Factors Determining the Stability, Resolution, and Precision of a Conventional Raman Spectrometer

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We verified the performance of a conventional Raman spectrometer, which is composed of a 30 cm single polychromator, a Si based charge-coupled device (CCD) camera, and a holographic supernotch filter. For that purpose, the time change of the peak positions of Raman spectra of naphthalene and fluorescence spectra of ruby (Cr-doped Al₂O₃) were monitored continually. A time-dependent deviation composed of two components was observed: a monotonous drift up to 0.4 cm⁻¹ and a periodic oscillation with a range of 0.15 cm⁻¹. The former component was stabilized at approximately 2000 s after the CCD detector was cooled, indicating that incomplete refrigeration of the CCD detector induced the drift. The latter component synchronized with the periodic oscillation of the room temperature, indicating that thermal expansion or contraction of the whole apparatus induced this oscillation. The implemental deviation is reduced when measurements are conducted using a sufficiently cooled CCD detector at a constant room temperature. Moreover, the effect of the room temperature oscillation is lowered in a spectrum acquired over a duration that is longer than one cycle of this oscillation. Applying the least squares fitting method to carefully measured spectra enhanced the precision of the determination of the peak position to 0.05 cm⁻¹ using the spectrometer with pixel resolution of 1.5 cm⁻¹.

Index Headings: Spectrometer; Charge-coupled device detectors; CCD detectors; Resolution; Precision; Raman spectroscopy; Stability; Temperature effect.

INTRODUCTION

Raman spectroscopy has been applied to a wide range of scientific and engineering fields using miniaturized and simplified spectrometers comprising a notch filter, a CCD detector, and a single polychromator. These spectrometers have high signal throughput at low laser power. Consequently, they are useful for micro Raman spectroscopy, including scanning near-field optical microscopy (SNOM), which detects weak photon signals from the sample surface with a spatial resolution of less than 0.5 μm.

In some cases, high resolution in wavenumber is also necessary for Raman spectroscopy. For example, stress distributions of materials are studied by observing subtle frequency shifts in Raman spectra using micro Raman spectrometry.1-3 Pressure dependences of Raman and fluorescence spectra are used to estimate stress.4-9 Residual stresses in geological samples have also been studied using micro Raman spectrometry.10-15

The resolution of spectral measurements generally depends on the focal length of the spectrometer, its dispersion, and the pixel density of the CCD detector. Using a larger spectrometer attains a higher resolution, but the use of such large devices is limited to specific Raman users in terms of their space and cost. Furthermore, the low signal efficiency of such large spectrometers can be a disadvantage for analyses of low Raman signals. Alternatively, curve-fitting techniques are widely used to produce apparent high resolutions. This technique can enhance the practical frequency resolution for peak positions by approximately ten times.10 Such a high spectral resolution is effective only when it is associated with the high precision of Raman analyses and frequency calibration of the relevant accuracy. However, these factors (resolution, precision, and accuracy) are affected by slight changes in instrumental conditions. For example, the alignment of a spectrometer drifts because of slight changes in room temperature, electric power conditions, etc.16,17

We have encountered two kinds of unstable behavior when measuring Raman spectra using our conventional downsized Raman spectrometer. One was a monotonous drift of a peak position. Figure 1 shows the Raman peak position of the O–H stretching mode (3677 cm⁻¹) of a natural mineral: talc (Mg₃Si₄O₁₀(OH)₂). These data were obtained as a function of time after starting the cooling of the CCD detector. Each data point is an averaged value of three repeated measurements. The peak position shifted monotonously for approximately 0.2 cm⁻¹ (corresponding to 0.13 pixel number in the condition of this experiment) in several hours (about 15 000 s); that value was considerably larger than the standard deviation of the measured values (approximately 0.05 cm⁻¹).

Another unstable behavior was detected as periodic noise in mapping data. Figure 2 depicts fluorescence intensity (Fig. 2a) and the peak position (694 nm) mapping (Fig. 2b) of the fluorescence spectrum of an Al₂O₃/ZrO₂ eutectic composite. The details on the measurements will be published elsewhere.18 These mapping data were obtained simultaneously using SNOM. Since the peak position of the fluorescence line (694 nm) of Al₂O₃ is widely used as a pressure scale,19 distributions of local residual stress are expected to be visualized in Fig. 2b. However, the obtained image was remarkably perturbed by periodical noise. In this experiment, scanning was undertaken along each horizontal line every 66 s. Spectra were acquired on the 128 (vertical direction) × 40 (horizontal direction) grids. Results show that the periodic noise was observed only in the mapping of the peak position. Its oscillation range was approximately 9 lines (corresponding to approximately 10 min), indicating that the noise is unrelated to the sample heterogeneity. It is caused by the spectrometer itself.

