

Laser Spectroscopy II. Raman Scattering in Gases

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Abstract Using a He-Ne gas laser as the exciting source and a multiple reflection cell in the laser cavity, the rotational Raman spectra of CO₂ gas at the pressure of about 100 torr and the vibrational spectrum of N₂ in air were observed. The value of the rotational constant of CO₂ molecule was estimated to be 0.39 cm⁻¹.

Introduction

Since the appearance of the laser in 1960, many researches in the light scattering spectroscopy have been published, by using of the laser as an exciting light source. Thereafter, in addition to the development of more powerful laser, various detection techniques such as photon counting and noise voltage detection were also examined for weak spectra.

In 1962, Porto and his coworkers reported¹⁾ Raman data on gaseous media obtained by photoelectric detection system using a laser as the exciting source.

When spectral data on the Raman work with laser exciting source and counting method appeared, it seems likely that the technique for detecting Raman spectra was established, essentially. However, the observation of Raman scattering in gaseous molecules may be very difficult with He-Ne laser source.

In this report, some data will be presented on the pure rotational and the vibrational Raman spectra of some gaseous molecules obtained by using the He-Ne laser source and a specially designed cell of multiple reflection type.

Experimental Arrangement

An experimental arrangement employed in the present measurement is shown in

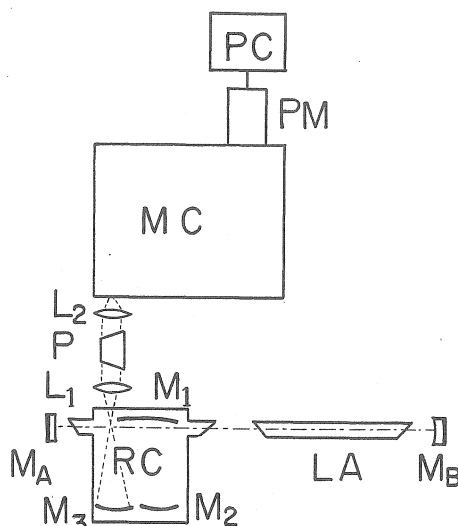


Fig. 1. Experimental arrangement for laser Raman scattering in gaseous molecules. LA: Laser, RC: Raman gas cell, M: Mirrors, L: Lenses, P: Dove prism, MC: Monochromator, PM: Photomultiplier, PC: Photon counting system.

Fig. 1, diagrammatically.

A He-Ne gas laser 1.8 meter long, of Tokyo Kōdenshi Kōgyo, K. K., was used as an exciting source. The laser resonator is terminated by the mirrors \$M_A\$ and \$M_B\$. The laser oscillates at 6,328 Å and the power inside the laser cavity is about 500 mW.

A Raman gas cell is positioned in the laser cavity in order to get higher scattering efficiency, on which discussion will be given later again.

A Dove prism P and lenses \$L_1\$, \$L_2\$, are used to rotate the horizontal image of the Raman-scattered light so as to coincide it with the vertical slit of a monochromator. The monochromator is of the Echelle grating type and was described in the earlier paper.²⁾



Fig. 2. Block diagram of photon counting system. PM: Photomultiplier, PA: Preamplifier, D: Discriminator, WA: Wide band amplifier, PS: Pulse shaper, C: Counter, I: Integrator.

The photomultiplier is HTV-R376 and is cooled below -30°C with liquid air if necessary. The photon counting system as shown in Fig. 2, was employed mainly as a detection method. However, it is not essential³⁾ to S/N consideration of Raman spectra, what detection method is adopted.

Great care must be taken in order to obtain good S/N ratio, on the alignment of the laser, the Raman gas cell and the monochromator, and on the fine adjustment of

the mirror system in the gas cell. In general, the optical technique seems to be more important than the electrical for detecting Raman spectra.

Raman Gas Cell

For gaseous or vaporous samples, it was very difficult to obtain a good Raman spectrum. Although the development of powerful lasers such as Ar^+ -laser has made the observation of Raman spectra in gaseous molecules possible, in the case of the usage of a laser such as He-Ne laser which is not so powerful, it is still difficult. In such a case, a special sample cell must be designed. In 1966, Weber and his coworkers succeeded⁴⁾ in obtaining good Raman spectra in the gas by positioning a sample cell in a He-Ne laser cavity.

