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Investigation on Optical Bistability and Excited State Absorption in Laser Grade Coumarine Dye

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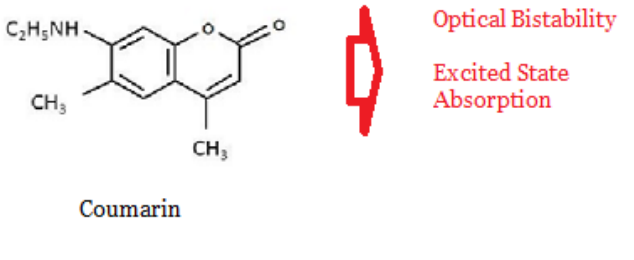
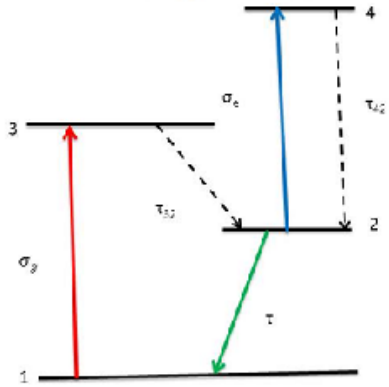
ABSTRACT





The recent advances in science and technology have a great demand to study optical bistability behavior. There are certain processes that are based on nonlinear optical interactions of intense light with the use of suitable optical material. Optical bistability is one of the phenomena representing non-linearity in the systems of prime importance. The phenomenon varies with the choice of materials and environmental conditions. In this paper we have developed Coumarin-450 doped polymeric (PMMA) samples of the varying concentration. Efforts have been made to demonstrate the non-linear behavior of optical materials in solid form using 532 nm of Nd:YAG lasers. The nonlinearity in terms of optical-bistability and excited state absorption has been discussed.

Keywords: optical bistability, excited state absorption, Fabryperot cavity, optical switching

INTRODUCTION

Optical bistability has got importance because of its potential applications in all optical switching, optical modulation and optical memory. The phenomenon of optical bistability was first reported by Gibbs et al in 1976.[1] As the name indicates, the phenomenon involves two stable states of a non-linear system. Mostly optical bistability have been reported in many types of laser systems.[2-5] The bistability in an intracavity saturable absorber have been the subject of interest as absorption characteristics are different depending on whether incident pump power is increasing or decreasing.[6] In another type, the bistability depend on thermally that induces changes in resonator optics where the absorption coefficient or the index of refraction is temperature dependent.[7] The bistable output comes from the combined effects of non-linear saturation of ground state re-absorption, the energy transfer up-conversion and the excited state absorption. The experimental observations of optical bistability in non-linear Fabry-perot cavity show that the effect on nonlinear refraction dominates over non-linear absorption that gives rise to bistability. It is worth nothing that only infinitesimally small changes in the index of refraction are required because of interferometric nature to the Fabry-Perot cavity. Therefore to fully explain the experimental results, it is necessary to include non-linear refraction along-with saturable absorption.[8]

Sincere efforts have been done in recent years to identify suitable materials for optical switches, optical bistable devices and

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spatial light modulators for the development of optical computers.[9-10] The lack of appropriate materials to implement theoretical designs of optical hardware is considered as a bottleneck in realizing the potential of the field.[11] These materials must be transparent not only at laser frequency but also should have the following features[12-13]:

- Large non linearity
- Resistant to optical damage
- High mechanical hardness
- Exhibit good thermal and chemical stability
- Capable of growing in useful size
- Appropriate phase matching properties
- Faster response time that offered by more photochromic systems

During the last two decades organic chromophores have been investigates as potentially promising candidates as optically non-linear materials,[14,15]. In many chromophores, complications due to dimer formation may destroy the desired non-linear optical response.[16] Therefore, in order to observe optical bistability in a molecular absorber due to either absorption saturation or excited state absorption, a system free from higher molecular aggregates need to be chosen. In this way the optical bistability response of a molecular absorber is expected to depend on the optical density of the medium.[17] To examine this dependence one need to analyze the bistability loop is a characteristic of intensity-induced increasing absorption. The bistabilty loop is reversed due to change in the electronic absorption mechanism, that is, a purely electronic route that changes the level populations and requires the resonator for feedback for the induction of optical bistability.[18]

