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1 December 1998

OPTICS  
COMMUNICATIONS

Optics Communications 157 (1998) 177–181

# Spectral features of hyper-Rayleigh scattering in chloroform-d

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Received 9 June 1998; accepted 1 September 1998

## Abstract

Measurements of hyper-Rayleigh scattering (HRS) in chloroform-d indicate that interaction induced contributions account for more than half of the scattered intensity from the liquid phase. The effective hyperpolarizability obtained from the entire liquid HRS spectrum in the VV polarization geometry is  $\langle \beta_{VV}^2 \rangle^{1/2} = 15.7 \pm 0.6$  au. The unimolecular hyperpolarizabilities obtained from the Lorentzian components of the HRS spectrum are  $\langle \beta_{VV}^2 \rangle^{1/2} = 10.2 \pm 0.7$  au and  $\beta_{\parallel} = 10.8 \pm 0.5$  au. This value for  $\beta_{\parallel}$  differs substantially from that previously inferred from electric field induced second harmonic generation (EFISH) measurements, calling into question previous HRS results calibrated using chloroform as a standard. © 1998 Elsevier Science B.V. All rights reserved.

PACS: 42.65.Ky

Keywords: Nonlinear optics; Hyper-Rayleigh scattering; Chloroform

## 1. Introduction

Hyper-Rayleigh (HRS) or second harmonic light scattering measurements have become an important method for measuring first hyperpolarizabilities  $\beta$  of organic chromophores [1–3]. The HRS measurement is more flexible and much simpler than electric field induced second harmonic generation (EFISH), which is the principal alternative method for determining  $\beta$ . However, unresolved difficulties [4] with the absolute calibration of EFISH measurements have not been avoided, because uncertain EFISH values are sometimes used to calibrate the HRS measurements and because different tensor elements of the hyperpolarizabilities are involved in the two experiments. Furthermore, HRS signals from molecular liquids can include large intermolecular contributions, which have usually been ignored although in fact they may dominate the nonlinear light scattering intensity [5].

Chloroform has frequently [6–13] been used as a HRS reference standard in which the liquid phase EFISH value

measured by Kajzar et al. [14] is used to calibrate the HRS signals. This EFISH value for  $\beta_{\parallel}$ , however, is dependent on the values of the nonlinear susceptibilities of quartz and glass, which are now believed [15–18] to be lower than the values used by Kajzar et al. Even given an accurate EFISH value of  $\beta_{\parallel}$  for chloroform, the liquid HRS calibration based on  $\beta_{\parallel}$  may still be inaccurate because of the large effect of molecular interactions on the  $\beta$  values obtained by HRS. In this Letter we provide accurate values of the HRS  $\beta$  of liquid chloroform, taking into consideration the effect of molecular interactions and calibrating the resulting  $\beta$  values against that for  $\text{CCl}_4$  [19].

## 2. Experiment

A detailed description of the experimental apparatus was given in a previous paper [20]. Briefly, chloroform-d (Cambridge Isotope Laboratories) was filtered through a 0.2- $\mu\text{m}$  micropore filter directly into a 1-cm spectroscopic fused silica cuvette. The laser (Quantronix 116) produced a train of  $\approx 150$  ns, 1 mJ pulses at 1064 nm at a repetition rate of 3 kHz, and was focused into the sample cell with a

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4 × microscope objective lens. The scattered light was collected at 90° with  $f/2.1$  optics and focused into a spectrometer (Jobin–Yvon Ramanor U 1000). The line-shape measurements were done with a spectral slit width of 2.4 cm<sup>-1</sup>. A maximum HRS signal of about 100 counts per second was observed in the VV polarization geometry.

