Hyper-Rayleigh Scattering in Isotropic Solution

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I. Introduction

The research into nonlinear optics started with the development of the first reliable lasers. In nonlinear optics, the frequency, phase, or amplitude of an electromagnetic field are modified through its nonlinear interaction with matter.[1] At the molecular level, this interaction is formulated in the nonlinear dependence of the induced dipole moment $\bar{\mu}$ on the electric field $\bar{E}$

$$\bar{\mu} = \alpha.\bar{E} + \beta:\bar{E}\bar{E} + ... \tag{1}$$

where α is the linear polarizability and β is the first hyperpolarizability. Mathematically, β is a third-rank tensor with 27 tensor components. Several material classes are currently being investigated for their nonlinear optical response, such as inorganic crystals and organic materials, (e.g., polymer films).[2]

According to the oriented gas model, the macroscopic nonlinear response of organic materials is proportional to the molecular hyperpolarizabilities. Therefore, the performance of important nonlinear optical devices, such as second-harmonic generators and electrooptic modulators, is proportional to β. Organic molecules combine

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Koen Clays obtained his Ph.D. in chemistry from the Catholic University of Leuven in 1989, for his work on hybrid multifrequency phasefluorometry with pulsed excitation under the supervision of Professor André Persoons. In 1991, he went to Corporate Research Laboratories of the Eastman Kodak Company in Rochester, NY, where he did postdoctoral research in the group of David J. Williams. He then returned to the University of Leuven, initially as a Senior Research Associate of the Fund for Scientific Research in Flanders, later as associate professor.

André Persoons obtained his Ph.D. in chemistry at the Catholic University of Leuven in 1965 under the supervision of Professor J. C. Jungers. After working with Leo De Maeyer on instrumental techniques for the study of fast reactions at the Max Planck Institute for Physical Chemistry in Göttingen, Germany, he returned to the University of Leuven, where, together with De Maeyer, he founded the Laboratory of Chemical and Biological Dynamics. He became full professor in 1977 and extraordinary professor at the University of Brussels in 1987. The research efforts of his group are currently focused on the nonlinear optical properties of organic and polymeric materials.

high nonlinearities with the flexibility of organic synthesis. Additionally, the organic nonlinear chromophores can be incorporated in a polymer matrix, yielding an inexpensive and easily processable material. Hence, organic materials are likely to replace the more traditional inorganic crystals in device applications.

The first step in the design of an organic material is the measurement of the molecular hyperpolarizabilities. Until 1991, the β of organic molecules in solution was routinely measured using Electric-Field-Induced Second-Harmonic Generation (EFISHG).[3] Because EFISHG relies on a strong electric field to break the centrosymmetry of the solution, it is limited to molecules with dipolar symmetry. Also, the magnitude of the molecular dipole moment is necessary to calculate β from an EFISHG measurement. In 1991, the Hyper-Rayleigh Scattering (HRS) technique was developed as an alternative method for the measurement of molecular hyperpolarizabilities.[4–6] Unlike EFISHG, HRS can be used to directly measure β of all molecules, irrespective of symmetry or charge. For dipolar molecules, the hyperpolarizability can be calculated without the knowledge of the dipole moment. In the last years, HRS has emerged as a very valuable measurement technique, and some inherent limitations have been identified and overcome. This review summarizes recent progress with HRS and improvements in the data analysis and the experimental setup. Section 2 explains theory and data analysis in HRS. Section 3 focuses on the experimental setup and the measurement of fluorescent molecules. Finally, Section 4 reviews a variety of HRS measurements performed on dipolar and octopolar molecules, and correlated chromophores.

II. Theory and Data Analysis

1. Theory. An HRS measurement is performed by measuring the intensity of the incoherently scattered light, at the second-harmonic wavelength, that is generated by an intense laser beam in an isotropic solution. HRS was observed first in 1965 by Terhune et al.[7] The theory of HRS was developed in the succeeding years.[8,9] The intensity of the light scattered by a single molecule at the harmonic wavelength 2ω can be calculated by performing an orientational average over β

$$I_s(2\omega) = \frac{32\pi^2}{c\epsilon_0{}^3\lambda^4 r^2} \langle \beta_{HRS}{}^2 \rangle I(\omega)^2 \tag{2}$$

The brackets indicate orientational averaging. As is the case in linear Rayleigh scattering, the intensity of the scattered harmonic is inversely proportional to the fourth power of the fundamental wavelength λ and to the square of the distance to the scattering molecule r.

