DISTRIBUTION OF INTENSITY IN THE ROTATIONAL RAMAN SPECTRA OF GASES.

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Received December 22, 1934.

1. *Introduction.*

In a series of communications (Bhagavantam, 1933 and Veerabhadra Rao, 1934) certain significant results have been described concerning the distribution of intensity within the rotational wings exhibited by liquids. Quantitative investigations have revealed that the phenomenon in liquids is characterised by certain prominent features which are ordinarily not to be noticed in the case of gases. In this respect the experimental results so far obtained with gases may be regarded as quite satisfactory inasmuch as they are in good agreement with the existing theories of the rotational Raman effect. In liquids, however, it is obvious from the results that complicating features have set in and no satisfactory and simple theoretical explanation is forthcoming as in the case of gases. It is of utmost importance, from the standpoint of the theory of the rotational Raman effect and its relation to the nature of the liquid state, to reconcile the two apparently different types of intensity distribution obtained in liquids and gases respectively. It is obvious that this can be done experimentally by following up the alterations produced in the rotational patterns consequent on either gradually (i) heating up a liquid subject to the pressure of its own vapour or (ii) compressing a gas at temperatures lower than its critical temperature. In the first case the liquid may be expected to develop the features characteristic of its vapour whereas in the second the gas may be expected to develop the features characteristic of the corresponding liquid. In the present paper, the problem is approached on the lines of the latter alternative and carbon dioxide and nitrous oxide are chosen for the investigation in view of their moderate critical pressures and the close proximity of their critical temperatures to the room temperature.

2. *Experimental Arrangements.*

The container used for the gas is a thick-walled transparent silica tube enclosed in steel casing. With suitably devised washers, the apparatus can be used without leak at pressures upto 50 atmospheres. Details of its construction have already been described in earlier papers by one of us

(Bhagavantam, 1932) and will not therefore be repeated here. Light from a mercury arc is condensed on to the gas tube, the length of the illuminated portion of the gas being about 5 inches. The scattered light is photographed with a 2 prism glass spectrograph of high light gathering power. Suitable apertures are placed in the track of the scattered beam so as to eliminate the stray light as completely as possible. This precaution is necessary as otherwise the Rayleigh line would be so heavily exposed as to mask the features of the rotational wing to a large extent. Several photographs of varying intensities of the rotational wing have been obtained with carbon dioxide and nitrous oxide at low and high pressures and the intensity distribution on each plate is computed with the help of a set of intensity marks recorded on the same plate by the method of varying slit widths. The best representative values are given in the next section. In each experiment a low pressure picture and a high pressure picture are photographed along with the intensity marks on the same plate keeping the other arrangements unaltered. The low pressure picture is exposed for a correspondingly longer period so as to obtain an intensity comparable with that in the high pressure picture. The long exposures involved have resulted in a broadening of the undisplaced line to an appreciable extent and points in its vicinity which are likely to be affected by such a broadening have not been taken account of.

3. *Results.*

Owing to the insufficient resolving power of the instrument, separate rotation lines have not been observed and the results in Table I represent the intensities in the continuous wing at various points whose respective wave number distances from the central line are given as $\Delta\nu$. The figures are only relative and have no absolute significance.

TABLE I.

$\Delta\nu$ (cm.$^{-1}$)		18·5	21·6	24·6	27·7	30·8	38·5	46·2	53·9	61·6	69·3	77·0	92·4
CO_2	Low pressure (7 atm.)	47·3	51·5	53·0	53·0	51·5	40·4	29·7	20·8	13·2	6·8	—	—
	High pressure (47 atm.)	62·6	58·8	54·6	51·7	48·5	38·8	30·2	21·5	15·6	12·7	—	—
N_2O	Low pressure (7 atm.)	—	—	47·0	48·3	48·3	43·0	35·0	26·7	18·6	13·2	7·2	2·2
	High pressure (37 atm.)	45·2	52·0	52·0	49·0	47·0	41·0	32·6	24·9	18·8	13·8	10·7	8·1

