

## Hyper-Rayleigh Scattering in Solution

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Hyper-Rayleigh scattering in solution is used for the determination of the hyperpolarizability of non-linear optical molecules. Obtaining the first hyperpolarizability  $\beta$  without having to independently determine the dipole moment  $\mu$  and the second hyperpolarizability  $\gamma$  is an advantage over the electric-field-induced second-harmonic generation technique. Values of the first hyperpolarizability  $\beta$  of  $23 \times 10^{-30}$  esu for *para*-nitroaniline,  $105 \times 10^{-30}$  esu for 4-methoxy-4'-nitrostilbene, and  $95 \times 10^{-30}$  esu for 4-hydroxy-4'-nitrostilbene dissolved in chloroform have been obtained. The equivalent-internal-field model is shown to hold for small saturated molecules.

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A problem with the experimental determination of the first-order optical hyperpolarizability  $\beta$  (second-order NLO polarizability) has been that centrosymmetric structures of individual molecules with a nonzero *microscopic hyperpolarizability*  $\beta$  do not possess a *macroscopic second-order NLO susceptibility*  $B$ . For this reason, the first measurements of  $B$  have been performed on crystals without centrosymmetry, Langmuir-Blodgett films, and poled polymers.<sup>1</sup> The Kurtz powder method has generated a substantial amount of second-harmonic powder efficiency data.<sup>2</sup> Electric-field-induced second-harmonic generation (EFISHG) is the only technique that allows the determination of optical hyperpolarizabilities in solution. The intrinsic symmetry of the isotropic solution is reduced by the application of an electric field. The quantity measured in EFISHG is  $\gamma + \mu\beta/5kT$ . Therefore, the values of the dipole moment  $\mu$ , the local-field correction factor, and the third-order hyperpolarizability  $\gamma$  are required to extract  $\beta$ .

Although second-harmonic generation in isotropic liquids is forbidden for reasons of symmetry,<sup>3</sup> second-order light scattering in isotropic samples has been observed.<sup>4</sup> Even second-order light scattering from centrosymmetric molecules in the liquid phase has been observed.<sup>5,6</sup> Hyper-Raman scattering around the hyper-Rayleigh line has also been reported.<sup>7</sup> The first reported use of the hyper-Rayleigh scattering of  $\text{CCl}_4$  in solution was in optimizing a hyper-Raman detection setup for  $\text{C}_2\text{Cl}_4$ .<sup>8</sup> However, hyper-Rayleigh scattering can be used to accurately measure NLO coefficients of solvent and solute molecules. To second order in the incident field, the induced dipole moment *for a single molecule* is, in Cartesian tensor notation,  $\mu_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k$ . Here,  $\mu_i$  is the component of the induced dipole moment along the molecule-fixed  $i$  axis,  $\alpha_{ij}$  is the  $ij$  component of the second-rank polarizability tensor  $\alpha$ ,  $\beta_{ijk}$  is the  $ijk$  component of the *microscopic* third-rank *hyperpolarizability* tensor  $\beta$ . A repeated subscript implies summation over the three components. The Fourier amplitude of the induced dipole moment *per unit volume* at  $2\omega$  is then

$$P_i(2\omega) = B_{ikl}(-2\omega; \omega, \omega)E_k(\omega)E_l(\omega),$$

where  $B_{ikl}$  is the  $ikl$  component of the *macroscopic second-order susceptibility*. In isotropic media, only the *average* value of  $B_{ikl}$  is zero, due to orientation fluctuations.<sup>4</sup> Correlation between the values of  $B_{ikl}$  for two different volumes 1 and 2 can be assumed to exist only over distances small compared to the wavelength.<sup>9</sup> The intensity of the second-harmonic scattered light is proportional to  $\langle B_{ikl,1}B_{jmn,2} \rangle_{av} dv$ . Next, the approximation is made that the scattering centers are randomly oriented individual molecules.<sup>4</sup> The intensity of the second-harmonic scattered light then becomes proportional to the number density  $N$  and to  $\langle \beta_{uvw}\beta_{xyz} \rangle_{av}$ . The transformation to molecular axes  $uvw$  for isotropic media is performed by averaging the products of the direction cosines over all directions.<sup>10</sup> Molecules with strong NLO activity are mostly conjugated  $\pi$ -electron systems with donor and acceptor groups in the *para* position. Therefore, the largest component of  $\beta$  is most likely  $\beta_{zzz}$ , the one in the direction of the molecular axis  $z$ . This has proven to be a good approximation for substituted benzenes.<sup>1</sup> Consequently, the element squared,  $\beta_{zzz}^2$ , is by far the largest term in  $\langle \beta_{uvw}\beta_{xyz} \rangle_{av}$ . The total intensity of the second-harmonic scattered light is then  $I_{2\omega} = gB^2I_0^2 = g\sum_s N_s \beta_s^2 I_0^2$ , where  $g$  depends upon the scattering geometry and contains the averages of the products of the direction cosines and the local-field corrections.  $N_s$  is the number density of species  $s$  with second-order NLO polarizability  $\beta_s = \beta_{zzz,s}$ . Because of the quadratic dependence of the hyper-Rayleigh signal, only absolute values of  $\beta$  can be deduced. Since no independent measurement of the dipole moment and the third-order hyperpolarizability is needed, this method can present an alternative for the measurement techniques cited above.

