The Slope Ratio Method: A Simple and Accurate Method to Extract the First Hyperpolarizability from EFISH Measurements

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The hyperpolarizabilities of organic molecules in solution have been determined using the method of the electric field induced second-harmonic generation (EFISH). In principle, the EFISH technique is capable of obtaining precise hyperpolarizabilities. However, the reported values of the hyperpolarizability for a given compound may vary by an order of magnitude. These variations arise because of the complications with the measurements of the nonlinear optical response, the coherence length, the permittivity, the density, and the refractive indices of a series of solutions with different concentrations and due to the variations in the external absolute reference, temporal overlap between the electric and laser pulses, choices of solvents, and the choices of the models of the local field factors. We have developed a method to extract accurate relative first hyperpolarizabilities from EFISH data, which eliminates most of the above problems. We plot the square root of the SHG intensity versus concentrations of the material of interest and of *p*-nitroaniline under identical experimental conditions. It is shown that the ratio of the slope of the sample to that of *p*-nitroaniline provides a simple and accurate characterization of the first hyperpolarizability of the solute under test. The measurements of the concentration dependent dielectric constant, density, coherence length, and refractive index of solutions are shown to be unimportant in the analysis of EFISH data by this method. The slope ratio method eliminates variability associated with lab-to-lab variations in the absolute reference, the overlap of the electric and optical pulses, and the solvent conductivity.

Introduction

Nonlinear optical (NLO) properties of organic and organometallic molecules are of widespread interest toward the development of photonic devices for telecommunication and optical computing.[1−5] NLO properties are characterized by molecular hyperpolarizabilities, which are most often measured with the electric field induced second-harmonic generation (EFISH),[6−9] hyper-Rayleigh scattering (HRS),[10,11] and third-harmonic generation (THG).[8] EFISH is a well-developed technique for measuring the first hyperpolarizability of organic molecules. In the EFISH experiment, a pulsed static electric field is used to align the molecular dipole moments of solutes in solution, thus removing the macroscopic centrosymmetry of the solution. Under this condition the second-harmonic response of the solution at frequency 2ω resulting from interaction with a strong optical field at frequency ω synchronized with the static pulse can be observed. Levine and Bethea initially reported the first hyperpolarizability measurements for organic molecules by EFISH.[6a] Singer and Garito developed the infinite dilute extrapolation procedure to accurately measure the first hyperpolarizability.[7] The first molecular hyperpolarizability can be determined from EFISH data along with the complementary measurements of density, refractive indices, dielectric constant, and the coherence length of a series of solutions of varying concentrations by this method. Cheng et al.[8] have conducted systematic measurements of the molecular hyperpolarizabilities of a broad range of compounds. In principle, EFISH measurements are capable of yielding precise values of the first hyperpolarizability. However, literature values may vary by an order of magnitude for a given compound.[12−15] These variations may arise as the result of complications with the measurements[7,8] of the nonlinear optical response, the dielectric constant, the density, the refractive indices, and the coherence length of a series of solutions with different concentrations, and the effects are particularly problematic when measurements are made at high concentrations. In addition, the variations also arise due to the lab-to-lab variations in the external absolute reference,[9,16,17] the shape of the static electric pulses, the temporal overlap between the static and optical pulses, the choice of the solvents,[18−24] the choice of the local field factor models,[7,16,18] the difference in fundamental frequencies,[25−29] the data reduction schemes,[8,17] and the dipole moment measurements.[30,31]

We have developed a method of data analysis that eliminates many of the above problems. We determine the slope of the square root of the SHG intensity versus the concentrations of the molecule of interest as well as that of *p*-nitroaniline as a reference in dilute solution. Under appropriate conditions the ratio of these slopes provides an accurate relative measure of the first molecular hyperpolarizability of the molecule under test. We demonstrate that measurement of solution coherence length, refractive index, permittivity, and density as a function of solute concentration play only a minor role in accurately determining the first hyperpolarizability by measuring the NLO response of three well-studied molecules, *p*-nitroaniline (PNA), *p*-(dimethylamino)benzaldehyde (DMABA), and nitrobenzene (NB) in *p*-dioxane solution. We also demonstrate that the ratio of the concentration dependent slope of the sample response to the standard response under identical experimental conditions provides a simple and accurate method for the determination of relative first hyperpolarizabilities from EFISH data.

