EFFECT OF TEMPERATURE ON THE RAMAN SPECTRUM OF LIQUID CC\textsubscript{4}.

Some Preliminary Considerations.

BY R. ANANTHAKRISHNAN.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received February 17, 1938.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.I.)

1. Introduction.

In a note published in *Current Science*, for June 1936, the author reported some preliminary observations relating to the spectral changes noticed when the Raman spectrum of liquid CC\textsubscript{4} was photographed at a series of temperatures extending over an interval of about 200° C. Although during the subsequent months time and attention were devoted towards a closer study of this problem, it has not been possible to pursue it in all its details, because of other lines of work which were on hand during this period, and the author’s subsequent departure from the Institute. Nevertheless, it is considered worthwhile to place on record the trend of ideas that have been pursued, and such experimental results as have been obtained during the course of the work.

The study of the effect of temperature on the Raman spectra of substances in general is a problem of interest because of its direct bearing on the important question concerning the nature of the changes brought about by heat in the condition of the molecules in such substances. Quantitative investigations in this direction have been comparatively rare, although we have a large mass of qualitative information. For instance, it is well known that the Raman spectra of polar substances often exhibit appreciable changes when the substances are examined over fairly wide intervals of temperature. These changes fall under two distinct categories, namely, (1) those due to change of state, and (2) those due to changes of temperature without change of state. For our present purpose, we shall confine our attention mainly to the latter class of phenomena. In polar substances these changes are attributed primarily to the mutual influence of the neighbouring molecules which presumably has a functional dependence on temperature. Such a disturbing factor is only of secondary importance in the case of non-polar substances, so that the explanation for the
observed spectral changes, if any, in the Raman spectra of such substances has to be sought for elsewhere.

By far the most important of the molecular properties the consideration of which is of importance from the standpoint of Raman spectra are the rotation and vibration of the molecules. The molecular rotation besides manifesting itself as a wing to the Rayleigh or unmodified line, also imparts a definite width to some of the vibrational Raman lines. The extent of such broadening increases with rise of temperature. Again, in so far as the anti-stokes Raman lines arise from transitions in which the excited vibrational levels of the molecules are involved as initial states, their intensity might be expected to show a pronounced increase at higher temperature. In order, however, to understand the quantitative aspect of the problem it is necessary to recall very briefly Placzek's polarisability theory of the Raman effect of polyatomic molecules (1931).

2. Theoretical.

It is well known that the Raman effect arises from the interaction between the nuclear and electronic motions of the molecules. In order to investigate this interaction, we consider the polarisability $\alpha$ of the molecule which is a magnitude characteristic of the scattering electrons and their binding with the nuclei. The effect of nuclear vibration is then to alter the polarisability of the molecule.

If $\nu_k$ and $\nu_e$ are the frequencies of the nuclear and the electronic vibrations respectively and $\nu$ the frequency of the incident light, Placzek's theory starts with the assumption that $\nu_k \ll \nu_e$, $\nu_k \ll \nu$, and $\nu_k \ll (\nu_e - \nu)$. Under these circumstances, the polarisability $\alpha$ is a function of the normal co-ordinates $q_j$ of the nuclei, so that we have,

$$\alpha(\mathbf{q}) = \alpha_0 + \sum_j \frac{\partial^2 \alpha}{\partial q_j^2} q_j + \frac{1}{2} \sum_{j,k} \left( \frac{\partial^2 \alpha}{\partial q_j \partial q_k} \right) q_j q_k + \cdots \quad (1)$$

where the suffix 0 refers to the equilibrium configuration. When the nuclei begin to vibrate, the quantities $q_j$ become periodic and introduce consequently a time-dependence upon $\alpha$. We have then to substitute for these quantities the well-known expressions for the harmonic oscillator. If the molecule is placed in the electric field $E$ of an incident light-wave of frequency $\nu$, the induced electric moment responsible for the scattering is $\alpha E$. From the expression for $\alpha E$, it can be easily seen that the term in $\alpha_0$ is responsible for the Rayleigh scattering, while the term in $\left( \frac{\partial \alpha}{\partial q} \right)_0$ give rise to the Raman effect. If we take the electric field of the incident light-wave to be parallel
to the $x$-direction, and confine our attention only to the induced moment responsible for the Raman effect, it can be shown that,

$$\left| M_{xx} \right|^2 (v_j \rightarrow v_j + 1) = \mathbb{E}^2 \left( \frac{\partial \alpha}{\partial q_j} \right)_{\alpha}^2 c_j (v_j + 1)$$

