

## Variations of Hydrogen Rotational Magnetic Moments with Rotational Quantum Number and with Isotopic Mass\*

R. G. BARNES, † P. J. BRAY, ‡ AND N. F. RAMSEY  
*Harvard University, Cambridge, Massachusetts*

(Received February 15, 1954)

Molecular beam observations have been made of the radio-frequency resonance spectra corresponding to reorientations of the rotational magnetic moment in hydrogen and deuterium molecules. For deuterium in the state  $I=J=1$ , these observations were made in magnetic fields of approximately 1800, 3500, and 5100 gauss. The direct result of these experiments is that the rotational magnetic moment of the deuterium molecule in the zeroth vibrational and first rotational states is  $\mu^D(\mu_R)_1 = 0.442884 \pm 0.000052$  nuclear magneton, and the dependence of diamagnetic susceptibility on molecular orientation is  $(\xi_{\pm 1} - \xi_0) = -(3.50 \pm 0.40) \times 10^{-21}$  erg gauss<sup>-2</sup> molecule<sup>-1</sup>. Combining these values with the recent theory of Ramsey on zero-point vibration and centrifugal stretching in molecules leads to an improved evaluation of the molecular susceptibility and quadrupole moment of the electron distribution. The experiments also provide a check on the values of the spin-rotational and spin-spin interaction parameters previously obtained from observations of the resonance spectrum corresponding to reorientations of the total nuclear spin.

The observations for hydrogen in the state  $I=0, J=2$  were made in magnetic fields of approximately 1800 gauss. The direct result of these experiments is that the rotational magnetic moment of the hydrogen molecule in the zeroth vibrational and second rotational states is  $\mu^H(\mu_R/J)_2 = 0.882265 \pm 0.000035$  nuclear magneton. This value in combination with the known value of  $0.88291 \pm 0.00007$  nuclear magneton for the first rotational state provides an independent check on the theory of zero-point vibration and centrifugal stretching in molecules and leads to an improved evaluation of the hydrogen molecular susceptibility.

### I. INTRODUCTION

THE radio-frequency spectra of H<sub>2</sub> and D<sub>2</sub> arising from changes in the rotational quantum number  $m_J$  have been measured previously by Ramsey.<sup>1</sup> In particular, he investigated the six-line spectra of H<sub>2</sub> and D<sub>2</sub> in the first rotational and zeroth vibrational state and with the nuclear quantum number  $I=1$ . From these measurements of resonance frequencies, values of the Hamiltonian interaction constants were derived and used as a check on the results obtained by Kellogg, Rabi, Ramsey, and Zacharias<sup>2</sup> from the  $I=J=1$  six-line spectra for H<sub>2</sub> and D<sub>2</sub> arising from changes in the nuclear quantum number  $m_I$ . In addition, he obtained values for the rotational magnetic moments in the two molecules in the first rotational state and for the diamagnetic interaction parameter  $(\xi_{\pm 1} - \xi_0)$ . An additional measurement of the hydrogen rotational magnetic moment was obtained from a resonance arising from the  $J=2, I=0$  state.

Recently, Harrick and Ramsey<sup>3</sup> have repeated the measurements for H<sub>2</sub> in the state  $I=J=1$ , using stronger magnetic fields than previously. The considerable increase in precision over the previous measurements arises from the longer homogeneous field magnet of the Harvard apparatus,<sup>4</sup> use of the Ramsey

separated radio-frequency field technique,<sup>5,6</sup> and the employment of more accurate frequency measuring equipment.<sup>7</sup>

The present paper contains the results of similarly improved measurements of the  $I=J=1$  rotational spectrum ( $\Delta m_I=0, \Delta m_J=\pm 1$ ) in D<sub>2</sub> and the  $I=0, J=2$  resonance in H<sub>2</sub>.

### II. APPARATUS

The apparatus employed in these experiments is essentially that built and described by Kolsky, Phipps, Ramsey, and Silsbee.<sup>4</sup> Some of the subsequent modifications and improvements made by the authors and Harrick are discussed in references 3 and 7, while others specifically required for the present measurements will be discussed in the following paragraphs.

The size of the  $I=J=1, \Delta m_I=0, \Delta m_J=\pm 1$  resonances in D<sub>2</sub> (detected as a decrease in beam intensity at the resonance frequency) is considerably smaller than that of the corresponding H<sub>2</sub> resonances. This is partly explained by the lower population of the  $I=J=1$  state for D<sub>2</sub> than for H<sub>2</sub>. In fact, the maximum possible number of molecules taking part in any given  $\Delta m_I=0, \Delta m_J=\pm 1$  resonance is<sup>2</sup> 5.4 percent of the total beam in the case of D<sub>2</sub> and 12.5 percent for H<sub>2</sub> when the effects of the velocity distribution among the molecules are taken into account. An additional decrease of resonance size for D<sub>2</sub> arises because of the smallness of its rotational magnetic moment. The force experienced by a molecule in the inhomogeneous fields of the *A* and *B* deflecting magnets is of the form  $F = \mu \partial H / \partial z$ . As a

\* This work was partially supported by the joint program of the U. S. Office of Naval Research and the U. S. Atomic Energy Commission.

