40

INFLUENCE OF TEMPERATURE ON THE INTENSITIES OF RAMAN LINES DUE TO SOME ORGANIC LIQUIDS

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ABSTRACT The intensities of a few Raman lines of benzyl alcohol, benzyl amine and benzoyl chloride at the room temperature and at higher temperatures, a few degrees below the boiling points of the liquids, have been measured quantitatively, using the method of photographic spectrophotometry. It has been observed that in the case of the lines 610, 794 and 1003 of benzyl alcohol and of the line 1003 of benzoyl chloride, the intensities increase with the increase of temperature in accordance with the predictions of the polarisability theory. In the case of the Raman lines of larger frequency-shifts the intensities are observed to remain almost constant with the increase in the temperature of the liquids as indicated by the said theory.

INTRODUCTION

It is well known that according to the theory put forward by Placzek (1931) the intensity of the Raman lines of frequencies $v-v_i$ should increase with the temperature in accordance with the relation $I_{(v-v_i)} \propto 1/(1-e^{-hv_i/kT})$ ... (1) Several attempts have been made to test the correctness of these predictions of the theory besides those regarding the ratio of the intensities of the Stokes and anti-Stokes Raman lines. Before this theory was published, Landsberg and Mandelstam (1930) had investigated the intensities of Raman line 465 of quartz at temperatures 22°C and 537°C. They observed that the intensity at the higher temperature was 1.29 times that at the lower temperature. The same problem was also studied qualitatively by Ney (1931) who reported that the influence of the increase of temperature on the intensities of the Raman lines of quartz was different for different Raman lines, so that the relative intensities of the Raman lines on the Stokes side were observed to change with the increase of temperature of the crystal. The microphotometric curves of the spectrogram reproduced by Ney show that the line 465 of quartz shifts to 458 and its intensity diminishes considerably at the higher temperature. Careful examination of the records, however, also shows that this line becomes much broader at the higher temperature than at the lower temperature. Ornstein and Went (1935), besides measuring the ratio of the intensities of Stokes and anti-Stokes Raman lines, also investigated quantitatively the changes in the intensities of the lines

2 —1455P VI

127 and 165 of quartz with the change of temperature of the crystal from 90°K to 426"K, and of the lines 153, 282, 714 and 1088 of calcite with the change of temperature from 293' K to 426°K. They observed that in the case of both the Raman lines of quartz mentioned above the intensity diminished with the increase of temperature, and the same effect was observed also in the case of the three lines 155, 282 and 714 of calcite, while the intensity of the line 1088 remained constant with the change of temperature. It has not been mentioned by these authors, however, whether they measured the integrated intensity or the peak intensity. It has been pointed out above that the microphotometric records reproduced by Ney indicate a broadening of the line 465 at the higher temperature. Hence the intensity is smaller at the higher temperature than at the lower temperature if the peak intensity is considered, but if the integrated intensity were taken into consideration the conclusion would probably be different, at least for this line.

The same problem was investigated in the case of some crystals more recently by Venkateswarlu (1941). He first studied the intensities of the Raman lines 465 of quartz, 1065 of sodium nitrate and 315 of mercuric chloride at different temperatures and observed in each case a diminution in intensity with the increase of temperature up to about 493"K. He mentioned that the width of the lines did not increase with the increase in temperature and hence only the peak intensities were measured. In a later paper Venkateswarlu (1942) reported the results of similar investigations in the case of calcite. In this case also the intensities of the Raman lines 155, 280, 710 and 1085 of calcite were observed to diminish with the increase of temperature from 305' K up to 493°K. It has been mentioned by him that the lines were of same width at the lower and higher temperatures and so only the peak intensities were measured. If, however, the spectrogram reproduced by him be examined carefully it is found that the line 280 of calcite becomes appreciably broader at higher temperatures. Besides this, the intensities of the Rayleigh lines also appear to diminish at the higher temperatures almost in the same ratio as those of the Raman lines mentioned above. If this be not due to any systematic diminution of the intensity of the incident light at higher temperatures, it is difficult to understand how the intensity of the Rayleigh scattering diminishes with the increase of temperature, because experimentally it has been observed by Landsberg and Mandelstam (1930) that in the case of quartz the intensity of the Rayleigh scattering is proportional to the absolute temperature of the crystal.