The intense infrared light pulses (8 ns, < 10 mJ, 1064 nm) of an injection-seeded  $Q$ -switched Nd-doped yttrium-aluminum-garnet laser are focused in a thermostated cylindrical cell. The experiments are performed well below the threshold for stimulated Raman and Brillouin scattering, and for self-focusing. A small fraction of the incident light beam is directed on a fast photodiode for monitoring pulse shape and stability, and incident light intensity. The scattered light is collected by

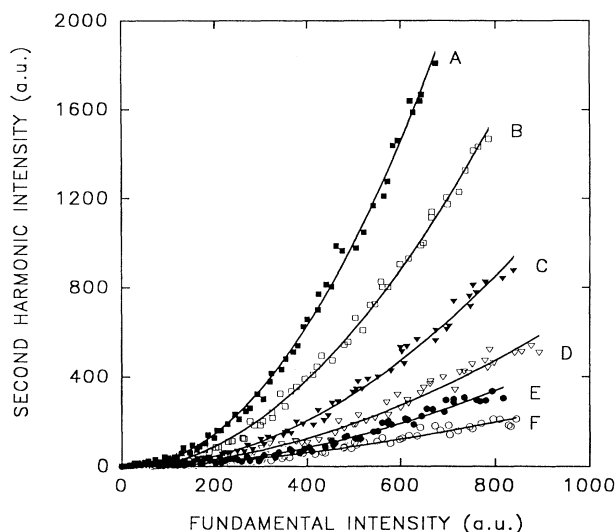


FIG. 1. Signal of nonlinear light scattering in solution for *para*-nitroaniline in methanol at 293 K at different number densities in units of  $10^{18} \text{ cm}^{-3}$ : curve A, 92; curve B, 46; curve C, 23; curve D, 9.2; curve E, 4.6; and curve F, 1.8; the solid lines are fitted curves.

an efficient condenser system. Spectral discrimination of the second-order scattering from the linear counterpart is accomplished by low-pass optical filters and a 3-nm-bandwidth, 532-nm interference filter. Gated integrators are used to retrieve actual values for the intensities of the incident and second-order scattered light pulses. Experimental details will be published elsewhere.

A quadratic dependence of the hyper-Rayleigh signal  $S_{2\omega}$  on the incident light intensity  $I_0$  is always observed, according to  $S_{2\omega} = GB^2 I_0^2$ , with  $G$  a proportionality constant, containing geometrical and electronic factors. For a two-component system,

$$B^2 = N_{\text{solvent}}\beta_{\text{solvent}}^2 + N_{\text{solute}}\beta_{\text{solute}}^2.$$

For the low concentrations used, the presence of the solute molecules does not significantly change the number density  $N_{\text{solvent}}$  of the solvent molecules. Measurements at different number densities of the solute then show a linear dependence of  $GB^2$  on  $N_{\text{solute}}$ . From the intercept and the slope,  $\beta_{\text{solute}}$  is calculated when  $\beta_{\text{solvent}}$  is known, or vice versa. Since no external field directing the dipoles has to be applied, the local-field correction factor at zero frequency is eliminated. The only local-field correction factors needed are those at optical frequencies, which can be estimated by standard methods.<sup>1</sup> The internal reference method (IRM) eliminates the need for local-field correction factors, since these factors are divided out by calibrating and measuring in nearly the same local field, as long as the number density of the solute molecules present does not significantly change the refractive index of the solution.

