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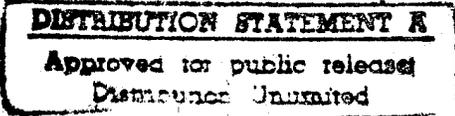
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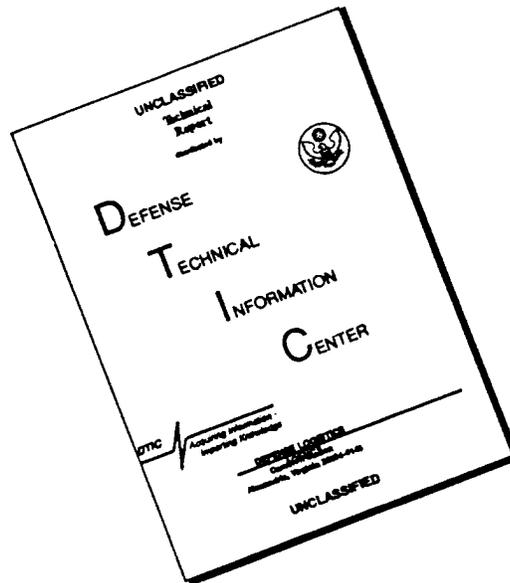
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Determination of First Hyperpolarizability of Nonlinear Optical Chromophores by Second Harmonic Scattering using an External Reference

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ABSTRACT

First hyperpolarizabilities (β) of two tricyanovinylthiophene chromophores were determined using second harmonic, hyper-Rayleigh, scattering. The use of an external standard in the determinations is compared with the previous use of an internal standard. A new method of analyzing the hyper-Rayleigh scattering signal by recording a histogram of the scattered energy is reported. This method is shown to give more reliable results in a shorter period of time than the usual static gate method. The histogram function provides additional information in the form of the histogram width which is shown to be an indication of the mean square concentration fluctuations of the chromophores in solution. The effects of molecular interactions on the concentration dependence of the hyper-Rayleigh scattering signal is discussed. It is shown that depending on the concentration

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range, the β value of *para*-nitroaniline, used as the external standard, can agree with two different values reported in the literature. Results on the depolarization ratio of the hyper-Rayleigh scattered light from one of the tricyanovinylthiophene chromophores are presented. At low concentration the depolarization ratio agrees with the theoretically predicted value based on C_{2v} symmetry. However, at higher concentration the measured depolarization ratio increases indicating molecular interactions.

INTRODUCTION

Organic molecules consisting of a strong electron donor and acceptor group at either ends of a long π -conjugation are known to exhibit large first hyperpolarizabilities, β , along the molecular axis.¹ The large β values of these chromophores are due to asymmetry in the charge distribution associated with the excited charge-transfer state. Incorporation and proper processing of these large β chromophores in a polymer could result in a material with a large second-order nonlinear optical susceptibility $\chi^{(2)}$. Due to important technical applications of these nonlinear optical (NLO) materials, significant efforts have been directed to the design, synthesis and characterization of the chromophores.^{2,3,4}

Up to the present, the β values of most NLO molecules have been determined by an infinite dilution extrapolation method⁵ using electric field induced second harmonic (EFISH) generation.^{6,7,8,9} In this technique, the chromophore of interest is first dissolved in a solvent of low viscosity. A strong, pulsed, external DC electric field is applied to remove the macroscopic centrosymmetry of the chromophore solution. When laser pulses, synchronized with the DC field pulses, are applied to the sample at frequency ω , a second harmonic generation (SHG) signal at frequency 2ω is induced. By measuring the induced SHG signal intensity from the solution as a function of the NLO chromophore concentration and then extrapolating the data to zero chromophore concentration, one obtains the $\beta\mu$ value of the chromophore in solution, where μ is the ground state (permanent) dipole moment of the chromophore. To extract the β value, one needs to know the value of μ . Obtaining β also requires knowledge of local field factors at the

