RAMAN SPECTRUM OF DEUTERIUM : I.

By S. Bhagavantam.

(*From the Department of Physics, Andhra University, Waltair.*)

1. Introduction.

In two earlier papers (Bhagavantam, 1932), the author studied the Raman spectrum of ordinary hydrogen in all its aspects in great detail using a specially constructed high pressure gas tube as the container for the gas. It is felt that these investigations should be extended to the case of heavy hydrogen as of all the other molecules that are amenable to such studies, it comes next in simplicity. The necessity of making a complete experimental survey of the Raman spectrum in such a case so as to include all the important features such as the intensity relationships, polarisation characters and fine structure of the lines, need not be overstressed here. It may, however, be pointed out that ordinary and heavy hydrogen constitute the only two cases which may be expected to furnish unique experimental evidence on a variety of points in favour or otherwise of the existing theories of the Raman effect. This, of course, is intimately connected with the very low moments of inertia and the simplicity of structure of these molecules. The present paper is the first of a series dealing with the Raman spectrum of deuterium which the author proposes to publish and contains the preliminary results obtained in this direction.

2. Experimental.

Preparation of Deuterium.—The following procedure is adopted for preparing deuterium under high pressure. About 5 grammes of heavy water supplied as 99·5% pure by the Ohio Chemical and Manufacturing Company is further purified by slow distillation in an evacuated and sealed double bulb of pyrex glass. The water thus purified is transferred to a thin wall glass capsule. The glass capsule is sealed off and carefully inserted into a specially prepared steel bomb. About 6 grammes of sodium and a small steel hammer are introduced into the bomb which is then closed. Through a pin valve connected to the bomb all the enclosed air is removed thoroughly by means of an efficient oil pump, till a manometer connected in the circuit showed that any air that may have been left inside the bomb is only at a pressure of a fraction of a millimeter. The pin valve is then closed and the

303

steel hammer dropped, by suitably tilting the bomb, on to the water bulb. The bulb breaks and the water at once reacts with the sodium thus generating deuterium inside the bomb at a high pressure. The volume chosen for the bomb is such that the above quantities of heavy water and sodium have generated a pressure of about 100 atmospheres. The reaction is almost instantaneous and is accompanied by the evolution of a large quantity of heat. The total volume of the deuterium generated is about 3 litres at atmospheric pressure.

The gas is then allowed to cool and is transferred into the experimental tube designed for a study of the Raman effect in gases at high pressures and described by the author in the earlier papers already referred to. The connecting tubes used in transferring the gas and the experimental tube are thoroughly evacuated beforehand through pin valves. In this way the experimental tube is filled with fairly pure (nearly 100%) deuterium at a pressure of about 17 atmospheres.

Exposure.—Light from a six-inch quartz mercury arc is condensed by means of a large glass condenser on to the gas tube. The scattered light is focussed with a short focus lens on the slit of a Hilger 2 prism glass spectrograph of high light gathering power. Using a slit width of 0·05 mm. a continuous exposure of about 72 hours is found necessary to record the Raman spectrum with reasonable intensity. Golden Isozenith plates have been used for photographing the spectra.

3. Results.

Table I gives the various lines recorded and measured in the Raman spectrum of deuterium in the present investigation. The plate shows other feeble lines which are not included in the table and these will be measured and interpreted in subsequent communications after obtaining more intense photographs. Figs. (*a*) and (*b*) in the Plates are respectively the Raman spectrum of deuterium and a microphotometric record of the same. The transitions are given for some of the rotation lines that are easily seen in the reproductions. V.R. indicates the vibration Raman line excited by λ 4046. The microphotometric record is confined only to the rotation lines in the neighbourhood of λ 4358 and is intended to exhibit the approximate relative intensities of these lines. The most remarkable feature s the alternation of intensities, lines representing transitions between even rotational quantum numbers being stronger than those that represent transitions between odd rotational quantum numbers. The nearly equal intensity of the 0→2 and the 2→4 lines may also be noted and is of special significance.

