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Some Applications of cw Dye Laser to Spectroscopic Study

Masayoshi SATO, Nobukimi OHASHI
and
Shin-ichi MATSUOKA

Institute of Spectroscopic Study of Matter, Faculty of Science, Kanazawa University

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The appearance of the tunable dye laser has made a considerable progress in the high resolution optical spectroscopy. The fruitful applications of the dye laser to the spectroscopic study on unstable molecules have been well known. [1]

Some experimental studies using the tunable dye laser have been made on unstable molecules in our laboratory for a few years. Experimental methods and preliminary results obtained so far are described briefly in this article.

Laser excitation spectroscopy

The excitation spectrum gives important information on the electronic excited state of molecules. The experimental apparatus for the laser excitation spectrum measurement is shown in Fig. 1 schematically. The exciting source is a ring dye laser (Spectra Physics, Model 380A) which is optically pumped by an Ar^+ laser (Spectra Physics, Model 164). The wavenumber of the dye laser is scanned in 200 MHz mode-hopping by sweeping the electric field applied to the piezoelectrical element attached to an etalon placed within the laser cavity. The single mode scanning is available in the wavelength range of 570 nm to 620 nm with use of Rhodamine 6G as the dye. The output power of the dye laser is 380 mW maximum at 580 nm in the single mode operation when pumped by 4 Watts output from the Ar^+ laser in the all-line mode. The wavenumber calibration is made by recording the iodine spectral lines which have been precisely known. [2] The precision in the wavenumber determination for the excitation spectrum is about $\pm 0.02 cm^{-1}$. The dye laser mode is monitored by means of a spectrum analyzer which consists of a piezoelectrically driven Fabry-Perot interferometer (confocal type, FSR = 0.75 GHz) and a ramp generator. The fluorescence cell is made of a Pyrex glass tube of 35mm in outer diameter and 600mm long, sealed with a pyrex-glass Brewster-angle window at each end. A 2450 MHz microwave discharge cavity is placed upstream of the cell. The discharged products and the reactant are mixed at the entrance to the cell and pumped out continuously from the cell by a mechanical booster pump followed by a rotary pump. For the detection of the fluorecence

signal a photomultiplier (HTV R666S) is placed by the wall of the cell. The scattered laser light is reduced by light baffles inside the cell and is blocked by sharp-cut filters in front of the photomultiplier. The laser beam is mechanically chopped at 390 Hz and the signal from the photomultiplier is detected by a lock-in amplifier (NF, LI-570).

As an example of the excitation spectrum, $\tilde{A}^2A'$,(004)←$\tilde{X}^2A''$(000) vibronic transition of HSO radical is shown in Fig. 2. For the generation of the HSO radical, the following reaction system was used;

$C_2H_5SH + O_2$ (MW discharge).

(30m Torr) (100m Torr)

The details of this spectrum will be published elsewhere.

