

Excited State Enhancement of Nonlinear Optical Properties

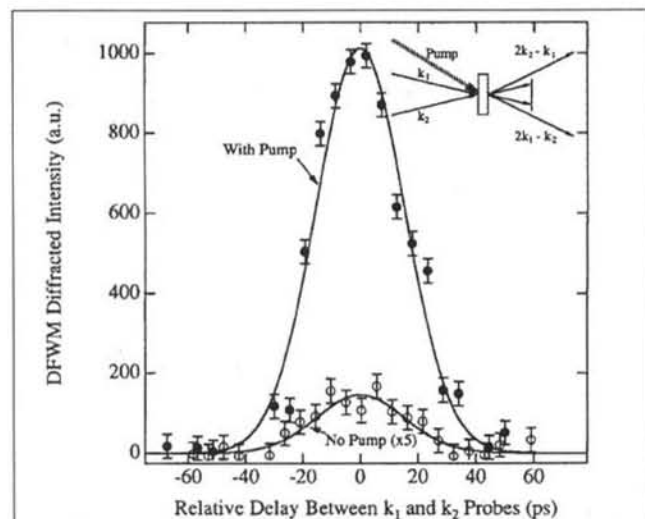
By D.C. Rodenberger, J.R. Heflin,* and A.F. Garito, Department of Physics, University of Pennsylvania, Philadelphia, Pa., and

*Department of Physics, Virginia Polytechnic Institute and State University, Blacksburg, Va.

In the search for efficient materials for all-optical photonic devices based on the third order optical susceptibility $\chi^{(3)}$, organic and polymeric materials are being intensely investigated because nonresonant virtual excitation of the delocalized π -electron systems of these materials can result in large ultrafast nonlinear optical responses with minimal background absorption. We have recently shown through theoretical and experimental studies that $\chi^{(3)}(-\omega_4; \omega_1, \omega_2, \omega_3)$ can be increased by orders of magnitude over the normally observed ground state values by population of electronic excited states.

The excited state enhancement mechanism was theoretically predicted¹ by many-electron, configuration interaction calculations of the molecular susceptibility $\gamma_{ijkl}(-\omega_4; \omega_1, \omega_2, \omega_3)$ of one-dimensional chains when either the first or second π -electron excited state is occupied. The principal reasons for the enhancement are (1) larger optical transition moments μ_{nr} , (2) smaller transition energies between the occupied excited state S_n and other excited states S_m , and (3) a reduced degree of competition between virtual excitation processes that has been shown to be a limiting factor in the ground state (S_0) $\gamma_{ijkl}(-\omega_4; \omega_1, \omega_2, \omega_3)^{2,3}$.

The first experimental observation⁴ of enhanced nonlin-



Typical DFWM signal of DPH in dioxane with pump on and pump off as a function of time delay between the two 1064 nm probe beams. The pump delay is set such that the 355 nm pump pulse precedes the probes by 100 psec and the relative delay between the probe pulses is varied. The unpumped data, which has been multiplied by a factor of 5 for clarity, corresponds to the background signal from the dioxane solvent since the ground state contribution from DPH is smaller than the detection resolution of the experiment. An enhancement of a factor of 37 in intensity is shown here for a concentration of 3×10^3 molar. The inset diagram illustrates the forward scattering DFWM experiment.

ear optical response by excited state population was made in third harmonic generation (THG) measurements of the conjugated disk-like structure, silicon naphthalocyanine (SINC). When solutions of SINC were optically pumped at $\lambda=770$ nm in the strong Q absorption band to populate the first electronic excited state (S_1), and then probed by 30 psec pulses at $\lambda=1543$ nm, the THG Maker fringe amplitude was seen to change significantly because of a very large and negative $\gamma^{S_1}(-3\omega; \omega, \omega, \omega)$ of $1,640 \pm 100 \times 10^{-36}$ esu from the S_1 excited state of SINC. This is orders of magnitude larger than the ground state $|\gamma^{S_0}(-3\omega; \omega, \omega, \omega)|$ which is $< 10 \times 10^{-36}$ esu.

More recently, excited state degenerate four wave mixing (DFWM) measurements⁵ have shown an increase as large as a factor of 100 in the completely nonresonant two beam⁶ DFWM signal at $\lambda=1064$ nm when solutions of the conjugated linear chain diphenylhexatriene (DPH) are optically pumped by 30 psec pulses at $\lambda=355$ nm into the first optically allowed electronic excited state (S_2). Both with and without the pump beam present, the DFWM signal is non zero only when the two probe pulses temporally overlap in the sample (see figure). However, a large increase in the signal is observed when the sample is pumped due to a large $\gamma^{S_2}(-\omega; \omega, \omega, -\omega)$ of $12,000 \pm 1700 \times 10^{-36}$ esu compared to the ground state $|\gamma^{S_0}(-\omega; \omega, \omega, -\omega)|$ which is $< 50 \times 10^{-36}$ esu. Importantly, separate transient absorption experiments show there is no excited state absorption at 1064 nm with excitation at 355 nm. Therefore, upon population of the excited state, the microscopic third order optical susceptibility of DPH is increased by orders of magnitude without introducing any optical loss at the probe wavelength.

The excited state enhancement mechanism is generalizable to other nonlinear optical processes and to other material structures. The measurements reported to date were made in solutions where the small number density of excited state molecules with large optical nonlinearity results in a smaller $\chi^{(3)}(-\omega_4; \omega_1, \omega_2, \omega_3)$ than would be observed with a pure, single substance. Studies are currently underway on pure polymer thin films where typical nonresonant ground state $\chi^{(3)}$ values on the order of 10^{-10} esu are expected to be enhanced by orders of magnitude, potentially leading to figures of merit sufficient for practical photonics devices.

ACKNOWLEDGMENTS

This research was generously supported by the U.S. Air Force Office of Scientific Research, DARPA, the Penn Research Fund, and Pittsburgh Supercomputing Center.

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