These results are represented graphically in Figs. 1 and 2. The crosses are the observed points at high pressures and the circles with dots inset are

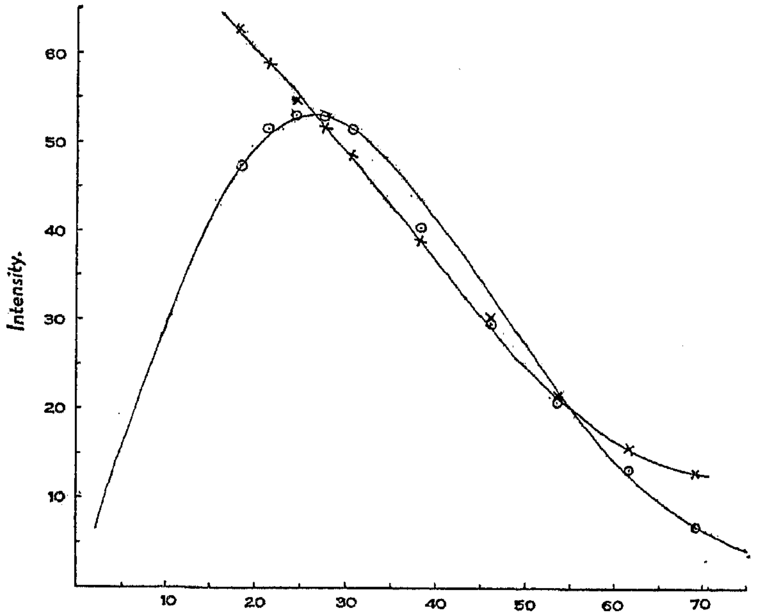


FIG. 1. CO_2 $\Delta\nu$ cm.$^{-1}$

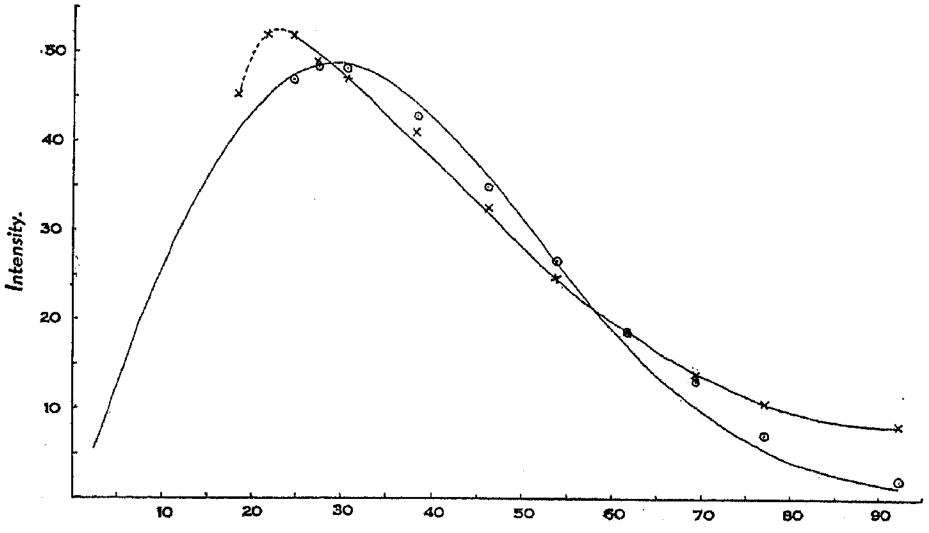


FIG. 2. N_2O $\Delta\nu$ cm.$^{-1}$

the observed points at low pressures. The smooth curves starting from zero intensity at the centre in each case and extending to $\Delta\nu=75$ in CO_2 (Fig. 1) and to $\Delta\nu=90$ in N_2O (Fig. 2) are drawn on the basis of the theory of the rotational Raman effect developed by Manneback (1930) assuming $70 \cdot 2 \times 10^{-40}$ and $59 \cdot 4 \times 10^{-40}$ respectively for the moments of inertia of CO_2 and N_2O molecules. In the case of CO_2, only alternate rotation lines representing transitions between even levels are assumed to be present

(Houston and Lewis, 1931). In N_2O no such assumption need be made and all the lines are given the same weight factor (Plyler and Barker, 1931).