The quadratic dependence of the observed hyper-

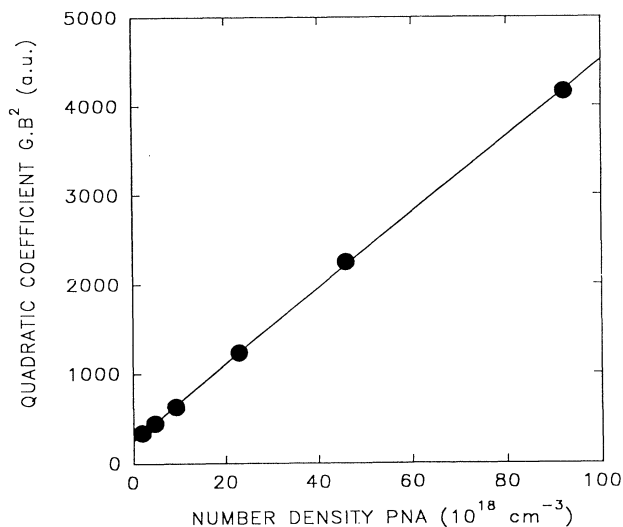


FIG. 2. Quadratic coefficient  $GB^2 = G[N_{\text{solvent}}\beta_{\text{solvent}}^2 + N_{\text{solute}}\beta_{\text{solute}}^2]$ , obtained from the curves in Fig. 1, vs  $N_{\text{solute}}$ , the number density of PNA in methanol at 293 K.

Rayleigh signal  $S_{2\omega}$  at optical frequency  $2\omega$  on incident intensity  $I_0$  at frequency  $\omega$  is illustrated in Fig. 1 for *para*-nitroaniline (PNA) in methanol. The  $\delta$  spectral response at  $2\omega$  was confirmed by checking with different optical fibers. Figure 2 shows the expected linear dependence of the retrieved value for the quadratic coefficient  $GB^2$  on the number density  $N_{\text{solute}}$ . With the known value of  $\beta_{\text{solvent}} = -0.49 \times 10^{-30} \text{ esu}$  for  $\text{CHCl}_3$ ,<sup>11</sup> we were able to check the method of extracting accurate values for  $\beta_{\text{solute}}$  by the IRM. We calculated a value for  $\beta_{\text{PNA}}$  of  $23 \times 10^{-30} \text{ esu}$ ,  $105 \times 10^{-30} \text{ esu}$  for 4-methoxy-4'-nitrostilbene (MONS), and  $95 \times 10^{-30} \text{ esu}$  for 4-hydroxy-4'-nitrostilbene (HONS), all in  $\text{CHCl}_3$ . These values are in good agreement with previously reported values for  $\beta$  in different solvents (Table I and Fig. 3). The dependence of  $\beta$  on the polarity of the solvent, as measured by the dielectric constant  $\epsilon$ , has been used in solvatochromic measurements of  $\beta$ .<sup>12</sup> The factor  $(\epsilon - 1)/(2\epsilon + 1)$  is related to the reaction field, experienced by the permanent dipole moment of the solute molecule due to the interaction with the permanent dipole moment of the solvent molecules.<sup>13</sup> The theoretical limits for  $\beta_{\text{PNA}}$  in different solvents, deduced from Fig. 3, are in good agreement with the range of reported values from  $6 \times 10^{-30}$  to  $40 \times 10^{-30} \text{ esu}$ .<sup>14</sup> Consequently, a maximum value of  $140 \times 10^{-30} \text{ esu}$  is inferred for  $\beta_{\text{MONS}}$  in highly polar media [ $(\epsilon - 1)/(2\epsilon + 1)$  close to 0.5].

With a solute molecule with an accurately known value for  $\beta_{\text{solute}}$  as the internal reference, the proposed technique is the method of choice for the determination of the small value of  $\beta$  for solvents. From the value of  $\beta_{\text{PNA}} = 34.5 \times 10^{-30} \text{ esu}$  in methanol,<sup>15</sup> an absolute value of  $0.69 \times 10^{-30} \text{ esu}$  for  $\beta_{\text{MeOH}}$  has been deduced. When no internal reference is present, e.g., when the solvent

TABLE I. Dielectric constant  $\epsilon$ ,  $(\epsilon-1)/(2\epsilon+1)$ , and second-order polarizability  $\beta$  for PNA, MONS, and HONS in different solvents. Values in parentheses are estimated uncertainties.

Solvent	$\epsilon$	$(\epsilon-1)/(2\epsilon+1)$	$\beta$ ( $10^{-30}$ esu)		
			PNA	MONS	HONS
Dioxane	2.2	0.22	16.9(0.4) <sup>a</sup>	81(8) <sup>b</sup>	
Chloroform	4.8	0.36	23(3)	105(35)	93(30)
1,2 dichloroethane	10.6	0.43		119(17) <sup>c</sup>	
Methanol	32.6	0.48	34.5(4) <sup>d</sup>		

<sup>a</sup>From Ref. 13.

<sup>b</sup>From Ref. 23.

<sup>c</sup>From Ref. 14.

