Unforgettable Raman*

Mitsuo Ito

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

C. V. Raman is one of the greatest scientists produced in India. His discovery of the Raman effect in 1928 was a revolution in modern science. His contribution and influence on mankind and our society are still obvious. On the other hand, Sanichiro Mizushima was a great scientist from Japan. He is famous for his work on rotational isomerism and internal rotation of molecules. He discovered for the first time, the existence of two rotational isomers, *trans* and *gauche* forms, for 1,2-dichloroethane. This work was the beginning of modern structural chemistry and spectroscopy in Japan. It is noteworthy that the concept of rotational isomerism was established in 1936 by application of Raman spectrocopy[1]. In this sense, the two great men, Raman and Mizushima, had a very close connection. Since then, ties between India and Japan in the field of molecular science were greatly strengthened and now we are enjoying very good relations between the two countries.

I have not known either Raman or Mizushima personally. However, I always feel a strong bond with them. My scientific career started from the Raman experiment. I was also involved in rotational isomerism and internal rotation problems in my later work. In the first Mizushima–Raman Lecture, I spoke about my old work, somewhat related to the work of Raman and Mizushima. This manuscript is based on my talk there. However, only the part about Raman is reproduced here and the part related to Mizushima is omitted.

My first encounter with Raman effect was in 1950, almost fifty years ago, when I was a university student. One of the subjects of student laboratory experiments was Raman spectrum of liquid carbon tetrachloride. At that time, the light source was a low pressure mercury lamp and the atomic line of mercury at 435.8 nm was used for Raman excitation. The Raman spectrum was taken photographically with a very simple prism spectrograph as shown in Figure 1. The spectrograph shown in the figure is the one used by Raman in his early work and it is now preserved in the Indian Association for the Cultivation of Science in Calcutta. At least one hour exposure time was necessary even if a high sensitive photographic plate was used. One year later, I graduated from the university and was appointed an assistant in the chemistry department. One of my duties was to take care of students doing the Raman experiment. I taught them how to take the Raman spectrum, especially how to install a photographic plate into a plate cassette in a dark room. An important part is to identify the photosensitive emulsion side of the plate using a finger under complete darkness. This side must be exposed to Raman scattering light. One day, a group of students carried out their Raman experiment under my direction. After the experiment, they showed me a completely black plate. I ordered them to repeat the experiment thinking they must have gone wrong. Then, again, a black plate resulted. I thought that the photographic plate I gave them was so old that it was already exposed to light. So I gave them a fresh new plate, with which they repeated the experiment. Again a black plate was obtained. I carefully checked their experimental procedures. There was no mistake. Finally, I asked them how they installed the photographic plate in the dark room. They said that they correctly installed the plate on the cassette after confirming the emulsion side by finger. 'Are you sure?' I asked. Then, one of the students said, 'Because you repeatedly advised us to confirm the emulsion side, after confirming the side by finger, we also confirmed it by eye by turning on the room light!' This is a real story. They were really lovely students. Later, some of them became university professors in chemistry.

