EFFECT OF TEMPERATURE ON THE INTENSITIES OF RAMAN LINES

Part IV. Liquids *(Contd.)*

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1. Introduction

The author has taken up a critical and exhaustive study of the verification of Placzek's theory of Raman Effect[1] and in the first two parts[2,3] of this series, results relating to the effect of temperature on the intensities of Raman lines in some typical crystals like calcite, quartz, etc., were given. In the third part[4] the author published some results regarding the effect of temperature on the intensities of the Stokes, the anti-Stokes as well as the ratio of intensities of the Stokes and the anti-Stokes Raman lines in some typical liquids like carbon tetrachloride, chlorobenzene, etc. These investigations were defective inasmuch as the range of temperature employed was very small. It is now proposed to study the changes in intensities over a wider range of temperature. On account of the comparative simplicity of the spectra and the chemical stability of the molecules, carbon tetrachloride and benzene are best suited for the study and so these liquids are again taken up but temperatures of 250° C. in the former case and 150° C. in the latter have been reached.

Available literature on the subject has been reviewed in the earlier papers of the author. Mention may, however, be made here of a recent paper by Sirkar[5] who studied the effect of temperature on the intensities of Raman lines in some organic liquids, and concluded that the observed values, when corrected for the expansion, agree fairly well with the values calculated on the basis of Placzek's expressions.

2. Experimental

Distilled carbon tetrachloride is taken in a thick-walled pyrex tube capable of withstanding high pressures. Sufficient space has been left in the tube for the expansion of the liquid at higher temperatures and the tube is sealed off after removing the air. The tube containing the liquid is

surrounded by an electric heater and the temperature of the liquid could be read by a thermometer kept in contact with the tube within an accuracy of $\pm 5°$ C. Light from a 6-inch quartz mercury arc lamp is focussed on the liquid by an 8-inch glass condenser and the scattered light coming from the window of the tube is condensed on to the slit of a Hilger two-prism glass spectrograph by means of a lens. Only a portion of the liquid has been illuminated and the illuminated portion is kept the same while obtaining the spectra at different temperatures.

As the lines may broaden at higher temperatures, a wide slit (0·5 mm.) has been used to photograph the spectra at different temperatures and intense and clear spectra were obtained by giving comparatively short exposures. Care has been taken to see that the slit is not so wide as to cause overlapping of the adjacent Raman lines. The time of exposure and the intensity of the source are kept constant while obtaining the Raman spectra of the liquid at different temperatures. As a wide slit has been used in all the cases and as there is no further broadening of the lines, the peak intensities have been compared. In order to study the frequency and structural changes of the Raman lines, the spectra at different temperatures are photographed using a narrow slit (0·06 mm.). In this case, the aggregate intensities of the various lines at different temperatures have been compared, the aggregates being obtained from the microphotometric records. As there is no appreciable difference between the results thus obtained by comparing the aggregate intensities of the lines at different temperatures using a narrow slit and those obtained by comparing the peak intensities using a wide slit, only the latter results are given in the paper. The experimental arrangements are just the same for benzene also, but in this case the results obtained by comparing the aggregate intensities of the lines at different temperatures using a narrow slit are given.

3. Results

Table I contains the results regarding the effect of temperature on the intensities of the Stokes Raman lines in CCl_4.

In Table II are given the results relating to the effect of temperature on the intensities of the anti-Stokes Raman lines in CCl_4.

In Table III are given the results regarding the effect of temperature on the ratio of intensities of the Stokes and the anti-Stokes Raman lines in CCl_4.

Table IV contains the results regarding the effect of temperature on the widths of the Raman lines in CCl_4.

TABLE I

Frequency cm.$^{-1}$	Temperature °K.	$\frac{I_T}{I_{313}}$ obs.	$\frac{I_T}{I_{313}}$ calc.	Quotient
215	313	1·00	1·00	1·00
	383	0·86	1·13	1·31
	443	0·76	1·25	1·64
	523	0·65	1·40	2·15
315	313	1·00	1·00	1·00
	383	0·89	1·10	1·24
	443	0·77	1·20	1·56
	523	0·69	1·32	1·91
460	313	1·00	1·00	1·00
	383	0·86	1·07	1·24
	443	0·73	1·13	1·55
	523	0·61	1·23	2·00
775	313	1·00	1·00	1·00
	383	0·81	1·03	1·27
	443	0·67	1·05	1·57
	523	0·55	1·10	2·00

TABLE II

Frequency cm.$^{-1}$	Temperature °K.	$\frac{I_T}{I_{313}}$ obs.	$\frac{I_T}{I_{313}}$ calc.	Quotient
− 215	313	1·00	1·00	1·00
	383	1·15	1·36	1·18
	443	1·21	1·56	1·29
	523	1·28	2·09	1·63
− 315	313	1·00	1·00	1·00
	383	1·23	1·44	1·17
	443	1·32	1·83	1·39
	523	1·39	2·36	1·70
− 460	313	1·00	1·00	1·00
	383	1·31	1·57	1·20
	443	1·44	2·11	1·47
	523	1·51	2·86	1·89

