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The Raman Spectra of the Isotopic Molecules H_2 , HD, and D_2

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The Raman spectra of H_2 , HD and D_2 gases, at 3 atmospheres pressure, were excited by Hg 2537 and photographed with a high dispersion quartz prism spectrograph. A total of 42 lines were analyzed. The positions of the pure rotation lines for H_2 agree with the measurements of Rasetti but the lines in the Q vibration band do not. New vibrational constants calculated from the Raman and emission spectrum data of H_2 and HD give calculated

values of the positions of the rotational-vibration Raman lines in good agreement with the values observed for the three isotopic molecules. Contrary to the theoretical predictions, the 0,0 line of the Q vibrational band of HD was observed. A source of error in Raman measurements, namely, the movement of the spectrum due to variations of the barometric pressure during the exposure of a plate, was detected and eliminated.

INTRODUCTION

THE large mass ratios and low moments of inertia of the three hydrogen molecules H_2 , HD, and D_2 make them particularly suited for a demonstration of isotopic effects expected in the Raman spectra of diatomic molecules. Several years ago the Raman spectrum of the H_2 molecule was investigated by Rasetti,¹ who succeeded in photographing lines in the pure rotational and the 0-1 rotation-vibration bands. Observation of two rotational lines and the unresolved Q vibrational branch of D_2 was recently reported in a note by Anderson and Yost.² In this paper we wish to report measurements of lines in the pure rotation and the 0-1 rotation-vibration bands of the H_2 , HD, and D_2 molecules.

In the course of this work, a serious difficulty was encountered, namely, a shift in the spectrum due to fluctuations in the barometric pressure. Merton,³ working in the visible with a high dispersion glass spectrograph, appears to be the only one to have reported this effect. Although we have found it a serious source of error in Raman measurements, especially for gases where the exposure times are longest, a search has revealed no previous mention of it in the literature on the Raman effect. For this reason we report it in rather greater detail than might otherwise seem necessary.

¹ F. Rasetti, Phys. Rev. **34**, 369 (1929).

² T. F. Anderson and D. M. Yost, J. Chem. Phys. **3**, 243 (1935).

³ T. R. Merton, Proc. Roy. Soc. **A113**, 704 (1926).

EXPERIMENTAL

The first photographs of the Raman spectrum of hydrogen, taken in the region 2450 to 2850 Å with a Hilger E-1 quartz prism spectrograph, were entirely unsatisfactory for the measurement of the Raman displacements. The lines on two of the plates appeared to be incompletely resolved doublets and on others they appeared diffuse and the rotational structure of the vibrational branch was incompletely resolved. This loss of resolution was found to be due to fluctuations in the barometric pressure during the exposures. Such fluctuations are accompanied by changes in the refractive index of the air in contact with the prism and by consequent changes in the path of the light entering and emerging from it. By photographing the iron arc spectrum through adjacent holes of a Hartmann diaphragm, it was found that shifts of the order of 0.1 Å frequently occurred during the three hours between successive exposures. Measured values of the shift observed in this way agreed closely with those calculated from the change of the index of refraction of the air with pressure. The shifts were too large to be accounted for on the basis of a pressure effect on the frequency of the lines emitted by the iron arc.

To eliminate the above difficulty, the spectrograph was encased in a pressure-tight steel box having removable ends of aluminum. A crystal quartz window admitted the light to be analyzed. A rack and pinion device was provided for changing the position of the Hartmann diaphragm without opening the box. The instrument was barostatted at 739 mm by use of a mercury

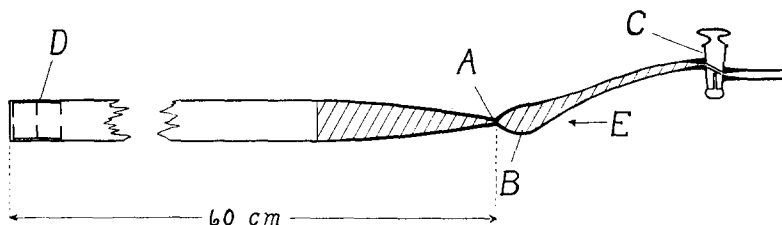


FIG. 1. Raman cell.

manometer contact and a relay controlling a Hyvac oil pump connected to the box. The pressure was maintained constant to within less than 0.1 mm. The instrument was also thermostatted at 32°C to within a few hundredths of a degree.