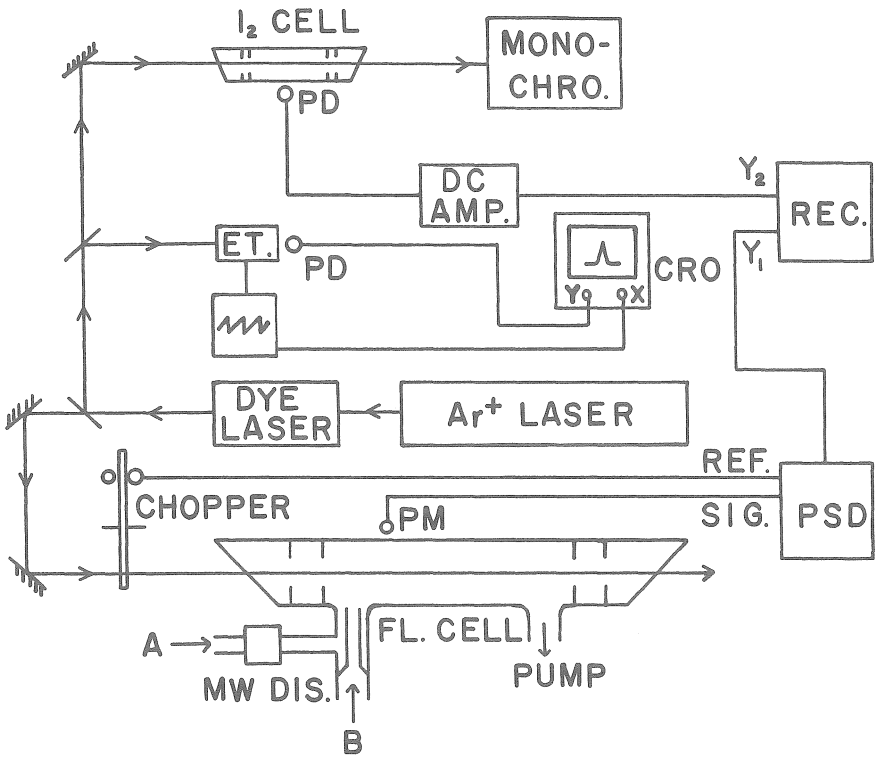

Fig. 1. Schematic of experimental apparatus for laser excitation spectra.

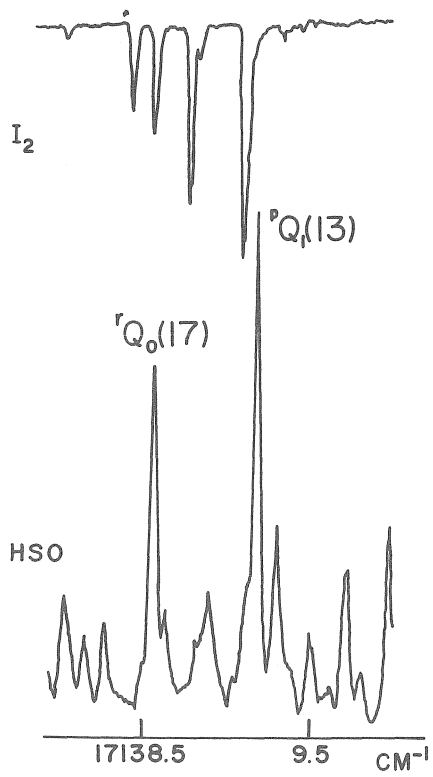

Fig. 2. An example of the excitation spectrum. The $\tilde{A}^2A'(004) \leftarrow \tilde{X}^2A''(000)$ vibronic trasition of HSO is shown in the lower trace. The upper trace is the iodine spectrum recorded for the wavenumber calibration.

Laser induced fluorescence spectroscopy

Information on the energy levels of the lower electronic state can be obtained by observing fluorescence following the excitation of individual rotational levels of selected vibronic states. [3] In Fig. 3 the experimental arrangement is shown. The fluorescence is analyzed with a Nikon Echelle grating monochromator and is detected by a cooling photomultiplier (HTV R712) followed by a photon counting system. In Fig. 4 the fluorescence spectrum of HCF recorded following the selective excitation of the 7_{25} rotational level of the $\tilde{A}^1A''(000)$ vibronic state is shown. In addition to resonance fluorescence lines, collision-induced lines are observed. For the generation of the HCF radical, the following reaction system was employed:

$$CH_3Cl + CF_4 \text{ (MW discharge).}$$
(15 mTorr) (290 mTorr)

At present time the precise measurement of this radical is in progress. The results will be published elsewhere.