(2)

$$\left| M_{yx} \right|^2 (v_j \rightarrow v_j + 1) = \mathbb{E}^2 \left( \frac{\partial \alpha}{\partial q_j} \right)_{\alpha}^2 c_j (v_j + 1)$$

and

$$\left| M_{xx} \right|^2 (v_j \rightarrow v_j - 1) = \mathbb{E}^2 \left( \frac{\partial \alpha}{\partial q_j} \right)_{\alpha}^2 c_j v_j$$

(3)

$$\left| M_{yx} \right|^2 (v_j \rightarrow v_j - 1) = \mathbb{E}^2 \left( \frac{\partial \alpha}{\partial q_j} \right)_{\alpha}^2 c_j v_j$$

where $c_j = \frac{\hbar}{8\pi^2 \mu_j \nu_j}$, $\mu_j =$ reduced mass, $\nu_j =$ vibrational frequency, $v_j =$ vibrational quantum number corresponding to the normal co-ordinate $q_j$. $\left| M_{xx} \right|^2$ and $\left| M_{yx} \right|^2$ represent respectively the mean square of the $x$ and $y$ components of the electric moment which give rise to the Raman radiation of frequency shift $\pm \nu_j$, during the quantum transition $v_j \rightarrow v_j \pm 1$.

From (2) and (3) we obtain the total intensity corresponding to the transition $v_j \rightarrow v_j \pm 1$, by multiplying by the number of molecules in the initial state $v_j$, and transforming the moments to the corresponding intensities. If we neglect the effect of anharmonicity, then irrespective of the initial quantum number $v_j$, all transitions $\Delta v_j = \pm 1$ give rise to radiations of the same frequency $\nu \pm \nu_j$. We therefore obtain the aggregate intensity of the stokes and the anti-stokes components by summing up over all the initial states $v_j$ from 0 to $\infty$. The result is

$$I (\nu - v_j) = \frac{64\pi^2}{3c^3} (\nu - v_j)^4 \left\{ 4 A_{1j}^2 - 7 B_{1j}^2 \right\} \frac{1}{1 - e^{-\frac{\hbar \nu_j}{kT}}}$$

(4)

$$I (\nu + v_j) = \frac{64\pi^2}{3c^3} (\nu + v_j)^4 \left\{ 4 A_{1j}^2 - 7 B_{1j}^2 \right\} \frac{1}{\frac{\hbar \nu_j}{e^{\frac{kT}{\hbar}} - 1}}$$

(5)

where $A_{1j}$ and $B_{1j}$ are the invariants of the symmetric tensor $\left( \frac{\partial \alpha}{\partial q_j} \right)_{\alpha}^2$.

From (4) and (5) it follows that not only the anti-stokes Raman line $(\nu + v_j)$ but also the stokes component $(\nu - v_j)$ increases in intensity as the temperature is elevated. This is because of the factors $(v_j + 1)$ and $v_j$ in equations (2) and (3) which show that transitions between the higher vibrational states give rise to larger intensity of scattering. Fig. 1 gives a graphical representation of the variation of the intensity of the
Effect of Temperature on the Raman Spectrum of Liquid CCl₄

stokes and the anti-stokes Raman lines corresponding to the frequency shift $v_i$ as a function of $\frac{v_i}{T}$.

The ratio of the intensity of the stokes to that of the anti-stokes component is given by:

$$\frac{I(v - v_i)}{I(v + v_i)} = \left(\frac{v - v_i}{v + v_i}\right)^4 \frac{h v_i}{e^{h v_i / k T}}.$$  

(6)

From (6) we see that the intensity of the stokes and the anti-stokes components tend to approach each other for high temperatures in conformity with the classical theory.

In the case of diatomic molecules, on account of the symmetry about the nuclear axis, the constants $A_{1j}$ and $B_{1j}$ in formulae (4) and (5) can be further simplified. If we denote the polarisability of the molecule parallel and perpendicular to the nuclear axes by $\alpha$ and $\beta$ respectively, and the inter-nuclear distance by $R$, and also put $\alpha - \beta = \gamma$ and $\frac{\alpha + 2\beta}{3} = \mu$, then it follows that

$$4 A_{1j}^2 - 7 B_{1j}^2 = 15 \left(\mu' + \frac{7}{45} \gamma''\right),$$  

(7)