fundamental optical frequency, the second harmonic frequency and at zero frequency and the refractive index of the solution and the solute chromophore. Although one can make an independent measurement to obtain the chromophore's permanent dipole moment, complete knowledge of the local field factors, especially the one at zero frequency, is presently not available. In addition, there is also a contribution to the second harmonic signal in the EFISH experiment from the second hyperpolarizability, γ , that is difficult to quantify and whose contribution is therefore often neglected in the calculation of β .¹⁰ Thus, besides experimental uncertainty from the dipole moment measurement, incomplete knowledge of the local field factors and the second hyperpolarizability make a β value determined by the EFISH method subject to great uncertainty. Another shortcoming of the EFISH method is that it cannot be used to determine the beta value of a chromophore that does not possess a permanent dipole moment (for the reason that such molecules would not respond to the orienting DC field pulses). For these types of molecules, an alternate method must be used.

Second harmonic light scattering, or *hyper-Rayleigh* scattering (HRS), is another technique that can be used to determine the β value of an NLO chromophore and can be used regardless of whether or not the molecule under study has a permanent dipole moment. Incoherent light scattering from a solution occurs as a result of fluctuations in the local refractive index. If the incident radiation at frequency ω has a high intensity, the induced polarization in the medium can acquire an appreciable amplitude at the second harmonic frequency 2ω . Thermal fluctuations in the induced polarization (or refractive index) would remove local centrosymmetry and allow a scattering field at 2ω to

propagate. Terhune, Maker and Savage first reported in 1965 hyper-Rayleigh scattering from H₂O, CCl₄ and fused quartz.¹¹ After nearly three decades of inactivity in this field, Persoons has recently initiated a revival of interest in HRS by using it as a method to determine first hyperpolarizabilities of a number of NLO chromophores.^{12,13,14,15,16}

The intensity of the HRS radiation, $I(2\omega)$, from a binary NLO chromophore/solvent solution is given by

$$I(2\omega) = K(\rho_s\beta_s^2 + \rho_c\beta_c^2)I^2(\omega) \quad (1)$$

where $I(\omega)$ is the intensity of the fundamental light and K is a constant determined by the scattering geometry, local field factors at ω and 2ω and other optical and instrumental quantities. The quantities (ρ_s, β_s) and (ρ_c, β_c) denote (concentration, first hyperpolarizability) of solvent molecules and chromophores, respectively. The method used in refs. 12-16 to determine β_c , and which will be henceforth referred to as the

internal standard method (ISM), is to measure $\frac{I(2\omega)}{I^2(\omega)}$ as a function of the chromophore concentration, which gives a linear plot at low ρ_c . Extrapolation to zero chromophore concentration yields the intercept, $K\rho_s\beta_s^2$. Dividing the slope of the $\frac{I(2\omega)}{I^2(\omega)}$ versus ρ_c

plot by the intercept, one obtains $\frac{\beta_c^2}{\rho_s\beta_s^2}$. One notes that in the ISM, the quantity K , which

depends on local field factors at ω and 2ω , is canceled by division; this removes the uncertainties that might be introduced by those factors. In order to determine the β value of the chromophore unknown, β_c , one must know β_s (and ρ_s which can be determined with accuracy and which is assumed to remain constant due to the low concentration of

the dissolved molecules). Since β_s is often several orders of magnitude smaller than β_c , a small uncertainty in β_s can result in a large uncertainty in the value of β_c , as β_s is in the denominator. The ISM is further hampered by the fact that the chromophore being tested must be dissolved in a solvent with a nonzero β value (if β_s is zero then the quotient $\frac{\beta_c^2}{\rho_s \beta_s^2}$ is undefined); therefore, the ISM can not be directly applied to solutions with centrosymmetric solvents such as benzene.