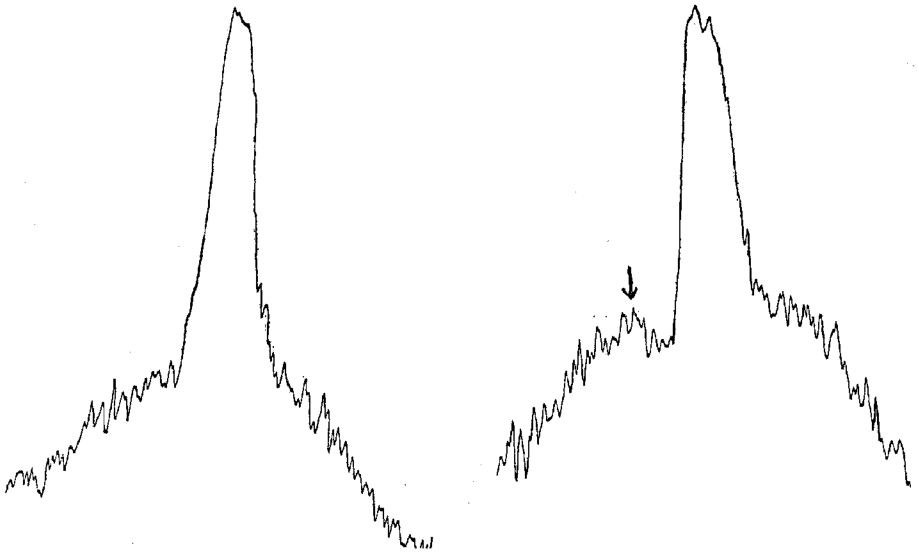
4. *Discussion of the Results.*

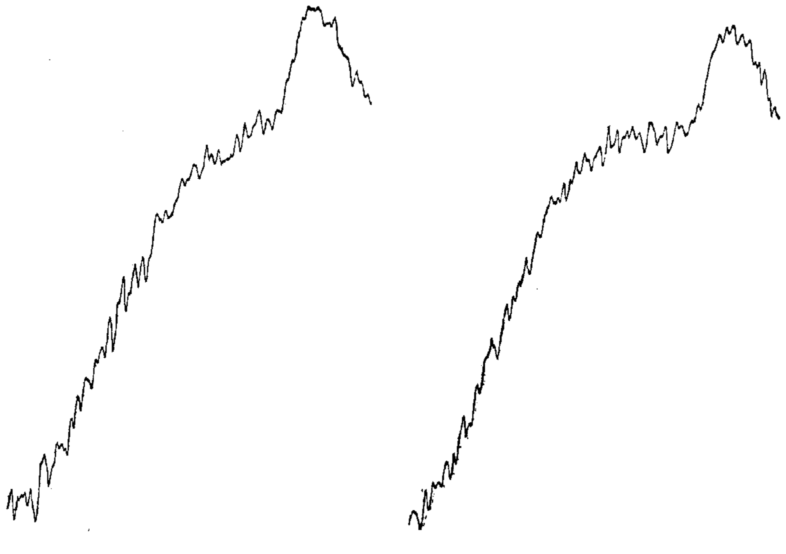
The following prominent features, easily noticeable from Figs. 1 and 2, may be recorded here. The experimental points obtained at low pressures for both the gases deviate very little from the courses of the corresponding theoretical curves. Although it has not been found possible to obtain reliable points close to the Rayleigh line, the observations distinctly show that at the expected place, there is a maximum of intensity and that on either side of this maximum is a fading off of the wing in satisfactory accordance with the theory applicable to gaseous molecules. The positions of the intensity maxima in the low pressure pictures are measured from the microphotometric records and they correspond to a moment of inertia 69×10^{-40} for CO_2 and 62×10^{-40} for N_2O in good agreement with $70 \cdot 1 \times 10^{-40}$ and $59 \cdot 4 \times 10^{-40}$ deduced respectively for these molecules earlier from infra-red absorption spectra (Adel and Dennison, 1933 and Plyler and Barker, 1931).