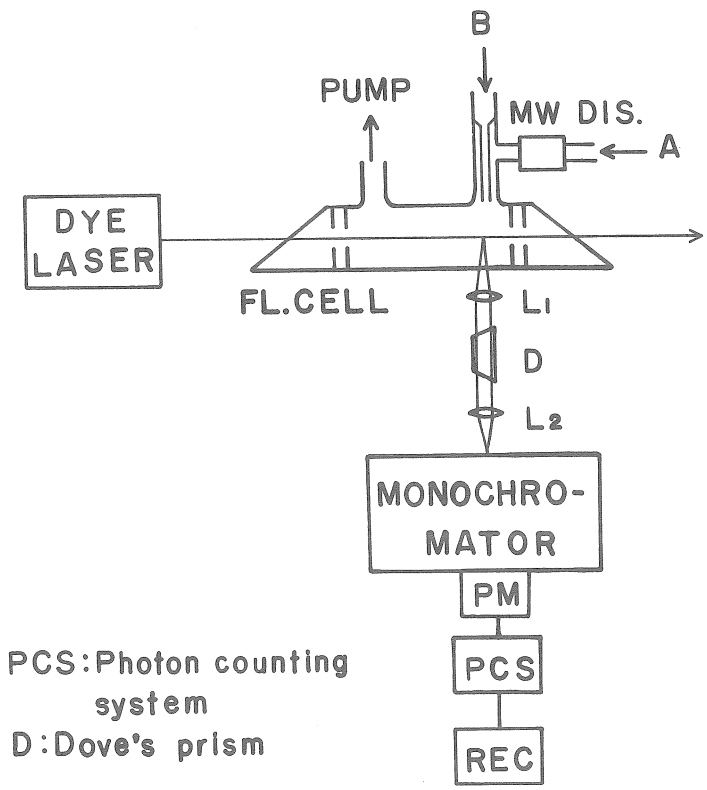

Fig. 3. The experimental arrangement for analyzing the laser induced fluorescence.

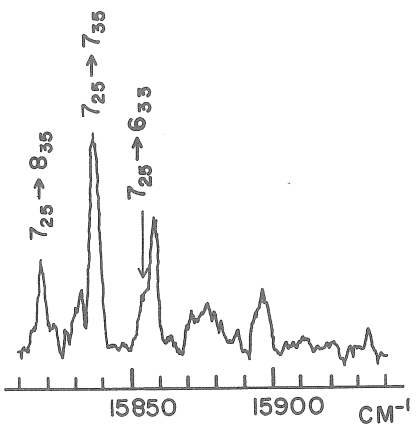

Fig. 4. The fluorescence spectrum of HCF terminating on the $\tilde{X}^1A'(010)$ level, observed following the selective excitation to the 7_{25} level of the $\tilde{A}^1A''(000)$.

Opto-galvanic spectroscopy

An opto-galvanic effect has been utilized mainly in atomic spectroscopy using the cw tunable dye laser. [4] As the application to molecular spectroscopy there is a work made by Suzuki et al who observed and analyzed the transition between the Rydberg levels of N_2 [5]. In the aim of obtaining the spectra of unstable molecules and molecular ion, we started the experiment of the opto-galvanic effect. As preliminary stage of this

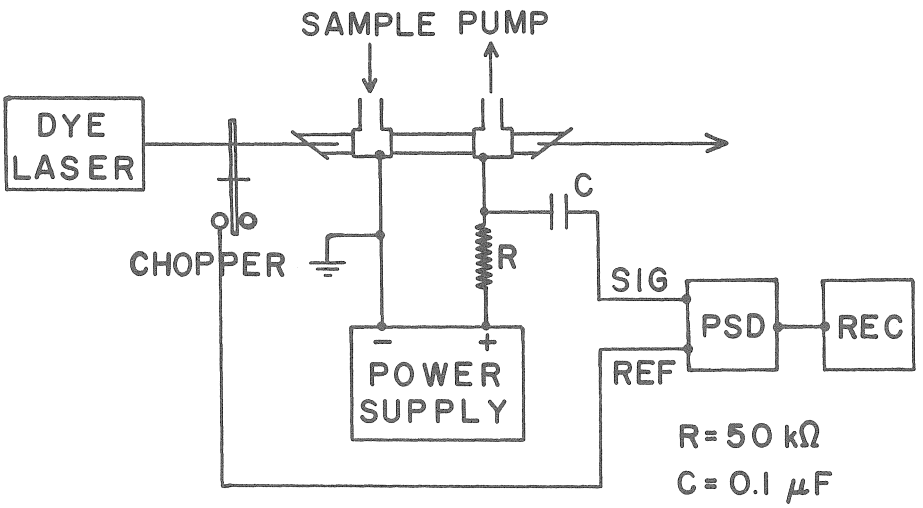

Fig. 5. The experimental arrangement used for the opto-galvanic measurement.