Another way of performing hyper-Rayleigh scattering experiments would be to use a chromophore with a known β value as a standard. This new external standard method (ESM) involves measuring hyper-Rayleigh scattering from two series of solutions, one of the unknown and the other of an NLO chromophore with a known β value (to our knowledge it has not yet been discussed in the literature). $\frac{I(2\omega)}{I^2(\omega)}$ vs. ρ_c plots are constructed for each solution series and the slopes are obtained. The ratio of the slopes is then $\frac{\beta_c^2}{\beta_{st}^2}$, where β_{st} is the β value of the standard chromophore and β_c is the β value of the unknown. Assuming β_{st} is known, the value of β_c can be determined. Furthermore, since the standard chromophore can be chosen such that its β value is of the same order of magnitude as the unknown's, a very accurate value for β_c can be obtained (for this reason we have found that the ESM gives more reproducible results than the ISM). To be sure, to obtain the ratio, one assumes that the constant K given in Eq. (1) is the same for both solution series. (The same type of approximation is also used in the ISM, where K is assumed to be the same for both the solvent and the dissolved chromophore) Thus, it is

important when using the ESM that experimental conditions not be altered between measurements on the two solution series so that the instrumental quantities imbedded in K do not change. It can be inferred from the standard local-field Lorentz expression, though, that the cancellation of the local field factors will not be complete. Since the local field factors involved in the HRS experiment are those at ω and 2ω , they could be explicitly taken into account by using the Lorentz expression if highest accuracy is required.

To demonstrate the external standard method we here report results of hyper-Rayleigh scattering measurements performed on two tricyanovinylthiophene derivative chromophores.¹⁷ The β values of these chromophores have been recently measured in our laboratory in two different solvents by using the ISM.¹⁸ In this paper, we show that the ESM method significantly improves the accuracy of the results. Using this data we also show how an assumption, made both in our previous paper¹⁸ and in others,^{12,13} that the value of K [in Eq. (1) above] is constant for the same chromophore in different solvents (as long as experimental conditions remain exactly the same) should be used with caution. Also introduced in this paper is a previously unreported method of data analysis for the hyper-Rayleigh scattering experiment, specifically the recording of a histogram of the scattering signal from the detector. We show how the concentration dependence of the width of the histogram is a sensitive indicator of the onset of chromophore-chromophore molecular interactions. We also discuss the concentration dependence of the measured β value of the chromophore, *para*-nitroaniline (*p*NA) used as the external standard in the

above measurements. Finally, we report on results regarding the concentration dependence of the depolarization ratio of one of the tricyanovinylthiophene derivatives.

EXPERIMENT

The structure and synthesis of the two tricyanovinylthiophene derivatives used in this study have been reported previously.¹⁷ The IUPAC names of the chromophores are (E)-[5-[2-[4-(diethylamino)phenyl]ethenyl]-2-thienyl]ethenetriacarbonitrile (chromophore-I) and (E)-[5-[2-[4-(diphenylamino)phenyl]ethenyl]-2-thienyl]ethenetriacarbonitrile (chromophore-II). *Para*-nitroaniline (Aldrich catalog no. 18,223-0; purity 99+%) was used as received. The solutions used in the experiments were made by first preparing a stock solution of the chromophore in an appropriate solvent (either chloroform or benzene for chromophores-I and -II and these two solvents plus dioxane for *p*NA) and then making a concentration series by successive dilution. Solution concentrations were on the order of 10^{15} - 10^{18} molecules/cm³ for all solutions and were verified by measuring the absorbance at λ_{max} with an ultraviolet/visible spectrometer. To remove undissolved particulates, which could be the source of spurious scattering signals,¹¹ all solutions were filtered through a 0.2 μ m FTEP filter (Watterman) before measurements were made. Glass cells, which did not yield an SHG signal, were used as sample holders. When experiments were done using the ESM, extreme care was taken to not change any of the experimental conditions between measurements of the chromophore and standard as this would have affected the value of K [Eq. (1)] and hence produced incorrect results.