Subsequent to the barostatting of the spectrograph, additional exposures were made to determine more exactly the magnitude of the pressure effect. During two successive exposures of a plate to the mercury arc, the pressure in the spectrograph was maintained at 595 mm and then at 745 mm. Measurements of the displacement of corresponding lines in the superimposed spectra gave a value of approximately 2.6Å/cm change in pressure as compared to the calculated value of 1.7Å. The discrepancy between the observed and calculated values is probably to be attributed to the approximate character of the calculations and to strains set up in the spectrograph mounting.

The fused quartz cell in which the gas under study was placed was constructed as indicated in Fig. 1. It was approximately 60 cm long and had an inside diameter of 2.5 cm. The walls of the cell, which were approximately 2 mm thick, were calculated to withstand, with a safety factor of three, two atmospheres in excess of the atmospheric pressure. One end was drawn down symmetrically along the axis of the cell to the 1 mm (I.D.) constriction *A*, to which the subsidiary light horn *B* was added. The Pyrex vacuum stopcock *C* was attached to the cell by means of a seven-step seal. The gas contained in the cell was illuminated by three low pressure Hanovia 2537 Mercury Arcs, the radiating elements of which were quartz tubes (1 cm in diameter and 133 cm long) bent into the shape of

closed S's. The arcs were held firmly against the Raman tube by a polished aluminum reflector which was bound around them. Each arc was supplied approximately 100 milliamperes by individual high voltage (0.5 kva) transformers. The arcs maintain a low temperature and therefore were sufficiently cooled by the use of two fans.

The illumination of the spectrograph slit by light coming directly from the walls of the quartz cell was minimized by a series of three platinum diaphragms *D* spun and spot-welded into a platinum sleeve and blackened by the electrodeposition of a thin film of platinum by the method of Lorch.⁴ The diaphragms allowed uniform illumination of a 3-mm length of the slit when the tube was placed about three centimeters from it. The cell was easily and accurately aligned along the optical axis of the spectrograph by sighting through a temporarily unblackened portion *E* of the subsidiary light horn and through the constriction *A* and the diaphragms *D* at light sent through the spectrograph in the reverse direction.

The mercury arcs were found to produce high concentrations of ozone resulting in the absorption of $\lambda 2537$ and also the scattered light. In order to reduce this loss of light, a moderate stream of nitrogen was allowed to flow between the cell and the reflector. It is estimated that this method of eliminating the envelope of ozone around the cell decreased the exposure time by a half or two-thirds. The actual exposure times were from 100 to 200 hours.

The exciting line that was scattered without change of wave-length was partially absorbed by

⁴ A. Lorch, Thesis, Columbia University, 1932.

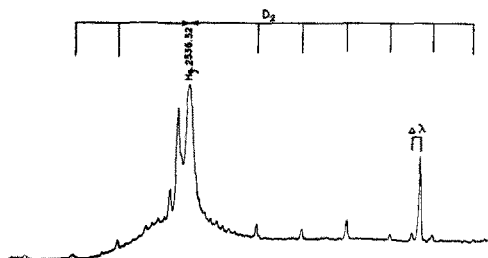


FIG. 2.

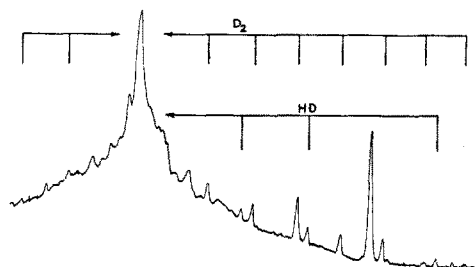


FIG. 3.

vapor from a small quantity of mercury placed in the spectrograph.

The deuterium content of the gas samples used for obtaining Plates I, II, and III was 99, 70, and 60 percent, respectively.

The iron arc was used as a reference spectrum.

