Appl. Phys. B 67, 569–572 (1998)

Applied Physics B
Lasers
and Optics

Determination of resonance Raman scattering cross sections of laser dyes using a traveling-wave amplifier

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Received: 1 April 1998/Revised version: 20 April 1998

Abstract. A new technique for enhancing resonance Raman lines of materials having strong luminescence is described. The applicability of this method is demonstrated by investigating three different laser dyes. The dependence of Raman line intensities on the experimental conditions is measured and analysed. The absolute values of resonance Raman scattering cross sections have been determined by solving a simple rate-equation model.

PACS: 33.20.Fb; 33.50.Dq; 42.62.Hk

The investigation of resonance Raman scattering (RRS) is difficult for fluorescent molecules, because of the strong luminescence background. One possibility of avoiding the disturbance of the fluorescence is to put the signal onto the other side of the pump to the fluorescence that is using anti-Stokes scattering methods, for example CARS [1, 2]. Another possibility is to enhance the RRS signal compared to the fluorescence. A surface-enhanced method [3] was applied for Rhodamine 6G dye adsorbed on colloidal silver. Here RRS was enhanced while the fluorescence was quenched by the metal surfaces. An intracavity arrangement was applied to measure inverse resonance-Raman-scattered and resonance-Raman-amplified spectra of a few laser dyes [4]. Resonance induced Raman scattering was used for studying the scattered spectra of several dyes [5]. It was demonstrated that RRS of Rhodamine 6G dye embedded in micro-droplets could be enhanced when gain is achieved at the Raman lines [6]. It is well known [7] that in traveling-wave amplifiers (TWA) [8] the gain can be extremely large. A Raman line of Rhodamine 6G dye was early identified in the spectrum of a TWA [9].

In this paper we investigate the necessary experimental conditions to reach the strongest Raman lines in TWA. Using the optimized arrangement a number of new Raman lines are identified for different dyes. An extended version of the rate-equation model used earlier [10] to describe the TWA makes it possible to measure the RRS cross sections of laser dyes.

1 Experimental setup

The TWA prismatic arrangement, which was suggested in [11] and applied in [7, 9, 12] has been modified by replacing the glass prism with a liquid prism. A smaller dye cell (1 cm × 1 cm) containing the investigated dye is placed into another cell (4 cm × 2 cm) filled with glycerol (see Fig. 1). This arrangement makes it possible to optimise the Raman signal intensity by simultaneous changing of the incidence angle (α) and the refractive angle (φ) of the glycerol prism. The angle φ is set to be about 81°. In this case the TW condition is satisfied (resulting in a large gain [7]) and the angle between the pump and TW-amplified spontaneous emitted (TWASE) beams is minimized at the same time. The dye solution is pumped by pulses of a dye laser system [13] producing 6-ps-long pulses at 608 nm with energy of 60 μJ. The exciting beam is focused to a line by a 93-mm focal length cylindrical lens. The excited volume has a length of 7 mm, a height of 0.1 mm, and a penetration depth of about 30 μm.

We notice that the pump pulse duration has to be 5–10 ps in order to ensure a relatively good spectral resolution of Raman lines, and keeping small sizes for the arrangement.

The intensity of the Raman lines in the TWASE beam depends on the pumping direction as is shown in Fig. 2, for the

