CHAPTER II

Measurement Techniques for Nonlinear Optical Effects in Engineering Applications

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Introduction

There is a great deal of interest in discovering materials having significant yet fast nonlinearities. As a result, this database requires expansion. Throughout the book section, methods for determining nonlinear coefficients are described. This interest, which is largely motivated The look for materials for applications such as sensor protection and all-optical switching results in two categories: nonlinear absorption (NLA) and nonlinear refraction (NLR). In many situations, the database for nonlinear optical characteristics of materials, particularly organic materials, is insufficient for establishing trends to guide synthesis efforts.

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Organic nonlinear optics offers numerous exciting opportunities for basic study as well as real-world applications. Similar to other high-tech industries microelectronics and genetic engineering are two examples. Technical and scientific advances are likely to interact fundamentally in a way that promotes improvements in the other. Nonlinear optical phenomena, for example, are increasingly being used in optical and laser technology.

Methods for Studying of Optical Nonlinearity of Materials Applications

Certain methodologies are used in practice to explore one or more nonlinear effects. One of these methodologies, Z-scan methods, is particularly well suited for the simultaneous investigation of two nonlinear phenomena, nonlinear absorption and nonlinear refraction, both of which are related to material dielectric permeability. This technique has been updated in two ways: open aperture Z-scan is used to examine optical nonlinear absorption, and closed aperture Z-scan is used to study material nonlinear refraction.

- Degenerate Four Wave Mixing, DFWM: Used to measure the amplitude of a third order nonlinear response.
- Third Harmonic Generation: Only used to measure third order nonlinearity.
- Z-Scan: Used to determine the magnitude and sign of third order nonlinearity.
- Electro-absorption method: This approach is used to study third order nonlinearity dispersion.
- Time-Resolved Optical Kerr Effect and Transient Absorption Techniques: These techniques are used to present photophysical processes that determine nonlinearity.

A z-scan measurement is used in nonlinear optics to determine the nonlinear index n_2 Kerr nonlinearity and the nonlinear absorption coefficient using the "open" and "closed" approaches,

respectively. Because nonlinear absorption might impact nonlinear index measurement, the open approach is commonly used in conjunction with closed technique to correct the computed value (Artkin F., 2014).

Degenerate Four Wave Mixing (DFWM)

Essentially, the physical explanation of degenerate four-wave mixing is comparable to that of harmonic generation, also known as frequency mixing. The distinction here is that three spatially distinct waves of fields E1(ω,t), E2(ω,t), and E3(ω,t) at the same frequency ω interact to produce a fourth wave, E4(ω,t), in an alternate direction of transmission, yet at the same frequency.

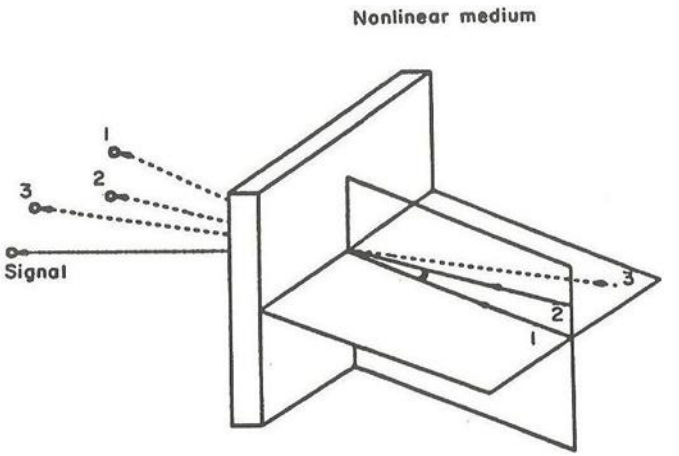


Figure 1. The illustration shows beams for degenerate four-wave mixing in the forward-wave setups.

