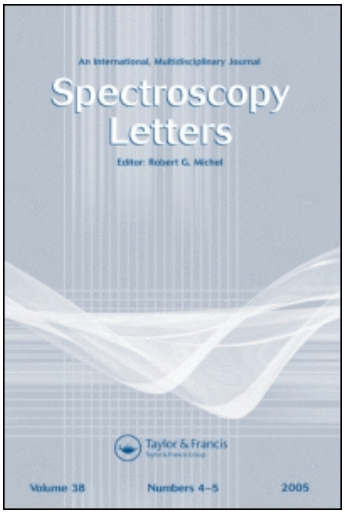

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BROADBAND SINGLE PULSE COHERENT ANTI-STOKES RAMAN SCATTERING IN LIQUIDS

key words: Coherent anti-Stokes Raman Scattering

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ABSTRACT

A scheme satisfying CARS phase matching condition in dispersive media at every laser shot in a broadband wavelength region is suggested and is experimentally verified for liquid water.

INTRODUCTION

Frequently in the study of particular problems by the method of Coherent anti-Stokes Raman Spectroscopy (CARS), it is needed to generate spectra of tens, even hundreds of wavenumbers. Thus, in order to determine gas species concentration and temperature in combustion

systems several spectral lines should be simultaneously detected[1 - 6]. The investigation of the complicated O-H stretching band in water[7, 8] and of C-H bands in alcohols and in other organic compounds are examples for application of broadband CARS in liquids.

Up to the middle of the seventies all CARS experiments were carried out employing two narrow band lasers[1-3, 7]. The spectra were recorded point by point using a scanning dye laser[1] or optical parametric oscillator[7] as a Stokes source. The angle between the pump and the Stokes beam was adjusted for every spectral point in order to satisfy the phase matching condition. Consequently, hundreds of laser pulses scanning the Stokes region were required in order to generate the studied spectrum. In addition, lasers having very narrow bandwidths and high power stability are necessary to generate high-resolution spectra without distortion. These requirements are extremely difficult to satisfy. For the first time a broadband Stokes laser in conjunction with a narrowband pump laser was used by Roh and coworkers[9] to record the CARS spectrum of H_2 lines in a single laser pulse. This method, single pulse CARS, has been employed widely, but only in gases. In strong dispersive media such as liquids, the phase matching condition limits the width of the single pulse CARS spectra.

In this report we propose a scheme with a broadband Stokes beam, in the cross section of which the components are laterally shifted by two conjugated prisms. By focusing the broadband beam and the pump beam into the sample, the phase matching condition has been satisfied for every Stokes spectral component. The scheme is demonstrated experimentally. CARS spectrum from the water O-H stretching band is obtained.

SCHEME AND EXPERIMENTAL

The phase matching condition for two crossed beam technique is:

$$\Delta\mathbf{k} = 2\mathbf{k_p} - \mathbf{k_s} - \mathbf{k_{as}} = 0,$$

where $\mathbf{k_p}$, $\mathbf{k_s}$ and $\mathbf{k_{as}}$ are wavevectors of the pump, Stokes and anti-Stokes waves with corresponding frequencies ω_p, ω_s and ω_{as}. This condition defines the angle θ between $2\mathbf{k_p}$ and $\mathbf{k_s}$ so that $\Delta\mathbf{k} = 0$. Experimentally, this is realized by focusing with a lens both parallel beams - of the pump and the Stokes into the sample. Usually, the pump beam coincides with the lens optical axis and the Stokes beam is aligned at a distance h from the axis. The distance h is conditioned by the refractive index of the sample and the lens focal length. If the full width of the studied Raman band is $\Delta\omega = \omega_{s1} - \omega_{s2}$, the phase matching angle θ_{si} is different for various spectral components ω_{si}

($\omega_{S2} < \omega_{Si} < \omega_{S1}$). Thus, the distances h must be different, too. This means that the spectral components of the Stokes beam must be laterally shifted with respect to each other and parallel to the pump beam (Fig. 1). Let the wavelength of the pump source be 532 nm. In the case of liquid water, the O-H stretching band is spread over the range from 2850 cm^{-1} to 3800 cm^{-1} [10], therefore the Stokes source should give a broadband emission of 40 nm, covering the interval from 627 nm to 667 nm. Our Stokes source, however, emits a band of 20 nm on the interval from λ_{S1} = 630 nm to λ_{S2} = 650 nm. This Stokes band corresponds to the O-H stretching vibration wavenumbers from 2924 cm^{-1} to 3412 cm^{-1}. Taking into account the dispersion of the water refractive index, the angles θ_S are 2.95° and 3.49°, respectively. We use 200 mm focal length achromatic lens L_i to focus incident beams into the sample (Fig. 1). The separation h between the pump and the Stokes beams varies from 10.3 mm to 12.2 mm for λ_{S1} and λ_{S2}, respectively.

