RAMAN SPECTRUM OF DEUTERIUM: II.

Intensity and Polarisation Characters.

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1. *Introduction.*

In Part I of this series (Bhagavantam, 1935), the author described a preliminary investigation of the Raman spectrum of deuterium. In the present paper a quantitative study of the intensity and polarisation characters of the various Raman lines is made and the results are compared with the conclusions of the existing theories of Raman scattering by gaseous molecules (Manneback, 1930 and Placzek, 1934). More intense and satisfactory photographs of the scattered light have incidentally been obtained and a complete analysis is made of all the new lines appearing in the scattered spectra.

2. *Experimental.*

Measurement of Relative Intensities.—The preparation of deuterium under pressure, the experimental tube and the illuminating arrangements, have all been already described in earlier papers. In this investigation an intense picture is obtained by giving a continuous exposure of about 6 days for purposes of measuring the relative intensities of the lines. The Plate is run through a Moll microphotometer and the densities of the various lines are obtained in the usual way. A set of intensity marks is recorded on the same Plate by the method of varying slit widths using the continuous radiation emitted by a standard quartz globe tungsten ribbon lamp as the source. A steady current of 14·8 amperes is maintained in the lamp by feeding it from a battery of 220 volts. The colour temperature T of the lamp corresponding to this current is given by the makers as 2660 and the radiation emitted by the lamp is therefore assumed to obey the Wien's law $I_\lambda = A\lambda^{-5} e^{-c_2/T\lambda}$ where $c_2 = 1 \cdot 432$, $T = 2660$ and A is a constant. The density at any desired wave-length is obtained for each of the intensity marks by running the Plate through the microphotometer under the same conditions as above and the corresponding intensities are taken as proportional to their respective slit widths. In this way, the density-log intensity curves are drawn for each wave-length at which the various Raman lines that are to be compared with each other appear. The intensity of any line as a fraction of the standard radiation having the same wave-length as the line itself is easily read off from the above curves and the relative intensities of the various lines are then computed from a knowledge of the intensity distribution in the radiation emitted by the lamp. It may easily be seen that this procedure totally eliminates errors due to variations in the photographic sensitivity of the Plate in different regions of the spectrum.

Polarisation Characters.—For this purpose, a suitably oriented double image prism is introduced in the path of the scattered light and the two images representing respectively the vertical and the horizontal components are focussed one above the other on the slit of the spectrograph. They are thus simultaneously photographed (see Plate XXV) and fluctuations in the intensity of the incident radiation are not therefore of any consequence. On the same Plate is recorded as before a set of intensity marks by the method of varying slit widths using the standard tungsten ribbon lamp. Density–log intensity curves are drawn for each one of the wave-lengths at which the Raman lines appear and a knowledge of the densities of the horizontal and vertical components of any particular line enables us to obtain the depolarisation ratio from the corresponding density–log intensity curve. Depolarisation factors obtained in this manner are subject to corrections arising from (i) depolarisation introduced by oblique refraction at the prism surfaces, and (ii) a certain lack of transversality between the incident and scattered rays. The method of determining and applying these corrections has already been described by the author in earlier papers (Bhagavantam, 1932) and the values given in the following pages are obtained after applying these corrections.

3. *The Raman Spectrum of Deuterium.*

The main frequency shifts observed in the Raman spectrum of deuterium have already been given in Part I. In a subsequent paper (Bhagavantam, 1935), a further set of faint lines have been reported and attributed to the presence of a small proportion of hydrogen deuteride molecules in the sample under investigation. The relation of the observed frequency shifts to the molecular constants has been discussed. In more intense pictures that have since been obtained, all these frequencies are confirmed and some of them are found to be excited by two or even three different lines of the incident spectrum. It may be noted that using the full range of the mercury lamp in the visible region, no fewer than about 28 lines have been recorded with this simple substance. A complete list of the observed lines and their assignments to the various exciting radiations are given below in Table I.

