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LETTERS

Solvent Dependence of the First Molecular Hyperpolarizability of *p*-Nitroaniline Revisited

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The solvent effect on the molecular first hyperpolarizability, β, of *p*-nitroaniline (*p*NA) has been investigated. Using the hyper-Rayleigh scattering technique, we have also determined β of *p*NA in DMSO using 1064 nm laser radiation. This β value has not been previously reported. With the help of Onsager's theory, we have arrived at a correction factor to account for the solvent dependence of the values of the intrinsic hyperpolarizability β_0. The Onsager model significantly removes the strong solvent dependence of β (or β_0) on the dielectric constant.

Introduction

The essence of second-order organic nonlinear optical (NLO) materials are chromophores that exhibit large first hyperpolarizabilities, β, usually through an electronic donor−acceptor arrangement with an extended conjugation sequence in between.[1] In order to make intelligent choices of the chromophores for devices based on the NLO response, it is necessary to be able to accurately characterize them. Until recently, electric field induced second-harmonic (EFISH) generation[2,3] has been the standard technique to determine β via the measurement of $\mu\beta$ in a solvent of negligible β, where μ is the amplitude of the ground state dipole moment of the chromophore. The EFISH method thus requires one to make an independent measurement of μ in order to obtain β. Moreover, to obtain $\mu\beta$, one needs to make assumptions regarding local field factors, both at zero frequency and at optical frequencies, in addition to assumptions about the molecular second hyperpolarizability γ. Since it is difficult to obtain precise values for these quantities, error is easily introduced into the determination of β; this is most likely the cause of the inconsistencies in β values reported in the literature.[3]

Another source of inconsistency in reported β values is due to the solvent effect. The solvent dependency arises from a number of sources. One of them is the chromophore dipole-induced reaction field which modifies the local field experienced by the NLO chromophores. Another source is the effects of intermolecular interactions on the transition dipole associated with the charge transfer transition band. Clays and Persoons[4] have suggested that the solvent effect of β can be accounted for by using an empirical linear relationship between β and $(\epsilon - 1)/(2\epsilon + 1)$, where ϵ is the static dielectric constant of the solvent used in the measurement of β. Due to complex dependencies of the transition dipole, the resonance frequency of the charge transfer band, and the permanent dipole moment of the chromophore on the solvent, it is surprising that such a simple solvent dielectric constant dependence for β should exist. In this Letter, we show the inadequacy of the Clays and Persoons model and suggest another correction factor that can be used to account for the solvent dependence. We have chosen the β data of *p*-nitroaniline (*p*NA) for this study, since *p*NA has been extensively studied in a number of solvents. To include the result of high dielectric constant solvents, we have also carried out the measurement of the β value of *p*NA in dimethyl sulfoxide (DMSO) using the technique of hyper-Rayleigh scattering (HRS). To the best of our knowledge, the β value of *p*NA in DMSO has not previously been available in the literature.

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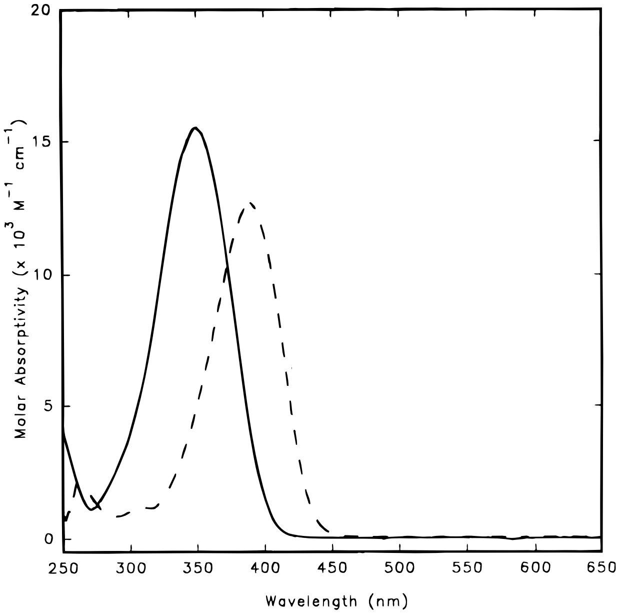

Figure 1. Molar absorptivity spectra for *p*NA dissolved in $CHCl_3$ (solid line) and DMSO (dashed line). Note that there is no detectable absorption present at the second-harmonic wavelength, 532 nm.