A schematic of the optical setup used during the experiments has been previously reported.¹⁸ Basically, it consisted of a Q-switched Nd:YAG laser (Spectra-Physics GCR-11) at 1.064 μm operating at 10 Hz and the associated optics. Beam power stability was assured by allowing the laser a warm-up period of at least one hour before measurements were made. The hyper-Rayleigh scattered light was detected at 90° relative to the incident beam using a side window photomultiplier tube. A 532 nm (10 nm bandwidth) interference filter (Newport) at the entrance to the photomultiplier tube housing prevented any Rayleigh scattered 1064 nm light and any light generated via fluorescence from reaching the detector. In addition, all measurements were made with lights in the laboratory turned off so as to eliminate the possibility of stray 532 nm light being measured by the detector. The signal from the PMT was analyzed with a microprocessor-based boxcar integrator (EG&G 4400, 4402) which was triggered by the Q-switch of the laser. The boxcar was interfaced to a personal computer. For the measurements of the polarization dependence of the scattered light, a polarizer was inserted into the beam path before the sample cell and an analyzer, mounted in a computer-controlled motorized rotation stage, was placed after it.

To obtain the HRS intensity with a boxcar integrator, the standard method is to use a "static gate" mode that integrates the total signal intensity that falls within the boxcar's gate. When this method is used, all information about the dynamics associated with hyper-Rayleigh scattering¹⁹ is lost. However, with each laser shot the scattered photons that reach the detector do so with a combined energy that reflects the instantaneous concentration distribution in the solution. A histogram of the signal

intensity from the PMT would yield detailed information about the energy distribution of the scattered photons. This, in turn, would provide information about the fluctuation of chromophore concentration in solution; the width of the histogram would indicate the extent of the mean square concentration fluctuations. In this study, the boxcar integrator was programmed to record a histogram of the signal intensity from the PMT during the gate time for a specified number of laser shots.

A sample histogram from one of the tricyanovinylthiophene chromophores in benzene is shown in Fig. 1. The signal level used for the calculation of β was found by performing a Gaussian fit to the data (PeakFit™ by Jandel Scientific) and then taking the calculated center of the Gaussian peak as the HRS intensity (this would represent the most probable energy of the scattered photons during the data acquisition time). The equation used in the Gaussian fit was

$$y(x) = a_0 \exp \left[-0.5 \left(\frac{x - a_1}{a_2} \right)^2 \right]. \quad (2)$$

Here the parameter a_0 is the amplitude of the histogram; a_1 is the center of the Gaussian peak and is the parameter taken as the scattering signal; the width of the histogram is given by parameter a_2 . It should be noted that for the calculation of β it would not matter whether a Gaussian, Lorentzian or Pearsons' equation is used in the fit.

As stated above, the usual method to obtain the HRS intensity would be to simply integrate the total signal intensity that falls within the boxcar's gate. However we have found that by using the histogram method as described above, we not only obtain extra information (the width of the histogram) but are also able to reduce the data collection

time necessary to obtain reproducible data. All of the HRS data presented in this paper was obtained with measurement of only 500 to 1000 laser shots (50 to 100 sec) per solution rather than the 4000 laser shots (6.6 min.) often needed in the static gate mode. To find the relative HRS intensity one could also integrate the data that defines the histogram. However, we have found this method not to be suitable, especially for chromophores with small β values, as the results of an integration can be adversely skewed by only a few high intensity spurious signals.

Since the tricyanovinylthiophene solutions absorbed slightly at the second harmonic wavelength (532 nm)¹⁸ the hyper-Rayleigh scattering intensities from these solutions had to be corrected for absorption before calculations were made (*p*NA has negligible absorption at 532 nm). This was done by using a Beer's law expression:

$$I_f = I_i e^{-\epsilon c l} \quad (3)$$

Here I_f is the intensity of the hyper-Rayleigh scattering as measured by the PMT, I_i is the corrected ("true") signal intensity, ϵ is the extinction coefficient of the sample (L/M-cm), c is the concentration of the sample (moles/L) and l is the optical path length (cm) of the scattered light. Since the excitation beam is defocused into the center of the scattering cell, the optical path length is one-half of the cell diameter.

