# Nonlinear optical undergraduate experiments with porphyrin solutions and low power lasers

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Abstract. We present various nonlinear phenomena that can be visualized directly as variations of the beam cross section with laser beam powers beginning from a few miliwatts. Self-action effects like self-defocusing, and the measurement of the nonlinear refractive index can be performed using low power cw lasers and organic solutions of porphyrins. These experiments are suitable for undergraduate standard laboratories where nonlinear optical phenomena are to be demonstrated in a practical and simple fashion. Porphyrins solutions exhibit a sensitive photorefraction and are characterized by a large nonlinear coefficient.

Resumen. Presentamos varios fenómenos no lineales que pueden visualizarse directamente como variaciones de la sección transversal del haz de un láser cuya potencia es de sólo algunos milivatios. Algunos efectos de autoacción como autodesenfocamiento y la medición del índice de refracción no lineal pueden efectuarse usando láseres de onda continua de baja potencia y soluciones orgánicas de porfirinas. Estos experimentos son adecuados para laboratorios ordinarios de nivel de licenciatura donde se desea demostrar los fenómenos ópticos no lineales de una manera simple y práctica. Las soluciones de porfirinas exhiben una fotorrefracción sensible y se caracterizan por tener un gran coeficiente no lineal.

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## 1. Introduction

Nonlinear optics (NLO) is a field that arose largely due to the advent of the laser, with its characteristic high degrees of intensity, monochromaticity and directionality. Particularly, the very high power levels attainable by means of pulsed lasers were necessary to observe higher order nonlinarities that were too weak to be detected with thermal sources, even with presently available low power continuous wave lasers in commonly available non-linear optical materials. NLO research, on the other hand, is emerging as an interdisciplinary area of increasing importance for applications in optical computing and all-optical signal processing. Therefore, it is foreseeable that the educational aspect of this field be gaining increasing importance in the curricula of many careers including physics and engineering. However, the high cost of powerful laser systems and of sensitive materials, their complexity, and the safety considerations involved, have been an obstacle for bringing the simplest NLO phenomena to the undergraduate classroom or laboratory. Although the wealth of NLO phenomena is large, we are concerned here with those effects which are connected with changes in the real part of the [complex] dielectric constant.

Alternatively, these effects may be described by the dependence of the refractive index on the light intensity: $n_2 = n_0 + \gamma I$.

Unlike other NLO effects, such as harmonic generation and parametric conversion, where waves with very different frequencies exchange energy, we will consider self-induced effects by a wave that remains quasi-monochromatic; in this sense the interactions are sometimes termed degenerate. Our purpose here is to show that a number of demonstrations and laboratory experiments based on self-action effects can be implemented for the undergraduate, without sophisticated apparatus or expensive substances, but using commonly available low power cw visible lasers and porphyrin type dyes dissolved in organic solvents that are relatively easy to obtain. For instance, we observed evidence of self-defocusing with an average irradiance of approximately 6 watts/cm$^2$ produced by a 1 mW He-Ne laser at the focus of a 55 mm focal length lens. The medium being a solution of Manganese$^{III}$ Tetra phenylporphyrin Acetate, termed Mn$^{III}$:TPP[acetate] in acetone with a concentration by weight of the order of $10^{-5}$.

## 2. The nonlinear medium

Some liquids exhibit a refractive index that changes spatially with the presence of an intense laser beam. Intensity-dependent contributions to the refractive index may result from a variety of physical mechanisms. For a discussion of such mechanisms, the reader is referred to the literature [1–3]. A large contribution to the nonlinear refractive index, specially under continuous wave operation, is due to thermal effects. Heating of a medium by light absorption produces a change in the refractive index due to a change of molecular density in the medium. Initially, light is absorbed producing a large number of electrons in excited states. Subsequent decay to lower energy states produces temperature changes that eventually result in change of the refractive index. Media with large thermal nonlinearity are convenient for this purpose, although other artificial media posses a large nonlinearity too, such is the case of dielectric microspheres in suspensions [4]. Optical bistability experiments for educational purposes with solutions of laser dyes were also reported recently [5].

The use of substances of the porphyrin chemical complex for this application is a question that we would like to stress further.

