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Ultrafast nonlinear optical and spectroscopic studies at the University of Hyderabad, India

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Dedicated to Professor D N Rao for his significant contributions and pioneering works in the fields of spectroscopy, optics, nonlinear optics and photonics

This mini-review presents the results from our various efforts on the nonlinear optical (NLO) and ultrafast studies from the year 1997-2014 at the University of Hyderabad, India under the leadership of Prof Narayana Rao Desai. Our group was one of the first to work on the third-order nonlinear optical properties of novel organic materials such as porphyrins and phthalocyanines using nanosecond, picosecond, and femtosecond laser pulses. Further, a summary of the second order NLO studies performed along with femtosecond laser direct writing studies are summarized. Some of the important results accomplished during this period from our group were also highlighted.

Keywords: Nonlinear Optics, Z-scan, DFWM, Porphyrins, Phthalocyanines, Femtosecond, Two-photon absorption, Three-photon absorption

1 Introduction

Nonlinear optics is the subdivision of optics that interprets the nature of light in a nonlinear optical (NLO) media, in which the induced polarization is responsible for the nonlinear response to the applied electric field [1]. When intense laser pulses interact with materials NLO effects are manifested beyond certain input peak intensities of the light. The electrons oscillations follow anharmonicity which produces light with different frequency and amplitude from the fundamental beam. Since its discovery in the 1960's, second harmonic generation (SHG) was found via the combination of two photons, generating a single photon at two times the frequency. Generally, a single intense light pulse is adequately enough to generate nonlinear optical phenomena. However, some of the nonlinear effects were found earlier than the development of lasers, including, Pockel's cell effect and electro-optic effect. To infer the NLO phenomena including second harmonic generation (SHG), third harmonic generation (THG) etc. in the material, it is required to include the nonlinear terms in the dielectric polarization equation, that is, the dielectric polarization is proportional to higher power of the applied electric field. This equation is described as

$$\tilde{P}(t) = \epsilon_0 [\chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}^2(t) + \chi^{(3)} \tilde{E}^3(t) + \cdots]$$

The quantity ϵ_0 is the electric permittivity of vacuum, $\chi^{(1)}$ is linear optical susceptibility, $\chi^{(2)}$ and $\chi^{(3)}$are referred as second and third order NLO susceptibilities, respectively. $\tilde{P}(t)$ and $\tilde{E}(t)$ are known as induced polarization and applied electric field, respectively. The second order susceptibility can be provided by the non-centrosymmetric media only since these media do not exhibit property of inversion symmetry (for example SHG crystals such as BBO, KTP, KDP etc). Second harmonic generation, sum frequency generation

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and difference frequency generation phenomena occur due to second order nonlinear optical susceptibility $\chi^{(2)}$. The inversion symmetry property can be demonstrated by other samples such as liquid media, solids with amorphous phase and some of the inorganic crystals etc. and therefore, $\chi^{(2)}$ cancels out identically. But, both media exhibit third order NLO interactions and provide third order nonlinear optical susceptibility $\chi^{(3)}$.

2 Experiments developed at the University of Hyderabad (UoH), India

2.1 SHG studies (*Kurtz-Perry method*)

We established the Kurtz-Perry method for measuring the SHG strength of novel organic molecules [2-7]. The materials investigated were push−pull/chiral quinonoid compounds, *N*-alkyl-*p*-nitroanilines, and bis (*n*-alkylamino) dicyanoquinodimethanes

2.2 Z-scan (cw, nanosecond, picosecond, femtosecond)

Our group at the University of Hyderabad was one of the first groups in the country to have performed continuous wave (cw), nanosecond (ns), picosecond (ps), and femtosecond (fs) Z-scan studies in solutions, thin films, nanomaterials, and nanocomposites [8-23]. We were one of the first groups in India to have developed a complete understanding of the nonlinear absorption/refraction changes with input intensity, concentration of molecules studied, wavelength, and pulse duration [10,11,19]. A first demonstration of switching behavior in nonlinear absorption [saturable absorption (SA) to reverse saturable absorption (RSA) and vice-versa] was from our group [11]. Figure 1 shows a schematic of all the NLO studies performed in our group during the 1990-2010 period.

