Laser Spectroscopy.I.A Trial Arrangement for Detecting Laser Raman Scattering in Gases.

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for Detecting Laser Raman Scattering in Gases

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§ 1. Introduction

Raman spectroscopy is concerned with the phenomenon of a change of frequency when light is scattered by molecules. The phenomenon is that, when monochromatic light of frequency ν_0 is used, the spectrum of the scattered light shows a pattern of lines of shifted frequency. The shifts are independent of the exciting frequency ν_0 and are characteristic of the species giving rise to the scattering.

Since the phenomenon was discovered, Raman spectroscopy has played an important role in researches of molecular science. Experimentally, much Raman work has been done with specially designed mercury lamp using the intense blue line.

The search for a more intense monochromatic source for the Raman spectroscopy has been the task of many scientists for a long time, and from the moment the laser was invented, the application of the use of the laser for a Raman source has been researched.

After Raman spectra of organic compounds were successfully observed by Porto and Wood[1] with excitation by pulsed ruby laser, a large amount of laser-excited Raman studies has appeared[2].

Now, in our institute, a project is carrying on spectroscopy of scattered light in gaseous molecules contained in a specially designed multiple reflection cell, and excited with a stabilized cw-gas laser of a single frequency.

In this report, some features of main elements of our arrangement and discussion on the photoelectric detection of the scattered light in gaseous molecules are described.

§ 2. Laser

In contrast with the property of conventional mercury lamp, the laser contains the

energy in a very narrow parallel beam which can be manipulated in any direction one wants. The polarization and intensity are well controlled, while the half-bandwidth of the laser line is smaller than those of the lines of the mercury or any other light sources. So, it is expected that the laser beam is probably the most ideal light source for Raman spectroscopy, provided that the power level and the operating frequency are satisfactory.

Laser became available a few years ago and a number of Raman experiments has already been performed with these devices.[3]~[8]   The first use of the pulsed ruby laser for exciting Raman spectra was reported by Porto and Wood.[1]   This exciting source, however, had disadvantages in that it required 50~100 laser flashes to obtain a reasonable Raman spectra of tetrachlorocarbon and benzene and had to be cooled with liquid nitrogen.

In 1963, Raman data were published by Kogelnik and Porto[3] who used the helium-neon gas laser oscillating at 6,328 Å as a Raman source. Although the helium-neon gas laser can be operated at a number of frequencies, the most suitable frequency for Raman spectroscopy is the line at 6,328 Å, because of its highest intensity and lowest wavelength.

In our experiment, a stabilized helium-neon gas laser oscillating at a single mode of 6,328 Å is used as the exciting source, for the reason to make resonate to a specially designed sample cell of multiple reflection type. The laser is of a modified JLG-06 type of the Japan Electron Optics Laboratory and its frequency stability is seemed to be kept in about 10^{-8} per a day with a temperature regulator. Distance between two mirrors is about 25 cm and 6,328 Å line oscillates in TEM_{00} mode, but the output power is poorer than multimode oscillation and is about 0.2 mW. The stability of the output power level, estimated from running records of 25 hours, was about 2×10^{-3}.
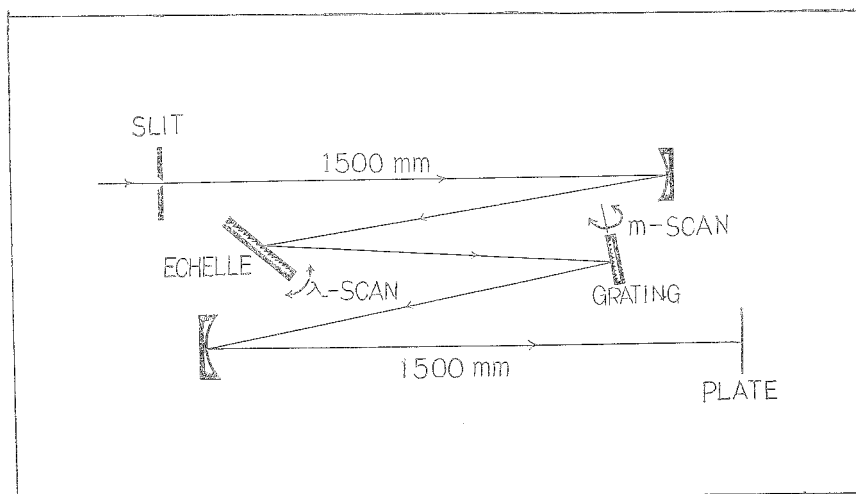

Fig. 1. The optical diagram of the Echelle monochromator.

