

System for Precise Measurement in Inverse Raman Spectroscopy

Y. Taira*, S. Amano**, and H. Takuma

The Institute for Laser Science, The University of Electro-Communications,
Chofugaoka 1-Chome, Chofu, Tokyo, 182 Japan

Received 8 December 1988/Accepted 24 December 1988

Abstract. A system for precise measurement was developed for inverse Raman spectroscopy, using a cw argon laser and a pulsed dye laser pumped by a YAG laser. The frequency accuracy was assured by monitoring the frequency of both of the lasers with an iodine fluorescence cell or a Fabry-Perot etalon dynamically calibrated by a stabilized HeNe laser. The spectrometer system employed a digitally controlled mechanism to handle the complicated measurement procedure and hence to reduce the overall measurement time. The performance of the system was tested by measuring the CH_4 ν_1 lines and the H_2 Q(1) line.

PACS: 07.65. – b, 33.20.Fb, 35.80. + s

Both high resolution and high signal intensity in Raman spectroscopy are obtainable by methods of coherent Raman spectroscopy [1, 2]. Of these methods, Stimulated Raman Gain (SRG) techniques, including inverse Raman spectroscopy [3], have several advantages, such as laser-linewidth-limited high resolution and no requirement for phase-matching. The signal is proportional to the differential Raman cross-section, whereas in the Coherent Anti-Stokes Raman Spectroscopy (CARS) method [4], it is the square of the third-order nonlinear optical susceptibility. Since the real part of the nonlinear susceptibility contains a nonresonant term, interference between the Raman term and the nonresonant term in CARS sometimes makes interpretation of the result complicated. Furthermore, SRG techniques are more suited to high-resolution measurement. Because the signal intensity is proportional to the intensity of the probe beam in SRG, a single-mode cw probe can be used without any loss of sensitivity. Therefore a combination of a single-mode cw laser and a narrow-band pulsed laser is widely used for high-resolution SRG measurement.

One of the difficulties of using nonlinear optical spectroscopy to achieve high resolution is that the frequency of the lasers tends to drift during lengthy measurements. Although the frequency stabilization of lasers is desirable in an ultra-high-resolution measurement, simple monitoring of the frequency is sometimes sufficient in a moderate resolution of over 100 MHz. Since the line width of a pulsed dye laser of several nanoseconds is usually several hundred MHz, the monitoring technique is widely applicable to coherent Raman spectrometers based on such a pulsed dye laser. A study of the drift of the pulsed dye laser and the single-mode argon laser placed in our laboratory with usual air-conditioning showed that the center of the oscillating frequency is stable in the short term but tends to drift unidirectionally in a period of one hour, and also that the frequency is quite different from day to day. Because ordinary point-by-point measurement took a few hours in our case, reduction of the overall measurement time is also important for improving the accuracy as well as the monitoring of the frequency.

In our stimulated raman gain measurement system using a cw probe laser and a pulsed pumping laser, a frequency drift of a few GHz in a single-mode cw argon laser can be monitored by a repetitively scanning Fabry-Perot (FP) interferometer. The frequency of the dye laser in a sweeping operation can be monitored by

* Present address: IBM T. J. Watson Research Center, P.O. Box 218 Yorktown Heights, NY 10598, USA

** Present address: Hoya Co., Akishima, Tokyo, Japan

an iodine fluorescence spectrum. In combining these monitoring systems with the basic Raman gain spectrometer, it is very convenient to use a computer system for a prototype measurement system. With the computer system it is possible to collect data from various parts of the system and control the equipment according to the prescribed experiment procedure. According to this concept we have developed an inverse Raman spectrometer with good frequency stability. Its constitution, operation, and performance will be described in this report.

1. Detailed Constitution

The optical part of the system was based on the inverse Raman spectrometer that was used to measure the ν_1 Raman line of CH_4 [4, 5]. A frequency monitoring system for a dye laser and an argon laser and controller including a computer were added to the basic spectrometer. The complete setup for measurement is shown schematically in Fig. 1. The probe beam was the frequency-fixed output of a cw argon laser (Spectra-Physics SP 161) with an intra-cavity etalon (SP 589), where the line width was from 10–50 MHz. The pulsed pumping beam was tunable light from a pulsed dye laser (Moletron DL 18P) pumped by a Q-switched YAG laser (Moletron MY 34), which operates at 10 Hz. The line width of this Hänsch-type dye laser output was about 0.03 cm^{-1} when its optional intra-cavity etalon was used. The fine tuning of the dye laser was carried out by means of a pressure scan.

