REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection data needed, and completing and reviewin burden, to Washington Headquarters Serv Budget, Paperwork Reduction Project (07	of information is estimated to average 1 hour per response, g collection of information. Send comments regarding this nees, Directorate for Information Operations and Reports 1 704-0188), Washington, DC 20503.	including the time for reviewing instructions, se burden estimate or any other aspect of this collo 215 Jefferson Davis Highway, Suite 1204, Arlin	earching existing data sources gathering and maintaining the ection of information, including suggestions for reducing this gton, VA 22202-4302, and to the Office of Management and	
1. AGENCY USE ONLY (Leave blank) 2. REPORT DATE June 20, 1995	3. REPORT TYPE AND DATES COVE Technical	RED	
4. TITLE AND SUBTITLE Dicarbocyanine Dyes in Methanol Solution Probed by Rayleigh and Hyper- Rayleigh Light Scattering.			5. FUNDING NUMBERS #313H030 Kenneth J. Wynne	
6. AUTHOR(S) Ok-Keun Song and C.H. W	ang			
7. PERFORMING ORGANIZATION N 632 Hamilton Hall Department of Chemist University of Nebraska Lincoln, NE 68588-030-	AME(S) AND ADDRESS(ES) Try -Lincoln 4	IC CTE 711995	8. PERFORMING ORGANIZATION REPORT NUMBER 36	
9. SPONSORING / MONITORING AC Office of Naval Researc 800 N. Quincy Street Arlington, VA 22217-50	SENCY NAME(S) AND ADDRESSIES JULY Ch	B	10. SPONSORING/ MONITORING AGENCY REPORT NUMBER Office of Naval Research	
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17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

Dicarbocyanine Dyes in Methanol Solution Probed by Rayleigh and Hyper-Rayleigh Light Scattering

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Abstract.

The hyper-Rayleigh scattering (HRS) intensity of two symmetric carbocyanine dyes (1122DEDC and 1144DEDC, full names given in the text) in methanol is measured as a function of dye concentration. These dye molecules at equilibrium show no permanent dipole moment. The low concentration data showing the HRS intensity is proportional to the dye concentration are used to determine the first order hyperpolarizability for each of these dyes. However, above a concentration $\rho_b=0.1{\times}10^{-3}$ M, the HRS intensity shows an anomalous concentration dependence. Above ρ_b , the HRS shows a saturation behavior and even decreases with increasing concentration at high dye concentration. The HRS intensity depolarization ratio is also measured as a function of dye concentration. At lowest concentration, the depolarization ratio obtained is consistent with that expected for molecules with C_{2v} symmetry. As the dye concentration increases, the depolarization ratio also increases rapidly but the increase quickly saturates as concentration exceeds ρ_b . The concentration dependence of the HRS intensity and depolarization ratio are interpreted as due to formation of molecular aggregates. The depolarized Rayleigh scattering (DRS) intensity is also measured as a function of dye concentration. The result of DRS corroborates well that found of HRS.

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Introduction.

Organic molecules consisting of a π -electron delocalization group having strong electron donor and electron acceptor groups attached to the ends of the π -system are known to exhibit a large first order hyperpolarizability β .¹ The large β value arises from large transition dipole moment and asymmetry in the charge distribution of the charge-transfer excited state. Various methods have been devised to assemble organic molecules in polymer to form materials having a large second order optical susceptibility. This is presently an active area of research because of potential applications in nonlinear optics (NLO). Efforts leading to the determination of the β value of the chromophore and also understanding of the effect of the chromophorechromophore interaction to help the design of an effective nonlinear optical material are of interest.

Up to the present time, the method of electric field induced second harmonic generation (EFISH) has been most used for characterizing the β value of the NLO chromophore.² In the application of the EFISH method, NLO chromophores are dissolved in a solvent of low viscosity to form a solution. An external DC electric field is then applied to orient the chromophores in solution from which a laser radiation at fundamental frequency ω is used to induce an optical field at the second harmonic frequency 2 ω . The induced second harmonic generation (SHG) is measured as a function of chromophore concentration. The result is extrapolated to zero concentration to yield the value for calculating β . In order to determine the β value, one also needs local field factors at fundamental frequency ω ,

second harmonic frequency 2ω , and at zero frequency. Since an external electric field is applied to the sample, the EFISH method also relies on the existence of a permanent (or ground state) dipole moment of the NLO chromophore to orient and remove the macroscopic centrosymmetry of the chromophore solution. However, there exists a class of materials consisting of molecules that do not have permanent dipole moments but have a large transition dipole moment and a dipole moment in the excited charge transfer state. These types of molecules are of potential interest because they might also possess large β values.³ To determine the β values of these type of molecules, an alternative method must be used.