The laser was invented in 1960 and was thought to be an ideal source of light for Raman spectroscopy. However, we had to wait for several years until a laser of practical use became available. In 1966, I saw for the first time a hand-made argon laser in the laboratory of a Japanese electronics company. I requested the company to give it for use in the Raman experiment. As a test, I observed the Raman spectrum of liquid carbon tetrachloride by using the 514.5 nm Ar lasing line as an exciting source. When observing the Raman spectrum dispersed by a prism spectrograph, I had a great surprise. There, I saw with my naked eye, in bright colours the Raman spectrum of carbon tetrachloride as shown in Figure 2. It was my belief that Raman lines could never be seen by the naked eye and that they could be observed only by accumulating the light energy on a photographic plate for a long time. So, the bright Raman lines were a great shock and a great revelation for me. Since
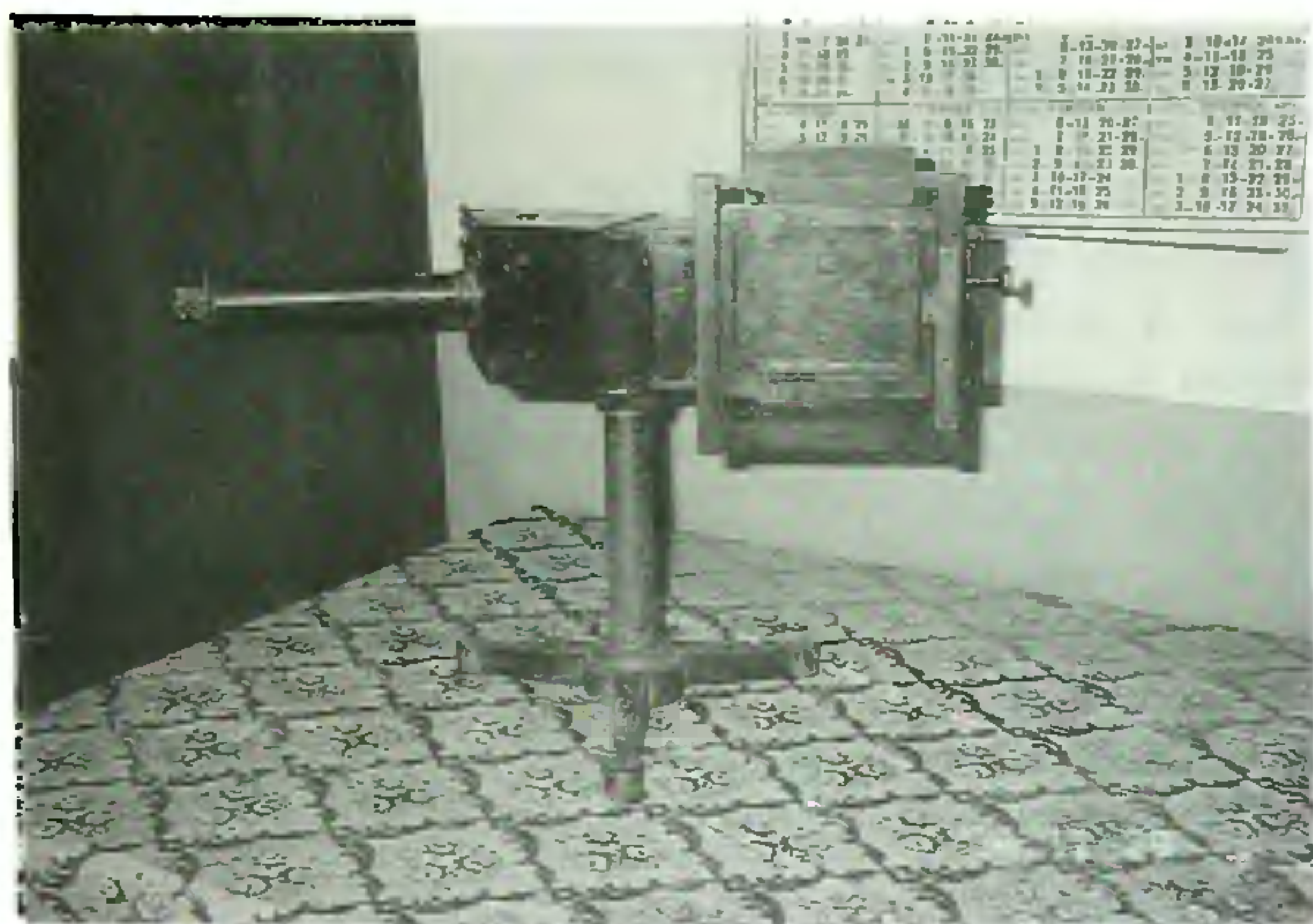