The probe beam was partially reflected and was directed to the scanning Fabry-Perot interferometer (Burleigh RC-110) with a mirror spacing of 1 cm, which gave a free spectral range of 15 GHz. Since the thermal drift of the FP monitor was not negligible even when

we put a thermo-shield box over the FP, a beam from a stabilized HeNe laser (Tropel model 100), which has a frequency stability of less than 100 MHz, was used to calibrate the spacing of the FP etalon. A part of the beam of the dye laser was also set to pass the FP as a reference and as a monitor of the dye laser line width. Because the mirrors of FP were of a type with a wideband reflectivity of over 400–700 nm, we were able to use a single FP with an aperture of 50 mm to measure three beams of different wavelengths simultaneously. Another part of the dye laser beam was set to pass through an iodine fluorescence cell. The fluorescence intensity was detected by a photo transistor, whose signal was recorded in the computer after AD conversion.

The sample cell was made of a stainless steel pipe of 20 mm inner diameter and two side flanges with a fused silica window of 10 mm thickness. This sample was tested at pressures of up to 70 atm and was normally used at pressures of up to 40 atm. The main beams of the dye laser and the argon laser were combined carefully by using a dichroic mirror so that they were parallel, and were then introduced into the sample cell without any focusing lenses. A dichroic mirror and two prisms were placed at the exit of the sample cell so that beams other than probe beam would be blocked before detection. Assuming that the two beams are well overlapped within the interaction space and that the small signal assumption holds, the absolute Raman gain coefficient γ is determined using the relation

$$\gamma L = \frac{\int_{-\infty}^{\infty} (I_2(t)/I_1 - 1) dt}{\int_{-\infty}^{\infty} I_0(t) dt}, \quad (1)$$

where $I_2(t)$ is the output probe light intensity, I_1 the unperturbed probe intensity, $I_0(t)$ the intensity of the pumping pulse, and L the interaction length. The

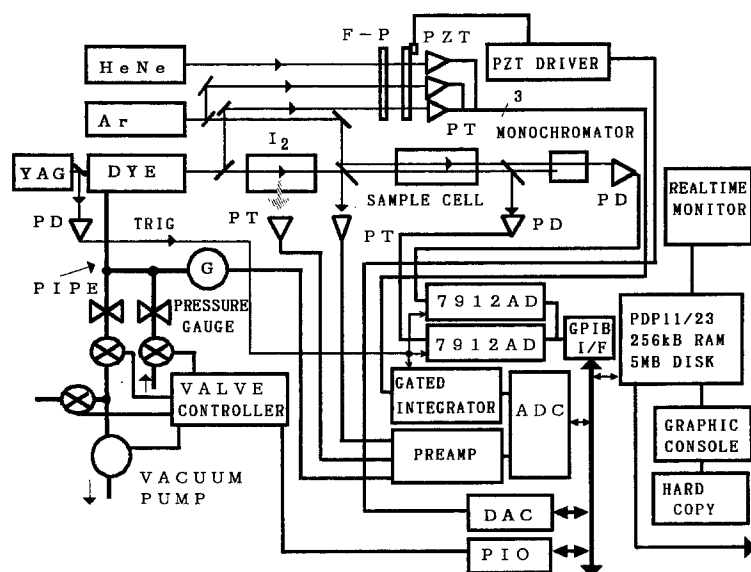


Fig. 1. Experimental setup for the inverse Raman spectroscopy and computer-controlled data recording system. (PT: photo transistor, PD: photo diode, F-P: Fabry-Perot interferometer, ADC: analog to digital converter, DAC: digital to analog converter, PIO: parallel input and output)

intensities of the fluorescence and the beams through the FP were all monitored with photo-transistors. The Raman gain or inverse Raman signal in the probe beam was detected by a PIN diode connected to an FET probe (Tektronix P 2910) with a $470\ \Omega$ termination load connected. The magnitude of the load register was set in order to obtain maximum voltage sensitivity while keeping the rise and fall times of the detection system at less than 2 ns. The part of the dye laser beam used as a reference was also detected by a PIN diode. The outputs of these two PIN diodes for the probe output and the dye laser pulse were connected to two transient digitizers (Tektronix 7912 AD).

