

# PHOTOMETRY OF RAMAN SPECTRA OF CRYSTALS—PART II

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## 1. INTRODUCTION

IN earlier communication which appeared in these *Proceedings* (and which will be referred to as Part I) the author (Narayanan, 1948) outlined a new method of determining accurately the relative intensity of Raman lines and also the ratio of intensity of the Stokes and anti-Stokes components of a Raman line by the use of an ultraviolet Spekker photometer. However, as the instrument then available was not in perfect order, it was not possible to use it for accurate measurements in the case of high frequency Raman lines. Recently, the work was resumed with a new Spekker photometer. Using this instrument, Krishnan and Narayanan (1950) measured the relative intensities of the Raman lines in diamond.

## 2. EXPERIMENTAL RESULTS AND DISCUSSION

For an accurate determination of the relative intensities by photographic photometry, it is well known that the only correct method is to attempt to produce the two images to be of equal density on the same plate and with the same time of exposure (Fabry and Buisson, 1913; Harrison, 1924; Twymann and Allsop). However, as it is not possible to make the lines under comparison to be of the same density purely by an adjustment of the calibrated drum, they were made as nearly equal as possible consistent with the accuracy of setting on the drum and the resulting images compared. Under such conditions, it is obvious that the photographic error introduced is a minimum.

In the case of diamond, the specimen could be held at the spark gap itself thereby ensuring proper alignment without much difficulty. In the case of the three crystals, namely, calcite, barytes and gypsum, investigated here, the scattering was comparatively weaker and it was found that the scattered light had to be focussed on the spark gap after adjusting the specimen to be in a line with the collimator of the spectrograph and the Spekker

photometer. But the choice of the condensing lens was determined by the condition that the divergence of the beam should be sufficient to make the scattered light falling on the quartz rhombs to be of uniform intensity. Though fairly big crystals were employed, only a small portion of the crystal was in focus at the spark gap.

Since the comparison was made between one line (approximately) at  $\lambda 2460$  and another at  $\lambda 2625$ , it was necessary that the specimen employed should be free from all trace of colour and should not exhibit increased absorption at the shorter wavelengths. This correction for differential absorption is obviously different from that necessary when the exciting radiation is close to one of the characteristic ultraviolet absorption frequencies. For gypsum this effect was negligible. In the case of barytes and calcite, however, the absorption in the  $\lambda 2460$  region was slightly higher than that in the  $\lambda 2625$  region. The relative absorption in the two regions were therefore estimated by using the Spekker photometer and the correction necessary was found to be about 5% for barytes and for 8% for calcite. The intensity ratios of the Stokes—to the anti-Stokes component of the principal Raman lines of gypsum, barytes and calcite are given in Table I.

TABLE I

Crystal	Frequency shift of the line in $\text{cm.}^{-1}$	$\frac{h\nu_i}{e kT}$	$\left(\frac{\nu - \nu_i}{\nu + \nu_i}\right)^4$	$\frac{h\nu_i(\nu - \nu_i)^4}{e kT(\nu + \nu_i)^4}$	Experiment
Gypsum ..	1006	121.6	.815	99	92.3
Barytes ..	988	115	.818	93.8	97
Calcite ..	1085	183.1	.802	147	151

The theoretical formula for the ratio of intensity of the Stokes and

anti-Stokes components is given by  $e^{\frac{h\nu_i}{kT}} \left(\frac{\nu - \nu_i}{\nu + \nu_i}\right)^4$  where the Boltzmann factor is predominant for lines with frequency shift less than  $600 \text{ cm.}^{-1}$ . It is obvious from the figures given in Table I that the method used here enables not only to study the high-frequency Raman lines, but also offers an invaluable means of confirming the dependence of the intensity on the fourth power of the emission frequency.

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SUMMARY

The relative intensities of the Stokes and anti-Stokes components of the most intense and high frequency shift Raman lines in calcite, gypsum, and barytes have been studied by a spectrophotometric method and the results confirm the dependence of the intensity of a Raman line on the fourth power of the emission frequency.

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