The lightwave intensity variation along the propagation distance is negligible on the scale of light wavelength, and negligible pump beam depletion. The phase-matching condition $k_1 + k_2 + k_3 + k_4 = 0$ is likewise yielded by the wave equation, just like in the case of harmonic creation. Various beam geometries have been employed in degenerate four-wave mixing (DFWM) applications. Figures 1 and 2 show off the two common geometries. The forward-wave geometry configuration is depicted in Figure 1, where the incident

beams (E1, E2, and E3) are all traveling moving in the same way from right to left. It also displays the output beam's (signal's) phase-matched direction. In Figure 2, a backward-wave geometry is depicted. The forward and backward beams, Ef and Eb, are represented by beams E1 and E2, respectively, while the probe beam, Ep, is represented by beam E3, which is incident at a tiny angle θ with respect to E1. Since kf = - kb in this geometry, ks = kp would be necessary for the phase-matching requirement. Stated differently, in Figure 2, the phase-matched signal will be generated counterpropagating to the probe beam.

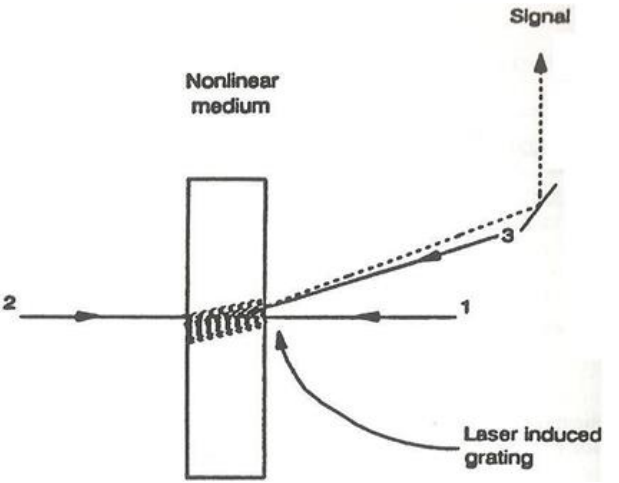


Figure 2. Diagrams showing the four beams in the backward-wave configuration for combining degenerate four waves.

Optical phase conjugation and the reverse wave geometry technique of DFWM are interchangeable (Fisher, R.A., 1983). They create a phase conjugate mirror, is taken into consideration in this respect. When a probe beam impacted on it, it can exchange energy with the other beams but is reflected back to retrace itself. The conjugate of the probe beam Ip is known as the signal Is. As a result, beam Is reconstructs any phase distortion experienced by the probing beam Ip. Dynamic holography with great contrast may be achieved with this approach. The effectiveness of the DFWM process is

commonly expressed in terms of nonlinear reflectivity R = Is/Ip in the phase-conjugation image. The following expression for the reflectivity R results from solving wave equation 1 (Yariv, A., 1978). Under the assumptions of a weak probe beam field Ep, minimal pump beam depletion, and uniform pump amplitude along the probe beam's interaction path length:

$$R = \tan^2(k|E_f E_b|l) \quad (1)$$

The overall appearance of a laser-induced grating may also be utilized to grasp the DFWM process cognitively (Eichler, H., et al., 1986). In this case, intensity modulation is caused by the relationship between a material's two coherent beams. Because a nonlinear medium's intensity changes its refractive index, the result is index modulation, This is just a diffraction grating. When the real component of the refractive index of a material with a complicated refractive index is changed, a phase grating is created (Fayer, M. D., 1982). The refractive index's imaginary component is present when changed, an amplitude grating is created. In the event of a DFWM with a reverse wave form, each two-beam pair generates three distinct gratings, However, only two of these gratings are present, provide phase-matched conjugate signals (Shen, Y.R., 1984).

Third Harmonic Generation (THG)

When the phase velocities of the fundamental and third-harmonic waves are the same. Fundamental and third-harmonic wave phase velocities, however, differ due to dispersion in the refractive indices (i.e., $n_{3\omega}$ and n_{ω} are, generally, different). As a result, $I_{3\omega}$ experiences damped oscillations for phase mismatch finite values, reducing based on its worth at $\Delta k = 0$.

