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Time-resolved hyper-Rayleigh scattering: measuring first hyperpolarizabilities β of fluorescent molecules

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Abstract

Time-resolved hyper-Rayleigh scattering experiments using a femtosecond mode-locked Ti-sapphire laser are presented. The technique is capable of discriminating between hyper-Rayleigh scattered light and fluorescent emission induced by multiphoton absorption with a time resolution of 80 ps. Measurements on the non-fluorescent organic molecules crystal violet and calix-[4]arene demonstrate that the technique can measure first hyperpolarizabilities β consistent with experiments using a Q-switched Nd:YAG laser. The first hyperpolarizability β of a fluorescent molecule, which is often overestimated when using a nanosecond laser system, can be corrected for long-term fluorescence using the time-resolved technique as is demonstrated for the octupolar molecule 1,3,5-tris[(4-pyridyl)ethynyl]benzene.

1. Introduction

A major issue in the research on quadratic non-linear optics is the determination of the first hyperpolarizability β of organic molecules. Until a few years ago the common method for measuring β of molecules was electric field induced second harmonic (EFISH) generation [1,2]. In 1991 Clays and Persoons [3] introduced the hyper-Rayleigh scattering (HRS) technique. This technique is capable of more direct measurement of the first hyperpolarizability β , not only for dipolar but also for non-dipolar and ionic molecules. Furthermore, depolarised HRS measurements offer the opportunity to measure individual tensor components [4], while the EFISH technique is limited to measurement of the β component projected along the dipole moment of the molecule.

Unlike EFISH the HRS process is an incoherent process. A phenomenon like fluorescence is also an

incoherent process. Therefore, for molecules exhibiting both hyper-Rayleigh scattering and fluorescence, induced by multiphoton absorption, it is not possible to distinguish between the two processes spatially. The contribution of multiphoton fluorescence can cause unrealistically high HRS values for β as pointed out by Flipse et al. [5].

Hyper-Rayleigh scattering is an instantaneous process, while fluorescence occurs generally on a nanosecond time scale. In this Letter we present results using a time-resolved hyper-Rayleigh scattering experiment which allows a discrimination between the two processes in time.

2. Experiment

The hyper-Rayleigh scattering technique is most often performed with a Q-switched Nd:YAG laser

system generating typically 10 ns pulses at a repetition rate of 10 Hz. In order to have sufficient time resolution for discriminating between fluorescence and hyper-Rayleigh scattering, much shorter pulses are needed. Therefore, it was decided to use a mode-locked titanium–sapphire laser (Spectra Physics, Model 3960 Tsunami). This system generates typically 80 fs pulses at a repetition rate of 82 MHz and an average power of 0.5–1 W. The resulting peak power of the pulses is of the order of 100 kW. This is one order of magnitude lower than for the Q-switched nanosecond system, which is limited to typically 1 MW by breakdown in the solution, and will result in two orders of magnitude less second harmonic intensity. This loss in peak power is com-

pensated for, however, by the difference in duty cycle of the Ti–sapphire and Nd:YAG lasers, 7×10^{-6} and 1×10^{-7} , respectively. In conclusion, it is expected that comparable amounts of signal are observed for both types of hyper-Rayleigh experiments. Recently, Clays and Persoons [6] demonstrated HRS results using a mode-locked Ti–sapphire laser in combination with phase sensitive detection.

A schematic drawing of the apparatus is shown in Fig. 1. In this study the fundamental wavelength was 900 nm. Because of the short pulses the corresponding spectral width is typically 15 nm. In order to avoid broadening of the pulse in time, resulting in a lower peak power, as few as possible optical components are used before focusing the laser beam in a

Fig. 1. Femtosecond hyper-Rayleigh scattering apparatus using the time-correlated single photon counting technique. C: cell; CFD: constant fraction discriminator; FPD: fast photodiode; GT: Glan–Taylor polariser; IF: interference filter 450 nm; L1–L4: positive lenses; LPF: low-pass filter; MCP: microchannel plate photomultiplier tube; ND: neutral density filter; PD: photodiode; TAC: time to amplitude converter; WP: half-wave plate.

cylindrical cell containing the solution of interest. The fundamental beam power is changed by a computer-controlled rotating half-wave plate that is followed by a Glan–Taylor polariser. The average beam power is monitored by an integrating photodiode.

The scattered signal is collected by a high numerical aperture lens and imaged onto a fast microchannel plate (MCP) photomultiplier tube by a second lens. The Rayleigh scattered infrared light is filtered out by a low-pass filter. Additionally, an interference filter at a central wavelength of 450 nm and a transmission bandwidth of 10 nm is used in order to detect the second harmonic and eliminate most of the fluorescence.

