

PERIODIC NONLINEAR REFRACTIVE INDEX OF CARBON DISULFIDE VAPORS

by

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A thesis submitted in partial fulfillment of the requirements
for the Honors in the Major Program in Physics
in the College of Sciences
and in the Burnett Honors College
at the University of Central Florida
Orlando, Florida

Spring Term, 2014

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ABSTRACT

The purpose of this thesis is to explore the nonlinear refractive index of carbon disulfide vapors as opposed to its liquid form. With CS₂ vapors, the vapors are less dense so they will rotate longer than liquid CS₂ because there are less intermolecular interactions. The electric field of the beam causes the molecules to align with the electric field and applies a torque to the molecules. After this excitation, the molecules continue rotating. The rotations change the index of refraction of the material. Continuous rotation of the molecules causes the index of refraction to be periodic which means the molecules are going through multiple revivals. I will analyze this periodic nonlinear index of refraction. However, some problems occurred while the experiment was being done as well as some issues of measuring CS₂ because of white light continuum generation in the cell walls. To avoid these issues we measured the air in the lab and were able to observe the periodic change of index of refraction for O₂ and N₂.

DEDICATION

For my loving parents
my brother, Quinn
my sister, Ruby
and supportive boyfriend, Kevin.

ACKNOWLEDGMENTS

I am grateful to Dr. Hagan and Dr. Van Stryland for allowing this great learning experience and opportunity. They helped me to achieve my dream of working in CREOL and without Dr. Hagan's suggestion to write this paper I would not have had this amazing research experience.

Thank you to my group members that have helped me along the way: Trenton, Matt, Jenn, Peng, Manny

Thank you to my high school Physics teacher who sparked this interest and without him I would not be studying this beautiful science.

I would also like to thank my Dad for helping me throughout college and always being extremely supportive of my goals.

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Introduction

Much research has been done on the nonlinear optical (NLO) properties of Carbon Disulfide (CS_2) in liquid form. However, little work has been done on gaseous CS_2 vapors. Therefore, I want to differentiate the third order nonlinear refraction (NLR) of the vapors from the liquid by studying the NLO properties, specifically the NLR of CS_2 vapors. The molecules behave differently when in a liquid form than when in a vapor form, causing the dynamics of the NLR to change between forms. CS_2 is a symmetric molecule making it simple to examine and its interaction with light can also be simulated classically. It has a carbon atom bonded to two sulfur atoms by double bonds, making the molecule centrosymmetric and linear. Since the molecule is symmetric, as shown in Figure 1a, the electrons are evenly distributed throughout the molecule. Therefore, it does not have a permanent dipole moment [1]. Once introduced to an electric field, a dipole moment will be induced by the field which ultimately causes the molecule to reorient with its long axis, the longitudinal axis, parallel to the applied field [2]. If a pump beam reorients the molecules, a probe beam can monitor this reorientation. In liquid form, the molecules interact with other molecules rapidly because they are close together and this interaction causes the molecules to stop rotating [3]. However, in the vapor phase where intermolecular interaction is minimal, the probability of molecules colliding is much lower, thus allowing them to rotate for a longer duration of time before the next collision and therefore do not stop rotating as quickly as in the liquid form.

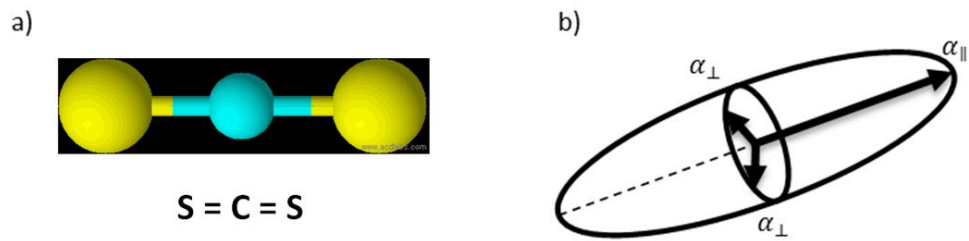


Figure 1 a) A diagram of the CS₂ molecule; b) The CS₂ molecule with the corresponding transverse and longitudinal polarizability [1].