Experimental Section

To ascertain the β value measurement of *p*NA in DMSO by HRS, we have also carried out the HRS measurement of *p*NA in chloroform for comparison. *p*NA (Aldrich, 99+% purity) was used as received without further purification. Both solvents used were reagent grade. Solutions were prepared by dissolving *p*NA in chloroform and DMSO to form concentrated stock solutions. Samples with different concentrations were obtained from these stock solutions via successive dilution. All diluted solutions were filtered with 0.1 μm filters (Whatman) to remove any undissolved particulates or dust. The experimental setup used for the HRS measurements has been described elsewhere,[5] with one modification: A beam splitter that directed a small fraction of the incident beam toward a fast photodiode (ET2000, Electro-Optics Technology) was added along the fundamental beam path to facilitate the point-by-point monitoring of the laser intensity during the HRS experiment. This addition allows the direct measurement of the quantity ($I_{2\omega}/I_{\omega}^2$) while eliminating the measurement of fluctuations in laser intensity that contribute to a variation in the measured HRS intensity. The output of a Nd:YAG (Spectra-Physics, GCR-11, 1064 nm, 10 Hz) was filtered through two low-pass filters and focused into a 3.5-mL glass sample cell. The scattered radiation at 90° was collected with a camera lens, focused with a biconvex lens (*f*/1.3), filtered through a band-pass filter centered at 532 nm with a 10-nm bandwidth, and focused onto a photomultiplier tube. Refractive index measurements were carried out on a Reichert Abbe Mark II refractometer at the sodium D line (589.3 nm). It was calibrated using distilled water ($n_D = 1.3327$ at 23.4 °C). Molar absorptivity measurements were carried out on a Hewlett-Packard 8452A diode array UV/visible spectrophotometer.

Results and Discussion

Figure 1 shows the molar absorptivity plotted as a function of wavelength for *p*NA dissolved in both chloroform and DMSO. One notes a large red shift of about 40 nm for *p*NA in DMSO relative to chloroform: $\lambda_{max}(CHCl_3) = 350$ nm, $\lambda_{max}(DMSO) = 390$ nm. Since both the fundamental frequency (1064 nm) and the second harmonic (532 nm) of the HRS experiment are far from resonance in both solvents, additional second-order effects, such as two-photon fluorescence,[6,7] that may plague the HRS method in the determination of β should be absent here, and the intensity detected at 532 nm should accurately represent the HRS intensity for *p*NA in these solvents.

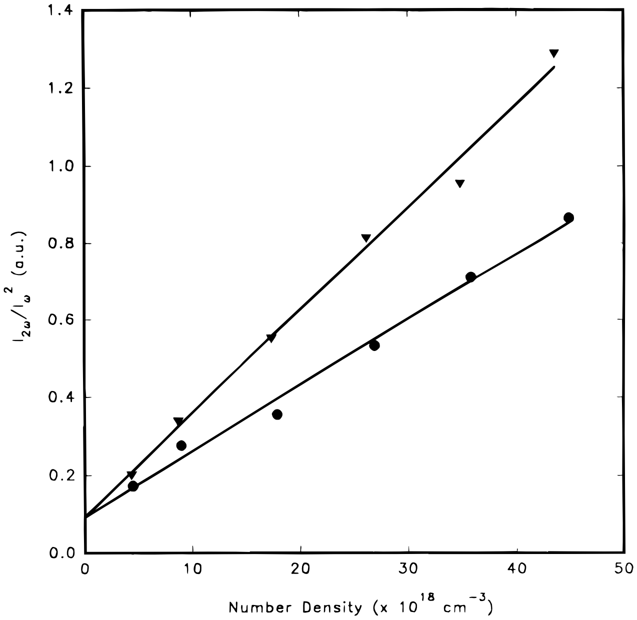

Figure 2. Hyper-Rayleigh scattering intensity, ratioed by the square of the fundamental intensity, vs *p*NA number density in $CHCl_3$ (circles) and in DMSO (triangles); corrected for local field factors. The solid lines indicate a least-squares fit through the experimental data.

Figure 2 shows the HRS concentration dependence data collected for *p*NA in $CHCl_3$ and in DMSO, in this dilute concentration regime. Using the data given in Figure 2 and standard procedures using the internal reference method (IRM),[4] we have obtained the β value of *p*NA in $CHCl_3$ to be 23.4×10^{-30} esu, in excellent agreement with the literature value of 23×10^{-30} esu.[4] Using the *p*NA/$CHCl_3$ result, we have determined the β value of *p*NA in DMSO to be 28.8×10^{-30} esu using a modified version of the external reference method (ERM).[8] Since we are comparing HRS intensities from different solvents ($CHCl_3$ and DMSO), one needs to correct for the different local fields experienced by the *p*NA molecules in each solvent. It should be noted that if we use the IRM to calculate β for *p*NA in DMSO, using $\beta = 0.19 \times 10^{-30}$ esu for DMSO,[9] we obtain a value of 28.9×10^{-30} esu. This value is in good agreement with the β value obtained with the ERM given above.