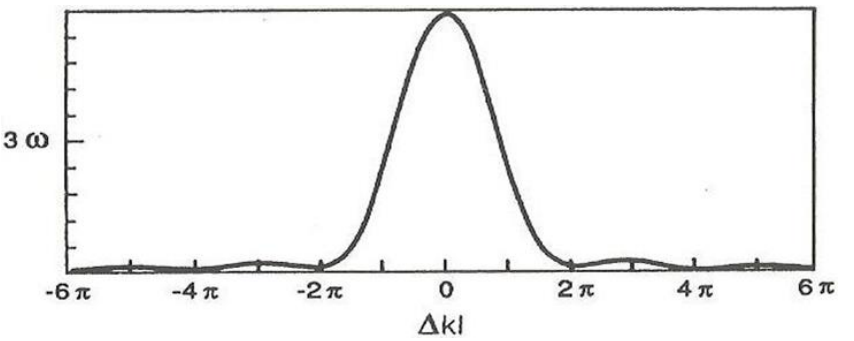


Figure 3. Plotting the third-harmonic intensity, $I_{3\omega}$, for every unit, Δk, as a function of Δkl.

$\Delta k_{1/2}$, the whole value of $I_{3\omega}$, is a helpful measure for an acceptable wave-vector mismatch in a medium that allows a significant amount of third-harmonic production. The value of this quantity is (Reintjes, J F., 1984).

$$\Delta k_{1/2} = 5.6/\, l \qquad (2)$$

The intrinsic birefringence of anisotropic media, such birefringent crystals, able could be applied for phase matching, as is the case for effective second-harmonic production. For instance, one can decide on a propagation direction for which where amazing and ordinary rays are denoted by the letters e and o. However, owing to the fundamental and third harmonic waves have radically different frequency values and there is inadequate birefringence, it is extremely difficult to accomplish

$$ne(3\omega) = no(\omega) \qquad (3)$$

Phase matching for the practical generation of third harmonics in a crystal. To the best of our knowledge. As far as we know, no crystal has been shown to exhibit phase-matched third-harmonic generation.

Dispersion effects on refractive index prevent phase matching in pure isotropic media, such as liquids, gases, or amorphous polymers. Nonetheless, combining two isotropic media

A and B (such as two gases) might theoretically result in phase matching (Reintjes, J F., 1984). So that

$$n_A(\omega) + n_B(\omega) = n_A(3\omega) + n_B(3\omega) \quad (4)$$

As a result of the normal dispersion relation, $n(\omega) < n(3\omega)$. In order for equation 4 to hold, one of the materials must compensate for $n_B(\omega) < n_B(3\omega)$ and display anomalous dispersion, which characterizes the condition $n_A(\omega) > n_A(3\omega)$. Alkali metal vapors have been known to exhibit this kind of anomalous dispersion (Reintjes, J F., 1984), (Bloom, D. M., 1975).

If phase-matching is not present, the interaction length can be changed to maximize third-harmonic generation. When the interaction length is altered, either by translating a wedge-shaped sample or rotating the sample as in the Maker fringe approach, the harmonic intensity oscillates for a fixed value of Δk. The coherence length Ic is given by (Reintjes, J F., 1984) as follows:

$$I_c = \pi/\Delta k \quad (5)$$

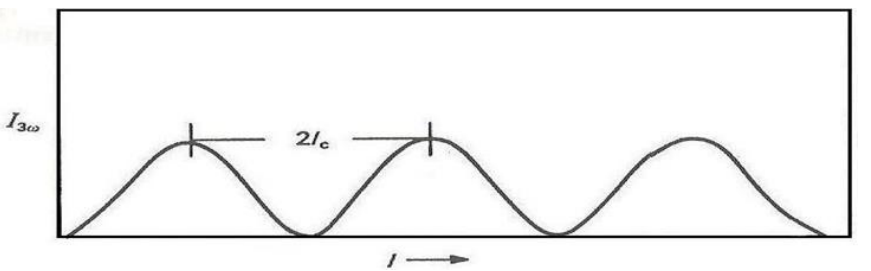


Figure 4. To alter the route length l, the wedge fringe pattern for the third-harmonic signal $I_{3\omega}$ which is acquired as a sample, is translated.