Harmonic light scattering, or more commonly known as hyper-Rayleigh scattering (HRS) is an alternative technique for the determination of β .⁴ Light scattering occurs as a result of fluctuations in the local refractive index. If the incident radiation inducing light scattering has a high intensity, the induced polarization in the medium could acquire an appreciable amplitude in the optical field at second harmonic frequency 2ω . Thermal fluctuations in the local refractive index would then give rise to incoherent scattering light at 2ω at all scattering angles. By measuring the scattered light intensity at 2ω as a function of the NLO chromophore concentration, the β value of the chromophore can be deduced.⁵ Since no external dc electric field is applied in HRS, in contrast to the EFISH technique, no permanent electric dipole moment of the molecule is needed. Hence, the HRS method applies to all molecular systems whether or not they possess permanent dipole moments.⁶

In this paper, we have employed the HRS technique to determine the β values of two carbocyanine dyes: 1,1'-diethyl-4,4'-dicarbocyanine

(1144DEDC) and 1,1'-diethyl-2,2'-dicarbocyanine (1122DEDC). Due to symmetry and π -electron delocalization, the cations of these carbocyanine dyes have practically no permanent dipole moment. Moreover, since the carbocyanine dyes are known to associate,⁷ forming molecular aggregates even at low concentration, one expects the HRS intensity to sensitively reflect the aggregate formation as the concentration of the chromophore changes. Furthermore, because of more spherical shape, molecular aggregates have less optical anisotropy. Depolarized Rayleigh scattering depends on the anisotropy of the polarizability tensor of the scatterer. As the aggregates are formed, the optical polarizability anisotropy inside the scattering volume is expected to decrease, hence decreasing the depolarized Rayleigh scattering intensity. To corroborate the HRS result, we have also measured the depolarized Rayleigh scattered light intensity as a function of the concentration of the carbocyanine dye.

Experimental.

1122DEDC and 1144DEDC were purchased from Kodak company and used directly without further purification. Solution with different concentrations were prepared from a stock solution (1 mM in methanol) by successive dilution. The stock solution was filtered with a 0.2 µm filter to remove dust and undissolved particulate. Because quartz cells were found to give rise to a strong SHG signal, glass cells which give rise to negligible SHG signal were used as light scattering cells for the HRS experiment. The optical setup used for the present HRS measurement was similar to that described in

our previous publication.⁸ Briefly, a Nd:YAG laser (10 Hz and 3-8 ns pulse width) was used as an excitation source. The intensity of the incident beam from the Nd:YAG laser, after it was filtered by a long pass filter to remove the second harmonic component at 532 nm, was varied by the combination of a polarizer and a half wave plate. The incident beam was focused onto the sample with a f/10 lens and the scattered light was collected by a f/1.3 camera lens followed by a biconvex lens of 30 cm focal length. The collected signal from scattered light was directed to a photomultiplier tube having attached in the front an interference filter and a sharp bandpass filter set at the second harmonic frequency. A boxcar integrator was used to process the signal. To measure the depolarization ratio of the HRS intensity, we set the excitation radiation always in the s polarization. The polarization of the light analyzer was selected by a Glan-Taylor polarizer either in the s (polarized) or p (depolarized) polarization. All HRS experiments were carried out at room temperature and the scattering angle was 90°. The depolarized Rayleigh scattering experiment was carried out by using a continuous wave (cw) argon ion laser oscillating at 514.5 nm. The depolarized scattered light also at 90° scattering angle selected by an analyzer was measured through a double grating monochromator allowing only the intensity at 514.5 (\pm 0.02) nm to pass. The intensity of the scattered light was detected by using a photon counting system. The depolarization of the scattered light was calibrated with CCl₄.

Results and Discussion.

Hyper-Rayleigh scattering is due mainly to fluctuations in the orientation and the number density of the optical chromophores. The fluctuations instantly remove the optical isotropy of the solution and induce the second harmonic scattering in the solution. Orientational fluctuations are responsible for the depolarization of the HRS intensity. The hyper-Rayleigh intensity at 2ω can be written as

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

where G is an experimental constant determined by the scattering geometry, local field factors and is also proportional to $(2\omega)^4$ associated with the scattering process. (ρ_s , β_s) and (ρ_c , β_c) are the (concentration, hyperpolarizability) of the solvent molecule and chromophore, respectively. In this experiment, methanol is used as an internal standard as well as a solvent. The first hyperpolarizability of methanol has been found to be 0.69×10^{-30} esu.⁹ This value was used as an internal standard to calculate the first order hyperpolarizability of 1122DEDC and 1144DEDC using the method described elsewhere.⁸ The HRS intensity is certified by the quadratic dependence of the HRS signal on the incident laser power intensity I(ω). The β_c values for 1144DEDC and 1122DEDC are found to be 802×10^{-30} esu and 486×10^{-30} esu, respectively. Comparing the β values of reported NLO chromophores, the β values of these carbocyanine dyes are rather substantial.