As mentioned above, to account for the solvent effect, Clays and Persoons[4] have proposed an empirical linear relationship between the β value of the chromophore and the dielectric factor $D = (\epsilon - 1)/(2\epsilon + 1)$ of the solvent. In Figure 3, we plot the β values of *p*NA in various solvents vs D. Values for β and ϵ for *p*NA in various solvents are taken from the paper by Stähelin et al.[10] and are given in Table 1. The results show rather poor agreement between β and D, in contrast to what has been proposed in ref 4. For the *p*NA/DMSO system, the β value clearly lies well below the line proposed by Clays and Persoons.[4]

Since the major contribution to β is due to the charge transfer band, we adopt a classical two-state model expression for β given by[1]

$$\beta = \frac{\beta_0}{(1 - \omega^2/\omega_{eg}^2)(1 - 4\omega^2/\omega_{eg}^2)} \qquad (1)$$

where β_0 is the intrinsic molecular hyperpolarizability, ω is the excitation frequency of the fundamental beam, ω_{eg} is the

TABLE 1: Intrinsic Hyperpolarizability (β_0) Data for *p*NA Dissolved in Various Solvents (Whose Refractive Indices and Dielectric Constants Are Also Given)

solvent	ϵ^a	n^b	$\frac{n^2+2}{3}\frac{2\epsilon+1}{2\epsilon+n^2}$	β^a ($\times 10^{-30}$ esu)	$\beta_0{}^a$ ($\times 10^{-30}$ esu)	$\beta_0 \Big/ \left[\frac{n^2+2}{3}\frac{2\epsilon+1}{2\epsilon+n^2}\right]$ ($\times 10^{-30}$ esu)
1,4-dioxane	2.21	1.422	1.128	16.3	8.1	7.18
chloroform	4.81	1.446	1.237	16.8	8.6	6.95
tetrahydropyran	5.61	1.4211	1.237	22.5	10.8	8.73
ethyl acetate	6.02	1.372	1.212	22.6	11.0	9.08
tetrahydrofuran	7.58	1.407	1.251	21.4	10.2	8.16
2-methoxyethyl ether	7.63	1.4097	1.253	23.8	11.0	8.78
dichloromethane	7.77	1.424	1.264	16.9	8.5	6.72
acetone	20.7	1.359	1.257	25.9	11.9	9.47
N-methylpyrrolidone	32.0	1.488	1.379	38.4	15.8	11.5
methanol	32.63	1.328	1.240	32.0	14.5	11.7
dimethylformamide	36.71	1.43	1.330	30.0	12.6	9.48
acetonitrile	37.5	1.344	1.256	29.2	13.6	10.8

[a] From ref 10. [b] From ref 12.

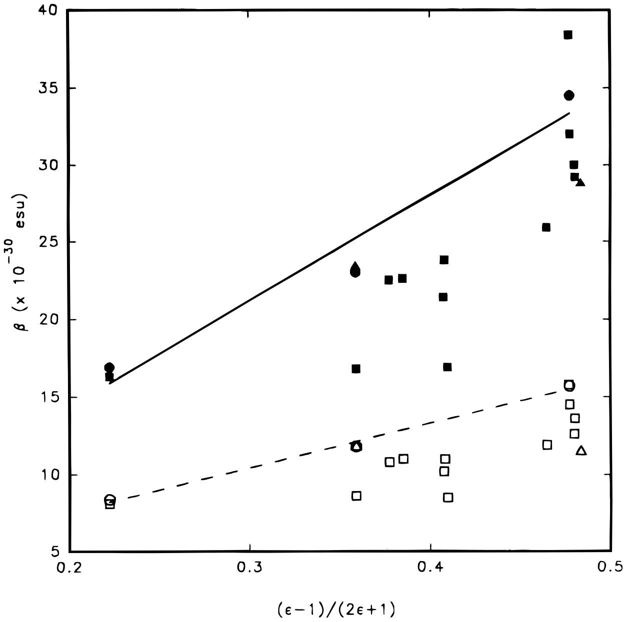

Figure 3. β (solid symbols) and β_0 (open symbols) vs $(\epsilon - 1)/(2\epsilon + 1)$. The solid circle data and the solid line are from ref 4, measured by using HRS; the open circle data are β_0 values calculated using $\lambda_{\max}$ values from ref 4. The solid and open square data are from Table 1, measured by using EFISH. The solid and open triangle data represent new experimental data measured by HRS. The dashed line is drawn from the solid line after removing the dispersion factor.

