we present an investigation on the mechanism for the observed limiting effects in the nanotubes (NTs). We have performed the following experiments at 532-nm wavelength. (1) Energy-dependent transmission measured with pico- and nano-second laser pulses; (2) picosecond time-resolved pump-probe; and (3) nonlinear scattering detected with nanosecond laser pulses. The energy-dependent transmission of the NTs shows strong limiting action on the nanosecond time scales but no limiting behavior in the picosecond regime even with an input fluence as high as 3 J/cm². This is different from the behavior of C₆₀ but similar to that of carbon black suspension (CBS) [3,4]. The pump-probe experiments indicate that it takes about 0.5 ns for the nonlinear transmission to take place for both the NTs and CBS. In addition, the pump-probe experiments show that the smaller the external diameters of the NTs, the faster and larger are the changes of the transmission. One of the suggested mechanisms for the limiting action in CBS is that it is a result of the breakdown of absorbing micro-particle, due to the heating by the intense pulses, and consequent plasma absorption and nonlinear scattering. Another suggested model is the formation of micro-bubbles that subsequently scatter light. The similarities that we observed between the NTs and CBS suggest that the same process(es) that occur(s) in CBS also play an important role in the limiting behavior of the NTs. To confirm that nonlinear scattering exists in the NTs, we have measured the energy dependence of the scattered light and found that it is very similar to that seen with CBS. [1] X. Sun, R. Q. Yu, G. Q. Xu, T. S. A. Hor, and W. Ji, Appl. Phys. Lett. 73, 3632 (1998). [2] P. Chen, X. Wu, X. Sun, J. Lin, W. Ji, and K. L. Tan, Phys. Rev. Lett. 82, 2548 (1999). [3] K. Mansour, M. J. Soileau and E. W. Van Stryland, J. Opt. Soc. Am. B 9, 1100-1109 (1992). [4] O. Durand, V. Grolier-Mazza, and R. Frey, Opt. Lett. 23,1471 (1998).

4:30 PM *PP6.8

ELECTRICALLY SWITCHABLE HOLOGRAPHIC POLYMER-DISPERSED LIQUID CRYSTAL FILTER. Lalgudi V. Natarajan, R.L. Sutherland, V.P. Tondiglia, M. Schmitt, S. Siwecki, R. Pogue, Science Applications International Corporation, Dayton, OH; and T.J. Bunning, Air Force Research Laboratory, Wright-Patterson Air Force Base, Dayton, OH.

Liquid crystals have proven to be desirable electro-optical materials for developing wavelength rejection filters due to their high birefringence and large electro-optical response. We have developed filters based on holographic reflection gratings recorded on polymer dispersed liquid crystals. Reflection gratings in blue, green and red colors were written in thin polymer films exhibiting diffraction

efficiency ~70% and transmittance >80%. The reflection grating was electrically switched with a field of ~12V/um and a contrast ratio >100. The response time for electrical switching was on the order of ~100 msec. The fast response time and the high switching field are attributed to the presence of small nematic droplets on the order of 50-100 nm. The band width of the grating was controlled by varying the cell thickness and index modulation. By stacking up thin films of the gratings in a tandem fashion, optical densities >3 are obtained. We have demonstrated the potential of using the thin film stack as a laser rejection filter by electrically switching the stack.

SESSION PP7/BB12: JOINT SESSION: ORGANIC PHOTOREFRACTIVES

Chair: Joseph W. Perry
Friday Morning, December 3, 1999
Salon G (M)

8:30 AM *PP7.1/BB12.1

HIGH SPEED AND INFRARED SENSITIVE PHOTOREFRACTIVE POLYMERS. N. Peyghambarian, E. Hendricks, K.B. Ferio, J.A. Herlocker and B. Kippelen, Optical Sciences Center, University of Arizona, Tucson, AZ; Y. Zhang, V. Alain, S. Thayumanavan, S.R. Marder, J.W. Perry, Chemistry Department, University of Arizona, Tucson, AZ.