Figure 1. The prism spectrograph used by Raman in his early work.
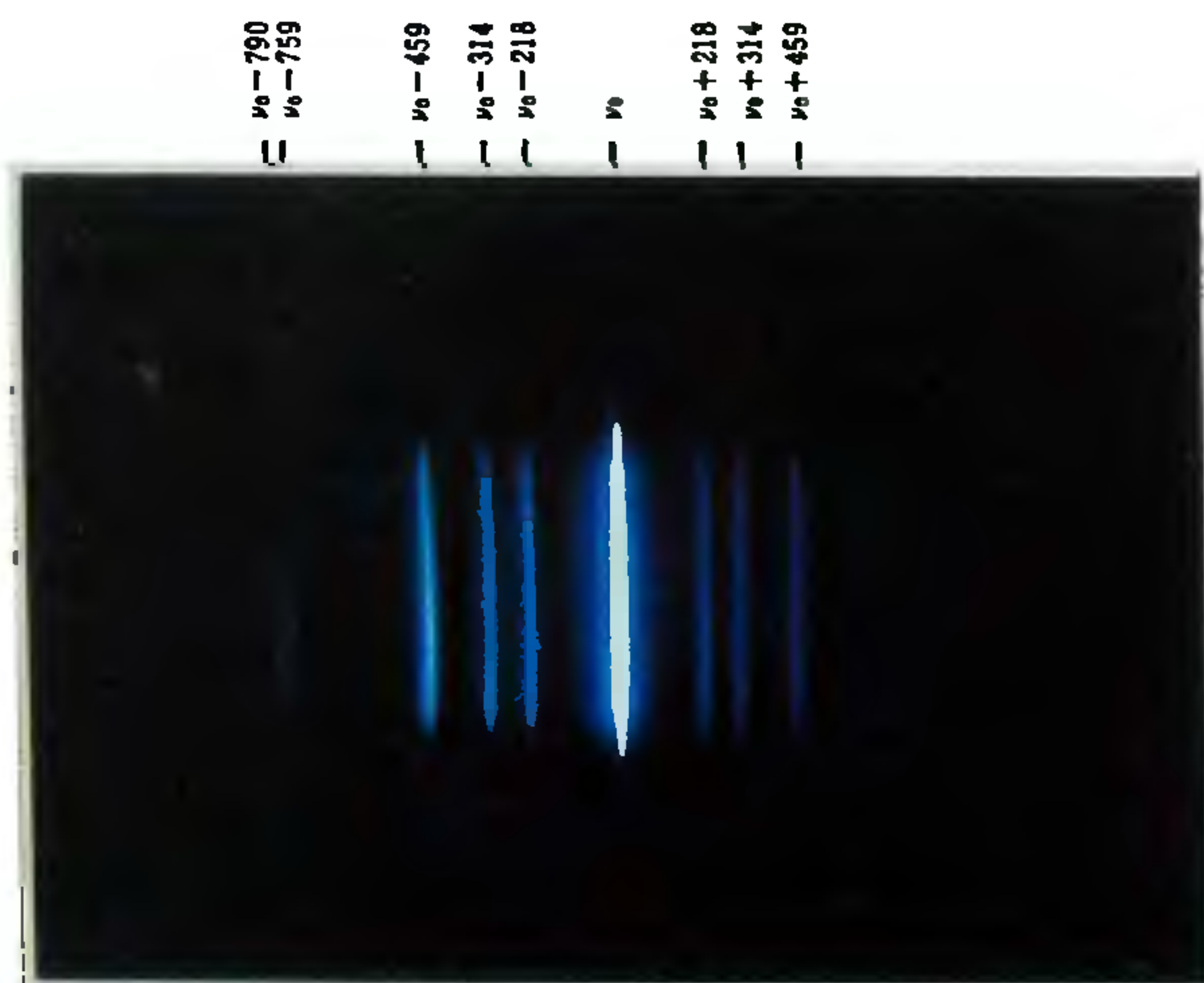
Figure 2. Raman spectrum of liquid carbon tetrachloride excited by Ar laser light at 448.0 nm.