Significance

My purpose for performing this experiment is to determine the different behaviors that CS₂ in vapor phase show when introduced to optical electric fields compared to their liquid counterparts. There have been few measurements of optical nonlinearities of vapors. Using a newly developed Optical Beam Deflection technique [1], explained in a subsequent section, I should be able to measure the NLR of CS₂ vapors. The beam deflection technique offers unique advantages as it offers time dynamic NLR, the polarization of the two beams used can be changed with respect to one another, and the beams can be non-degenerate. Ultimately, however, finding the nonlinearities of dilute materials, such as CS₂ vapors, could possibly lead to the exploration of atmospheric gas nonlinearities. “The nonlinear responses of atmospheric gases are of interest because they can lead to applications such as remote sensing, spectral broadening and shaping of ultrashort laser pulses, terahertz generation, and guiding of electrical discharges” [9].

Hypothesis

In equilibrium, the molecules will be randomly oriented until an electric field is applied. As stated above, the liquid molecules collide with each other. Since vapor is not as dense, the

molecules are more spread out allowing them to reorient freely. This will cause them to continue to rotate until they collide with each other or collide with the walls of the cell, which will occur less frequently than in the liquid form. As the molecule rotates, it aligns parallel with the electric field and also aligns perpendicular to the electric field and will continue in this cycle as shown in Figure 2. The NLR depends on the electric field interacting with the electrons in the molecule. The NLR will increase as the molecules align parallel to the electric field and decrease as it becomes perpendicular to the field. Due to this, the change in NLR should be periodic [4]. In addition to measuring the NLR, I can also extract the time it takes for the molecules to decay and randomly realign, once they have interacted with other molecules to keep them from rotating. This is known as the decoherence time [4].

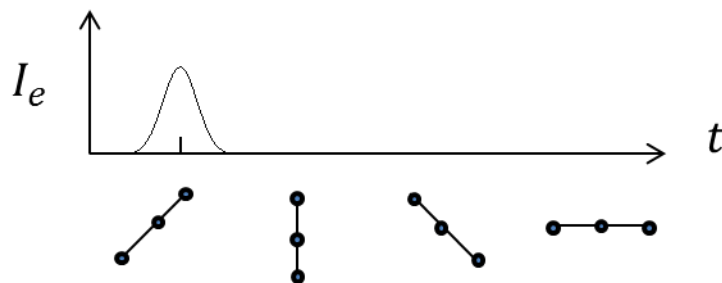


Figure 2: Diagram of the excitation pump acting on a “randomly” oriented molecule, which is shown as 45° for simplicity, and the progression of the rotation of the molecule rotating where the top Sulfur atom is moving counterclockwise in space and time. The rotation of the molecules is dependent of the irradiance of the beam, therefore the axis shows irradiance against time.

Definitions of terms

The index of refraction is defined as $\eta = n + i\kappa$, where the real part, n , is the linear index of refraction :

$$n = \sqrt{\frac{1}{2}(|\epsilon_r| + \text{Re}(\epsilon_r))} \quad (1)$$

and the imaginary part , κ , is related to the absorption coefficient α ,

$$\alpha = \frac{4\pi\kappa}{\lambda_0} = \frac{4\pi}{\lambda_0} \sqrt{\frac{1}{2}(|\epsilon_r| - \text{Re}(\epsilon_r))}, \quad (2)$$

where λ_0 is the wavelength in vacuum and ϵ_r is the relative permittivity of the material. Once third order susceptibility are involved there are different indexes of refraction which are no longer linear. The nonlinear index of refraction is represented by n_2

$$n_2(\omega_p; \omega_e) = \frac{1}{2n^2 c \epsilon_0} \text{Re} \left(\chi^{(3)}(\omega_p; \omega_e) \right). \quad (3)$$

