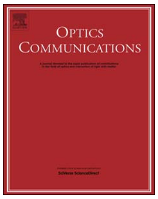
ARTICLE IN PRESS

Optics Communications xx (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Optics Communications

journal homepage: www.elsevier.com/locate/optcom



Spectrally- and polarization-resolved hyper-Rayleigh scattering measurements with polarization-insensitive detection

P. Němec[a,*], F. Pásztor[a], M. Brajer[a], I. Němec[b]

[a] Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, 121 16 Prague 2, Czech Republic
[b] Faculty of Science, Charles University, Hlavova 8, 128 40 Prague 2, Czech Republic

ARTICLE INFO

Keywords:
Harmonic generation
Hyper-Rayleigh scattering
First hyperpolarizibility
Crystal engineering

ABSTRACT

Determination of the molecular first hyperpolarizability by hyper-Rayleigh scattering (HRS) is usually significantly complicated by a presence of the multiphoton excited fluorescence which has to be separated from HRS to obtain a meaningful values of the hyperpolarizability. We show, by performing a spectrally-resolved measurement, that the intensity and spectral shape of the fluorescence can depend strongly on the fundamental laser wavelength. Consequently, a properly selected excitation wavelength can significantly simplify the process of separation of HRS from the detected signal. We tested the developed experimental setup with a polarization-insensitive detection by measuring HRS generated in water and in aqueous solutions of 2-aminopyrimidine (AMP) and its monocation (HAMP). The effective hyperpolarizability of AMP and HAMP was measured experimentally and compared with that obtained by quantum chemical calculations. The polarization-resolved HRS measurement was performed for AMP and the experimentally obtained depolarization ratio agrees well with that predicted theoretically, which confirms that routine density functional theory computations of static hyperpolarizability tensor components can be considered as a sufficient approach suitable for non-interacting molecules dissolved in water.

1. Introduction

Hyper-Rayleigh scattering (HRS) [1,2] is currently the most versatile experimental method for a determination of the molecular first hyperpolarizability β, which describes the second order nonlinear optical response at the molecular level. Before the discovery of HRS, the electric-field-induced second-harmonic generation (EFISHG) technique was used for this purpose [3,4]. However, there are several strong limitations of the EFISHG technique. The electric field, which is applied over the solution to partially orient the molecules, does not allow the measurement of ionic species and octupolar molecules. Moreover, the application of electric field in EFISHG complicates the cell design and also the difference between the externally applied field and the internal field has to be considered. In contrast, in HRS technique no electric field is applied and, therefore, also octupolar molecules and ionic species can be measured. The internal reference method [1], when HRS generated by the investigated solute molecules is compared with that produced by the reference solvent, also eliminates the need for a local-field correction factors estimation.

The efficiency of HRS, i.e. incoherently scattered second-harmonic generation, in isotropic solutions is rather small. Therefore, the development of HRS measurement techniques is very closely linked with the advancement of available optical and optoelectronical technologies. Originally, the nanosecond laser pulses produced by Q-switched Nd:YAG lasers at one wavelength at low repetition rate (≈10 Hz) were used as excitation source and the HRS-generated photons were detected using fast gated detection electronics [5]. Later, femtosecond laser pulses produced by mode-locked Ti:Al_2O_3 lasers started to be used [6]. One of major advantages of these femtosecond lasers is their high repetition rate (≈80 MHz) that enables an utilization of continuous-wave phase-sensitive detection techniques using lock-in amplifiers, which significantly increases the signal-to-noise ratio in the measured data and makes the detection setup rather simple: The photons generated by HRS are spectrally separated from the excitation ones by an usage of low-pass and band-pass optical filters and they are converted to electrical signals by a photomultiplier (PMT) [6]. However, it was discovered later that the hyperpolarizabilities measured by this relative simple detection technique can be seriously overestimated due to a presence of a multiphoton excited fluorescence in studied materials [7]. This problem can be suppressed by performing a time-resolved experiments [8] because HRS is an instantaneous process, while the decay of excited fluorescence occurs