Experimental Section

All reagents and solvents were obtained from Aldrich and used without further purification. The excitation source for the EFISH experiment is a mode-locked and Q-switched Nd:YAG laser which operates at a wavelength of 1.06 μm. The Q-switch

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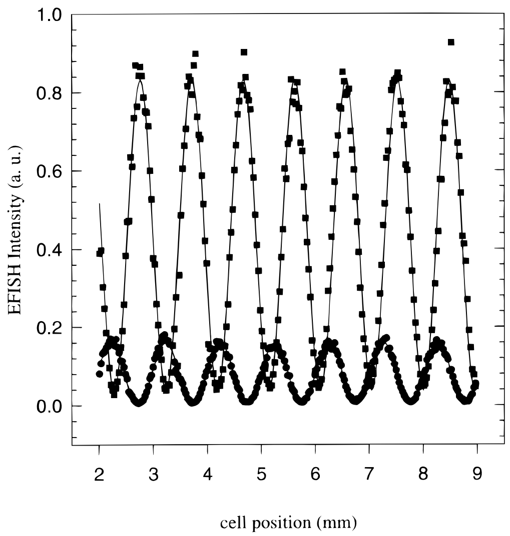

Figure 1. Experimental Maker fringe pattern measured for 0.041 M *p*-(dimethylamino)benzaldehyde (DMABA) in *p*-dioxane solvent. The small oscillation at the bottom of the figure is the pure solvent response. The lines are best fits of the data.

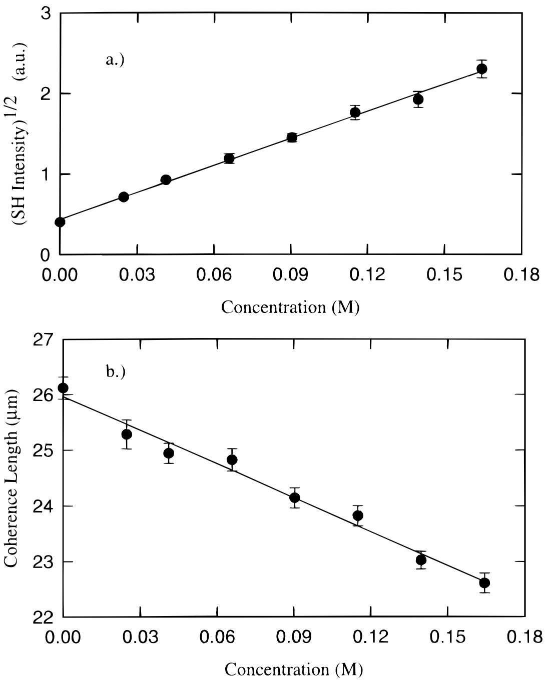

Figure 2. Concentration dependence of (a) the square root of the measured intensity of the second harmonic signal at 532 nm and (b) the coherence length of solutions of *p*-(dimethylamino)benzaldehyde in *p*-dioxane solvent. The data are determined from the best fits of the Maker fringe oscillations such as that shown in Figure 1.

operates at a repetition rate of 200 Hz, and each of the Q-switch laser pulses contains about 20 mode-locked laser pulses of 80 ps duration separated by 12 ns. The beam intensity is adjusted with a half-wave plate and a Brewster angle reflector. The main beam is split into two beams: the reference arm which excites a quartz crystal and the sample arm which excites the sample in an EFISH cell. The SHG signal generated from the quartz plate is used to correct for laser intensity fluctuations. The EFISH cell is a standard wedge-type cell.[6,8,9,32] The wedge angle of the glass plates is about 2.55−3.00° and is measured with an accuracy of 0.005°. High-voltage pulses are applied to the electrodes by a Lasermetrics, Inc. Model 8006 Q-switch driver. The peak voltage is set to about 7000 V during the measurement, and the pulse has a width of 300 ns at half-intensity.

The signal from the sample is collected through a monochromator by a photomultiplier tube, and the reference signal is measured with an avalanche photodiode. Both signals are sampled and held simultaneously, then amplified before being digitized with an analog-to-digital converter, and processed with a personal computer. A home-built digital delay circuit allows us to maintain synchronization of the firing of the Q-switch, the high-voltage pulser, and the sample and hold triggers to within 10 ns, and these events are also synchronized with the analog-to-digital conversion and translation of the EFISH cell. Each data point in the Maker fringe trace is the average of 400 measurements, which takes about 2 s. The cell position is then incremented by 30 μm using a computer-controlled stepper motor and a precision translation stage, and the next point is collected. An entire Maker fringe trace can be collected within 10 min. Figure 1 shows a trace of the experimental data of 0.041M DMABA in *p*-dioxane and pure dioxane with a typical signal-to-noise ratio.