We report on a photorefractive polymer with better than 2ms response time. We will also report on two-photon induced photoconductivity in PVK-sensitized with nonlinear absorbers. The results of photorefractive response at 800nm will be presented and efforts to extend the response to longer wavelengths will be summarized. Our recent work on compounds that exhibit 100 percent photogeneration efficiency at 633nm will be reviewed.

9:00 AM *PP7.2/BB12.2

PHOTOREFRACTIVITY IN NEMATIC LIQUID CRYSTALS DOPED WITH A CONJUGATED POLYMER: MECHANISMS FOR ENHANCED CHARGE TRANSPORT. Michael R. Wasielewski, Dept. of Chemistry, Northwestern Univ, Evanston, IL; Gary P. Wiederrecht, Chemistry Div, Argonne Natl. Lab., Argonne, IL.

A new mechanism for space-charge field formation in photorefractive liquid crystal composites containing poly(2,5-bis(2'-ethylhexyloxy)-1,4-phenylenevinylene) (BEH-PPV) and the electron acceptor N,N'-dioctyl-1,4:5,8-naphthalenediimide, NI, is observed. Using asymmetric energy transfer (beam coupling) measurements that are diagnostic for the photorefractive effect, the direction of beam coupling as a function of grating fringe spacing inverts at a spacing of 5.5 microns. We show that the inversion is due to a change in the dominant mechanism for space-charge field formation. At small fringe spacings, the space-charge field is formed by ion diffusion in which the photogenerated anion is the more mobile species. At larger fringe spacings, the polarity of the space charge field inverts due to dominance of a charge transport mechanism in which photogenerated holes are the most mobile species due to hole migration along the BEH-PPV chains coupled with interchain hole hopping. Control experiments will be presented, which use composites that can access only one of the two charge transport mechanisms. The results show that charge migration over long distances leading to enhanced photorefractive effects can be obtained using conjugated polymers dissolved in liquid crystals.

9:30 AM PP7.3/BB12.3

ENHANCEMENT OF PHOTOREFRACTIVITIES IN MONOLITHIC PHOTOREFRACTIVE POLYMERS. Tatsuo Wada^{1,2}, Takafumi Sassa², Tetsuya Aoyama², Yadong Zhang¹, Atsushi Gunji^{1,2} and Hiroyuki Sasabe^{1,2,3}, ¹Core Research for Evolutional Science and Technology (CREST), JST, ²Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama, JAPAN, ³Chitose Institute of Science and Technology, Bibi, Chitose, Hokkaido, JAPAN.

We have developed carbazole oligomers and polymers as monolithic photorefractive materials in which single multifunctional chromophore meets all the requirement of photorefractive. Carbazole oligomers show better photorefractive performance than polymeric ones and provide molecular level of tuning. In order to improve the photorefractive properties of carbazole polymers, additional hole-transporting and electro-optic chromophores were introduced into the side chain, 9-position of the 3-6-linkaged main-chain polymer. In these main- and side-chain polymers, photoconductive properties were enhanced by factor of 10. Electro-optic coefficients and second-harmonic coefficients also increased. Asymmetric energy transfer in two beams with 90° phase shift was observed and the great enhancement of photorefractive was obtained in main- and side-chain polymers. The two-beam coupling net gain of 103 cm⁻¹ was obtained

without an external electric field in carbazole main-chain polymer with p-nitrostilbene in the side chain. The enhancement of two-beam coupling gain can be explained by the refractive index change estimated from the diffraction efficiency in four-wave mixing.

9:45 AM *PP7.4/BB12.4

NANOPHOTONICS: MATERIALS, INTERACTIONS AND APPLICATIONS. P.N. Prasad, J. Swiatkiewicz, D. Jakubczyk, Y. Shen, Y. Jiang, M. Lal, L. Levy, C. Friend and A. Biswas, Photonics Research Laboratory, Department of Chemistry and Physics, State University of New York at Buffalo, Buffalo, NY.