The study of nonlinear behavior of single organic molecules is quite simple. The basic requirement is that the single molecule as a basic unit of these structures should have favorable high cross-section σ in the applied spectral range for nonlinear optics. The higher the cross sections, the lower the necessary excitation intensity I_{exc} for the required σI_{exc} product. The cross section of the particles in the sample can be increased by aggregation and other special arrangements of single molecules by many orders of magnitude. In other cases with pulse widths and modulation time much longer than the characteristic relaxation time τ of the matter, the product τ σ can be as large as possible to allow small excitation intensities. Thus the relaxation time can be large for low intensities but on the other hand fast for the required application.[19] Various research scientists are exploiting nonlinear optical properties of laser grade dyes in four wave mixing experiments,[20] real time holography,[21,22] optical phase conjugation,[22,23] and in optical-bistability experiments.[23-25]

Silica/polymeric samples doped with dye molecules are being considered as an appropriate medium for device fabrication. Out of various dye molecules, excellent lasing properties of substituted coumarin molecules as such are non-fluorescent but it exhibits intense fluorescence on substitution of various groups at different positions. During the present course of investigation, efforts have been made to study the optical bistability effects in Coumarin-450. Normally an excite coumarin molecule in solution can exist in two states with different conformation: a planar excited molecule or a planar intramolecular charge transfer state (ICT) or twisted (TICT). This particular molecule is a free-rotor molecule as the florescence emission takes place from either a planar excited molecule or from an ICT or TICT. The TICT state is a non-fluorescent state arising due to rotation of the attached functional group at position 7. However, in some cases intensity depending upon time nature of the solvent whether the solvent used is polar or non-polar. During the present course of investigation, experimental observations of optical bistabiltiy in Coumarin-450 dye molecule entrapped in polymeric host inside Fabry-Parot cavity is reported. The results show that the effects on non-linear refraction dominate over non-linear absorption in giving rise to the bistability.

THEORETICAL CONSIDERATION

Figure.1 shows a four level diagram for a saturable dye with an unsaturable absorption loss D. Mohan et al,[26] have established a theory for the estimation of various photo physical parameters viz. intensity gain coefficient, saturation parameter, absorption and emission cross sections and threshold conditions in 1989. They have further compared -450, and C460 dye molecules,[27] and found that C-450 is more stable than C-460 because C-450 has a methyl group in the 6th position and is capable of pushing the amine group out of planarity (Figure. 2) The steady state populations in levels 1 and 2 in the rate equations are,[23]:

$$N_1 = N\left(1+\frac{I}{I_s}\right)^{-1} \quad \text{.....[1]}$$

$$N_{2=}N - N_1 = N\left(\frac{I}{I_S}\right)\left(1+\frac{I}{I_S}\right)^{-1} \quad \text{..... [2]}$$

Where N is the total density of absorbers, I is the incident laser intensity and $Is = h\nu/\sigma_{13}\tau$ is the saturable absorption intensity at photon energy hν for the dye with relaxation time τ. The total absorption coefficient is given by

$$\alpha_a = N_1\sigma_{13} + N_2\sigma_{24} = \mathrm{N}\sigma_{13}\left(1+\frac{\mathrm{I}}{\mathrm{Is}}\right)^{-1}\left(1+\frac{\sigma_{24}}{\sigma_{13}}\right).\left(\frac{\mathrm{I}}{\mathrm{Is}}\right) \text{ ... ... [3]}$$

$$= \alpha_0(1+p)^{-1}(1+\eta p) \text{ ... ... [4]}$$

Where η is the ratio of excited state and ground state cross sections and $\alpha_0 = N\sigma_{13}$

The excited state absorption cross-section is of the order of 10^{-17} cm^2 as has been reported by D. Mohanet al,[27] . Further the condition for absorptive bistabiltity is[28-29]

$$= \frac{\alpha_0 L}{(1-R)+\eta\alpha_0 L} \geq 10 \text{.....} \quad [5]$$

Where L is the Fabry-Parot cavity length and R is the reflectivity of the mirror.

