P1-10 Small Absorption Spectroscopic Measurements in Transparent Liquids

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1. Introduction

It is very important today to measure the transperancy in water for drinking, washing, swimming, and for monitering the environments in rivers, lakes and seas. In general, it may be very difficult to observe very small absorption coefficients less than $10^{-3}cm^{-1}$, since on transmission measurement the intensity reduction to 1/e must require a long path cell over 10m. So, some investigaters already reported the absorption coefficients of 10^{-3} or $10^{-5}cm^{-1}$ for some pure liquids, such as benzene, hexane, and acetone, by use of the photo-thermal lens method, the photo-accoutic method, and the optical interference method[1-3]. For the water, however, the coefficient under $10^{-3}cm^{-1}$ was not reported, that may be according to the sample in law purity. On the other hand, for the benzene, the smaller value of $10^{-6}cm^{-1}$ was observed by the photo-thermal deflection technique[4].

Now we will report the small visible absorption spectra of water in high quality, coming from the 5 or 6th overtones of infrared vibrations in about $3000cm^{-1}$, that are observed by the photo-thermal deflection spectroscopy with a pulsed red dye laser. The additive effects, such as chloride and glucose, are also detected.

2. Experimental Setup

Figure 1 shows the experimental setup of the photo-thermal deflection spectroscopy. A tunable dye laser with 0.4nm width for the local excitation in liquid samples, benzene and waters, was pumped by a double frequency Q-switched Nd:YAG laser. The fine beam of a He-Ne laser was past through the sample cell of 1 cm thick for probing the photo-thermal lens effect, being deflected by the thermal lens due to the optical absorption or the relaxation of excited states rapidly pumped by the dye laser. The deflection sensitivity related to the absorbance was increased with the arm distance from the cell to the knife edge.

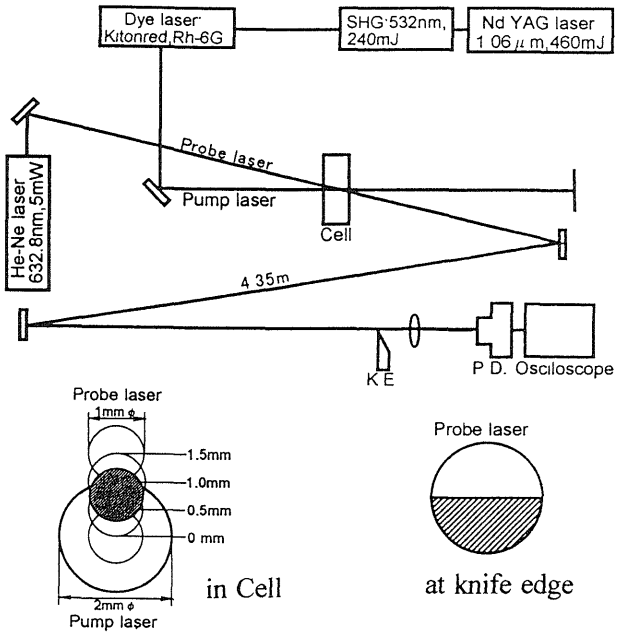

Fig.1 Experimental setup

3. Experimental Results

Figure 2 shows the experimental result on benzene. The two peaks of absorption were observed at 583nm as well as 604nm. The latter was already measured by W.B.Jackson[4] to be in the order of

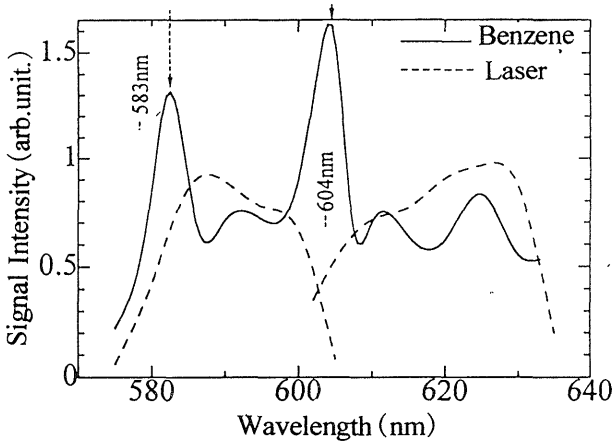

Fig.2 Photo-thermal deflection of absorption spectra on benzene.