### 3. Results and discussion

The nonlinear optical response of an isolated molecule irradiated with light of high intensity may be written as a Taylor series for the induced dipole moment,  $\mu_i = \alpha_{ij}E_j + \frac{1}{2}\beta_{ijk}E_iE_j + \dots$ , where the molecular tensors  $\alpha$  and  $\beta$  describe the linear polarizability and the first hyperpolarizability of the molecules, respectively. The second harmonic light intensity for a collection of  $N$  non-interacting molecules without orientational correlations, in the electric dipole approximation, is given by  $I^{2\omega} \propto N \langle \beta_{IJK} \beta_{LMN} \rangle$ , where the quadratic forms  $\langle \beta_{IJK} \beta_{LMN} \rangle$  of the microscopic molecule-fixed-axis hyperpolarizability components,  $\beta_{ijk}$  are averaged over all possible molecular orientations. Spatial fluctuations of molecular orientation are responsible for the non-vanishing intensity of incoherent HRS from molecular fluids, while temporal fluctuations of molecular orientation govern the spectral distribution of HRS. Reorientational dynamics and consequently the spectrum are strongly influenced by intermolecular interactions in dense media. The fluctuating molecular field seen by the interacting molecules also leads to a perturbed value of  $\beta_{ijk}$ . Since the interaction between nearest neighbors varies rapidly with distance, molecular motion causes rapid fluctuations of the first hyperpolarizability and gives rise to an additional broad ‘collision induced’ HRS spectral component.

The HRS spectra of chloroform-d in the VV and HV polarization geometries are shown in Fig. 1. The main features are a narrow Lorentzian peak superimposed on a broad exponential wing. The broad exponential wing strongly suggests collision induced HRS, since a nearly exponential profile is typical of collision induced light scattering, but the complete theory is complicated and incompletely developed [21]. On the other hand, the Lorentzian lineshape  $g_M^J(\Delta\nu)$  is readily understood as HRS from rotationally diffusing molecules [22,23],

$$g_M^J(\Delta\nu) = \frac{2c\tau_M^J}{1 + (2\pi c\Delta\nu\tau_M^J)^2} \quad (1)$$

where the frequency shift  $\Delta\nu$  in wavenumbers (cm<sup>-1</sup>) is measured from the second harmonic of the incident laser frequency (negative  $\Delta\nu$  for the Stokes side). In the general case (molecules of C<sub>1</sub> symmetry) there are 10 relaxation times  $\tau_M^J$  of which three are of ‘dipolar’ symmetry ( $J = 1$ ,

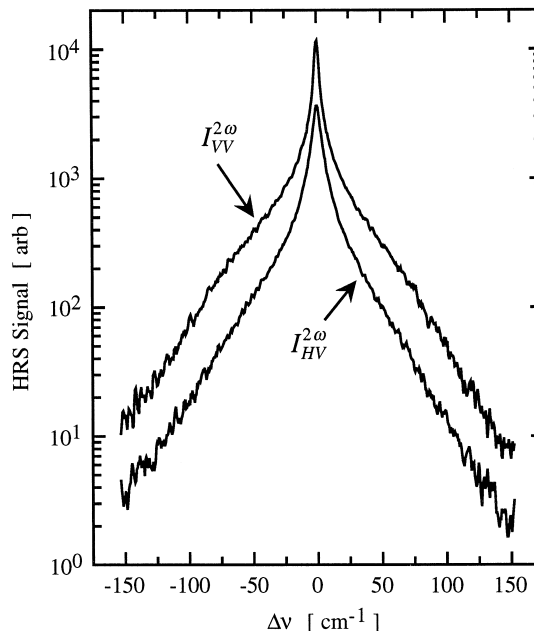


Fig. 1. HRS from chloroform-d at 22°C with irradiation at 1064 nm. The Lorentzian components contribute 42% of the total scattering for  $I_{VV}^{2\omega}$  and 48% for  $I_{HV}^{2\omega}$ . The polarization ratio  $I_{VV}^{2\omega}/I_{HV}^{2\omega}$  at  $\Delta\nu = 0$  is  $3.2 \pm 0.1$ . Integration of the total scattering gives a polarization ratio  $I_{VV}^{2\omega}/I_{HV}^{2\omega} = 2.5 \pm 0.1$  whereas integration of only the Lorentzian terms gives a ratio  $I_{VV}^{2\omega}/I_{HV}^{2\omega} = 2.2 \pm 0.2$ .

