# The first Hyperpolarizability of 2,5-Dimethyleaniline through the Hyper-Rayleigh Scattering Technique

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**Abstract:** *The first order hyperpolarizability (β) of Organic Monomer like 2,5-Dimethyleaniline (DMA) dissolved in Methanol has been measured using Hyper-Rayleigh Scattering technique. An Argon Ion Laser operating at 514 nm was used as the excitation source to generate the second harmonic scattered light. The results show that Organic Monomer have large β values and found that the β value is $7.05 \times 10^{-30}$ esu for 2,5-Dimethyleaniline (DMA). The calculated results indicated DMA has a potential for SHG device applications, owing to its remarkable β value.*

**Keywords:** *DMA; HRS technique; non-linear optical (NLO); first hyperpolarizability; EFISHG technique.*

## 1. INTRODUCTION

An important research area is to understand the linear and nonlinear optical (NLO) properties of materials. Nonlinear materials are of great technological importance for use in future application within electronics and photonics [1-2].The second-harmonic generation (SHG) is of particular interest and to investigate this property many studies have been devoted. The SHG properties of organic molecules are characterized in terms of their molecular first hyperpolarizability (β), which can be measured using electric-field-induced second-harmonic generation (EFISH) [3-5] or hyper-rayleigh scattering (HRS) techniques [6-7]. These experiments are usually performed in solution.

Due to their large value for the first hyperpolarizability, typical organic chromophores which are of interest are the so-called push-pull or donor-accepter molecules [1,8]. *Para*-nitroaniline (*p*-NA) is the prototype push-pull molecule and it has been found that the first hyperpolarizability of *p*-NA depends strongly on the solvent both in the EFISH and the HRS methods [7,10,14,16]. Pa (phenanthrene), a conjugated polymer that lacks the push–pull (D–p–A) substitution pattern shows an extremely high hyperpolarizability, has been studied by hyper-rayleigh scattering [9].

Through the second harmonic generation (SHG) process, the doubling of the frequency of the incident beam constitutes one example of NLO phenomena that is currently exploited in laser components as well as in optical information processing and data storage devices [17-19]. For a series of donor-acceptor substituted π-conjugated organic compounds, a comparison of first hyperpolarizabilities (β) determined by Hyper-Rayleigh scattering (HRS; $\beta_{HRS}$) and Electric Field Induced Second Harmonic Generation (EFISH; $\beta_{EFISH}$) shows a marked discrepancy between $\beta_{HRS}$ and $\beta_{EFISH}$ values for NLO-chromophores which fluoresce in the frequency-doubled wavelength region (532nm) [20]. An improved method for measuring first order hyperpolarizadility of organic NLO materials in solution by hyper-rayleigh scattering technique was provided by Nam Woong Song and co-workers [21].

HRS technique was applied by Ernesto V. Rodriguez and co-workers to measure the first-order hyperpolarizability (β) of ferroelectric $BaTiO_3$ and $PbTiO_3$ nanoparticles (NPs) dissolved in methanol and the first hyperpolarizability (β) value per unit volume of NPs was two orders of magnitude larger than that observed for antiferroelectric $NaNbO_3$ nanoparticles [22]. Contribution of bipolar and quadrupolar to the first hyperpolarizability of DMA was measured by an experiment for the angular distribution at second harmonic frequency. Effect of electric dipole in the hyperpolarizability is the most and more than 90% [23].

## 2. RESEARCH METHOD

The description of the Hyper-Rayleigh Scattering technique is based on a review article by Clays and Persoons [24]. The experimental Hyper-Rayleigh Scattering set-up section overviews an article recently published by I. Asselberghs, J. Pérez-Moreno and K. Clays [25]. Since Hyper-Rayleigh Scattering is a forbidden process in isotropic solution, the efficiency is very low as the output arises from rotational fluctuations. As a consequence, optical fields with high optical power-density are needed together with an efficient collection system to detect the Hyper-Rayleigh Scattering signal. In this experiment we use multiline Argon Ion Laser. This Argon Ion Laser has following properties:

- Maximum output is 150mW
- Wavelength range is 457 to 514nm.
- Beam diameter is 0.65mm
- Divergence is 0.95mrad
- Coherent length is 10cm

The fundamental light beam is passed through a grating scale that helps to split the beam in different wavelengths or different frequencies. Then the beam of wavelength 514nm was taken. The green beam was focused in the cell by a convex lens. The collection system consists of a concave mirror, a convex lens and a power detector. A schematic view of setup is shown in figure 1.