Once the nonlinear refractive index is known for the material you can also analyze it based on the polarization of the beam. For a co-polarized case, the nonlinear index of refraction by $n_{2,\parallel}$

$$n_{2,\parallel}(\omega_p, \omega_e) = \frac{N}{n^2 \epsilon_0^2 c} \frac{(\bar{\alpha}_{\parallel} - \bar{\alpha}_{\perp})^2}{45k_b T} f^{(1)4}. \quad (4)$$

and for the cross polarized case you represent it by $n_{2,\perp}$

$$n_{2,\perp}(\omega_p, \omega_e) = -\frac{N}{n^2 \epsilon_0^2 c} \frac{(\bar{\alpha}_{\parallel} - \bar{\alpha}_{\perp})^2}{90 k_b T} f^{(1)4} = \frac{1}{2} n_{2,\parallel}(\omega_p, \omega_e), \quad (5)$$

where ω_p is the probe frequency, ω_e is the pump frequency, ϵ_0 is the permittivity of vacuum, c is the speed of light, N is the number density of molecules, k_b is Boltzmann constant, and $\bar{\alpha}_{\parallel}$ is the longitudinal polarizability and $\bar{\alpha}_{\perp}$ is the transverse polarizability.

Polarizability relates an induced dipole moment to the applied electric field [5]. As the electric field is applied, it interacts with the molecules' electrons and the electrons move in the opposite direction as compared to the electric field. This creates a dipole moment.

Polarizability is shown by the equation

$$P(t) = \epsilon_0 \chi^1 E(t) \quad (6)$$

the permittivity of free space. χ^1 is the first order, linear, electric susceptibility that describes the ease of polarization of a charge in a specific medium when a field E is applied. $E(t)$ is the applied electric field and $P(t)$ is the induced charge polarization. In the classical analogy, the electrons move along their imaginary spring away from the nucleus. The further away they get from the nucleus the larger the polarization, which can become nonlinear the further away from equilibrium.

Methodology

The beam deflection technique, depicted in Figure 3 and outlined in Refs. [1], was preferred in this experiment for many reasons. Beam deflection uses a pump beam, also called the excitation beam, and a probe beam, which is significantly weaker than the excitation beam. Having two beams allows for measurement of non-degenerate NLR which means that one beam will have a different energy, therefore different frequency, than the second beam. Time dynamics can also be measured using the beam deflection technique, which helps determine decoherence time and the rotational constant.

In beam deflection, the induced polarization from the pump beam creates a dipole in the molecule which is reoriented by the electric field. Measuring CS_2 vapors there will be a negligible amount of absorption measured, so NLR will strictly be measured. The pump meets the sample at a small angle to the probe. Meeting at a small angle allows separation of the pump beam from the probe beam incident on the detector. An aperture placed before the detector allows for the pump beam to be blocked but allows the probe beam to be detected. The change in NLR can only be observed when the pump and probe are spatially and temporally overlapped within the sample.

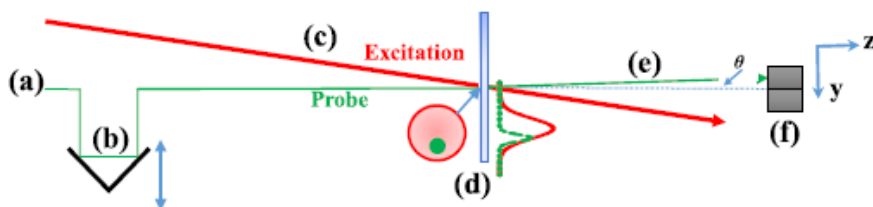


Figure 3:Diagram of the Excitation and Probe beam set up, where a) is the probe beam, b) delay line, c) excitation beam, d) sample and where the pump and probe overlap, e) deflected probe beam to show the nonlinearity, f) quad cell detector, and θ is the deflection angle [1].

The probe beam must be much less intense than the pump beam for this experiment. After a single beam comes out of the laser at 800nm a beam splitter was used to get two separate beams. The weaker beam from the two was used as the probe. The probe beam was then directed into a lens followed by a water cell to generate white light. This created the visible spectrum from a single beam which allowed us to filter out 650nm as the probe's wavelength. The stronger beam was then aligned through mirrors and apertures to reach the sample.

Ultimately, when the pump beam and the probe beam hit at the stage which held the sample, they were overlapped temporally and spatially. Once overlapped temporally, zero delay can be found. Zero delay was found using (SiNc). SiNc (silicon 2, 3-naphthalocyanine) is an organic dye with a long lifetime. After the pump excites the electrons in the sample of SiNc, they stay excited long enough for the probe's transmission to be effected by the excited electrons which is then detected.