$M = 0, \pm 1$ ) and seven are of ‘octupolar’ symmetry ( $J = 3$ ,  $M = 0, \pm 1, \pm 2, \pm 3$ ). For molecules of higher symmetry, the number of relaxation times is lower. By using the rotational diffusion coefficients perpendicular,  $D_{\perp}$ , and parallel,  $D_{\parallel}$ , to the 3-fold rotation axis, the relaxation times for a symmetric top molecule can be written as

$$\frac{1}{\tau_M^J} = J(J+1)D_{\parallel} + M^2(D_{\perp} - D_{\parallel}) \quad (2)$$

thus giving  $\tau_M^J = \tau_{-M}^J$ . The distinct relaxation times for molecules of C<sub>3v</sub> symmetry consist of one with dipolar symmetry ( $J = 1$ ,  $M = 0$ ) and two with octupolar symmetry, ( $J = 3$ ,  $M = 0, 3$ ).

Maker [22] and subsequently, Alexiewicz [23], have discussed the expansion of  $\beta_{ijk}$  in terms of a spherical tensor representation where  $\beta_M^{[J]}$  is the  $M$ th element of a tensor of rank  $J$ . This representation is useful for the description of HRS as the individual elements of  $\beta_M^{[J]}$  are invariant under molecular coordinate frame rotations. In general, the dipolar,  $\beta_M^{[1]}$ , and octupolar,  $\beta_M^{[3]}$ , contributions to HRS can be constructed in terms of the VV and HV spectra. For a molecule with C<sub>3v</sub> symmetry undergoing rotational diffusion, the spectral broadening of the

dipolar HRS spectrum is described by a single Lorentzian  $g_0^1$ ,

$$6 \left( I_{VV}^{2\omega} - \frac{3}{2} I_{HV}^{2\omega} \right) \propto |\beta_0^{[1]}|^2 g_0^1(\Delta\nu) = \frac{5}{3} \beta_{\parallel}^2 g_0^1(\Delta\nu), \quad (3)$$

whereas the octupolar spectrum should be a sum of two Lorentzians,  $g_0^3(\Delta\nu)$  and  $g_3^3(\Delta\nu)$ ,

$$\begin{aligned} \frac{63}{2} \left( I_{HV}^{2\omega} - \frac{1}{9} I_{VV}^{2\omega} \right) \propto \sum_M |\beta_M^{[3]}|^2 g_M^3(\Delta\nu) \\ = \frac{2}{5} (\Delta\beta)^2 g_0^3(\Delta\nu) + 4\beta_{yy}^2 g_3^3(\Delta\nu). \end{aligned} \quad (4)$$

Symmetry restrictions on the dipolar and octupolar hyperpolarizabilities imply  $\beta_M^{[J]} = \beta_{-M}^{[J]}$  for a symmetric top molecule. The molecular hyperpolarizability invariants for a molecule with  $C_{3V}$  symmetry are [24]

$$\beta_{\parallel} = \frac{3}{5} (\beta_{zzz} + 2\beta_{zzx}), \quad \Delta\beta = \beta_{zzz} - 3\beta_{zzx},$$

and  $\beta_{yyy}$ , (5)

with  $z$  coincident with the 3-fold symmetry axis of the molecule. The expressions for the hyperpolarizability components of  $\langle \beta_{VV}^2 \rangle$  and  $\langle \beta_{HV}^2 \rangle$  in terms of these invariant are:

$$\langle \beta_{VV}^2 \rangle = \frac{1}{3} \beta_{\parallel}^2 + \frac{4}{175} (\Delta\beta)^2 + \frac{8}{35} \beta_{yyy}^2, \quad (6a)$$

$$\langle \beta_{HV}^2 \rangle = \frac{1}{27} \beta_{\parallel}^2 + \frac{8}{525} (\Delta\beta)^2 + \frac{16}{105} \beta_{yyy}^2, \quad (6b)$$