In this experiment, first convex lens had focal length of 10cm and in collection system 7.56cm focal length convex lens were used. The concave mirror had a focal length 4.5cm. We used power meter in place of photomultiplier tube. Because of this power P(2ω) of the scattered beam was found in place of intensity $I_{2w}$. As a sample holder rectangular quartz cell was used, where the transmission coefficient of the glass was very good and the reflection coefficient was very poor. The Laser light, grating, lens, concave mirror, photo detector or power detector and sample holder were aligned manually as accurately as possible.
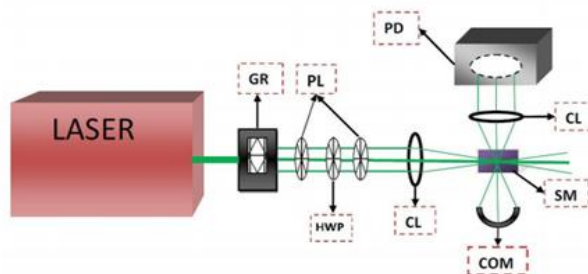


**Figure1.** *Schematic view of the experimental Hyper Rayleigh Scattering setup. Where Gratting (GR), Polarizer (PL), Convex Lens (CL), Concave Mirror (COM), Power Detector(PD), Sample (SM)*

### 2.1. The Internal Reference Method

To take advantage of the linear dependence on the chromophores concentration ($N_2$), a series of different concentrations are prepared. The quadratic coefficient for each concentration, $Q$ is then obtained. If the first hyperpolarizability of solvent$< \beta^2_{HRS} >_1$is known and the experimental conditions are well characterized, first hyperpolarizability of solute$< \beta^2_{HRS} >_2$can be obtained by calculating the slope of the quadratic coefficients as a function of concentration. This is referred as the internal reference method [26].In the internal reference method a plot of the quadratic coefficients (Q) vs. as a function of $N_2$ yields a straight line with a slope $b_1$ and an intercept $b_0$.
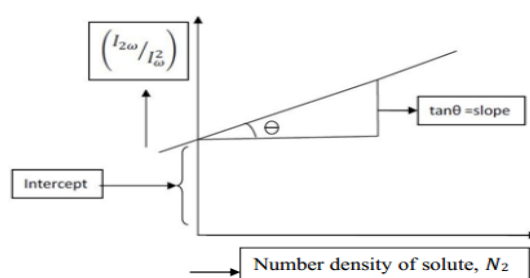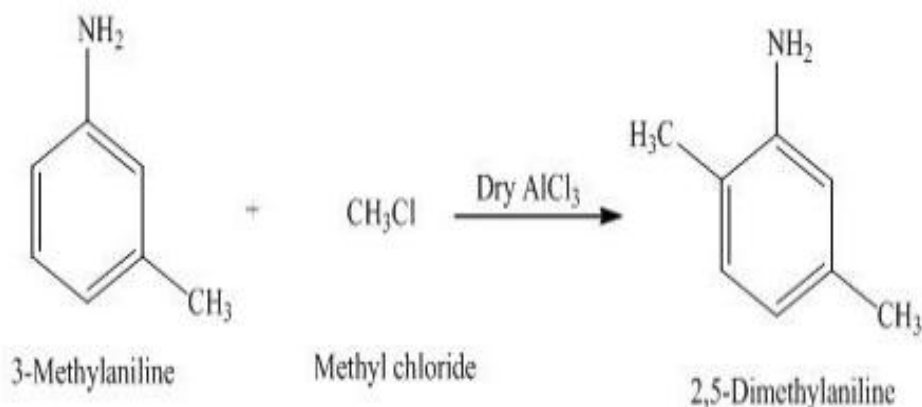


**Figure2.** *A schematic plot of ($I_{2\omega}/I_\omega{}^2$) Vs number density of solute ($N_2$) showing the intercept and slope*

The working equation is given by:

$$< \beta^2{}_{HRS} >_2 = \frac{b_1}{b_0} N_1 < \beta^2{}_{HRS} >_1 = \frac{b_1 N_A \rho_1}{b_0 M_1} < \beta^2{}_{HRS} >_1 \tag{1}$$