† Now at the University of Delaware, Newark, Delaware.

‡ Now at Rensselaer Polytechnic Institute, Troy, New York.

<sup>1</sup> N. F. Ramsey, Phys. Rev. **58**, 226 (1940).

<sup>2</sup> Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **56**, 728 (1939); **57**, 677 (1940).

<sup>3</sup> N. J. Harrick and N. F. Ramsey, Phys. Rev. **88**, 228 (1952).

<sup>4</sup> Kolsky, Phipps, Silsbee, and Ramsey, Phys. Rev. **87**, 395 (1952).

<sup>5</sup> N. F. Ramsey, Phys. Rev. **78**, 695 (1950).

<sup>6</sup> N. F. Ramsey and H. B. Silsbee, Phys. Rev. **84**, 506 (1951).

<sup>7</sup> Harrick, Barnes, Bray, and Ramsey, Phys. Rev. **90**, 260 (1953).

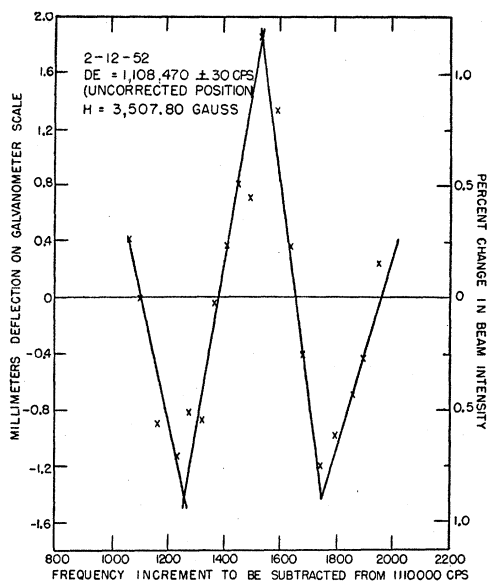


FIG. 1. Typical  $D_2$  rotational resonance,  $I=J=1$ .

result, when resonance is reached, the reoriented molecules of small moment may not be sufficiently deflected from the nonresonance path to prevent their entering the detector. Harrick experienced this difficulty in obtaining the  $H_2$  rotational spectrum measurements<sup>3</sup> and since the  $D_2$  rotational moment is smaller by a factor of two, the effect is very pronounced in the present case.

Increasing the deflecting magnets' field strength would remedy the problem in principle but is not a good solution in practice. The homogeneous  $C$ -magnet field is definitely influenced by the flux stolen from the deflecting magnets. Larger deflecting magnet fields increase the difficulty of achieving a uniform field over the entire length of the  $C$ -magnet and increase field regulation problems.

The  $D_2$  rotational resonances when found were approximately 1.5 to 2 mm peak-to-peak on the change in intensity *versus* frequency plot obtained using the Ramsey separated field<sup>5</sup> and  $0^\circ$ - $180^\circ$  phase shifting technique<sup>6</sup> (see Fig. 1). The beam is detected by a Pirani gauge with four heated platinum ribbon elements in a Wheatstone bridge arrangement. The output from the bridge is measured with a Leeds and Northrup HS

galvanometer of 12.32-cm/microvolt sensitivity as used. Previous to the preparations for the present measurements, thermal variations, mechanical vibrations, and other disturbances had introduced "noise" and drift into the galvanometer spot location on the scale amounting to 1 to 2 mm and 1 cm/minute, respectively, at times of best behavior. Since it is necessary to take readings to  $\pm \frac{1}{4}$  mm in order to determine the shape and center of a resonance measuring 2 mm at its maximum, considerable improvement of the apparatus was required. Rebuilding of the detector circuits with painstaking attention to clean, tight contacts and complete shielding from air currents, magnetic fields, rf fields, and vibration reduced the circuit noise to  $\frac{1}{4}$  mm on the galvanometer scale during periods of days and even weeks.

Vacuum system modifications, including the replacement of the previous mechanical pump<sup>4</sup> with a 9 liter/second Kinney VSD 8811 water-jacketed model, made possible a stable main chamber pressure of  $3 \times 10^{-7}$  mm Hg even with the use of a 4- or 5-mm Hg input gas pressure in the source (compared to the 3-mm Hg maximum previously used).

Modifications of the  $C$ -magnet current regulator achieved a regulation of five parts in one million in the magnetic field.