TABLE I.

Raman Spectrum of Deuterium.

-length	Approx. Rel. Intensity	Exciting line	Frequency shift	Quantum transition	
				J	n
4·27	2	4046	2992·7	$\begin{cases} 0 \to 0 \\ 1 \to 1 \\ \text{etc.} \end{cases}$	0→1
4·13	1	4358	643·5	4 → 6	
L·58	1	,,	530·8	3 → 5	
3·69	5	,,	415·2	2 → 4	
)·58	3	,,	297·4	1 → 3	
)·74	5	,,	179·5	0 → 2	
;·77	0	,,	−178·1	2 → 0	
·54	0	,,	−297·5	3 → 1	
·67	4	4046	414·9	2 → 4	
·02	3	,,	298·4	1 → 3	
·01	0	,,	−175·4	2 → 0	

Discussion of Results and their Comparison with Theory.

quency *Shifts and the Molecular Constants.*—The Raman spectrum
m at a pressure of 2·5 atmospheres has been investigated by
nd Yost (1935) recently using λ 2537 of mercury as the exciting
These authors have reported two rotation lines having frequency
9·6 and 298·3 and a vibration line having a frequency shift
These figures are in satisfactory agreement with those obtained
ior. In the present investigation use is made of λ 4358 as the
iation and it has been possible to record several other rotation
ome antistokes lines as the gas is obtained at a much greater
litherto there existed no direct experimental evidence for the
onstants of deuterium. These have been derived by Urey and
only indirectly by making use of the data available for the H_2 and
es with the help of the usual relations between the constants of

F

isotopic molecules. Anderson and Yost have shown that these constants satisfactorily predict the positions of the two rotation lines observed by them in the Raman spectrum of deuterium. This agreement may be regarded as the first direct experimental evidence for the molecular constants of deuterium but cannot be considered complete as the anharmonic constants and the small correction terms do not make themselves felt appreciably until we reach large rotation quantum numbers. The fact that in the present investigation, five lines have been recorded and measured, enables us to make the comparison much more complete and the results provide a most satisfactory confirmation of the constants derived by Urey and Teal. The rotational energy of a diatomic molecule in a specified electronic state and zero vibrational state is given by the following equation

$$\frac{E_J}{hc} = \left[B_e - \frac{\alpha_e}{2} + \frac{\gamma}{4} - \frac{\delta}{8} \right] J(J+1) + \left[D_e + \frac{\beta}{2} \right] J^2(J+1)^2 + F_e J^3(J+1)^3 \qquad .. \quad (1)$$

In this equation J is the rotational quantum number and B_e is the moment of inertia of the molecule in a state of vibration of infinitesimal amplitude and is related to B_0 the moment of inertia of the molecule in the zero vibrational state by the equation

$$B_0 = B_e - \frac{\alpha_e}{2} + \frac{\gamma}{4} \text{ etc.} \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \quad (2)$$

The other constants are all small and enter only as correction terms. Assuming, in accordance with Urey and Teal, that $B_e = 30.459$; $\alpha_e = 1.0858$; $\gamma = 0.01713$; $\delta = 0.00115$; $-D_e = 0.01121$; $\beta = 2.39 \times 10^{-4}$, the rotational energies pertaining to the various J values are calculated from (1) and the frequency shifts of the Raman lines $0 \to 2$, $1 \to 3$, etc. are deduced. These are given in Table II along with the frequency shifts observed in the present investigation for comparison. Since the antistokes rotation lines and those excited by λ 4046 are somewhat weak, in giving the figures in Table II, only the lines excited by λ 4358 are taken into consideration.

TABLE II.

Comparison with Theory.