---

[*] Corresponding author.
E-mail address: nemec@karlov.mff.cuni.cz (P. Němec).

http://dx.doi.org/10.1016/j.optcom.2016.10.072
Received 2 August 2016; Received in revised form 25 October 2016; Accepted 29 October 2016

Please cite this article as: Nemec, P., Optics Communications (2016), http://dx.doi.org/10.1016/j.optcom.2016.10.072

on rather long (typically nanosecond) time-scales. However, this time-resolved approach is rather time consuming and, therefore, it is not widely applicable. Another possibility is to suppress the multi-photon fluorescence contribution in the measured data by a high-frequency demodulation technique [9,10]. The disadvantage of this technique is that the excitation laser has to be equipped with an active stabilization of the repetition frequency, which is not a common feature in the $Ti{:}Al_2O_3$ – based lasers. Moreover, the finite bandwidth of the used PMTs, which is typically ≈300 MHz, limits the applicability of this technique only to fluorescence with a lifetime longer than ≈1 ns [9], while in many material systems fluorescence decay components with much faster decay times are present [11]. Alternatively, the separation of fluorescence and HRS signal can be performed in a spectral domain [11–14] because the fluorescence is typically spectrally much broader than HRS, whose width is given mainly by the spectral width of the excitation laser pulses (especially for the case of femtosecond excitation laser pulses). The necessary spectral resolution can be achieved by using a scanning monochromator with PMT [12–14] but this approach is again rather time consuming. Much faster measurements can be performed by a spectrograph equipped with a charge-coupled device (CCD) where the whole selected spectral range around the second harmonic wavelength is detected in parallel [11].

Another advantage of HRS is that it could provide information about ratios between several hyperpolarizability tensor components, including their sign, if the polarization-resolved experiment is performed [7,14–17]. Moreover, the polarization-resolved HRS can be used to reveal intermolecular interactions [16,18,19]. From the experimental point of view, however, the polarization-resolved measurement of HRS is rather challenging. In fact, the complete separation of fluorescence and HRS signals is of uttermost importance in this type of experiment because fluorescence and HRS usually have completely different polarization properties, as we illustrate below. Therefore, even seemingly small admixtures of fluorescence can considerably distort the measured depolarization ratios of HRS in the investigated molecules. Consequently, the combined spectrally- and polarization-resolved measurements of HRS should be performed. However, the optical gratings, which provide the spectral-resolution in spectrographs, have strongly polarization-dependent diffraction efficiencies (see, e.g., Fig. 2 in Ref. [14]). Therefore, to address this issue, it is necessary to perform a post-measurement recalibration of the measured data which inevitably increases the experimental uncertainty in the obtained depolarization ratios. Moreover, to define which polarization component of HRS is actually experimentally measured, a polarizer has to be inserted in the signal detection path. This in turn reduces even further the number of detectable photons, which carry information about HRS. In this paper we describe several approaches that can be used to increase the HRS measurement precision and/or to decrease the measurement time, which is necessary to obtain the required information. First of all, we illustrate that the intensity of the spectrally-broad fluorescence background can dependent substantially on the fundamental laser wavelength and, therefore, that a careful selection of a wavelength provided by the broadly spectrally tunable femtosecond $Ti{:}Al_2O_3$ lasers is strongly advisable. Secondly, if the HRS-related photons are carried into the spectrograph by a bundle of optical fibers (rather than by focusing them directly to the spectrograph input slit), the optical response of the spectrograph starts to be polarization-independent. This polarization-insensitivity of the detection apparatus can be consequently utilized in the determination of hyperpolarizability tensor components in the investigated molecules, as we show below.