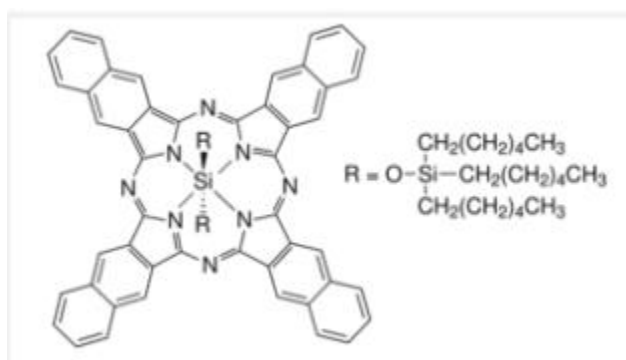


Figure 4: molecular structure of SiNc (Sigma- Aldrich)[8]

The probe beam met at the material and saw a 'prism-like' effect and is then deflected [1]. There was temporal overlap so that they arrive at the sample at the same time using spatial translation stages for example 1 mm delay is ~3.3 ps of temporal delay since light travels at

$3 \times 10^8 \text{ m/s}$. Lock-in amplifiers are also used to filter out the noise so the probe signal, which is small, can be detected [1]. The Lock-in reads the frequency that the chopper was set to. The chopper rotated at a certain frequency, in this case 285 Hz, so that any scattering from any other source at different frequencies could not be detected. The pump is the beam that was chopped because the pump is what caused the probe to be deflected and any other light was filtered out by the lock-in. We modulated the pump beam to see how it affects the probe. The pump beam then changes the index of refraction and creates an index gradient in the material which is detected by the deflection of the probe beam. A Silicon Quad cell detector was used to detect the deflection of the probe. It contains a quad cell diode made of 4 parts, once the probe beam hits the diode it generates an electric current and is then amplified by a differential amplifier to see the signal. There are three outputs of this detector which are total, left minus right, and top minus bottom, and those differences detect the deflection. The detector is connected to the Lock-in amplifier which reduces noise from the detector at the frequency the chopper was set at.

Preliminary calculations were made to determine what n_2 signal the vapors would be able to be seen. With a Density of 1.261 g/cm^3 and using Molar Mass of 76.139 g/mol also using the Liquid $n_2 = 3 * 10^{-19} \frac{\text{m}^2}{\text{w}}$ and Liquid $N = 9.97 * 10^{27} \frac{\text{molecules}}{\text{m}^3}$, I was able to calculate the approximate n_2 for the vapors to show how much smaller the vapor signal would be than the liquid signal. Using the general ratio $\frac{n_2}{N} = \text{constant}$, the calculated constant is $3.01 * 10^{-47} \frac{\text{m}^5}{\text{W} * \text{molecules}}$. I then found the $n_{2\text{vapors}}$ to be $3.86 * 10^{-22}$ compared to $n_{2\text{liquid}} = 3 *$

10^{-19} it is about a factor of 1000 times less of a signal with all the same parameters in both situations.

Data

CS₂

The fused silica cell posed a problem during this experiment because the cell signal overpowered the CS₂ signal. With the following parameters we were not able to see CS₂ vapor signals.

$$\begin{aligned}\lambda_p &= 532 \text{ nm (Water} \\ &\quad \text{- WL)} \\ \lambda_e &= 800 \text{ nm (Laser)} \\ E_e &= 18 \text{ } \mu\text{J} \\ I_{0,e} &\approx 160 \text{ GW/cm}^2 \\ w_e &= 302 \text{ } \mu\text{m} \\ w_{0,p} &= 82 \text{ } \mu\text{m} \\ \tau_{xcorr} &= 118 \text{ fs (FWHM)} \\ \tau_{xcorr}/\sqrt{2} &= 83 \text{ fs (FWHM)}\end{aligned}$$

Figure 5: Where λ is the wavelength of the probe and the excitation beam respectively, E is the energy of the beam, w is the spot size of the excitation beam and the probe respectively and τ is the pulse width of the cross correlation of the beam.