The time-correlated single photon counting technique [7] is widely used in fluorescence lifetime measurements. The essential part of this technique is a time to amplitude converter (TAC) (EG&G Ortec Model 566), which is started by a pulse from the MCP and stopped by a pulse from a fast photodiode which monitors the laser beam. The influence of fluctuations in pulse amplitude is eliminated by using constant fraction discriminators. The TAC converts the time difference between the arrival of the start and stop pulses into a voltage which is fed into a PC through an A/D converter. The reason to use the pulses from the MCP as the start pulse is that in this way the TAC only starts in the case of detecting a photon on the MCP and the dead time is as small as possible.

The response function of the system was measured to have a full-width at half-maximum of 80 ps. This should be sufficient to discriminate between instantaneous hyper-Rayleigh scattered light and fluorescence with a nanosecond lifetime.

The hyper-Rayleigh scattered intensity $I_{2\omega}$ is expected to follow the relation [3,8]

$$I_{2\omega} = g(N_s \beta_s^2 + N_c \beta_c^2) e^{-N_c A_c} I_\omega^2, \quad (1)$$

where g is a geometry factor determined by the apparatus, N the number density, β the first hyperpolarizability, and I_ω is the fundamental intensity. The factor $e^{-N_c A_c}$ takes account of absorption at the second harmonic wavelength, with A_c the product of chromophore absorption and the optical pathlength in the cell. Subscripts s and c denote the solvent and chromophore, respectively.

3. Results

First, experiments were performed on the octupolar molecule crystal violet. Octupolar molecules [9] form a special class of molecules whose hyperpolarizability β can only be studied by HRS because of the absence of a static dipole moment. Fig. 2 shows a typical time dependence of the scattered signal from a solution of crystal violet in chloroform. It is observed that the signal has equal shape and width as the system response function and therefore originates from the second harmonic.

The fundamental intensity has been varied for a range of solutions with different concentrations, including the neat solvent chloroform, in order to have accurate results when using the internal reference method [8]. Fig. 2 shows apart from the sharp peak also a flat background, which is caused by dark counts which are not correlated with the laser pulses. Most of the dark counts are eliminated from the measured signal by introducing a 0.3 ns wide window around $t=0$. Only counts inside this window are considered as signal. In Fig. 3 the sum of the counts inside the window as a function of fundamental beam intensity is shown for the different concentrations. Quadratic dependence is observed as expected from Eq. (1). The offset in the quadratic dependence is due to the residual contribution of dark counts inside the window. From the quadratic coefficient as a function of concentration a β_{HRS} value for crystal violet of $500 \pm 100 \times 10^{-30}$ esu is calculated using Eq. (1) with $\beta_s = \beta(\text{CHCl}_3) = -0.49 \pm 0.05 \times 10^{-30}$ esu [10] as internal reference. This value is somewhat lower than the value $866 \pm$

Fig. 2. Time-dependent scattered signal from a solution of crystal violet in chloroform. Inset: crystal violet.

Fig. 3. Scattered signal in 0.3 ns window around $t = 0$ versus fundamental intensity for a range of concentrations of crystal violet in chloroform. Inset: quadratic coefficient (q.c.) versus concentration fitted with Eq. (1).

260×10^{-30} esu reported by Verbiest et al. [11]. Direct comparison is not possible because the fundamental wavelength (872 nm) and solvent (methanol) are different. However, based on the dielectric constant of both solvents, a 25% lower β value is expected [3,8] when using chloroform instead of methanol.

The dipolar molecule tetranitrotetrapropoxycalix [4]arene [12–14] has been studied before by hyper-Rayleigh scattering in a solution in chloroform using a Q-switched Nd:YAG laser. The β_{HRS} value at the fundamental wavelength of 1064 nm has been determined at $28 \pm 3 \times 10^{-30}$ esu [4]. Using the time-resolved apparatus at a fundamental wavelength of 900 nm a time-dependent signal equal in shape and width to the system response is observed. Thus the presence of fluorescence in the signal can be excluded. The β_{HRS} value determined from measurements of the quadratic coefficient for a range of concentrations and using the internal reference method, is $34 \pm 6 \times 10^{-30}$ esu. The time-resolved method apparently is capable of measuring β 's consistent with the values obtained with nanosecond laser systems. The effect of resonance enhancement is negligible in this case as both the chromophore and the solvent have an absorption maximum below 300 nm and the expected resonance enhancement, according to the two-level model [15], is of the order of the experimental error.