The relation between $\langle \beta_{HRS}{}^2 \rangle$ and the components of the molecular hyperpolarizability tensor depend on the polarization state of the fundamental and harmonic

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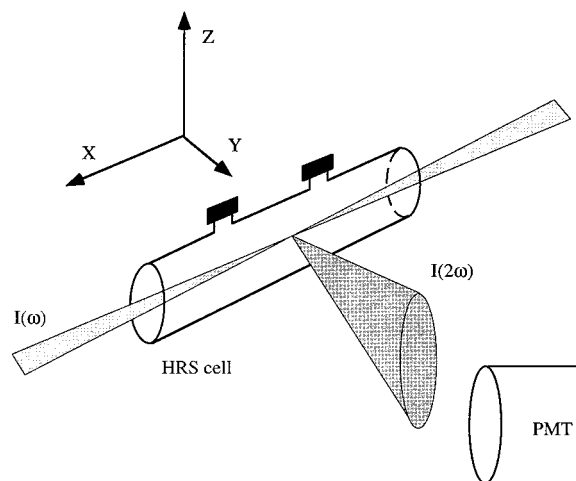[†] University of Leuven.
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FIGURE 1. Sketch of a hyper-Rayleigh scattering setup. An intense infrared laserbeam is brought to focus or collimated in a cell containing an isotropic liquid and the frequency-doubled light is detected under 90°.

beams, the experimental geometry, and the molecular symmetry. If the molecules have no absorption at either fundamental or harmonic wavelength, the components of the hyperpolarizability tensor are real quantities. In this case, the detailed analysis of Bersohn et al.[9] showed that no additional information can be gained by looking in any direction but the classic 90° angle. Therefore, as shown in Figure 1, we can assume that the incident fundamental beam travels in the X-direction and the scattered light is detected in the Y-direction. The relations between the orientationally averaged tensor components and the components of the β tensor are given in Table 1 of ref 9. A total of six functions of the tensor components can be determined using linearly, circularly, and elliptically polarized light. Because these functions are linearly dependent, the number of independent observables is limited to five.

If fundamental and harmonic frequencies are far from material resonance frequencies, Kleinman's symmetry condition $\beta_{ijk} = \beta_{kij} = \beta_{jki}$ applies. In addition, the symmetry convention for second-harmonic generation can be used, $\beta_{ijk} = \beta_{ikj}$. This reduces the analysis by Bersohn et al. to that of Cyvin et al.[8] For a fundamental beam polarized in the Z-direction, the orientationally averaged hyperpolarizabilities are given by

$$\langle \beta_{ZZZ}{}^2 \rangle = \frac{1}{7}\sum_i \beta_{iii}{}^2 + \frac{6}{35}\sum_{i \neq j} \beta_{iii}\beta_{ijj} + \frac{9}{35}\sum_{i \neq j}\beta_{iij}{}^2 + \frac{6}{35}\sum_{ijk,\text{cyclic}}\beta_{iij}\beta_{jkk} + \frac{12}{35}\beta_{ijk}{}^2 \quad (3)$$

$$\langle \beta_{ZZZ}{}^2 \rangle = \frac{1}{35}\sum_i \beta_{iii}{}^2 - \frac{2}{105}\sum_{i \neq j} \beta_{iii}\beta_{ijj} + \frac{11}{105}\sum_{i \neq j}\beta_{iij}{}^2 - \frac{2}{105}\sum_{ijk,\text{cyclic}}\beta_{iij}\beta_{jkk} + \frac{8}{35}\beta_{ijk}{}^2 \quad (4)$$

The first subscript (X or Z) refers to the polarization of the frequency-doubled light. If both polarizations are

detected with equal sensitivity, then

$$\langle \beta_{HRS}{}^2 \rangle = \langle \beta_{ZZZ}{}^2 \rangle + \langle \beta_{XZZ}{}^2 \rangle \quad (5)$$

Equations 3 and 4 are correct only if the scattered light is collected under an angle of 90° in the Y-direction. Correction factors have to be introduced if the collection system collects light under a large angle.[10-12] Morrison et al.[12] have calculated that for accurate measurements of the scattering anisotropy, the numerical aperture of the collection system should be <0.15.