### III. HAMILTONIAN

The Hamiltonian operator for a homonuclear  $^1\Sigma$  diatomic molecule in a magnetic field is given<sup>8</sup> by

$$\begin{aligned} \mathcal{H}/h = & -(1-\sigma_{mJ})a(\mathbf{I}_z) - [1-\sigma_J(J)]b(\mathbf{J}_z) - c(\mathbf{I} \cdot \mathbf{J}) \\ & + \{5d/[(2J-1)(2J+3)]\} \times \{3(\mathbf{I} \cdot \mathbf{J})^2 + \frac{3}{2}(\mathbf{I} \cdot \mathbf{J}) \\ & - I(I+1)J(J+1)\} - \{5f/[3(2J-1)(2J+3)]\} \\ & \times \{3(\mathbf{J}_z)^2 - J(J+1)\} - g. \quad (1) \end{aligned}$$

The quantity  $\sigma_{mJ}$  denotes the nuclear shielding when the molecule is in the state with  $(\mathbf{J})_z = m_J$  and is the same as  $\sigma_i(\mathbf{J})$  of reference 8. The remaining symbols appearing in Eq. (1) are defined and discussed in references 1, 2, and 8.

### IV. THEORY OF DEUTERIUM ROTATIONAL SPECTRUM

For deuterium molecules in the state  $I=J=1$ , the following six transition frequencies may be found<sup>8</sup> from Eq. (1) by the use of third-order perturbation theory and the condition that  $\Delta m_J = \pm 1$ ,  $\Delta m_I = 0$ :

$$AB/KL - (\sigma_{\pm 1} - \sigma_0)a + b' \pm (-c + 3d/2) \mp f - C_2', \quad (2)$$

$$BC/GK \quad (\sigma_{\pm 1} - \sigma_0)a + b' \mp (c + 3d/2) \pm f - (C_2 - C_2') \pm C_3, \quad (3)$$

$$DE/EF \quad b' \quad \mp 3d \quad \mp f - C_2' \quad \mp 2C_3, \quad (4)$$

where

$$C_2 = [(c + 3d/2)^2 + 9d^2/2]/(a - b'),$$

$$C_2' = (c - 3d/2)^2/(a - b'),$$

$$C_3 = (c + 3d/2)^2(c - 9d/2)/(a - b')^2,$$

$$b' = (1 - \sigma_{11})b.$$

The upper sign in each equation goes with the upper transition (such as  $AB$ ).  $\sigma_{11}$  is  $\sigma_J(J)$  for the case  $J=1$  and  $m_J = \pm 1$ .

<sup>8</sup> N. F. Ramsey, Phys. Rev. 85, 60 (1952).

### A. Determination of the Deuterium Rotational Magnetic Moment

In order to eliminate the magnetic field value  $H$ , the deuteron resonance frequency  $\nu_D = (1 - \sigma_D)a$  is obtained from the molecules in the  $J=0, I=2$  state. Then, from Eqs. (2)–(4), one finds the values

$$b'/(1 - \sigma_D)a = (1 - \sigma_{11})\mu_{RD}/(1 - \sigma_D)\mu_D$$

$$= \frac{AB + KL}{2(1 - \sigma_D)a} + \frac{C_2'}{(1 - \sigma_D)a} + \frac{\sigma_{\pm 1} - \sigma_0}{1 - \sigma_D} \quad (5)$$

$$= \frac{BC + GK}{2(1 - \sigma_D)a} + \frac{C_2 - C_2'}{(1 - \sigma_D)a} - \frac{\sigma_{\pm 1} - \sigma_0}{1 - \sigma_D} \quad (6)$$

$$= (DE + EF + 2C_2')/2(1 - \sigma_D)a. \quad (7)$$

Here the symbol  $\mu_{RD}$  is equal to the quantity  $v^x(\mu_R/J)_J$  of Ramsey's paper<sup>9</sup> which denotes the expectation value of the rotational moment divided by the rotational quantum number  $J$  where, in the present case,  $x=D$  (i.e., a deuterium molecule),  $v=0$  (the zeroth vibrational state of the molecule), and  $J=1$ .

It is apparent from Eqs. (5)–(7) that use of the transitions  $DE$  and  $EF$  will avoid the term  $(\sigma_{\pm 1} - \sigma_0)/(1 - \sigma_D)$  arising from nuclear shielding and not accurately known. Furthermore, if the two average values of  $b'(1 - \sigma_D)a$  obtained independently from  $AB + KL$  transition frequency sums and  $BC + GK$  transition frequency sums are again averaged, Eqs. (5) and (6) show that the unwanted term  $(\sigma_{\pm 1} - \sigma_0)/(1 - \sigma_D)$  will be cancelled. This procedure will be used, but in the selection of a final "best value" for  $b'/(1 - \sigma_D)a$ , more reliance will be placed on the values obtained from the  $DE$  and  $EF$  transition frequencies.

The value of the deuterium rotational moment (in the first rotational state) in nuclear magnetons may be obtained from the relation,

$$(\mu_{RD})_{NM} = (1 - \sigma_D)(\mu_D/\mu_H)(\mu_H)_{NM} \times [\mu_{RD}/(1 - \sigma_D)\mu_D], \quad (8)$$

where the value of Smaller, Yasaitas, and Anderson<sup>10</sup> for  $\mu_H/\mu_D$  and that of Sommer, Thomas, and Hipple<sup>11</sup> for  $(\mu_H)_{NM}$  can be employed. The value of  $b'(1 - \sigma_D)a$  is used for  $\mu_{RD}/(1 - \sigma_D)\mu_D$  by neglecting the small unknown correction  $\sigma_{11}$ .

