

RAMAN SPECTRUM OF HYDROGEN DEUTERIDE.

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1. Introduction.

IN an earlier paper in this Journal* the author had described the results of a study of the Raman spectrum of deuterium. Subsequent to this, a particularly intense picture of the scattered spectrum is obtained using the same sample of the gas as in the previous investigation with a view to complete the work in all its aspects. This photograph, besides showing the Raman lines of D_2 very intensely, is found to exhibit another feeble series of lines excited by λ 4358. Measurement revealed that these have their origin in the HD molecules. The extreme feebleness of the lines in comparison with the D_2 lines indicates that the HD molecules are present in a very small proportion in the sample under investigation. A search is made for the well-known Raman lines of the H_2 molecule but none has been found. It may, therefore, be concluded that the sample contains no appreciable proportion of H_2 molecules. In the present paper the results of the measurements relating to the HD series of Raman lines are given.

2. Results.

TABLE I.

Raman Spectrum of Hydrogen Deuteride.

Wave-length	Exciting line	Approx. rel. intensity	Frequency observed	Frequency calculated	Transition $J \rightarrow J'$
4479.0	4358	0	618	614.8	$2 \rightarrow 4$
4443.9	„	$\frac{1}{2}$	442	442.1	$1 \rightarrow 3$
4409.6	„	0	267	266.5	$0 \rightarrow 2$
4308.7	„	0	-264	„	$2 \rightarrow 0$

The lines having frequency shift of 442 is the strongest of the series and the corresponding line excited by λ 4046 is also seen and measured on the plate.

* See page 303 of this number.

3. Discussion of Results.

W. H. Rindesbush, *Phys. Rev.*, 1934, 45, 480. Beutler and Mie² (1934) have analysed the bands of HD molecule in the ultra-violet. Urey and Teal³ (1935) have given the following constants for the normal state of this molecule to account for the experimental data of the above authors.

$$\begin{aligned} \nu_0 &= 6549; \alpha = 1.9928; \gamma = 0.03850; \delta = 0.00317; -D_e = 0.02602; \\ \beta &= 6.58 \times 10^{-4}; F_e = 2.19 \times 10^{-5}. \end{aligned}$$

These constants are used in calculating the frequencies of the various Raman lines $0 \rightarrow 2$, $1 \rightarrow 3$ and $2 \rightarrow 4$ as in the foregoing paper and the results are given in Table I for comparison. The agreement between observed and calculated frequency shifts is very satisfactory in view of the feebleness of the lines.

Another outstanding feature of the spectrum is the absence of the alternation of intensities. The intensity rises to a maximum at the second rotation line corresponding to $1 \rightarrow 3$ † and then falls off. This is in accordance with what may be expected as the molecule is composed of identical atoms. The relative intensities of the rotation lines that are to be expected on the basis of Manneback's expressions (Manneback,⁴ 1930) are calculated and given in Table II. Same statistical weight is assigned to

TABLE II.

Calculated Relative Intensities of the Rotation Lines.

PP Series $J \rightarrow J-2$		RR Series $J \rightarrow J+2$	
Transition	Intensity	Transition	Intensity
$2 \rightarrow 0$	0.188	$0 \rightarrow 2$	0.666
$3 \rightarrow 1$	0.095	$1 \rightarrow 3$	0.786
		$2 \rightarrow 4$	0.483
		$3 \rightarrow 5$	0.176
		$4 \rightarrow 6$	0.040

W. H. Rindesbush, *Phys. Rev.*, 1934, 45, 480.

Beutler and K. Mie, *Naturwiss.*, 1934, 22, 418, and subsequent papers.

Urey and G. K. Teal, *Rev. Mod. Phys.*, 1935, 7, 34.

† It is noted that in D_2 , this line is weaker than the first rotation line $0 \rightarrow 2$.

Manneback, *Z. f. Phys.*, 1930, 62, 224; and 65, 574.

both even and odd rotational states. The calculations are for a temperature of 30°C. and the value of B_0 is taken as 44.67.

The fact that the intensity reaches a maximum at the second line and then falls off is nicely confirmed. A more detailed comparison is not at present possible owing to the feebleness of the lines. The stokes lines represented by $3 \rightarrow 5$ and $4 \rightarrow 6$ and the antistokes line $3 \rightarrow 1$ have not been recorded.

In conclusion the author desires to express his grateful thanks to Sir C. V. Raman for his kind interest in the work.

4. Summary.

Using $\lambda 4358$ as the exciting radiation, frequency shifts of 267, 442 and 618 arising respectively from the rotational transitions $0 \rightarrow 2$, $1 \rightarrow 3$ and $2 \rightarrow 4$ have been recorded in the Raman spectrum of hydrogen deuteride gas. The figures compare well with 266.5, 442.1 and 614.8 which are calculated on the basis of the molecular constants given by Urey and Teal for the HD molecule. The antistokes line arising from the transition $2 \rightarrow 0$ is also recorded. The phenomenon of alternating intensities is not observed and the line corresponding to $1 \rightarrow 3$ is the most intense one in the series as may be expected.