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Study on The Third-Order NLO Properties of Trace Metal Ions in Nitric Acid Solution by Closed-Aperture Z-scan Technique

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Abstract. Discovery of materials which exhibit large real third-order optical nonlinearities have recently become the topic of a broad scientific interest, due to its potential applications in many areas especially in the field of all-optical signal-processing. Here in this work, we report a preliminary investigation on the third-order nonlinear optical (NLO) response of different type of trace metal ions in nitric acid standard solution. A facile and rapid single beam z-scan technique incorporating 532nm diode pump solid state laser was employed to study the response of Lead (Pb), Cadmium (Cd), Mercury (Hg), Zinc (Zn), Aluminum (Al) ions towards NLO properties. Nonlinear refraction (NLR) response of the heavy metal samples were recorded from closed-aperture output and the maximum values of nonlinear refractive index, n_2 for all Pb, Cd, Hg, Zn, Al were recorded at 1.96355x10^{-9}, 3.38228x10^{-9}, 9.36907x10^{-9}, 8.67559x10^{-10},3.28211x10^{-9} cm^2W^{-1} respectively. Based on the experimental findings, the negative sign of the nonlinear refractive index values successfully indicates that the samples exhibit nonlinear self-defocusing effect, which is further expected to have potential applications in all-optical devices

1. Introduction

The need for novel material with relatively high nonlinear optical (NLO) behaviour has caused increasing interest in the field of photonics due to its potential in applications in diverse areas such as optical data storage [1], telecommunications [2], and information processing [3]. Many materials including organic and inorganic types have been studied for its third-order NLO susceptibility, due to the high demand from industrial sectors [4]. To date, various nonlinear properties and behaviour exhibited by metal nanoparticles (NPs) have been reported. Metal nanoparticles with relatively high third order nonlinearity have been extensively investigated, for instance gold [5,6] and silver [7,8]. On top of that, many researches related to heavy metals such as, calcium-halide [9], metal-organic e.g. dibromo(4-hydroxy-L-proline)cadmium (II) [10], Ni(II) [11] and metal Nitride e.g. TiN [12] were studied towards NLO response. In this study, five different metal ions of Pb Zn, Al, Cd and Hg in nitric acid solution were selected to its study its third order NLO response.

A single beam Z-scan technique based on diode pump solid state laser with excitation wavelength of 532nm were utilized for nonlinear characterization due to its ability to determine the nonlinearity of different heavy metal samples in the form of liquid solution. Another reason Z-scan technique is preferable in this research over other nonlinear setups is that the general conditions that are easily fulfilled, data analysis is quick and simple, making it a good method for screening on both NLO responses from absorption and refraction in solids and liquids [13,14]. On top of that, this technique also able to provide values of third-order nonlinear susceptibility$\chi^{(3)}$, simultaneously along with its magnitude and sign. In this research, we report the value of nonlinear refractive index, and real part of third-order nonlinear susceptibility, $\chi^{(3)}$ of five different heavy metals samples.

2. Methods and materials

2.1. Linear optical response
UV-vis absorbance characterization was taken for all heavy metal samples, the corresponding values of linear absorption coefficient, α were calculated at 532nm absorption. The value of linear refractive index, n of all samples were measured using a digital hand-refractometer (KRUSS-DR101-60)