Thermal nonlinearity in liquids has been known and understood for more than two decades. Using the fact that the refractive index change $\Delta n = \Delta T(dn/dt)$ and that the temperature change $\Delta T$ is proportional to the linear absorption coefficient $\alpha$, one obtains $\Delta n \propto \alpha(dn/dT)$. Therefore, liquids with large $(dn/dT)$ are expected to have a large thermal refractive nonlinearity. This can be achieved also by adding absorbing agents to increase their absorptivity in the spectral region of interest. In this respect, organic dyes like Porphyrins are suitable for this goal because they posses a large nonlinear refractive index when dilute in several organic solvents. By using this type of media it is not difficult to observe self-action effects, with a 5 mW He-Ne laser, as reported by Zhang *et al.* [6] using chlorophyll. Porphyrins are molecular analogue of chlorophyll, and they posses a nonlinear coefficient some 4 to 6 times larger than that of chlorophyll solutions [7]. Because of this significant thermally induced effect it is possible to use low power lasers to demonstrate nonlinear phenomena, in the milliwatt regime. The rationale of using this type of dyes resides also on their versatility. These compounds are often synthesized. In the process of synthesis it is possible to incorporate molecularly a metal atom (such as Fe, Ni, Co, Cu, Mn, Zn, V) at the center of the main porphyrin ring to produce a compound, metalloporphyrin, with drastically different spectral absorptance (see Fig. 1 in Ref. [7] and comments therein). Thus, by judiciously choosing the metal we can tailor the absorptance of our medium to a desired laser wavelength and power level in hand. Metalloporphyrins are dissolved easily by many organic solvents. We used acetone and chloroform in 1 cm cells with a concentration by weight of the order of $10^{-6}$ to a saturated solution. Note that the solvent can be chosen to enhance the effect in proportion to its thermal expansion coefficient.

## 3. EXPERIMENTAL

We arranged the experiments in order of increasing complexity.

a) Observation of self defocusing.

b) Interferometric observation of self-defocusing.

c) Measuring $n_2$.

d) A bistable Fabry-Perot interferometer.

a) Thermal defocusing can be observed using the experimental set up illustrated in Fig. 1. the laser beam is focused by the lens into a cell filled with the nonlinear medium $K$. The beam trajectory through a cell containing the nonlinear medium is shown with full trace and it features in increased divergence due to the induced negative lens effect. The dotted trace shows the beam trajectory when the cell contains the solvent only, which behaves linearly. The screen is used as an observation plane and may be substituted with a camera, the effect obtained is shown in Fig. 2. As the power of he incident beam is increased the added divergence produces a larger beam spot size. In this fashion, the array acts as a laser power monitor in real time. Variations of the incident flux will produce corresponding beam diameter changes. A plot of beam diameter versus incident power is desirable in this case for assessing the sensitivity of the technique.

b) The laser-induced change of refractive index can be measured interferometrically with the aid of a Mach-Zehnder interferometer, for example, as shown in Fig. 3. The cell containing the nonlinear solution is positioned in one of the arms of the interferometer. The interferometer is adjusted so as to produce straight parallel fringes, that serve as reference, when the pump beam is off. A low power He-Ne laser beam is used as the interferometer beam to probe the zone were the nonlinearity is produced. It must carry a much lower power than the pump beam to avoid introducing another nonlinearity in the medium. Figure 4 shows the fringe patterns produced under the action of the pump. The quantitative determination of the nonlinear index of refraction is obtained from the relation given by $n_2 = \lambda\Delta/2dE_0^2$, where $\Delta$ is the fringe shift, $\lambda$ is the wavelength of the laser beam, $d$ the length of the interaction region, and $E_0$ the field amplitude. The