§ 3. Monochromator

In our study, a 1.5 meter Echelle monochromator of the Nippon Kogaku K. K. is used, where two gratings of the Bausch and Lomb Optical Co., are mounted in Czerny-Turner type as shown in Fig. 1.   One is a plane grating ruled with 600 grooves/mm and its effective area is 102 mm × 102 mm, and the other is an Echelle grating[9] with 73.25 grooves/mm of which effective area is 102 mm × 208 mm and the blaze angle is 63° 26′.

The resolving power of the monochromator is nominally about 300×10^3. Actually, two lines at 5,460.644 Å and 5,460.677 Å of the isotope fine structures in mercury *e*-line, were resolved, so that the resolving power better than 200×10^3 was certainly attained.

A spectrum can be scanned by rotation of gratings with sine-bars driven automatically or manually. That is, a choice of an order number *m* of the spectrum is made by an inclination of the plane grating about a horizontal axis and the wavelength is scanned by rotation of the Echelle grating about a vertical axis.

The full ranges covered by the scanning mechanism are from $m\lambda = 251,321$ to $m\lambda = 243,082$ or from $\lambda \sim 2,000$ Å to 8,000 Å.   The scanning speeds are 20 Å/min. and 2 Å/min., and the product $m\lambda$ is indicated by a digital counter.

Both photographic and photoelectric detections can be employed.   A photograph of the arc spectrum of iron is shown in Fig. 2, where the center of the plate is at $m = 66$ and $m\lambda = 246,504.72$ and Fuji spectroscopic plate is used.
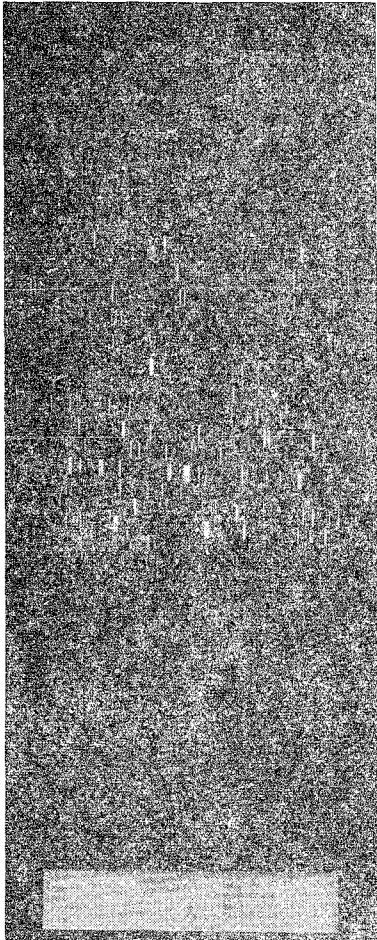

Fig. 2.   The arc spectrum of iron taken with the Echelle monochromator. The spectrum is dispersed in length by *m* and in width by λ.

§ 4. Sample Cell and Discussion

For liquid samples and light in the visible region, the total intensity of molecular scattering may be of the order of 10^{-5} of the incident intensity, and of this, perhaps, only about 1 % may contribute to Raman spectrum.   For gases, where the molecular population density is lower, the intensity of molecular scattering is correspondingly lower, and in general, larger sample volumes must be used.

In most cases of measurements in gases, therefore, a cell of multiple reflection type has been

used, because if the incident light is reflected n times at each reflector in the cell, the intensity I becomes effectively nI.