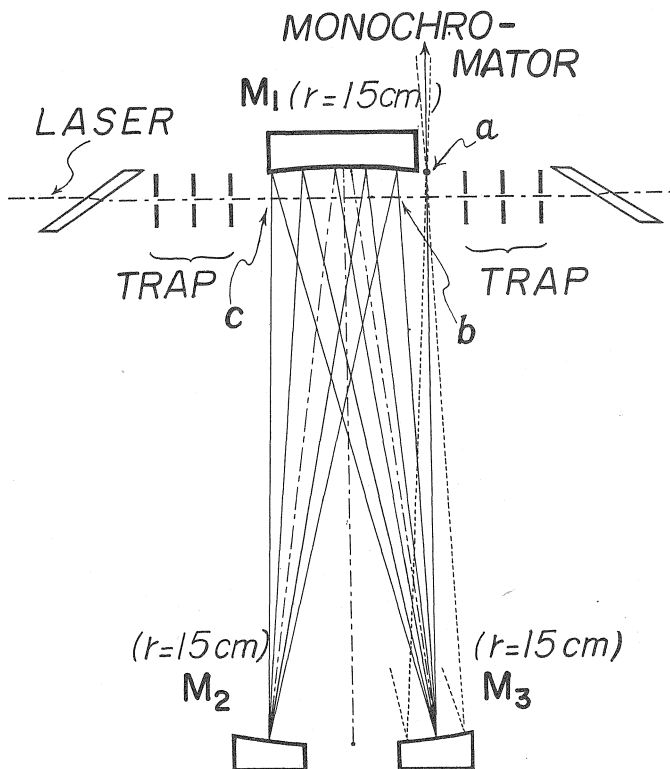


Fig. 3. Schematic diagram of the Raman gas cell with a multiple reflection mirror system.

As a gas sample cell for a mercury-arc lamp, the multiple reflection cell designed by Yoshino and Bernstein⁵⁾ is probably most effective one. Their idea was adopted for design of our cell. The diagram of our sample cell is shown in Fig. 3, and this was manufactured by Nippon Ryōshi Kōgaku K. K. The effectiveness of the mirrors M_1 , M_2 , and M_3 , would be understood by considering as follows; the scattering light from

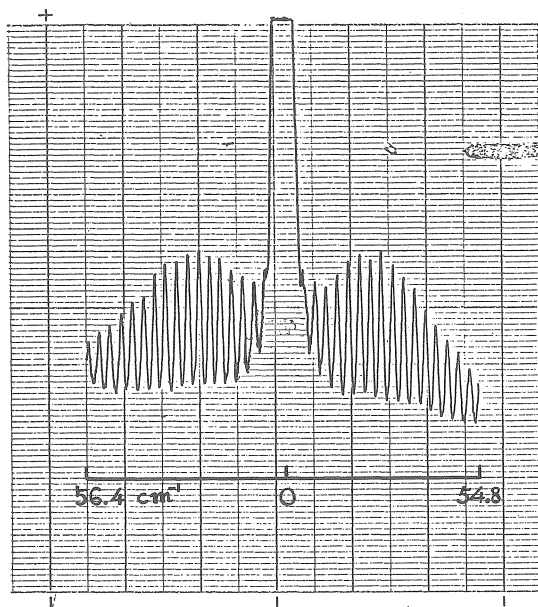


Fig. 4. Pure rotational Raman spectrum of CO₂.
Pressure: 100 torr, slit width: $500\mu=1\text{cm}^{-1}$, time constant: 50 sec.

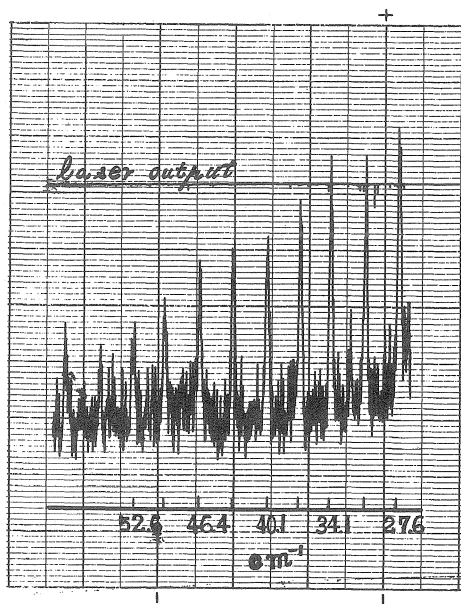


Fig. 5. Pure rotational Raman spectrum of CO₂.
Pressure: 100 torr, slit width: $100\mu=0.2\text{cm}^{-1}$, time constant: 10 sec.