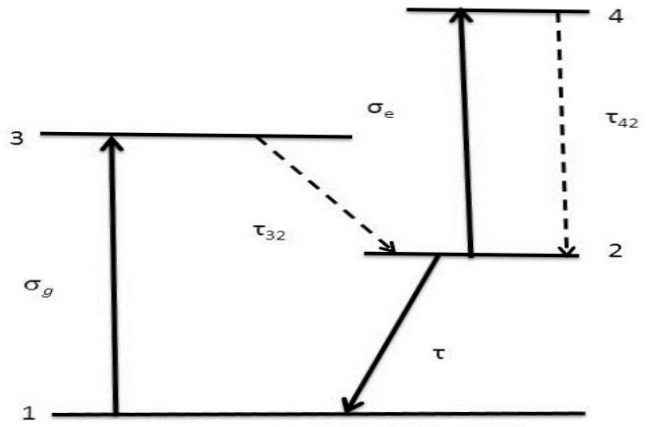

Figure.1: A theoretical consideration of Energy level scheme for a system with three successive absorption transitions,[28]

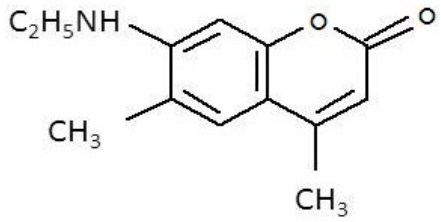

Figure.2: Structure of Coumarine-450

This implies that the ratio of excited state and ground state cross sections must be less than 10. There is also an intensity dependent phase shift that allows the optical bistability to exhibit. This phase shift is due to the contribution of non-resonant dispersion.

As the laser pulse width σ with is greater than τ at input intensities for above the ground state saturable absorption intensity and most of the dye population is in the metastable state and this population remains constant during the laser pulse. When the intensity inside the cavity (Ic) is much larger than the saturable absorption intensity, then N1<<N2 and consequently the steady state susceptibility is reduced to

$$\chi = N_1\chi^1 + N_2\chi^2 \sim N_2\chi^2 \quad \text{[6]}$$

Where χ^1 and χ^2 are the molecular susceptibilities of the respective levels.

Therefore the non-resonant susceptibility is proportional to the metastable state population and with the change in distribution a large phase shift change is observed,[23,30]

$$\chi = NPc(1 + Pc) - \chi^2 \quad \text{[7]}$$

where $P_c=I_c/I_s$.

With the increase in pump power, the excited state absorption process plays an important role and it decreases population of the upper level 2 and therefore the value of threshold pump power increases. Therefore, the storable absorption provides a population redistribution to observe the non-linear indeed of refraction and hence the optical bistability.

EXPERIMENTAL

Preparation of the samples

Chemicals used are spectroscopic grade obtained from Sigma Aldrich, C-450 (molecular weight 479.02) from Lambda Physics, U.S.A. are used as procured without further purification. Methyl methacrylate (MMA) is washed three times with 20% sodium chloride and 5% Sodium hydroxide solution to remove foreign inclusions till the solution is clear. A few pellets of anhydrous sodium sulphate are added to the MMA and kept for 24 hrs before filtration. As Coumarin dye has limited solubility in the monomer MMA, Methyl Alcohol is used as a solvent. For the preparation of dye doped samples, he monomer MMA is mixed with the dye dissolved Methyl Alcohol in the ratio 4:1. The addition of Methanol as a plasticizer also increases the laser damage threshold of PMMA. Further, one gram of benzyl peroxide per 100 ml of the solution is used as an initiator for polymerization. The monomer-alcohol mixture containing the dye and the initiator is put in covered glass tubes and kept in a constant temperature bath maintained at 50°C for polymerization. Necessary precautions like proper mixing of the dye solution in PMMA, temperature control etc is taken for homogeneous distribution of the dye in polymeric matrix. The completely polymerized samples (pure as well as dye impregnated of different concentrations) having dimensions 15x6x6 mm^3 are removed from the water bath after around 6 days.[31]