### B. Deuterium Molecular Susceptibility

The high-frequency term of the deuterium molecular susceptibility in the zeroth vibrational and first rotational states can be written as [Eq. (14) of reference 9]

$${}^0\text{D}\langle\chi\rangle_1^{\text{hf}} = \frac{e^2 L}{12mc^2} R_e^2 {}^0\text{D}\langle(R/R_e)^l\rangle_1 / {}^0\text{D}\langle(R/R_e)^{l-2}\rangle_1 \times [1 - 2(\mu_D'/M) {}^0\text{D}\langle\mu_R/\mu_{NM}\rangle_1]. \quad (9)$$

<sup>9</sup> N. F. Ramsey, Phys. Rev. **87**, 1075 (1952).

<sup>10</sup> Smaller, Yasaitas, and Anderson, Phys. Rev. **81**, 896 (1951).

<sup>11</sup> Sommer, Thomas, and Hipple, Phys. Rev. **82**, 697 (1951).

The quantity  ${}^0\text{D}\langle(R/R_e)^l\rangle_1 / {}^0\text{D}\langle(R/R_e)^{l-2}\rangle_1$  can be calculated from Eq. (21) of reference 9 after determination of the exponent  $l$ . The determination of  $l$  is achieved from the relation

$$\frac{{}^0\text{H}\langle(R/R_e)^{l-2}\rangle_1}{{}^0\text{D}\langle(R/R_e)^{l-2}\rangle_1} = 1 + \frac{1 - (\mu_H'/\mu_D') {}^0\text{H}\langle\mu_R/\mu_{NM}\rangle_1 / {}^0\text{D}\langle\mu_R/\mu_{NM}\rangle_1}{(M/2\mu_D') {}^0\text{D}\langle\mu_R/\mu_{NM}\rangle_1^{-1} - 1}, \quad (10)$$

which is a specific case of Eq. (23), reference 9. All quantities on the right side of Eq. (10) are known or are measured in these experiments. Comparison of the numerical value achieved for the right-hand side of Eq. (10) with the plot of Fig. 2 of reference 9 permits evaluation of  $l$ .

$R_e$  is determined from the relation [Eq. (13), reference 9]

$$R_e^2 = h / (8\pi^2 c \mu_H^H B_0) \cdot {}^0\text{H}\langle(R/R_e)^{-2}\rangle_0, \quad (11)$$

where  ${}^0\text{H}\langle(R/R_e)^{-2}\rangle_0$  is found from Eq. (21) of reference 9.

### C. Deuterium Diamagnetic Interaction

For molecules in the first rotational state, the diamagnetic interaction parameter  $f$  is related<sup>8</sup> to the diamagnetic susceptibilities  $\xi_{\pm 1}$  and  $\xi_0$  by

$$f = (\xi_{\pm 1} - \xi_0)H^2/2h, \quad (12)$$

where the subscripts  $\pm 1$  and  $0$  refer to the value of  $m_J$  in the state  $J=1$ . It is evident that  $(\xi_{\pm 1} - \xi_0)$  measures the dependence of the diamagnetic susceptibility on molecular orientation. Each pair of the transition frequencies Eqs. (2)–(4) may be used to evaluate  $f$ , as follows:

$$2f = (KL - AB) - 2c + 3d, \quad (13)$$

$$2f = (BC - GK) + 2c + 3d - 2C_3, \quad (14)$$

$$2f = (EF - DE) - 6d - 4C_3. \quad (15)$$

The deuterium  $I=2, J=0$  single resonance frequency  $\nu_D$  is used to monitor the magnetic field  $H$  during operation, since

$$\nu_D = (1 - \sigma_D)(\mu_D/\mu_H)(\gamma_H/4\pi)H. \quad (16)$$

The nuclear shielding factor  $\sigma_D$  in Eq. (16) can be neglected here in calculating the magnetic field from  $\nu_D$  since the uncertainty in  $(\xi_{\pm 1} - \xi_0)$  is entirely determined by that in  $f$ . The third-order correction  $C_3$  is calculated from Eq. (21) below.

### D. Quadrupole Moment of the Deuterium Electron Distribution

For the deuterium molecule in the first rotational and zeroth vibrational states the quadrupole moment of

the electron distribution is given by

$${}^0\text{D}\langle Q_e \rangle_1 = -\frac{20mc^2}{e^2} [(\xi_{\pm 1} - \xi_0) - \frac{3}{5} {}^0\text{D}\langle \xi \rangle_1^{\text{hf}}]. \quad (17)$$

Here,  ${}^0\text{D}\langle \xi \rangle_1^{\text{hf}}$  is the high-frequency part of the diamagnetic susceptibility per molecule and is obtained from Eq. (9) by division by  $L$ .