The experimental values for the SHG intensity and coherence length of the solution can be obtained with the best fit parameters of the Maker fringe oscillation to the equation $I = a/2[1 + \cos f\pi + \phi)] + b$, where the fitting parameters a, b, ϕ and f are the peak-to-peak intensity, intensity offset, phase offset, and spatial frequency of the oscillation, respectively. The relationship of the coherence length l_c to the spatial frequency f is given by $l_c = \tan(\alpha)/f$, where α is the wedge angle of the solution cell. The magnitude of the SHG response is the peak-to-peak intensity, a, and the deviation is the average deviation of the peak-to-peak intensity from the best fit pattern over all of the peaks in the trace. The nonzero background b is usually very small compared with the peak-to-peak intensity a under our experimental conditions and arises from the finite spot size of the fundamental beam. The refractive index of the solution at 1.06 μm is determined from the refractive index measured at 532 nm and the coherence length l_c with the relationship $n_{1.06} = n_{532} - \lambda/4l_c$, where $\lambda = 1.06$ μm. The accuracy of this approach has been checked for a few pure solvents by directly measuring the refractive index at 1.06 μm.

For the purpose of testing the method described below, we have made careful measurement of permittivity, refractive index, and density for each of the solutions tested. Density was measured at room temperature with a pycnometer. Refractive indices were measured with a home-built Abbe-type refractometer at 532 nm. We estimate the precision of the instrument to be ±0.0001 refractive index units. Solution permittivity was measured with a precision instrument of our own design, which has been described in detail previously.[30] This instrument also allowed us to make accurate determinations of solute dipole moments, which are required for EFISH data analysis. The differential resolution of the instrument is as high as 0.000 02 units relative to that of the pure solvent. Linear dependencies of all of the complementary parameters on concentration are observed over the concentration range used in this study. Solution values for the complementary parameters that are used in various calculations described below are taken from the values determined from best fit lines to the data versus concentration.

Results and Analysis

Figures 2 and 3 show the concentration dependence of the square root of SHG intensity, the coherence length, permittivity, density, and refractive index of DMABA in *p*-dioxane. The molecular hyperpolarizability of DMABA can be extracted from this set of experimental data. Similar data sets for PNA and NB in *p*-dioxane have also been collected under identical experimental conditions. A rigorous formula for the magnitude of the nonlinear optical susceptibility from EFISH intensity has

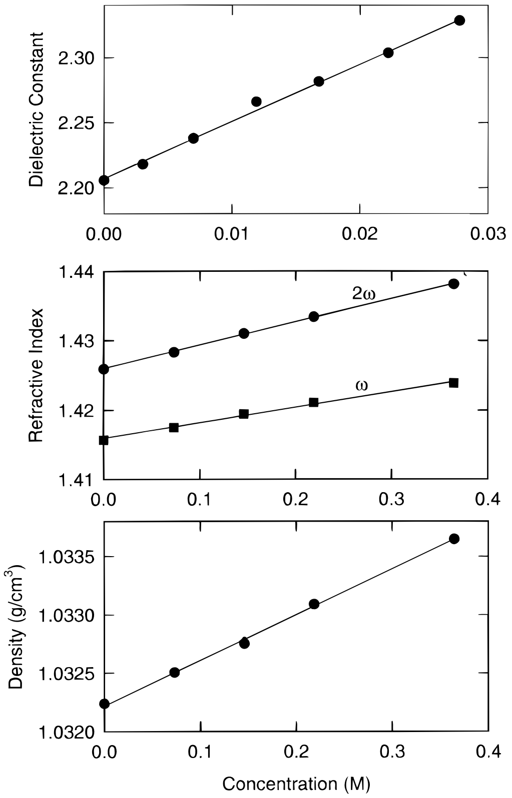

Figure 3. Concentration dependence of the experimentally determined dielectric constant, refractive index, and density of DMABA in *p*-dioxane solvent. The lines are the results of linear regression analysis.