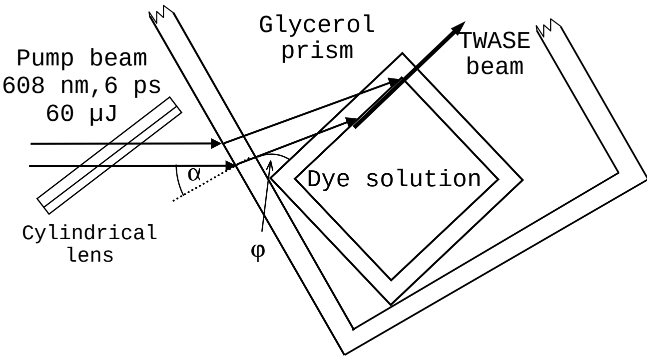

Fig. 1. Traveling wave amplifier arrangement with liquid prism

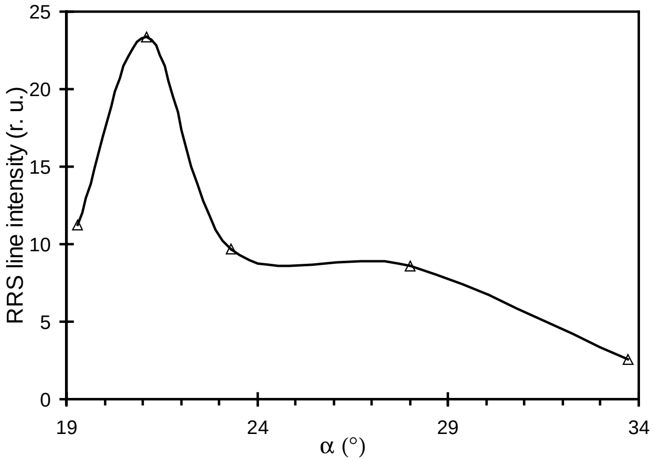

Fig. 2. Measured RRS line intensity of TWASE for Sulforhodamine 101 dye versus the incidence angle of pump beam

1512-cm^{-1} line of Sulforhodamine 101 dye. The condition of TW excitation holds at $\alpha = 20.9°$ according to (13) of [11]. It can be seen that the large maximum appears at this angle of incidence. The shoulder for larger α can be explained by taking into account the dependence of the Fresnel losses on surfaces, and the penetration depth on α, as well as the angular distribution of Raman scattering [14].

2 Experimental results

Measurements were carried out for three different dyes: Sulforhodamine 101 (10 g/l), Cresyl Violet (5 g/l), and DODCI (5 g/l). All of them were dissolved in methanol. The spectra of single pulses were recorded by a CCD matrix with spectral resolution of 5 cm^{-1}. Besides the Raman lines, the spectrum of the TWA contains lines of fluctuating position and intensity [9]. In order to suppress this noisy background, spectra of 10 pulses were averaged. Such averaged spectra are displayed in Fig. 3. Narrow Raman lines with high intensity rise from the broad TWASE background. When the pump wavelength was changed these lines shifted over the permanent TWASE background keeping the wavenumber difference between the pump and the Raman line constant, as expected. The polarisation of the Raman lines is the same as that of the pump beam. For comparison, in the top of Fig. 3 lines of earlier Raman measurements [3–6], which are in accordance with the lines detected by us, are also indicated (carried out for the same (Cresyl Violet) or similar (Sulforhodamine 101 and DODCI) dyes).

An interesting result for the Cresyl Violet is that the wavenumbers of all lines are a multiple of the 596 cm^{-1} line. For DODCI dye the 876-cm^{-1} and 1081-cm^{-1} lines are the harmonics of 438-cm^{-1} and 541-cm^{-1} lines, respectively.

Raman-scattered lines of the solvent do not appear in the TWASE spectra in spite of the fact that the 1033-cm^{-1} and 1071-cm^{-1} lines of methanol fall into the spectral gain band of TWA and the number of methanol molecules is larger by about three orders of magnitude than that of the dyes.

3 Determination of resonance Raman cross sections

The measured temporal properties of TWASE have been compared with results of model calculations and good agreement was found [10]. Our calculation is based on a similar model. However, the system of equations in [10] is completed with an equation taking into account the amplified Raman-