RESULTS

In Figs. 2 and 3 are shown the microphotometer curves of the pure rotational spectra on Plates I and II. Plates I and III were taken after the spectrograph was barostatted. Due to the failure of the relay controlling the pump connected to the barostat, the pressure in the spectrograph was reduced from 739 mm to about 600 mm for approximately 10 to 12 hours during the exposure of Plate I. The resultant pressure shift of one of the mercury lines is indicated in the microphotometer curve of Fig. 2 as an apparent change in wave-length $\Delta\lambda$. Plate II is the only one satisfactory for measurement obtained previous to the barostatting of the spectrograph. Even for this plate, however, the line width was somewhat greater than obtains when the pressure is controlled, as may be seen by comparing the curves of Plates I and II in Figs. 2 and 3, respectively.

While photographing the iron spectrum on Plate I an accidental jarring of the spectrograph caused a movement of the plate and resulted in a shift of the reference spectrum with respect to the Raman spectrum. In determining the frequencies of the Raman lines, allowance for this shift was made by determining its value for the Rayleigh scattered mercury lines. It was considered best to obtain the apparent frequency of the irradiating mercury line from the Stokes and

anti-Stokes Raman lines on each plate, the values 39,411.9 cm^{-1} , 39,412.43 cm^{-1} and 39,412.35 cm^{-1} being found for Plates I, II, and III, respectively.

The error in measurement of the lines varies from 0.5 to 1.0 cm^{-1} except for several very weak lines. It is estimated that the average values of the three plates are good to approximately 0.3 cm^{-1} .

In order to calculate the frequencies, the following expression for the energy⁶ was used:

$$\begin{aligned} E/hc = & \bar{\omega}_e(v + \frac{1}{2}) - x\bar{\omega}_e(v + \frac{1}{2})^2 \\ & + y\bar{\omega}_e(v + \frac{1}{2})^3 - z\bar{\omega}_e(v + \frac{1}{2})^4 \\ & + [B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 - \delta_e(v + \frac{1}{2})^3]J(J+1) \\ & + [D_e + \beta_e(v + \frac{1}{2})]J^2(J+1)^2 + F_eJ^3(J+1)^3; \end{aligned}$$

The constants used are those of Jeppesen^{6, 7} as recalculated by Urey and Teal.⁸ Below is given, in Tables I and II, a comparison of the calculated and observed values of the frequencies in wave numbers in vacuum.

It will be seen in Table I that there is good agreement between the observed and calculated values of the pure rotational lines. Though a trend in the values for D_2 indicates that the rotational levels for this molecule may be closer together than predicted by theory the variation from the theoretical values is within the experimental error for most lines. Very good agreement is had between the values for H_2 in Table I and those found by Rasetti¹ and Bhagavantam.⁹ For

⁶ W. Jeavons, *Report on Band Spectra of Diatomic Molecules*, Cambridge (1932).

⁷ C. R. Jeppesen, *Phys. Rev.* **44**, 165 (1933).

⁸ C. R. Jeppesen, *Phys. Rev.* **45**, 480 (1934).

⁹ H. C. Urey and G. K. Teal, *Rev. Mod. Phys.* **3**, 243 (1935).

⁹ S. Bhagavantam, *Ind. J. Phys.* **6**, 319 (1931); **7**, 105 (1932).

TABLE I.

ν	J	PLATE I	PLATE II	PLATE III	AVERAGE	CALC.	DIFFERENCE
H ₂	0-0	3-1	—	586.3	586.3	587.0	-0.7
		2-0	—	354.3	354.3	354.3	0.0
		0-2	—	354.5	354.5	354.3	+0.2
		1-3	587.1	586.9	586.9	586.9	0.0
		2-4	—	815.3	815.3	814.4	+0.9
		3-5	—	1034.5	1034.5	1034.5	-0.1
HD	0-0	4-2	—	616.0	616.0	616.2	-0.2
		3-1	444.2	442.5	443.3	443.1	+0.2
		2-0	—	268.0	268.0	267.1	+0.9
		0-2	267.9	265.4	267.1	267.1	0.0
		1-3	443.0	442.9	443.0	443.1	-0.1
		2-4	—	616.0	616.0	616.2	-0.2
		3-5	785.4	784.5	784.9	785.2	-0.3
		4-6	—	949.3	949.3	949.1	+0.2
D ₂	0-0	6-4	—	642.2	642.2	643.5	-1.3
		5-3	528.2	530.2	529.2	530.3	-1.1
		4-2	—	416.1	414.2	414.9	+0.1
		3-1	297.5	297.5	296.4	297.3	-0.6
		2-0	178.7	178.9	179.3	179.0	-0.1
		0-2	178.7	179.0	178.7	179.1	-0.3
		1-3	297.2	298.0	297.1	297.7	-0.3
		2-4	414.6	415.3	414.5	414.8	-0.1
		3-5	530.0	530.3	530.1	530.3	-0.2
		4-6	642.1	642.3	642.4	643.5	-1.2
		5-7	752.2	752.6	752.9	754.1	-1.5