To clarify the causes of the large drifts and periodic noise in the peak positions of the spectra, we monitored the spectrometer in detail using semi-continuous measurements of Raman spectra at an identical sample point. Based on those results, the precision in determining the peak positions for the conventional Raman spectrometer was evaluated.
EXPERIMENTAL PROCEDURES

In the present study, all spectra were obtained in the confocal mode using a Raman microprobe spectrometer. This system is composed of a 30 cm single polychromator (250is; Chromex), an Ar ion laser (5500A; Ion Laser Technology Inc.), and a Si based charge-coupled device (CCD) camera with 1024 × 128 pixels (DU-401-BR-DD SH; Andor Technology). The CCD camera was electronically cooled at −70 °C using a Peltier device. The Rayleigh line was removed using a holographic supernotch filter (HIPF-514.5-1.0; Kaiser Optical Systems, Inc.). The entrance slit width of the spectrometer was 130 μm. Scattered light was dispersed using a grating with 1800 grooves per millimeter. The spectral resolution was approximately 1.5 cm⁻¹ per pixel. Samples were excited using 514.5 nm emission of an Ar ion laser. The laser power was 5 mW at the sample surface, which is sufficiently below the threshold for the heat-induced spectral change.

Five Raman bands of naphthalene (C₁₀H₈) at 513.8 (v1), 763.8 (v2), 1021.6 (v3), 1382.2 (v4), and 1464.5 (v5) cm⁻¹ (Fig. 3a) were used for investigating the initial large drift and periodic noise. Measurements were begun soon after the completion of cooling by the Peltier device (software allows measurements when the device reaches the preset temperature of −70 °C). Each Raman spectrum was obtained continually every 6.2 s with a 6-s exposure time. Each band was fitted with one Gaussian curve for determining the peak position, except for the asymmetrical peak at 1464.5 (v5) cm⁻¹, which was fitted with three Gaussian curves and was represented by the position of the most intense component.

Fluorescence bands of ruby at 693 and 694 nm (Fig. 3b) were adopted for monitoring the periodic noise as a function of time. The intense signal of the ruby fluorescence achieved continuous analyses with short acquisition time. A natural ruby sample derived from Morogoro, Tanzania, was crushed into a size of approximately 1 mm. Fluorescence spectra of ruby were measured every 0.8 s with an exposure time of 0.6 s. Each spectrum was fitted with two Lorentzian curves for estimating the peak height, width, and position precisely. Each fitting analysis of the naphthalene and ruby bands was held using the least squares method.

The room temperature was measured simultaneously every 2 s using a thermo recorder (RS-11; Espec Mic Corp.) with a resolution of 0.1 °C. The time response of this recorder is a few minutes. The recorder was located near the spectrometer, within a distance of approximately 10 cm. All measurements were conducted during May–June 2005. The laboratory was air-conditioned at 24 °C with cooling-mode operation.

RESULTS AND DISCUSSION

Raman Spectra of Naphthalene: Time-Dependency in the Overall Pixel Range. Figure 4 shows the peak position of each Raman line of naphthalene and the peak distance (Δ(v4 − v2)) between 1382.2 (v4) and 763.8 (v2) cm⁻¹ as a function of time. In that figure, the Raman shift in the vertical axis is plotted on a relative scale. The profiles of peak positions show that the wave fluctuations in a cycle of 1000 s were followed by a decrease in Raman shift during the initial 2000 s. Deviations of the peak positions were mutually synchronous in their direction and amplitude. We can partition these profiles into two components: a monotonous decrease in wavenumber observed from the beginning of the measurement, and

![Figure 1](image1.png)

**Fig. 1.** The peak position of a talc Raman band (3677 cm⁻¹) as a function of time after the cooling of the CCD detector has started. The error bars on the x-axis indicate the summed time for taking the three measurements (about 200 s); those on the y-axis indicate the standard deviations of the measurements.

![Figure 2](image2.png)

**Fig. 2.** (a) Total photon mapping and (b) the peak-position mapping of the fluorescence spectrum of Al₂O₃/ZrO₂ eutectic obtained using scanning near-field optical microscopy (SNOM). The pixel sizes of (a) and (b) are 128 × 128 and 128 (longitudinal) × 40 (lateral), respectively. In the photon mapping (a), the brighter region corresponds to the region indicating more intense fluorescence. In the peak-position image (b), the brighter region corresponds to the region indicating the peak position of higher wavelength. A striped shading pattern with about 0.5 micrometer cycle, which corresponds to the scanning time of approximately 10 minutes, is seen in the peak-position map (Fig. 2b). This implies that a periodical drift took place in addition to the peak shifts originated from the sample property.
a periodic oscillation. The amount of the initial monotonous
decrease was up to 0.4 cm$^{-1}$ (corresponding to 0.30 pixel) from
the beginning of measurement. The range of this periodic
change was approximately 0.15 cm$^{-1}$ (corresponding to 0.10
pixel number) and its cycle was approximately 1000 s. It is
noteworthy that these subtle changes in Raman shift are
apparent using the downsized conventional spectrometer.