The validity of relation (1) in the case of liquids was first tested by Ananthakrishnan (1938) who investigated the intensities of the Raman lines of CCl_4 at temperatures ranging from 25°C to 200°C. He observed that the integrated intensity of the Stokes Raman lines of CCl_4 does not increase with the increase of temperature. He has also discussed various other changes, e.g., broadening, and change of frequency of the Raman lines which are observed with the increase of temperature as well as the difficulties which are experienced in making the experimental conditions identical at both high and low temperatures.

Besides the difficulties mentioned by Ananthakrishnan, *e.g.*, the widening of the lines, the change of refractive index of the liquid causing a change in the intensity of the incident light, and the expansion of the liquid, there is another difficulty not mentioned by him, namely, the birefringence of the window of the tube containing the liquid caused by high pressures developed when the liquid is heated much above its boiling point in the closed tube. The present investigation was undertaken with the object of testing the validity of relation (1) given by Placzek in the case of a few aromatic liquids having high boiling points so that no high pressure could be developed inside the tube containing them. Some of the other sources of error have also been taken into account as will be evident from the discussions of the results.

<center>E X P E R I M E N T A L</center>

The liquids chosen for the present investigation are benzyl alcohol, benzyl-amine and benzoyl chloride. These were obtained from Kahlbaum's sealed bottles. They were distilled in vacuum before use. The experimental tube had a plane window and its other end was bent into the form of a horn terminating in a bulb to hold the increased volume of liquid at the higher temperature. A narrow tube was joined to the bulb and after the tube was filled with the distilled liquid upto a level below the bottom of the bulb, the tube was evacuated and a constriction in the narrow tube was sealed off. The heater consisted of a few coils of nichrome wire enclosed between two coaxial brass cylinders, insulated by asbestos and a window was left open parallel to the length of the cylinder. This gap was closed by a transparent thin sheet of mica. The tube was thrust into the heater through one of its mouth and the scattered light was observed through the other mouth, the open regions of which were closed with asbestos packing. Light from a horizontal Heraus type mercury arc condensed by a five-inch glass condenser was used as the incident light which passed through the mica window. The arc was started before the commencement of the exposure and was allowed to run at a stretch undisturbed throughout the exposure for both the hot and the cold liquid. As the room was closed on all sides, the intensity of the arc did not fluctuate during the exposure. Also, as the liquids were heated upto temperatures a few degrees below their boiling points, the plane windows of the experimental tubes did not develop any extra birefringence at the higher temperature. The levels of the liquid in the tail of the experimental tube at the room temperature and at the higher temperatures were noted and from the measured volumes upto these levels the increase in the volume of the liquid was estimated. The temperature was measured with a mercury thermometer which was placed in contact with the glass tube containing the liquid inside the heater.

The Raman spectrum for the hot liquid was photographed first in order to take into account any chemical change in the liquid which might take place with the rise of temperature. The current in the heater was switched off and

the spectrum for the cold liquid was next photographed on the same plate using the same time of exposure as for the hot liquid. A few intensity marks were also obtained on the same plate using different known widths of the slit of the spectrograph and light from an ordinary tungsten filament lamp reflected by a piece of thick white paper as source of continuous radiation. A Hilger two-prism spectrograph of high light-gathering power was used. Microphotometric records of the spectrograms were obtained with the help of a Kipp and Zonen self-recording microphotometer. The intensities of the background on both sides of each line relative to the unexposed portion of the plate were determined in the case of each line in question with the help of the blackening log.-intensity curves and were subtracted from the total intensity of both the background and the line in order to obtain the intensity of the line. In the case of each liquid only a selected few Raman lines have been taken into consideration. Also, in order to investigate the question whether the intensity of the Rayleigh lines increases with the increase of the temperature of liquids, the intensities of the line λ_{4916} recorded at the two temperatures have been compared. The results are discussed in the following section.