We noted the following features in the experimental condition: (1) The steady-state intensity level of the argon laser fluctuated rather slowly with a period of a second; (2) the observed signal dip in the argon laser intensity was very small (less than 5%) compared with the dc intensity level, and thus the small-signal assumption would be appropriate for the analysis [5]. We therefore made the signal connected to the transient digitizer ac-coupled in order to magnify the dip by offsetting the ground level far below the viewing range. Since the dc-level variation of probe light in the PIN diode was difficult to detect with the transient digitizer in the ac-coupling mode, we also used another slow detector of a photo transistor to record the dc-level independently.

We took the following steps for relative calibration of detectors for the probe light: (1) we determined the height of the argon laser dc-level by setting the coupling mode dc-coupled and the sensitivity low enough so that the ground (null) level and dc level were both seen within a display range of the transient digitizer; (2) we measured the dc-level of the photo transistor with the AD converter; and (3) we compared these two values and obtained the conversion coefficient. The use of the transient digitizer was very effective for determining the area of the dip in the probe beam by calculating the area surrounded by the base level and the waveform. Since the base-level (dc-level) position change was taken into account in every measurement cycle, the obtained area was correct even when the intensity of the cw probe light fluctuated appreciably. The base level of the probe light was determined from the leading part of its waveform recorded in the transient digitizer. Then we were able to obtain a time integral of the deviation of the waveform from the base level by adding the appropriate parts of the digitized waveform and subtracting the base level. We obtained the energy of the dye laser pulse in a similar way except that the base level was always constant. In this way we obtained both the area of the dip and the energy of the dye laser pulse in every measurement cycle. We recorded these values in the

disk file of the controller computer, together with the input and output levels of the beams to the FP and the output of the pressure transducer connected to the dye laser tuning vessel.

Because a preliminary test showed that 250 ms was necessary to complete one cycle of the measurement including waveform digitization, transfer, analysis, and recording, at most a third of the laser shots could be used for measurement in our 10 Hz repetition rate system. We decided to use a fourth of the laser shots for obtaining the Raman signal so as to allow some margin in the processing system. The outputs from the frequency monitoring system included outputs from the FP and the signal from the iodine fluorescence cell. All these signals were amplified, sampled, held, and then AD converted. The timing of the sampling and conversion was set by using a built-in trigger-delay generator. The FP was piezoelectrically scanned synchronously to the laser shot. A cycle of sawtooth ramp voltage for FP scanning was usually set to end after 400 laser shots. The total span of the sweep was set so that at least three peaks would be visible in all the FP traces for three independent beams. Although only a fourth of the laser shots could be utilized for obtaining Raman gain in the speed of the present data collection system, we also used the remaining three fourths of the laser shots to improve the accuracy of the frequency monitoring. Thus all the laser shots contributed to the frequency monitoring.

The frequency of the dye laser was set prior to the measurement by using a grating and an intra-cavity etalon. A tuning range of more than $4\ \text{cm}^{-1}$ was covered by scanning the pressure from 100 to 600 Torr of air. The pressure in the vacuum vessel was controlled by powered valves and was monitored continuously by means of a pressure transducer. We tried two measurement procedures: stepwise scanning and continuous scanning of the dye laser pressure. The continuous scanning was superior in overall time and accuracy and was eventually adopted. In the stepwise scanning mode of the dye-laser frequency, it was difficult to set the tuner pressure to the predetermined value by a simple on-off control of valves because of the needed time of the pressure to settle. Therefore a period was required for pressure adjustment. Furthermore, this time was wasted because we could not make any measurements, and the total measurement time was longer than in the other case. In the continuous scanning mode the speed of the frequency sweep was controlled by adjusting the opening of the leak valves in the pressure controller. We set the opening so that the entire scanning would be completed in 15 min. We chose to increase the mode of the pressure scanning rather than decrease it, because in this way the operation of the vacuum pump to