where

$$\mu' = R \left(\frac{\partial \mu}{\partial R}\right)_0$$  

and

$$\gamma' = R \left(\frac{\partial \gamma}{\partial R}\right)_0.$$

A further approximate simplification is effected if we denote the polarisability of the individual ions (considered as isotropic) by $\alpha_1$ and $\alpha_2$ respectively;
then it can be easily shown that

\[ a = \frac{a_1 + a_2 + \frac{4a_1a_2}{R^3}}{1 - \frac{4a_1a_2}{R^6}} \]

\[ \beta = \frac{a_1 - a_2 - \frac{2a_1a_2}{R^3}}{1 - \frac{a_1a_2}{R^6}} \]

and hence

\[ \mu' = - (a_1 + a_2) \frac{12a_1a_2}{R^6} \]

\[ \gamma' = - \frac{18a_1a_2}{R^3} \left( 1 + \frac{a_1 + a_2}{R^3} \right) \] (8)

From (4), (5), (7) and (8) we see that it is possible as a first approximation to express the intensity of the Raman lines of a diatomic molecule in terms of the polarisability of the individual atoms and the equilibrium internuclear distance.

In general, the magnitude \( \left( \frac{\partial a}{\partial q} \right)_0 \) is a measure of the intensity of the corresponding Raman radiation of frequency \( \nu \pm \nu_i \). If for any particular normal mode \( a (q_j) = a (-q_j) \), then \( \left( \frac{\partial a}{\partial q} \right) = 0 \), and so the intensity of the corresponding Raman radiation vanishes.


From the above consideration, it will be seen that an experimental investigation comprising the measurement of the absolute and relative intensities of the stokes and the anti-stokes lines as a function of temperature is of great interest because it would afford a direct experimental test of the relations (4), (5) and (6) and hence also of the polarisability theory. The major part of the work in this direction has been directed towards the verification of formula (6) which gives the theoretical intensity relationship between the stokes and the anti-stokes Raman lines. The agreement between theory and experiment has been found to be generally satisfactory in this respect. It must nevertheless be clearly stressed that such an agreement by no means constitutes a crucial experimental test of Placzek’s theory, because of the preponderance of the Boltzmann factor in the expression on the right-hand side of equation (6). The more difficult measurement of the variation of the absolute intensity of the stokes and the anti-stokes Raman lines might be expected to furnish some information on this point.
As early as 1928, Krishnan pointed out in a note in *Nature* that in the Raman spectrum of liquid CCl₄ photographed at 81° C. the stokes lines are weaker and the anti-stokes lines brighter than in the spectrum photographed at the room temperature (34° C.). Such a result appeared to be in conformity with the semi-classical explanation of the Raman effect which existed at that time. Similar conclusions were arrived at by Brickwedde and Peters (1929) who investigated the Raman spectrum of crystalline quartz between 180° C. and 550° C. We know now that the above result, if genuine, is at variance with the demands of the quantum theory, which predicts an increase of intensity with increasing temperature for the stokes as well as for the anti-stokes Raman lines, the ratio between the two intensities at any temperature being given by the relation expressed by (6).

In 1930 Landsberg and Mandelstamm took up an experimental re-investigation of the problem in the case of crystalline quartz, and reported an increase of intensity for the stokes component of the Raman line at 465 cm⁻¹ in the ratio 1:1.29 when the temperature was raised from 295° abs. to 810° abs. Although the expected increase was in the ratio 1:1.6, they concluded that the deviation was within the limits of accuracy attainable in the measurements.

More recently, Ornstein and Went (1935) published the results of an investigation of the influence of temperature on the Raman lines of crystalline quartz and calcite over a range of temperature extending from that of liquid air up to about 150° C. They noticed that while the ratios of the intensities of the stokes and the anti-stokes Raman lines were in fair agreement with equation (6), a wide discrepancy existed between theory and experiment in respect of equation (4). The absolute intensity of all the stokes lines studied by them showed a marked diminution, with rising temperature instead of the expected increase. In particular, the ratio of the intensity of the Raman line 465 cm⁻¹ of quartz at 90° abs. to the intensity of the same line at 420° abs., was found to be as 1:0.57, while according to Placzek’s theory, this ratio ought to be as 1:1.25. The observed diminution of intensity was much greater for the lower frequencies than for the higher frequencies. The Raman lines also showed small frequency diminutions and structural changes with increasing temperature, these being much more pronounced in the region of low frequencies. The above authors did not attempt to give an explanation of the deviations in intensity, but only remarked that due to the correspondingly small magnitude of the elastic forces between the nuclei, the low frequencies might naturally be expected to be deranged by temperature much more easily than the higher ones, and
that it is probable that Placzek's theoretical considerations are inapplicable
to the lines in question.