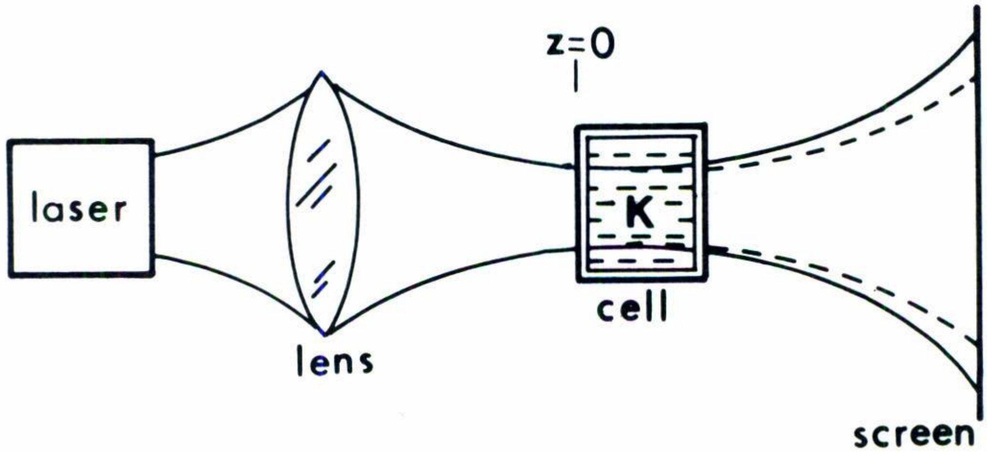


FIGURE 1. Experimental setup to show the diverging lens effects produced by a focused laser beam incident upon a Porphyrin solution with intensity dependent refractive index. The defocused beam is shown with full line. The dashed line shows the beam profile when the medium is linear, *i.e.*, when the cell contains solvent only.

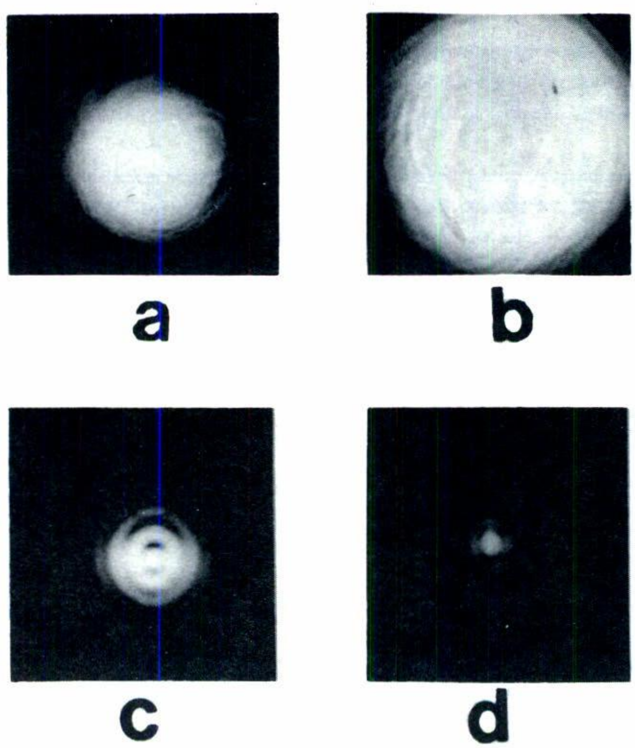


FIGURE 2. Beam patterns at an observation screen placed 15 cm from the cell. (a) Linear medium, (b) Self-defocusing. Here the beam waist is at the entrance face ($z = 0$), producing a maximum divergence. (c) Ring pattern produced when the beam waist is at the exit face of the cell, (d) Laser beam suffering spherical abberration. The waist is 3 mm outside of the exit face of the cell. These pictures correspond to a 10 mW incident power focused with a 55 mm focal length lens into a 1 cm cell.

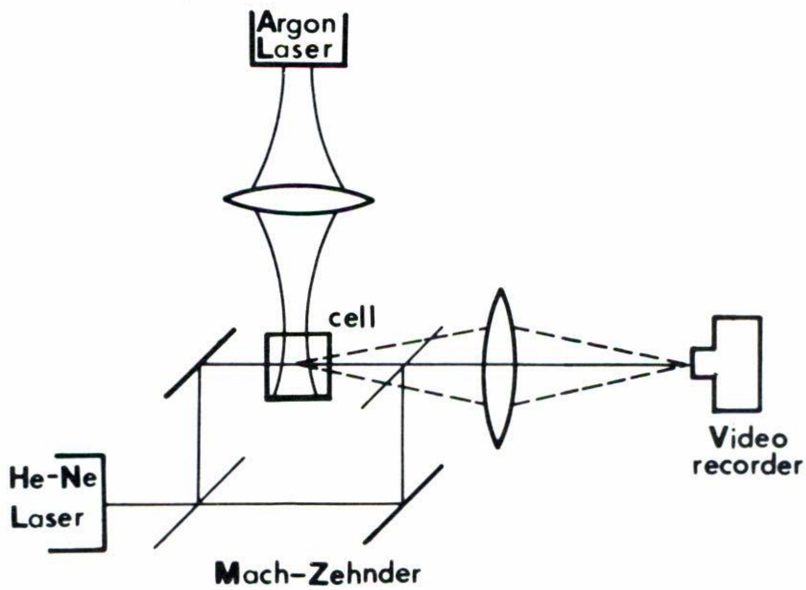


FIGURE 3. Measuring the nonlinear refractive index by means of a Mach-Zehnder interferometer. The beam of an argon laser is used as the pump. The index change is spatially and temporally monitored with a low power He-Ne laser, perpendicularly to the pump beam.