<sup>d</sup>From Ref. 15.

molecules are centrosymmetric, calibration against a standard solution with known  $B^2$  enables the calculation of  $\beta_{\text{solution}}$ . In this way, a value of  $\beta = 1.8 \times 10^{-30}$  esu was obtained for nitromethane. Reported values for the same and other small saturated molecules, in gas or liquid phase, are given in Table II for comparison.

A linear relationship between  $\beta$  and the dipole moment for *monosubstituted* benzene derivatives has been derived on the basis of the equivalent-internal-field (EIF) model.<sup>16</sup> Figure 4 shows that this relationship is also qualitatively fulfilled by small methane derivatives. This case has not been considered in the EIF theory where the second-order NLO hyperpolarizability  $\beta$  is shown to be equal to  $\beta = 3(\gamma_\pi/\alpha_\pi)\Delta\mu_x$ , with  $\Delta\mu_x = \alpha_\pi E_0$  the *mesomeric* moment<sup>16</sup> caused by the substitution on the polarizable  $\pi$ -electron system. The same concept can be applied to a nonconjugated molecule where only a  $\sigma$ -electron-related polarizability is present. For the case of methane, one has an induced dipole moment equal to  $\mu_{\text{ind}} = \alpha_\sigma E_{\text{tot}} + \gamma_\sigma E_{\text{tot}}^3$ . This leads to an analogous expression for  $\beta$  in terms of  $\alpha_\sigma$  and  $\gamma_\sigma$ ,  $\beta = 3(\gamma_\sigma/\alpha_\sigma)\Delta\mu_x$ , with  $\Delta\mu_x$  now the *electromeric* moment. The dipole moment originates solely from localized but polarizable  $\sigma$  electrons. The assumption can then be made that  $\Delta\mu_x$  is

simply the static dipole moment  $\mu$  of the molecule.<sup>17</sup> This theory predicts a linear relationship of  $\beta$  as a function of dipole moment with a slope of  $3\gamma_\sigma/\alpha_\sigma$ . For the methane derivatives, the experimentally determined slope is  $0.50 \times 10^{-12}$  esu; the slope according to  $3\gamma_\sigma/\alpha_\sigma$  with  $\alpha_\sigma = 2.6 \times 10^{-24}$  esu (Ref. 18) and  $\gamma_\sigma = 0.42 \times 10^{-36}$  esu for methane<sup>19</sup> is  $0.48 \times 10^{-12}$  esu. In view of this agreement, it seems justified to extend the concept of the EIF model from conjugated  $\pi$ -electron systems to fully saturated molecules.

In solution, attention should be paid to the importance of the reaction field, caused by the dipole moment themselves, and to the associated increase of the dipole moment under the influence of its own reaction field.<sup>20</sup> The uncertainty of the value of the effective, interacting dipole moment hinders the retrieval of accurate values for the second-order NLO polarizability  $\beta$ . Since the hyper-Rayleigh signal is directly proportional to  $\beta^2$ , the knowledge of the dipole moment is not required, if the sign of  $\beta$  is irrelevant.

It has not escaped our attention that the proposed technique could be used to measure the effective reaction-field amplitude  $E_{\text{RF}}$ . Since this amplitude can amount to values comparable to the amplitude  $E_{\text{opt}}$  of the optical fields in intense laser beams, the measurement of the third-order NLO polarizability (second hy-

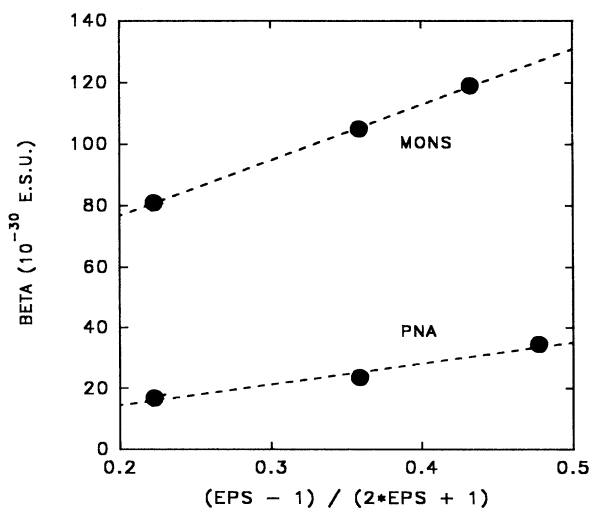


FIG. 3. Second-order nonlinear optical polarizability (first hyperpolarizability)  $\beta$  for PNA and MONS vs  $(\epsilon-1)/(2\epsilon+1)$ .