transition frequency associated with the charge transfer band, and the quantity in the denominator represents the dispersion effect. Since β_0 is equal to $3\mu_{\mathrm{eg}}^2\Delta\mu/(\hbar\omega_{\mathrm{eg}})^2$, where μ_{eg} is the transition dipole moment and $\Delta\mu$ is the change in the permanent dipole moment of the ground and excited states, the solvent-induced effect on β may arise from the induced shift in the absorption maximum that changes the resonance frequency of the charge transfer band and the change of the dipole matrix elements μ_{gg}, μ_{ee}, and μ_{eg} that enter into the hyperpolarizability expression. One can remove the effect due to the red shift ($\omega_{\mathrm{eg}} = 2\pi c/\lambda_{\max}$) in DMSO relative to $CHCl_3$ by using the frequency dispersion factor and then comparing the β_0 values of *p*NA in these solvents. Using eq 1, we obtained $\beta_0 = (11.5 \pm 1.5) \times 10^{-30}$ and $(11.8 \pm 1.5) \times 10^{-30}$ esu for *p*NA in DMSO and $CHCl_3$, respectively. The agreement in the β_0 values obtained in these solvents is within the experimental uncertainty. The fact that β_0 is not sensitive to the solvent perturbation in the case of $CHCl_3$ and DMSO suggests that the solvent effects on the resonance frequency and dipole matrix elements (transition dipole *as well as* permanent dipole) cancel each other out in these two systems. However, if β_0 values obtained from other solvents are plotted vs *D*, as also shown in Figure 3, there is also a significant scatter of data. For *p*NA/DMSO, the β_0 value also lies below the line of the β_0 vs *D* plot.

As originally shown by Onsager,[11] a polar molecule which is placed in an evacuated spherical cavity of radius *a* and which is then immersed in a dielectric continuum composed of polar solvent molecules and subjected to a static electric field **E** will experience two electric fields in response to the continuum: a cavity field $\mathbf{G} = [3\epsilon/(2\epsilon + 1)]\mathbf{E}$ caused by the accumulation of surface charge around the spherical cavity of the solute and a reaction field $\mathbf{R} = [2(\epsilon - 1)/(2\epsilon + 1)]\boldsymbol{\mu}/a^3$ caused by the response of the solvent molecules to the dipole moment of the solute molecule. Here ϵ represents the static dielectric constant of the medium, $\boldsymbol{\mu}$ is the intrinsic (i.e., gas-phase) ground-state dipole moment of the solvent molecule, and bold lettering indicates vector quantities. One can then combine the relations for **G** and **R** and make use of the Clausius−Mossotti relation to obtain an expression for **m**, the dipole moment of the molecule immersed in the solvent (the "liquid moment") as

$$\mathbf{m} = \frac{n^2+2}{3}\,\frac{2\epsilon+1}{2\epsilon+n^2}\boldsymbol{\mu} \tag{2}$$

where *n* is the refractive index of the solution measured far from resonance. The coefficient for $\boldsymbol{\mu}$ in eq 2 can be considered to be a "correction factor" in describing the effects of the environment on the intrinsic dipole moment of the molecule. We have analyzed the β_0 data presented in Table 1 and divided each β_0 value by this factor; the results are also presented in Table 1. Clearly, after dividing β_0 by this correction factor, the variation in β_0 is no longer as sensitive to the solvent polarity, despite a consistent upward increasing trend with increasing dielectric constant. This upward increase is possibly related to the effect of the solvent dielectric constant on the transition dipole moment, which we have not yet considered.

Conclusion

We have studied the solvent dependence of the hyperpolarizability of *p*NA. Using an external reference method, we obtain a β value of 28.8×10^{-30} esu for *p*NA in DMSO, which has not been available in the literature. By removing the solvent effect on the frequency dispersion factor involving a two-state model, we have obtained an intrinsic molecular hyperpolarizability β_0 that appears to be largely insensitive to the solvent perturbation for the cases of DMSO and $CHCl_3$. The major solvent effect in the charge-transfer type of NLO chromophores, as represented by *p*NA, arises from the frequency dispersion factor. We have further investigated the solvent dependence of β_0 using Onsager's reaction field theory. Correction made by using the Onsager theory significantly narrows the variation of β_0 values in different solvents.

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