TABLE I. Nonlinear refractive index $n_2$ for meso-tetraphenylporphine and its transition metal complexes at Ar-laser wavelengths of 488 and 514 nm.

| compound[a] | $n_2$(esu) $\times 10^5$ | | $(n_2)$ rel[b] | |
|---|---|---|---|---|
| | $\lambda$488 | $\lambda$514 | $\lambda$488 | $\lambda$514 |
| Chlorophyll | 1.18 | 1.01 | 1.00 | 1.00 |
| $TPPH_2$ | 1.91 | 5.98 | 1.62 | 5.92 |
| $Mn^{III}TPP(CH_3CO_2^-)$ | 5.19 | 3.31 | 4.40 | 3.28 |
| $Fe^{III}TPP(Cl^-)$ | 2.36 | 2.07 | 2.00 | 2.05 |
| $Ni^{II}TPP$ | 1.18 | 0.84 | 1.00 | 0.83 |
| $Co^{II}TPP$ | 1.18 | 0.82 | 1.00 | 0.81 |
| $Cu^{II}TPP$ | 1.42 | 1.72 | 1.20 | 1.70 |

[a]TPP: Meso-tetraphenylporphyne (2-) ligand.
[b]Relative value referred to the $n_2$ of chlorophyll.

values obtained for different compounds are given in Table I. This experience results particularly appealing because it yields us the spatial index distribution within the medium in real time. The student can use this set up to measure the nonlinear refractive index interferometrically using the relationships given above.

Using this method the relative values of $n_2$ for different substances can be compared in straightforward manner by measuring fringe distortions solely. Another measurement of

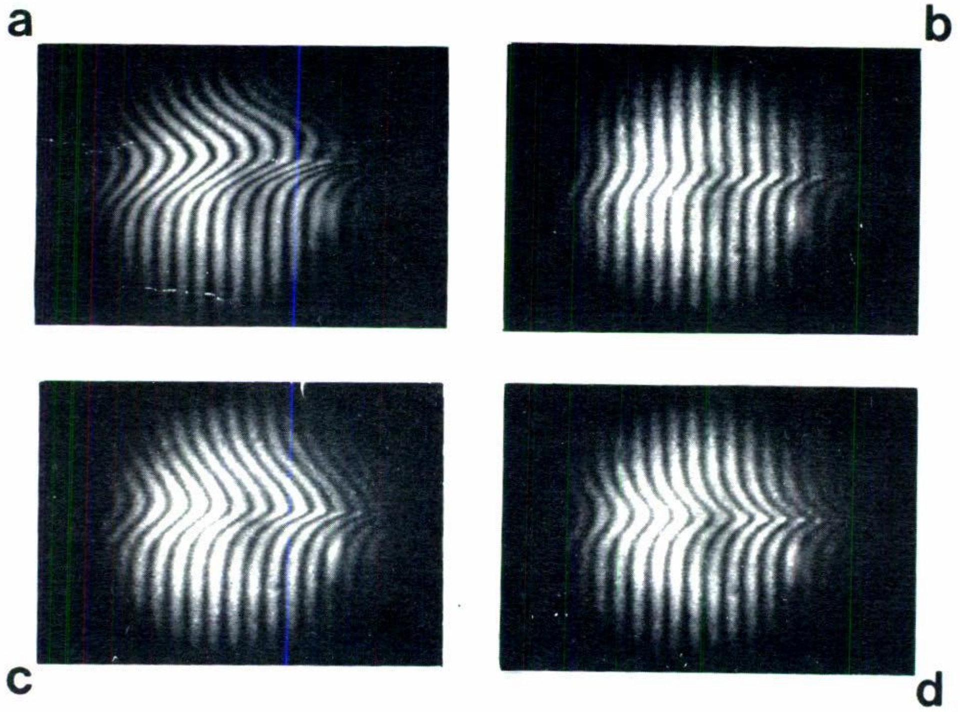


FIGURE 4. Mach-Zehnder interferograms showing the response of $[Mn^{III}:TPP](CH_3CO_2^-)$ to a 50 mW, 514 nm laser beam. In these pictures the pump beam enters the medium from the right-hand side. (a) and (c) show the development of a convection current. (b) shows a stationary pattern that turned stable in approximately 400 ms after laser turn on shown in (d). A fringe motion towards the right hand side indicated a decrease of the refractive index. An unperturbed medium showed straight parallel fringes whose separation was taken as the unit in fringe shift measurements.

