

INTENSITY RATIO OF THE RAMAN LINES IN DIAMOND

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Received October 23, 1950

1. INTRODUCTION

As is well known, with moderate exposures the Raman spectrum of diamond consists of only one intense line with a frequency shift of 1332 cm^{-1} . With the use of the $\lambda 2537$ radiation of the mercury arc for excitation and long exposures, the most striking feature noticeable in the spectrum is the appearance of a whole series of sharply defined lines belonging to the second order spectrum and also the anti-Stokes line corresponding to the principal frequency shift 1332 cm^{-1} . An accurate determination of the intensity ratio of the first and second order Raman lines in diamond is of great theoretical interest. Besides, a measurement of the intensity ratio of the Stokes and anti-Stokes lines of the principal frequency affords a reliable verification of the dependence of intensity of Raman line on the fourth power of the emission frequency (Placzek, 1934). Diamond is the most suitable case for this purpose as it is the one substance in which the anti-Stokes line corresponding to the highest frequency shift has so far been recorded.

According to Placzek's theory of the scattering of light, the ratio of the intensities of the Stokes to the anti-Stokes Raman line is given by

$$\frac{I_S}{I_{AS}} = \left(\frac{\nu - \nu_i}{\nu + \nu_i} \right) e^{\frac{h\nu_i}{kT}}, \quad (1)$$

where $\nu - \nu_i$ and $\nu + \nu_i$ are the respective emission frequencies. Experimental verification of this relation has so far been carried out for Raman lines with frequency shifts less than 500 cm^{-1} . For lines with $\nu_i < 600 \text{ cm}^{-1}$, the first term on the right-hand side of equation (1) will be very nearly equal to unity and the preponderance of the exponential term makes an experimental verification of the dependence of the ratio on the emission frequency very difficult. Though for high-frequency-shift Raman lines and visible radiations of the mercury arc for excitation, the frequency factor deviates considerably from unity, it is not experimentally possible to record the anti-Stokes components of these Raman lines with sufficient intensity on a clear

background under excitation in the visible region. Another serious limitation is that for an accurate determination of heterochromatic intensity ratios, the photographic density ratio should not exceed 6-8. The first difficulty is easily overcome by the use of λ 2537 for exciting the Raman spectrum. In order to measure accurately the ratio of the intensities of the Raman lines, it is necessary to employ the new method of using a Spekker photometer outlined by one of us in an earlier communication (P. S. Narayanan, 1948), especially when the Stokes-anti-Stokes ratio exceeds 10. Using this method the relative intensities of the Stokes and anti-Stokes components of the 1332 line and also of the prominent second order lines of diamond have been measured. The results are given below.

2. EXPERIMENTAL DETAILS AND RESULTS

A semi-circular piece of diamond (Catalogue No. N.C. 174 in Sir C. V. Raman's personal collection) 1.5 mm. thick was employed. It was transparent to the ultra-violet region with a sharp cut off at λ 2350. By the use of the continuous radiations of a hydrogen lamp it was confirmed that the specimen had no appreciable absorption till the very absorption limit. The plate of diamond was held in the spark gap of a Hilger ultra-violet Spekker photometer with its broad face vertical and its straight edge facing the quartz rhombs. The λ 2537 radiation of a quartz arc was focussed on the diamond with a short focus lens of aperture 2". By suitable adjustment of the focussing lens and the plate of diamond, the scattered light was made to be of uniform intensity over both the apertures of the Spekker photometer. The light emerging from the photometer was allowed to fall on the slit of a medium quartz spectrograph. The graduated drum of the photometer was set exactly at 2 so that the variable aperture had an area 1/100 that of the fixed aperture. In the spectra obtained thereby, one could effect a direct comparison of the Stokes and anti-Stokes Raman lines and also the second-order lines. The Stokes component of the 1332 Raman line in the spectrum obtained through the fixed aperture appeared in 5 minutes, while the second order lines and the anti-Stokes of 1332 were recorded with an exposure of two days.

The relative intensities were computed using the density-log intensity curve for a mean λ 2540. As mentioned in the previous paper, in the case of the photographic plates used by the authors, the variation of photographic sensitivity in the region λ 2450-2650 was very small. Even if there is any slight decrease of sensitivity with decrease of λ , it would tend to increase the Stokes-anti-Stokes ratio—a point which will be discussed later in the paper. The results are summarised in Tables I and II. In the case of the

TABLE I. *Stokes-anti-Stokes ratio for the 1332 Raman line*

| $\Delta\nu = \nu_i$ | $e^{\frac{h\nu_i}{kT}}$ | $\left(\frac{\nu - \nu_i}{\nu + \nu_i}\right)^4$ | $\left(\frac{\nu - \nu_i}{\nu + \nu_i}\right)^4 e^{\frac{h\nu_i}{kT}}$ Theoretical | Observed value |
|---------------------|-------------------------|--|---|----------------|
| 1332 | 581 | 0.763 | 443 | 426 |

TABLE II. *Relative intensities of the principal second-order Raman lines*

| cm^{-1} . | $I_{1332}/I_{\text{s.o.}}$ |
|--------------------|----------------------------|
| 2160 | 590 |
| 2480 | 130 |
| 2665 | 270 |

second-order spectrum, there is a group of closely spaced lines at about 2460 cm^{-1} . Their peak intensity has been estimated.

