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SENSITIVITY CALIBRATION OF A RAMAN SPECTROMETER USING THE ROTATIONAL RAMAN SPECTRA OF DEUTERIUM

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The dependence of the sensitivity of a Raman spectrometer on the wavelength of light was examined by comparing the observed and calculated intensity distributions of the rotational Raman spectra of deuterium (D_2). Relative sensitivity curves were obtained in the region of the wavelength of the five lines of the argon ion laser.

The sensitivity of a Raman spectrometer generally depends strongly on the wavelength of light and it often causes serious errors in the measurement of Raman intensities, especially when one compares the intensities of two or more Raman lines having much different Raman shifts. Thus, the sensitivity calibration of a Raman spectrometer plays an important role when accurate measurement of Raman intensities is intended. In this note, a description of a convenient method of calibrating a Raman spectrometer is given, and the results obtained by this way are reported.

A rotational Raman spectrum of D_2 is shown in Fig. 1. Five Stokes and three anti-Stokes lines have the intensities comparable one another, and these eight lines cover a region of about 1000 cm^{-1} near the wavelength of the exciting line (from -415 cm^{-1} to 643 cm^{-1} of the exciting line). We chose D_2 because this pattern of the spectrum is ideal for the purpose of the sensitivity calibration using rotational Raman spectra.

According to Placzek and Teller (1), the intensity of a rotational Raman line of a diatomic molecule whose electronic ground state is Σ is given by the followings if the Boltzmann distribution is assumed among the rotational levels.

$$I(J \rightarrow J+2) \propto \frac{(J+1)(J+2)}{2J+3} g_J \exp(-F_0(J)/ kT) \nu^3 \qquad \text{(Stokes lines)}$$

$$I(J\rightarrow J-2)\propto\frac{(J-1)J}{2J-1}\,g_J\,\exp(-F_0(J)/kT)\,\nu^3 \qquad \text{(anti-Stokes lines)}$$

I denotes the intensity of a rotational Raman line (number of the scattered photons), J is the rotational quantum number of the initial state, g_J is the statistical weight of the initial state due to nuclear spin, T is the temperature which determine the population among the rotational levels, $F_0(J)$ is the energy of a rotational level and ν is the absolute frequency of the scattered Raman light. In the case of a diatomic molecule, $F_0(J)$ is given in a good approximation by the following equation;

$$F_0(J) = B_0J(J+1) - D_0J^2(J+1)^2 + H_0J^3(J+1)^3$$

where B_0, D_0, and H_0 are the rotational constants of the vibrational ground state. The rotational Raman spectra of H_2, HD, and D_2 were studied precisely by Stoicheff (2), and the rotational constants were obtained as follows;

$$B_0 = 29.910\ \mathrm{cm}^{-1},\ D_0 = 0.0113\ \mathrm{cm}^{-1},\ \text{and}\ H_0 = 0.36\times10^{-5}\ \mathrm{cm}^{-1}$$

These values allow us to calculate the intensity distribution of the rotational Raman spectra of D_2 in a sufficient accuracy for the present purpose.

There are two ways of measuring the intensity of a Raman line on the spectrum chart. One is to take the peak height as the intensity (peak intensity) and the other is to measure the area under the peak (area intensity). The former is more convenient but is less accurate than the latter, because the former is affected by the change in the spectral slit width. In order to obtain the area intensity directly from the peak height we set the intermediate and exit slit widths of the monochromator (s_2 and s_3 respectively) much larger than the width of the entrance slit (s_1). Fig. 2 shows the change of the observed shape of the 0 → 2 rotational line of D_2, when s_2 and s_3 change from 200 μ to 1000 μ while s_1 is kept constant at 200 μ. It is clearly seen from the figure that if s_2 and s_3 exceed 600 μ, further increase in their values produces no change in the peak height, showing that the whole of the monochromatic image of the Raman line reaches to the detecter without any loss due to the intermediate and exit slits. Thus, if s_1, s_2, and s_3 are set 200, 1000, and 1000 μ respectively, the peak height of the observed line directly corresponds to the area intensity. A typical pattern of the rotational spectra of D_2 with such slit setting is shown in Fig. 3. The separations between the adjacent lines are much larger than their widths, and each line is completely isolated in the spectrum.

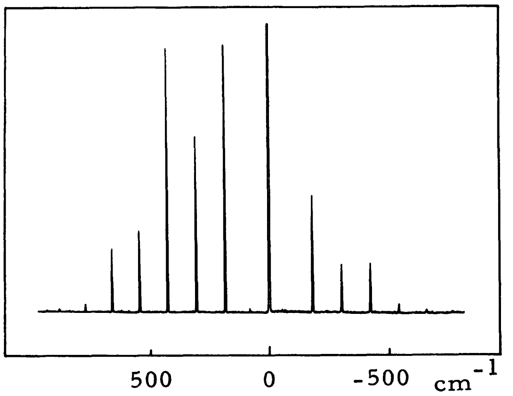

Figure 1. Rotational Raman spectrum of D_2 excited by the 4880 A line of the argon ion laser. Slit widths; 150-150-150 μ. Scan speed; 25 cm^{-1}/min. Integration time; 0.5 sec. Smoothing; 4 points.