TABLE II. Dipole moment  $\mu$  and absolute value of first hyperpolarizability  $\beta$  for some small saturated molecules. Values in parentheses are estimated uncertainties.

Solvent	$\mu$ ( $10^{-18}$ esu)	$ \beta $
		( $10^{-30}$ esu)
Methane	0.0	0.0 <sup>a</sup>
Chloroform	1.01	0.49(0.05) <sup>b</sup>
		0.5(0.4) <sup>c</sup>
		0.39 <sup>c</sup>
		13 <sup>d</sup>
Methanol	1.70	0.005(0.011) <sup>c</sup>
Nitromethane	3.46	0.69(0.07) <sup>c</sup>
		1.82(0.33) <sup>c</sup>

<sup>a</sup> $\beta_{xyz} = 0.01 \times 10^{-30}$  esu, from Ref. 6.

<sup>b</sup>Solution value, from Ref. 11.

<sup>c</sup>Gas-phase value, from Ref. 24.

<sup>d</sup>Liquid-phase value, from Ref. 24.

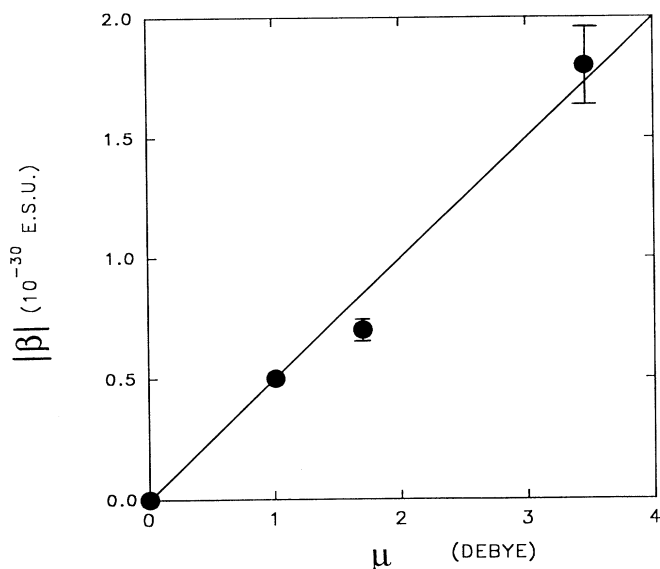


FIG. 4. Absolute value of second-order nonlinear polarizability (first hyperpolarizability)  $\beta$  vs dipole moment  $\mu$  for  $\text{CH}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{OH}$ , and  $\text{CH}_3\text{NO}_2$ . ●, experimental points; —, fitted curve with slope  $(0.50 \pm 0.02) \times 10^{-12}$  esu.

perpolarizability),

$$\gamma(-2\omega_{\text{opt}} \pm \omega_{\text{RF}}; \omega_{\text{opt}}, \omega_{\text{opt}}, \omega_{\text{RF}}) E_{\text{opt}} E_{\text{opt}} E_{\text{RF}},$$

functions as a local probe for the reaction-field strengths as well as for the dynamics in solution.

We propose the use of a centrosymmetric solute molecule as a probe of the internal field strength to which the solute molecule is subjected in solution with a dipolar solvent. The observed hyper-Rayleigh signal at  $2\omega$  will be proportional to the square of the reaction-field strength  $E_{\text{RF}}$ , while it is hypothesized that spectral broadening will reflect orientation fluctuations in solution. This situation is different from hyper-Rayleigh scattering due to intermolecular interactions between centrosymmetric molecules in the liquid phase.<sup>21</sup>

In conclusion, we have explored the feasibility of hyper-Rayleigh scattering in solution for the determination of second-order NLO polarizabilities of organic molecules in solution. The second-order NLO behavior of small saturated molecules has been rationalized in terms of the previously reported equivalent-internal-field model.

Finally, there are no theoretical difficulties in expanding the induced dipole moment  $\mu_{\text{ind}}$  to higher order in the oscillating electric field  $\mathbf{E}$ ,  $\mu_{\text{ind}} = \alpha \cdot \mathbf{E} + \beta : \mathbf{E}\mathbf{E} + \gamma : \mathbf{E}\mathbf{E}\mathbf{E}$ . This implies third-order hyper-Raman scattering at the third harmonic, proportional to  $\gamma^2$  and to  $I_0^3$ . Detection of the scattered signal at  $3\omega$  should then be proportional to  $\Gamma^2 = \sum_s N_s \gamma_s^2$ . Since coherent generation of the third harmonic in the forward direction has been observed ex-

perimentally,<sup>22</sup> detection of the incoherently scattered light at the third harmonic should be feasible.

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