EFFECT OF TEMPERATURE ON THE INTENSITIES OF RAMAN LINES

Part III. Liquids

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PLACZEK'S theory indicates that both the Stokes and the anti-Stokes Raman lines should increase in intensity with increase of temperature. The expressions for the intensities of the Stokes and the anti-Stokes lines as a function of temperature are given by (1) and (2).

$$I_{(\nu-\nu_j)} \propto (\nu-\nu_j)^4 \frac{1}{1-e^{-\frac{h\nu_j}{KT}}} \quad (1) \qquad I_{(\nu+\nu_j)} \propto (\nu+\nu_j)^4 \frac{1}{e^{\frac{h\nu_j}{KT}}-1} \quad (2)$$

Not much work has been done as regards the effect of temperature on the intensities of the Raman lines either in solids or in liquids. The early work of Landsberg and Mandelstamm[1] in the case of quartz, shows that the intensity of Stokes lines increases with temperature while the more recent work of Ornstein and Went[2] in the case of calcite and quartz, on the other hand, shows a marked decrease of intensity with increase of temperature. In two previous communications,[3,4] the author has published some results in the case of a few typical crystals. The following are the main features observed by the author in the cases he has studied. The Stokes lines decrease in intensity with increase of temperature. The anti-Stokes lines generally increase in intensity with increase of temperature but not to the expected extent. The ratio of the intensities of the Stokes and the anti-Stokes lines in all cases is in conformity with the theoretically expected results. Some special features observed in the case of calcite are that the low frequency lines decrease in intensity more rapidly than the others and that the anti-Stokes lines show slight decrease in intensity. Small shifts of the low frequency lines towards the exciting line have also been noticed.

As regards liquids, Krishnan[5] pointed out that in the Raman spectrum of liquid carbon tetrachloride, the Stokes lines become weaker and the anti-Stokes lines stronger in intensity with increase of temperature. Ananthakrishnan[6,7] concluded from the spectrograms he has obtained in the case of liquid CCl_4 over an interval of temperature extending from 25° C. to 200° C. that the integrated intensities of the Stokes lines do not increase with increasing temperature and also that the anti-Stokes lines increase in intensity but not to such an extent as is required by Placzek's theory.

The work so far done in the case of liquids is very meagre and purely qualitative. As such and to fall in a line with the previous work done by the author in the solids, the present investigation regarding the effect of temperature on the intensities of Raman lines in some typical liquids like carbon tetrachloride, benzene, chlorobenzene, etc., has been taken up.

2. *Experimental*

The experimental arrangements are the same as those described by the author in the previous communications. Light from a 6-inch quartz mercury arc lamp condensed by an 8-inch condenser is allowed to fall on the slit of the Raman tube containing the liquid under investigation. The scattered light coming out from the window of the tube is focussed on to the slit of a Fuess spectrograph. The Raman tube containing the liquid is heated by a specially made electric heater and a thermometer placed in contact with the tube indicated the temperature with an accuracy of $\pm 2°$ C. Intense and clear spectrograms are obtained in a very short time. The intensity of the source and the time of exposure are kept constant while obtaining the spectra at different temperatures. The Raman spectra at various temperatures along with a set of intensity marks given by the method of varying slit widths using the standard quartz globe tungsten ribbon lamp as the source are recorded on the same plate. The intensities of the various lines are computed in the usual way. As the lines did not show any appreciable broadening in the temperature region studied, only peak intensities have been compared.

3. *Results and Discussion*

Tables I, II, III and IV contain the results regarding the effect of temperature on the intensities of the Stokes Raman lines in liquid carbon tetrachloride, benzene, normal butyl alcohol and chlorobenzene respectively.

TABLE I. *Carbon Tetrachloride*

Frequency cm.$^{-1}$	Temperature °K.	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
215	305	1·00	1·00	1·00
	340	1·05	1·07	1·02
315	305	1·00	1·00	1·00
	340	0·94	1·05	1·12
460	305	1·00	1·00	1·00
	340	0·90	1·04	1·16
760	305	1·00	1·00	1·00
	340	0·84	1·01	1·20
790	305	1·00	1·00	1·00
	340	0·84	1·01	1·20

TABLE II. *Benzene*

Frequency cm.$^{-1}$	Temperature °K.	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
605	305	1·00	1·00	1·00
	345	0·89	1·03	1·16
850	305	1·00	1·00	1·00
	345	0·93	1·01	1·09
990	305	1·00	1·00	1·00
	345	0·97	1·01	1·04
1180	305	1·00	1·00	1·00
	345	0·90	1·01	1·12
1585	305	1·00	1·00	1·00
	345	0·89	1·00	1·12
1605	305	1·00	1·00	1·00
	345	0·91	1·00	1·10
3055	305	1·00	1·00	1·00
	345	0·97	1·00	1·03