Figure 3. Polarized Raman spectra of naphthalene single crystal.

then, I became crazy about laser Raman spectroscopy, and spent almost all my time doing the Raman experiment for about two years. At that time, I was an Assistant Professor of Tokyo University and a part of the laboratory of S. Nagakura who is practically a founder of this lectureship together with C. N. R. Rao. I escaped from all duties in Tokyo University where I draw my salary. I appreciate very much the tolerance of Nagakura, which allowed me to concentrate on the laser Raman experiment.

One of the achievements at that time was the study of polarized Raman spectra of organic single crystals. Lasers have many excellent characteristics such as good monochromaticit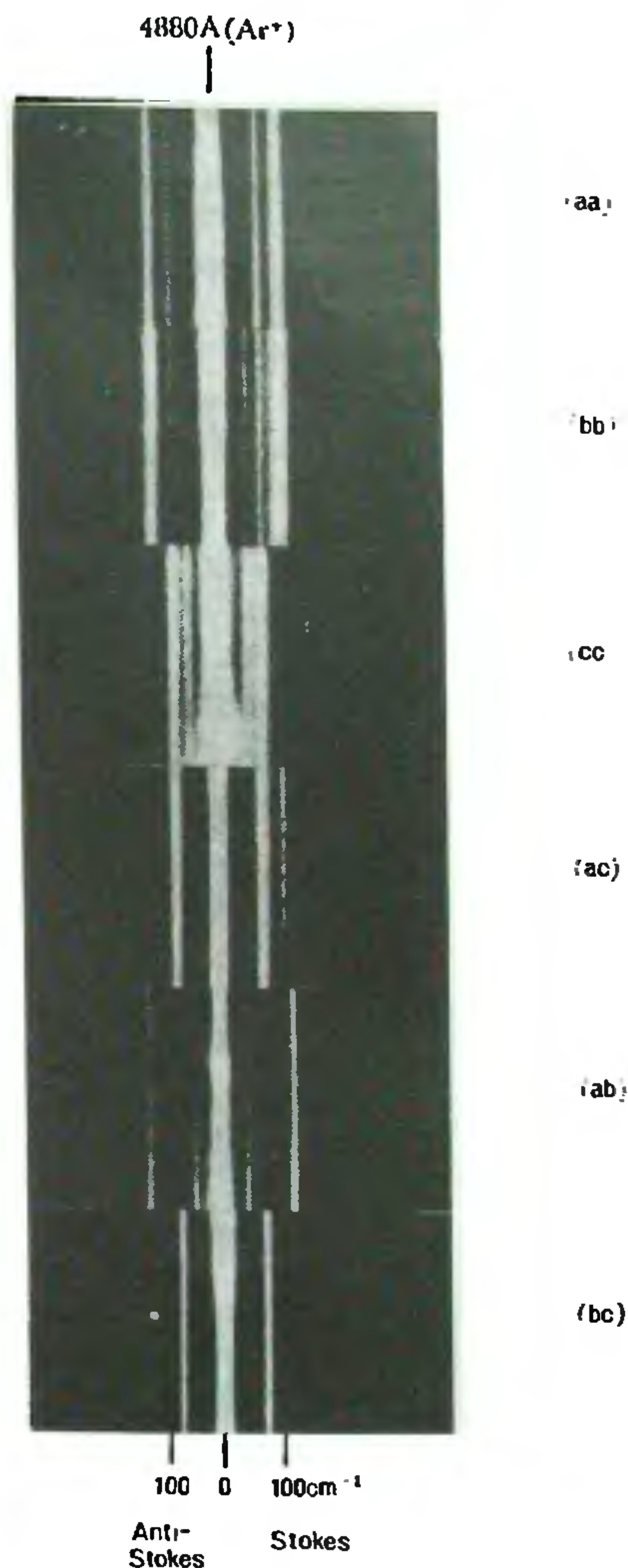y, well-defined beam direction and high intensity. In addition, laser light has excellent polarization. By using these polarization characteristics, a new type of Raman experiment became possible. Figure 3 shows the polarized Raman spectra of a single crystal of naphthalene obtained photographically[2]. The center line is the Rayleigh line of the Ar laser at 488.0 nm. The observed low-frequency Raman lines appearing on both sides of the Rayleigh line are Stokes and anti-Stokes Raman lines due to the lattice vibrations of the molecules in the crystal. Each of the six polarized spectra in Figure 3 was obtained by exciting the single crystal with Ar laser light polarized along a particular crystal axis and observing Raman scattered light polarized along one of the crystal axes. For example, the spectrum (ab) in Figure 3 was obtained by exciting the single crystal with laser light polarized along the a axis of the crystal and