A fringing curve describes the oscillatory behavior of $I_{3\omega}$ when the interaction duration is varied. When a wedge-shaped sample is translated, the interaction length changes, resulting in the wedge fringe pattern seen in Figure 4. Harmonic creation, or, more broadly, frequency mixing, is a coherent process as there's a clear

correlation between the phase of the input waves and the out wave generated at the new frequency.

Z-Scan

The Z-scan technique has become a standard for isolating the nonlinear variations in absorbance and index and has been rapidly embraced by the nonlinear optics community. Generally speaking, Any nonlinear optical method that alters the absorption coefficient and/or refractive index can be detected using a Z-scan approach making it impossible to identify the underlying physical processes that are present (Paras N. Prasad., et al., 1991).

A nonlinear sample causes a change in the overall refractive index that is proportional to both the nonlinear refractive index of the material and the beam intensity as it passes through it. This leads to the following modification in the most basic scenario, when there are just third-order nonlinearities:

$$n = n_0 + n_2 I \quad (6)$$

In this case, I represents the excitation intensity, The linear refractive index is denoted by n_0, the third-order nonlinear refractive index by n_2, and the overall refractive index is represented by n. When a lens is applied to a Gaussian incoming beam, the intensity profile of the beam will cause a nonlinear refractive index change in the profile of the beam. Consequently, a refractive index lens is being produced in the nonlinear medium by the beam propagation.

Sheik Bahae et al.'s (M. Sheik-Bahae et al., 1990) transmission Z-scan technique is a simple and accurate single beam methodology for detecting the amount and sign of the real and imaginary components of third order nonlinear susceptibility.

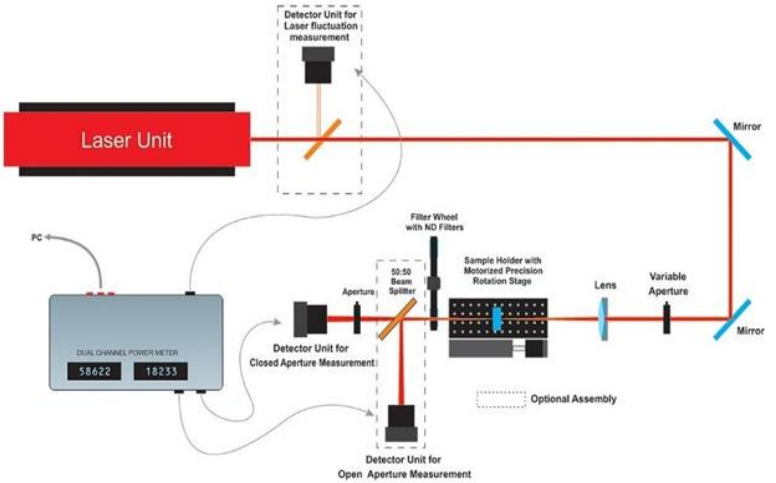


Figure 5. Experimental Z-scan setup (holmarc.com, 2023).

The foundation a lens's focal plane (the focusing lens L1 in Figure 5). A detector positioned behind the sample in the far field with an aperture in front of it (closed aperture Z-scan) tracks the refractive index lens effect as the sample moves. As a result, the sample's varying focusing/defocusing caused by the light-induced lens is assessed. The focusing lens, the translation stage, the three primary components are the detector, the detector, and the detector of the experimental setup for transmission Z-scan investigations, which is shown in Figure 5.

Electro-absorption Method (EA)

An effective method for examining a material's third-order nonlinear optical susceptibility $\chi^{(3)}$ dispersion is electro-absorption (EA) spectroscopy. It modifies a material's absorption spectra by applying an electric field, revealing details about alterations in the material's optical and electronic structure.