### E. Evaluation of $c$ and $d$ for Deuterium

From Eqs. (13)–(15) one can deduce the relations

$$(EF - DE) + (AB - KL) = -2c + 9d + 4C_3, \quad (18)$$

$$(EF - DE) + (GK - BC) = 2c + 9d + 2C_3, \quad (19)$$

$$(GK - BC) - (AB - KL) = 4c - 2C_3, \quad (20)$$

where the small third-order term,

$$C_3 = (c + 3d/2)^2(c - 9d/2)/(a - b')^2, \quad (21)$$

can be evaluated using the best values of  $c$  and  $d$  from nuclear spectrum measurements,<sup>7</sup> the relation

$$a - b' = \mu_D H [1 - (1 - \sigma_{11})\alpha]/h, \quad (22)$$

where  $\alpha = \mu_{RD}/\mu_D$ , and the fact that

$$\mu_D H/h = \nu_D/(1 - \sigma_D). \quad (23)$$

The ratio  $(1 - \sigma_{11})\alpha/(1 - \sigma_D)$  is obtained in the present measurements and the deuterium  $I=2$ ,  $J=0$  single resonance frequency  $\nu_D$  is measured repeatedly during any operational period in order to monitor the magnetic field  $H$ . The nuclear shielding factor  $\sigma_D$  may be neglected in computing the small term  $C_3$ .

### V. THEORY OF HYDROGEN ROTATIONAL SPECTRUM IN THE SECOND ROTATIONAL STATE

For hydrogen molecules in the state  $I=0$ ,  $J=2$  the Hamiltonian operator Eq. (1) reduces to the simpler form

$$\mathcal{H}/h = -[1 - \sigma_J(J)]b(J)_z - (5/63)f\{3J_z^2 - 6\} - g. \quad (24)$$

The matrix elements of this operator are all diagonal, and the energy levels can accordingly be written down directly. The differences between these levels corresponding to the selection rule  $\Delta m_J = \pm 1$ ,  $\Delta m_I = 0$  are the transition frequencies in the rotational spectrum:

$$\begin{aligned} \nu_1 &= (1 + \sigma_{21} - 2\sigma_{22})b - (5/7)f, \\ \nu_2 &= (1 - \sigma_{21})b - (5/21)f, \\ \nu_3 &= (1 - \sigma_{21})b + (5/21)f, \\ \nu_4 &= (1 + \sigma_{21} - 2\sigma_{22})b + (5/7)f. \end{aligned} \quad (25)$$

Note that  $f$  in Eq. (25) can be related to  $(\xi_{\pm 1} - \xi_0)$  of the first rotational state by Eq. (12) if the change in  $f$  due to centrifugal distortion is small.

### A. Hydrogen Rotational Magnetic Moment

The transitions Eq. (25) average to the value  $(1 - \sigma_{22})b = b''$ . In terms of the rotational magnetic moment,

$$b = \mu_{RH}H/Jh. \quad (26)$$

The value of the magnetic field is determined from the deuteron resonance frequency  $\nu_D$  in the  $J=0$ ,  $I=2$  state of deuterium, Eq. (16). Combining Eqs. (16) and (26) gives for the value of the rotational magnetic moment in nuclear magnetons

$$(\mu_{RH}/J)_{NM} = (1 - \sigma_D)(\mu_D/\mu_H)(\mu_H)_{NM}\{b/\nu_D\}. \quad (27)$$

The quantity actually observed is the ratio  $(b''/\nu_D)$  but the correction  $\sigma_{22}$  for the difference between  $b$  and  $b''$  is negligible for the present accuracy. The values of the other quantities are those mentioned in connection with Eq. (8).

### B. Hydrogen Molecular Susceptibility

The high-frequency term of the hydrogen molecular susceptibility in the zeroth vibrational and  $J$ th rotational states can be written as [Eq. (14) of reference 9]

$${}^0\text{H}\langle \chi \rangle_J^{\text{hf}} = \frac{e^2 L}{12mc^2} R_e^2 {}^0\text{H}\langle (R/R_e)^l \rangle_J / {}^0\text{H}\langle (R/R_e)^{l-2} \rangle_J \times \{1 - {}^0\text{H}\langle \mu_R/J\mu_{NM} \rangle_J\}. \quad (28)$$

In order to evaluate the quantities of the form  ${}^0\text{H}\langle (R/R_e)^n \rangle_J$  from Eq. (21) of reference 9, the value of  $l$  must be determined. This can be done from the hydrogen results by comparing the values of the quantity  $(\mu_R/J)_{NM}$  or  $(b/\nu_D)$  in the first and second rotational states. According to reference 9, this gives the ratio

$$\frac{{}^0\text{H}\langle (R/R_e)^{l-2} \rangle_1}{{}^0\text{H}\langle (R/R_e)^{l-2} \rangle_2} = 1 + \frac{1 - {}^0\text{H}\langle \mu_R/J\mu_{NM} \rangle_1 / {}^0\text{H}\langle \mu_R/J\mu_{NM} \rangle_2}{{}^0\text{H}\langle \mu_R/J\mu_{NM} \rangle_2^{-1} - 1}, \quad (29)$$

whereas this same ratio has the theoretical value<sup>9</sup>

$$\frac{{}^0\text{H}\langle (R/R_e)^{l-2} \rangle_1}{{}^0\text{H}\langle (R/R_e)^{l-2} \rangle_2} = \frac{1 + 8(l-2)(B_e/\omega_e)^2}{1 + 24(l-2)(B_e/\omega_e)^2}. \quad (30)$$