Although with these specific parameters the results were expected, there were other problems as well. CS₂ is easily combustible, so with high enough energy, the CS₂ may have combusted inside the cell causing the cell to break and the toxic CS₂ to leak. This was not tested for the sake of the lab safety. Some other problems that came up during this experiment was that the air ionizes at 200 μ J, this would also have overshadowed the vapor signal within the air ionization signal. Another possible interference with the vapor signal was white light continuum generated by the cell walls. Using the theory in the paper by Heritage, we were able to see their theoretical calculations for CS₂. They also successfully measured the revivals of CS₂ vapors in a

meter cell to avoid the cell wall interference of the vapor signal. They also used different beam parameters [10].

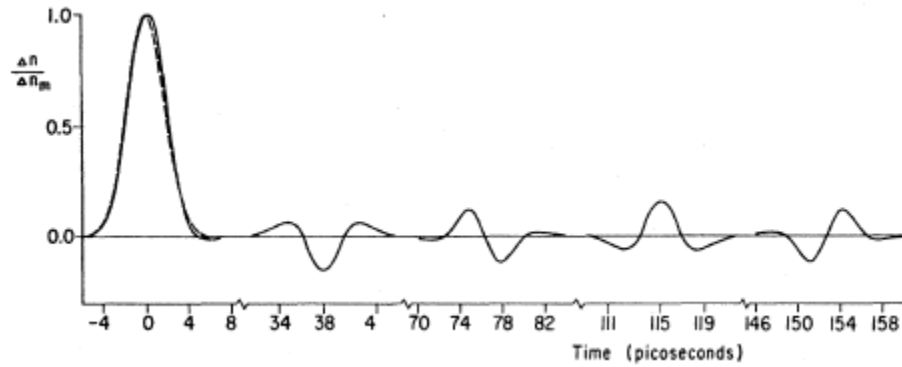


Figure 6: This is the Heritage paper's theoretical calculation of the time dependent change of nonlinear index of refraction [10].

Air

To avoid these potential and probable issues caused by the cell walls and CS₂, the CS₂ sample was removed and the revivals of air molecules was tested.

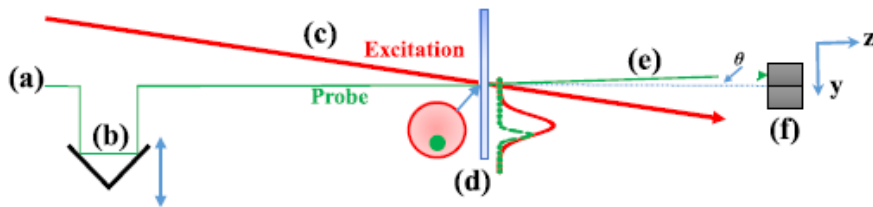


Figure 7: part d) is the sample. This sample was removed completely from the set up and the excitation beam and probe beam were allowed to interact in the open air in the lab.

The beam was allowed to propagate through the air to the detector and revivals were able to be seen.