The electrons in the material interact with this electric field. This is noticed as a shift in the transmitted light's intensity at various wavelengths. The EA spectrum is useful for figuring out the

distribution of $\chi^{(3)}$ over a variety of wavelengths. The third-order nonlinearity dispersion of many different materials, such as organic semiconductors, polymers, nanomaterials, and quantum dots, has been extensively studied using the EA approach. New materials with improved nonlinear optical characteristics for use in optical communications, lasers, and other technologies can be developed using the data gathered from EA experiments.

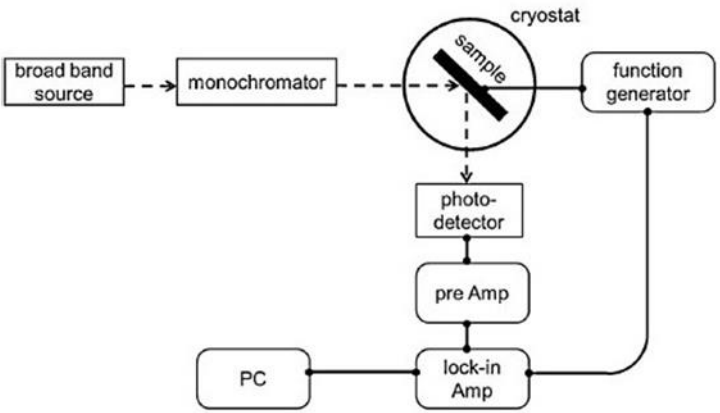


Figure 6. Diagram showing the Electro Absorption (EA) spectroscopic setup (Lai T.H., et al. 2013).

The EA spectrum is frequently analyzed using the Kramers-Kronig relations. It measured absorption change, these relations help distinguish the real and imaginary components of $\chi(3)$. Additional nonlinear optical characteristics, such as the nonlinear susceptibility of second order $\chi^{(2)}$, can also be studied using the EA approach. The EA approach comes in a variety of forms, each having pros and cons of its own. Photocurrent spectroscopy (PCS), differential electro-absorption (DEA), and linear electro-absorption (LEA) are a few popular versions.

To sum up, the electro-absorption technique is a useful instrument for researching the dispersion of materials with third-order nonlinearity. It gives researchers a way to quantify the alterations in electronic structure and optical characteristics brought

about by the utilization of an applied electric field, important information for creating novel materials with improved nonlinear optical functions **(**Lai T.H., et al., 2013; Loukos, P., et al., 2014).

Time-Resolved Optical Kerr Effect and Transient Absorption Techniques

Transient absorption (TA) and time-resolved optical Kerr effect (OKE) are two effective methods for examining the ultrafast dynamics of materials, especially in condensed phases. These methods provide complementary insights into molecular interactions, structural alterations, and excited state dynamics. In isotropic materials, A third-order nonlinear optical phenomenon is the OKE. The material becomes optically anisotropic upon contact with power laser sources, leading to a transient birefringence. The laser pulse's electric field produces the atoms in the material to distort their electron clouds, which results in a transient dipole moment and birefringence.

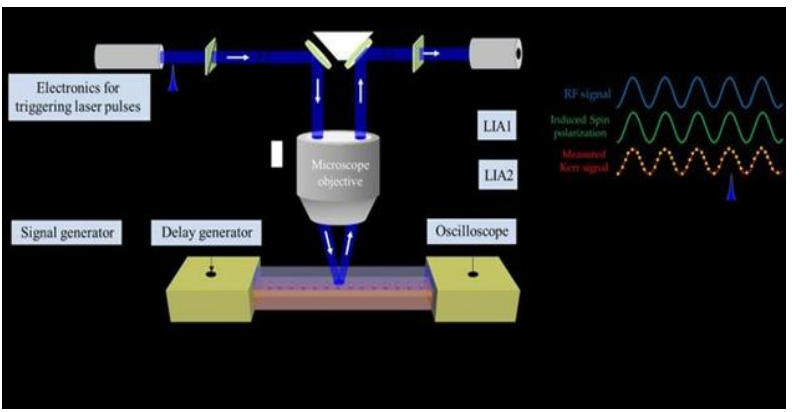


Figure 7. Transverse magneto-optical Kerr effect measurements with time resolution (TR-TMOKE) experimental configuration (Auvray F., et al., 2018).