An essential assumption underlying Placzek's theory is a chaotic
distribution of the scattering centres, which, of course, can be considered
to be approximated only by a liquid or a gas. It therefore appeared to be
of interest to take up an investigation of the above nature with a liquid
over an interval of temperature not hitherto attempted.

4. Experimental Technique and Results.

The liquid chosen was carbon tetrachloride which is specially suited
for an investigation of the present type on account of the comparative
simplicity of its spectrum and the remarkable chemical stability of the
molecule. A convenient quantity of the liquid was distilled in vacuum into
a thick-walled pyrex tube about 8 inches long and 2 cm. internal bore,
capable of withstanding pressures as high as 25 atmospheres. The tube
was initially degassed by heating to a high temperature with continuous
evacuation by a Cenco Hyvac pump. Leaving sufficient space for expansion
of the liquid at high temperatures, the tube was sealed off. The conical
and rounded ends were darkened by deposition of soot, leaving a small
circular aperture at the latter end for the exit of the scattered light. The
tube containing the liquid was placed inside a cylindrical electrical heater
which consisted of a tube of pyrex glass with sparsely wound nicrome wire,
and was supported in a horizontal position at a suitable distance in front
of the slit of a Hilger two-prism spectrograph. By passing suitable currents
through the wire, the liquid could be maintained at any desired temperature
up to 250° C. within ± 5°. The illumination was supplied by a quartz
mercury arc which was focussed on the liquid by means of a 6-inch glass
condensing lens.

(a) Frequency and Structural Changes.—In order to follow the structural
changes of the Raman lines on heating the liquid, it is necessary to work
with a very narrow slit. A slit width of 0.04 mm. was employed in the present
work. Photographs of the Raman spectra with sufficient intensity could be
secured in 24 hours. The observed results may be summarised as follows:—

It is well known that the Raman spectrum of liquid CCl₄ consists of
the following principal frequencies:—

218 cm.⁻¹ ... \( v₂ \) (doubly degenerate).
314 cm.⁻¹ ... \( v₃ \) (triply degenerate).
459 cm.⁻¹ ... \( v₁ \) (totally symmetric).
762 \( \) cm.⁻¹ ... \( v₄ \) (triply degenerate).
Effect of Temperature on the Raman Spectrum of Liquid $CCl_4$

The most striking and easily observed change brought about in the spectrum on heating the liquid is the rapidly increasing broadening and diffuseness of the Raman lines $v_4$. As was first pointed out by Fermi, the splitting of $v_4$ is caused by the accidental degeneracy $v_4 \approx (v_1 + v_3)$. At the room temperature $v_4$ is a well-resolved doublet, but at 200°C it is a broad and diffuse band extending over some 50 wave-numbers, the two components having considerably spread out and practically run into each other. The other two degenerate frequencies which are fairly sharp at room temperature also become broad and diffuse at higher temperature and extend roughly over some 20 wave-numbers at 200°C. On account of this considerable broadening it is difficult to say with any degree of precision whether there is a change in frequency or not. In the case of the totally symmetric vibration which is ordinarily about 10 wave-numbers broad with an intensity maximum at 459 cm$^{-1}$ and shading off in intensity towards the side of the exciting line, the observed changes are of a somewhat different nature. It is slightly more diffuse at the higher temperature, and shows a definite though small diminution in frequency (about 2 to 3 wave-numbers) on careful examination with a comparison iron arc.

(b) Intensity Changes.—When we pass on from considerations of frequency and structural changes to changes in intensity undergone by the Raman lines on heating the liquid, the problem is one of much greater difficulty. In this connection, we have to bear in mind a fundamental difference between liquids, on the one hand and crystalline solids like quartz, calcite, etc., on the other. The expansion of liquids at high temperatures is very large, and gives rise to an appreciable diminution in the density and refractive index of the scattering medium. In making comparative estimates of the intensity of a Raman line at two different temperatures, we have to allow for these two factors; while the diminution in the density of liquid due to expansion causes a decrease in the number of effective scattering centres per unit volume, the change in the refractive index profoundly modifies the path of the light beam traversing the medium. It is therefore obvious that alone for these two reasons, the conditions of exposure cannot be identical at the lower and the higher temperatures. Fluctuations in the intensity of the light source during the exposure and broadening of the line under consideration at the higher temperature are two other disturbing factors in the accurate estimation of the intensity of a Raman line at two different temperatures.