TABLE III. *Normal Butyl Alcohol*

Frequency cm.$^{-1}$	Temperature °K.	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
825	305	1·00	1·00	1·00
	373	0·60	1·02	1·70
960	305	1·00	1·00	1·00
	373	0·72	1·02	1·42
1300	305	1·00	1·00	1·00
	373	0·76	1·01	1·33
1450	305	1·00	1·00	1·00
	373	0·75	1·00	1·33
2865	305	1·00	1·00	1·00
	373	0·76	1·00	1·32
2910	305	1·00	1·00	1·00
	373	0·80	1·00	1·25
2935	305	1·00	1·00	1·00
	373	0·82	1·00	1·22
2960	305	1·00	1·00	1·00
	373	0·82	1·00	1·22

TABLE IV. *Chlorobenzene*

Frequency cm.$^{-1}$	Temperature °K.	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
200	305	1·00	1·00	1·00
	358	0·88	1·10	1·25
	395	0·73	1·18	1·62
420	305	1·00	1·00	1·00
	358	0·87	1·06	1·22
	395	0·74	1·10	1·49
700	305	1·00	1·00	1·00
	358	0·92	1·02	1·11
	395	0·85	1·05	1·24
1000	305	1·00	1·00	1·00
	358	0·90	1·01	1·12
	395	0·78	1·02	1·31
1020	305	1·00	1·00	1·00
	358	0·91	1·01	1·11
	395	0·82	1·02	1·24
1080	305	1·00	1·00	1·00
	358	0·88	1·01	1·15
	395	0·75	1·02	1·36
1580	305	1·00	1·00	1·00
	358	0·92	1·00	1·09
	395	0·85	1·00	1·18
3065	305	1·00	1·00	1·00
	358	0·87	1·00	1·15
	395	0·73	1·00	1·37

Tables V and VI contain the results regarding the effect of temperature on the intensities of the anti-Stokes Raman lines in carbon tetrachloride and chlorobenzene respectively.

TABLE V. *Carbon Tetrachloride*

Frequency cm.$^{-1}$	Temperature °K.	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
−215	305	1·00	1·00	1·00
	340	1·12	1·19	1·06
−315	305	1·00	1·00	1·00
	340	1·18	1·24	1·05
−460	305	1·00	1·00	1·00
	340	1·22	1·31	1·07

TABLE VI. *Chlorobenzene*

Frequency cm.$^{-1}$	Temperature °K.	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
−200	305	1·00	1·00	1·00
	358	1·18	1·27	1·08
	395	1·25	1·45	1·16

Tables VII and VIII contain results regarding the effect of temperature on the ratio of the intensities of the Stokes and the anti-Stokes Raman lines in carbon tetrachloride and chlorobenzene respectively.

TABLE VII. *Carbon Tetrachloride*

Frequency cm.$^{-1}$	Temperature °K.	$e^{\frac{h\nu_j}{KT}}$	$\left(\frac{\nu - \nu_j}{\nu + \nu_j}\right)^4 \cdot e^{\frac{h\nu_j}{KT}}$	$\frac{I_S}{I_{AS}}$ obs.
215	305	2·75	2·55	2·50
	340	2·48	2·30	2·34
315	305	4·40	3·95	4·08
	340	3·78	3·39	3·26
460	305	8·71	7·41	7·52
	340	6·97	5·93	5·60

TABLE VIII. *Chlorobenzene*

Frequency cm.$^{-1}$	Temperature °K.	$e^{\frac{h\nu_j}{KT}}$	$\left(\frac{\nu - \nu_j}{\nu + \nu_j}\right)^4 \cdot e^{\frac{h\nu_j}{KT}}$	$\frac{I_S}{I_{AS}}$ obs.
200	305	2·56	2·39	2·53
	358	2·23	2·08	1·89
	395	2·07	1·93	1·48

From the results given above, the following conclusions may be drawn:—

(1) The Stokes lines decrease in intensity with increase of temperature excepting the line at 215 cm.$^{-1}$ in CCl_4.

(2) The anti-Stokes lines increase in intensity with increase of temperature but not to the expected extent.

(3) The ratio of the intensities of the Stokes and the anti-Stokes lines at various temperatures is in good agreement with the expected results.

In liquids, the large expansion at high temperatures causes a diminution in the density of the scattering medium and to that extent there will be a decrease in the number of effective scattering centres per unit volume. The effect of taking density into consideration is to increase the observed intensities of the Stokes lines. But in the cases studied in the present paper it can easily be seen that the intensities even after applying the correction for density, taking that the number of effective scattering centres per unit volume is inversely proportional to the density, are not equal to the calculated values.

A detailed explanation of the results obtained by the author both in solids and liquids will be dealt with in a separate communication.

4. *Summary*

The effect of temperature on the intensities of the Raman lines in some typical liquids like carbon tetrachloride, benzene, normal butyl alcohol and chlorobenzene has been studied. It has been found that the Stokes lines in all the cases studied, excepting the line at 215 cm.$^{-1}$ in CCl_4, decrease in intensity with increase of temperature whereas the anti-Stokes lines increase in intensity but not to the expected extent. The ratio of the intensities of the Stokes and anti-Stokes lines, however, is in good agreement with the calculated value. The intensities of the Stokes lines, even after applying the correction for the change in density on the assumption that the number of effective scattering centres will be inversely proportional to the density, are not equal to the calculated values.

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