interest is the time response of the medium which can be determined by recording the time evolution of the shape of a fringe, for example. In the case of our samples, their response constant is approximately 0.4 seconds, sufficiently slow to be noticed and followed by the eye.

c) The measurement of the nonlinear refractive index is a laboratory project in itself, and also an interesting parameter to determine in many substances. Numerous techniques exist for this purpose (see, *e.g.*, Ref. [8] and references therein) with various degrees of complexity. However, a simple yet sensitive method [8], that relies on the transformation of phase distortions to amplitude distortion during beam propagation seems appropriate for this level. This single beam technique is useful for determining both the sign and magnitude of refractive nonlinearities. In this technique the sample is moved along the $z$-direction (see Fig. 1) of a focused Gaussian beam while the laser emission is kept constant.

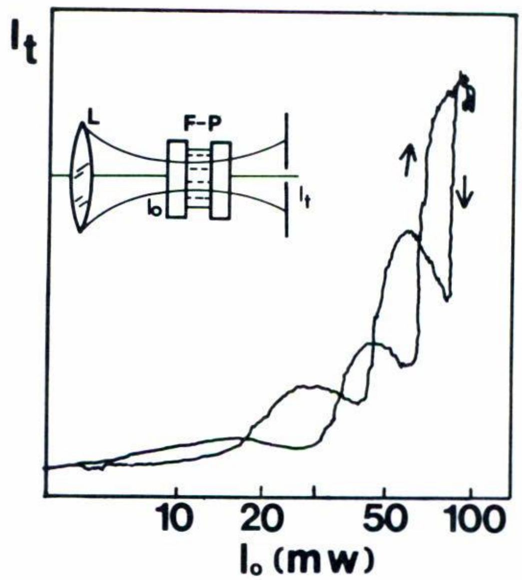


FIGURE 5. Optical bistability experiment with a student FP interferometer. The recorder trace was obtained with the experimental setup shown at the inset. The beam power is gradually increased up to 100 mW, then decreased. The incident flux and the on-axis transmitted intensity are simultaneously recorded. The curve shown was obtained with a FP whose mirrors had $R \simeq 80\%$, a 10 cm focal length focusing lens, and a 2 mm cell. The solution was $[Mn^{III}:TPP](CH_3Co_2^-)$ diluted in acetone with a concentration of the order of $10^{-6}$ by weight.

The resultant plot of transmittance through an aperture in the far field versus $z$, yields a dispersion-shaped curve from which $n_2$ can be calculated. The nonlinear index of refraction of the compounds of Table I were measured with the interferometric technique and in some cases the $z$-scan method was also used. The results agreed within the experimental error.

d) In another experiment the student places a cell with the solution between the mirrors of a Fabry-Perot (FP) interferometer. A recording of the on axis output power versus incident power shows bistability loops as shown in Fig. 5. The equipment used to obtain these curves includes a regular student interferometer with FP optics; A variable power $Ar^{3+}$ laser capable of producing controlled emission from 0 to 100 mW. If the laser power control is unavailable, an otherwise nominally constant flux laser would have to be continuously modulated or attenuated to show the loops. If very precise measurements are intended in this experiment, care should be taken to ensure a minimum air spacing inside the cavity for air would contribute additional third-order nonlinearity. The quantitative information that can be obtained in this experiment include the trace of Fig. 5 which can be compared with the theoretically calculated.

## 4. CONCLUSION

In summary, we presented a set of experiments that should provide the student with a lively experience of the concepts of intensity-dependent index of refraction, self-action effects, and optical bistability. The necessary experimental equipment and substances are unsophisticated, and are generally available in undergraduate laboratories, or hobbyist's shop. We hope that the realization of the experiments outlined here would help to bring the excitement of nonlinear effects to the undergraduate student and to the general public as well.

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