The experimental setup of the single pulse broadband CARS spectrometer is based on a single mode, Q-switched Nd:YAG laser with two amplifiers. Two KDP crystals as second harmonic generators supply two beams with wavelength of 532 nm and 10 ns pulse duration. The first beam with an energy up to 6 mJ is used as a pump

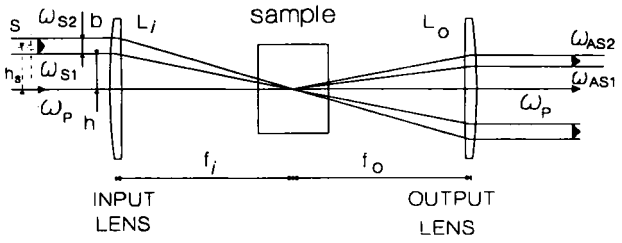

FIG. 1. A sheme for broadband single pulse CARS in dispersive media.

beam in the CARS process. The second one (with an energy up to 12.5 mJ) is expanded by a telescope and is used for generation and amplification of the Stokes wave.

A nanosecond dye laser operating by the scheme of spatially-dispersive resonator[11], but with two prism pairs, is used as a broadband Stokes source. Each pair is composed of one TF1 and one SF104 glass prism. The first pair is conjugated to the second one. The prism apexes are 60 degrees and the distance between prism pairs is 12 cm. The cavity is plane-parallel with 60 % reflectance of the output mirror and 0.6 mm aperture diameter. The rays in the resonator are incident under almost Brewster's angle with respect to the prisms and are deflected at minimum deviation from them. Our first experiments were to record the broadband CARS spectra of the water O-H band. For that purpose the most appropriate laser as a Stokes source is a DCM dye oscilla-

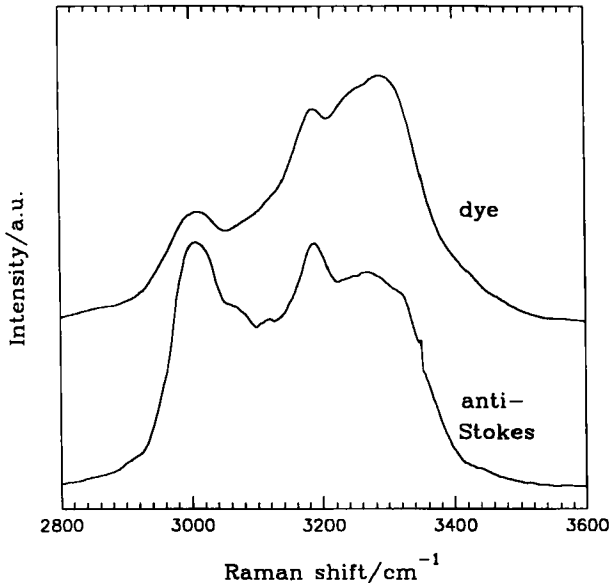

FIG. 2 a) Spectra of the dye laser and simultaneously detected anti-Stokes signal of liquid water.

tor. The dye laser beam exits the dispersive cavity end with a lateral shift of 1.1 mm between the components at 630 nm and 650 nm. The radiation is amplified and afterwards additionally spatially dispersed by two conjugated prisms made of SF104 glass up to size b (about 2 mm). This guarantees the phase-matching condition and reduces the spectral narrowing in the second dye amplifier. Both the dye oscillator and amplifiers were operated with DCM dissolved in methanol (10^{-3} mol/l). The flow speed of the solution was 2 ml/s. The output energy of the Stokes wave was up to 0.5 mJ.

