

# RELATIVE INTENSITIES OF STOKES AND ANTI-STOKES RAMAN LINES IN CRYSTALS

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## 1. Introduction

THE existence of the anti-Stokes lines in the Raman spectrum of a substance proves that, at ordinary temperatures, there will be some oscillators at a higher energy level than the normal and that the incident light induces a return of these to the normal state. Raman and Krishnan<sup>1</sup> showed that the relative intensities of the Stokes ( $\nu - \nu_{mn}$ ) and the anti-Stokes ( $\nu + \nu_{mn}$ ) lines,  $\nu$  being the frequency of the incident light and  $\nu_{mn}$  the transition frequency,

are given by the relation  $e^{\frac{h\nu_{mn}}{kT}}$  where  $h$  is the Planck-constant,  $k$  is the Boltzmann-constant per molecule and  $T$  is the absolute temperature. Landsberg and Mandelstam<sup>2</sup>, Tamm<sup>3</sup> and Ornstein and Rekveld<sup>4</sup> obtained a slightly modified expression, namely,  $\left(\frac{\nu - \nu_{mn}}{\nu + \nu_{mn}}\right)^4 e^{\frac{h\nu_{mn}}{kT}}$  for this ratio. Placzek<sup>5</sup> considered the effect of absorption bands on this ratio and obtained an expression which may be shown to reduce to the above one, if the substance has no absorption bands in or near the region of investigation.

Considerable amount of work has been done by Ornstein and Rekveld<sup>6</sup> and Sirkar<sup>7</sup> in respect of the ratio of intensities between Stokes and anti-Stokes lines in liquids. The measurements of Ornstein and Rekveld in  $\text{CCl}_4$

agree with the ordinary Boltzmann distribution function  $e^{\frac{h\nu_{mn}}{kT}}$  while those of Sirkar in the same liquid are in conformity with the modified formula

$\left(\frac{\nu - \nu_{mn}}{\nu + \nu_{mn}}\right)^4 e^{\frac{h\nu_{mn}}{kT}}$ . Landsberg and Mandelstam made some estimates of the above ratio in quartz at different temperatures and showed that the behaviour of the Stokes and anti-Stokes Raman lines was in conformity with the requirements of the ordinary Boltzmann distribution function. Ornstein and Went<sup>8</sup> determined the ratio of the Stokes and anti-Stokes lines in the Raman spectra of quartz and calcite. Their results, which are confined to the 465 line only in the case of quartz, are in good agreement with those calculated

on the basis of the modified expression while discrepancies are found in the case of calcite. In view of these discrepancies, it is proposed to study the cases of calcite and quartz in this paper.

## 2. *Experimental Details*

Light from a 6-inch quartz mercury arc lamp is condensed by means of an 8-inch glass condenser on to one face of the crystal and the scattered light emerging out of one of the other faces of the crystal is focussed on the slit of a two-prism glass spectrograph of high light gathering power with a suitable lens. In both the cases of calcite and quartz, cut and polished crystals of appreciable size (one-inch cubes) have been used and with suitable precautions, which are usually employed for obtaining good Raman spectra, intense and clear spectrograms showing the Stokes and the anti-Stokes lines have been obtained.

The plates are run through a Moll microphotometer and the densities of the various lines are obtained in the usual way. A set of intensity marks is recorded on each plate by the method of varying slit widths using the continuous radiation emitted by a standard quartz globe tungsten ribbon lamp as the source. A steady current of 15.1 amperes is maintained in the lamp in both the cases by feeding it from a battery of 220 volts. The colour temperature  $T$  of the lamp corresponding to the current drawn is given by the makers as 2695 and the radiation is assumed to obey Wien's law  $E_\lambda = A \lambda^{-5} e^{-c_2/T\lambda}$  where  $c_2 = 1.432$ ,  $T = 2695$  and  $A$  is a constant. The density at any desired wave-length is obtained for each of the intensity marks by running the plate through the microphotometer under the same conditions as above and the corresponding intensities are taken as proportional to the respective slit widths. In this way, the density-log intensity curves are drawn for each wave-length at which the various Raman lines that are to be compared with each other appear. The intensity of any line as a fraction of the standard radiation having the same wave-length as the line itself is easily read from the above curves and the relative intensities of the various Stokes and anti-Stokes lines are then computed from a knowledge of the energy distribution in the radiation emitted by the lamp. It may easily be seen that this procedure totally eliminates the error due to variations in the photographic sensitivity of the plate in different regions of the spectrum. Since the crystals are not very large and since they are perfectly colourless, no corrections need be made on the score of absorption by the crystal itself. This correction will, however, be of importance only in the case of long columns of liquid.

A few remarks may be made here on the question of measuring the peak intensities of the lines in preference to the integrated intensities or *vice versa*. This point is of special importance when we compare the intensities of different lines having different breadths or the intensities of the same line at different temperatures when the sharpness of the line in question changes with temperature. Since, in this investigation, we are comparing the intensity of a Stokes line with that of the corresponding anti-Stokes line, it is immaterial whether we measure the peak intensities or the integrated intensities because the Stokes lines have the same breadth characters as those possessed by the corresponding anti-Stokes lines. Accordingly, in the present paper, only the peak intensities are measured and compared.

### 3. Results and Discussion

The ratio of intensities between the Stokes and anti-Stokes lines in calcite and quartz obtained by the author are given in the last column of the following tables.

TABLE I

*Calcite*

Temperature	$\nu_{mn}$ $\text{cm}^{-1}$	Excitation A.U.	$\frac{h\nu_{mn}}{e^{kT}}$	$\left(\frac{\nu-\nu_{mn}}{\nu+\nu_{mn}}\right)^4 \frac{h\nu_{mn}}{e^{kT}}$	$\frac{I_s}{I_{A.S.}}$ Observed
303° K.	155	4358	2.08	1.97	1.93
		4046	2.08	1.98	1.86
	280	4358	3.77	3.42	3.32
		4046	3.77	3.44	3.53

TABLE II

*Quartz*

Temperature	$\nu_{mn}$ $\text{cm}^{-1}$	Excitation A.U.	$\frac{h\nu_{mn}}{e^{kT}}$	$\left(\frac{\nu-\nu_{mn}}{\nu+\nu_{mn}}\right)^4 \frac{h\nu_{mn}}{e^{kT}}$	$\frac{I_s}{I_{A.S.}}$ Observed
303° K.	465	4358	9.04	7.69	7.53
	127	4046	1.82	1.75	1.67

The values given in the last three columns of both the tables clearly reveal that the observed values of  $\frac{I_s}{I_{A.S.}}$  agree more closely with the expression

$\left(\frac{\nu - \nu_{mn}}{\nu + \nu_{mn}}\right)^4 \frac{h\nu_{mn}}{e^{-kT}}$  than with  $e^{\frac{h\nu_{mn}}{kT}}$  alone. Especially the ratios in the case of  $\nu_{mn}$  280 in calcite and of  $\nu_{mn}$  465 in quartz serve as deciding tests in favour of the former, the discrepancies between the observed results and those deduced on the basis of the latter expression being quite large in comparison with the possible experimental errors.

#### 4. Summary

The ratios of intensities of various Stokes and anti-Stokes lines in the Raman spectra of calcite and quartz have been determined and the observed values are in better agreement with the values calculated on the basis

of the expression  $\left(\frac{\nu - \nu_{mn}}{\nu + \nu_{mn}}\right)^4 e^{\frac{h\nu_{mn}}{kT}}$  than with  $e^{\frac{h\nu_{mn}}{kT}}$  alone.

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