The relations given in Eqs. (3) and (4) assume that the HRS spectra can be described in terms of the hyperpolarizability components of the independent, unperturbed molecules alone. In our previous work with  $\text{CCl}_4$  [5], we have identified other contributions to the HRS intensity that arise from the intermolecular interactions. For example, there is an ‘octupole-induced-dipole’ contribution due to the fields of the permanent octupole moments on neighboring molecules. These contributions to HRS are expected to be present in chloroform as well and are typically characterized by a non-Lorentzian spectral profile.

Maker has shown that the Debye–Stokes approximation to the viscous drag describing the rotational diffusion of the molecules gives a poor estimate of the relaxation times  $\tau_M'$ , at least when using the shear viscosity values [22]. Therefore, we used the previous HRS measurement of  $\text{CCl}_4$  [5] and Eq. (2) to predict the Lorentzian linewidths of chloroform. The HRS spectra of  $\text{CCl}_4$  contain a single Lorentzian of type  $g_0^3$  with a spectral linewidth  $1/\pi c\tau_0^3 = 9.2 \text{ cm}^{-1}$  (FWHM). Assuming that the rotational diffusion coefficients are inversely proportional to the moments of inertia of the free molecules, Eq. (2) calibrated with the Lorentzian  $g_0^3$  of  $\text{CCl}_4$  predicts that the Lorentzian components of chloroform should be characterized by

linewidths of 1.5, 9.2 and  $14 \text{ cm}^{-1}$  (FWHM) corresponding to  $g_0^1$ ,  $g_0^3$ , and  $g_3^3$ , respectively.

Fig. 2 shows the experimental spectra constructed according to Eqs. (3) and (4). Both a Lorentzian and an exponential component are necessary to adequately fit either the dipolar or the octupolar spectrum. The exponential components report the changes in  $\beta$  due to intermolecular collisions, while the Lorentzian components provide the  $\beta$  values for the undistorted molecule. The experimental spectra were fit with the following expression:

$$\begin{aligned} I_J^{2\omega}(\Delta\nu) = \left\{ \sum_M I_{JM} \frac{2g_M^J(\Delta\nu)}{1 + \exp|\Delta\nu/v_0|} \right. \\ \left. + I_J \frac{\exp(-|\Delta\nu/v_J|)}{2v_J} \right\} \exp(-\Delta\nu/2kT), \end{aligned} \quad (7)$$

with  $J = 1$  and  $J = 3$  for the spectra constructed according to Eqs. (3) and (4), respectively, and where  $I_{JM}$  and  $I_J$  are the integrated intensities of the corresponding components of  $I_J^{2\omega}$ . The final exponential factor accounts for the Stokes/anti-Stokes intensity asymmetry ( $2kT = 410 \text{ cm}^{-1}$  at  $22^\circ\text{C}$ ). The Lorentzian function in Eq. (7) has its far wings clipped; at large  $|\Delta\nu|$  it becomes an exponential. For chloroform, the transition is expected to occur at about  $\nu_0 \approx 100 \text{ cm}^{-1}$ , corresponding to a time of about 0.05 ps, because the reorientational motion is ballistic rather than diffusive at times shorter than the mean time between collisions. The best fit is achieved with  $\nu_0 = 90 \pm 10 \text{ cm}^{-1}$ .