The initial drift was similar to the result for talc (Fig. 1).
These drifts took place in a limited time span after cooling of
the detector, indicating thermal effects that are related to the
Peltier device. A possible cause is a subtle temperature drift of
the CCD detector caused by incomplete cooling. Until reaching
the stabilized condition, the alignment of the CCD array
presumably deviates in micrometer order. The initial monot-
onous drifts observed in the experiments of talc (Fig. 1) and
naphthalene (Fig. 4) showed similar behavior. The quantity of
drift, however, was different between the results of talc (0.2
cm$^{-1}$) and naphthalene (0.4 cm$^{-1}$). The data on naphthalene
(Fig. 4) were collected soon after finishing the cooling of the
CCD detector and the initial drift was quantified. In contrast,
the measurement of talc (Fig. 1) did not involve the very initial

drift. Therefore, the downshift in Fig. 1 appears to be smaller
than that in Fig. 4.

Fluorescence Spectra of Ruby and the Relationship
Between Peak Position and Room Temperature. We carried
out detailed monitoring using the fluorescence spectra of ruby
to investigate the cause of periodic oscillation observed in the
SNOM mapping (Fig. 2) and in Raman spectra of naphthalene
(Fig. 4). The room temperature was measured simultaneously.
Figure 5 shows the time change of the R1 peak center of ruby
and the room temperature. These results indicate clearly that
the peak position of the R1 peak changes synchronously with
the room temperature variation. Figure 5 actually demonstrates
that the temperature profile maxima are subtly shifted with
respect to peak position maxima. This is explained by the slow
response of the thermo recorder (a few minutes). The peak
center shifted to a higher wavelength (nm) concomitant with
the increased room temperature. The R1 peak center and room
temperature oscillated in phase: its cycle was about 1100 s. The
range of the oscillation of the R1 peak center was

![Fig. 3. (a) Raman spectrum of naphthalene and (b) the fluorescence spectrum of ruby.](image-url)
approximately $5 \times 10^{-3}$ nm (corresponding to 0.104 cm$^{-1}$ and 0.13 pixel number). The corresponding range of temperature deviation was 0.8 °C. These changes are consistent with the relationship between Raman spectra of naphthalene and temperature (data not shown) in terms of the direction and amplitude of the deviation.

Similar spectral shifts attributable to changes in room temperature have already been pointed out in several studies.$^{16,17}$ Gaufres et al.$^{16}$ described that the periodic oscillation of the peak positions of neon emission lines with amplitude of 0.015 cm$^{-1}$ synchronized with a 25-min cycle of the temperature regulation. Mestari et al.$^{17}$ described the monotonous change of the peak position of a neon line with the monotonous change of the room temperature using a double monochromator. They concluded that shifts in peak positions that were induced by the change of the room temperature varied according to operating modes of the spectrometer; for the ‘Normal’ mode, ‘Direct’ mode, and ‘High dispersion’ mode, the respective average values of the shifts per degree were 0.3628, 0.2415, and 0.1785 cm$^{-1}$. However, those previous papers did not show the actual relationship with the oscillating temperature. In contrast to those previous studies, the present study directly showed the simultaneous changes of the peak position and temperature. Moreover, the shift of peak positions of the ruby (R1) induced by the change of room temperature for our spectrometer was $6.3 \times 10^{-3}$ (nm °C$^{-1}$) (corresponding to 0.13 (cm$^{-1}$ °C$^{-1}$)). These results suggest that the room temperature change causes the thermal expansion or contraction of the entire apparatus. In addition, the downsized spectrometer exhibits a small temperature-induced shift in frequency compared with a large double monochromator.

**Suggestions for Precise Acquisition of Spectra.** The above instrumental deviations can engender considerable experimental error. For acquiring spectra more precisely, the following two measures, at least, should be considered during sample analyses. One is to take sufficient time before starting measurements for stabilizing the CCD detector. According to the results of this study, it takes a longer time than expected to cool and stabilize the CCD detector from the indicated temperature condition. The time profile for stabilizing the CCD should be verified carefully for each apparatus by monitoring the peak positions of Raman spectra or fluorescence bands over time. Then, data collection must be started after the complete stabilization of an equipped detector. The other measure is to minimize the room temperature deviation. Our present results suggest that the most straightforward method to reduce the spectrometer fluctuation is to maintain the room temperature as constant. Covering the apparatus will minimize the temperature deviation.