been derived by Levine and Bethea,[6a] which includes contributions from the glass plates of the cell as well as the response of the solution under test relative to a crystaline quartz plate. If glass plates are chosen that have negligible EFISH response, and if one assumes that the refractive index of the solution is independent of solute concentration, then the result of Levine and Bethea can be written

$$\Gamma_{\mathrm{L}} = \frac{A(I^{\mathrm{L}}_{2\omega})^{1/2}}{l^{\mathrm{L}}_{\mathrm{c}}(l^{\mathrm{Q}}_{2\omega})^{1/2}} = \mathrm{A}\,\frac{(I^{\mathrm{S}}_{2\omega})^{1/2}}{l^{\mathrm{L}}_{\mathrm{c}}} \tag{1}$$

where Γ_{L} is the third-order optical susceptibility of the solution, A is an instrument constant, and $I^{\mathrm{S}}_{2\omega}$ is the ratio of the sample-second harmonic response to the response of quartz which corrects for pulse-to-pulse fluctuations in the laser intensity. The conventional analysis to convert the measured third-order optical susceptibility to a first hyperpolarizability of the solute is based on the addition principle of the optical susceptibilities of different species,[6−9]

$$\Gamma_{\mathrm{L}} = \Gamma_0 + \Gamma_1 = 1000N_{\mathrm{A}}C_0 f^{\mathrm{dc}}_{\mathrm{o}}(f^{\omega}_{\mathrm{o}})^2 f^{2\omega}_0 \gamma_0 + 1000N_{\mathrm{A}}C_1 f^{\mathrm{dc}}_1(f^{\omega}_1)^2 f^{2\omega}_1 \gamma_1 \tag{2}$$

where the subscripts 0 and 1 represent the solvent and solute, respectively, C is concentration in mol/L, N_{A} is Avogadro's number, the *f*'s are the local field factors, and, γ_i is the second hyperpolarizability of molecules of type i contained in the solution. The concentration of solvent C_0 is a function of the solute concentration and is calculated from the known concentration of solute, C_1, and density of the solution, ρ.

The local field factors account for the difference between the field experienced by the molecules and the field applied to the electrodes. We use the Onsager local field factor to correct the influence of each field:[9,21]

$$f^{\mathrm{dc}}_i = \frac{\epsilon(n^2+2)}{2\epsilon + n^2}$$
$$f^{\omega}_i = \frac{n^2(\omega)+2}{3} \tag{3}$$
$$f^{2\omega}_i = \frac{n^2(2\omega)+2}{3}$$

where the unsubscripted refractive indices and permittivities refer to solution values. We assume that solvent and solute local field factors are identical over our concentration range. To clarify the dependence of second hyperpolarizability on density, dielectric constant, refractive index, coherence length, and SHG measurement, eq 2 can be written as the following equation

$$A\left[\frac{(I^{\mathrm{S}}_{2\omega})^{1/2}}{l^{\mathrm{L}}_{\mathrm{c}}\, f^{\mathrm{dc}}_1(f^{\omega}_1)^2 f^{2\omega}_1} - \frac{(I^{\mathrm{S},0}_{2\omega})^{1/2}}{l^{0}_{\mathrm{c}}\, f^{\mathrm{dc},0}_0(f^{\omega,0}_0)^2 f^{2\omega,0}_0}\,\frac{C_0}{C^0_0}\right] = \Gamma^* = 1000N_{\mathrm{A}}C_1\gamma_1 \tag{4}$$

where the parameters with superscript 0 indicate values determined for the pure solvent. All parameters in brackets on the left side of eq 4 can be measured directly, and the resulting effective third-order optical susceptibility, Γ^*, is equal to the value of the quantity in brackets scaled by A, the instrument constant.

The slope of a plot of Γ^* versus solute concentration is $1000N_{\mathrm{A}}\gamma_1$. Rigorous calculation of the local field factors as well as the solvent contribution to the overall response at various solute concentrations demands that a set of complementary measurements including coherence length, density, refractive index, and permittivity be measured versus concentration for the solutions under test, as well as the instrument constant. In order to examine the importance of the concentration dependence of each of these quantities in the calculation of the local field factors on the determination of γ_1 from Γ^*, we have calculated Γ^* versus concentration where Γ^* is calculated using various levels of approximation. (We set $A = 1$.) These levels of approximation involve ignoring the influence of solute concentration on solution density, refractive index, permittivity, or coherence length or combinations of these parameters. When a parameter is ignored, the pure solvent value is used at all concentrations in place of the measured concentration dependent quantities.