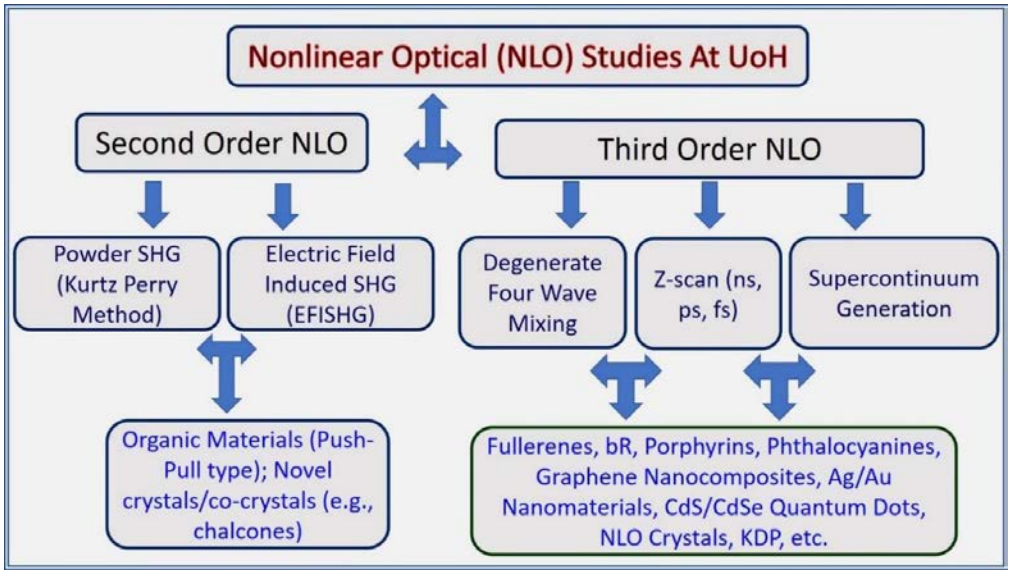

Fig 1. A schematic of various NLO techniques developed at UoH and a variety of molecules, compounds, nanocomposites investigated using these techniques.

2.3 Degenerate Four Wave Mixing (*DFWM*, (*ps*, *fs*))

We were also one of the first groups to develop degenerate four wave mixing (DFWM) setup using incoherent laser pulses (ns) and ps laser pulses (in collaboration with Prof G Ravindra Kumar, Prof Deepak Mathur, Dr Reji Philip, TIFR). We investigated several organic molecules [9,15,24] for their third-order NLO properties and time response (in collaboration with Prof B G Maiya, School of Chemistry, University of Hyderabad).

2.4 EFISHG (ns)

Electric field induced second harmonic generation (EFISHG) and powder SHG measurements were performed in our lab in the late nineties [25]. A new sample cell was designed and developed [see Figs 2 (a) and 2 (b)] and the analysis protocol was formulated to analyse the EFISHG results [19]. This formed a valuable first step in characterizing the molecule for its further applications (e.g., in bioimaging). Most of this work has been performed in collaboration with Prof T P Radhakrishnan, School of Chemistry, UoH [19].

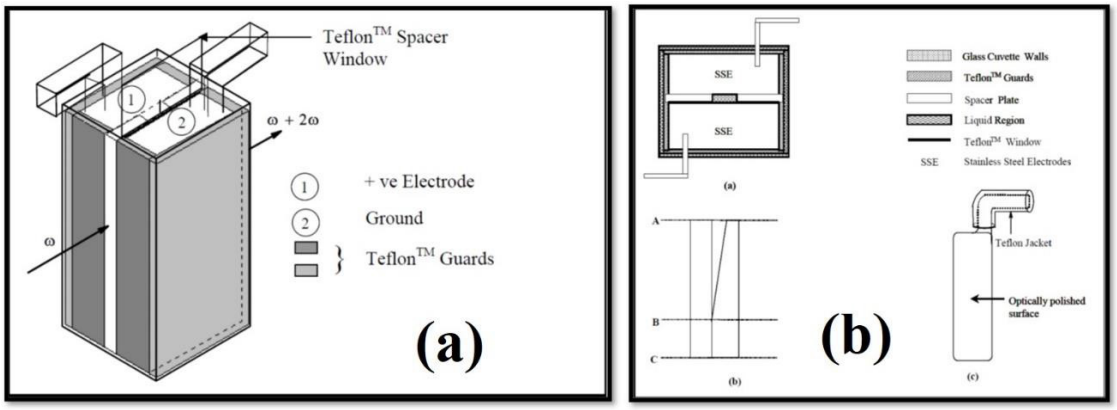

Fig 2. (a) Design of the EFISHG cell and (b) top/side views. Reproduced with permission from Ph D thesis of Dr N K M Naga Srinivas, University of Hyderabad, India, 2004..