Direct comparison of the right-hand sides of Eqs. (29) and (30) yields the value of  $l$ . The recent spectroscopic results of Herzberg may be used for  $B_e$  and  $\omega_e$ .  $R_e$  in Eq. (28) is determined from Eq. (11).

### C. Quadrupole Moment of the Hydrogen Electron Distribution

Equation (17) can be carried over directly to the case of hydrogen in the zeroth vibrational and first rotational states. The value of  ${}^0\text{H}\langle \xi \rangle_1^{\text{hf}}$  is obtained from Eq. (28) by division by  $L$ .

**VI. EXPERIMENTAL RESULTS**

Table I contains measurements of the deuterium rotational transition frequencies at three distinct magnetic field strengths (approximately 1800, 3500, and 5100 gauss). Subscripts affixed to each pair of transition frequencies are for ease in distinguishing the values calculated in later sections. The measurements on *DE* and *EF* at 5100 gauss were obtained only once due to subsequent continuing detector noise and other problems. All measurements reported here, however, display a clear line shape, low dispersion of points, and complete symmetry of line shape within experimental error. These properties were obtained for such very small resonances by painstaking adjustment of the apparatus

TABLE I. Measurements of deuterium rotational transition frequencies in the first rotational state in strong magnetic fields.

Number of observations of each transition	Transition	Position of resonance (cps)
3	$\nu_D$	1 140 935±20
	<i>KL</i> <sub>I</sub>	558 642±30
	<i>AB</i> <sub>I</sub>	616 981±30
2	$\nu_D$	1 240 906±20
	<i>KL</i> <sub>II</sub>	610 339±40
	<i>AB</i> <sub>II</sub>	668 708±40
	<i>DE</i> <sub>II</sub>	565 190±30
	<i>EF</i> <sub>II</sub>	713 956±35
3	$\nu_D$	2 292 652±20
	<i>DE</i> <sub>III</sub>	1 108 476±30
	<i>EF</i> <sub>III</sub>	1 258 565±30
2	$\nu_D$	2 270 692±20
	<i>KL</i> <sub>IV</sub>	1 142 750±30
	<i>AB</i> <sub>IV</sub>	1 201 584±30
	<i>BC</i> <sub>IV</sub>	1 121 968±35
	<i>GK</i> <sub>IV</sub>	1 216 271±40
1	$\nu_D$	3 362 905±20
	<i>DE</i> <sub>V</sub>	1 661 760±40
	<i>EF</i> <sub>V</sub>	1 811 447±30

and by averaging techniques involving four to eight galvanometer spot deflections for each experimental point. Figure 1 is a typical line trace.

Table II contains measurements of the observed hydrogen rotational transition frequency in the second rotational state and of the deuteron resonance frequency in D<sub>2</sub> in magnetic fields of approximately 1680 and 1865 gauss. The line width listed is measured at the points of zero galvanometer deflection of the 0°-180° phase-shifting resonance pattern. The statements previously made with regard to the line shape and symmetry and low point dispersion of the deuterium data apply equally to the hydrogen rotational data. Figure 2 is a typical line trace.

**VII. ANALYSIS OF EXPERIMENTAL DEUTERIUM ROTATIONAL SPECTRUM**

**A. Deuterium Rotational Magnetic Moment**

When the data of Table I are used in Eqs. (5)-(7), the values of  $b'/(1-\sigma_D)a$  displayed in Table III are ob-

TABLE II. Hydrogen rotational resonance  $I=0, J=2$ , and deuterium nuclear resonance  $I=2, J=0$ .

Transition	Time	Position of resonance (cps)	Line width (cps)
$\nu_D$	10:50 P.M.	1 095 728±20	350
$b''$	12:00	1 127 522±20	600
$\nu_D$	1:30 A.M.	1 095 716±20	405
$b''$	2:10	1 127 535±20	560
$b''$	2:40	1 127 493±20	570
$\nu_D$	3:15	1 095 720±20	400
$b''$	3:45	1 127 500±20	560
$b''$	4:15	1 127 495±20	580
$\nu_D$	4:40	1 095 735±20	400
$b''$	5:10	1 127 542±20	550
(Above data taken with a magnetic field, $H \cong 1680$ gauss)			
$\nu_D$	5:20 P.M.	1 219 842±20	370
$b''$	6:05	1 255 240±20	500
$b''$	6:45	1 255 242±20	575
$\nu_D$	7:15	1 219 836±20	425
$\nu_D$	11:40	1 214 335±20	410
$b''$	12:15 A.M.	1 249 577±20	600
$b''$	12:45	1 249 565±20	590
$\nu_D$	1:15	1 214 322±20	450
$b''$	1:45	1 249 552±20	575
$b''$	2:05	1 249 542±20	580
$\nu_D$	2:30	1 214 335±20	420
(Above data taken with a magnetic field, $H \cong 1865$ gauss)			