If the molecules show absorption at the fundamental or harmonic wavelength, the components of the hyperpolarizability tensor are complex numbers. By expanding the orientational averages in terms of rotational invariants, Kauranen and Persoons[13] have shown that the maximum number of observables for a complex hyperpolarizability tensor is equal to six. Here, it is necessary to use scattering geometries with a scattering angle other than 90°. A measurement scheme to determine the six observables by varying the polarization of the incoming beam and detecting both linearly and circularly polarized hyperscattered light at an angle of <135° is presented. The number of independent observables can also be reduced by the symmetry of the molecular scatterer. For a planar molecule, where the tensor components that would generate an induced dipole moment perpendicular to the plane of the molecule can be neglected, the number of observables is reduced to five for a complex and to four for a real hyperpolarizability tensor. Again, if the hyperpolarizability tensor is real, the analysis in ref 13 reduces to that of Bersohn et al.[9]

An isotropic solution consists of a large number of randomly oriented molecules. The total scattered intensity can be calculated by summing the electric fields scattered by the individual molecules in the scattering volume and squaring the result. Assuming the molecules in the scattering volume are completely independent, the total intensity is proportional to the sum of the intensity scattered by the individual molecules:

$$I_s(2\omega) = BNf(\omega)^4 f(2\omega)^2 \langle \beta_{HRS}{}^2 \rangle I(\omega)^2 \quad (6)$$

where B groups a number of constants, N is the concentration, and $f(\omega)$ and $f(2\omega)$ are the local field factors:

$$f(\omega) = \frac{n(\omega)^2 + 2}{3} \quad (7)$$

$$f(2\omega) = \frac{n(2\omega)^2 + 2}{3} \quad (8)$$

If the molecules in the scattering volume are correlated, a coherent term that averages over relative distances and mutual orientations of pairs of molecules is added to eq 6.[9] Recent HRS measurements have not given direct evidence of the importance of this term in solutions of dipolar or octopolar chromophores.

2. Data Analysis. In the analysis of the data, the product of B and the local field factors in eq 6 can be
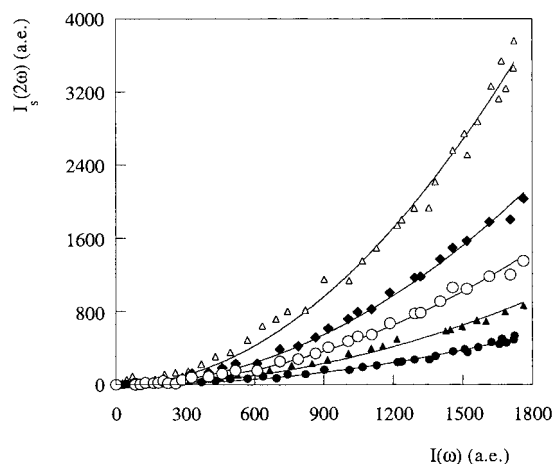
FIGURE 2. Intensity of the hyperscattered light versus the intensity of the fundamental beam for a dilution series of *para*-nitroaniline in chloroform. From a quadratic fit to the data, the quadratic coefficient $G[N_S \langle \beta_{HRS}^2 \rangle_S + N_c \langle \beta_{HRS}^2 \rangle_c]$ can be determined.
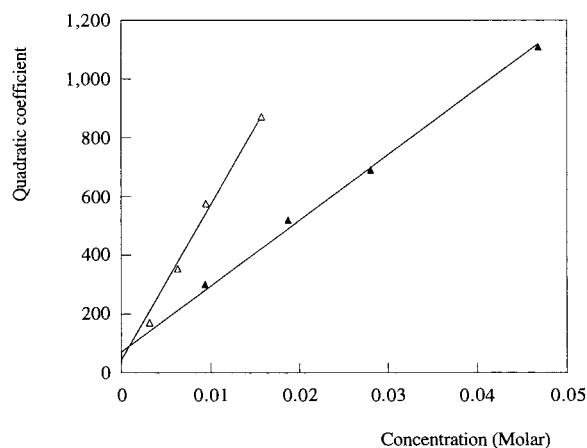

FIGURE 3. Quadratic coefficient versus concentration for *para*-nitroanisole (solid triangles) and *para*-nitroaniline (open triangles) in dioxane. The ratio of the two slopes is proportional to the ratio of the orientationally averaged hyperpolarizabilities.

treated as a calibration constant, G. For a solution of chromophores, eq 6 can be written as:

$$I_s(2\omega) = G[N_S \langle \beta_{HRS}^2 \rangle_S + N_c \langle \beta_{HRS}^2 \rangle_c] I(\omega)^2 \qquad (9)$$

where the subscript S refers to the solvent and the subscript c to the chromophore. If the chromophores absorb the hyperscattered light, a Lambert–Beer term is introduced in eq 9.[14] A typical HRS measurement can be performed by measuring the quadratic dependence of $I_s(2\omega)$ on $I(\omega)$ for a dilution series of the chromophore in an organic solvent (Figure 2). From a fit to a quadratic equation $y = ax^2$, the product of G and the term between brackets can be determined. The product is a linear function of the chromophore concentration in the absence of absorption (Figure 3).