To standardize experimental procedure, first hyperpolarizability values were determined for important molecular systems in dimethyl sulfoxide (DMSO) and N-Methyl-2-pyrrolidone (NMP) and were found to match well with those reported in literature. The calibration experiments carried out using 4-nitroaniline in DMSO and NMP confirmed the first hyperpolarizability value of DMSO to be $-(0.19\pm0.029)\times10^{-30}$ esu. A novel strategy was developed by making use of electric field dependency of SH signal for the EFISHG experiment and verified by measuring the first hyperpolarizability values for pNA and NPP in DMSO and in NMP. The measured μβ value of BPDQ in DMSO was -2546×10^{-48} esu and in NMP was -2066×10^{-48} esu. Detailed studies reported from our laboratory on the relaxation dynamics of polar molecules in solutions, using the EFISHG setup, suggest a close link between the size and dipole moment of the molecules and their reorientation/relaxation under the influence of the applied electric field.

2.5 DFWM-ILS (ns)

A new spectroscopic method (incoherent laser spectroscopy) was developed in 1980-1990 decade, which used incoherent light as the source. A temporally incoherent light has a very short coherence and, hence, correlation time. This kind of light appears as a short pulse of duration τ_c in auto correlation measurements and is, therefore, expected to play similar role to a short pulse in the nonlinear regime utilizing the correlation technique. Accordingly, experiments with extremely high temporal resolution were performed with incoherent light. Here, the time resolution is independent of pulse width and the identified advantages of this technique were (1). incoherent light was much easier to generate compared to ps/fs lasers during those days (2). tunability was large with such systems by appropriately changing the dye species, concentration, solvent, pumping power, pumping source etc. (3). time resolution was not degraded by dispersion. A first experimental setup based on this spectroscopic method was commissioned in India at UoH [8,26-29]. A schematic of the setup is presented in Fig 3. The molecules investigated were tetratolyl porphyrins, C_{60}, dyes, etc.

2.6 Electro-absorption Technique

Electroabsorption spectroscopy is capable of determining the dispersion of $\chi^{(3)}$ components. Further, it can offer information about a NLO chromophore orientation in the material. Electroabsorption experiments were setup at UoH [30] and initial spectra were obtained for the sample of free-base hydrogen tetratolylporphyrin (dispersed in PMMA) and third order NLO susceptibility was evaluated.

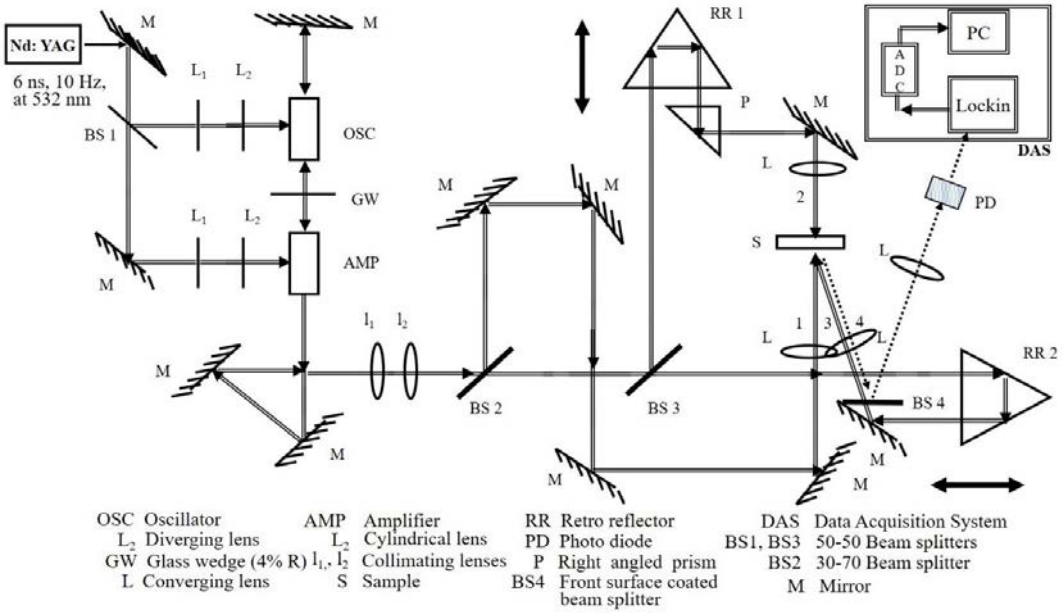

Fig 3. A schematic of DFWM experiments with incoherent laser pulses setup at UoH. Reproduced with permission from [27].

2.7 Femtosecond laser direct writing

We have developed the fs laser direct writing (LDW) facility at UoH using ~2 mJ, ~100 fs, ~ 1 kHz pulses at 800 nm [31-40]. We used different microscope objectives (20X, 40X, 60X etc.) to achieve micron-sized and submicron-sized features on and beneath various materials' surfaces. Several microstructures and nanostructures (e.g., 1-D/2-D gratings, holes) were created on the surface and sub-surface in a variety of materials such as polymers (PMMA, PVA, PS etc.), glasses (Baccarat etc.), metals using this setup. Figure 4 illustrates the typical surface structures produced in PMMA and PDMS.