RESULTS AND DISCUSSION

Shown in Fig. 2 are plots of the concentration dependence of the hyper-Rayleigh scattering intensity from chromophore-II and the external standard *p*NA in benzene. (The quadratic power dependence of the hyper-Rayleigh signal from appropriate solutions of

both chromophores-I and -II as well as *p*NA, indicating that the measured signal was indeed HRS, was previously verified) It must be stressed that the data for this graph was obtained in one run, making sure that no experimental conditions were altered between the measurement of the chromophore and standard as this could have lead to some change in the value of the *K*'s, as mentioned above. Measurements similar to this were also performed on chromophore-I in benzene and on chromophore-II in both solvents so that a comparison could be made between the values measured in this study by the ESM and those measured previously using the ISM. Table I summarizes the measured β values for both chromophores in the two solvents.

For the calculation of the β values of chromophores-I and -II using the ESM, the β value of the *p*NA standard in benzene and chloroform must be known. The β value of *p*NA in chloroform has been reported in the literature, although there is some discrepancy between the values obtained by different authors (see below). For this study the exact β value of *p*NA in chloroform used in calculation was verified at the time of experiment (it's value was determined from the $\frac{I(2\omega)}{I^2(\omega)}$ vs. ρ_c plots of *p*NA in chloroform using the ISM).

The β value of *p*NA in benzene is not known in the literature and cannot be obtained directly by the ISM (for the reason that benzene has a zero β value). For this reason we obtained it using a method suggested by ref. 12 where an empirical relationship between the β value of a chromophore and (a function of) the dielectric constant, ϵ , of the solvent is demonstrated. By using values of β reported in the literature for *p*NA in different solvents with varying dielectric constants, we obtained a β value for *p*NA in benzene of

16.4×10^{-30} esu by interpolation.²⁰ This value was then used as the value of β_{st} in the calculations of β of the chromophore unknowns in benzene.

Upon examination of Table I, it can be seen that although the measured β values of the two chromophores in chloroform (as determined with the ISM and ESM) agree to within experimental error, those measured in benzene do not. Since benzene is a centrosymmetric solvent and thus possesses a zero β value, with the previous measurements, the chromophore/benzene solutions had to be calibrated against solutions with known values of K (following a method given in refs. 12 and 13). Specifically, the assumption was made that the value of K in Eq. (1) above would not change too much with solvent for a particular chromophore as long as experimental conditions remained exactly the same. (For instance, K was first determined for a chromophore-I/chloroform solutions series; this value was then assumed to describe a chromophore-I/benzene solution series) As explained above, however, the constant K contains local field factors that depend upon the dielectric constant of the solution. Since chloroform and benzene have different dielectric constants [$\epsilon(0)_{CHCl_3} = 4.806$,²¹ $\epsilon(0)_{C_6H_6} = 2.284$ ²¹] the assumption that K is the same in both solvents was probably a poor one. Note that the results calculated with this assumption are very sensitive to it. On the other hand, in the ESM, the same solvent is used for the chromophore and the standard and the uncertainty introduced by solvent substitution in the ISM is avoided. Thus, the ESM is definitely a superior method in this regard since the solvent remains the same during the determination of a particular β and thus the effects of local field factors should more completely cancel out. From the data presented in the table, one notes that the β value of chromophore II is

larger than that of chromophore I in both solvents. Furthermore, for a given chromophore, the β value in chloroform is larger than that in benzene (as determined by the ESM). This solvent dependence is consistent with the higher dielectric constant of chloroform.