## 2.2. Sample Preparation

2,5-Dimethylaniline (DMA) is an organic chemical compound, a substituted derivative of aniline. It can be produced by well known Fridel-Craft alkylation reaction as following:



Substitution of the aniline monomer with alkyl (-R) or alkoxy (-OR) groups improves the solubility in organic solvents such as methanol. Molecular weight of DMA is 121.18. Melting and boiling point of DMA are 11.5 °C(lit.) and 218 °C(lit.) respectively. Density of DMA is 0.973 g/mL at 25 °C(lit.). DMA may be sensitive to prolonged exposure to air and almost insoluble in water. DMA ignites on contact with fuming nitric acid. It neutralizes acids in exothermic reactions to form salts plus water. May be incompatible with isocyanates, halogenated organics, peroxides, phenols (acidic), epoxides, anhydrides, and acid halides .It is combustible. It is dark brown and very poor transparent liquid. Due to the low transparency of DMA, it was dissolved in methanol and eight solutions of DMA in methanol were made.

## 3. RESULT AND DISCUSSION

0.50ml DMA was taken and dissolved in methanol. At first, it was mixed with 0.50ml methanol. Then it was mixed with 1.0ml, 1.25ml, 1.50ml, 1.75ml, 2.0ml methanol respectively as solvent. As a result the concentration of DMA was changed. For a input power, three sets of output power were measured. Finally we calculated the mean output power

**Table1.** *Mean output power for different concentration of DMA dissolved in methanol*

| $(Input power)^2$ $in W^2 (\times 10^{-12})$ | Mean output power in $W$ $(\times 10^{-12})$ (for 0.5ml DMA+0.5ml methanol) | Mean output power in $W$ $(\times 10^{-12})$ (for 0.5ml DMA+0.75ml methanol) | Mean output power in $W$ $(\times 10^{-12})$ (for 0.5ml DMA+1.0ml methanol) | Mean output power in $W$ $(\times 10^{-12})$ (for 0.5ml DMA+1.25ml methanol) | Mean output power in $W$ $(\times 10^{-12})$ (for 0.5ml DMA+1.5ml methanol) | Mean output power in $W$ $(\times 10^{-12})$ (for 0.5ml DMA+1.75ml methanol) | Mean output power in $W$ $(\times 10^{-12})$ (for 0.5ml DMA+2.0ml methanol) | Mean output power in $W$ $(\times 10^{-12})$ (for 0.5ml DMA+2.25ml methanol) |
|---|---|---|---|---|---|---|---|---|
| 0.6651 | 122.57 | 107.57 | 72.20 | 52.15 | 33.89 | 32.50 | 30.77 | 32.58 |
| 0.6612 | 121.69 | 106.44 | 71.08 | 50.96 | 33.30 | 32.20 | 30.39 | 32.233 |
| 285.2045 | 128.28 | 111.15 | 74.45 | 51.48 | 36.17 | 35.10 | 34.81 | 35.04 |
| 1833.5781 | 136.38 | 126.28 | 86.07 | 60.27 | 45.24 | 41.30 | 41.96 | 40.48 |
| 4839.1084 | 144.82 | 141.81 | 97.40 | 69.54 | 54.73 | 48.38 | 47.45 | 43.75 |
| 9018.7881 | 169.50 | 157.09 | 108.77 | 77.96 | 63.14 | 56.50 | 55.59 | 50.38 |
| 19097.3882 | 212.18 | 180.01 | 129.93 | 103.69 | 78.43 | 71.36 | 69.05 | 70.28 |