the Q vibrational branch of H₂, however, discrepancies appear between the values found in this work and the measurements of Rasetti. The possibility that the differences between these values and Rasetti's might be due to the effect of pressure was considered since Rasetti's observations were made at approximately 12 atmospheres whereas the values in Tables I and II are for gas at 3 atmospheres. Bhagavantam did not observe an effect on the lines of hydrogen when the pressure was varied from 13 to 50 atmospheres, but no previous measurements at lower pressures, as used here, are available.* The cause of the

differences is not yet understood. The discrepancies are not cleared up by the measurements of Bhagavantam since these latter values agree in part with the measurements given in Table II and in part with those of Rasetti. Since agreement was had between the measured values obtained from three plates and the discrepancies between the observed and calculated values, given in Table II, were consistent, it was concluded that the vibrational constants were incorrect. New vibrational constants were therefore calculated. Least-square solutions of the ΔG values for the first seven states were obtained for H₂ from the data of Jeppesen,⁶ Rasetti¹⁰ and this study and for HD from the data of Jeppesen,⁷ Mie¹¹ and this study. Our experimental values for ΔG_1 are:

$$\Delta G_1(\text{H}_2) = 4160.2 \pm 0.2 \text{ cm}^{-1},$$

$$\Delta G_1(\text{HD}) = 3631.4 \pm 0.2 \text{ cm}^{-1},$$

$$\Delta G_1(\text{D}_2) = 2993.5 \pm 0.2 \text{ cm}^{-1}.$$

The emission spectrum data and Rasetti's and the present Raman data were weighted 1, 3, and 5, respectively. The best values of the constants thus obtained are listed in Table III. The relationship observed between the ω_e 's of H₂ and HD agrees excellently with the theory and the agreement for the $x\omega_e$'s, $y\omega_e$'s, and $z\omega_e$'s, is about as good as could be expected from the accuracy of the data and from the number of levels used in

TABLE II.

ν	J	PLATE I	PLATE II	PLATE III	AVERAGE	CALCULATED U. & T.	CALCULATED T. & M.	DIFFERENCE U. & T.	DIFFERENCE T. & M.
H ₂	0-1	0-0	—	—	—	4162.4	4160.4	—	—
		1-1	—	4154.1	4154.1	4156.5	4154.5	-2.4	-0.4
		2-2	—	4143.2	4143.2	4144.6	4142.6	-1.4	+0.6
		3-3	—	4124.5	4124.5	4127.2	4125.2	-2.7	-0.7
HD	0-1	0-0	—	3630.8	3630.8	3634.2	3631.5	-3.4	-0.7
		1-1	3628.8	3627.5	3628.1	3630.5	3627.7	-2.4	+0.4
		2-2	3620.0	3619.9	3620.0	3622.8	3619.9	-2.8	+0.1
		3-3	3609.6	3608.2	3608.9	3611.3	3608.5	-2.4	+0.4
		4-4	3592.8	3592.3	3592.5	3596.1	3593.2	-3.6	-0.7
		5-5	—	2963.6	2961.6	2962.3	2964.6	-2.3	+0.5
D ₂	0-1	0-0	—	—	—	2996.1	2993.2	—	—
		1-1	2992.1	2992.1	2992.2	2994.0	2991.1	-1.8	+1.1
		2-2	2986.4	2986.0	2987.2	2986.9	2989.7	-2.8	0.0
		3-3	2980.8	2979.8	2980.0	2980.1	2983.4	-3.3	-0.4
		4-4	2972.6	2971.9	2972.6	2972.4	2975.1	-2.7	+0.2
		5-5	—	2948.3	2948.3	2952.2	2949.3	-3.9	-1.0
		6-6	—	3167.5	3165.0	3166.3	3168.9	-2.6	+0.3
		0-2	—	3278.5	3278.5	3281.1	3278.2	-2.6	+0.3
		1-3	—	3385.9	3387.1	3386.5	3390.0	-3.5	-0.6
		2-4	—	—	—	—	—	—	—