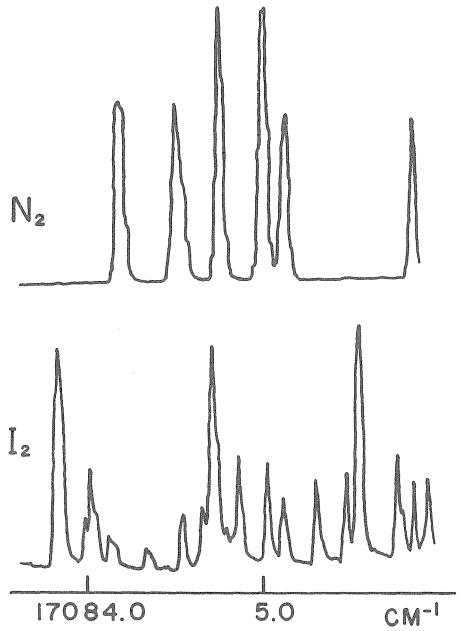

Fig. 6. Opto-galvanic spectrum of N_2 (upper trace).

experiment we could observe the spectra of Ar, Ne and N_2. In Fig. 5 the experimental arrangement is shown and in Fig. 6 the spectrum of N_2 is presented. The discharge cell is made of Pyrex glass tube of 10mm outer diameter and two pieces of T-type valve fitting which form electrodes.

Thermal lens effect

The highly vibrational levels of the ground electronic state have attracted much attention as one of the applications of the tunable dye laser to spectroscopic study. The

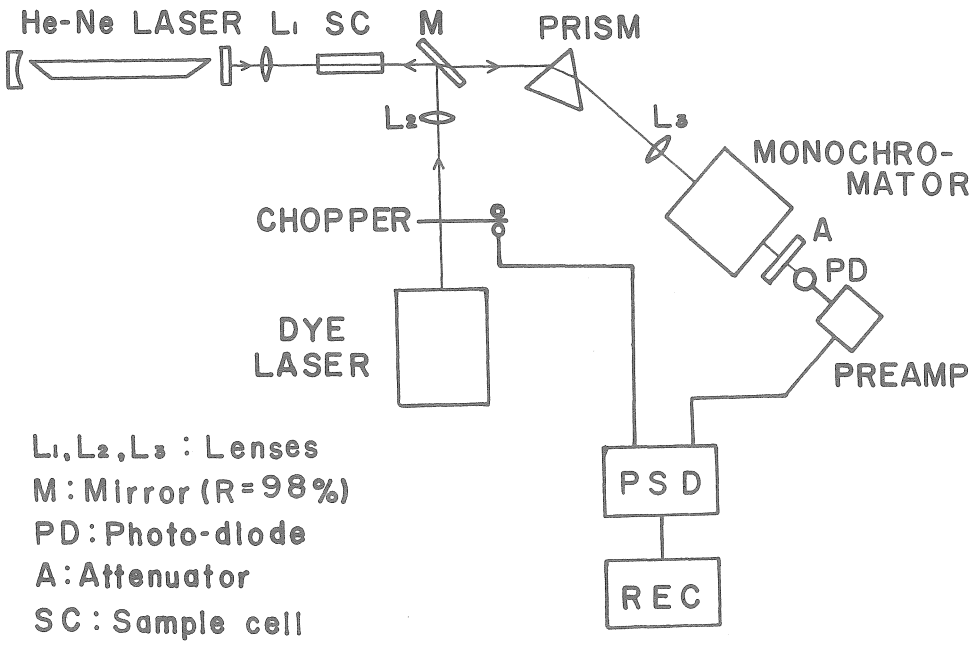

Fig. 7. Experimental setup used for the thermal lens effect measurement.

techniques utilyzing thermal lens effect and opto-accoustic effect, are available to observe the transitions including these levels. As the first step of the study on the highly vibrational level, we observed the thermal lens effect of liquid benzene which corresponds to the absorption of the sixth harmonics of the CH stretching mode. In Fig. 7 and Fig. 8, the experimental apparatus and the spectrum are shown, respectively. In order to study the highly vibrational state of gaseous state we are preparing a multi-pass cell.

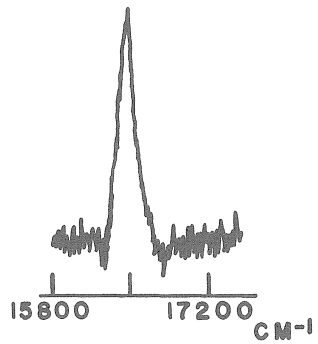

Fig. 8. Absorption spectrum of benzene-h_6 obtained by means of thermal lens technique.

References

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