$10^{-6}cm^{-1}$ and discussed to come from the 6th overtone of C-H bond stretching of $3040cm^{-1}$. Therefore, the former seems to be resulted from the other of $3096cm^{-1}$.

Figure 3 shows the experimental results on pure water in 10M Ω, and including chloride of 200/cc. The peak at 583nm corresponds to the O-H bond vibration of $3610cm^{-1}$, while another peak at 587nm seems to that blue-shifted by the additive effects of chloride.

Figure 4 shows the additive effects of glucose on water in 18M Ω. The absorption peak of water was red-shifted slightly with increasing glucose. For the water including glucose of 30% at weight, the peak was shifted up to 585nm.

4. Discussions

As concerned with the sixth overtones of benzene, we can estimate the anharmonic constants χ of 0.013 and 0.011 for the peaks at 604nm and 583nm, respectively, as expected reasonably [5]. we can get also the value of 0.029 as the anharmonicity of the O-H bond, as shown in Table I.

On the additive effect of chloride, the anion of large radius of 0.169nm will cut off the hydrogen bond and the water molecules may move easily. This results in activating the vibration and rotation to shift the peak slightly to higher frequency. On the other hand, the addition of glucose will attract the water molecules about it, since that is very large molecule and resembles the structure of water . This will put down the motions of water molecules to shift the peak slightly to lower frequency.

Table I Fundumental vibration, 6th overtone, and anharmonic constant for benzene, water.

	peak (nm),	mode (cm^{-1}),	χ
benzene	604	3040	0.013
benzene	583	3096	0.011
water	583	3640	0.029
water+Cl	578		
water+gl	585		

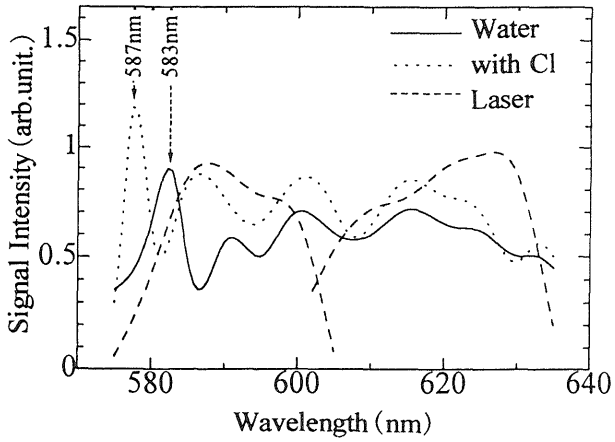

Fig.3 Photo-thermal deflection of absorption spectra on pure water and with chloride.

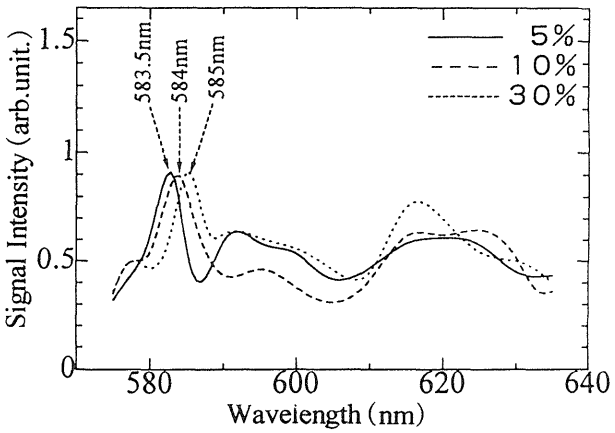

Fig.4 Photo-thermal deflection of absorption spectra on water with the addition of glucose.

5. Conclusion

Anyway, we can get the very small absorption spectra of $10^{-6}cm^{-1}$ coefficients on benzene and water in visible region, that are attributed to the higher harmonics of normal modes in infrared region.

References

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