tained. The average values obtained from the different transition frequency sums are given in Table IV. Averaging of the first two values in Table IV yields

$$b'/(1-\sigma_D)a = 0.516547 \pm 0.000027, \quad (31)$$

which is in very satisfactory agreement with the determination from *DE*+*EF* transition frequency sums (see Table IV).

The best value from the present measurements is taken to be

$$b'/(1-\sigma_D)a = 0.516550 \pm 0.000016. \quad (32)$$

The corresponding value obtained from Eq. (8) for  $\mu_{RD}$

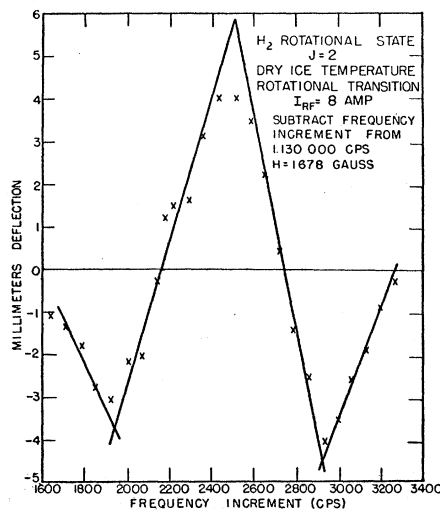


FIG. 2. Typical H<sub>2</sub> rotational resonance,  $I=0, J=2$ .

TABLE III. Values of  $b'/(1-\sigma_D)a$  obtained from different transition frequency sums. Subscripts are those appearing in Table I.

Transition frequency sum involved	$b'/(1-\sigma_D)a$
$(AB+KL)_I$	$(0.516544 \pm 0.000035) + (\sigma_{\pm 1} - \sigma_0)/(1-\sigma_D)$
$(AB+KL)_{II}$	$(0.516504 \pm 0.000041) + (\sigma_{\pm 1} - \sigma_0)/(1-\sigma_D)$
$(AB+KL)_{IV}$	$(0.516555 \pm 0.000018) + (\sigma_{\pm 1} - \sigma_0)/(1-\sigma_D)$
$(DE+EF)_{II}$	$(0.516543 \pm 0.000035)$
$(DE+EF)_{III}$	$(0.516555 \pm 0.000019)$
$(DE+EF)_V$	$(0.516555 \pm 0.000013)$
$(BC+GK)_{IV}$	$(0.516558 \pm 0.000021) - (\sigma_{\pm 1} - \sigma_0)/(1-\sigma_D)$

in units of nuclear magnetons is

$$\mu_{RD} = 0.442884 \pm 0.000052 \text{ nuclear magneton.} \quad (33)$$

Here use has been made of the value

$$\sigma_D = (2.64 \pm 0.04) \times 10^{-5} \quad (34)$$

found from the theory of Ramsey<sup>9</sup> and measurements on the H<sub>2</sub> and D<sub>2</sub> nuclear spectra.<sup>7</sup>

The value of  $\mu_{RD}$  in Eq. (33) can be compared with the value

$$\mu_{RH} = 0.88291 \pm 0.00007 \text{ nuclear magneton} \quad (35)$$

found by Harrick and Ramsey<sup>8</sup> for hydrogen in the first rotational state.

The ratio

$$\mu_{RH}/\mu_{RD} = 1.99355 \pm 0.00022 \quad (36)$$

[obtained from Eq. (32) and Harrick's<sup>8</sup> value for  $\mu_{RH}/(1-\sigma_D)\mu_D$ ] differs from  $1.999008 \pm 0.000006$ , which is the ratio  $M_d/M_p$  of the deuteron mass to that of the proton. In fact,

$$(M_d/M_p)(\mu_{RD}/\mu_{RH}) = 1.00274 \pm 0.00011, \quad (37)$$

which departs from unity by twenty-five times the probable error. Part of this difference may be attributed to the fact that the electrons contribute in part to the moment of inertia of the molecule, in which case the proper comparison ratio is intermediate between the nuclear mass ratio and the atomic mass ratio. However, even if the atomic masses are used in Eq. (37) the resulting value is  $1.00247 \pm 0.00011$ , which differs from unity far beyond the experimental error. As discussed in the next paragraph, the departure is probably due to the differences in zero point vibration and in centrifugal stretching for the two molecules.