The first procedure that was used to determine the calibration constant G is the internal reference method. The calibration constant is calculated from the intercept in Figure 3 and the known hyperpolarizability and number density of the pure solvent:

$$\frac{1}{N_S \langle \beta_{HRS}^2 \rangle_S} \left| \frac{I_s(2\omega)}{I^2(\omega)} \right|_{N_c=0} = G \qquad (10)$$

The slope, or $G\langle \beta_{HRS}^2 \rangle_c$ can then be used to calculate $\langle \beta_{HRS}^2 \rangle_c$. As pointed out by a number of authors, this method is difficult to use.[12,15–17] A more reliable method is the external reference method. Here, the quadratic dependence of $I_s(2\omega)$ on $I(\omega)$ is measured for a dilution series of a chromophore with an unknown hyperpolarizability and for a reference chromophore with a known hyperpolarizability in the same solvent. Both are plotted as a function of chromophore number density and, in the absence of absorption the ratio of the two slopes, is directly proportional to the ratio of the orientationally averaged hyperpolarizabilities:

$$\frac{\text{slope}(1)}{\text{slope}(2)} = \frac{\langle \beta_{HRS}^2 \rangle_1}{\langle \beta_{HRS}^2 \rangle_2} \qquad (11)$$

A typical molecule used for calibrations is *para*-nitroaniline (PNA).

The spectral profile of the HRS line contains information about the dynamics of the molecules. Spectral measurements of the hyperscattered light have shown that it is composed of a narrow, Lorentzian peak that is superimposed on a broad background. The total width of the spectrum is $\sim$100 cm^{-1}. The narrow peak is generated by the orientational fluctuations of the molecules in solution. Maker's[18] analysis expands both the rotational motions and the hyperpolarizabilities of the molecules into a dipolar and an octopolar term and relates the rotational relaxation time to the width of the Lorentzian profile. Because the rotational relaxation times are of the order of $(2-20) \times 10^{-12}$ s, the line width of the narrow profile is typically a few cm^{-1}. Molecular interactions, that induce a temporary dipole moment in a molecule, influence its symmetry and hence its ability to frequency-double light. The broad background is related to intermolecular interactions and has been fitted to a broad Lorentzian-type profile[19] and an exponential decay.[11] Both these papers report that, at high frequencies, the HRS profile decays exponentially. Kielich et al.[20] have reported on the observation of HRS by liquids of centrosymmetric molecules, such as tetrachloroethylene. Later, a weak and broad hyper-Rayleigh band was also observed in benzene and attributed to collective scattering.[21] Theoretically, this was explained by assuming that the centrosymmetric molecules are in a strongly fluctuating molecular field that can briefly destroy the centrosymmetry.

III. Experimental Details

1. HRS with Nanosecond Pulse Excitation. A general layout of the HRS setup is shown in Figure 4.[5] A fundamental wavelength of 1064 nm is obtained from an injection seeded, Q-switched Nd:YAG laser (Quanta-Ray DCR3, 10 ns, 220 mJ, 10 Hz). A 2–3-mJ portion of this energy is focused into a cylindrical cell (volume, 8–9 mL).
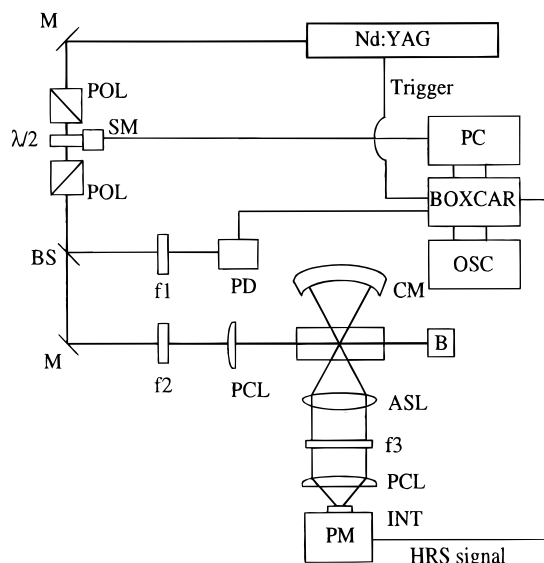
FIGURE 4. Traditional HRS setup with nanosecond pulse excitation: ASL, aspheric lens; B, beamdump; CM, concave mirror; BS, beam splitter; f1, 98% IR filter; f2, visible light filter; f3, IR-filter; PD, photodiode; PM, photomultiplier; INT, 532 nm interference filter; $\lambda/2$, half-wave plate; SM, motor; OSC, oscilloscope; PCL, plano-convex lens; POL, polarizer; M, mirror.