Figure 1 shows the chemical structures of 1122DEDC and 1144DEDC. Two canonical resonance structures contribute equally to the ground-state configuration of the molecule. Clearly, the transition dipole of cyanine

molecule is along the long π axis of the molecule. Figure 2 shows the UV/Vis spectra of 1122DEDC and 1144DEDC in methanol. The spectra show that 1122DEDC and 1144DEDC have a negligible absorption in the 500-535 nm region. Because of two equal resonance structures contributing to the ground state configuration of dicarbocyanine dyes, one can safely assume that these molecules are nonpolar in the ground state. To certify the zero dipole moment hypothesis, we have investigated the solvatochromic effect of the two carbocyanines and compared the results with other well known NLO molecules such as disperse red 1 (DR1) and paranitroanilne (PNA) in methanol, 2-propanol, and dimethylsulfoxide (DMSO). The comparison of the solvatochromic shift of 1122DEDC with that of DR1 and PNA in these solvents are shown in Table I. Since the dielectric constants of these solvents vary greatly, molecules with permanent dipole moments are expected to display a large solvatochromic shift, as exhibited by the case of DR1 and PNA. On the other hand, 1122DEDC only shows a very small spectral shift in these solvents. A similar observation is also found for 1144DEDC. The results thus indicates that the ground state dipole moment of 1122DEDC (or 1144DEDC), if it exists, is negligibly small.

Figure 3 and 4 show the hyper-Rayleigh signal as a function of the number density of 1122DEDC and 1144DEDC, respectively. One sees that the intensity of the second harmonic scattered light increases linearly with increasing chromophore number density in the very low concentration range $(<10\times10^{16} \text{ molecules/cm}^3 \text{ or } 1.7\times10^{-4} \text{ M})$. Above this concentration its increase is slower and as the number density exceeds 300×10^{15} molecules/cm³ the HRS intensity even gradually decreases. Since

1122DEDC and 1144DEDC show negligible absorption at 532 nm, the decrease in the second harmonic intensity is not due to absorption of the scattered light by the molecules. We have also tested the photomultiplier saturation range which might also give rise to an abnormal intensity behavior if the intensity of the scattered light is large; however, the magnitude of the second harmonic signal observed in this experiment is much lower than the photomultiplier saturation range. Thus, we conclude that the anomalous intensity behavior is due to the intermolecular effect affecting the hyper-Rayleigh scattering intensity as the chromophore concentration is greater than 10×10^{16} molecule/cm³. Using the β values determined from the linear region of the HRS intensity versus concentration plot as given above (β =802×10⁻³⁰ esu for 1144DEDC and 486×10⁻³⁰ esu for 1122DEDC), and the strength of the optical field employed in the present experiment, ¹⁰ we have estimated the pair contribution due to orientational correlation as discussed by Bersohn.¹¹ The orientational pair correlate contribution is found to be rather insignificant.

To obtain additional information concerning the intermolecular interaction effect we have carried out the HRS depolarization experiment. The polarization ratio is defined as

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

When $I_{2\omega}(sp)$ and $I_{2\omega}(ss)$ indicate the HRS intensity induced by using the incident radiation in the s-polarization and scattered light detected at p (depolarized) and s (polarized) radiation, respectively. Results of the