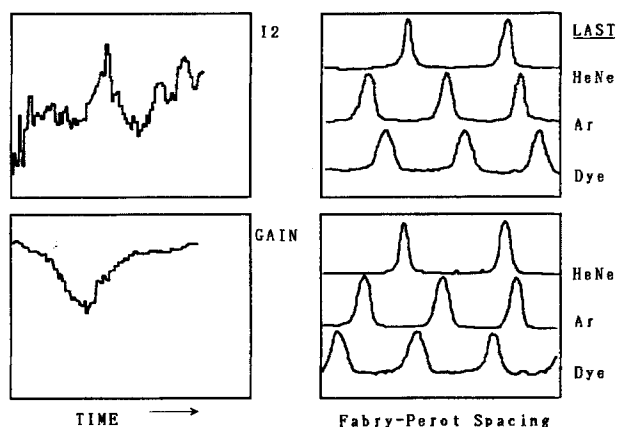


Fig. 2. Example of an online monitor display. Successive two traces of the Fabry-Perot fringes of the dye, argon, and HeNe lasers are shown on the right. Iodine fluorescence and the inverse Raman signal are shown on the left. The traces are repetitively renewed and re-scaled when overflow happens

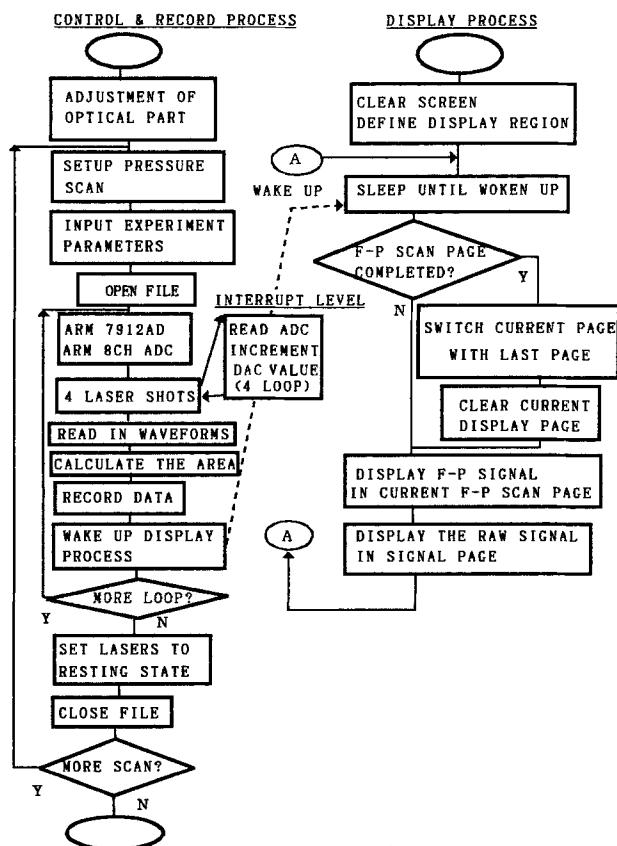


Fig. 3. Flowchart of the measurement. The control and record process (job) and the display process (job) proceed independently

evacuate the vessel was necessary only in the presetting period but not at the time of measurement.

An online monitor display was included in the system so that we could see what spectrum had been recorded and the real time status of the laser line widths. The screen of the online monitor was divided

into two parts, one for a display of the raw values of the Raman signal and the iodine fluorescence, and the other for the three FP outputs for the three lasers. The latter part had two areas that could be switched, one for the data being currently renewed, and one for the previous scan, so that we could see an entire page of the FP monitor at any time, as shown in Fig. 2. The essential operation of the measurement is shown in Fig. 3 as a flowchart. The program was divided into two separate jobs, one for controlling and recording and the other for monitoring. These jobs were set to run simultaneously, and only the former is essential for measurement. Finally the collected data were analyzed after the completion of the measurement.