The slopes of the calculated Γ^* values versus concentration for various levels of approximation of the complementary measurements are given in Table 1 for the three solutes studied. Figure 4 shows the calculated values of Γ^* versus concentration at various levels of approximations for DMABA in *p*-dioxane along with the best fit lines. The solute concentration dependence of the solution permittivity and the coherence length were found in all cases to most strongly influence the slope of Γ^* versus concentration. The solution permittivity increases with increasing concentration, whereas the coherence length decreases with increasing concentration. As a result, if one neglects the concentration dependence of both of these parameters in calculating Γ^*, a cancellation of errors will result. In fact the deviation that results when ignoring the solute concentration dependence of all of the parameters is less than 10% of the correct value in all cases, and the deviation decreases as the slope increases. For PNA the observed deviation is about 0.1%, which is within the uncertainty of the measurement. On the other hand, neglecting the dependence of solution density and refractive index on solute concentration appears to have a minor influence on the extracted value Γ^*, which indicates that to a

TABLE 1: Slopes of the Effective Nonlinear Susceptibilies of Solutions under Test versus Solute Concentration under Various Approximations in *p*-dioxane at 1.06 μm

values used for parameters required to calculate Γ*	*p*-nitroaniline	*p*-DMABA	nitrobenzene
solution values for all parameters	17.69 ± 0.35	11.72 ± 0.26	0.911 ± 0.055
solvent value for solution density, all other values are solution values	17.97 ± 0.35	11.88 ± 0.26	0.950 ± 0.057
solvent value for solution refractive index, all other values are solution values	17.74 ± 0.36	11.86 ± 0.26	0.946 ± 0.054
solvent value for solution refractive index and density, all other values are solution values	18.02 ± 0.36	12.02 ± 0.26	0.986 ± 0.056
solvent value for solution permittivity, all other values are solution values	18.80 ± 0.44	13.01 ± 0.25	1.191 ± 0.053
solvent value for solution coherence length, all other values are solution values	16.40 ± 0.25	9.8 ± 0.31	0.683 ± 0.058
solvent values for solution permittivity and coherence length, all other values are solution values	17.60 ± 0.40	11.41 ± 0.26	0.937 ± 0.057
solvent values for all parameters	17.79 ± 0.30	11.19 ± 0.27	0.983 ± 0.053

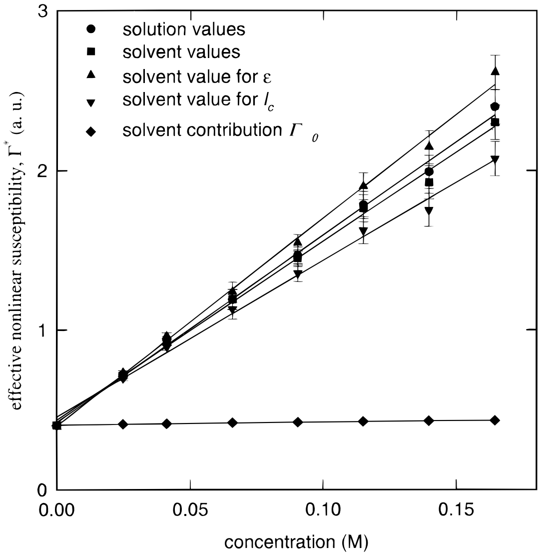

Figure 4. Concentration dependence of calculated values for Γ* under various levels of approximation. (●) All parameter (ϵ, n, ρ, and l_c) values used in the calculation of Γ* (eq 4) are the experimental values for the solutions at the indicated concentrations. (■) All values in the calculation are pure solvent values at all solute concentrations. (▲) All values used in the calculation except the solution permittivity are solution values, and the solvent permittivity is substituted for the solution values at all solute concentrations. (▼) All values used in the calculation except the solution coherence length are solution values, and the solvent coherence length is substituted for the solution values at all solute concentrations. (◆) Calculated solvent only comtribution to the effective nonlinear susceptibility of the solution. Error bars indicate the uncorrelated uncertainties of each data point propagated from uncertainties of all parameters used in the calculation of Γ*. Lines are the results of linear regression analyses of the data under each approximation. The slopes of the lines are given in Table 1. A constant offset equal to the value of the pure solvent response has been added to each calculated value of Γ*.

good approximation the contribution of the solvent to the overall response can be assumed to be independent of solute concentration. Again this approximation becomes better as the solute response increases. Under these circumstances knowledge of the concentration dependence of the second-harmonic response alone appears to be sufficient to determine Γ_L within experimental uncertainty.