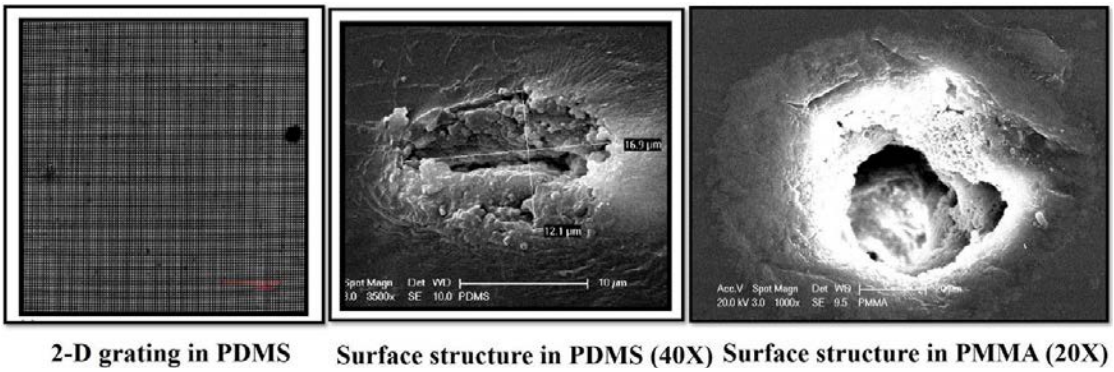

Fig 4. Femtosecond (1 kHz, 800 nm, maximum energy of 2 mJ) laser direct writing of different structures (gratings, holes) in PDMS and PMMA at UoH [32].

3 Results and Discussion

Third-order NLO phenomena do not need structural constraints such as non-centrosymmetry in materials and, hence, NLO properties/coefficients have been comprehensively investigated in various organic molecules due to their excellent potential in optical data storage and optical limiting applications. Numerous organic molecules with a large number of π-electrons such as porphyrins, phthalocyanines, corroles and porphycenes possess exciting third order NLO properties. Further, their ultrafast excited state dynamics have been widely explored by various groups in the recent years [9-22]. Many research reports have been unsuccessful to divulge the more important concerns such as (a) wavelength dependent nonlinearities (b) pulse width dependent nonlinearities and (c) resolving the pure electronic nonlinearity and thermal nonlinearity values [9-22]. So far, our group has demonstrated the methods to overcome these concerns (especially in above-mentioned organic molecules) and our detailed studies revealed important information [9-22,24].

3.1. Nonlinear optical studies of porphyrins

The third order NLO properties and relaxation dynamics of porphyrins and porphyrins conjugates have been investigated by Z-scan and time resolved degenerate four wave mixing (DFWM), respectively. The nonlinear absorption coefficients including, two photon absorption and three photon absorption coefficients; negative and positive nonlinear refractive index; magnitude of third order susceptibility and relaxation dynamics have been figured out. In 1997, our group was one of the first to start on NLO studies and relaxation dynamics in India and reported the reverse saturable absorption or excited state absorption from cobalt tetratolylporphyrin (CoTTP) and related molecules [26]. Population-relaxation times of the excited states of metalloporphyrins, for instance zinc meso-tetra-phenylporphyrin (ZnmTPP), zinc meso-tetra (*p*-methoxyphenyl)tetrabenzoporphyrin (ZnmpTBP), tetratolylporphyrin (TTP), CoTTP and nickel tetratolylporphyrin (NiTTP), as acquired by DFWM technique with incoherent emission of a nanosecond dye laser. The values of relaxation dynamics obtained were of 48, 32, 40, 37, and 45 ps for ZnmTPP, ZnmpTBP, TTP, CoTTP and NiTTP, respectively [26]. Furthermore, our group studied the optical limiting behavior of porphyrins using nanosecond pulses in the visible regime [9]. The outcomes of the effective excited state absorption cross-section values obtained over the visible region 500–700 nm in the range of 0.5×10^{-16} cm^2 to 2.5×10^{-16} cm^2 [9]. By the contribution of other central ions in TTP molecules, our group has investigated third-order nonlinearity in several Tetra(tolyl)porphyrin molecules (TTP) in the ns and ps domain, using DFWM and Z-Scan techniques [9,24]. The results of DFWM measurements suggested a third order effect of the AuTTP molecules with a susceptibility coefficient of 10×10^{-12} esu at a lower input intensity (100 MW/cm^2) and 30×10^{-12} esu at a higher input intensity (300 MW/cm^2), and also measured slope values from log-log plots are of ~3 and ~5 at lower and higher intensities, respectively. The slope value at higher intensity was suggesting the nonlinear contribution from higher excited states. It was also reported the excited state dynamics of TTP with different central metal ions, investigated by DFWM incoherent light (DFWM-IL) and picosecond DFWM (DFWM-PS). We determined that there are three relaxation times for the photo-excited molecules in the case of DFWM-IL and estimated t_1 to be < 170 ns (fast component), t_2 ~3–6 ps and t_3 ~ 20–60 ps, which are attributed to vibrational relaxation in the higher excited states, vibrational relaxation in Frank-Condon states (S_1) and population relation, respectively. In the case of DFWM-PS, TTP molecules with some central metal ions depicted single relaxation time t ~ 40 –550 ps due to population relaxation [24]. We, further reported the wavelength dependent nonlinear absorption in zinc *meso*-tetra-(*p*-methoxyphenyl)tetrabenzoporphyrin (ZnmpTBP) using open aperture *Z*-scan over the visible region from 480 nm to 600 nm with ns optical parametric oscillator (OPO). The five-level model was used to analyze the data and evaluated various NLO coefficients. The two-photon absorption coefficients were found to be 0.18 -1.48×10^{-8} cm/W in the 480–600 nm spectral range. The other excited states absorption coefficients were also estimated [10]. By the introduction of structural modification in two systems P(V)TTP and Sn(IV)TTP scaffold, we were able to notice that the molecules reveal RSA behavior