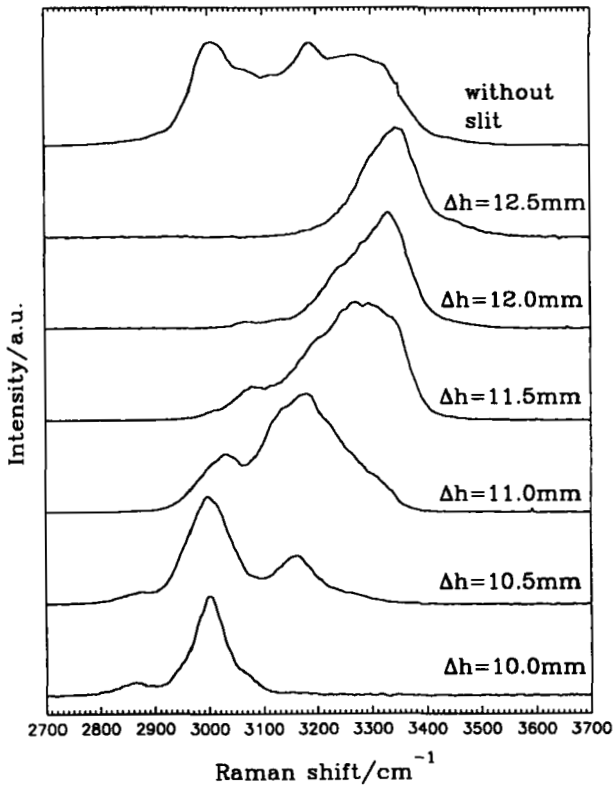

FIG. 2 b) Spectra demonstrating the satisfaction of the phase matching condition.

The anti-Stokes signal is detected with a vidicon based optical multichannel analyzer OSA 500 (B&M Spectronik) mounted on a polychromator, whereas the dye spectrum is simultaneously recorded by a diode array coupled to another polychromator. Both detectors are connected to a PC computer and are calibrated by Ne and Hg spectra. The spectral resolution was about 2.7 cm^{-1} per channel.

RESULTS

Fig. 2a displays a typical spectrum of the dye laser and simultaneously recorded anti-Stokes spectrum of the water. The polarization of the pump and Stokes beams, as well as the polarization of the CARS signal are parallel, and rejection of the background signal is not used. Although the dye laser generates from 2900 cm^{-1} to 3500 cm^{-1}, the anti-Stokes signal is limited on the side of the high wavenumbers because of the interference between the resonant and nonresonant part of the third order nonlinear susceptibility $\chi^{(3)}_{iiii}$[12].

In order to demonstrate the proposed scheme for satisfaction of the phase matching condition (Fig.1) we used a slit S, which can be moved by a micrometer translation stage in the direction of the Stokes beam dispersion (perpendicularly to the ω_S beam and in the plane of Fig. 1). Thus only one part of the dye beam (therefore only a selected part of the dye spectrum) was incident at established position h on the input lens L_i. The slit width was 0.5 mm, which means that about 110 cm^{-1} wide part of the dye spectrum could pass through the sample. Fig. 2b demonstrates some of the recorded spectra, corresponding to different distances h_S of the slit from the pump beam. The great value of the dye laser divergence (about 10 mrad) allows transmission of wider Stokes signal through the slit.

Combined with the diffraction from the slit this broadens the CARS spectra so that their width is more than twice greater than 110 cm^{-1}. The spectrum at h_S = 10 mm is broadened least of all because of the decreased intensity in the dye spectrum wing. The spectra corresponding to h_S = 10.5 mm and 11.0 mm are well over broadened, but each of them has two maxima. Their structure reflects the shape of the dye laser spectrum in the corresponding spectral range. The whole CARS spectrum of water possesses a dip from about 3400 cm^{-1} to 4000 cm^{-1} due to the negative interference between the resonant and the nonresonant parts of the third order nonlinear susceptibility[12]. This dip conditions two peculiarities in the behavior of our spectra in the high wavenumber region. The first peculiarity is that the spectrum at h_S = 12.5 mm is less broadened in comparison with the spectra at h_S = 10.5 mm and 11.0 mm. The second one consists in the strongly reduced distance between the maxima of the spectra at h_S = 12.0 mm and 12.5 mm. The two maxima almost coincide, as it is seen in Fig. 2b.

The spectra obtained show that the proposed scheme has satisfied the phase matching condition and has permitted us to record broadband CARS spectra in dispersive media by a single laser shot.

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