Given the above results, it appears that variability in β values due to approximations made in the data reduction is minimal when measurements are made in dilute soltuions, particularly when solutes with large β values are studied. Note from eq 4 that in order to generate a true γ value from the measured slope, one must determine the instrument parameter *A*, and in our view the difficulty associated with this determination is responsible for the variability in literature values reported for the same compound by different labs. This arises, for example, as a result of the need to consider the relative shapes of the excitation pulse and the high-voltage static pulse as well as their temporal and spatial overlap. The value of *A* can also be influenced by differences in solvent conductivity between two labs. When measured against crystalline quartz as an absolute reference, several other instrument properties such as laser polarization purity, crystal orientation, and crystal quality become important. These instrumental qualities are extremely difficult to control and characterize from one lab to the next and are therefore expected to vary significantly between different laboratories. On the other hand they are expected to be constant within a particular lab over the course of a typical experiment, and it is therefore appropriate to consider the development of a method by which the second hyperpolarizability of a sample under test can be measured relative to a standard measured under identical conditions within a particular laboratory by the EFISH technique.

The Slope Ratio Method

Here we present a method for determining relative first hyperpolarizabilities from EFISH data which eliminates the effect of lab-to-lab variation in the instrument constant on reported values. Experimentally we measure the concentration dependent EFISH response of the solution under test and the concentration dependent response of PNA as a reference on the same day under identical conditions. (No experimental variables are adjusted between these two measurements, and the same solvent is used.) Equation 4 illustrates that the calculation of the true value of the slope of Γ* versus solute concentration, and therefore the absolute second hyperpolarizability, requires knowledge of the instrument constant. However the instrument parameter is eliminated in the ratio of the slope of Γ* of the solution under test to the slope of a reference measured under identical conditions. The contribution of the first hyperpolarizability to the value of γ dominates for molecules whose β value exceeds that of the solvent and therefore[6-9]

$$\gamma = \gamma_e + \gamma_v + \mu\beta/(5kT) \approx \mu\beta/(5kT) \qquad (5)$$

Thus the slope ratio of the solution under test to that of the reference can be written

$$\frac{\mathrm{slope}_{\mathrm{test}}}{\mathrm{slope}_{\mathrm{ref}}} = \frac{\mu_{\mathrm{test}}\beta_{\mathrm{test}}}{\mu_{\mathrm{ref}}\beta_{\mathrm{ref}}} \qquad (6)$$

and the calculation of β_{test} for a molecule of interest can be made from measurement of the slope ratio of the square root of its EFISH response relative to a well-characterized and accepted standard along with its dipole moment.

The slope ratios of DMABA and NB to PNA at various levels of approximation with respect to the other measurable parameters are listed in Table 2. The meaning of these approximations are identical to those of Table 1 and are calculated from the ratio of the slopes determined under various levels of approximation in Table 1 for both test and reference solutions. Again we observe that neglect of density and refractive index variations with concentration have little effect on the slope ratio. We also observe that neglect of either solution permittivity or coherence length variations with concentration has the largest

TABLE 2: Slope Ratios[a] of Solutes under Test to PNA at Various Levels of Approximations in *p*-Dioxane at 1.06 μm

values used for parameters required to calculate Γ^*	*p*-DMABA	nitrobenzene
solution values for all parameters	0.66 ± 0.02	0.052 ± 0.003
solvent value for solution density, all other values are solution values	0.67 ± 0.02	0.053 ± 0.003
solvent value for solution refractive index, all other values are solution values	0.67 ± 0.02	0.053 ± 0.003
solvent value for solution refractive index and density, all other values are solution values	0.68 ± 0.02	0.055 ± 0.003
solvent value for solution permittivity, all other values are solution values	0.69 ± 0.02	0.063 ± 0.003
solvent value for solution coherence length, all other values are solution values	0.60 ± 0.02	0.042 ± 0.003
solvent values for solution permittivity and coherence length, all other values are solution values	0.65 ± 0.02	0.053 ± 0.003
solvent values for all parameters	0.63 ± 0.02	0.055 ± 0.003
experimental slope ratio $(\mu\beta)_x/(\mu\beta)_{pna}$ in literature	0.56 ± 0.08^{b}	0.057 ± 0.012^{d1}
	0.45 ± 0.07^{c}	0.053 ± 0.010^{d2}
		0.046 ± 0.010^{d3}