If N molecules to be studied, are contained in $1\ mm^3$ of the sample, the luminous flux, or the radiant flux, Φ watt, reaching the detector through the monochromator, is expressed as

$$\Phi = (1/4\pi)I\sigma Nl U\eta, \tag{1}$$

where, I is the intensity in $watt/mm^2$ of the light in the cell, σ is the cross section in mm^2 of Raman scattering and $(I\sigma N/4\pi)$ is the volume brightness of Raman light. l is the effective length of the cell and η is the total transmittance. U is the luminosity in mm^2 and is given by

$$U = (2\ ha b\ \sin\ \varphi \cdot \varDelta\lambda)/\lambda F, \tag{2}$$

for the Echelle monochromator, where h is the slit-length, $a \times b$ is the effective area of the Echelle grating and F is the focal length of the collimator. λ is the used wavelength and $\lambda/\varDelta\lambda$ is the resolving power and φ is the blaze angle of the Echelle grating. Substituting the values already described for the monochromator and $h=12$ mm, $\lambda=6,000\mathring{A}$ and $\varDelta\lambda=0.02\ \mathring{A}$ into eq. (2), the following estimate was obtained for the Echelle monochromator,

$$U \sim 1 \times 10^{-3}\ mm^2. \tag{3}$$

Now, to estimate the order of the value of eq. (1), it is necessary to obtain the value of N. The rotational energy of molecule is given by

$$E_{J,K} = BJ\ (J+1)\ +\ w\ (J,\ K), \tag{4}$$

$$J = 0,1,2,\cdots;\ K = -J,\ -J+1,\ \cdots,\ +J,$$

where, B is the rotational constant of the molecule and J, K are quantum numbers. By neglecting the second term in eq. (4) for simplification, the following relation is obtained,

$$N_0 = N\sum_\infty (2J+1)\ \exp\ [-BJ\ (J+1)/kT], \tag{5}$$

where Boltzmann distribution is assumed, and N is the number of molecules in $J=0$ level and N_0 is the total number of molecules.

Replacing the summation in eq. (5) by the integral, we have

$$N/N_0 \sim B/kT, \tag{6}$$

where k is the Boltzmann constant and T is the temperature of the gas. At room temperature $T=300\ °K$, the value of kT is of the order of $200\ cm^{-1}$, and if the similar molecule as cyanogen $C_2\ N_2$ is considered, the rotational constant B is nearly equal to 6 Gc or $0.2\ cm^{-1}$. Then for such molecules, the value of N becomes approximately $2 \times 10^{13}\ mm^{-3}$, because N_0 is nearly equal to $2 \times 10^{16}\ mm^{-3}$.

Therefore, substituting this value and $l = 100\ mm$, $\eta=0.2$, $\sigma = 10^{-26}\ mm^2$ into eq.

(1), the luminous flux is estimated as

$$\Phi \sim 5 \times 10^{-20} \text{ watt}, \qquad\qquad (7)$$

with $I \sim I_0 = 0.2$ mW/mm^2 and I_0 is the intensity of the laser.

In the case of photoelectric detection with these arrangements and a cell of 100 mm length, the luminous flux of this order is considerably smaller than the noise power of the photomultiplier. Then if reflectors are placed at each side of the cell and if the the beam is reflected about 100 times, the intensity of the beam in the cell is 100 times as large as as the incident intensity. So, with the multiple reflection cell, the luminous flux is of the order of

$$\Phi \sim 5 \times 10^{-18} \text{ watt}. \qquad\qquad (8)$$

If the lock-in technique is employed as the photodetection method, a dc dark current is given by[10]

$$I_d = [2 I_a{}^2 / e\mu B(S/N)^2] - I_a, \qquad\qquad (9)$$

where, I_a is a signal current, e is the electronic charge, μ is the gain of the photomultiplier for signal current and B is the bandwidth of the lock-in amplifier about a reference frequency. Using the value of $I_d \sim 10^{-9}$ A of EMI 9558B photomultiplier, $\mu \sim 10^6$, $e = 1.6 \times 10^{-19}$ coulomb and $B = 0.1$ cps, the minimum detectable signal current, which corresponds to $S/N = 1$, was obtained as $(I_a)_{min} = 3 \times 10^{-12}$ A. With an average cathode sensitivity of EMI 9558B of 140 μA/lumen or 9×10^2 A/watt, this corresponds to an incident light power of 3×10^{-17} watt.

The scattered light power obtained above is, therefore, ten percent of the detectable power of the photomultiplier, so with these arrangements, it is almost impossible to detect photoelectrically Raman light in gases at the room temperature.

Then, a special sample cell, designed by Dr. S. Hattori, was constructed by the Kinmon Seisakusho K. K., of which the cross-section is drawn in Fig. 3. This cell consists of the sample container of fuzed quartz, indicated by A in the figure, a pair of mirrors, B and C, and lenses D and F. The end of the sample container has Brewster's angle windows and mirrors are coated so as to have the reflection coefficients of 100% and 98% at 6,328 Å. Both spherical mirrors have a radius of curvature of 76 mm and the distance between two mirrors is about (76×2) mm.