Nanophotonics is a new frontier dealing with nanoscale optical science and technology. Nanoscale optical interactions can be studied in two ways: (i) nanoscale confinement of radiation field and (ii) nanoscale confinement of the medium by nanostructuring. This paper will present our effort in both areas. Results will be presented from theoretical modeling and near field probing of linear and nonlinear optical processes. In nanostructured material design, two new directions taken by our group are development of photonic crystals and multistep organizational assemblies with enhanced photonic activities. Our work involving nanoscale photochemistry for applications will also be presented.

10:45 AM *PP7.5/BB12.5

TRAP DYNAMICS IN PHOTOREFRACTIVE POLYMER COMPOSITES. W.E. Moerner, D. Wright, A. Goonesekera, Stanford Univ, Dept of Chemistry, Stanford, CA; M.A. Diaz-Garcia, Univ of Calif San Diego, Dept of Chemistry, La Jolla, CA; R.J. Twieg, Kent State Univ, Dept of Chemistry, Kent, OH.

The high gain and index modulation reported for several new photorefractive polymer composites are due to a combination of factors, including high nonlinearity resulting from orientational enhancement, and the large internal electric fields that can be generated (~ 90 V/mm). In all models, the trap density plays a critical role in establishing strong space-charge fields. For composites based on poly(N-vinyl carbazole) containing amino-dicyanostyrene nonlinear optical (NLO) chromophores and sensitized with the fullerene C60, we have shown that the radical anion of C60 acts as the primary photorefractive hole trap. In addition, the NLO acts as a temporary reservoir for the photogenerated holes (compensator). The long-time dynamics of the trap density depend upon the position of the highest occupied molecular orbital (HOMO) of the NLO, as estimated by cyclic voltammetry. With this enhanced understanding, the overall trap dynamics can be controlled to an extent by changing the energetics of the NLO. Furthermore, we find that the speed of the photorefractive response is inversely correlated with the depth of the hole trap represented by the NLO, suggesting that the speed of the photorefractive effect is influenced by the possibility that mobile holes can become trapped in the NLO sites during transport. Time-of-flight mobility measurements will be utilized to attempt to quantify this effect. The overall picture that emerges provides an important step toward rational design of these materials, in which the actual trap concentrations and their influence on transport are controlled by composition and irradiation history.

11:15 AM PP7.6/BB12.6

SYNTHESIS AND PROPERTIES OF NOVEL PHOTOREFRACTIVE POLYMERS. C.D. Eisenbach, K. Ewert, Inst. Techn. Chemie II, Univ. Stuttgart, Stuttgart, GERMANY; D. Haarer, U. Hofmann, S. Schlöter, Exp.-Physik IV, Univ. Bayreuth, Bayreuth, GERMANY.

Polymers carrying both the photoconducting and nonlinear optically (NLO) active moieties along the polyester or polyurethane chain have been obtained by step-growth polymerization employing specially designed photoactive (NLO and photoconducting) building blocks. This strategy not only allowed to systematically vary the bulk and processing properties of the materials but also the photorefractive properties. The electrooptic properties were investigated by several techniques, and the polymers were found to be fast and stable photorefractive materials. The design and the synthesis as well as the advantageous photorefractive properties of the novel polymers will be discussed.

11:30 AM *PP7.7/BB12.7

PROGRESS IN FULLY FUNCTIONALIZED PHOTOREFRACTIVE POLYMERS. Luping Yu, The University of Chicago, Department of Chemistry, Chicago, IL.

In this talk, we will present our recent progress in the area of photorefractive (PR) polymers. Photorefractive polymers are multifunctional materials which combine the photoconductivity and electro-optic response to show a new phenomenon: reversible modulation of the index of refraction by light. Because of their

multifunctional features, designs, syntheses of these materials exhibiting high performances are an intellectual challenge. In the past year, our group has focused on the development of fully functionalized polymers, oligomers and small molecular materials. We have had success in identifying new materials and in gaining understanding in design principles of better materials. Several new PR material systems will be discussed, including conjugated PR polymers containing metalloporphyrin as photosensitizer, oligothiophene-NLO chromophore system exhibiting interesting physical properties and small molecular system containing NLO chromophore and carbazole moieties. All of these systems exhibit large net optical gain and minimized phase separation. The correlation between molecular structure and physical properties is the focal point of this presentation.