**Influence of Time-Integrated Acquisition on the Spectral Resolution and Precision.** Even if the room temperature oscillates, data accumulation during a long period might moderate the deviation of the peak-center estimation. For testing this assumption numerically, we prepared 80 sets of Lorentzian curves with a constant peak width of 3 nm and a constant intensity. Peak positions of the 80 curves were ranged sequentially from 692.9975 nm to 693.0025 nm. Furthermore, random noise, which is approximately 1% degree of the peak height, was added to each Lorentzian curve for modeling the actual system. Each spectrum was accumulated in sequence and the peak position of each spectrum was calculated using the least squares fitting method. Figure 6 shows the relationship between the integration time and the calculated peak position. This figure indicates that accumulation for a period including two cycles of temperature oscillation substantially reduces the deviation in wavelength down to 20%. In this study, the influence of periodic oscillation (corresponding to 0.15 cm$^{-1}$ and $5 \times 10^{-3}$ nm in the present study) is weakened to a value of 0.03 cm$^{-1}$ and $1 \times 10^{-3}$ nm, respectively. Longer time accumulation lessens the deviation. However, longer accumulation is not applicable to mapping measurements, which require rapid acquisition of each spectrum. Mapping-data are perturbed considerably by the periodic noise (see Fig. 2). When doing mapping experiments, room temperatures must be controlled strictly. Alternatively, a reference emission line (e.g., a neon lamp) should always be introduced with spectral acquisition. Calibration should be undertaken for each spectrum.

**Time Change of the Difference Between Two Periodically Oscillating Peak Positions.** The differences between the peak positions remain at constant values within the experimental uncertainties if the temperature variation shifts each peak in the same direction and with the same distance. The relative shifts between the peak position of 763.8 cm$^{-1}$ (v2) and 1382.2 cm$^{-1}$ (v4) are plotted on Fig. 4. This plot indicates that the fluctuation of the difference between two peak positions is several times smaller (about 0.05 cm$^{-1}$) than that of raw data (about 0.4 cm$^{-1}$). This result implies that the accuracy of differential shifts is better than single peak position analyses using calibration of a standard material.

In some cases, the difference values between peak positions within a Raman spectrum are useful as indicators of variations in the structure of materials.$^{13,20}$ Results of the present study support that such treatment is sound in accuracy. Estimating differences between a sample and a standard material is a ready means to avoid effects of unstable behaviors of spectrometers.

**Resolution and Precision of a Conventional Raman Spectrometer When Using a Fitting Method.** In this study, we observed periodic oscillation with an amplitude of 0.075 cm$^{-1}$ of the peak position using a spectrometer with a resolution of 1.5 cm$^{-1}$ per pixel, when applying the least squares curve-fitting method. Moreover, random noise as a residue after
excluding the periodic oscillation, corresponding to the precision in determining the peak-position value, was approximately 0.05 cm$^{-1}$ for the peak-position value of 1382.2 cm$^{-1}$ ($\gamma 5$). That is the strongest peak of the naphthalene bands. This value is comparable to the high-resolution spectrometer. Izraeli et al.$^{10}$ pointed out that the precision of the Raman shift value increases to over ten times that of the initial resolution with the curve-fitting method. The present value is thirty times better than the initial spectral resolution (1.5 cm$^{-1}$). These facts imply that the least squares fitting method is useful to increase the precision of a conventional Raman spectrometer. Figure 4 indicates that the precision of the peak-position value is better in the case of the stronger peak. It suggests that longer-time integration of spectral measurements enhances the precision of the peak-position value.

CONCLUSION

(1) Charge-coupled device camera of a Raman spectrometer is not thermally stabilized, even after the monitoring software indicates the completion of refrigeration. Data acquisition should be started after the device is completely stabilized (at least 2000 s in our laboratory).

(2) Periodic oscillation in room temperature induces the oscillation of the peak position of the spectrum. The periodic change of 0.4°C in room temperature (the maximum amplitude in our laboratory) gives rise to the shifts of peak positions with an amplitude of 0.0025 nm (corresponding to 0.052 cm$^{-1}$). This circumstance-induced deviation practically restricts the maximum error of the peak position in the case of short-time acquisitions.

(3) Peak-position deviations attributable to periodic room-temperature oscillation can be moderated by data acquisition that is longer than the cycle of room-temperature oscillation. Our simulation showed that accumulation for two cycles of temperature oscillation reduced the deviation to 20%.

(4) The difference between two peak positions can be determined with errors of about 0.05 cm$^{-1}$ (several times smaller than that of raw data) even if spectral fluctuations and an initial decrease exist.

(5) The least squares fitting method enhances the precision of the peak position to 1/30 times the value of the initial spectral resolution (from 1.5 cm$^{-1}$ to 0.05 cm$^{-1}$).

This study investigated the stability and precision of peak positions of spectra determination using our spectrometer. However, this investigation is applicable to all spectrometers used. We recommend that each user quantifies the spectrometer deviations and works to minimize circumstance-induced instrumental deviations.

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