then observing the scattered light polarized along the *b* axis. Therefore, the six spectra correspond to the six components of the Raman polarizability tensor of the single crystal. As seen from the figure, the Raman intensities of the lattice vibrations dramatically change by change of the polarization. From the observed polarization patterns, the individual Raman lines were uniquely assigned to the particular vibrational lattice modes. In this way, the complicated motion of the molecule in the crystal was elucidated in detail. It was also shown that the polarized Raman is very powerful in determining crystal structures.

This is only one example. Such new experiments became feasible by laser Raman and many new possibilities were opened. Then, the 1970s became a golden time of laser Raman called the Raman Renaissance. It was a pity that Raman passed away in 1970 when the Raman Renaissance had just started. He was 82 years old.

Since my first encounter with the Raman effect, I have always been puzzled about the mechanism of Raman scattering. According to Bohr's principle, light is emitted from a molecule when the molecule in an excited level undergoes a transition to a lower level. However, in the Raman effect, a molecule is not transformed to an excited level, because usually we have no level at the place reached by exciting light. Nevertheless, Raman scattered light is emitted as if such a level existed. The Raman effect is thus a strange phenomenon.

According to text-books, Raman effect is a phenomenon of interaction between a molecule and light explained by the second order perturbation theory. The theory shows that intensity of a Raman line due to the transition from *g* state to *f* state of a molecule (usually *g* and *f* states are the zero-point level and a vibrational level, respectively, of the electronic ground state of a molecule) is given by

$$I_{g \to f} \propto \sum_m \langle g|r|m \rangle \langle m|r|f \rangle / E_m - h\nu_{exc},$$

where *m* is an excited state of the molecule (practically an electronic excited state of the molecule), $\langle g|r|m \rangle$ is the transition moment between *g* and *m* states and $\langle m|r|f \rangle$ is the transition moment between *m* and *f* states. To have Raman intensity, the matrix elements should be simultaneously non-zero. We need such an electronic excited state from which transition is allowed to both *g* and *f* states. E_m is the energy of *m* state, $h\nu_{exc}$ is the energy of exciting light. The Raman intensity is a sum of contributions of all possible *m* states, that is, all possible electronic excited states. Therefore, the mechanism of Raman scattering is very complicated. However, when we can select the exciting light whose energy is very close to a particular *m* state, a term associated with this particular *m* state becomes dominant because the de-

nominator of this term becomes very small. The Raman spectrum observed under such a condition is called Resonance Raman.