2.2. Third order NLO Characterization.

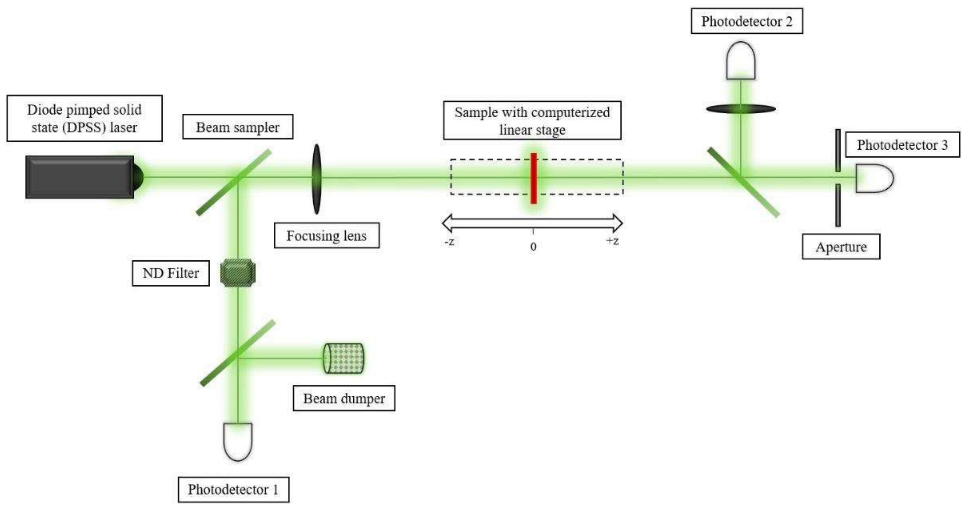

Figure 1: The Z-scan schematic diagram

A schematic diagram of Z-scan setup is shown in Figure 1. A continuous-wave frequency doubled diode pumped solid state (DPSS) laser (Coherent Verdi-V5) at 532nm wavelength was used as the laser source of the setup. Silicon amplified photodetector (PDA55, Thorlabs) with adjustable gain were used to record the output for both open and closed signals. A converging lens of f=20cm was used to focus the beam into the sample and a laser beam profiler (Beam Master) was used to measure the radius of the Gaussian beam-spot at focal (23µm). The sample was filled in a quartz cuvette. The cuvette with a path length of 1mm was placed on a motorized stage (LTS-300, Thorlabs). The Rayleigh length (RL) of the laser beam was determined at 3.12 mm, and the pathlength of the cuvette was set at much smaller value around 1 mm to ensure the conformance with essential z-scan prerequisite. During the scanning which monitored by computer, the sample was moved along the z-direction and concurrently, the signal from the three photodetectors, PD1, PD2, and PD3 were recorded by an oscilloscope. The signal from PD1 acts as a reference to eliminate power fluctuation in the laser. The NLR response was studied from closed z-scan signal (PD3). Table 1 summarized the Z-scan parameters used in the experiment.

Table 1. Lists of Z-scan parameters.

Parameter	Value
f	20cm
r_a	0.19cm
w_0	0.0023cm
λ	532nm

The peak-valley normalized transmittance obtained from the closed aperture Z-scan is defined as $\Delta T_{P\text{-}V}$ which is the difference of peak and valley given as $T_P - T_v$. The formula of $\Delta T_{P\text{-}V}$ as a function of $|\Delta\varphi_0|$ is given as

$$\Delta T_{p-v} = 0.406\,(1 - s)^{0.25}|\Delta\varphi_0| \tag{1}$$

where $|\Delta\varphi_0|$ is define as the on-axis phase shift at the focus, while S is the aperture linear transmittance with r_0 represent the aperture radius and ω_0 represent the beam radius at the aperture in the linear regime.

$$S = 1 - exp\,(-\frac{2r_0^{\,2}}{\omega_0^{\,2}}) \tag{2}$$

Then formula of nonlinear refractive index, n_2 is,

$$n_2 = \frac{\Delta\varphi_0\lambda}{2\pi I_0 L_{eff}} \tag{3}$$

where λ is the laser wavelength, I_0 is the intensity of the laser beam at focus,

$$L_{eff} = \frac{[1 - exp(-\alpha L)]}{\alpha} \tag{4}$$

L_{eff} is the effective thickness of the sample, α is the linear absorption coefficient and L is the thickness of the cuvette. The real part of the third-order nonlinear optical susceptibility $\chi^{(3)}$ is evaluated from the value n_2 . The relation of n_2 and real part of $\chi^{(3)}$ are as below

$$Re\,\chi^{(3)}(esu) = 10^{-4}\,\frac{\varepsilon_0 c^2 n_0^{\,2}}{\pi} n_2 \quad \left(\frac{cm^2}{W}\right) \tag{5}$$

3. Results and discussion

3.1. UV-vis absorption spectra and linear absorption coefficient

Figure 2 shows the UV-VIS absorption spectra recorder from all the heavy metal ions samples. The absorptions are prominent in the green region with two broad shoulders around 500nm and 550nm appearing. Linear absorption coefficient, α at 532nm was calculated for each sample according to the absorbance and tabulated in Table 2.