Transition	J : 0 → 2	1 → 3	2 → 4	3 → 5	4 → 6
Observed frequency	179·5	297·4	415·2	530·8	643·5
Calculated frequency	179·1	297·7	414·9	530·3	643·5

lent agreement between the two sets of values up to the fifth
.ne must be regarded as a satisfactory confiimaticn of both the
:cular constants and the correction terms as well.

lative Intensities of the Rotation Lines, Spins and Statistics of the
rom observations on the alternation of intensities in the α
euterium, Lewis and Ashley (1933) have concluded that the nucleus
m obeys the Einstein-Bose statistics, and that the spin cannot be
phy and Johnston (1934) working on the Fulcher spectrum of D_2
uded that the statistical weight of the symmetric states is twice
ɛ antisymmetric states. This would mean that the spin of the
nucleus is 1. These results indicate that in the Raman spectrum
m, unlike the case of ordinary hydrogen whose nuclei obey the
c statistics, the lines representing transitions between even rota-
itum numbers should be stronger than those that correspond to
between odd rotational quantum numbers. This is most satis-
nfirmed in the present investigation as may be seen from Figs.
in the Plates. The formulæ originally developed by Manneback
subsequently also given by Placzek (1934) for the relative intensi-
rotational Raman lines in the case of a diatomic molecule are
f in calculating the intensities given in Table III. It is assumed
ules with even rotational quantum numbers have a statistical
:e as large as that possessed by those having odd rotational
umbers. The calculations are for a temperature of 30° C. and
: $B_0 = 29\cdot916$.

TABLE III.

Calculated Relative Intensities of the Rotation Lines.

P P Series : $J \rightarrow J - 2$.		R R Series : $J \rightarrow J + 2$	
Transition	Intensity	Transition	Intensity
$2 \rightarrow 0$	0·571	$0 \rightarrow 2$	1·333
$3 \rightarrow 1$	0·220	$1 \rightarrow 3$	0·904
$4 \rightarrow 2$	0·202	$2 \rightarrow 4$	1·467
		$3 \rightarrow 5$	0·407
		$4 \rightarrow 6$	0·322
		$5 \rightarrow 7$	0·020

S. Bhagavantam

The figures are only relative and have no absolute significance. It is easily seen from the pictures that the relative intensities experimentally obtained are in qualitative agreement with the above figures. The fact that the lines $0 \rightarrow 2$ and $2 \rightarrow 4$ are to be expected to be of nearly the same intensity, both being more intense than $1 \rightarrow 3$ is beautifully confirmed in the microphotometric record of Fig. (b) in the Plates. The intensity distribution amongst the various lines is a very exceptional one and has not been observed in any of the Raman spectra so far studied.

(c) *The Vibration Line and Its Fine Structure.*—The vibration line $n : 0 \rightarrow 1$ should consist of several fine structure components arising from different molecules belonging to different rotational states. The spacing of these may be calculated using the constants given by Urey and Teal. In the present investigation, however, the resolution employed and the exposure given are sufficient only to bring out the strongest of these components and a detailed calculation of the positions and the relative intensities of these components is therefore postponed to a later communication. The strongest line should have a frequency shift of 2991·2* and the observed value of 2992·7 is in good agreement with this figure. Anderson and Yost have given 2989·5 for the frequency shift of this line.

5. Summary and Conclusion.

The paper describes the results of a study of the Raman spectrum of deuterium at a pressure of about 17 atmospheres using λ 4358 of mercury as the incident radiation.

Rotation lines having frequency shifts ±179·5, ±297·4, 415·2, 530·8 and 643·5 and a vibration line with a shift of 2992·7 have been observed. These shifts are in excellent agreement with and provide for the first time a direct experimental confirmation of the molecular constants given by Urey and Teal for the D_2 molecule.