Similar to our previous results^{18,19} we found in the present work that the intensity of the scattered second harmonic light increases linearly with concentration at low concentration levels but that at higher concentrations, the signal intensity levels-off (Fig. 2). This behavior was observed for chromophores-I and -II in both chloroform and benzene. Since the scattering intensity data had been corrected for absorption, this leveling-off was not due to the absorption of scattered light by the chromophores. In addition, we have ascertained that the signal level measured in these experiments was well below the saturation level of the PMT used. Since the hyper-Rayleigh scattering signal results mainly from the breakdown of local centrosymmetry owing to concentration fluctuations in the medium,¹⁹ this leveling-off in signal as the chromophore concentration increases indicates that at higher concentrations the solution becomes more isotropic than at lower concentrations. Thus, the result suggests the presence of chromophore-chromophore intermolecular interactions which suppress chromophore concentration fluctuations as the chromophore concentration exceeds a certain value.

The concentration dependence of the HRS scattering intensity will affect the determination of the β value. Fig. 3 shows the concentration dependence of the hyper-Rayleigh scattering intensity of the *p*NA standard in chloroform. As can clearly be seen, the HRS intensity increases linearly at low concentration but then bends over above the

concentration of 28×10^{18} molecules/cm³. As indicated in the figure, one may approximate this result with two linear regions, one at very low concentration and the other at a higher concentration. The β value calculated for *p*NA will obviously depend upon which concentration region is used. Using the data shown, we have calculated a value for β of 34×10^{-30} esu from the lower concentration region and a value of 23×10^{-30} esu for β in the higher concentration region (using the ISM). Clearly, the different slopes observed in the two regions are due to *p*NA-*p*NA molecular interactions that become important at higher concentration. It is interesting to note that two different β values of *p*NA in chloroform obtained using HRS have recently been reported in the literature. Persoons et. al reported a value of 23×10^{-30} esu¹³ and Heesink et. al reported a value of 34×10^{-30} esu.²² Also, Stählein, et. al have recently reported a value of 16.8×10^{-30} esu for *p*NA in chloroform obtained from EFISH measurements.¹⁰ It is apparent that the β value obtained using HRS (and also that obtained using EFISH) depends sensitively on the concentration range that is used in the extrapolation. In general, the data at high chromophore concentration will yield a lower β value than that at low concentration. To avoid the intermolecular effect, one needs to carry out the HRS experiment in as dilute a concentration range as possible in order to obtain a true single-molecule β value. In this study, we were careful to keep the standard *p*NA solutions in the dilute concentration range.

As mentioned above, the width of the histogram (HW) of the scattering signal indicates the extent of the mean square concentration fluctuations of the chromophores in solution. Thus, a HW versus ρ_c plot would be expected to exhibit the concentration

dependence of the mean square concentration fluctuations of the chromophore. Such a plot is shown in Fig. 4, which shows the concentration dependence of the HW as derived from the Gaussian fit [parameter a_2 in Eq. (2)] for a series of *p*NA/dioxane solutions. At low chromophore concentration the HW increases rapidly with increasing concentration. The HW reaches a maximum at about 18×10^{17} molecules/cm³ and decreases above this concentration. Above the concentration that shows the maximum HW, intermolecular interactions decrease the mean square fluctuations. With the help of a HW versus concentration plot, one can determine a chromophore concentration range that exhibits minimal intermolecular interactions and which can then be used to obtain the β value of a single molecule. As clearly shown here HRS is rather sensitive to intermolecular effects. In fact, hyper-Rayleigh scattering was originally proposed as a method to study molecular interactions.¹¹

There are many types of intermolecular interactions that could lead to a decrease in chromophore concentration fluctuations. Considering the fairly large permanent dipole moments of these molecules,¹⁸ one would expect dipole-dipole interactions to play an important role in enhancing the correlation between chromophores. In addition, due to the large optical fields applied, induced dipole-induced dipole interactions may also play a role. Bersohn has discussed the pair orientation correlation arising from the induced dipole associated with the first hyperpolarizability,²³ however, considering the hyperpolarizability value that we have measured and the optical fields used in the experiment, we estimate that the magnitude of this correlation will be very small. The formation of dimers and higher molecular aggregates of the NLO chromophores may be

also be important. Our recent study of the HRS intensities from carbocyanine dye solutions has shown dimerization and the formation of higher aggregates to be the cause for the decrease of the HRS intensity as the chromophore concentration is increased above a certain value.¹⁹ It is possible that chromophore aggregation is also responsible for the effect observed here.