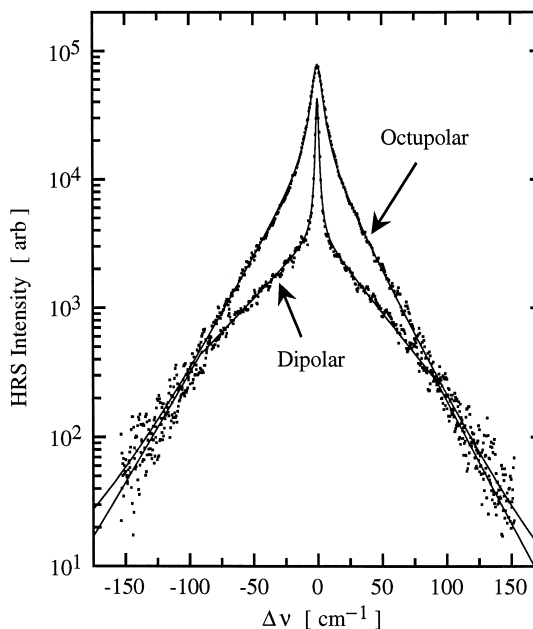


Fig. 2. Decomposition of the HRS spectra of chloroform-d at  $22^\circ\text{C}$  into the dipolar and octupolar contributions, as in Eqs. (3) and (4).

Table 1

Linewidth parameters of the HRS spectra of chloroform-d obtained from the dipolar and octupolar HRS spectra constructed in accordance with Eqs. (3) and (4) and analyzed with Eq. (7)

Linewidth	Measured [ $\text{cm}^{-1}$ ]	Predicted [ $\text{cm}^{-1}$ ]
$1/\pi c\tau_0^1$	$1.6 \pm 0.2^a$	1.5
$1/\pi c\tau_0^3$	$9.0 \pm 0.4$	9.2
$1/\pi c\tau_3^3$		14
$\nu_0$	$90 \pm 10$	100
$\nu_1 (\Delta\nu < \nu_0)$	$39 \pm 3$	
$\nu_1 (\Delta\nu > \nu_0)$	$23 \pm 2$	
$\nu_3$	$25 \pm 2$	

The rotational diffusion relaxation times  $\tau_M^J$  are obtained from the Lorentzian components of the spectra. The corresponding predicted values are in good agreement with the measured values. The parameters,  $\nu_j$ , of the exponential profiles of the HRS spectra are related to the timescale of intermolecular interactions.

<sup>a</sup>Spectral slit width deconvolved.

The dipolar spectrum constructed as in Eq. (3) has three distinct regions comprised of a narrow Lorentzian of width  $1/\pi c\tau_0^1 = 1.6 \pm 0.2 \text{ cm}^{-1}$  (spectral slit width deconvolved), and a complex broad component fit by a shallow exponential term with  $\nu_1 = 39 \pm 3 \text{ cm}^{-1}$  for  $\Delta\nu < 90 \text{ cm}^{-1}$ , which switches to a steeper exponential profile with  $\nu_1 = 23 \pm 2 \text{ cm}^{-1}$  for  $\Delta\nu > 90 \text{ cm}^{-1}$ . The octupolar spectrum could be fit with a single narrow Lorentzian of width  $1/\pi c\tau_0^3 = 9.0 \pm 0.4 \text{ cm}^{-1}$  and an exponential term with  $\nu_3 = 25 \pm 2 \text{ cm}^{-1}$ . A fit of the octupolar spectrum with two Lorentzians of widths  $1/\pi c\tau_0^3 = 9 \text{ cm}^{-1}$  and  $1/\pi c\tau_3^3 = 14 \text{ cm}^{-1}$  gives zero amplitude for the latter. According to Eq. (4), this indicates that  $\beta_{yyy} = 0$ . Table 1 summarizes the linewidth parameters obtained using this analysis.

Table 2

Hyperpolarizability values obtained from the HRS measurements

Hyperpolarizability	[au]
$\langle \beta_{VV}^2 \rangle^{1/2}$ total	$15.7 \pm 0.6$
$\langle \beta_{HV}^2 \rangle^{1/2}$ total	$9.9 \pm 0.4$
$\langle \beta_{VV}^2 \rangle^{1/2}$	$10.2 \pm 0.7$
$\langle \beta_{HV}^2 \rangle^{1/2}$	$6.9 \pm 0.5$
$\beta^{[1]}$	$13.9 \pm 0.6$
$\beta^{[3]}$	$33 \pm 2$
$\beta_{  }$	$10.8 \pm 0.5$
$\beta_{zzz}$	$32 \pm 2$
$\beta_{zzx}$	$-7.0 \pm 0.5$
$\beta_{yyy}$	$0.0 \pm 0.5$

The total integrated HRS intensities are listed first and were obtained in comparison to the integrated HRS intensities of  $\text{CCl}_4$ . The remaining hyperpolarizability values are obtained from just the Lorentzian contributions to the HRS spectra of chloroform-d. The relative signs of all hyperpolarizability components are determined from the measurements and Eq. (5), but the absolute signs are undetermined.

