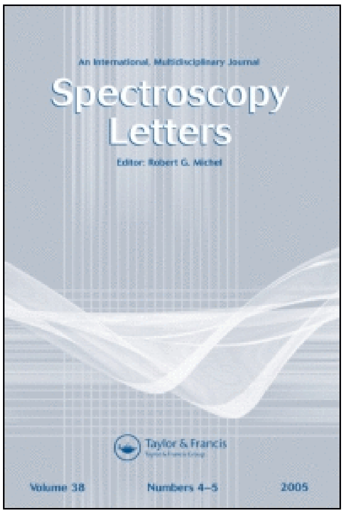

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Detection of Trace Iodine in Solution by Phase Conjugate Reflection

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DETECTION OF TRACE IODINE IN SOLUTION BY PHASE CONJUGATE REFLECTION

Keywords: Absorption spectrometry, Degenerate four wave mixing, Phase conjugation, Thermal grating.

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ABSTRACT

The phase conjugation of degenerate four-wave mixing (DFWM) was observed by irradiating an excimer laser pumped dye laser to iodine/benzene solution. It is confirmed that the generated light intensity shows quadratic proportion to the absorbance of solution.

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INTRODUCTION

Phase conjugation of light attained by DFWM is one of the important subject in the recent optical phisics or chemistry[1-5]. This non-linear process was explained as the thermally induced refractive index change, the Kerr effect, and saturable absorption[1]. The detection of phase conjugate wave due to DFWM is also important on the stand point of measuring small absorption of solution. When a thermal effect is limited as a cause of this phenomena, the two crossing laser beams produce the holographic grating which is due to the heterogeneous distribution in refractive index of solvent, and the third beam is reflected by this grating. In this case, the generated light from a phase conjugate media is the reflection of the third beam by a thermally induced grating.

Recently, Pelletier and Harris observed thermal grating diffraction, where a cw Ar^+ or a pulsed Nd:YAG laser was used for inducing a grating in the solution and a He-Ne laser was used as the probe for observing reflection by the grating[6,7]. Although this system has a different configulation from the phase conjugation by DFWM, it has been shown that the observation of thermal grating diffraction is quite effective to measure the small absorption of solution.

In the present paper, a wavelength-tunable pulse laser has been employed for observing the phase conjugation on the standpoint of measuring the small absorption of solution. Also, it is theoretically and experimentally confiemed that the diffraction light intensity shows quadratic proportion to the absorbance of solution.

THEORY

Suppose the thermal process was dominant as a cause of the grating in the solution, the phase conjugate reflectivity(R) was given by Caro and Gower[1] as

$$R = |\phi D \tau I_p \exp(-\alpha L')[1-\exp(-\alpha L)]|^2 \quad ---(1)$$

in the condition of R being small. In this equation, ϕ is the fraction of absorbed radiation converted to heat, τ is the duration of the electromagnetic fields, I_p is the intensity ofthe pumping laser, α is the absorption coefficient of solution, L and L' are the lengths of pump and prove beams in the sample, respectively, and D is a constant specific to the solvent and given by

$$D = (\omega/c\rho C_p)(dn/dT) \quad ---(2)$$

where is the frequency of laser beam, and ρ and C_p are the density and specific heat of solvent, respectively. Suppose that L is equal to L' and that the absorbance of analyte given by αL is much less than one, i.e., $\exp(-\alpha L') \simeq 1$ and $[1 - \exp(-\alpha L)] \simeq \alpha L$, the equation (1) can be simplified as

$$R \propto [I_p \cdot \alpha L \cdot D]^2 \quad ---(3)$$

The equation (3) means that the reflectivity is proportional both to the squares of absorbance of solution(αL) and the change of the refractive index of solvent against the temperature (dn/dT). When phase conjugate reflection is mainly due to the grating produced by the two laser beams (crossing angle is about 4 degree in the present case) and diffraction of the counterpropagating third beam by this grating, it can be considered that the laser source doubles as pumping and probing of the thermal grating. In this case, the intensity of diffracted light(S) is proportional to the cubic of the laser power as

$$S \propto I_p^3 \cdot (\alpha L)^2 \quad ---(4)$$

EXPERIMENTAL

Iodine(I_2) was dissolved into benzene solution. As other solvents, carbon disulfide, ethyl alcohol, acetone, and water were also tested: carbon disulfide gave strong diffraction without iodine according to non-thermal effect(such as Kerr effect). On the other hand, the induced grating effect is extremely small in acetone, ethyl alcohol, and water, being not preferable for observing small absorbance of solution. This seems to be due to low (dn/dT) of these solvents. As a result, benzene was chosen as the solvent in the present experiment because of the exceptionally high sensitivity and low background reflection in benzene.