The intensity of the fundamental beam is varied by rotating a half-wave plate between crossed polarizers and is monitored with a photodiode. The harmonic light generated in the focus is collected by a condenser system (a concave mirror and two lenses), and measured by a photomultiplier. A 532 nm interference filter selects light with frequency at the second harmonic. Gated integrators are used to retrieve actual values for the intensities of fundamental and harmonic light.

A major disadvantage of the setup in Figure 4 is its inability to discriminate between hyperscattered light and light that is generated by multiphoton-absorption-induced fluorescence. In the high optical power densities used in the HRS experiment, chromophores can be excited by the simultaneous absorption of two or even three photons. Flipse et al.[22] have shown that the anti-Stokes fluorescence of two-photon excited dimethylaminonitrostilbene and methoxynitrostilbene overlaps with the HRS light. For *trans*-retinol, a broad emission peak, starting at a wavelength higher than the second-harmonic frequency, was observed.[15] The excitation mechanism involved is three-photon excitation and the emission also overlaps with the hyperscattered light. If a setup as shown in Figure 4 is used, it has to be verified if the observed intensity is hyperscattered light only. This verification can be easily done by replacing the 532 nm interference filter with a 550 or 500 nm interference filter or by using a monochromator. Morrison et al.[12] tested for fluorescence by tilting the 532 nm interference filter to shift its transmission by a few nanometers and by measuring the time dependence of the observed pulse.

By pumping an optical parametric power oscillator with the third harmonic of a Nd:YAG laser, Stadler et al.[23] were able to shift the excitation wavelength to 1500 nm. This shift in excitation wavelength reduces the resonance enhancement of the hyperpolarizability and permits a more direct determination of the static hyperpolarizability. Measurement of the hyperpolarizabilities of fluorescent molecules can still be done in the nanosecond regime by replacing the interference filter with a monochromator and recording the spectral profile.[24] The broad emission background is then subtracted from the narrow HRS peak.

2. HRS with Femtosecond Pulse Excitation. To make an unambiguous distinction between hyperscattered light and multiphoton fluorescence, one can exploit the difference in temporal characteristics between scattering and fluorescence. Fluorescence is characterized by a fluorescence lifetime, resulting from the finite lifetime of the excited state. The result is that a large part of the fluorescence photons is emitted after the excitation pulse. Scattering however is immediate, and occurs only when the excitation pulse is still present. This difference in temporal behavior can be exploited to discriminate between (hyper)scattering and (multiphoton) fluorescence. Typical values for fluorescence lifetimes, or the average time over which fluorescence is delayed, are in the nanoseconds. It should be clear that a nanosecond pulse laser will not offer the necessary time resolution. Femtosecond pulse lasers offer both the required temporal resolution and the necessary peak power. The use of femtosecond pulse lasers for HRS had been demonstrated for nonfluorescent molecules previously.[25] It has been extended with narrow and early gating and fast-photon counting to discriminate between scattering and fluorescence directly in the time domain. Because a substantial part of the fluorescence photons is still arriving in the temporal window of the excitation, overlapping with scattered photons, a fitting to a single-exponential decay for the fluorescence, followed by subtraction of this contribution from the early photons, gives the amount of scattered photons due to HRS.[26]
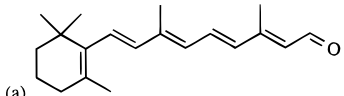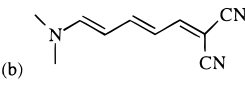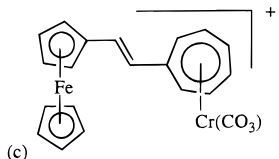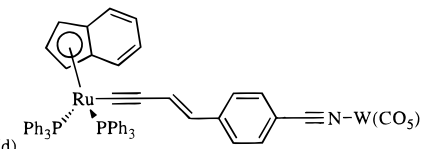
Recently, the Fourier transform of this technique has been implemented in the frequency-domain. In this domain, fluorescence is characterized by a phase shift φ between excitation and fluorescence and a demodulation M (ratio of fluorescence amplitude F over excitation amplitude E) at a certain modulation frequency $\omega = 2\pi f$.

$$\tan\varphi = \omega\tau \tag{12}$$

$$M = \frac{F}{E} = \frac{1}{\sqrt{1 + \omega^2\tau^2}} \tag{13}$$

This phase shift φ and demodulation M tend to 90° and zero, respectively, in the limit for high frequencies or long lifetimes. This result means that a distinction between immediate scattering and delayed fluorescence in the time domain can be made in the frequency domain based on phase and demodulation. Because we are not interested in the fluorescence contribution, we eliminate it by performing the HRS experiment with a very high modulation frequency for the fundamental laser light. For the nanosecond fluorescence lifetimes, the frequency necessary for essentially complete demodulation, is in the