The relative intensities of the rotation lines are in agreement with the fact that the deuterium nucleus has a spin of one unit and obeys the Bose-Einstein statistics. States characterised by even rotational quantum numbers are given a statistical weight twice as large as that of those having odd rotational quantum numbers.
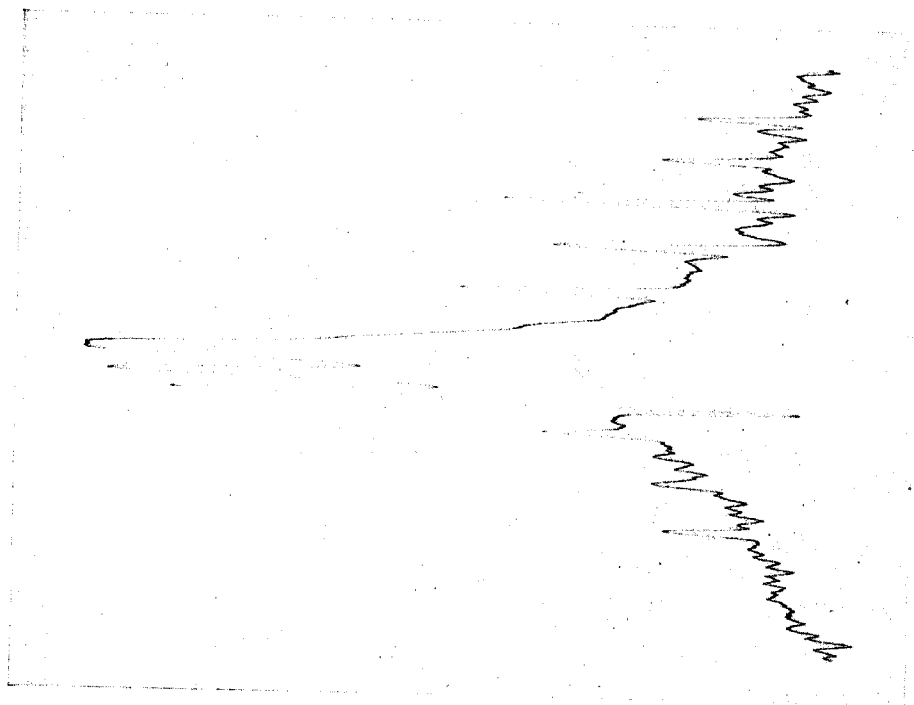
The intensity distribution is in qualitative agreement with that predicted by the theory developed by Manneback for the rotational Raman scattering in diatomic molecules.
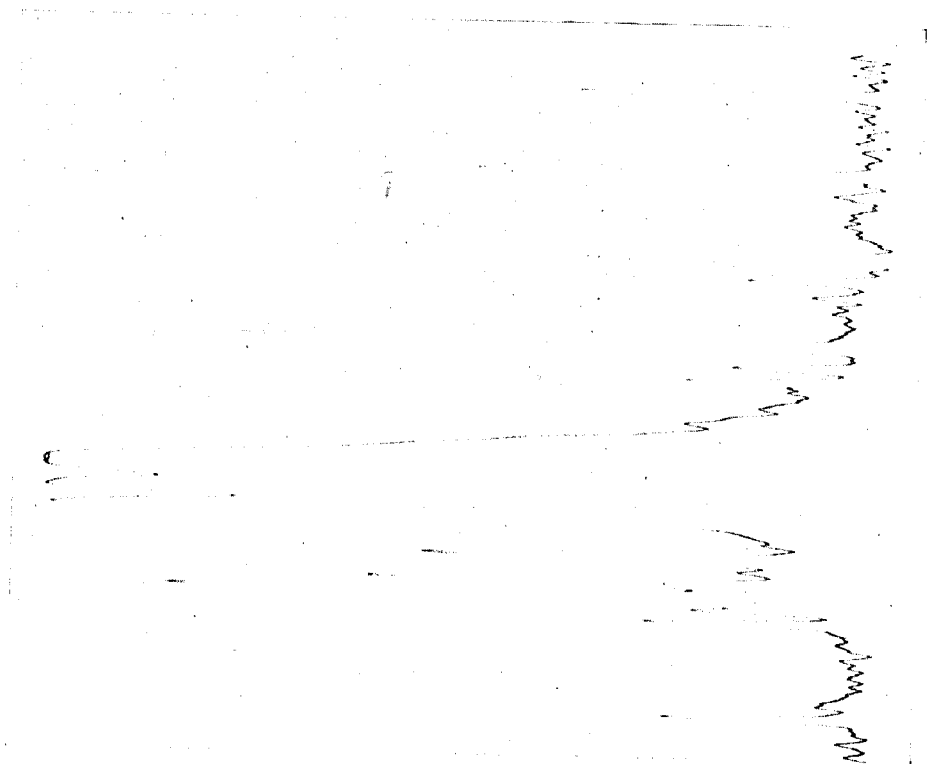
---