TABLE I. *Raman Spectrum of Deuterium.**

Wave-length	Approx. Rel. intensity	Exciting line	Quantum transition	
			J	n
3979·4	1	4046	4 → 2	
3999·1	1	,,	3 → 1	
4017·9	2	,,	2 → 0	
4090·0*	0	,,	0 → 2	
4096·3	4	,,	1 → 3	
4097·8	1	3650	..	0 → 1
4104·5	1	3654	..	0 → 1
4115·7	5	4046	2 → 4	
4121·5*	½	,,	1 → 3	
4128·0	½	4077	1 → 3	
4135·1	2	4046	3 → 5	
4147·6	½	4077	2 → 4	
4154·9	2	4046	4 → 6	
4281·3	1	4358	4 → 2	
4302·5	1	,,	3 → 1	
4308·7*	0	,,	2 → 0	
4324·5	2	,,	2 → 0	
4392·7	4	,,	0 → 2	
4409·6*	0	,,	0 → 2	
4415·6	3	,,	1 → 3	
4438·7	5	,,	2 → 4	
4443·8*	½	,,	1 → 3	
4461·6	2	,,	3 → 5	
4478·9*	0	,,	2 → 4	
4484·1	2	,,	4 → 6	
4604·3	4	4046	..	0 → 1
4644·7	½	4077	..	0 → 1
5009·5	0	4358	..	0 → 1

* Lines marked with an asterisk arise from hydrogen deuteride molecules.

4. *Relative Intensities of the Rotation Lines.*

In Table II the observed intensities of the various rotation lines are compared with the calculated values. The calculations, details of which are to be found in Part I, refer to a temperature of 30° C. The figures are only relative and have no absolute significance.

TABLE II.

Relative Intensities of the Rotation Lines.

Transition	PP Series		Transition	RR Series	
	Calculated	Observed		Calculated	Observed
$2 \rightarrow 0$	0·57	0·69	$0 \rightarrow 2$	1·33	1·34
$3 \rightarrow 1$	0·22	0·4	$1 \rightarrow 3$	0·90	0·82
$4 \rightarrow 2$	0·20	0·4	$2 \rightarrow 4$	1·47	1·40
$5 \rightarrow 3$	0·01	..	$3 \rightarrow 5$	0·41	0·46
			$4 \rightarrow 6$	0·32	0·38
			$5 \rightarrow 7$	0·02	..

The agreement between the two sets of values is fairly satisfactory. Appreciable discrepancies are, however, to be noticed in connection with the two relatively faint antistokes lines but these may be attributed to the fact that errors in photometric measurements are more likely in cases of such faint lines. According to the theory we should expect the $2 \rightarrow 4$ line to be the most intense and this is confirmed. The calculations clearly show that the intensity of the rotation lines rapidly falls off from the sixth line onwards on the stokes side and the fourth line onwards on the antistokes side and in order to obtain these, one would have had to expose the picture for about fifteen times the normal period. The non-appearance of these lines in the photographs (Plate XXV) is thus fully explained.

The fact that the rotation lines representing transitions between even levels are stronger than those representing transitions between odd levels is contrary to what is observed in ordinary hydrogen and shows that the nuclei obey Bose-Einstein statistics. The quantitative agreement between the observed results and the detailed calculations as given in Part I further confirms the view that the deuterium nucleus has a spin moment of one unit. The deuterium nucleus thus differs from the hydrogen nucleus in these two important respects as the latter conforms to Fermi-Dirac statistics and has a spin moment of only half a unit.

5. *Polarisation of the Raman Lines in Deuterium.*

The Raman spectrum obtained for this purpose with a double image prism in the path of the scattered light is reproduced in the Plate accompanying this paper. The vertical and horizontal components are clearly separated from each other. The almost complete depolarisation of all the rotation lines stands out in marked contrast with the nearly perfect state of polarisation of the three vibration lines marked V. R. and excited respectively by λ 3654, 4046 and 4358 radiations of the mercury arc. The vibration line excited by λ 3650 falls nearly on the top of a rotation line $1 \to 3$ and the admixture consequently exhibits a state of polarisation which is intermediate. The results obtained are given in Table III.

TABLE III.

Depolarisation of the Raman Lines.

Transition	$J: 2 \to 0$	$0 \to 2$	$1 \to 3$	$2 \to 4$	$3 \to 5$	$n: 0 \to 1$ $J: 0 \to 0$, $1 \to 1$, etc.
Depolarisation	0·84	0·86	0·84	0·84 0·88	0·83	0·18

All the values, with the exception of 0·88 for $2 \to 4$ rotation transition and 0·18 for the vibration transition, refer to lines excited by λ 4358. The latter two are obtained with lines excited by λ 4046. A depolarisation factor of 0·86 is to be expected for all rotation lines when unpolarised incident light is used and the observed results closely agree with this expectation. The low value of 0·18 for the vibration line compares well with 0·13 reported earlier by the author for the vibration line in ordinary hydrogen (Bhagavantam, 1932).