Table 1. Static Hyperpolarizability, Solvent in which the Measurement was Done, and Reference β Value used of Dipolar Molecules Determined by HRS Measurements

Structure	β	Solvent	Reference
(a)	300	CHCl$_3$	β CHCl$_3$ = 0.49
(b)	34	1,4-dioxane	β PNA,dioxane = 16.9
(c)	105	CH$_2$Cl$_2$	β PNA,dioxane = 16.9
(d)	150	CH$_2$Cl$_2$	β PNA,CH$_2$Cl$_2$ = 16.9

[a] From ref 33. [b] From ref 34. [c] From ref 38. [d] From ref 39. [e] The extrapolation of the experimental β to the resonance-free (static field) β_0 is usually performed with the dispersion factor in the two-state model (see e.g., ref 2, pp 53−54).

hundreds of MHz. This frequency can be obtained from the high harmonic content of a repetitive femtosecond pulse. The result is that when performing HRS at MHz frequencies, the only signal that can be detected at these frequencies is coming from scattering, because the amplitude of the fluorescence contribution is essentially zero. This approach to the problem of multiphoton fluorescence in HRS was tested on well-characterized model compounds.[27]

IV. Molecules

1. Molecules with Dipolar Symmetry. For molecules with dipolar symmetry, quantum chemical calculations have shown that the main hyperpolarizability tensor component is β_{zzz}, where z is in the direction of the molecular dipole moment.[28] The relative magnitude and sign of the molecular hyperpolarizability tensor components can be estimated from a polarization analysis of the hyperscattered light. Alternatively, the HRS depolarization ratio can be calculated from quantum chemical calculations and compared with the experimental values.[29] For a dipolar molecule, such as PNA, Heesink et al.[29] have measured $\langle\beta_{XZZ}^2\rangle = 0.225 \langle\beta_{ZZZ}^2\rangle$. Assuming Kleinman and C_{2v} symmetry, it follows from the rotational averages that

$$\beta_{zyy} = \beta_{yyz} = -0.07\beta_{zzz} \qquad (14)$$

where the molecule is in the zy plane and z is in the direction of the dipole moment. Under the same assumptions, the EFISHG-hyperpolarizability is

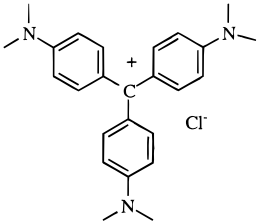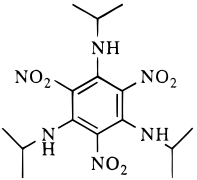$$\beta_{\text{EFISHG}} = \beta_{zzz} + \beta_{zyy} \qquad (15)$$

A list of EFISHG hyperpolarizabilities of PNA in a variety of solvents is listed in ref 30. From these values, and eqs

14 and 15, β_{zzz} and β_{zyy} can be determined and used as a reference value for $\langle\beta_{\text{HRS}}^2\rangle$ in eq 11. Note that the hyperpolarizabilities in ref 30 were measured versus an SHG coefficient for quartz of $d_{11} = 0.5$ pm/V.

We have studied the hyperpolarizabilities of bacteriorhodopsin (bR), and retinal and organometallic compounds. bR is the light-energy transducing protein present in the purple membrane of the extreme halophilic bacterium *Halobacterium Salinarium*. bR has a purple color due to the presence of a chromophore, the protonated Schiff base of retinal, in a complex ionic binding site. When photoexcited, bR runs through a complex photocycle that involves a deprotonation and reprotonation of the Schiff base and cis−trans isomerizations. Because of its thermal stability and unique photochemical properties, bR is an excellent candidate for use in optoelectronics.[31] EFISHG could not be used because of the presence of charged amino acid residues on the protein. A direct measurement of β was done with HRS on a solution of solubilized bR.[32] The HRS β value of 2100×10^{-30} esu at a fundamental wavelength of 1.06 μm is in good agreement with the values measured in two other, indirect, experiments.

The large β of bR could be attributed entirely to the presence of the protonated Schiff base of retinal. A systematic study involving HRS and INDO/CI/SOS (intermediate neglect of differential overlap/configuration interaction/sum-over-states) calculations on retinal and related molecules later showed that these polyenes follow the same tendencies as the more traditional donor−acceptor-substituted NLO chromophores; that is, β strongly depends on the position of the absorption maximum and the length of the conjugated system.[33] It was also noted that trans-to-cis isomerization of double bond 13 or 9 leads to a 30% decrease in β and that the β of retinal strongly increases with the solvent polarity (Table 1a).