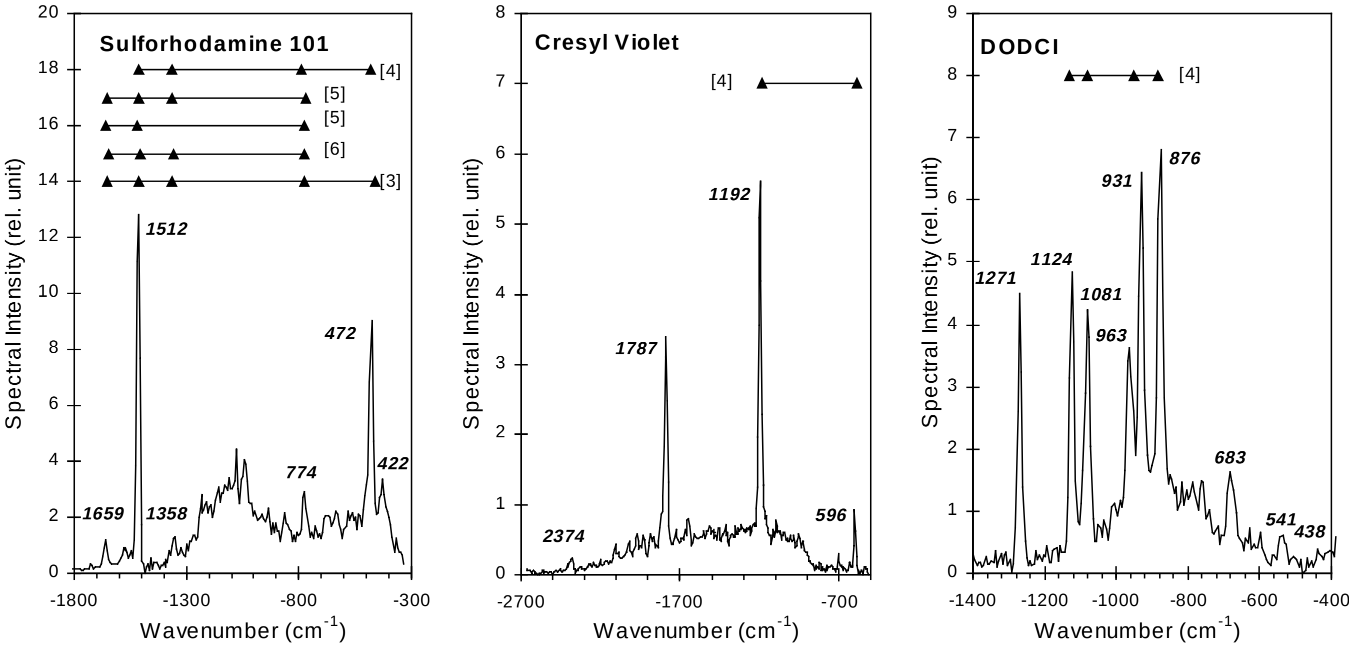

Fig. 3. Measured spectra of the TWA for three laser dyes. The Raman shifts of the RRS lines are indicated in wavenumbers. In the *top* of the figure the Raman lines observed earlier are also indicated

scattered light [15]. Furthermore, in order to take into account the spectral dependence of the emission cross section of the dye, eleven separate equations are used to describe the photon current densities of the different spectral components of the TWASE. These equations are coupled to each other through the excited state population. The equation describing the excited state population contains corresponding new terms. The set of equations is then as follows:

$$\begin{aligned}\frac{\partial n}{\partial t} &= I_{\mathrm{p}}\sigma_{\mathrm{p}}\,(n_0-n)-\frac{n}{\tau}\\ &\quad -\sum_j\left(I_j^{+}+I_j^{-}\right)\left(\sigma_{\mathrm{e},\,j}n-\sigma_{\mathrm{a},\,j}\,(n_0-n)\right)\\ &\quad -\sum_i\left(I_{\mathrm{R}i}^{+}+I_{\mathrm{R}i}^{-}\right)\left(\sigma_{\mathrm{e,R}i}n-\sigma_{\mathrm{a,R}i}\,(n_0-n)\right)\,,\end{aligned} \tag{1}$$

$$\begin{aligned}\frac{\mathrm{d}I_j^{\pm}}{\mathrm{d}x} &= \sigma_{\mathrm{e},\,j}nI_j^{\pm}-\sigma_{\mathrm{a},\,j}\,(n_0-n)\,I_j^{\pm}+S_j\frac{\Omega}{4\pi}\frac{n}{\tau}\,,\\ &\quad j=1,2,\ldots 11\,,\end{aligned} \tag{2}$$

$$\begin{aligned}\frac{\mathrm{d}I_{\mathrm{R}i}^{\pm}}{\mathrm{d}x} &= n\sigma_{\mathrm{e,R}i}I_{\mathrm{R}i}^{\pm}-(n_0-n)\,\sigma_{\mathrm{a,R}i}I_{\mathrm{R}i}^{\pm}\\ &\quad +S_{\mathrm{R}i}\frac{\Omega}{4\pi}\frac{n}{\tau}+n_0\frac{\mathrm{d}\sigma_{\mathrm{R}i}}{\mathrm{d}\Omega}\Omega I_{\mathrm{p}}\,,\\ &\quad i=1,2,\ldots N\,.\end{aligned} \tag{3}$$