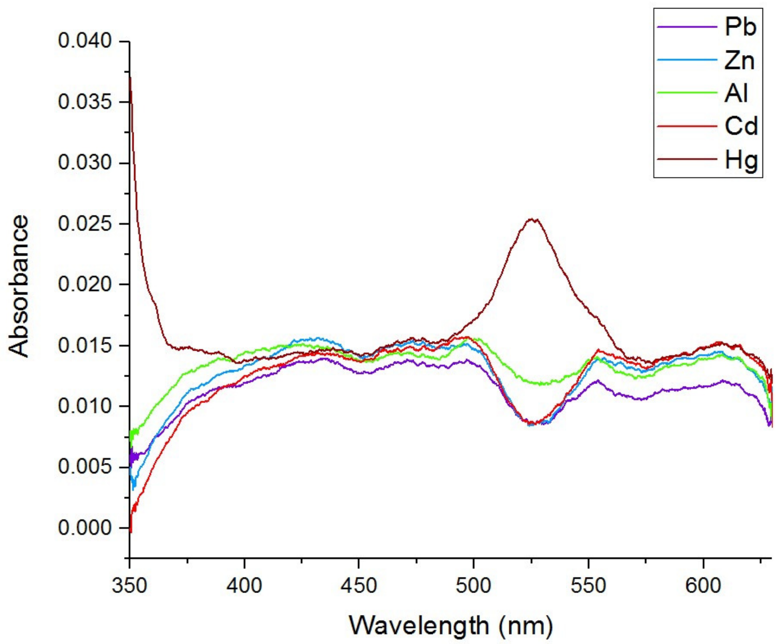

Figure 2: UV-Vis absorbance spectra of heavy metals

Table 2. The value of α for different heavy metal samples

Element	α (cm^{-1})
Pb	-0.013818
Zn	-0.016121
Al	-0.02303
Cd	-0.006909
Hg	0.048363

3.2. Nonlinear z-scan measurement

To eliminate the cuvette and the solvent effect in the signal, we first run the background z-scan on the cuvette only and cuvette filled with the solvent. Both signals show non-nonlinear signal and the background effects are minimal. Both closed and open z-scan was performed simultaneously on the sample with the help of 50:50 beam splitters at increasing focal intensity from 1.60 to 36.2 kW/cm^2. The NLR response of the sample was characterized via closed z-scan setup with 0.19cm radius of aperture. Result of normalized transmission against z displacement for all samples of Pb, Zn, Al, Cd and Hg were plotted as shown in Figure 3.

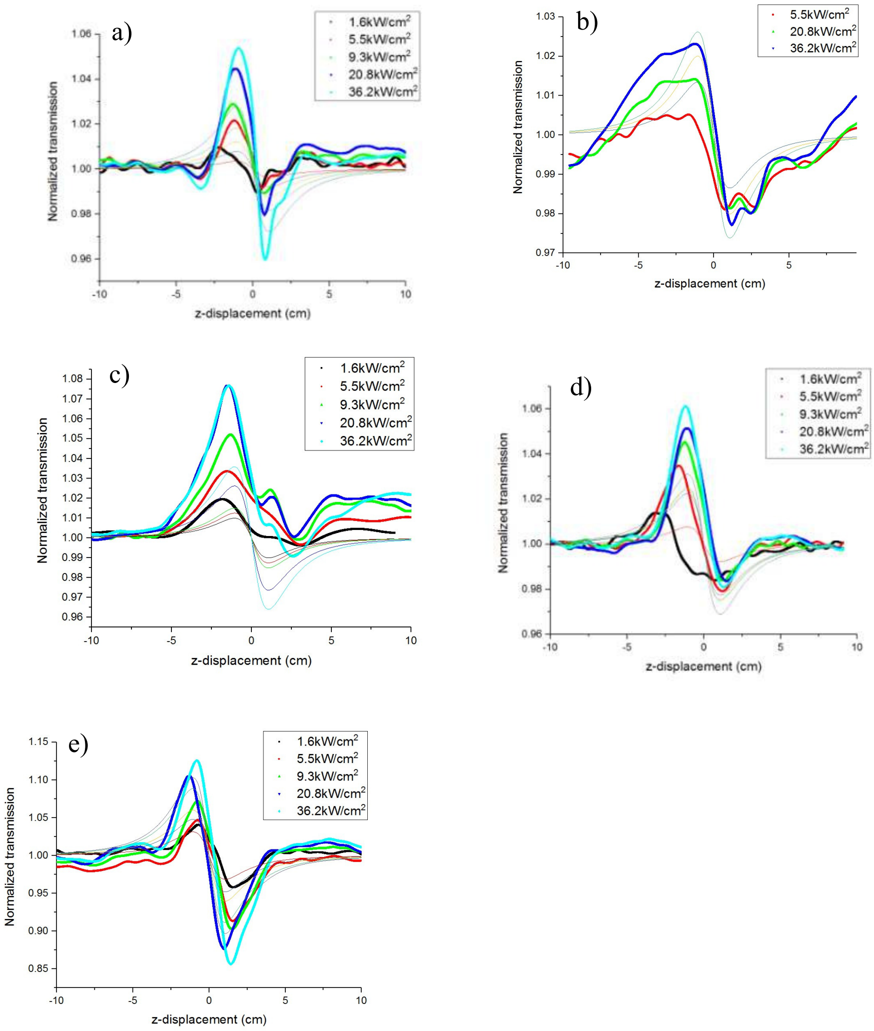

Figure 3: NLR response from closed aperture signals correspond to (a)Pb, (b)Zn, (c)Al, (d)Cd and (e)Hg respectively.