In the 1970s, laser technology showed great progress and lasers of various lasing frequencies became available. As a result, it became possible to carry out resonance Raman experiment for many molecules. In 1972, we carried out resonance Raman experiment for pyrazine ($C_6H_4N_2$) (refs 3, 4). The electronic absorption spectrum of pyrazine vapour is shown in Figure 4. There are two absorption regions at 320 nm and 260 nm. The absorption at 320 nm is due to the transition from the ground electronic state to the lowest electronic excited state of $n\pi^*$ character, while the absorption at 260 nm is due to the transition to the second lowest excited state of $\pi\pi^*$ character. At that time, we had an argon laser whose lasing line was 514.5 nm, which is far from these electronic excited states. Therefore, the Raman spectrum obtained by using the Ar 514.5 nm line is one under non-resonant condition, which is the usual condition for the ordinary Raman experiment. The Raman spectrum obtained is shown at the top of Figure 5. In 1972, we hand-made a nitrogen pulsed laser whose lasing line was at 337.1 nm. As seen from Figure 4, this line is very close to the $n\pi^*$ electronic excited state. Therefore, by using the nitrogen laser, we can obtain the Raman spectrum resonant to this particular $n\pi^*$ excited state. The spectrum obtained is shown in the middle of Figure 5. As is obvious, the relative intensities of the Raman lines in the spectrum excited by the nitrogen laser are entirely different from those of the spectrum obtained by Ar laser. A most surprising thing is the great intensity enhancement of the Raman line at 980 cm^{-1} denoted by 10a. This Raman line is very weak in the spectrum of 514.5 nm excitation, but it becomes the strongest Raman line in the spectrum of nitrogen laser excitation. Two years later, another home-made laser became available. It was
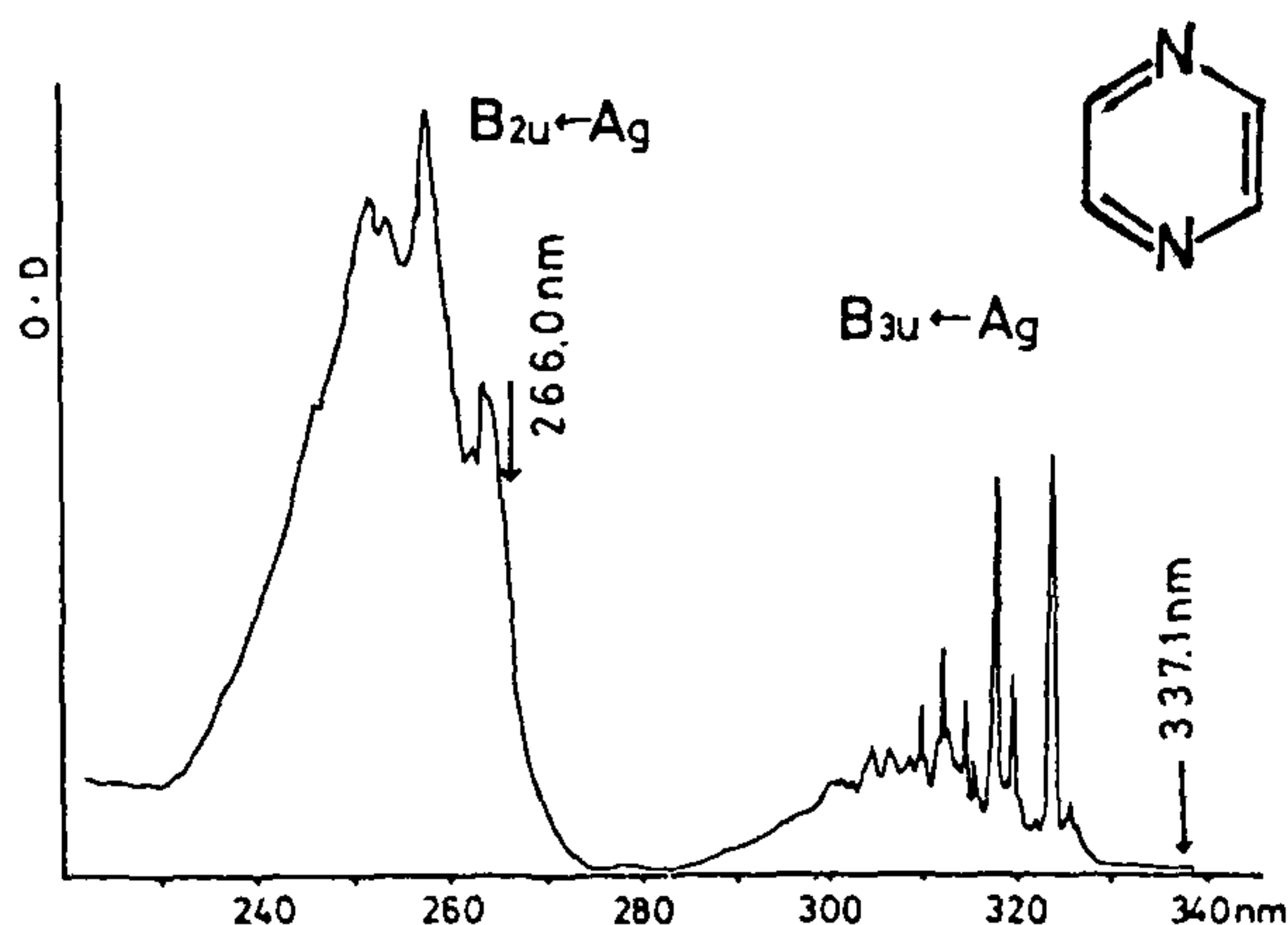