Another octupolar molecule, 1,3,5-tris[(4-pyridyl)ethynyl]benzene, has been measured. The absorption spectrum of the molecule shows a first peak at a wavelength of 302 nm. For purposes of second harmonic generation in the 400–500 nm wavelength range it is, therefore, a more suitable molecule than crystal violet as the latter shows strong absorption in this wavelength range. A typical time-dependent signal as measured on a solution of this molecule in chloroform is shown in Fig. 4. It is clearly observed that the signal has a long-term fluorescence contribution. In order to determine the origin of this fluorescent signal the power dependence of the signal is measured. Therefore, two time windows are set in the histogram. The first is a 0.3 ns window around $t = 0$. The signal inside this window is expected to be scattered second harmonic light and a contribution from the fluorescent signal. The second window has a width of 2.5 ns and is chosen such that it does not overlap with the system response and therefore only a fluorescent signal is detected. In Fig. 5 the sum of the counts in both windows is given as a function of the fundamental beam power. The data is fitted with the function

$$I_{\text{scattered}} = A + B(I_{\omega})^C, \quad (2)$$

where A , B and C are fitting parameters. The value of C found for window 1 is 2.07 ± 0.06 which is close to 2 as is expected for second harmonic generation. The small deviation from 2 is likely to be caused by the fluorescence contribution which has a

Fig. 4. (*) Time-dependent signal from octupolar molecule 1,3,5-tris[(4-pyridyl)ethynyl]benzene. (—) Single exponential fit. Inset: molecular structure.

Fig. 5. Dependence on fundamental intensity of second harmonic (window 1) and fluorescence (window 2) and the coefficient C obtained by fitting with Eq. (2).

C value of 2.24 ± 0.07 , as is found for the fit of window 2. The fluorescence apparently is caused mainly by a two-photon absorption process but also has a contribution from three-photon absorption. The presence of two-photon absorption corresponds with the presence of an absorption tail at the second harmonic wavelength.

From the time-dependent signal it is possible to determine a value for β . The signal from four different solutions with different concentrations of the chromophore, including neat chloroform, was measured for a fixed fundamental intensity. The quadratic dependence of the second harmonic signal on the fundamental intensity was already verified and has not been measured again for this reason. In order to eliminate the fluorescent contribution the signal not overlapping with the system response is fitted with a convolution of a single exponential decay and the system response for the three solutions containing the chromophore. The fluorescent lifetime turned out to be independent of the concentration in the range used in this experiment. A typical result of this fit is shown in Fig. 4. The β value of the molecule is calculated using two different methods. The first method sums all the signals in window 1 after subtracting the fluorescent contribution and the background of dark counts. The result of fitting and subtracting the fluorescence is accurate for fluorescent lifetimes longer than typically 1 ns. The second method integrates the complete time-dependent signal with subtraction of the background of dark counts. The latter will overestimate the β of the chromophore considerably. The value of β_{HRS} deter-

mined from the data using the internal reference method, is $31 \pm 5 \times 10^{-30}$ esu and $89 \pm 10 \times 10^{-30}$ esu, respectively, for the first and second method.

4. Conclusions

The results with the time-resolved hyper-Rayleigh scattering technique show that for non-fluorescent molecules it is possible to measure β values that are consistent with previous experiments using a nanosecond Nd:YAG laser. Advantages of the Ti:sapphire compared with an Nd:YAG laser are the tunability of the wavelength, making available dispersion studies, and the absence of breakdown in the solution due to the shorter pulses with lower peak power.

The main advantage of femtosecond pulses compared with nanosecond pulses is evidently the possibility of discriminating in time between hyper-Rayleigh scattered light and fluorescence induced by multiphoton absorption. Measurements on the octupolar molecule 1,3,5-tris[(4-pyridyl)ethynyl]benzene show that when the fluorescent contribution is not subtracted the β value in the case of this molecule is overestimated by a factor of 3. The signal after subtraction still shows a contribution from a fast exponential decay as is shown in Fig. 4. Due to the width of the system response of 80 ps it is difficult to discriminate between hyper-Rayleigh and contributions from fast (< 200 ps) fluorescent emission. The β_{HRS} value of $31 \pm 5 \times 10^{-30}$ esu calculated in the case of subtracting the fluorescence therefore must be considered as the upper limit.

In general, it is concluded that the time-resolved hyper-Rayleigh scattering technique gives more insight into the β 's of organic molecules and the influence of fluorescence induced by multiphoton absorption. The technique is therefore preferable to hyper-Rayleigh scattering with nanosecond pulses.

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