We have recently begun a detailed study of the polarization dependence of hyper-Rayleigh scattered light. In general, the first hyperpolarizability tensor consists of 10 elements (assuming Kleinmann symmetry), although the major component is the one along the molecular axis. As has been shown in detail elsewhere, by resolving the hyper-Rayleigh signal into different polarization components, various rotational invariant elements of the β tensor can be resolved.^{11,23,24,25,26} This information is of interest as the determination of the magnitude of the tensor components will shed light on molecular structure. Performing the polarization dependence experiments is also expected to yield data useful for the molecular engineering of NLO chromophores with higher β values. We have studied the polarization dependence of the HRS intensity using continuous rotation of the analyzer polarization axis; however, we present here only results of the *depolarization ratio at 90° scattering angle*. The complete resolution of the β tensors for these chromophores will be presented elsewhere.²⁷

The depolarization ratio at 90° scattering angle is given by the expression

$$\sigma = \frac{I_{2\omega}(sp)}{I_{2\omega}(pp)}$$

where, $I_{2\alpha}(sp)$ and $I_{2\alpha}(ss)$ indicate, respectively, detected p and s polarized HRS radiation induced by s polarized incident radiation. Recently, Heesink et. al. have completed a study of the hyperpolarizability tensor components of a molecule that possesses C_{2v} symmetry and in which they measured the depolarization ratio of p NA.²² Their result of $\sigma = 0.23$ is in good agreement with the theoretically predicted value of $\frac{1}{5}$,²³ assuming only one dominant β tensor element and also assuming that Kleinmann symmetry is valid.¹⁴ Experimentally, they found that their value for the depolarization of p NA was independent of both solution concentration and solvent, thus indicating that molecular interactions were negligible in their work. This is consistent with the higher β value for p NA (34×10^{30} esu) that they reported leading one to suspect that the β value of 23×10^{30} esu reported by Clays and Persoons¹³ is low due to the presence of intermolecular interactions.

Table II gives results from our depolarization ratio measurements on two different concentrations of chromophore-II in chloroform. Although the exact symmetry of this molecule is complicated, as a zero order approximation it can be considered to be effectively C_{2v} due to long π -electron conjugation. Our experimental result of $\sigma = 0.23$ at low concentration is consistent with this approximation. However, at higher concentration, the depolarization ratio increases to 0.32. This increase over the predicted value is another indication of chromophore-chromophore intermolecular effects that become important at high chromophore concentration. The delineation of the nature of the intermolecular interactions will be a subject of future studies.

CONCLUSIONS

In summary, we have performed hyper-Rayleigh scattering measurements on two tricyanovinylthiophene NLO chromophores. We have developed and demonstrated the use of an external standard method. We have found this method to yield more reliable results than the previously used internal standard method. The ESM has the additional advantage of being able to be directly used with solvents that possess a zero β value. Furthermore, we have also demonstrated the utility of a histogram of the HRS intensity. We have shown that the width of the histogram provides information concerning the range of solution concentration that one can safely consider to minimize the intermolecular effects and that it reflects the effects of chromophore concentration fluctuations. In addition, we have shown that the leveling-off of the HRS intensity as the concentration of the tricyanovinylthiophene solutions increases above a certain concentration is due to intermolecular effects, possibly due to the dipole/dipole interactions and formation of dimers or higher molecular aggregates in solution.