2. Experimental setup

As a light source we use a diode-pumped mode-locked Ti:sapphire laser (Spectra-Physics, Mai Tai HP) which enables a computer-controlled spectral tunability of the excitation laser from 690 to 1040 nm with an average power up to ≈3 W, repetition rate 80 MHz, and pulse duration ≈100 fs. The implemented experimental setup for HRS measurements is shown in Fig. 1. We use a high-power polarizing beamsplitter cube (P_1) and two achromatic half wave plates (HWP_1 and HWP_2) to control the excitation laser intensity and linear polarization

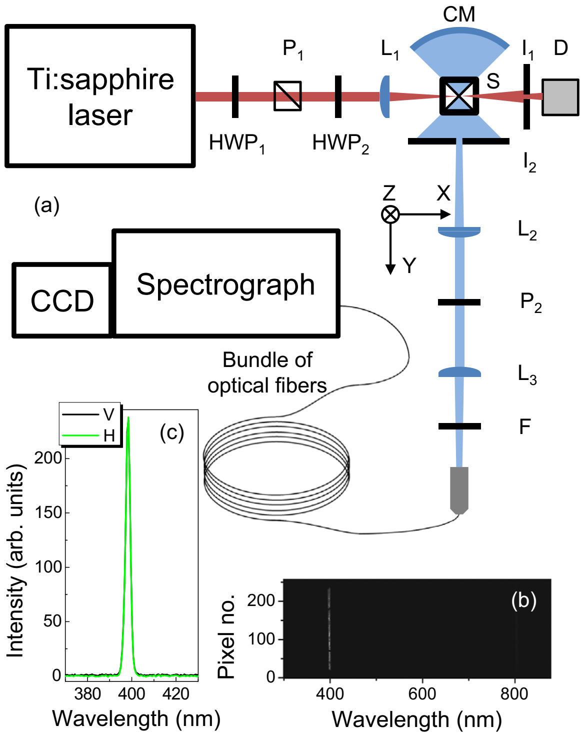


Fig. 1. (a) Experimental setup for spectrally- and polarization-resolved hyper-Rayleigh scattering measurements with a polarization-insensitive detection. HWP: half wave plate, P: polarizer, L: lens, S: sample, CM: concave mirror, I: iris, D: detector, F: short wavelength pass filter. Excitation laser light (with frequency ω) propagates along the X direction and scattered photons (with frequency 2ω) are detected along the Y direction. (b) Image of the output from fiber optic bundle taken by the CCD chip. (c) Measured spectra of vertically (V) and horizontally (H) linearly polarized photons obtained by Full Vertical Binning in the CCD chip are identical which illustrate the polarization insensitivity of our optical fiber-based detection system.

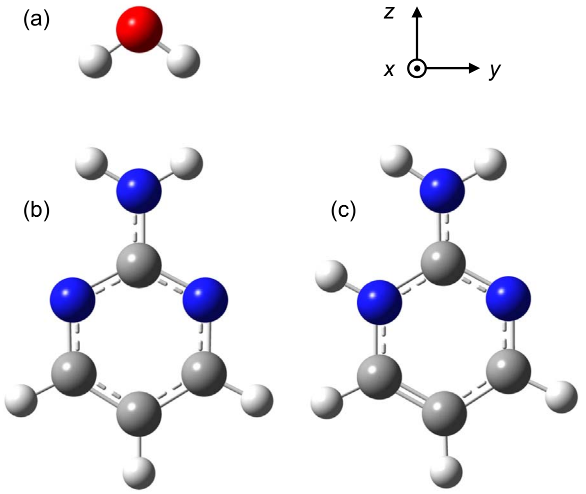


Fig. 2. Schematic depiction of studied molecules. (a) Water, point group C_{2v}; (b) 2-Aminopyrimidine (AMP), point group C_{2v}; (c) Monocation of 2-aminopyrimidine (HAMP(1+)), point group C_s. The selected coordinate system corresponds to molecules on the *yz* plane. For water and AMP C_2 axis is along the *z* axis. Color code: oxygen: red; nitrogen: blue; carbon: dark gray; hydrogen: light gray. (For interpretation of the references to color in this figure legend,the reader is referred to the web version of this article.)