Table 2. Static Hyperpolarizability, Solvent in Which the Measurement was Done, and Reference β Value Used of Octopolar Molecules Determined by HRS Measurements

(a) — 470 — MeOH — $\sqrt{\langle \beta_{PNA}^2 \rangle} = 15.9$

290 — MeOH — $\beta\,MeOH = 0.69$

(b) — 16 — $CHCl_3$ — $\beta\,PNA,dioxane = 16.9$

[a] From refs 12 and 42. [b] From ref 42.

HRS was also used to study the solvent effect on the β of the push−pull polyene 1,1-dicyano-6-(dibutylamino)-hexatriene (Table 1b).[34] For this molecule, β exhibits a peak as a function of solvent polarity. EFISHG measurements also showed a peak in $\mu\beta$ as a function of solvent polarity,[35] but because μ is difficult to measure by capacitance measurements in very polar solvents, β could not be calculated.

The search for organometallic compounds with large hyperpolarizabilities has started only recently. Apart from regular $\pi-\pi^*$ transitions, organometallic molecules can exhibit strong absorption bands, due to, for example, metal-to-ligand charge transfer transitions, that possibly contribute to β. Also, a large family of compounds can be synthesized by systematically changing substituents of the central metal ions. Review papers containing the data gathered so far are available.[36,37] A group used frequently in organometallics is the ferrocene group. The donor strength of ferrocene approximately matches that of the organic methoxyphenyl group and large hyperpolarizabilities have been reported for bimetallic Fe−Cr sesquifulvalene complexes (Table 1c).[38] Complexes with a ruthenium bis(triphenylphosphine)−(indenyl)acetylide donor had the largest β value for bimetallic compounds measured so far (Table 1d).[39]

2. Molecules with Octopolar Symmetry. The concept of octopolar molecules for nonlinear optics was introduced by Zyss.[40] If Kleinman symmetry applies, the third-rank β tensor can be decomposed in the sum of two irreducible components: a vector or dipolar term, and a septor or octopolar term. For octopolar molecules, all dipolar quantities, including the ground-state dipole moment, vanish and the octopolar term is the only contribution to β. Because of the absence of the molecular dipole moment, EFISHG cannot be applied and HRS must be used to determine β in solution. Compared with dipolar molecules, the only difference in the data analysis is the orientational average $\langle \beta_{HRS}^2 \rangle$. From eqs 3 and 4 it can be calculated that for a scatterer with C_{3v} or D_{3h} symmetry and nonzero β components $\beta_{zzz} = -\beta_{zxx} = -\beta_{xzx} = -\beta_{xxz}$ that

$$\langle \beta_{ZZZ}^2 \rangle = \frac{24}{105} \beta_{zzz}^2 \qquad (16)$$

$$\langle \beta_{XZZ}^2 \rangle = \frac{16}{105} \beta_{zzz}^2 \qquad (17)$$

Thus, the depolarization ratio of the hyperscattered light using a fundamental beam polarized in the Z-direction is equal to 1.5.
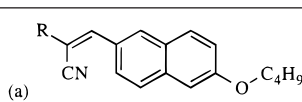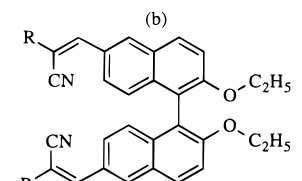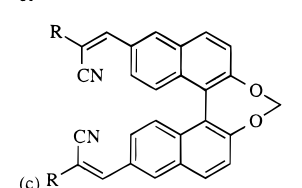
With the exception of organotin compounds,[41] most of the molecules with a large octopolar term have D_{3h}, C_3, or C_{3v} symmetry. Verbiest et al.[42] measured the β of hexasubstituted benzenes (Table 2b), a cyclopropenylium cation and the tricyanomethanide anion.[43] The depolarization ratio of these molecules was shown to be 1.5. The crystal violet cation was studied by various authors (Table 2c).[12,42]