TABLE III

Frequency cm.$^{-1}$	Temperature °K.	$e^{\frac{h\nu_j}{kT}}$	$\left(\frac{\nu-\nu_j}{\nu+\nu_j}\right)^4 e^{\frac{h\nu_j}{kT}}$	$\frac{I_R}{I_{As}}$ obs.
215	313	2·67	2·48	2·70
	383	2·23	2·07	2·01
	443	2·07	1·92	1·70
	523	1·80	1·67	1·38
315	313	4·23	3·79	3·98
	383	3·25	2·91	2·88
	443	2·77	2·48	2·32
	523	2·37	2·12	2·00
460	313	8·20	6·98	7·15
	383	5·58	4·75	4·70
	443	4·42	3·76	3·63
	523	3·52	3·00	2·88

TABLE IV

Frequency cm.$^{-1}$	Widths at different temperatures (cm.$^{-1}$)			
	313° K.	383°	443°	523°
215	12	15	18	23
315	13	16	19	25
460	11	16	20	25
775	747–768 780–800	..	..	728–800

There is no marked change in the frequency for the first three lines.

In Table V are given the results regarding the effect of temperature on the intensities of Raman lines in benzene.

TABLE V

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
	363	0·84	1·04	1·24
	423	0·63	1·08	1·71
850	305	1·00	1·00	1·00
	363	0·86	1·02	1·19
	423	0·67	1·04	1·55
990	305	1·00	1·00	1·00
	363	0·90	1·01	1·12
	423	0·78	1·03	1·32
1180	305	1·00	1·00	1·00
	363	0·84	1·01	1·20
	423	0·63	1·02	1·62
1585	305	1·00	1·00	1·00
	363	0·85	1·00	1·18
	423	0·67	1·00	1·49
1605	305	1·00	1·00	1·00
	363	0·84	1·00	1·19
	423	0·62	1·00	1·61
3055	305	1·00	1·00	1·00
	363	0·89	1·00	1·12
	423	0·77	1·00	1·30

4. DISCUSSION OF THE RESULTS

The Raman spectrum of carbon tetrachloride presents a simple case wherein we can get both the Stokes and the anti-Stokes lines with reasonable intensity. It consists of the lines at 215 (ν_2, doubly degenerate), 315 (ν_3, triply degenerate), 460 (ν_1, total symmetric) and 760 and 790 cm.$^{-1}$ (ν_4, triply degenerate). Fermi pointed out that the splitting of ν_4 is due to the accidental degeneracy $\nu_4 \approx \nu_1 + \nu_3$. As can be seen from Table IV, the fairly sharp lines at 215, 315 and 460 cm.$^{-1}$ at the room temperature have slightly

broadened at higher temperatues but there is no change in frequency. Of these three, the line at 460 cm.$^{-1}$, which is shading off in intensity towards the exciting line, is slightly more diffuse than either of the other two lines. ν_4 is a well resolved doublet at the room temperature but at 250° C. the two components have become broad and diffuse and practically merged into each other to become almost a single band extending over about 70 wavenumbers. The above conclusions are in fair agreement with those of Ananthakrishnan.[6]

Placzek's theory indicates that both the Stokes and the anti-Stokes lines increase in intensity with increasing temperature, the intensities becoming infinitely large at very high temperatures. The observed results show that the Stokes lines decrease in intensity and the anti-Stokes lines increase but not to the expected extent. According to the author, the intensities of the Stokes and the corresponding anti-Stokes Raman lines tend to meet each other at some finite intensity but not at infinite intensity as predicted by the theory. This observation indicates a very serious departure from Placzek's theory and the theory has to be suitably modified to account for the observed facts in liquids and solids.

It has already been mentioned in the previous paper, where the author has worked at temperatures below the boiling points of the liquids, that the observed values even when corrected for the expansion do not show an increase as is expected in Placzek's theory. The present investigations confirm this conclusion. It may be mentioned here that the densities of carbon tetrachloride and benzene decrease in the ratio of 1·30 : 1 and 1·16 : 1 respectively when these liquids are heated from the room temperature to the highest temperatures employed in this investigation. Since the illuminated volume has been kept constant, this would mean that the maximum correction to be applied to the observed intensities on this score will result in their being increased as per the above ratios. The recorded discrepancies are, however, far in excess of such corrections. The intensities of the Rayleigh lines on the other hand, when corrected for the expansion, show a definite increase with the increase of temperature. The line at 215 cm.$^{-1}$ in carbon tetrachloride, which has been reported by the author in the previous communication to have shown a slight increase in intensity with increase of temperature from 305° to 340° K, also decreased in intensity at higher temperatures. The ratio of intensities of the Stokes and the anti-Stokes lines tend to approach more and more towards unity with increasing temperatures and the ratios at all temperatures are in conformity with the theoretically expected results.

5. Summary

The author has studied quantitatively the effect of temperature on the Raman spectrum of liquid CCl_4 from 40° to 250° C. and on the Raman spectrum of benzene from 32° to 150° C. It has been observed that the Stokes lines decrease in intensity and the anti-Stokes lines increase but not to the expected extent, with the increase of temperature. The ratios of the intensities of the Stokes and the anti-Stokes lines are in conformity with the results calculated from Placzek's theory at all temperatures. In the case of CCl_4 the lines have broadened out and the widths of the lines at various temperatures are given.

In conclusion, the author takes great pleasure in expressing his grateful thanks to Prof. S. Bhagavantam, Hon. D.Sc., for his interest in this investigation.

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