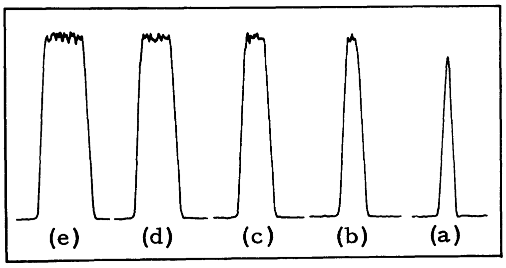

Figure 2. Change of the observed shape of the 0 → 2 Raman line with the change in the slit widths. See text.

	s_1	s_2	s_3	
(a)	200	200	200	μ
(b)	200	400	400	μ
(c)	200	600	600	μ
(d)	200	800	800	μ
(e)	200	1000	1000	μ

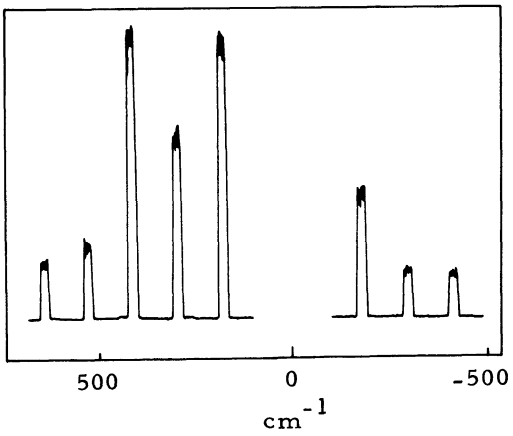

Figure 3. Rotational Raman spectrum of D_2 excited by the 4880 A line of the argon ion laser. Slit widths; 200-1000-1000 μ. Scan speed; 10 cm^{-1}/min. Integration time; 'laser monitor' (see text). Smoothing; 8 points.

Comparing the observed and calculated intensity distributions, we obtain a sensitivity curve of the spectrometer near the wavelength of the exciting line. The positions of 37 rotational Raman lines excited by the five lines of the argon ion laser (5145, 4965, 4880, 4765, and 4579 A) are schematically shown in Fig. 4. Five series of Raman lines give five sensitivity curves, which overlap one another at least at one region of the wavelength. In a overlapped region of the sensitivity curves, we have two independent values for the curvature which are obtained from the two different series of Raman lines. These two values must agree with each other, if the right value of the temperature is used in the calculation of the intensity distribution. Inversely, we can determine the temperature so that the curvature of the two sensitivity curves in the

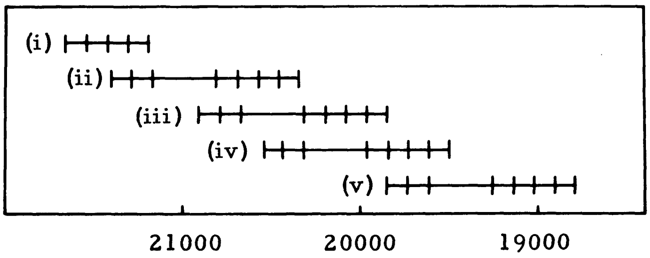

Figure 4. Positions of the 37 rotational Raman lines of D_2 excited by the five lines of the argon ion laser. (i) 4579 A, (ii) 4765 A, (iii) 4880 A, (iv) 4965 A, (v) 5145 A.

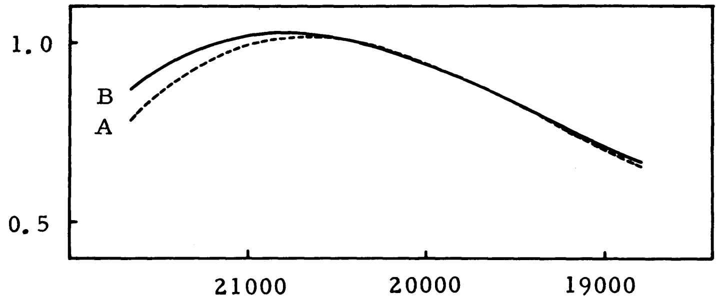

Figure 5. Relative sensitivity curve for the 400 D spectrometer. A shows the sensitivity curve with the analyzer and B without it.