Table 3

Comparison of hyperpolarizability values obtained from EFISH and HRS measurements at a fundamental wavelength of 1064 nm

$\beta_{  }$ [au]	Method	Ref.
$10.8 \pm 0.5^a$	liquid phase HRS	This work
$+1.0 \pm 4.2$	gas phase EFISH	[19]
$-68 \pm 7$	liquid phase EFISH <sup>b</sup>	[14]

The hyperpolarizabilities are given in atomic units ( $1 \text{ au} = 3.20636 \times 10^{-53} \text{ C}^3 \text{ m}^3 \text{ J}^{-2} = 3.6213 \times 10^{-42} \text{ m}^4 \text{ V}^{-1} = 8.6392 \times 10^{-33} \text{ esu}$ ).

<sup>a</sup>Sign undetermined.

<sup>b</sup>Calibration requires  $\chi^{(2)}$  of quartz and  $\chi^{(3)}$  of glass and  $\text{CHCl}_3$ .

The absolute values of the integrated intensities were calibrated with respect to the total intensity of the VV HRS spectrum, which was previously referenced to the HRS signal from  $\text{CCl}_4$  [19]. The hyperpolarizabilities were then calculated with Eqs. (3), (5), (6a) and (6b), using only the integrated intensities of the Lorentzian components. Table 2 summarizes the hyperpolarizabilities obtained from the integrated intensity measurements. Note that the appropriate reference value for calibration of HRS intensities is the effective hyperpolarizability  $\langle \beta_{VV}^2 \rangle^{1/2}$ .

In Table 3, we compare values of the first hyperpolarizability  $\beta_{||}$  of chloroform from previous gas- and liquid-phase EFISH measurements along with the present value obtained from HRS. The HRS  $\beta_{||}$  has been obtained from just the Lorentzian components of the HRS spectra (thus excluding intermolecular collision effects) to make it directly comparable to EFISH  $\beta_1$  values. Despite this, the HRS  $\beta_{||}$  differs from the gas-phase  $\beta_{||}$  [19]. However, the present result is corroborated by direct comparison of liquid- and gas-phase  $\text{CDCl}_3$  HRS intensities, which gives  $\beta_L/\beta_G = 1.70 \pm 0.10$  for the ratio of effective hyperpolarizabilities  $\langle \beta_{VV}^2 \rangle^{1/2}$  [19]. This implies  $\beta_{||} = 9.8 \pm 0.7 \text{ au}$  for the undistorted molecule in liquid  $\text{CDCl}_3$ , in agreement with the results of the HRS spectral decomposition analysis but not with the gas-phase EFISH result. Further study is needed to resolve the discrepancy between the HRS and gas-phase EFISH results.

The HRS liquid-phase value also differs substantially from the liquid-phase EFISH value, although the published value of the latter may contain large systematic errors due to inaccurate values of the reference nonlinear susceptibilities, and needs to be recalibrated [15–18]. In particular, since  $\gamma$  dominates the EFISH signal, the result for  $\beta_{||}$  is very sensitive to any error in the value of  $\gamma$  used in the analysis. This could even change the sign of  $\beta_{||}$  obtained from the liquid-phase EFISH measurement.