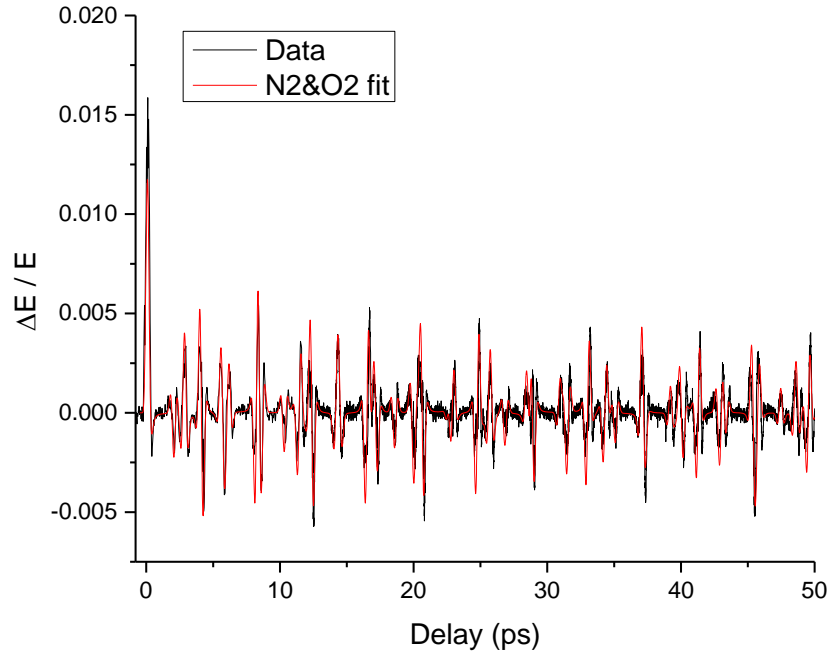


Figure 8: N₂ and O₂ revivals in air. The Measured and reference parameters: $T = 296\text{K}$, $\Delta\alpha_{\text{N}_2}=0.93\text{e-}30\text{m}^3$, $\Delta\alpha_{\text{O}_2}=1.14\text{e-}30\text{m}^3$, $L = 20\text{mm}$, $w_e=150\mu\text{m}$, $w_p=87\mu\text{m}$, $E = 332\text{uJ}$ and the fitting parameters are: $B_{\text{N}_2}=202/\text{m}$, $B_{\text{O}_2}=146/\text{m}$, $\text{Dephasing}_{\text{N}_2} = 1/80\text{ps}$, $\text{Dephasing}_{\text{O}_2} = 1/100\text{ps}$, $\text{Tau}_{\text{pump}} = 100\text{fs}$, $\text{Tau}_{\text{probe}} = 350\text{fs}$ ($<500\text{fs}$). The symbols correspond to the previous figure but now include T which is temperature, $\Delta\alpha$ which is polarizability and B is the rotational constant.

The red line is the fit of the air revivals based on the Heritage paper [10]. Since this technique is sensitive, we were able to see the revivals for up to 50 ps. Without this time sensitivity we would not be able to see the amount continuous revivals that we have.

Conclusion

The beam deflection technique allows for a temporal and spatial overlap in a sample that can cause an index gradient in the material which is caused by the pump and detected by the probe. The probe deflects at a small angle due to this detection of the gradient and that angle can determine the change in nonlinear refractive index. Since CS_2 is a linear molecule and since vapors are less dense than liquid, the CS_2 molecules would have less intermolecular interactions than in the liquid and therefore rotate. However some issues came across with the fused silica cell walls that would drown out the signal of the vapor reorientations, so the air in the lab was tested. This proved that the N_2 and O_2 in the air did indeed show rotational change of nonlinear refractive index.

List of References

1. Ferdinandus, M.R., *Techniques for characterization of third order optical nonlinearities*. 2012.
2. Stegeman, G.I. and R.E. Stegeman, *Nonlinear Optics: Phenomena, Materials and Devices*. Wiley Series in Pure and Applied Optics, ed. G. Boreman. 2012, Hoboken: Wiley.
3. McMorro, D., W.T. Lotshaw, and G.A. Kenney-Wallace, *Femtosecond optical Kerr studies on the origin of the nonlinear responses in simple liquids*. Quantum Electronics, IEEE Journal of, 1988. 24(2): p. 443-454.
4. Chen, Y.H., Varma, S., York, A., and H.M. Milchberg, *Single-shot, space-andtime-resolved measurements of rotational wavepacket revivals in H_2 , D_2 , N_2 , O_2 and N_2O* . Opt. Exp., 2007. 15(18): p. 11341-11357
5. Boyd, R.W., *Nonlinear Optics*. 3rd ed. 2008, New York: Academic Press.
6. Fox, M., *Optical Properties of Solids*. Oxford Master Series in Condensed Matter Physics, ed. M. Fox, S. Blundell, and J. Stevenson. 2001, New York: Oxford University Press.
7. Ferdinandus, M.R., et al., *Beam deflection measurement of time and polarization resolved ultrafast nonlinear refraction*. Opt. Lett., 2013. **38**(18): p. 3518-3521.
8. SiNc, Sigma- Aldrich, CAS 92396-88-8,
<http://www.sigmaaldrich.com/catalog/product/aldrich/389935?lang=en®ion=US> .
9. Yu-hsin Chen, *The Ultrashort Nonlinear Response of Air Molecules and its Effect on Femtosecond Laser Plasma Filaments in Atmosphere*. ProQuest Dissertations and Theses, 2011.
10. Heritage, J.P., Gustafson, T.K., and C.H. Lin, *Observation of Coherent Transient Birefringence in CS_2 Vapor*. Physical Review Lett., 1975. **34**(21): p. 1299-1302.