Figure 4. Absorption spectrum of pyrazine vapour. The positions of the Raman exciting lines of Figure 5 are shown by arrows.
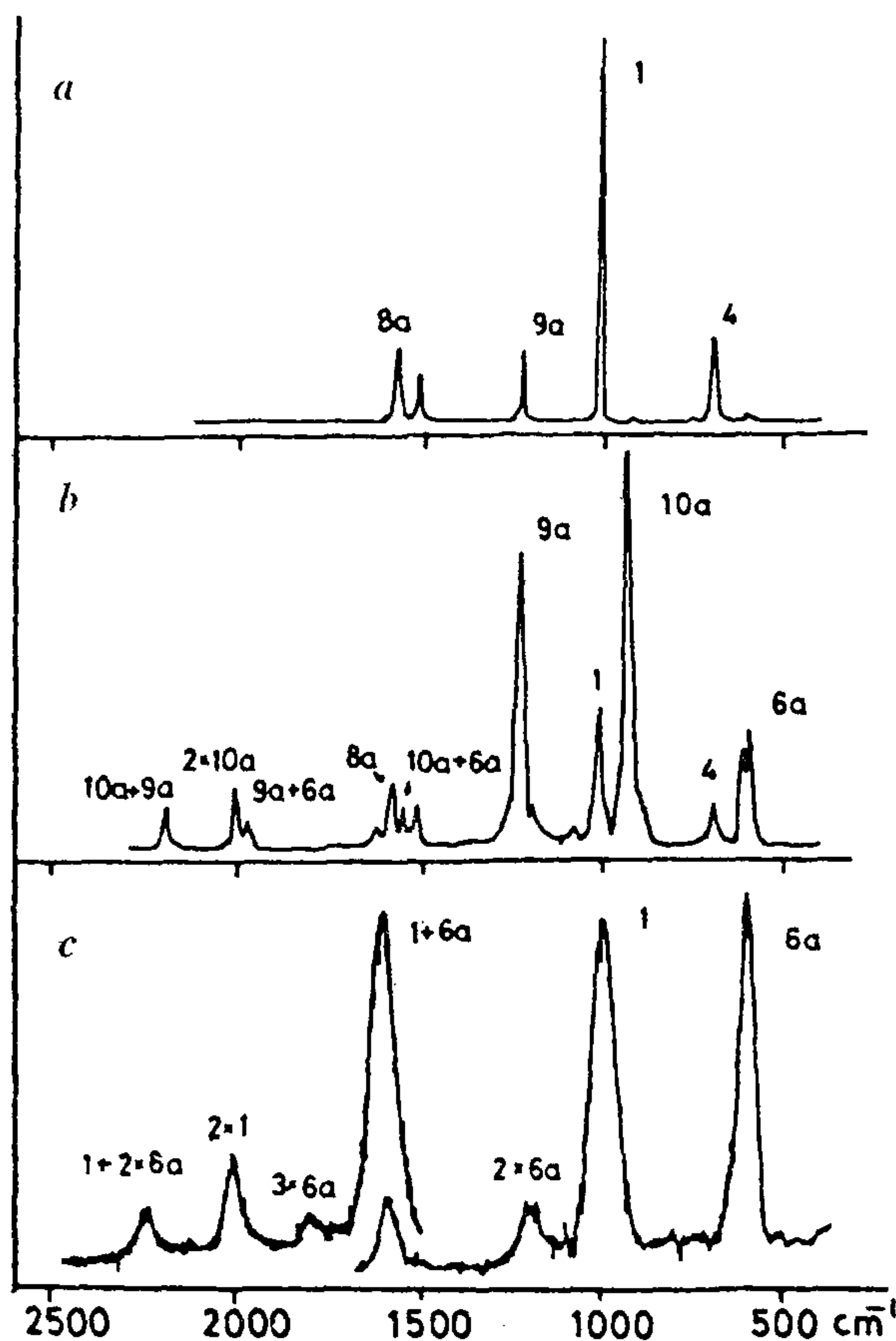
Figure 5. Raman spectra of pyrazine excited by 514.5 (a), 337.1 (b), and 266.0 nm (c) laser lines.