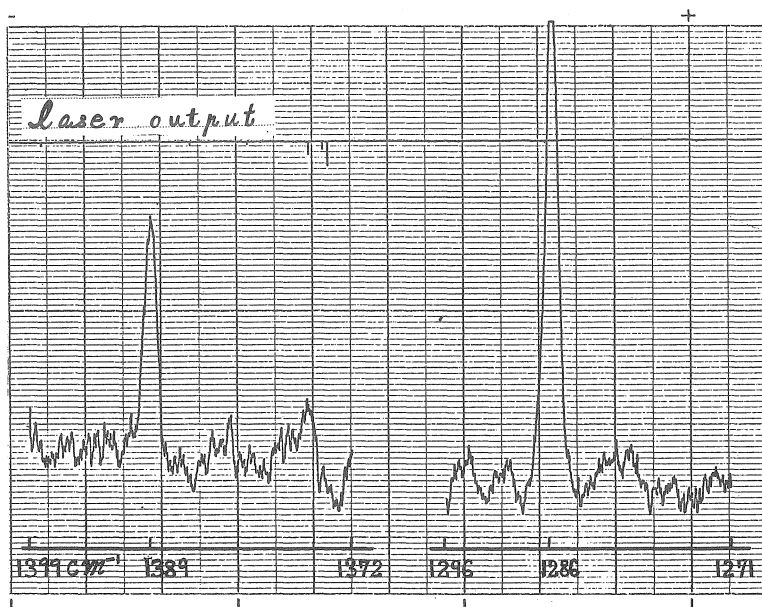


Fig. 6. Vibrational Raman spectrum of CO₂.
Pressure: 400 torr, slit width: $500\mu=1\text{cm}^{-1}$, time constant: 50 sec.

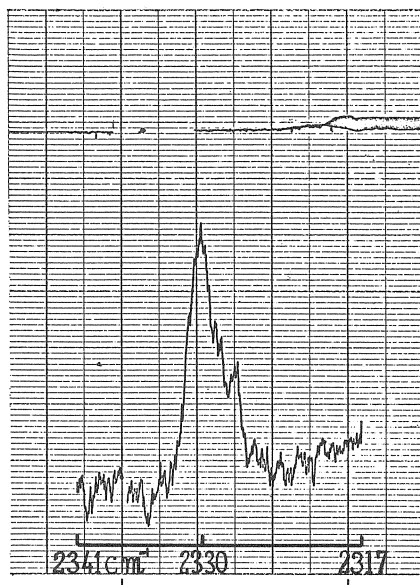


Fig. 7. Vibrational Raman spectrum of N₂ in air.
Slit : $500\mu = 1\text{cm}^{-1}$, time constant : 50 sec.

each part between b and c in the incident laser beam is collected to the part a by multiple reflection at the mirrors M_1 , M_2 and M_3 . Namely, in addition to the bright pencil of part a in the incident beam, that of the part between b and c also contributes to the observation of Raman scattering. Each mirror was adjusted with four screws mounted on the back of the mirror so carefully as to obtain best spectrum.

Raman Spectra of Gases

Some Raman spectra using the gas cell mentioned above were obtained as shown in Fig. 4 to Fig. 7. The pure rotational Raman spectra of CO₂ at the pressure of 100 torr was observed with the slit width of 0.2 cm^{-1} and the time constant of 10 sec (Fig. 5). The value of the rotational constant B was estimated to be 0.39 cm^{-1} for CO₂. This agrees with the tabulated value.⁶⁾

More refined discussion will be published elsewhere together with detailed analysis of the Raman gas cell.

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References

- 1) S. P. S. Porto and D. L. Wood, *J. Opt. Soc. Am.*, **52**, 251 (1962).
- 2) S. Matsuoka, N. Ohashi, A. Chimoto and K. Senda, *Sci. Rep. Kanazawa Univ.*, **13**, 83 (1968).
- 3) R. R. Alfano and N. Ockman, *J. Opt. Soc. Am.*, **58**, 90 (1968).
- 4) A. Weber, S. P. S. Porto, L. E. Cheesman and J. J. Barrett, *J. Opt. Soc. Am.*, **57**, 19 (1967).
- 5) T. Yoshino and H. J. Bernstein, *J. Mol. Spectry.*, **2**, 213 (1958).
- 6) J. J. Barrett and A. Weber, *J. Opt. Soc. Am.*, **60**, 70 (1970).