in both ns and ps regimes. Especially, in the ps domain, RSA was observed at lower intensity and saturated two-photon absorption (SA in RSA) at higher intensity due to the saturation of higher excited states [41,42]. Recently, our group has started working on dispersed wavelength dependent third order NLO studies of unsymmetrical β-functionalized 'push–pull' porphyrins using femtosecond 80 MHz pulses. The results of broadband nonlinear absorption and nonlinear refractive index studies of the materials, MTPP$(TPA)_2NO_2$ and MTPP $(TPA)_2CHO$ (M = 2H and Zn(II)) demonstrated the strong two photon absorption and negative nonlinearity with coefficients of ~10^{-8} cm/W and ~10^{-13} cm^2/W, respectively [43]. Because of high repetition rate of laser pulses, the acquired nonlinearities have strong thermal contributions, which could be avoided by using femtosecond 1 kHz pulses in the Z-scan measurements [43]. In continuation, we have investigated femtosecond 1 kHz nonlinear optical properties of a new series of "Push-Pull" meso-substituted trans-A2BC porphyrins, where A = mesityl, B = phenothiazine (push) and C = o/p-nitrophenyl moiety (pull) and M = 2H, Ni(II), Cu(II), and Zn(II) at 800 nm, and revealed the strong two photon absorption with coefficients of ~0.082-0.0953 cm/GW and cross-sections (~1.71–1.95×10^3 GM). Additionally, we have done some comparison studies on NLO properties of similar porphyrin molecules and the results have been revealed that a new series of "Push-Pull" meso-substituted trans-A2BC porphyrins showed a superior performance compared with other porphyrin molecules [44].