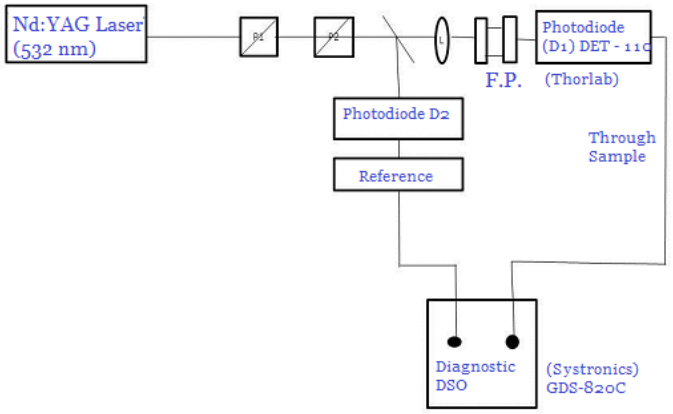

Figure 3: Block diagram for the study of optical bistability

To study the optical bistability the experimental set up suggested by Zhang et al,[32] is used. Figure 3 shows a set-up for the demonstration of optical bistability using a dye filled etalon. Nd:YAG laser: light source; P_1 and P_2: two polarizing cubes; L: lens; F.P: Fabry-Perot etalon (optical Bistable Device); D_1 and D_2; two silicon photodiodes; and DSO: Digital storage Oscilloscope.

A Nd:YAG laser operation at 532 nm with an output power of~6 MW is employed as the light source. The light Intensity is varied by modulator consisting of two polarizing cubes, P_1 and P_2 delivering a maximum laser power at the etalon. Fabry-Perot cavity is filled with a nonlinear dye doped sample to form an optical bistable device. A lens L is used to focus the laser beam on the dye medium. Two silicon photo cells, D_1 and D_2 are positioned to detect the incident light and output light power. The output from D_1 which monitors the intensity I_o, is connected to the digital storage oscilloscope.

RESULTS AND DISCUSSION

Absorption Spectra

Absorption spectra of the liquid and polymeric samples of various concentrations of C-540 are recorded by using Varian make (Carry-5000) UV-VIS-IR spectrophotometer. Spectra obtained are similar for all concentrations of both liquid as well as polymeric samples except a small blue shift in the peak wavelength in polymeric samples. A typical absorption spectra of both polymeric and liquid samples with concentration 0.1 mM each is shown in the figures 4 and 5.

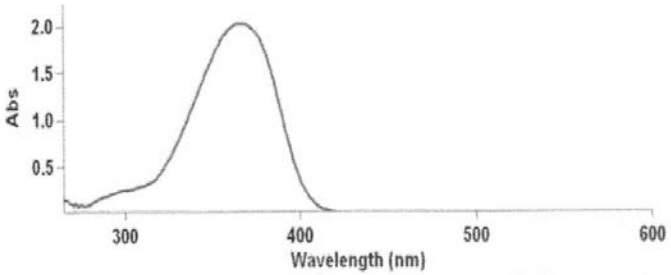

Figure.4: Absorption spectra of Liquid sample of concentration 0.1 mM.

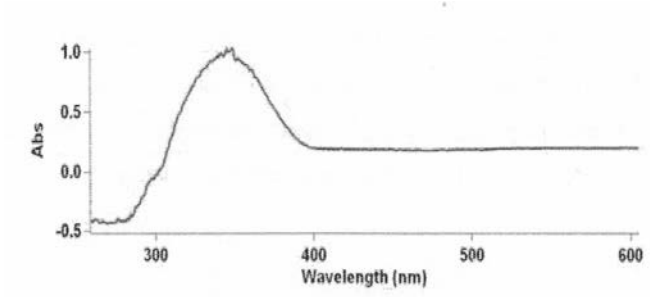

Figure.5: Absorption spectra of PMMA sample of concentration 0.1 mM.