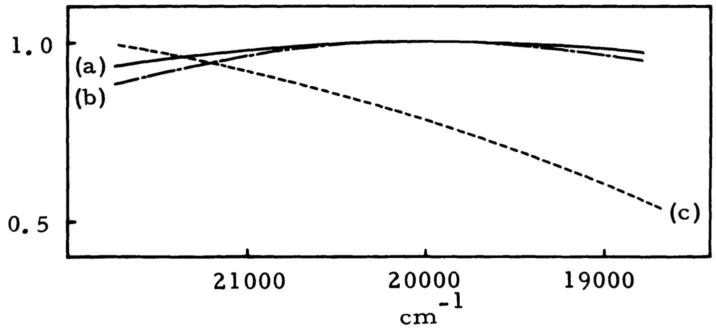

Figure 6. A typical transmittance curve for HN-32 sheet (a), a quantum efficiency curve for R-464 photomultiplier (b) and an estimated efficiency curve of a pair of holographic gratings (c). See text.

overlapped region coincide each other.

The Raman spectra were obtained using a Coherent Radiation CR-3 argon ion laser as the exciting source. The output powers were about 800 mW at 5145 A and a few hundred mW at the other wavelengths. A JEOL-400D Raman spectrometer consists of a 40 cm Czerny-Turner double monochromator equipped with two holographic gratings blazed at 5000 A(1800 grooves/mm) and a HTV R-464 bialkali-type photomultiplier and a standard photon counting system with a digital smoothing circuit. It has also a 'laser monitor system', which controls automatically the integration time of the photon counter and the stepwise rotation of the gratings simultaneously, so that the fluctuation of the output power of the laser is compensated. A sealed quartz tube containing 600 torr of D_2 was made by Daiko Seisakujo. It is 72 mm long, 30 mm in diameter and has a flat window of 18 mm in diameter. A polaroid HN-32 sheet was set as an analyzer in front of the entrance slit of the monochromator when the sensitivity for the linearly polarized light was examined.

Three kinds of measurements were carried out. For the first, the axis of the analyzer was set parallel to the grooves of the gratings (perpendicular to the direction of the polarization of the laser beam), for the second it was set perpendicular to the grooves and the third was done without the analyzer. Each measurement was composed of three independent observations at one exciting line. We assumed a value of the temperature and calculated the intensity distribution of the spectrum and obtained 3 X 5 = 15 sensitivity curves for each of the three measurements. A least squares calculation was carried out so that these fifteen curves were connected smoothly with one another by multiplying each of them by a proper constant multiplier, and a combined sensitivity curve was obtained. Then the assumed value of the temperature was changed from 20°C to 35°C by the interval of 0.5°C and a temperature was obtained which minimized the standard deviation of the observed sensitivity (which involves the temperature and the multipliers as parameters) from the combined curve. Because no appreciable differences exist between the first and second measurements[a], the least squares calculation was done using the two groups of data combined.

Fig. 5 shows the two relative sensitivity curves finally obtained. Curve A corresponds to the sensitivity with the analyzer, and curve B is the sensitivity curve without it. A was obtained with the temperature of 27.0°C and B, with 29.5°C. These values of temperature are about 5°C higher than the room temperature. If the values of the room temperature are used in the calculation, the standard deviation becomes to 0.031, while the minimized value is 0.018. Nevertheless, the curvature itself remains slightly changed (about 2 %) between the two cases.

The sensitivity of a Raman spectrometer is determined by the following quantities. They are the transmittance of the analyzer, the efficiency of the gratings and the quantum efficiency of the photomultiplier. Fig. 6 shows a typical transmittance curve for the HN-32 sheet (curve a) and a quantum efficiency curve for the R-464 photomultiplier (curve b) together with an esti-

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[a] This means that the linearly polarized light transmitted by the analyzer was completely scrambled by the Babinet's compensator which was set just at the back of the entrance slit of the monochromator. It is possible to make a precise measurement of depolarization degree by merely rotating the analyzer by 90 degrees. The average of the 12 values of the depolarization degree obtained for three Stokes lines excited by four laser lines (5145, 4965, 4765, and 4579 A) was found to be 0.747±0.026(2.58σ).

mated efficiency of a pair of holographic gratings with 2000 grooves/mm to the natural light (curve c). All the curves are normalized to the maximum values in the region of wavelength examined. The general trend of the relative sensitivity curves in Fig. 5 is reasonably deduced from the three curves in Fig. 6 though it is not appropriate to make a quantitative discussion using them.

Finally, we estimate that the obtained sensitivity curves are accurate within 2 %. The error is mainly due to the relatively low signal to noise ratio. If we use a multi-pass type gas cell, the signal to noise ratio will be increased by one order of magnitude and the sensitivity curve with higher accuracy will be obtained. Further improvement of the present method will be brought about, if we mix a little amount of nitrogen to the D_2 tube, and determine the temperature from the intensity distrbution of the rotational Raman spectrum of nitrogen.

It has been found that the sensitivity of a Raman spectrometer is well calibrated by the simple but accurate method described above.

We appreciate the cooperation of the members of our laboratory in the measurement of the intensities of many Raman lines.

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