3. DISCUSSION

The possible sources of error in the measurements described above are the following:

- (1) The difference in the sensitivities of the photographic plate for the regions $\lambda 2450$ and $\lambda 2625$ where the anti-Stokes and Stokes lines respectively fall.
- (2) The influence of the ultra-violet absorption frequency of diamond on the intensity.
- (3) General background arising from the long exposures used.

Although no accurate measurements of the relative photographic sensitivities for $\lambda 2450$ and $\lambda 2625$ were carried out, the indications were that the difference if any was very small. Even if there was a small difference, its effect would be to increase the Stokes-anti-Stokes ratio and thus bring the observed value closer to that given by the Boltzmann factor alone.

If one takes into consideration the influence of the absorption frequency of the scatterer, the intensity ratio is given by the following equation:—

$$\frac{I_S}{I_{AS}} = \left(\frac{\nu - \nu_i}{\nu + \nu_i}\right)^4 e^{\frac{h\nu_i}{kT}} \left(1 + \frac{4\nu\nu_i}{\nu_a^2 - \nu^2}\right), \quad (2)$$

where ν_a is the absorption frequency. The principal electronic frequency of diamond which is effective in dispersion corresponds to $\lambda 1750$. Besides, as there is no absorption even at $\lambda 2360$, it can be shown that the denominator in equation (2) is nearly equal to unity, *i.e.*, the intensity ratio is given by equation (1).

As for the third source of error, it may be pointed out that the chief advantage in using ultra-violet excitation is the fact that the Raman lines appear in the region of the spectrum which is free from any continuum. In the case of diamond, the Stokes component happens to coincide almost with the mercury line $\lambda 2652.2$. But by a proper adjustment of the arc and the aperture through which the scattered light was taken, it was found possible to cut down the parasitic illumination to an extent where the Raman line was brighter than even the strongest line of the mercury triplet with a mean wavelength 2653. Under such conditions it is needless to say that the contribution of the mercury line to the intensity of the Raman line in the spectrum obtained through the reduced aperture was practically zero.

The observed value of the Stokes-anti-Stokes ratio agrees well with that calculated using equation (1) confirming thereby in a decisive way the dependence of the intensity of the Raman line on the fourth power of the emission frequency.

A reasonably quantitative idea of the relative intensities of the first and second order lines in the case of C-C oscillation can be obtained by a calculation similar to that carried out by Bhagavantam (1939) in the case of some diatomic molecules. Using the values given by Jevons for ν_0 ($= 1641.5 \text{ cm.}^{-1}$) and $\nu_0 x$ ($= 11.67 \text{ cm.}^{-1}$) for C_2 from band spectra data, the ratio of intensity of the fundamental to that of the octave has been calculated and is given by

$$\frac{\nu_f^4 a_{01}^2}{\nu_k^4 a_{02}^2} = 318,$$

the frequency factor being calculated by taking $\lambda 2537$ as the exciting line. It is seen that the value obtained in the case of diamond for the 1332 line and its octave (Table II) is remarkably close to this. A rigorous calculation of the ratio, however, requires a knowledge of the potential energy and wave function in the case of diamond.

In conclusion, the authors wish to express their gratitude to Prof. C. V. Raman for a loan of the diamond and to Prof. N. Seetharaman of the Presidency College, Madras, for lending the Spekker photometer without which the above investigation would not have been possible.

SUMMARY

The relative intensities of the Raman lines in diamond have been studied by the spectrophotometric method, outlined in an earlier communication, using an ultra-violet Spekker photometer in conjunction with a medium quartz spectrograph.

The values obtained for the fundamental oscillation, 1332 cm.^{-1} are:—

$$I_{\text{Stokes}}/I_{\text{anti-Stokes}} = 426$$

$$I_{\text{Fundamental}}/I_{\text{Octave}} = 270$$

confirming thereby the dependence of the intensity of a Raman line on the fourth power of the emission frequency.

REFERENCES

1. Bhagavantam .. *Proc. Ind. Acad. Sci.*, 1939, **A10**, 224.
2. Harrison, G. R. .. *J.O.S.A.*, 1925, **11**, 341.
3. Jevons .. *Report on the Band Spectra of Diatomic Molecules*, 1932.
4. Krishnan, R. S. .. *Proc. Ind. Acad. Sci.*, 1946, **A24**, 25.
5. Narayanan, P.S. .. *Ibid.*, 1948, **A28**, 463.
6. Placzek .. *Handbuch der Radiologie*, 1934, **6**, 205.