It is understood that the Beer's law is observed at low concentrations and it is not obeyed at higher concentrations because of dimer of higher aggregate formations. Highly dimerised molecules exhibit non-linear absorption and they may set–up equilibrium between the dimmer and monomer and formation in liquid solutions while the restricted mobility of the molecules in PMMA may not allow such equilibrium. In order to observe optical bistabiltiy in a molecular absorber due to either saturation or excited state absorption one has to look for systems free of higher molecular aggregates. Therefore, the optical bistability response of a molecular absorber is expected to depend on the optical density of the medium,,[33] . The results of absorption spectra of doped PMMA samples show that the material is good candidate for the study of optical bistability using Nd:YAG laser, as is optically transparent at 532 nm.

Output-input characteristics of a bistable device

Optical bistability is exhibited by an optical device, which shows ideally two stable transmission values, T_1 and T_2 as a function of the input beam parameters, especially its intensity. Such device can be used for optical switching to obtain optical bistability and it requires an optical element and optical feedback.

These results of the output intensity as a function of incident intensity that crosses an unstable region between points 1 and 2, the output intensity jumps from point 1 to Point1' if the input intensity is increased and from point 2 to point 2' if the output intensity is decreased. At these points the transmission is changed rapidly. Thus the device is used for incident intensities between $I_{inc}/_{low}$ and $I_{inc}/_{high}$ for any kind of nonlinear effect that can be applied for such bistable optical device,[34]

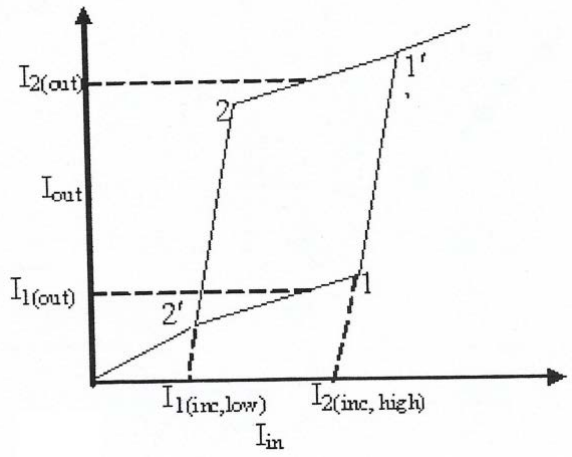

Figure. 6: output intensity of the beam verses input intensity

Empty cavity response at 532 nm is shown in figure 7 and figure 8 shows the results of the optical bistability in C-450 doped PMMA samples of different concentrations; 1.0, 0.10, 0.04, and 0.01nM.