#### 4. Conclusions

The HRS intensity in liquid chloroform is more than doubled by the interactions between nearest neighbor

molecules, similar to the case of carbon tetrachloride. For HRS in the VV polarization geometry, the portion of the total intensity that can be attributed to the intrinsic molecular hyperpolarizability contributes only about 42% to the total second harmonic light scattering. Thus, the interaction effects that modulate the second hyperpolarizability during intermolecular collisions are the major source of HRS in liquid chloroform. These contributions to the scattering must be considered when using chloroform as a reference material to obtain reliable estimates of the intrinsic molecular first hyperpolarizabilities from HRS measurements. The present analysis of the HRS spectra of liquid chloroform provides the hyperpolarizability value  $|\beta_{||}| = 10.8 \pm 0.5$  au. The existing liquid-phase EFISH hyperpolarizability value of chloroform differs considerably from this value, in part due to systematic calibration errors, and is unsuitable for calibrating HRS measurements.

## References

- [1] K. Clays, A. Persoons, L. De Maeyer, in: M. Evans, S. Kielich (Eds.), *Advances Chemical Physics*, Vol. 85, Wiley, New York, 1994, p. 455.
- [2] J. Zyss, I. Ledoux, *Chem. Rev.* 94 (1994) 77.
- [3] P. Kaatz, D.P. Shelton, *J. Chem. Phys.* 105 (1996) 3918.
- [4] A. Willetts, J.E. Rice, D.M. Burland, D.P. Shelton, *J. Chem. Phys.* 97 (1992) 7590.
- [5] P. Kaatz, D.P. Shelton, *Mol. Phys.* 88 (1996) 683.
- [6] K. Clays, A. Persoons, *Phys. Rev. Lett.* 66 (1991) 2980.
- [7] G.J.T. Heesink, A.G.T. Ruiter, N.F. van Hulst, B. Bölger, *Phys. Rev. Lett.* 71 (1993) 999.
- [8] T. Verbiest, K. Clays, C. Samyn, J. Wolff, D. Reinhoudt, A. Persoons, *J. Am. Chem. Soc.* 116 (1994) 9320.
- [9] M.A. Pauley, H.W. Guan, C.H. Wang, A.K.Y. Jen, *J. Chem. Phys.* 104 (1996) 7821.
- [10] M.C. Flipse, R. Jonge, R.H. Woudenberg, A.W. Marsman, C. Walree, L.W. Jenneskens, *Chem. Phys. Lett.* 245 (1995) 297.
- [11] E. Hendrickx, K. Clays, A. Persoons, C. Dehu, J.L. Brédas, *J. Am. Chem. Soc.* 117 (1995) 3547.
- [12] S. Stadler, G. Bourhill, C. Bräuchle, *J. Phys. Chem.* 100 (1996) 6927.
- [13] O.F.J. Noordman, N.F. van Hulst, *Chem. Phys. Lett.* 253 (1996) 145.
- [14] F. Kajzar, I. Ledoux, J. Zyss, *Phys. Rev. A* 36 (1987) 2210.
- [15] D.A. Roberts, *IEEE J. Quantum Electron.* QE-28 (1992) 2057.
- [16] K. Hagimoto, A. Mito, *Appl. Optics* 34 (1995) 8276.
- [17] I. Shoji, T. Kondo, A. Kitamoto, M. Shirane, R. Ito, *J. Opt. Soc. Am. B* 14 (1997) 2268.
- [18] A. Mito, K. Hagimoto, C. Takahashi, *Nonlinear Optics* 13 (1995) 3.
- [19] P. Kaatz, E.A. Donley, D.P. Shelton, *J. Chem. Phys.* 108 (1998) 849.
- [20] P. Kaatz, D.P. Shelton, *Rev. Sci. Instrum.* 67 (1996) 1438.
- [21] W.G. Rothschild, *Dynamics of Molecular Liquids*, Wiley, New York, 1984.
- [22] P.D. Maker, *Phys. Rev. A* 1 (1970) 923.
- [23] W. Alexiewicz, *Acta Phys. Polon. A* 47 (1975) 657.
- [24] A.D. Buckingham, B.J. Orr, *Quart. Rev. Chem. Soc.* 21 (1967) 195.