Here $I^{\pm}=I^{\pm}(x,t,\nu)$ and $I_{\mathrm{R}i}^{\pm}=I_{\mathrm{R}i}^{\pm}(x,t,\nu_{\mathrm{R}i})$ are the photon current density of TWASE and Raman light propagating in $+x$ and $-x$ direction, respectively. n_0 is the total density of dye molecules, and $n=n(x,t)$ is the density of dye molecules in the excited state, respectively. $I_{\mathrm{p}}=I_{\mathrm{p}}(x,t)$ is the photon current density of the pump pulse. It is assumed to have Gaussian temporal shape. σ_{p}, $\sigma_{\mathrm{a},\,j}$, $\sigma_{\mathrm{e},\,j}$, $\sigma_{\mathrm{a,R}i}$, and $\sigma_{\mathrm{e,R}i}$ are the absorption and emission cross sections of the dye at the wavelengths of the pump, TWASE and Raman light, respectively. τ is the fluorescence lifetime of the excited dye molecules. Ω is the solid angle in which the TWASE and amplified Raman light propagates. It depends on the sizes of the excited volume and is measured to be 2.7×10^{-3}. The quantities S and S_{R} determine which part of the fluorescence falls into the investigated spectral range of the TWASE and Raman lines, respectively. They are calculated with the formula

$$S=\frac{\sigma_{\mathrm{e}}(\nu)\,\Delta\nu}{\int\sigma_{\mathrm{e}}(\nu)\,\mathrm{d}\nu}\,. \tag{4}$$

N is the number of RRS lines, in our cases it is between 4 and 8 for the different dyes. Initial values were estimated for the $\mathrm{d}\sigma_{\mathrm{R}i}/\mathrm{d}\Omega$ differential RRS cross sections. Equations (1)–(3) were solved numerically using an implicit-Euler method. The calculated spectrum was compared to the measured spectrum of the TWA. Then (1)–(3) were solved again using modified values for the differential RRS cross sections. This iteration procedure was repeated until a good agreement between the calculated and measured spectra was found. Here we have to note that the $\sigma_{\mathrm{e},\,j}$, $\sigma_{\mathrm{e,R}i}$ emission cross sections of the dye were not known with sufficient accuracy. Therefore their values were also iterated.

The differential cross sections obtained in this way are summarised in Table 1. These values have the same order of magnitude as given for Betaine-30 dye [16, 17]. (Only the 596-cm^{-1} line of Cresyl Violet has a much larger value. This line is outside the gain region of TWA and here our model is not satisfactory.) However, they are larger by five orders of magnitude than the non-resonant $\mathrm{d}\sigma_{\mathrm{R}}/\mathrm{d}\Omega$ values of different solvents [18]. This latter observation explains why we did not observe the Raman line of methanol in the spectrum of the TWA.

4 Conclusion

A new method has been developed for the investigation of RRS. It uses a prismatic TWA. The experimental condition for achieving the largest Raman intensity is given. The optimised setup was used to determine the Raman lines of three laser dyes. A number of new lines were detected.

The RRS cross sections of the Raman lines were determined by comparing the measured spectra with the results of an iterative model calculation.

Table 1. Differential and integral RRS cross sections of the three investigated dyes

Dye	ν_{R} /cm^{-1}	$\mathrm{d}\sigma_{\mathrm{R}}/\mathrm{d}\Omega$ /m^2 sr^{-1}	σ_{R} /m^2
Cresyl Violet	1192	1.6×10^{-26}	4.2×10^{-29}
	1787	1.2×10^{-27}	3.1×10^{-30}
	2374	3.0×10^{-27}	7.9×10^{-30}
DODCI	541	4.9×10^{-27}	1.3×10^{-29}
	683	1.2×10^{-27}	3.3×10^{-30}
	876	9.6×10^{-28}	2.6×10^{-30}
	931	1.5×10^{-27}	4.0×10^{-30}
	963	8.4×10^{-28}	2.2×10^{-30}
	1081	3.9×10^{-27}	1.0×10^{-29}
	1124	7.4×10^{-27}	2.0×10^{-29}
	1271	2.5×10^{-26}	6.6×10^{-29}
Sulforhodamine 101	422	1.9×10^{-28}	5.1×10^{-31}
	472	4.2×10^{-28}	1.1×10^{-30}
	774	1.3×10^{-28}	3.3×10^{-31}
	1358	2.4×10^{-28}	6.3×10^{-31}
	1512	2.5×10^{-26}	6.6×10^{-29}
	1659	2.3×10^{-27}	6.2×10^{-30}

This new procedure is applicable for all Raman lines of different materials, which appear where it is possible to achieve a significant optical gain.

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