* See T. F. Anderson and D. M. Yost, *loc. cit.*
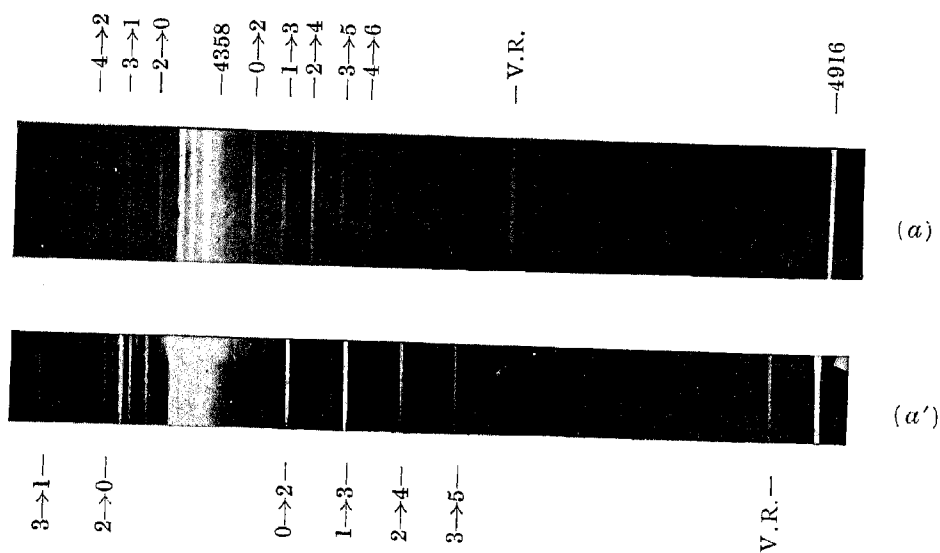
(a) Raman Spectrum of Deuterium.
(a') Raman Spectrum of Hydrogen on the same scale for comparison.

(b′) Microphotometric record of the Raman Spectrum of Hydrogen on the same scale.

(b) Microphotometric record of the Raman Spectrum of Deuterium.

re detailed and quantitative investigation of the intensity, fine
nd polarisation characters is in progress and will form the subject-
a further communication.

clusion, the author desires to express his grateful thanks to Sir
in for his kind encouragement and a loan of the heavy water used
:nt investigation.

REFERENCES.

derson and D. M. Yost	*Jour. Chem. Phys.,* 1935, **3**, 242.
ivantam	*Ind. Jour. Phys.,* 1932, **7**, 107 and 549.
ewis and M. F.	
.. ..	*Phys. Rev.,* 1933, **43**, 837.
eback	*Z. f. Phys.,* 1930, **62**, 224; and **65**, 574.
urphy and H. Johnston	*Phys. Rev.,* 1934, **45**, 500 and 761; and **46**, 95.
:k	*Handbuch Der Radiologie,* 1934, **6**, Part 2, 205.
ey and G. K. Teal ..	*Rev. Mod. Phys.,* 1935, **7**, 34.