We have also presented data indicating the concentration dependence of the β value of a chromophore in solution, in this case *p*NA in chloroform. We have demonstrated that depending on the concentration range of the *p*NA solution, the value for β could agree with two disparate values given in the literature. The present experiment using the histogram width method favors the higher β value for *p*NA in chloroform reported by Heesink et al.²² Finally, we have provided the value of the depolarization ratio of the HRS radiation. Our results from a low concentration solution of chromophore-II in chloroform have shown good agreement with the theoretical prediction for a molecule possessing C_{2v} symmetry. At a higher concentration, we have

found that the depolarization ratio increases, indicating the presence of intermolecular effects.

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TABLE I - β values, with estimated uncertainties, of the two tricyanovinylthiophene chromophores obtained previously and obtained here using the ESM

Chromophore	Solvent	ESM $\beta \times 10^{30}$ esu 1064 nm	Previous Results ¹⁸ $\beta \times 10^{30}$ esu 1064 nm
I	CHCl ₃	2800 (± 50)	3300 (± 500)
	C ₆ H ₆	1400 (± 30)	2600 (± 400)
II	CHCl ₃	3400 (± 70)	3000 (± 400)
	C ₆ H ₆	2700 (± 54)	3600 (± 500)

Table II - Depolarization ratios for two concentrations of chromophore-II in chloroform

Number Density (particles/mL)	σ	$\langle \sigma \rangle^{**}$
2.23×10^{15}	0.23	0.23 ± 0.04
	0.25	
	0.30	
	0.24	
	0.18	
4.45×10^{17}	0.30	0.32 ± 0.02
	0.34	

** $\langle \sigma \rangle$ indicates the average value of different measurements.

Figure Captions

1. Sample histogram of the hyper-Rayleigh scattering signal from chromophore-II in benzene. Filled squares represent data points; the solid line is a Gaussian fit to the data. Here the abscissa is the (integrated) energy at the 2 ns gate (placed at the

maximum of the temporal waveform) and the ordinate is number of counts for a given energy .

2. Demonstration of the use of the external standard method of hyper-Rayleigh scattering to calculate the β value of chromophore-II in benzene. Graph *A*) is a plot of the hyper-Rayleigh scattering signal vs. chromophore-II solution concentration; Graph *B*) is a plot of the same parameters but using the *p*NA standard. The data for these two graphs was measured sequentially with extreme care being taken not to change any experimental parameters during the measurement.
3. Concentration dependence of the β value of *p*NA in chloroform calculated using the ISM of hyper-Rayleigh scattering. Note the two distinct linear regions of the graph and how the β value calculated depends on which region is used.
4. Variation of the histogram width [see Eq. (2)] vs. sample concentration for a *p*NA in dioxane solution series.

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²⁰From the literature, the β values of *p*NA in dioxane [$\epsilon(0) = 2.209$]²¹, chloroform [$\epsilon(0) = 4.806$]²¹ and methanol [$\epsilon(0) = 32.63$]²¹ are 16.9×10^{-30} esu [C. C. Teng and C. F. Garito, *Phys. Rev. B*, **28**, 6766 (1983)], 23×10^{-30} esu (ref. 12) and 34.5×10^{-30} esu [J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, **66**, 2664 (1977)], respectively [$\epsilon(0)$ denotes the zero frequency dielectric constant of the solvent]. As shown in ref. 12, when the β value of the chromophore is plotted vs. $\frac{\epsilon - 1}{2\epsilon + 1}$, where ϵ is the dielectric constant of the solvent, a straight line is obtained. Knowing the dielectric constant of benzene [$\epsilon(0) = 2.284$]²¹, allowed us to interpolate the β value of *p*NA in that solvent to be 16.4×10^{-30} esu. [$\frac{\epsilon - 1}{2\epsilon + 1}$ is related to the reaction field experienced by the solute molecules as the result of interaction with the permanent dipole moment of the solvent molecules (C.C. Teng and A.F. Garito, *ibid.*)]

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