6. *Intensity of the Vibration Line.*

A direct comparison is made of the intensity of the vibration line excited by λ 4046 with the rotation line $2 \to 4$ excited by the same radiation. Since this rotation line has been found to be about 1·4/5·9 of the total rotational scattering (see Table II), it is easy to compute the intensity of the vibration scattering in relation to the aggregate rotational scattering. These figures are given in Table IV. If we further provisionally assume that the aggregate depolarisation of the scattered light in deuterium is the same as in hydrogen (about 2%), it follows that the aggregate rotational scattering will be about 3/100 of the Rayleigh scattering and an approximate estimate may be made of the intensity of the vibration scattering in relation to that of the Rayleigh line. The figure so obtained is given in column 4 of Table IV. This may be compared with the corresponding figure $4 \cdot 2 \times 10^{-3}$

TABLE IV.

Intensity of the Vibration Line.

Comparison	Vibration line ($n \cdot 0 \rightarrow 1$) / Rotation line (J: $2 \rightarrow 4$)	Vibration line (n : $0 \rightarrow 1$) / Aggregate rotation scattering	Vibration line (n : $0 \rightarrow 1$) / Rayleigh line
Relative Intensity	0·43	0·10	3×10^{-3}

obtained in ordinary hydrogen and shows that like hydrogen, the vibration Raman line in deuterium is about 1/300 of the Rayleigh line. Such a large intensity of the vibration scattering is exceptional in gases and has so far been observed only in hydrogen besides deuterium.

7. *Summary and Conclusion.*

Measurements have been made of the intensity and polarisation of the lines in the Raman spectrum of deuterium. The results, when compared with those calculated from the theory of rotational Raman scattering due to Manneback, show satisfactory agreement.

The vibration Raman line in deuterium is found to exhibit a depolarisation factor of 0·18 and an intensity of about one-tenth the aggregate intensity of the rotational scattering. From this result it is estimated that the intensity of the vibration line is about 1/300 of that of the Rayleigh line. This is an unusually large ratio for gases and has hitherto been found only in hydrogen.

Further work in relation to the fine structure of the vibration line and the inter-comparison of the P, Q and R branches is in progress and will form the subject-matter of the next paper in this series.

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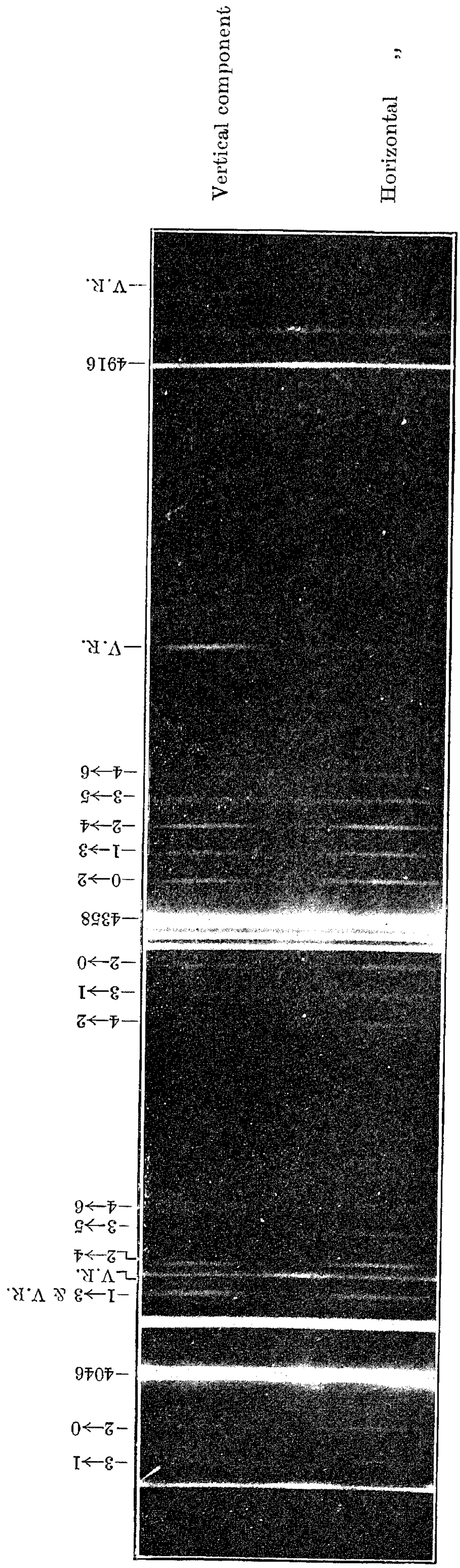

Raman Spectrum of Deuterium taken with a double image prism in the path of the scattered beam to show the state of polarisation of the various lines.