depolarization experiment are given in Table II for several chromophore concentrations. Depolarization ratios measured at ρ_c equal to 6.02, 1.13, and 0.05 (in the unit of 10^{17} / cm³) are 0.69, 0.64 and 0.18, respectively. One notes that the depolarization ratio decreases with decreasing chromophore concentration. The decrease is rather rapid at low chromophore concentration. Heesink et al. have studies the hyperpolarizability tensor components of a C_{2V} molecule and they have measured the depolarization ratio of PNA.¹² Their results show that at low PNA concentration, the second harmonic signal is linearly proportional to the PNA concentration, and σ is independent of the concentration and types of solvent. This indicates that the intermolecular contribution is negligible in their PNA results. Theoretically, the incoherent polarization ratio of C_{2v} molecule is 1/5, if only one of the β values along the pricipal axis is induced (assuming Kleinman symmetry).^{11,13} The effective symmetry of 1122DEDC and 1144DEDC is C_{2v} . Our result at low concentration is consistent with the value expected for a simple C_{2v} molecule but its value is smaller than the theoretical value including only the principal component. The discrepancy is presumably due to the contribution of other β tensor components and the assumption of Kleinman symmetry in theoretical calculations. Relaxing the Kleinman symmetry requirement tends to reduce the depolarization ratio, as shown by Lalama and Garito¹⁴ who have calculated five independent β tensor components of PNA at λ =1064 nm, not assuming Kleinman symmetry. Their result for σ (PNA) is 0.236. However, the deviation from the lowest concentration value found at higher concentration is thus due to intermolecular effects.

Due to extensive π -electron delocalization that can easily be polarized, strong intermolecular interaction exists between carbocyanine dye molecules. Strong intermolecular interactions result in the association of cyanine monomers, forming dimers, trimers and higher aggregates as the concentration of carbocyanine is increased. Due to the important role that these aggregates play in spectral sensitization, there has been extensive experimental and theoretical studies of the photoprocess of cyanines in solution as a function of concentration.¹⁵ The formation of aggregate is responsible for the increase of the depolarization ratio as the chromophore concentration increases.

As shown in Figure 2, the absorption spectra of 1144DEDC and 1122DEDC in methanol solution are characterized by an intense peak and a relatively weak peak at shorter wavelength. These spectral features are the characteristics of monomeric cyanine dyes.¹⁶ The formation of dimers and aggregates is accompanied by changes in the absorption spectrum due to strong electronic coupling (via transient dipoles) between molecules in these aggregates. The modification of the electronic structure as a matter of the aggregate formation is expected to change the value of molecular hyperpolarizability, hence affecting the HRS intensity. However, the more important consequence of the aggregation is the reduction of concentration fluctuations in the solution of carbocyanine dyes.

As is well known, regardless of the magnitude of the molecular hyperpolarizability, the second order optical susceptibility vanishes strictly in an isotropic system such as the liquid or solution. The presence of HRS in the carbocyanine solution as considered here arises from concentration fluctuations

which remove the micoscopic centrosymmetry at the site of the NLO chromophore. In cyanine dyes, both H-aggregate and J-aggregate are known to be present.¹⁶ The H-aggregate corresponds to a sandwich dimer and due to electronic coupling its absorption band is blue shifted from the monomer band. On the other hand, the J-aggregate is a linear (planer) dimer and its absorption spectrum exhibits a red shift.¹⁶ As one sees in Figure 2, there is practically no absorption at 532 nm (the second harmonic frequency) for both carbocyanine dyes studied. A blue shift from monomer band would result in an increase in absorption, hence giving rise to a resonance enhancement in the value of hyperpolarizability β . Time resolved picosecond absorption spectroscopic studies of aggregated diethylthiadicarbocyanine iodide (DTDCI) indicate the dominance of the blue-shifted absorption H-aggregate in methanol and ethanol solutions.¹⁷ Therefore, without a considerable reduction in the concentration fluctuations as a result of the intermolecular associations, one would expect to observe a greater HRS intensity from the spectroscopic data consideration alone. This prediction is contrary to the experimental result as shown in Figures 3 and 4, which show that the HRS intensity does not proportionally increase with the chromophore concentration.

Since the sandwich dimer of H-aggregates gives rise to a more or less spherical configuration and is expected to greatly decrease the optical anisotropy, the reduction in the optical anisotropy can be followed by depolarized Rayleigh scattering (DRS). The intensity of DRS is proportional to $|\delta \alpha_{ani}|^2$, where $\delta \alpha_{ani}$ is polarizability anisotropy.¹⁸ The DRS intensity (I_{ω}) for 1122DEDC and 1144DEDC are shown as a function of chromophore concentration (ρ_c) in Figures 3, and 4, respectively. One notes that for both