In the course of his experimental work the author has found that the last-mentioned difficulty can be easily overcome and the integrated intensity
of a Raman line can be readily obtained by the simple device of using a wide slit to photograph the Raman spectrum. This procedure also effects a considerable saving in the time of exposure, so that errors consequent on fluctuations in the source intensity can be better guarded against. Thus it was found that whereas a few hours were required to photograph the Raman spectrum of CCl₄ with reasonable intensity using a narrow slit (.04 mm.), a few minutes were sufficient when a wide slit as employed (about 0.6 mm.). In working with the wide slit, however, care should be taken to see that there is no overlapping between adjacent Raman lines. It might be pointed out in this connection that in the work of Landsberg and Mandelstamm already referred to, the time of exposure at the lower and higher temperatures was 5 days and some difficulty was experienced in assessing the integrated intensity of the Raman line in question at the two different temperatures on account of its slight broadening at the higher temperature.

The errors consequent on the expansion of the liquid are not capable of being eliminated in any simple manner, and it would seem that the only way of allowing for it is to choose the Rayleigh scattering as the standard of comparison at the higher and lower temperatures. This would involve a preliminary experiment in which the Rayleigh scattering of the liquid is investigated as a function of temperature by the well-known experimental technique. Unfortunately, for want of time, it has not been possible for the author to carry out this part of the work in the case of liquid CCl₄. However, qualitative observations which can only be regarded as preliminary, appear to show that there is hardly any perceptible increase in the intensity of the stokes lines of CCl₄—perhaps even a decrease in intensity—with rise of temperature.

5. Some General Remarks.

(a) Rotational Broadening of the Degenerate Vibrations.—Degenerate vibrations are associated with simultaneous changes in the vibrational and rotational quantum numbers of the molecule so that they are always accompanied by rotational structure which is seldom resolved. Consequently, such vibrational lines are generally somewhat broad and diffuse and exhibit the limiting depolarisation value of $6/7$ in Raman effect. Since more and more of the higher rotational levels are occupied at the higher temperatures, the rapidly increasing broadening of the degenerate vibrations on heating the liquid becomes quite intelligible.
(b) Effect of Anharmonicity of the Nuclear Vibrations.—At temperature $T$, the probability of a molecule existing in the vibrational state $v_i$ is proportional to $e^{-\frac{(v_i + 1)}{kT}}$, where $v_i$ is the vibrational frequency. Hence, if we denote by $N_0$, $N_1$, $N_2$, $\ldots$ the probable number of molecules in the vibrational states 0, 1, 2, $\ldots$ we have for $v_i = 459 \text{ cm}^{-1}$ (the totally symmetric vibration of $\text{CCl}_4$), the following percentage distribution of the molecules between various vibrational states at $25^\circ \text{C}$ and $200^\circ \text{C}$ respectively.

### TABLE I.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>$N_0$</th>
<th>$N_1$</th>
<th>$N_2$</th>
<th>$N_3$</th>
<th>$N_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$25^\circ \text{C.}$</td>
<td>89</td>
<td>9.8</td>
<td>1.07</td>
<td>0.11%</td>
<td>$\ldots$</td>
</tr>
<tr>
<td>$200^\circ \text{C.}$</td>
<td>75.36</td>
<td>18.46</td>
<td>4.67</td>
<td>1.13%</td>
<td>0.35%</td>
</tr>
</tbody>
</table>

If we denote by $I_0$, $I_1$, $I_2$, $\ldots$ the contribution to the total intensity arising from the transitions $0 \rightarrow 1$, $1 \rightarrow 2$, $2 \rightarrow 3$, $\ldots$ and if $I = I_0 + I_1 + I_2 + \ldots$ then, since $I_{v_i} \propto (v_i + 1) N_{v_i}$, we have,

### TABLE II.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>$I_0$</th>
<th>$I_1$</th>
<th>$I_2$</th>
<th>$I_3$</th>
<th>$I_4$</th>
<th>$I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$25^\circ \text{C.}$</td>
<td>89</td>
<td>19.6</td>
<td>3.21</td>
<td>0.44</td>
<td>$\ldots$</td>
<td>112.25</td>
</tr>
<tr>
<td>$200^\circ \text{C.}$</td>
<td>75.36</td>
<td>36.92</td>
<td>14.01</td>
<td>4.52</td>
<td>1.75</td>
<td>132.56</td>
</tr>
</tbody>
</table>

Hence

$$\frac{I_{200^\circ}}{I_{25^\circ}} = \frac{132.56}{112.25} = 1.18 : 1.$$  

Thus according to Placzek's theory the integrated intensity of the totally symmetric vibrational Raman line of $\text{CCl}_4$ at $200^\circ \text{C}$ should be $1.18$ times its intensity at $25^\circ \text{C}$.