[a] The error of the slope ratio is calculated with the formula $\Delta\text{ratio}/\text{ratio} = \sqrt{(\Delta m/m)^2_{\text{PNA}} + (\Delta m/m)^2_{\text{sample}}}$, where Δm and m are the slope error and slope of the effective nonlinear susceptibilities of the solutions. [b] Taken from ref 8a, pumped at 1.93 μm; PNA in acetone and DMABA in *p*-dioxane. Concentration ranges are unknown. [c] Taken from ref 35, $\lambda = 1.89$ μm in dimethyl sulfoxide. Concentration ranges are unknown. [d] Taken from ref 36, pumped at 1.06 μm. PNA in methanol to concentrations of 5% by volume: (1) NB in methanol to 17% by volume; (2) NB in benzene to 15% by volume; (3) NB in heptane to 15% by volume.

effect on the slope ratio, but that ignoring both of these effects results in close agreement between the approximate slope ratio value and the slope ratio value calculated using all concentration dependent quantities. The difference in these values is within the experimental uncertainty of the measurement. Furthermore we note that our slope ratios compare favorably to slope ratios extracted from literature values for DMABA[8a,35] and NB.[36] The literature slope ratios were calculated from values for DMABA and PNA or NB and PNA given in the same paper and were presumably measured under identical conditions. In both cases the slope ratios agree to within the experimental error of the measurements. Note on the other hand that the reported absolute values of $\mu\beta$ for PNA in these papers[8a,35,36] differ by a factor of 3−5 if the data are measured against the nonlinear coefficient of quartz, $d_{11} = 1.2 \times 10^{-9}$ esu at 1.06 μm. Note also that the experimental conditions such as wavelength and solvent and assumptions in data analysis such as choice of local field factor models differ significantly between the pairs of measurements for like solutes, and yet the differences in slope ratios are statistically insignificant. We suggest that better agreement will be achieved when the slope ratio method is used explicitly in other labs for relative first hyperpolarizability measurements.

Discussion

The approximations that have been explored experimentally above are aimed at simplifying the procedure of extracting β values from concentration dependent EFISH measurements. Equation 4 can be written

$$(I^{S}_{2\omega})^{1/2} = K_1 C_1 \mu_1 \beta_1 + K_2 \tag{7}$$

and the above approximations hold to the extent that K_1 is concentration independent. When K_1 is constant, a relative β value for a solute under test can be simply extracted as the ratio of the slopes of the square root of the EFISH intensity vs concentration of the test and reference solutions. When the approximations do not hold, Γ^* must be calculated from the NLO response using eq 4. Nevertheless the slope ratio method can still be applied to plots of Γ^* vs concentration and represents an improved method for the extraction of reliable comparative β values from EFISH data.

It is appropriate to consider the conditions under which the assumption that K_1 = constant will give an adequate β value. We note first that as the nonlinear response of the compound under test increases, one is able to reduce the maximum solute concentration required in order to measure β. This behavior is anticipated, and results from the relative importance of the solute and solvent contributions to the overall second-harmonic signal. As the required maximum concentration decreases, the effect of the solute on n, ρ, ϵ, and l_c diminishes. In the cases examined here the concentration dependence of n and ρ is observed to have little effect on the calculated value of Γ^*. This is expected as long as the solute concentration remains relatively low (<0.3 M) and the optical fields are far from resonance. The observation that the coherence length and permittivity dependencies on concentration tend to cancel one another greatly simplifies the data analysis necessary to extract relative first hyperpolarizabilities from EFISH data. This cancellation of errors appears to be fortuitous, and it is important to identify the conditions under which it is expected to occur.

The solution coherence length will generally decrease with increasing solute concentration, due to the relative proximity of the second-harmonic field frequency to the resonance frequency of the NLO active chromophore compared with its proximity to a resonance of the solvent. As long as the NLO active chromophore has stronger dispersion between the fundamental and second-harmonic frequencies than the solvent, the coherence length will decrease with concentration. In the case of the example given in Figure 3, the dioxane solvent exhibits a dispersion in the polarizability of about 2% between the fundamental and second-harmonic frequencies used in our measurements. The DMABA solute exhibits a dispersion of about 7% owing to the fact that DMABA has a resonance in the 300 nm range. This dispersion difference gives rise to a −20% difference in the coherence length of the solution over the 0−0.3 M concentration range. The coherence length changes by only −2% over the 0−0.03 M concentration range.