3.2. Nonlinear Optical Studies of Phthalocyanines

Phthalocyanines (Pcs) are macrocylic molecules which are identical with porphyrins structurally. Pcs and their derivatives have received considerable attention because of advancement of nonlinear optical techniques and their strong third order NLO properties. Pcs could also provide large nonlinearity with fast response time which is attributed to the existence of an extremely conjugated macrocyclic-electron system. The investigation of the optical limiting properties of Pcs in the nanosecond domain was reported in 1998 by our group for the first time in India [45]. The best territory for the optical limiting study is the low absorption or high transmission region. The outcomes of this research reveal that the Pcs are most applicable for optical limiting within the range of 475 nm – 680 nm compared with porphyrins (500 -600 nm) and C_{60} (430 – 650 nm). To the best of our knowledge, this was the first report on comparative studies on optical limiting properties of these molecules illustrating the dispersion behavior at similar conditions. The replacement of metal ion in the position of central atom (2H) demonstrated an advance tool for controlling the NLO properties and response times of the resulting MPcs. Our group reported excited state dynamics of metal Pcs using DFWM-IL [29]. The results of these studies reveal that the compounds Pc, CuPc, FePc, and ZnPc possessed three relaxation times: dephasing time (<170 fs), vibrational relaxation time (<5 ps) and population relaxation (<50 ps). Subsequently, we have explored structure-property relationship to advance the essential molecular properties for the establishment of potential device applications. Z-scan studies were performed on new class of alkyl and alkoxy Pcs in two different time domains (fs, ns) [12,13,46]. The results of the open aperture Z-scan measurements demonstrated three photon absorption for the 2(3), 9(10), 16(17), 23(24) tetra tert-butyl Pc and 2(3), 9(10), 16(17), 23(24) tetra-tert-butyl Zinc Pc with coefficients of ~9.1×10^{-5} and ~9.5×10^{-5} cm^3/GW^2 for the first time when pumped fs pulses at a wavelength of 800 nm. The ns data demonstrated strong two photon absorption and optical limiting properties while the continuous wave pumping indicated large negative nonlinear absorption coefficient at 633 nm. The fs DFWM study was utilized to evaluate third order susceptibility and dephasing time of the alkyl Pcs. The measured third order NLO susceptibility values were 4.26±0.42×10^{-14} and 4.31±0.43×10^{-14} esu and their dephasing time <<100 fs for 2(3), 9(10), 16(17), 23(24) tetra tert-butyl Pc and 2(3), 9(10), 16(17), 23(24) tetra-tert-butyl Zinc Pc, respectively [15]. We have also reported the NLO properties of two alkoxy Pcs specifically, 2,3,9,10,16,17,23,24-octakis-(heptyloxy) Pc and 2,3,9,10,16,17,23,24-octakis-(heptyloxy) Pc zinc(II) investigated by Z-scan technique at 532 nm using ns pulses and at 800 nm using fs pulses. In the ns domain, both the Pcs depicted strong third order nonlinearity of ~10^{-9} esu which was larger compared to

the other reported Pcs resulting in demonstration of a a great potential for their broad band optical limiting applications [13]. In the fs domain, mainly the open aperture data of Pc1 and Pc2 exhibited switching behavior over from saturable absorption (SA) to reverse saturable absorption (RSA) and RSA to SA. In those cases, excited state absorption, two photon absorption, three photon absorption and their saturations were observed to be responsible for the nonlinearity [13]. The Pc nanoparticles dispersed in water (PcN) and dissolved in chloroform (PcM) also showed the NLO property in the fs domain. Open aperture data of PcN exhibited strong three photon absorption whereas PcM exhibited saturable absorption at lower intensity and switching over SA to RSA at higher intensity. The sign of the nonlinearity of PcN and PcM were positive and negative, respectively [14]. Later on, our group continued the research on NLO studies of Pcs and their derivatives using Z-scan and DFWM techniques. Fs Z-scan open aperture data demonstrated that $(H_2)_2$SnPc (I), $Sn(OH)_2$Pc (II), and $Sn(Cl)_2$Pc (III) molecules displayed strong three photon absorption with the coefficients of ~4.0×10^{-5}, ~2.0×10^{-5} and ~1.5×10^{-5} cm^3/GW^2, respectively. We attributed large three photon absorption coefficient of $(H_2)_2$SnPc (I) at 800 nm to the large number of delocalized π-electrons for contributing to the nonlinearity which could be due to the existence of porphyrin molecules in the axial regions of Pcs [47]. Further, we have studied the NLO properties and excited state dynamics on the structural changes in the phthalocyanines comprise of (i) metallic Pcs (ii) alkyl Pcs (iii) alkoxy Pcs and (iv) symmetric and unsymmetrical PCs. The results of rest of our studies such as structural dependent and spectral dependent NLO studies of Pcs and their coefficients are well documented. Based on the data obtained from our investigations corresponding to the structural changes in Pcs we could provide some directions to accomplish the design and development of NLO device appropriate molecules [41-47].

3.3. Nonlinear optical studies of nanomaterials

Several nanomaterials were investigated at UoH during the last twenty years [49-61]. These include (a) Ag/Au nanomaterials prepared using simple, green chemical methods (b) phthalocyanine nanomaterials (c) CdS, CdSe quantum dots (d) graphene-based nanocomposites (e) bacteriorhodopsin (f) photonic crystals etc. Our group (in collaboration with U. Mass, Boston) has demonstrated low power optical limiting phenomenon using self-diffraction technique in films of bacteriorhodopsin (bR) [62]. We have also demonstrated all-optical logic gates using molecular states in a bR film [49]. We had successfully investigated the complete details of (a) nonlinear absorption (b) nonlinear scattering and (c) optical limiting properties of cadmium sulphide (CdS) nanoparticles dispersed in DMF (using ns pulses at 532 nm) [63]. Figure 5 shows the open aperture Z-scan and optical limiting data along with theoretical fits. This article [63] has been one of our highly cited articles on NLO. We have also performed NLO studies on Ag nanoparticles [53,54] prepared using simple chemical methods (extracts of Coriandrum sativum and Moringa oleifera leaf were used). We obtained strong NLO coefficients from these Ag nanoparticles. This article too [53] is another highest cited article from our group as per Google Scholar data (especially on NLO studies). A simple, effective protocol was developed for *in situ* generation of (a) highly monodisperse and (b) small (2−3 nm) Ag nanoparticles in PVA film. Further, we were successful in the fabrication of free-standing films [58,59] and the NLO studies were performed using nanosecond pulses. This was the first report of optical limiting with Ag nanoparticles-embedded polymeric thin film [58,59]. A limiting threshold of 0.83 Jcm^{-2} was obtained.