Figure above shows the closed aperture z-scan signals for all samples at different laser intensities. As shown, NLR response was observed in all heavy metal ions used with negative nonlinear refraction, n_2 as a result in the effect of self-defocusing when the sample passes through near to focal point of the excitation laser. Equation 3 and 5 were used to calculate the value of n_2 and $Re\ \chi^{(3)}$ correspond to the value of peak-valley transmission, ΔT_{P-V} from the closed aperture Z-scan respond. Thus, the values were tabulated in Table 3. The general pattern of the value of n_2 is inversely proportional against laser power as plotted in Figure 4. At a lower laser power, the values of n_2 show significant variation and easily can be distinguished. However, as the power rises, the recorded values of n_2 show very little variation and hard to differentiate from each other. Overall, all samples showed superior NLR response at 532nm excitation.

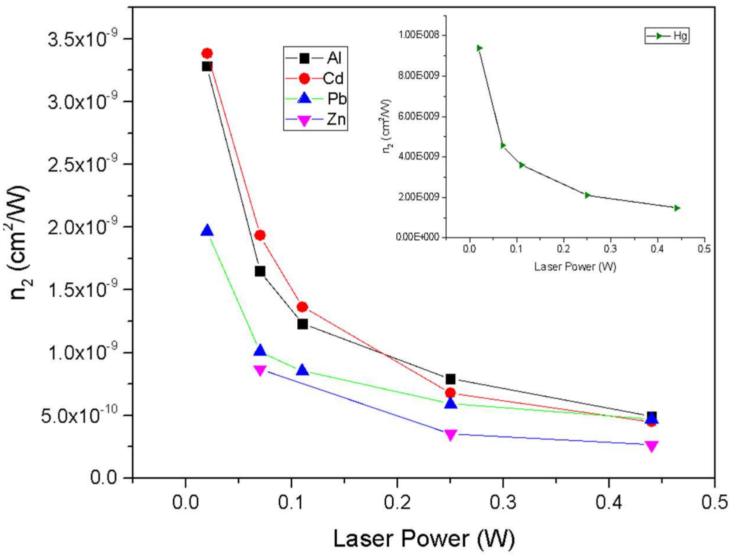

Figure 4: Nonlinear refractive index, n_2 for all samples at different laser power

Table 3. The comparison of linear, *n* and nonlinear refractive index, n_2 with respect to third-order nonlinear susceptibility, $\chi 3$ for each element

Solution	Laser Power (W)	Linear absorption coefficient, α (cm^{-1})	Linear refractive index, n	Nonlinear refractive index, n_2 (cm^2W^{-1}) (10^{-9})	Third-order nonlinear susceptibility, $\chi 3$ (esu) (10^{-8})
Al	0.02	-0.02303	1.3373	-3.28211	-14.89
	0.07			-1.65001	-7.48
	0.11			-1.22838	-5.57
	0.25			-0.78925	-3.58
	0.44			-0.49115	-2.23
Cd	0.02	-0.006909	1.3362	-3.38228	-15.32
	0.07			-1.93259	-8.75
	0.11			-1.36508	-6.18
	0.25			-0.67646	-3.06
	0.44			-0.44721	-2.03
Hg	0.02	0.048363	1.3459	-9.36907	-43.04
	0.07			-4.55275	-20.92
	0.11			-3.58881	-16.49
	0.25			-2.11189	-9.70
	0.44			-1.48088	-6.80
Pb	0.02	-0.013818	1.3353	-1.96355	-8.88
	0.07			-1.00676	-4.55
	0.11			-0.85077	-3.85

	0.25			-0.59041	-2.67
	0.44			-0.46745	-2.11
Zn	0.02			-	-
	0.07			-0.86756	-3.93
	0.11	-0.016121	1.3369	-	-
	0.25			-0.35275	-1.60
	0.44			-0.26463	-1.20

4. Conclusion
In summary, third order nonlinear effect was observed in heavy metal samples using 532nm excitation wavelength. Linear optical response of Pb Zn, Al, Cd and Hg samples were determined and the values of linear absorption coefficient and refractive index were calculated accordingly. For third order NLO characterization, nonlinear refractive index and nonlinear susceptibility of the samples were studied. Analysis from close-aperture signals confirms that the heavy metal ions exhibited self-defocusing effect with negative n_2 values and relatively high $\chi3$ recorded in the magnitude of 10^{-8}.

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