2. Performance of the System

First we tested the performance of the system by measuring the ν_1 line of CH_4 . The raw data for 25 atm of CH_4 is shown in Fig. 4. The raw data of the measurement was processed to give an entire spectral profile as a function of the tuner pressure, where the signal was normalized by the pumping energy and dc levels of the probe for each data point. The raw data of the fluorescence and FP monitors were processed in a similar way. The accumulated results indicated that the position of the argon laser was fixed relative to the HeNe laser during a single measurement lasting 15 min, and that the iodine fluorescence spectra for several scans were almost identical except for the horizontal position. Thus, as far as the central 2 cm^{-1} part is concerned, the inverse Raman signal profile could be adjusted simply by sliding the horizontal origin according to the indication of the fluorescence and the FP record for the argon laser. The processed Raman gain profile is shown in Fig. 5, where normalization and smoothing were applied. The measurement showed a good S/N ratio down to 100 Torr of a CH_4 sample, using a cell of 1 m in length. Use of a focused beam or use of multipass cell will improve the sensitivity further. The detailed results for CH_4 will be reported elsewhere [6].

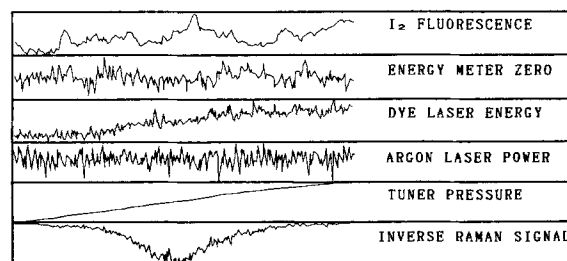


Fig. 4. Time series display of raw data stored in the disk file. The titles of each trace are shown on the right. Each trace has been normalized so that minimum and maximum fit exactly within its display region

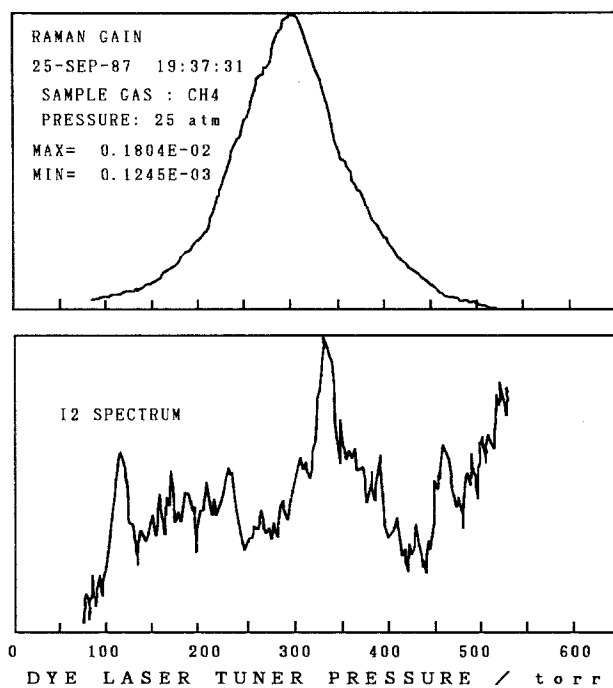


Fig. 5. A processed example of the inverse Raman gain profile (top) and the iodine fluorescence spectrum (bottom)

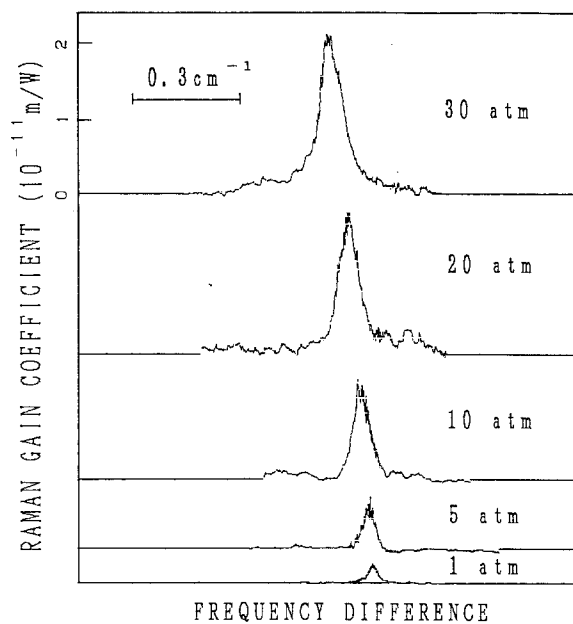


Fig. 6. Raman line shape of H_2 Q(1) line at several pressures. Note that the Raman shift decreases to the left in this graph