RESULTS AND DISCUSSION

The ratios of intensities of particular Raman lines at the higher temperature to the corresponding intensities at the room temperature as deduced from the blackening produced on the plate by the lines with the help of the blackening log.-intensity curves for the corresponding wavelengths are given in column 2 of tables I, II and III. These have been corrected for the dilatation of the liquid at the higher temperatures. The correction factors as calculated from the observed increase of volume of the liquids have been found to be approximately 1.09, 1.09 and 1.08 for benzyl alcohol, benzoyl chloride and benzyl amine respectively. The corrected values of the intensities are given in column 3 of the tables. These intensity-ratios as calculated from relation (1) are given in the last column of the tables. Only Raman lines excited by the Hg line λ_{4358} have been investigated in each case. The ratio of the intensity of the Rayleigh line λ_{4916} at the higher temperature to that at the room temperature as deduced from the spectrograms has also been entered in the last column of each of the said tables. The widths of the lines investigated are observed to remain unchanged at the higher temperatures and therefore the peak intensity has been measured in each case.

It can be seen from tables I, II and III that the intensity of the Raman lines 610, 794 and 1000 of benzyl alcohol and 1003 of benzoyl chloride increases with the rise of temperature of the liquids and the increase observed in each case is fairly in agreement with that predicted by the theory within experimental error. In the case of the lines 1001 and 3055 of benzyl amine the corrected intensity ratio is slightly lower than the calculated value, but this diminution is probably due to some experimental error, which taking into consideration

TABLE I

Benzyl alcohol. B. P. 478 K

Raman line.	$I_{466} I_{303}$ observed	$I_{466} I_{303}$ corrected for dilatation	$I_{466} I_{303}$ calculated
c-610	1.067	1.10	1.135
c-704	1.00	1.00	1.00
c-1000	0.96	1.05	1.03
c-3050	0.90	0.98	1.00
Rayleigh line 4916	1.05	1.14	...

TABLE II

Benzoyl chloride B. P. 470°K

Raman line.	$I_{453} I_{303}$ observed	$I_{453} I_{303}$ corrected for dilatation	$I_{453} I_{303}$ calculated
c-1003	0.953	1.04	1.03
c-1592	0.92	1.00	1.004
c-3067	0.90	0.98	1.00
Rayleigh line 4916	1.11	1.21	..

TABLE III

Benzyl amine. B. P. 457°K

Raman line.	I_{436}/I_{303} observed.	I_{436}/I_{303} corrected for dilatation.	I_{436}/I_{303} calculated.
c-1001	0.90	0.97	1.02
c-3055	0.88	0.95	1.00
Rayleigh line 4916	1.08	1.16	...

all the factors involved cannot be claimed to be much less than 5%. The results, however, show that there is no large diminution of the intensities of the Raman lines with the increase in the temperature of the liquids as observed by previous workers in the case of some crystals and also by Ananthakrishnan in the case of carbon tetrachloride. On the contrary, the intensity of the Raman lines of smaller frequency-shift increases more than that of the lines of larger frequency-shift with the rise of temperature of the liquid as indicated by relation (1), and therefore the relative intensities of these lines undergo changes with the change