The laser beam passes through the lens D, of which focal length is 100 mm, and reflects at each mirror. Then, the incident beam is collected[11] to the cylindrically symmetric region of the radius $r \sim (2 \lambda f / \pi r_0)$, where λ is the wavelength of the laser line used, f is the focal length of the focusing lens and r_0 is the mode radius of the laser beam. Hence the intensity of the beam in the cell will be effectively enhanced and become the order of $n I_0 r_0{}^2 / r^2$, where n is the number of reflection times and I_0 is the laser intensity. The Raman scattering is observed through the window at right angle and is detected through both the mirror E and the lens F.

The number of reflection times n is approximated to be $(1 - R)^{-1}$, where R is
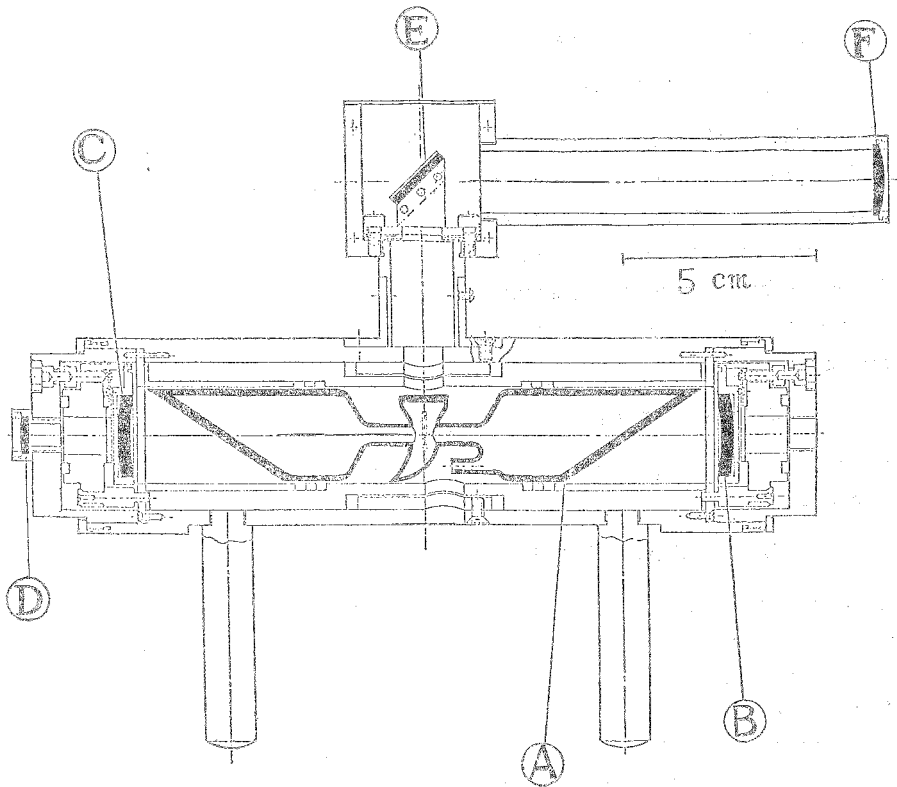
Fig. 3. The specially designed sample cell.

the reflection coefficient of the mirror, so that in the present case n becomes nearly 100. The mode radius r_0 of the laser beam is 0.5 mm and r was evaluated to be the order of 10^{-1} mm with $f=100$ mm and $\lambda=6,000$ Å. With these values, the luminous flux reaching the detector was estimated as

$$\Phi \sim 3 \times 10^{-17} \text{ watt,} \tag{10}$$

with the effective length of the cell of 10 mm.

This order of the luminous flux is comparable with that of the noise power in the photomultiplier, therefore it is not impossible to detect photoelectrically the scattered light in the gaseous molecule, because the dark current and external noise are enormously reduced by cooling photomultiplier to low temperature.

It is, however, difficult to detect photoelectrically more weaker light, for such cases it must be taken into account to accumulate the spectra by the computer or to employ the photon counting technique.[12]

Now, adjustments and preliminary experiments on the laser and the cell are in progress and some data will appear in the near future.

Acknowledgements

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