chromophore solutions the DRS intensity steadily decreases with increasing chromophore concentration. The I_{ω} vs. ρ_c plot for both solutions shows a break at $\rho_b \cong 0.1 \times 10^{-3}$ M). Contrasting the DRS result to that of the hyper-Rayleigh scattering, one further notes that beyond ρ_b the growth of the SHG intensity becomes slower; moreover, proceeds the decrease in the DRS intensity with increasing chromophore concentration with a different slope as the cyanine concentration is greater than ρ_b . The result clearly shows a decrease in the polarizability anisotropy, thus suggesting continuous formation of aggregates as the chromophore concentration increases beyond ρ_b . Above ρ_b the concentration dependence of both I_{ω} and $I_{2\omega}$ are different from that below ρ_b . Spectroscopic data have shown that cyanine dyes in methanol or ethanol solution at room temperature at concentration smaller than 0.1 mM exist exclusively in their monomeric form.¹⁵ If this is indeed the case, our DRS data would suggest that a strong interaction of 1122DEDC or 1144DEDC with methanol exists and the interaction reduces the optical anisotropy of the single moleculear cyanine prior to dimer formation. However, the DRS data could also be interpreted as formation of dimer at concentration below ρ_b . This would then contradict the prevalent view of the cyanine dyes at low concentration. Nevertheless, considering the high polarizable π -electron density of the cyanine dye, strong solvent-dye interactions via the OH proton is not unexpected for the single cyanine molecule in methanol. Above ρ_b , dimers. trimers, tetramers and higher aggregates are then expected to be formed, resulting in a continuous decrease in the optical anisotropy. As $\rho > 4 \times 10^{17}/cm^3$ $(6.6 \times 10^4 \text{ M})$, the HRS decreases with increasing chromophore concentration, indicating that above this concentration the concentration fluctuations are

considerably retarded, possibly suggesting the presence of interactions between dye aggregates.

Summary and Conclusion.

In summary, we have measured hyper-Rayleigh scattering (HRS) intensities of two carbocyanine dyes (1122DEDC and 1144DEDC) as a function of dye concentration. At low concentration, the intensity linearly increases with the number density of the dye molecule. Above 0.1×10^{-3} M (ρ_b) , the intensity increase becomes smaller and even gradually decreases at higher concentration. Using the linear region, we have determined the value of the effective hyperpolarizability β for these cyanine dyes to be 802×10^{-30} and 486×10⁻³⁰ esu for 1144DEDC and 1122DEDC, respectively. The depolarization ratio of the HRS intensity obtained at 90° scattering angle has also been determined as a function of concentration. The depolarization ratio has been found to increase with increasing dye concentration. At the lowest concentration, we have obtained a depolarization ratio value expected for a single molecule with C_{2v} symmetry. The increase of the depolarization ratio in conjunction with the leveling off of the HRS scattering intensity as the dye concentration is increased has been interpreted as due to formation of aggregates. The depolarized Rayleigh scattering (DRS) intensity in solution has also been measured as a function of the cyanine concentration. The observation of a decrease in DRS intensity as the dye concentration increases is consistent with the phenomenon of cyanine aggregate formation.

We have shown that the hyper-Rayleigh scattering technique provides not only a useful method for determining the molecular hyperpolarizability, but also a powerful method for studying the structure of dye molecules in solution.

Acknowledgment.

This work is supported by NSF (DMR 912993).

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Figure captions:

- Figure 1. Chemical structures of 1,1'-diethyl-2,2'-dicarbocyanine and 1,1'-diethyl-4,4'-dicarbocyanine.
- Figure 2. UV/Vis absorption spectra of 1,1'-diethyl-2,2'-dicarbocyanine (A: dotted line) and 1,1'-diethy-4,4'-dicarbocyanine (B: solid line).
- Figure 3. Intensities of Rayleigh (open circle) and hyper-Rayleigh (closed circle) in the function of concentration of 1,1'-diethyl-2,2'-dicarbocyanine chromophore.
- Figure 4. Intensities of Rayleigh (open circle) and hyper-Rayleigh (closed circle) in the function of concentration of 1,1'-diethyl-4,4'-dicarbocyanine chromophore.



1,1'-Diethyl-4,4'-Dicarbocyanine.



1,1'-Diethyl-2,2'-Dicarbocyanine.

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Fig 2. Song et al.



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Table I. Solvent effects on maximum absorption wavelengths of 1122DEDC, DR1, and PNA.

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Solvent	E	1122DEDC	DR1	PNA
2-propanol	18.3	710 nm	504 nm	 378 nm
Methanol	32.6	708 nm	500 nm	370 nm
DMSO	45.0	716 nm	534 nm	390 nm

∈: dielectric constant, DR1: disperse red 1, PNA: paranitroaniline.

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Number density (X 10 ¹⁷ /cm ³)	I _{ss}	I _{sp}	σ	
6.02	299.47	208.33	0.69	
1.13	283.54	180.64	0.64	ŧ.
0.05	69.43	12.70	0.18	

Table II. Depolarization ratios of 1144DEDC at different concentration.

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