3. Correlated Molecules. If a number of chromophores are covalently linked to each other and form a rigid structure, they no longer move independently and can be considered correlated.[44] The coupling of chromophores in a noncentrosymmetric unit can lead to an increase of the hyperpolarizability per molecule. The correlation between the chromophores can be accounted for by adding a coherent term to eq 6.[9] Mathematically, the coherent term can be calculated if the average relative orientation of all molecules is known. A more straightforward approach is to consider the multichromophoric molecules as independent scatterers. In eq 6, the number density and $\langle \beta_{HRS}^2 \rangle$ then refer to the multichromophoric molecules. The hyperpolarizability tensor of the correlated chromophores can contain several nonzero tensor components, depending on the exact geometry of the coupled molecules. If the molecular interactions between the coupled molecules can be ignored, the β tensor of the multichromophoric molecule can be estimated from the β tensor of the constituent chromophores

$$\beta_{IJK} = \sum_{ijk} \left(\sum_{s=1}^{n} \cos \theta_{Ii}^s \cos \theta_{Jj}^s \cos \theta_{Kk}^s \right) \beta_{ijk} \qquad (18)$$

where IJK refers to the multichromophoric molecule, n

Table 3. Hyperpolarizabilities (1064 nm, 10^{-30} esu) of Donor−Acceptor-Substituted Binaphthol Derivatives and Two Reference Molecules[a]

(a) structure			
64	64	79	87

(b) structure			
$\beta_{ZZZ} = \beta_{ZXX} = 59$	$\beta_{ZZZ} + \beta_{ZXX} = 118$	$\beta_{ZZZ} = \beta_{ZXX} = 68$	$\beta_{ZZZ} + \beta_{ZXX} = 135$
$\beta_{mono} = 83$		$\beta_{mono} = 96$	

(c) structure			
$\beta_{ZZZ} = 46$, $\beta_{ZXX} = 12$	$\beta_{ZZZ} + \beta_{ZXX} = 95$	$\beta_{ZZZ} = 54$, $\beta_{ZXX} = 14$	$\beta_{ZZZ} + \beta_{ZXX} = 65$
$\beta_{mono} = 32$		$\beta_{mono} = 37$	

[a] All measurements were performed in chloroform and the HRS setup was calibrated using $\beta_{PNA} = 23 \times 10^{-30}$ esu; the ratio between the tensor components was estimated from a vector model for the binaphthol ($\beta_{ZZX} = \beta_{XZX} = \beta_{XXZ} = 2(\cos \theta/2)(\sin \theta/2)^2 \beta_{mono}$ and $\beta_{ZZZ} = 2(\cos \theta/2)^3 \beta_{mono}$, where θ is the dihedral angle and β_{mono} is the β of the dipolar subunits); note the good agreement between EFISHG and HRS; all results are from ref 45.

to the number of coupled chromophores, and *ijk* to the individual uncoupled chromophores. The β_{IJK} tensor components are used to express $\langle\beta_{HRS}^2\rangle$ in terms of β_{ijk} and the molecular geometry.

Most of the correlated molecules studied so far were constructed by covalently linking two or more chromophores of dipolar symmetry, which considerably simplifies eq 18. A thorough study was made of binaphthol derivatives, that are built up by linking two donor−acceptor substituted naphthalenes (Table 3).[45,46] If the two naphthalenes are forced into a parallel geometry, the overlap between the oxygen donor orbitals and the aromatic bridge is reduced, which decreases the β of the subunit. The β tensor of the dimer was modeled assuming C_{2v} symmetry, which, according to eq 18, leads to four nonzero β tensor components for the dimer: β_{ZZZ} and $\beta_{ZXX} = \beta_{XZX} = \beta_{XXZ}$. The accuracy of the model used was verified by independent EFISHG measurements and by measuring the β of the monomeric naphthalene subunits.

More complex systems are the purple membrane of bR, functionalized polyisocyanides, and dendrimers. Purple membrane patches from *Halobacterium Salinarium* are composed of ~3000 bR proteins. The structure of the membrane patches is known in considerable detail and the size of the patches can be measured from atomic force microscopy (AFM) pictures. Even for these large structures, eq 18, in combination with depolarized HRS measurements, could be used to extract a value for the β of bR that is consistent with previously measured values.[47] The orientation of the protonated Schiff base chromophores in the purple membrane was found to be mainly octopolar. In functionalized polyisocyanides, the correlations are induced by rigidly linking chromophores to a helical backbone. An enhancement in the β of the polyisocyanide due to the noncentrosymmetric chromophore arrangement was observed.[48] In functionalized dendrimers, the chromophores are forced into a cen-

trosymmetric arrangement, which reduces the hyperpolarizability of the total structure.[49]

V. Conclusion

In summary, the efficacy of HRS has been demonstrated by its ability to measure the β of molecules that could not be measured by EFISHG, such as octopoles and molecular ions. Experimental improvements have been made, and the problem of multiphoton-absorption-induced fluorescence has been solved by using a monochromator or femtosecond excitation. Due to its simplicity and wide range of experimental possibilities, HRS is a powerful method for analyzing the molecular hyperpolarizability tensor.

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