3.4 Supercontinuum Generation (SCG)

We could also setup the SCG experiments with femtosecond laser pulses in our lab. We reported the first fs (~100 fs pulses) SCG in KDP crystal at an input wavelength of 790 nm. Owing to the quadratic nonlinearities of KDP an enhanced SCG bandwidth (385–960 nm) was generated [56]. Further enhancement of the white light was obtained [towards the blue wavelength regime (<400 nm)] by employing SCG and sum frequency generation (SFG) in tandem [55]. We have also investigated the polarization properties of the generated SCG [57].

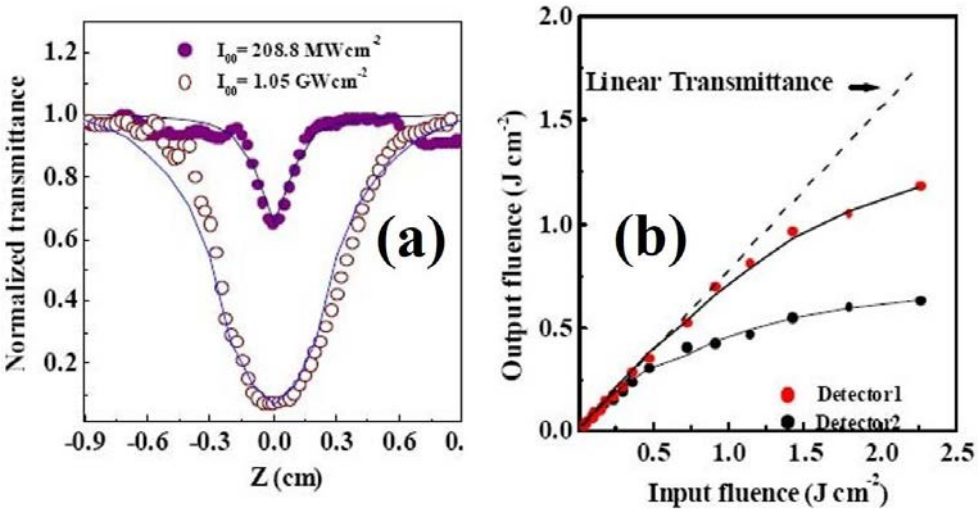

Fig 5. (a) Open aperture Z-Scan of CdS nanoparticles (4.5 nm) in DMF and theoretical fits (solid lines) (b) optical limiting data. Copyright @OSA; Reproduced with permission from [*Opt Express*, 13 (2005)867–872].

3.5. Femtosecond laser direct writing (fs LDW)

Major achievements using the fs LDW experimental setup at UoH include,

Achievement of waveguides and gratings in Baccarat glass [38]. A best propagation loss of ~0.9 dB cm^{-1} was obtained.

Accomplishment of 1-D and 2-D gratings in fused silica, GE 124, and Foturan™ glasses [40]. Good diffraction efficiencies (9–12%) were observed from these grating structures.

Achievement of femtosecond microstructuring and nanostructuring of various polymer materials (PVA, PMMA, PS). We reported the fabrication of (a) efficient and buried diffraction gratings and (b) micro-craters in bulk polystyrene using fs LDW technique [36]. Figure 4 illustrates a few typical structures in polymers.

We also reported fs microfabricated structures in the bulk/thin films of polystyrene (PS). An emission was observed from these structures [33,34]. We concluded that the emission was due to formation of optical centers resulting from fs irradiation. We have proved the existence of peroxide type free radicals (in the fs laser irradiated portions).

Photonic and microfluidic structures [35] were achieved on PMMA (poly(methylmethacrylate)) and PDMS (poly(dimethylsiloxane)).