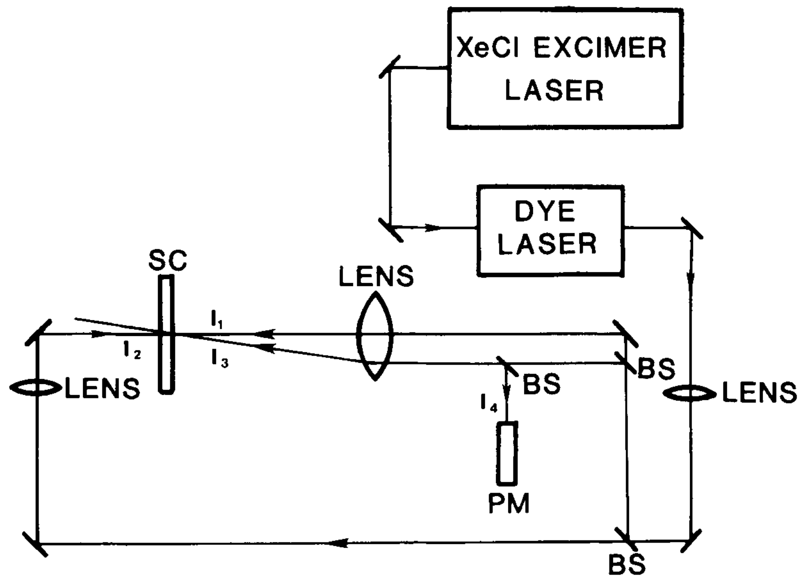

Figure 1 : Optical system for measuring phase conjugate diffraction by the DFWM process. I_1, I_2, and I_3:output beams of dye laser, I_4:diffracted light from phase conjugate media, SC:sample cell(1 mm thickness of solution for optical pathlength), BS:beam splitter, and PM: photomultiplier.

Figure 1 shows the system used in the present experiment. An excimer laser (XeCl, output 308 nm:Type C2540, Hamamatsu) pumped a dye laser (Type DLII, Molectron, and dye:fluorescein) was used as a light source. The wavelength of laser output was around 540 nm which is close to that of the absorption maximum of iodine in benzene. The laser was operated at 5 Hz, of which output energy was about 0.3 mJ/pulse. The output of dye laser was devided into 3 beams, i.e., I_1, I_2, and I_3

for inducing a DFWM process. The sample was placed in a cell of 1 mm pathlength, in which the optical geometry was as follows:I_1(horizontal diameter = 70 μm, vertical diameter = 40 μm), I_2(horizontal diameter = 50 μm, vertical diameter = 180 μm), and I_3(horizontal diameter = 50 μm, vertical diameter = 40 μm). The relative intensities of I_1, I_2, and I_3 beams were 0.5, 0.8, and 1, respectively at the sample cell.

The reflected light from the phase conjugate media (I_4 in Figure 1) was detected by a photomultiplier (Hamamatsu, type R928). The selection of wavelength of the detected light was done by placing a interference filter in front of the photomultiplier. Also the signal level was adjusted by ND filters. The output intensities of the dye laser and of the diffraction signal were stored in a transient memory (Kawasaki Electronika, type HR-1200) and read out by a personal computer(NEC, type PC8001-MKII). The details of the experimental apparatus will be shown in Ref(8).

RESULTS AND DISCUSSION

Figure 2 shows the signal output obtained by the system shown in Figure 1. Rather large fluctuation was found in the signal increment from the iodine solution. It can be considered in the pewsent system that the fluctuation in laser output provides a cubic fluctua-

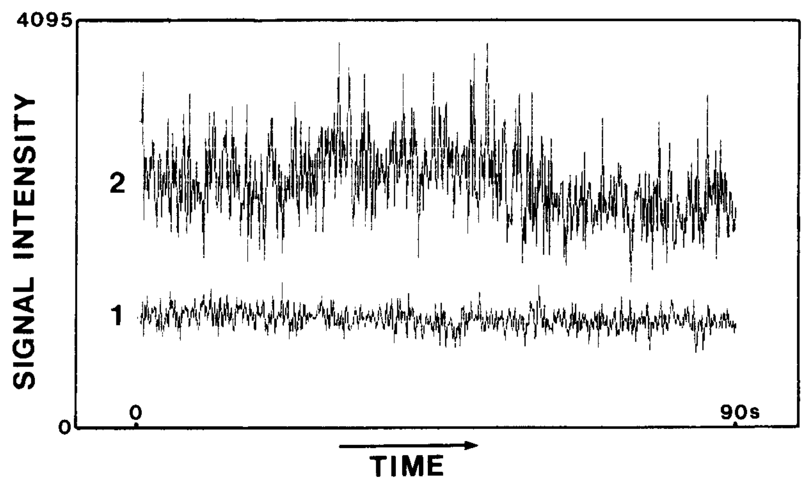

Figure 2 : Detected signal (450 laser shots/5 Hz). 1:benzene, 2:iodine/benzene solution(absorbance at a 1 mm cell = 0.0025).

tion in the magnitude in the detected signal according to the equation (4). For performing a quantitative measurement, the accumulation and averaging of the obtained signal at each laser shot is required. In the present case, 500 laser shots were irradiated to the sample solution (the signal was averaged against the 450 repetitive laser pulses with excluding initial 50 pulses for the sake of initial instability in the source light output).