For different concentration, the second harmonic response was measured. We calculated the value of Q from the graph of second harmonic power Vs square of incident power for different concentration of DMA dissolved in methanol.
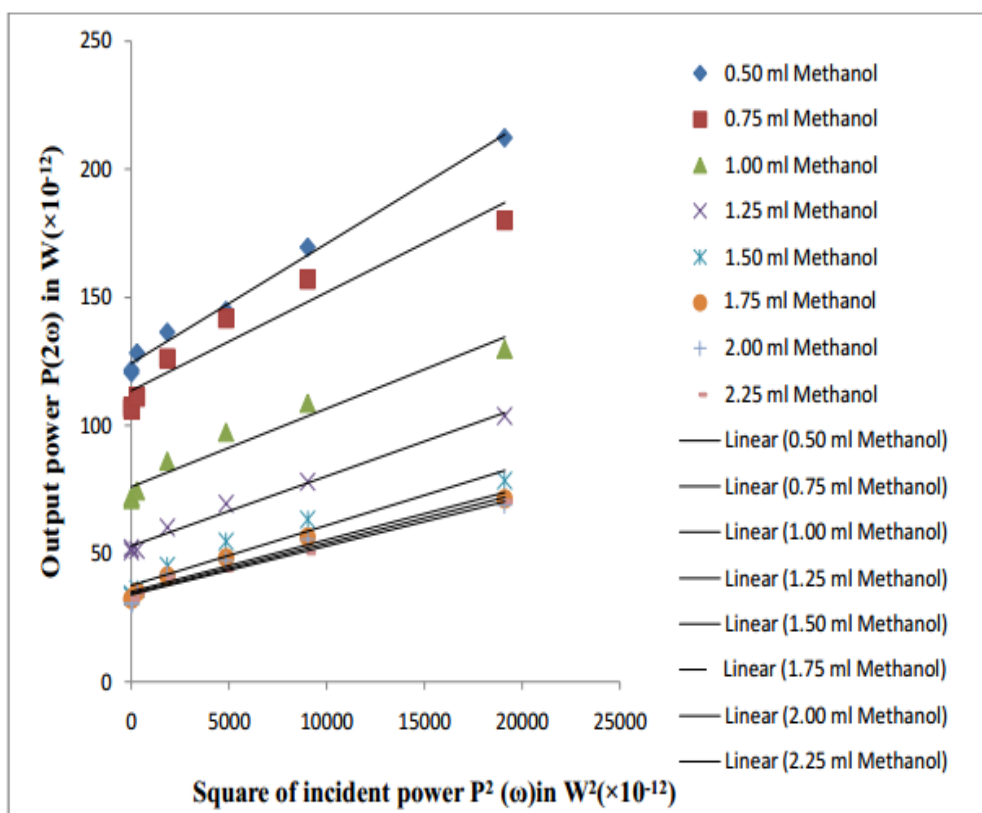
**Figure3.** *The second Harmonic power Vs Square of Incident power graph for different concentration of DMA dissolved in methanol*

Here,$r_1$ is the radius of the detector which is 0.564 cm and $r_2$ is the radius of the Gaussian laser beam which is 0.065 cm and the value of $k=\dfrac{4r_1{}^2}{\pi r_2{}^2}$ =2.2689× $10^4$.

1 a.u intensity = $3.51 \times 10^{16}\ \dfrac{w}{cm^2}$

Molecular mass of  DMA, M  = 121.18 gm/mol

Avogadro's number, $N_A$ = 6.023×$10^{23}$ per mol

Number density of methanol,  $N_1$ =   1.487×$10^{22}$   cm$^{-3}$  and

First hyper-polarizability of methanol, $(\beta^2{}_{HRS})_1$ = (0.69±0.07) ×$10^{-30}$ esu.

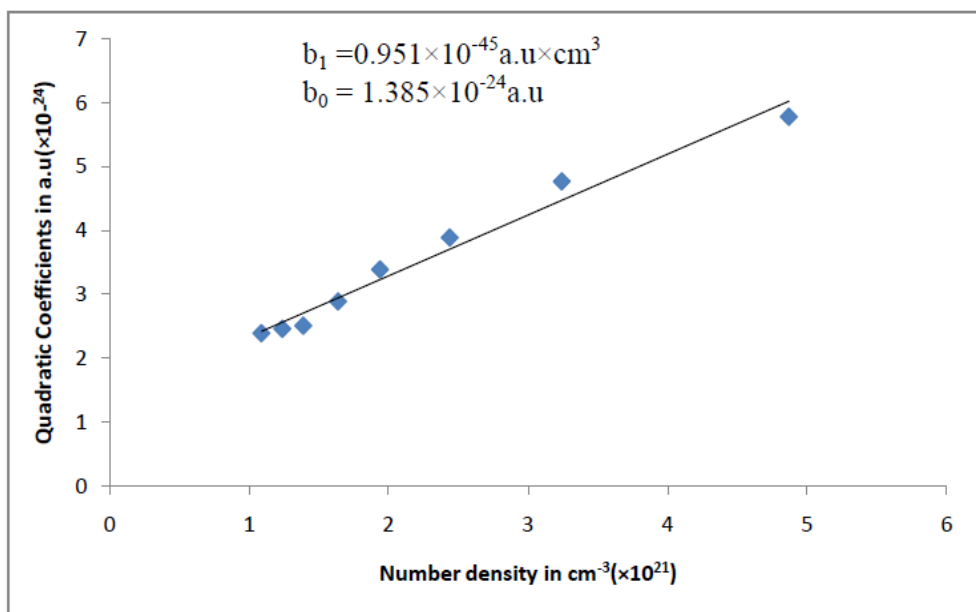We know,Number density,

$$N_2 = \frac{Density in the solution \times Avogedro's number}{Molecular mass}$$

$N_2$ was calculated for different density of solution ($\rho_2$).