Figure 6 shows a collage of the various lasers and NLO experiments setup at UoH. Several students contributed to these experimental setup. Over a period of more than 25 years, more than 20 students have graduated (Ph D) from these labs. Many others (project interns, M.Phil. students) were also benefitted from these facilities at UoH. Over the last two decades Prof D N Rao's group at UoH also ventured into other areas of NLO research such as

(a) surface enhanced Raman scattering (SERS) and glucose sensing,
(b) Preparation of 1-D, 2-D photonic crystals and their optical/NLO characterization,
(c) femtosecond laser micro- and nanostructuring in different materials including graphite, metals, semiconductors etc.,
(d) optical and NLO studies of glasses,

(e) Nanomaterials' preparation (using simple chemical methods and ultrafast lasers),
(f) interferometry in the spectral domain (using simple car headlight as the source) and
(g) biological applications of nanomaterials etc. (e.g., imaging of cancer cells).

Fig 6. A collage of various experiments and lasers developed during the last three decades in Prof D N Rao's Lab, at University of Hyderabad.

The ultrafast NLO group at UoH achieved many successful collaborations including (and not limited to): G S Agarwal, Suneel Singh, C Bansal, Ranjit Singh (SoP, UoH); B G Maiya, T P Radhakrishnan (SoC, UoH); D Mathur, G Ravindra Kumar, Reji Philip (RRI, Bengaluru); DVGLN Rao (U Mass., Boston), J A Akkara (US Army Labs).

Summary of a few important 2nd order and 3rd order NLO Results from Prof D N Rao's group @ UoH.

- A robust, indigenous **Raman shifter** (based on hydrogen gas) was developed at UoH with two Stokes and two Anti-Stokes lines observed when pumped with 532 nm.
- **A home made broadband** dye laser (oscillator and amplifier; Rhodamine B, Rhodamine 6G etc. were used as dyes) was developed for incoherent laser spectroscopic studies.
- **EFISHG** experiments were set up at UoH for the first time in the country [25].
- **First** demonstration of a double peak structure in the phase conjugate (DFWM) signal of porphyrins using incoherent ns laser spectroscopy [26,27].
- **Achieved** fs time resolution in excited state dynamics study of C_{60} using incoherent nanosecond pulses [28].
- A complete understanding of the nonlinear absorption in Rhodamine B achieved using experiments and modeling. A switching in nonlinear absorption (SA to RSA and RSA to SA) was reported by our group [11,16]. **[Highly cited articles]**
- **Developed** a general five-level theoretical model to characterize the complete nonlinear absorption behavior in C_{60} solution (using nanosecond excitation). [18] **[Highly cited article]**

- **Largest,** ultrafast nonlinearity and response times reported for several tetratolyl porphyrins using ns/ps pulses [9]. **[Highly cited article]**
- **First Demonstration** of STRONG three-photon absorption in alkyl phthalocyanines at 800 nm using fs pulses [46]. **[Highly cited article]**
- **First Demonstration** of gratings, waveguides in BACARRAT, a high quantum efficiency glass [31,38].
- **First Demonstration** of ultrafast nonlinear optical properties of alkyl phthalocyanine nanoparticles. [14]
- **Achieved large NLO figures of merit** for alkyl phthalocyanines studied using femtosecond pulses at 800 nm [15,46,21].
- **First report** on the nonlinear optical studies of silver nanoparticles synthesized using coriander leaves extract [54]. **[Highly cited article in Google Scholar: more than 560 citations, SCOPUS, and Web of Science]**
- **Demonstration of emission from microstructures** in PMMA, PDMS, PVA, PS using femtosecond direct writing [33,34]
- **First demonstration** of emission from fs laser written microstructures in PS and PVA [33].
- **First demonstration (in India):** Fabrication and optical characterization of microstructures in poly(methylmethacrylate) and poly(dimethylsiloxane) using femtosecond pulses for photonic and microfluidic applications
- **Demonstrated** strong nonlinear absorption, nonlinear scattering, and optical limiting in CdS quantum dots with 532 nm nanosecond pulses. [63] **[Highly cited article]**

Present Status

My group at Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderbad has been pursuing some of the above-mentioned areas of research and related studies including (a) ultrafast NLO and time-resolved studies of novel organic and perovskite materials (b) femtosecond ablation studies for various applications such as detection of hazardous materials using surface enhanced Raman scattering (SERS) technique [64-74].

The laser lab at the UoH, India was active, vibrant place and we took up several challenging NLO studies (e.g., SHG, incoherent laser spectroscopy, DFWM, Z-scan etc.). Our group was one of the first to delve into optical nonlinearities in different pulse domains (ns, ps, and fs) and in a variety of materials (e.g., organic and inorganic nanomaterials, crystals, biological materials, semiconductors, quantum dots etc.). Some of our works on the third-order nonlinearities (Z-scan, DFWM) are highly cited in the NLO literature. We had successfully collaborated with several groups within the school, across the schools in UoH and across the country/world. More than 50 students (Masters, Ph Ds, post-docs, summer interns) have contributed to various NLO studies performed at these Labs.

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