On the other hand, the observed points at higher pressures show considerable deviations from the courses of the theoretical curves and suggest that the intensity distribution within the wing has been appreciably affected by the increased pressure. In the case of carbon dioxide (Fig. 1) at a pressure of 47 atmospheres, we have not been able to locate any maximum at or near the expected place. The intensity falls off gradually and the gradient appears to be somewhat less than in the case of the same gas at lower pressures. Nitrous oxide (Fig. 2) at a pressure of 37 atmospheres exhibits similar characters. The observed points deviate considerably from the course of the theoretical curve. Maximum is not located at the expected place but much closer to the central line. The intensity falls off less rapidly at the higher pressure than at the lower pressure. It must, however, be noted that these characters are not so marked in N_2O as in CO_2, an observation which may be attributed to the fact that the pressure employed in the former case is only 37 atmospheres as against 47 atmospheres in the latter.

Two typical sets of curves obtained by us and reproduced in Figs. 3 and 4 bring out the above features in a very clear manner. Figs. 3*a* and 3*b* are the microphotometric records of the rotation wing accompanying the λ 4077 mercury line in carbon dioxide at 47 and 7 atmospheres respectively. The presence of a distinct maximum shown by the arrow at low pressures [Fig. 3(*b*)] and its absence at high pressures [Fig. 3(*a*)] are easily noticeable.

There is a redistribution of intensity at high pressures and the tendency is towards a concentration at points close to the central line. Exactly the same features are seen in Fig. 4 which contains the microphotometric records of the rotation wing accompanying the λ 4046 mercury line. The flatness of the curve in the vicinity of the central line [Fig. 4(*b*)] at low pressures and the relatively larger concentration of intensity in this region at higher pressures [Fig. 4(*a*)] is easily recognised. A relatively large concentration of intensity in the close neighbourhood of the Rayleigh line


(*a*) FIG. 3. (*b*)


(*a*) FIG. 4. (*b*)

and the absence of a maximum, contrary to what is indicated by the theory, have hitherto been regarded as features specially characteristic of the liquid state and it is of very great significance that these are now recognised also in gases but only at high pressures. Such phenomena are evidently connected with the fact that at the higher pressures employed both CO_2 and N_2O are near their critical states thus resembling the liquids in certain respects. This view is further supported by the fact that no such observations have been made with either hydrogen or oxygen although they have been investigated at reasonably high pressures (Bhagavantam, 1932; Trumpy, 1932).

REFERENCES.

Adel and Dennison .. .. .. *Phys. Rev.*, 1933, **44**, 99.
Bhagavantam .. .. .. *Ind. Jour. Phys.*, 1932, **7**, 107.
Do. .. .. .. *Ibid.*, 1933, **8**, 197.
Houston and Lewis .. .. .. *Proc. Nat. Acad.*, 1931, **17**, 229.
Manneback .. .. *Z. f. Phys.*, 1930, **62**, 224.
Plyler and Barker .. .. .. *Phys. Rev.*, 1931, **38**, 1827.
Trumpy .. .. *Z. f. Phys.*, 1933, **84**, 282.
Veerabhadra Rao .. .. .. *Proc. Ind. Acad. Sci.*, 1934, **1**, 274.