

RELATIVE INTENSITIES OF RAMAN LINES IN LIQUIDS

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1. INTRODUCTION

SOME of the earlier authors who have studied the intensity characters of the Raman spectra in carbon tetrachloride and benzene have given only the approximate relative intensities of the various Raman lines by estimating them visually. Daure,¹ Carelli and Went,² Dhar,³ A. V. Rao⁴ and B. P. Rao⁵ have made quantitative measurements of the intensities of the various Raman lines as compared to the corresponding Rayleigh line. The results of these authors show a great variance with one another. The greatest discrepancy in carbon tetrachloride is with respect to the well polarised total symmetric line at 460 cm.⁻¹

The data available are thus still meagre and the agreement among the values obtained by different authors is not altogether satisfactory. Hence an investigation of the relative intensities of Raman lines in some standard liquids has been taken up.

2. SPECIAL FEATURES OF THE PRESENT INVESTIGATION

When light passes through a prism it can be shown that the light polarised with its electric vector parallel to the refracting face of the prism is transmitted to a lesser extent than light polarised with its electric vector perpendicular to the refracting face. If we send a beam of unpolarised light through the spectrograph it comes out as partially polarised light as the horizontal and the vertical components are weakened to different extents. This instrument error affects the relative intensities of Raman lines of different polarisation characters.

A. V. Rao⁶ calculated the effect of oblique refraction on the intensities of Raman lines. If I_a and I_b denote the intensities of two Raman lines a and b before transmission, when the illumination is from the side, then $\frac{I_a}{I_b}$ becomes after transmission $\frac{I'_a}{I'_b}$ where

$$\frac{I'_a}{I'_b} = \frac{I_a}{I_b} \cdot \frac{(\rho_a + \sigma)(1 + \rho_b)}{(\rho_b + \sigma)(1 + \rho_a)}$$

where ρ_a and ρ_b are depolarisation factors of the lines a and b respectively and σ is the instrument correction. Thus well polarised lines suffer a greater loss of intensity than the unpolarised ones due to the passage through the spectrograph. This conclusion will be different in the case where the illumination is from the top.

Besides the above correction, when Raman lines having different breadth characters are compared, the aggregate intensities have to be taken into account. Both the above factors are taken care of in the present investigation. It is possible that it is only on account of the neglect of these two factors, very divergent results have been reported in the literature in the past.

3. EXPERIMENTAL

Light scattered by the liquid in the Raman tube which is illuminated by a mercury arc placed on the side in conjunction with a condenser is focussed on the slit of the spectrograph by a lens. The spectrum is photographed on a photographic plate on which is also recorded a set of graded intensity marks given by the method of varying slit widths. The continuous radiation employed for the purpose of giving the intensity marks is the light emitted by a tungsten ribbon lamp the characters of which are known.

The different Raman lines with the corresponding regions of the intensity marks are microphotometered and the aggregate intensities of the various lines have been obtained in the usual manner. Taking into consideration the known distribution of intensity, according to Wien's law, in the radiation emitted by the lamp, the relative intensities of the various Raman lines are calculated. The results obtained by the author are at the room temperature which is about 30° C. and for λ 4358 excitation.

4. RESULTS AND DISCUSSION

In the last column of Table I are given the results relating to the relative intensities of Raman lines in carbon tetrachloride obtained by the author. The results obtained by the others are also given for comparison.

TABLE I

Frequency cm. ⁻¹	Daure	Carelli and Went	Dhar	A. V. Rao	B. P. Rao	Author
215	0.77	0.82	0.56	0.83	0.89	0.84
315	1.00	1.00	1.00	1.00	1.00	1.00
460	0.46	0.73	0.88	0.70	1.11	1.24
760	} 0.58	0.27	0.35	0.23	..	0.46
790				0.21	..	0.46
1550	0.11

It is obvious from the above table that the greatest discrepancy is in respect of the well polarised line at 460 cm.^{-1} . This may be due to the fact that the earlier authors did not take the instrument correction into account.

B. P. Rao has made a study of the intensity of the overtone line at about 1550 cm.^{-1} in relation to one of the fundamental lines and has estimated the ratio of the fundamental to the overtone as 7.7:1. He might have compared the peak intensities of the two lines only. But the overtone line is a broad band extending to about 50 wave numbers, whereas either of the fundamentals has not got so much of breadth. When we compare two lines of entirely different breadth characters, the aggregate intensities should be compared. As has already been mentioned, the author has compared the aggregate intensities and has obtained the ratio of the fundamental to the overtone as 4.2:1. This is a very important result and has been obtained for the first time by comparing the aggregate intensities.

Table II contains the relative intensities of Raman lines obtained by the author in benzene along with the results of the earlier authors.

TABLE II

Frequency cm.^{-1}	Daure	Carelli and Went	Dhar	A. V. Rao	Author
605	..	0.53	0.78	0.88	0.82
850	..	0.39	0.42	0.42	0.34
990	3.33	4.54	2.11	8.40	5.80
1180	1.00	1.00	1.00	1.00	1.00
1585	} 1.67	0.75	0.84	0.28	0.58
1605				0.50	0.43
3045	} 4.67	2.75	..	2.46	} 5.10
3065				3.14	

In Table III are given the results regarding the relative intensities of Raman lines in chlorobenzene. This liquid has not been studied by any one before.

TABLE III

Frequency cm.^{-1}	..	200	420	700	1000	1020	1080	1580	3065
Relative intensities	..	1.00	0.69	0.51	1.93	0.84	0.72	0.82	2.47

5. SUMMARY

It is suggested that the discrepancies among the results of the various earlier authors in respect of the relative intensities of Raman lines are due

to neglecting the effect of oblique refraction and of the different breadth characters of the various lines on their relative intensities. In this investigation, the relative intensities of Raman lines in carbon tetrachloride, benzene and chlorobenzene are determined by comparing the aggregate intensities of the various lines and also taking into account the instrument correction. The fact that the intensity of the overtone line at about 1550 cm.^{-1} in carbon tetrachloride is about one-fourth the intensity of either of the fundamentals is an interesting observation of this investigation.

In conclusion, the author desires to express his grateful thanks to Prof. S. Bhagavantam, Hon.D.Sc., for his interest in this work.

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