OKE has a number of benefits. High temporal resolution: femtosecond timeframe dynamics may be measured. Non-invasive: No modifications or changes are required to the sample. Sensitive to

a variety of phenomena: It may examine structural alterations, vibrational motion, and changes in electronic structure. Also, OKE has some restrictions: Restricted spectral range: It usually extends only to the near-infrared spectrum. Indirect measurement: It excited state dynamics, more analysis is necessary as the refractive index variation affects the signal that is captured.

Using transient absorption spectroscopy, one may quantify a material's change in After being stimulated by a laser pulse, absorption occurs. The creation of excited states and environment cause this shift in absorption. TA measurements consist of: Pump pulse: The material is energized and excited states a femtosecond laser pulse produces. Probe pulse: The excited state population is examined by a weaker probe pulse that. Measuring the change in absorption: OKE and TA are two effective methods for examining the ultrafast dynamics of substances. Which method you chose to use will rely on the specific facts you are looking for.

In several instances, the combined use of OKE and TA yields a thorough understanding of a material's ultrafast dynamics. For instance, While OKE certain excited state species may be tracked using TA (Hosung, K., et al. 2021).

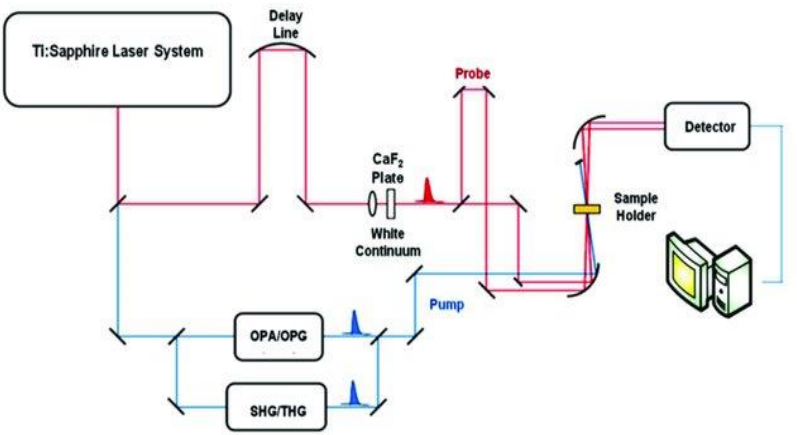


Figure 8. Diagram showing the general setup for Transient Absorption Spectroscopy (TAS) (Patrizi B., 2020).

Conclusion

Exciting opportunities arise from nonlinear optical phenomena for a variety of sophisticated technologies, from innovative materials with specialized features to all-optical signal processing. Precisely quantifying these impacts is essential to comprehending their fundamental physics and maximizing their utilization.

This review examined many methods that are often used to quantify nonlinear optical characteristics. It particular impact being researched, as well as required degree of precision and sensitivity. A straightforward and sensitive technique for figuring out optical coefficients, such as nonlinear refraction and nonlinear absorption, is the Z scan approach. Because of the ease of use and low cost of execute, it is extensively employed. In conclusion, precise and dependable measuring methods are crucial in the study of nonlinear optics. It is essential for researchers to comprehend their particular requirements and to successfully explore and make use of the intriguing phenomenon of nonlinear optics. This evaluation has focused mostly on third-order nonlinear effects. Higher-order nonlinearity measurement techniques are also available and under development. Aside from performance, other considerations that may impact the measuring technique choice include equipment availability, cost, and complexity. The limits can be measured are continually being pushed by developments in laser technology and apparatus, As a result, more complicated and sensitive measurement techniques have emerged.

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