The system were also tested for an H_2 Q(1) line, which has a Raman shift of 4155 cm^{-1} and a very narrow line width. The necessary scanning width was far less than for CH_4 . Slow scanning was easily achieved by throttling the needle valve in the pressure controller of the dye laser. The line shape, line width, and variation of the center position of H_2 are shown in

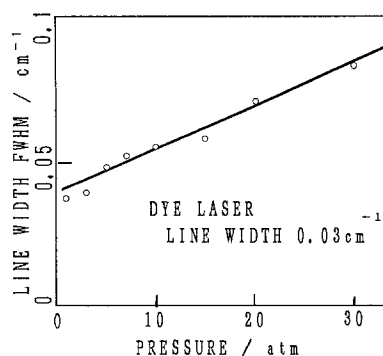


Fig. 7. Pressure dependence of the width of H_2 Q(1) line. Note that the observed width is shown in the graph, i.e. the line width includes the effect of finite width of the dye laser

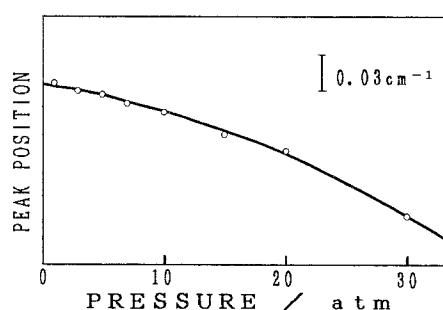


Fig. 8. Variation of the peak position of H_2 Q(1) line as a function of the pressure

Figs. 6–8. The peak position variation in several measurements over a few days showed that this type of measurement system allows us a reproducibility than 0.01 cm^{-1} , which is three times the line width of the laser. The absolute Raman cross-section of the hydrogen line was determined to be

$$(d\omega/d\Omega)_{488 \text{ nm}} = (7.0 \pm 0.7) \times 10^{-33} \text{ m}^2/(\text{mol} \cdot \text{ster}). \quad (2)$$

The line width increased linearly in relation to the pressure, with a proportional constant $0.016 \text{ (cm}^{-1}/\text{atm)}$ which agrees with the results of Toich et al. [7], while its zero-pressure width could not be determined since the value approached the resolution.

3. Future Extensions and Conclusion

The system performance will be greatly improved if we use all the laser shots at 10 Hz, instead of using a fourth of them as at present for Raman gain measurement. A preliminary test in which we replaced the current CPU board (DEC PDP 11/23), which has an FPU chip, with a higher-performance software-compatible PDP 11/73 CPU board, which has its optional floating point accelerator chip installed, showed that the total measurement time is halved even without any change in the software. A detailed study of the time spent on

the measurement cycle also showed that much time was wasted in the General Purpose Interface Bus (GPIB) transaction to transfer waveforms between the computer and the transient digitizers, and that further improvement in speed would be possible by changing the control scheduling to suit the faster CPU. These changes will enable full use to be made of 10 Hz laser shots, and as a result a single-scan measurement over 4 cm^{-1} with better than 1 GHz resolution will be completed in about 4 minutes.

To summarize, we developed a Raman-gain-type spectrometer with high accuracy and high speed. A frequency monitoring system was the key to assuring the accuracy of the frequency. We described the system constitution and the measurement procedure. The performance test in the inverse Raman measurement for the CH_4 ν_1 line and the Q(1) line of H_2 showed that

the frequency resettability was better than the system resolution of 0.03 cm^{-1} .

References

1. M.D. Levenson: *Introduction to Nonlinear Laser Spectroscopy* (Academic, New York 1982)
2. Y.R. Shen: *The Principle of Nonlinear Optics* (Wiley, New York 1984)
3. A. Owyong: In *Chemical Applications of Nonlinear Raman Spectroscopy*, ed. by A.B. Harvey (Academic, New York 1981) p. 281
4. Y. Taira, K. Ide, H. Takuma: *Chem. Phys. Lett.* **91**, 299 (1982)
5. Y. Taira, F. Uchikoba, H. Takuma: *Jpn. J. Appl. Phys.* **26**, 1807 (1987)
6. Y. Taira, S. Amano, H. Takuma: Submitted
7. A.M. Toich, D.W. Melton, W.B. Roh: *Opt. Commun.* **55**, 406 (1985)