* In this connection it is interesting to note that the nitrogen vibration line appeared on Plate III, and the measured value of its position was less than that recorded by Rasetti for nitrogen at 12 atmospheres by approximately

the same amount as observed for the hydrogen lines.

¹⁰ Data of Rasetti as recalculated by R. T. Birge and C. R. Jeppesen, *Nature* **34**, 463 (1930).

¹¹ K. Mie, *Zeits. f. Physik* **91**, 475 (1934).

TABLE III.

	H ₂	HD	D ₂	ρ'' : H ₂ —HD	
				Obs.	Theory
ω_e	4405.30	3817.09	3117.05	0.86648	0.86616
$x\omega_e$	125.325	94.958	63.034	0.7577	0.7502
$y\omega_e$	1.9473	1.4569	0.74526	0.748	0.650
$z\omega_e$	0.11265	0.07665	0.031573	0.680	0.563

calculating these constants.* The molecular constants of D₂ given in the table are the average values calculated from those of H₂ and HD, assuming the theoretical relationships between the reduced masses of H₂ and D₂ and of HD and D₂ to hold. The value of ΔG_1 (D₂) calculated by use of these constants is 2993.2 cm⁻¹, which differs from the experimental value of 2993.5 cm⁻¹ by only 0.1 cm⁻¹ more than the estimated accuracy of the experimental value. The agreement of the observed positions of the rotational vibration lines of the three isotopic molecules and the positions calculated from the new constants is very good, as may be seen from Table II.

The measurement of the heights of the intensity maxima of the microphotometer curves of

* It seems improbable that the theoretical relationships between the constants of the isotopic molecules could hold exactly due to differences to be expected in the potential energy curves from the differences in the electronic zero-point energies of the hydrogen and deuterium atoms as well as the molecules. This effect, however, should be small and not detectable in the constants in Table III.

Plates I and II shows an alternation of intensities of the pure rotational lines of D₂, the lines involving transitions from even states being more intense. This, in agreement with previous work on emission spectra,^{12, 13} allows one to conclude that the deuterium nucleus obeys the Einstein-Bose statistics and has a spin different from zero. The semi-quantitative measurements agree very well with those expected according to Placzek's theory¹⁴ if Murphy and Johnston's value of the spin equal to 1 is used. Though the theory predicts the absence of lines corresponding to V : 0-1, J : 0-0 transitions a line for this transition for HD was observed on Plate III.

ACKNOWLEDGMENT

We wish to express our appreciation to Professor H. C. Urey for advice and encouragement during the course of this investigation. One of us (G.E.M.) wishes to thank Professor Urey for financial assistance from the E. K. Adams Fellowship Fund. We are indebted to Dr. A. Dingwall for helpful suggestions and to the Physics Department for placing a spectrograph at our disposal.

¹² G. N. Lewis and M. F. Ashley, *Phys. Rev.* **43**, 837 (1933).

¹³ G. M. Murphy and H. Johnston, *Phys. Rev.* **46**, 95 (1934).

¹⁴ G. Placzek, *Handbuch der Radiologie VI* (1934), Vol. 2, p. 343.

On the Possibility of a Metallic Modification of Hydrogen

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Any lattice in which the hydrogen atoms would be translationally identical (Bravais lattice) would have metallic properties. In the present paper the energy of a body-centered lattice of hydrogen is calculated as a function of the lattice constant. This energy is shown to assume its minimum value for a lattice constant which corresponds to a density many times higher than that of

the ordinary, molecular lattice of solid hydrogen. This minimum—though negative—is much higher than that of the molecular form. The body-centered modification of hydrogen cannot be obtained with the present pressures, nor can the other simple metallic lattices. The chances are better, perhaps, for intermediate, layer-like lattices.