**Table2.** *Number Density of different concentration of DMA and for each concentration the value of corresponding quadratic coefficients (Q) are given below*

| 0.5ml DMA dissolved in methanol in ml | Number Density ($N_2$) in $cm^{-3}$ | Quadratic Coefficients(Q) in a.u |
|---|---|---|
| 0.50 | 4.87×$10^{21}$ | 5.78×$10^{-24}$ |
| 0.75 | 3.23×$10^{21}$ | 4.77×$10^{-24}$ |
| 1.00 | 2.44×$10^{21}$ | 3.89×$10^{-24}$ |
| 1.25 | 1.94×$10^{21}$ | 3.33×$10^{-24}$ |
| 1.50 | 1.64×$10^{21}$ | 2.89×$10^{-24}$ |
| 1.75 | 1.39×$10^{21}$ | 2.51×$10^{-24}$ |
| 2.00 | 1.24×$10^{21}$ | 2.46×$10^{-24}$ |
| 2.25 | 1.09×$10^{21}$ | 2.39×$10^{-24}$ |

**Figure4.** *Number density VS Quadratic Coefficients graph*

The experimental result of the Hyper-Rayleigh Scattering technique yields the value of first hyperpolarizability $< \beta^2_{HRS} >_2$ of DMA to be $7.05 \times 10^{-30}$ esu. In this paper, using Hyper-Rayleigh Scattering technique it has been shown that the organic monomers like DMA exhibit non-linear optical properties and the value of the first hyper-polarizability is $7.05 \times 10^{-30}$ esu. In general, octupolar molecules will have hyperpolarizabilities as large or larger than dipolar molecules [27]. D. V. Kanis and co-worker have shown that an extended π-organics dye molecule like 4- dimethylamino-4'-nitrostilbene (DMANS) has very large β value, which is about $(100 \text{ to } 1000) \times 10-30$ esu [8]. Organic polymer has a chain of an extended π-organics dye molecule, so the *β* value of organic polymer must be higher than DMANS. Koen Clays and Andre Persoons [28] have shown that the second harmonic intensity (SHI) increases exponentially with increasing incident intensity, but in a small region SHI increases linearly with increasing incident intensity. In this experiment we found that SHI increases linearly with increasing incident intensity or second harmonic power (SHP) increases linearly with increasing incident power. Koen Clays and Andre Persoons [28] have shown that the Second Harmonic Intensity (SHI) increases linearly with the square of the incident intensity and when incident intensity is zero then the SHI is zero. But in this experiment, a little value of SHI or SHP was found when incident intensity or incident power is zero due to the external radiation. The laser beam used in this experiment has multiple wavelengths, so a grating was used in front of laser beam to split the beam. Power meter detector was used in place of a photomultiplier tube. After detecting the input power, the powers for second harmonic scattering light (output power) were detected. The whole experiment was conducted at night in a dark room (as dark as possible) to avoid external light interfering with second harmonic scattered light. The lens and concave mirror were well focused. In this experiment, rectangular shaped sample holder (quartz) was used. The Laser light, grating, lens, concave mirror, photo detector or power detector and sample holder were aligned manually as accurately as possible. The Chemistry department is providing more samples so that this experiment can be repeated with different concentrations.

## 4. CONCLUSIONS

In conclusion, the experimental investigation shows that the organic monomer like DMA shows large βvalues.Hyper-Rayleigh scattering technique utilizing the Internal Reference Method was used to investigate the first hyperpolarizability (β) of organic monomer like DMA dissolved in methanol. Incoherentoptical second harmonic was generated and large first order hyperpolarizability associated with the DMA was determined. An Argon Ion Laser operating at 514 nm was used as the excitation source to generate the second harmonic scattered light. This could be an ideal material that could have potential applications in nonlinear optical devices like telecommunication, optical data storage and optical information processing etc.

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