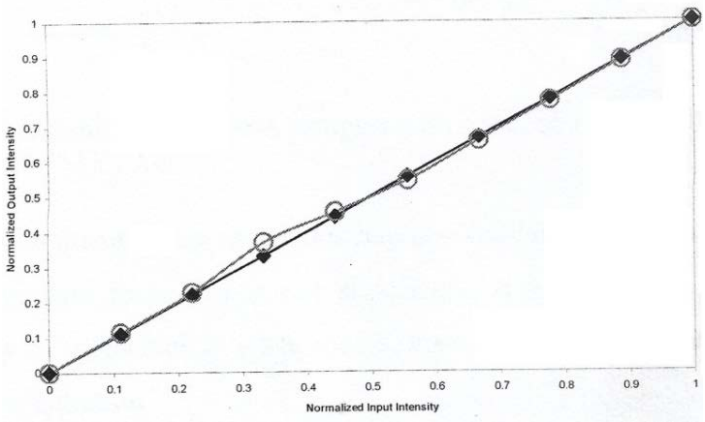

Figure. 7: Empty Cavity Response at 532 nm of Nd: YAG

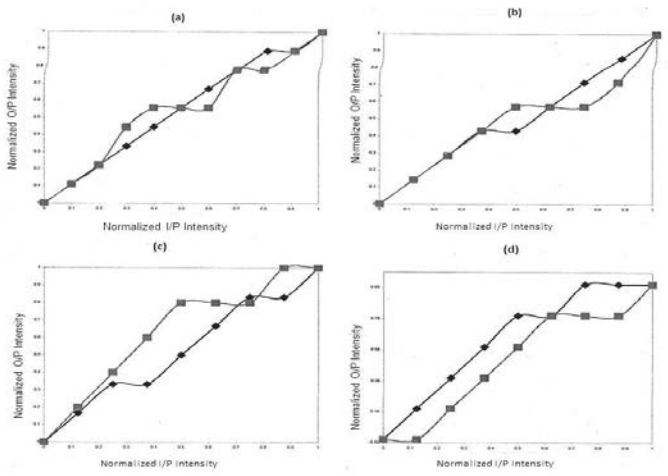

Figure. 8: Optical bistability of PMMA samples with concentration of (a) 1.0 (b) 0.1 (c) 0.04 and (d) 0.01 mM at 532 nm of Nd: YAg

As the environment of the molecules remains similar in the liquid and silica, it is expected that aggregate formation is not significant. It is further to add that due to restricted mobility of molecules in silica media, host aggregates are not formed even at slightly higher concentration.

Figure 8 depicts a hysteresis loop (two stages) observed in case of Coumarin- 450 doped samples of concentrations; 1.0, 0.1, 0.04, 0.01 mM, that is used to estimate nonlinear index of refraction (N2) by using the formula suggested by Zhang et al,[32]

$$n_2 \Delta I_o = \frac{\lambda}{2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [8]$$

The width between two adjacent hysteresis loops ΔI_o, corresponds to an optical path, the separation of $\lambda/2$ between two adjacent airy peaks. Thus the following parameters are shown in Table 1.

Table.1

Sr. No.	Concentration	Optical path length L (cm)	ΔI_o in W/cm^2	10^5 $n_2 = \lambda/2\Delta I_o L$ in 10^{-9} cm^2/W
1	1.00	1.203	0.160	1.384
2	0.10	1.309	0.160	1.271
3	0.04	1.301	0.194	1.053

During this study laser pulses with 5 ns time duration and repetition rate of 10 Hz were used. This repetition rate is sufficiently low to avoid sample overheating and accumulating effects. The orders of magnitude of the results for non-linear index of refraction are in good agreement as has been estimated by other researchers using z–scan technique particularly by Sunita et al.[31]

CONCLUSION

During the present course of investigations optical bistabiltiy phenomenon has been studied in organic dye molecules because the organic molecules satisfies the conditions of setting optical feedback provided by placing the nonlinear absorber inside a Fabry-Perot interferometer. The work presented in this chapter considers unique intensity dependence of the complex index of refraction manifested in the excited state absorption. Though different switching patterns have been reported by the various scientists, depending upon the particular switching parameter, viz. intensity variation, medium length, absorption coefficient etc, but the present work discusses the optical bistability characteristics depending upon the intensity variation.

The demonstration for optical bistability has been observed by optimizing the system by placing the dye solution of approximately ~ 1mM concentration in Fabry-Perot resonator and then by replacing the dye solution by solid material of dye doped silica materials synthesized by sol-gel technique. The method illustrates a Simple way to demonstrate the nonlinearity in optical materials by using a Nd:YAG laser operating at 532 nm with an output power of approximately ~ 6 MW. The experiment can be extended by using higher power lasers for obtaining better response from optical bistable devices. The interference fringes and hysteresis loops is loops fits many of the photo physical studies particularly the estimation of nonlinear refractive index of optical materials, that has been calculated during the present course of work.

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