The solution permittivity increases with increasing concentration for all solutes studied here, and this dependence will be observed as long as the dipole moment of a solute molecule exceeds the total dipole moment of the displaced solvent molecules. Second-order NLO chromophores typically have dipole moments in the range of 4−10 D. For a solute with a dipole moment of 6.5 D, model calculations indicate that solution permittivity will increase with increasing solute concentration for nonassociating solvents having dipole moments as large as 2.5 D (dielectric constants to values approaching 5). This may not hold for associating solvents in which the total dipole moment of the displaced solvent is enhanced by intermolecular solvent orientational effects. The magnitude of the permittivity dependence on solute concentration appears to scale monotonically with the difference in the dipole moments of solvent and solute. For DMABA $\Delta\mu = 6.5$, and we note that the change in permittivity over a 0−0.03 M concentration range is 7%, whereas the change in the dc local field factor is only 2.3%, equal in magnitude but opposite in sign to the change in coherence length over the same concentration range.

Γ^* includes as a factor the product of the coherence length and the local field factors. The factors for optical fields depend only on refractive index, and the concentration dependence of these factors has been shown to have negligible influence on the calculation of Γ^*. The product of the dc field factor and the coherence length ($l_c^L f_1^{dc}$) is the product of a positive linear quantity and a negative linear quantity, which results in an inverted parabolic concentration dependence. In the case of DMABA in dioxane the fact that the concentration dependencies of these quantities are equal in magnitude but opposite in sign conspires to position the shallow maximum of the inverted parabola in the center of the 0−0.3 M concentration range, resulting in a small (<0.6%) variation in the product over this entire concentration range. Although this cancellation is particularly fortuitous in the case of DMABA in dioxane, the observed trends are expected to occur under a wide variety of conditions. The coherence length will always decrease with concentration, and polarizability dispersion on the order of 5−10% is expected to be typical unless the second-harmonic frequency is very nearly resonant with a transition of the NLO chromophore. As $\Delta\mu$ decreases the position of the maximum in the inverted parabola shifts to lower concentration and $l_c^L f_1^{dc}$ exhibits a negative dependence on solute concentration. However, in model calculations utilizing the Debye, Onsager, and Lorenz−Lorentz equations and a solvent of dioxane's density with a permittivity of 2.6 ($\mu = 1$) the product $l_c^L f_1^{dc}$ still only varies by 1% over the 0−0.03 M concentration range, and with a permittivity of 4.5 ($\mu = 2.4$) $l_c^L f_1^{dc}$ varies by only about 2%. These variations are small compared with uncertainties in β values typically extracted from EFISH measurements, even in relatively polar solvents.

On the basis of the above results, we suggest that potential NLO chromophores can be adequately characterized through the slope ratio of the square root of their second-harmonic intensity with respect to solute concentration relative to PNA and that this method should be accurate to within measurement uncertainty for molecules whose response exceeds that of PNA. The slope ratio method should be adequate even for moderately polar solvents, but as the solvent polarity increases, it becomes increasingly important to minimize the range of concentrations used in the measurement. The 0−0.03 M concentration range appears to be suitable for nonpolar to moderately polar solvents. PNA provides an excellent standard against which to measure the first molecular polarizability from EFISH data because (1) it is inexpensive and readily available, (2) its NLO properties have been widely studied, and (3) it provides a benchmark against which the accuracy of a slope ratio determination can be judged. This last point is particularly important in screening of molecules for potential applications. The slope ratio method is an excellent screening tool since it (1) minimizes the number of measurements required to characterize a solute and (2) becomes more accurate as the response of the molecule increases. Using PNA as a reference, the slope ratio of a molecule under test which exceeds a value of 1 can be considered an accurate relative measure of the first molecular hyperpolarizability, without the need to perform additional measurements of solution properties. Typically researchers measure coherence length and second-harmonic response intensity simultaneously and also need to measure solution permittivity versus solute concentration in order to determine the solute dipole moment. Thus a slightly more accurate determination of the first hyperpolarizability from EFISH data can be made by using these results in the calculation of Γ^*.

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