Benzyl alcohol

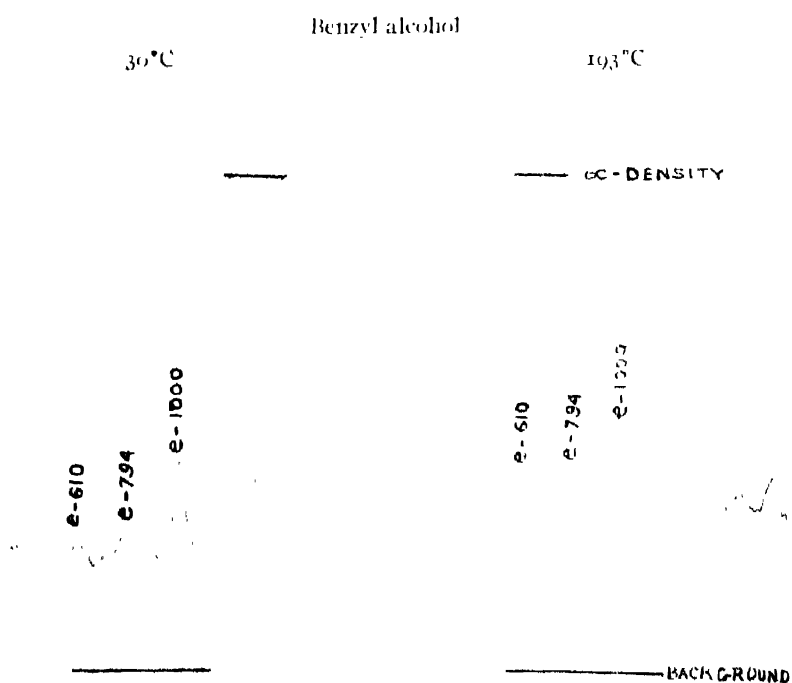30°C   193°C

Fig. 1

of temperature. The microphotometric records of the lines obtained in the case of benzyl alcohol are reproduced in Fig. 1 and it can be seen that the ratio of the intensity of the line 610 to that of the line 1003 increases at the higher temperature.

As regards the intensity of the Rayleigh line the results observed at the two temperatures for the line λ4916 in each case are given in the tables, because, there is no appreciable absorption in this region. It is observed that in each case the intensity of the Rayleigh line increases with the increase of temperature. Since the intensity of the Raman line due to C-H vibration excited by λ4358 and situated close to the line λ4916 does not change with the increase of temperature, the ratio of the intensity of the line λ4916 to that of the Raman line mentioned above increases with the increase of temperature. This can be seen from the microphotometric records reproduced in Fig. 2. Since there was some feeble stray light mixed with the scattered light, the observed increase is
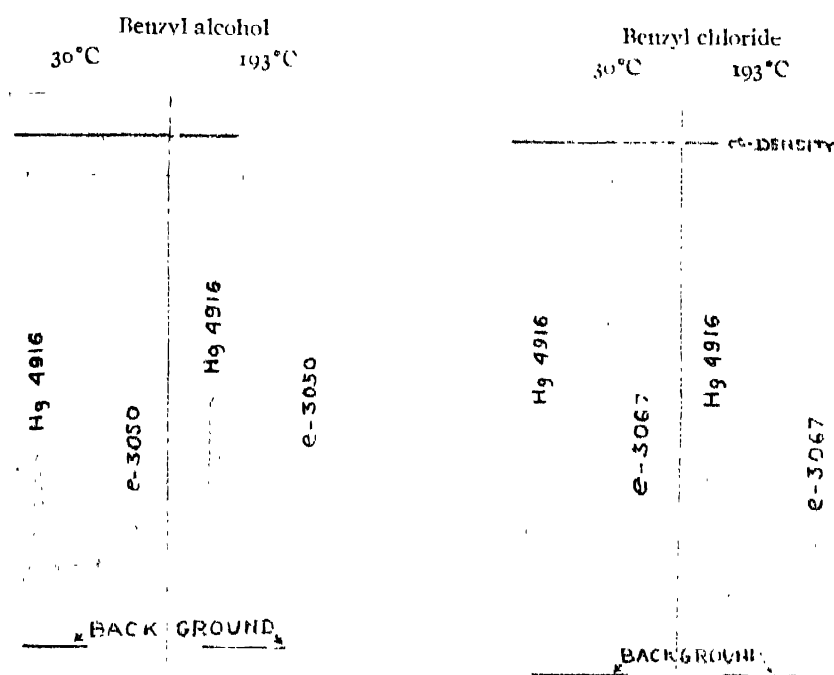
Fig. 2

slightly less than the actual increase in each case. The increase expected theoretically in these cases cannot be calculated, because the values of compressibility, and refractive index at the different temperatures are not known.

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