It has been already pointed out that the effect of anharmonicity of the nuclear vibration is not explicitly taken into account in Placzek's theory. Consequently, the frequencies arising from the transition $0 \rightarrow 1$, $1 \rightarrow 2$, etc., are assumed to be exactly superposable. We know, however, that the vibrational levels of a molecule approach each other more and more with increasing quantum numbers, so that the frequency arising from the transition $v_i \rightarrow v_i + 1$ diminishes with increasing $v_i$. Thus for the molecule of
chlorine in the ground state, band spectroscopic data shows that \( v (0 \rightarrow 1) = 557 \text{ cm}^{-1} \), and \( v (1 \rightarrow 2) = 549 \text{ cm}^{-1} \). The frequency observed in the Raman spectrum of liquid chlorine is 555 cm\(^{-1}\) and corresponds to the transition \( 0 \rightarrow 1 \). Now in the case of \( \text{CCl}_4 \) at room temperature, as we see from Tables I and II, the major contribution to the intensity of the line \( \nu_1 \) (about 80\%) comes from the transition \( 0 \rightarrow 1 \), while at 200\° C. the contribution from this transition is much less (about 56\%) and the contribution from the transition \( 1 \rightarrow 2, 2 \rightarrow 3, \ldots \) become correspondingly more important. Since these contributions are not strictly superposable we readily understand the increased diffuseness and the shift in the intensity maximum of the totally symmetric vibration at the higher temperature.

Again we saw in Section 2 that the intensity of a Raman line is determined by the value of \( \left( \frac{\partial a}{\partial q} \right)_0 \) for the vibration concerned and that this quantity is a function of the internuclear distance of the molecule, diminishing very rapidly with increasing nuclear separation. It is well known that the effect of vibration in the case of a di-atomic molecule is to increase the average distance between the nuclei since these are a greater proportion of the time at \( R > R_0 \) than at \( R < R_0 \), the potential energy curve \((V, R)\) being steeper to the left than to the right of the minimum. The centrifugal forces due to the rotation of the molecule also tend to increase the average distance of the nuclei. Now, the effect of increasing the temperature is to excite the higher rotational and vibrational states of the molecule and hence to increase the mean internuclear distance. As the contribution towards the intensity of the total Raman scattering from transitions involving higher quantum numbers becomes more and more important with increasing temperature in the case of relatively low Raman frequencies, it appears probable that in such cases the effect of the anharmonicity of the nuclear vibration and the centrifugal stretching due to rotation of the molecule, is to tend to cause a diminution in the intensity of such Raman lines.

In conclusion, the author's respectful thanks are due to Prof. Sir C. V. Raman for his kind interest and suggestions during the course of this work.


After a brief review of Placzek's theory of the Raman effect, the paper gives a short account of the experimental investigations that have been hitherto carried out to verify the intensity relationships predicted by the theory. The latter indicates that (i) the ratio of the intensities of the stokes and the anti-stokes components tend to approach more and more
Effect of Temperature on the Raman Spectrum of Liquid CCl₄ 207
towards unity with increasing temperatures, and (ii) that the absolute intensities of both the stokes and the anti-stokes lines increases with increasing temperature. While theory and experiment have been found to be in conformity as regards (i), considerable discrepancies have been noticed in respect of (ii). In the case of crystalline solids like quartz, calcite, etc., previous work shows that the stokes lines instead of showing the expected rise in intensity, exhibit a pronounced weakening at higher temperatures. In this connection, the Raman spectrum of liquid CCl₄ has been investigated over an interval of temperature extending from 25° to 200° C. and the spectral changes noticed are discussed. The degenerate vibrations manifest considerable broadening at higher temperatures, the doublet at (762–790) cm⁻¹, well resolved at the lower temperature, appearing as a single broad and diffuse band in the spectrum photographed at 200° C. The totally symmetric vibrational Raman line at 459 cm⁻¹ is also somewhat more diffuse at the higher temperatures and shows a small diminution in frequency. The integrated intensities of the stokes lines of CCl₄ seem to show no increase at the higher temperature. It is suggested that the effect of anharmonicity of the nuclear vibrations and the centrifugal stretching of the molecule due to rotation, is probably responsible for this departure from the expected increase in intensity.

REFERENCES.