a frequency doubled YAG laser, whose frequency is 266 nm. This lasing frequency is very close to the $\pi\pi^*$ excited state. Therefore, by using this laser, we can obtain the spectrum resonant to this $\pi\pi^*$ state. The spectrum obtained is shown at the bottom of Figure 5. Again, the intensities of the Raman lines change dramatically. This time, the Raman lines at about 1000 cm^{-1} and 600 cm^{-1} show great intensity enhancement.

The fact that the Raman intensity changes dramatically among the spectra resonant to different electronic excited states clearly proved the mechanism of Raman scattering predicted by theory. It should be emphasized that the Raman frequency itself is the frequency of

molecular vibration in the electronic ground state, but Raman intensity comes from electronic excited states, showing a close connection between molecular vibration and electronic states of a molecule. Since the Raman intensity comes from electronic excited states, we can obtain much valuable information on the electronic excited states from the Raman intensity. It should be stressed again that Raman spectroscopy which was a tool for the study of vibrational states of a molecule in its ground electronic state is also a very powerful tool for the study of electronic excited states of the molecule.

Until 1970, molecular spectroscopists in chemistry were broadly divided into two groups. One is spectroscopists who are mainly interested in vibrational states of molecules and their tool was infrared and Raman spectra. Another is those interested in electronic states of molecules and their tool was electronic absorption spectroscopy. The two groups were quite independent and their interaction was very weak. However, the situation completely changed with resonance Raman studies, which clearly showed a very close mutual relation. Since then, the boundary between the two groups, in other words, the Born–Oppenheimer approximation was removed. In this sense, Raman played a very important role in unification of vibrational and electronic spectroscopists.

My old experience with Raman spectroscopy has been mentioned. Since 1980, I have been more involved in other laser molecular spectroscopies. So my career in Raman spectroscopy was not further extended. However, many sophisticated laser molecular spectroscopies have recently been developed and they are widely used in various fields in chemistry, physics and biology. It is realized that many of these newly-developed spectroscopies are based on multi-photon processes. Since the Raman effect is a two-photon process, it is the most fundamental multi-photon process. The big harvest of new laser molecular spectroscopies we are now enjoying is simply produced by extension of the Raman effect. We should never forget that this wonderful harvest was first seeded by the great man, C. V. Raman.

1. Mizushima, S. and Morino, Y., Bull. Chem. Soc. Jpn., 1942, 17, 94–99.
2. Suzuki, M., Yokoyama, T. and Ito, M., Spectrochim. Acta, 1968, A24, 1091–1107.
3. Suzuka, I., Mikami, N., Udagawa, Y., Kaya, K. and Ito, M., J. Chem. Phys., 1972, 57, 4500–4501.
4. Suzuka, I., Udagawa, Y. and Ito, M., Chem. Phys. Lett., 1979, 64, 333–336.