Comparing with the iodine solution, the solvent (benzene) gave lower fluctuation. Convection due to the heat deposition in the iodine solution can be one of the cause of the fluctuation. In the case of the solution at absorbance of 0.04 (1 mm cell length), the relative standard deviation was 30-35 % in 450 signals. On the other hand, that of benzene (blank) was 21-23 %.

Figure 3 shows the relationship between the signal intensity vs absorbance of solution in a log-log diagram. In this figure, the ordinate shows the ratio of ($S - S_0$) and S_0, where S and S_0 are the siganl intensities from the iodine solution and that from the blank (solvent), respectively. The net signal of DFWM should be given by ($S - S_0$) because S_0 *includes the background* without DFWM such as the scattering light. Here, the signal intensity is expressed by a unit of the blank signal. The calibration curve of signal intensity due to the phase conjugate diffraction vs absorbance of solution was close to quadratic, proving the validity of the equation (4). This fact suggests that the diffracted light which is detected in the present system is mainly due to the thermal process.

After the signal averaging, the standard deviation in the four measurements was about 4.5 % for the solution of absorbance 0.004 (given by a cell of 1 mm length). When taking twice of the standard deviation in the five averaged signals from the solvent (benzene), the detection limit of absorbance was 0.0006 at a 1 mm cell, which corresponds to about 20 ng/mL of iodine in benzene solution.

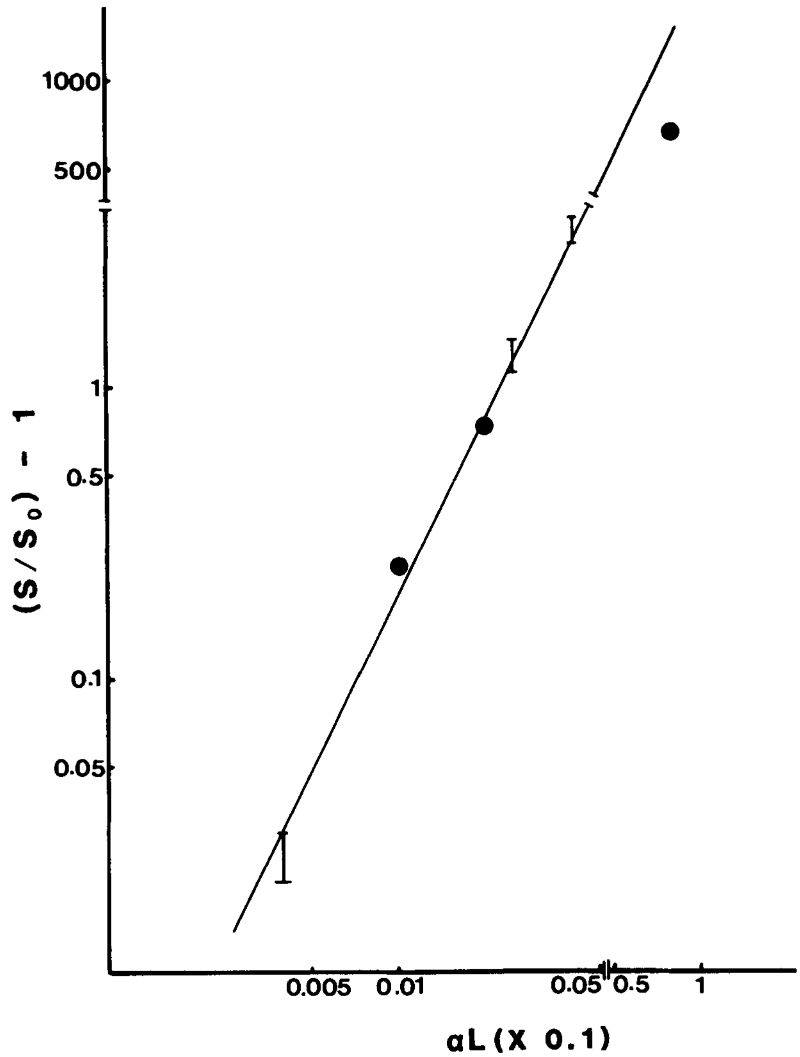

Figure 3 : Calibration curve for phase conjugate diffraction signal by DFWM vs absorbance of solution (αL) observed at a cell of 1mm pathlength. The solid line in the figure has an inclination of 2. Vertical bar shows the deviation in the triplicate measurements.

The phase conjugation of radiation has been applied to the colorimetric analysis in this paper. Although the geometry of light source and sample cell is not so flexible comparing to thermal lensing effect, it is effective to observe absorption in the small spot of sample. When the thermal effect is dominant, phase conjugation is in principle the same as the thermal lensing effect, i.e., the spatial distribution of refractive index change in the solvent is the origin of both effects. At present, thermal lensing effect is much developed and widely applied in the field of analytical chemistry than phase conjugation by DFWM process or the thermally induced grating effect. However the laser system shown in Figure 1 is rather simple and provides quite high precision when the accumulation and averaging of signal for a few hundred laser pulses has been done.

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