### B. Deuterium Molecular Susceptibility

Equation (10) is the specialization of Eq. (23) of reference 9 to the case of H<sub>2</sub> and D<sub>2</sub> in the state  $I=J=1$ . When the values of Eqs. (33) and (37) are substituted in Eq. (10), one finds

$$\{ {}^D\langle (R/R_e)^{l-2} \rangle_1 / {}^H\langle (R/R_e)^{l-2} \rangle_1 \} - 1 = (1/1.02108) - 1 \\ = - \left( \begin{array}{c} +0.0010 \\ 0.0206 \\ -0.0020 \end{array} \right), \quad (38)$$

where the asymmetry in the probable error arises from the uncertainty in the extent to which the electron contributes to the moment of inertia, as discussed in the preceding section. Use of Eq. (9) and Fig. 2 of reference 9 (which is a plot of  $\{ {}^D\langle (R/R_e)^n \rangle_1 / {}^H\langle (R/R_e)^n \rangle_1 \} - 1$  as a function of  $n$ ) determines the value of  $l$  as

$$l = d \ln \xi^{h^f} / d \ln R = 3.72 \begin{array}{c} +0.06 \\ -0.12 \end{array} \quad (39)$$

This result is in good agreement with the value,  $l=3.80 \pm 0.12$ , determined from measurements of the hydrogen rotational magnetic moment in the first and second rotational states [see Eq. (65) below].

From Eq. (39) above and Eq. (21) of reference 9, one finds

$${}^D\langle (R/R_e)^l \rangle_1 / {}^D\langle (R/R_e)^{l-2} \rangle_1 = 1.0949 \begin{array}{c} +0.0012 \\ -0.0030 \end{array} \quad (40)$$

Values of Herzberg<sup>12,13</sup> and Ramsey<sup>9</sup> are used for the necessary constants appearing in Eq. (21) of reference 9.

One now requires only the further value  $R_e$  in order to evaluate the high-frequency term of the deuterium molecular susceptibility in the zeroth vibrational and first rotational state, given by Eq. (9).  $R_e$  is found from the value

$${}^H\langle (R/R_e)^{-2} \rangle_1 = 0.9747 \quad (41)$$

[determined from Eq. (21) of reference 9] and Eq. (11) (combined with Herzberg's value of  ${}^H B_0$ ) to be

$$R_e = (0.7416 \pm 0.0001) \times 10^{-8} \text{ cm.} \quad (42)$$

Substitution of the values of Eqs. (33), (37), (40), and (42) into Eq. (9) yields

$${}^D\langle \chi \rangle_1^{hf} = (0.0978 \pm 0.0003) \\ \times 10^{-6} \text{ erg gauss}^{-2} \text{ mole}^{-1}. \quad (43)$$

A similar calculation for hydrogen, using the value of Eq. (35) for  ${}^H\langle \mu_R/\mu_{NM} \rangle_1$  gives

$${}^H\langle \chi \rangle_1^{hf} = (0.1036 \pm 0.0005) \\ \times 10^{-6} \text{ erg gauss}^{-2} \text{ mole}^{-1}, \quad (44)$$

with the value  $l=3.72$ . This value for  ${}^H\langle \chi \rangle_1^{hf}$  may be

TABLE IV. Average values of  $b'/(1-\sigma_D)a$  obtained from different transition frequency sums.

Transition frequency sum involved	$b'/(1-\sigma_D)a$
$AB+KL$	$(0.516536 \pm 0.000032) + (\sigma_{\pm 1} - \sigma_0)/(1-\sigma_D)$
$BC+GK$	$(0.516558 \pm 0.000021) - (\sigma_{\pm 1} - \sigma_0)/(1-\sigma_D)$
$DE+EF$	$0.516551 \pm 0.000023$

<sup>12</sup> N. F. Ramsey, Phys. Rev. **78**, 221 (1950).

<sup>13</sup> G. Herzberg, Can. J. Research **A28**, 144 (1950).

TABLE V. Data used in the evaluation of  $c$  and  $d$  and  $(\xi_{\pm 1} - \xi_0)$ . Values of  $(\xi_{\pm 1} - \xi_0)$  calculated from different sets of  $c$  and  $d$  values.

Magnetic field $H$ (gauss)	Transition frequency difference	Value thereof (cps)	$C_3$ (cps)	$(\xi_{\pm 1} - \xi_0)$ (from nuclear spectrum) ( $10^{-31}$ erg gauss $^{-2}$ molecule $^{-1}$ )	$(\xi_{\pm 1} - \xi_0)$ (from rotational spectrum) ( $10^{-31}$ erg gauss $^{-2}$ molecule $^{-1}$ )
1745.63 $\pm$ 0.07	$(AB-KL)_I$	58 337 $\pm$ 60		-(4.39 $\pm$ 1.82)	-(3.15 $\pm$ 1.50)
1898.61 $\pm$ 0.07	$(EF-DE)_{II}$	148 765 $\pm$ 60	-633	-(2.26 $\pm$ 1.10)	-(3.25 $\pm$ 1.15)
	$(AB-KL)_{II}$	58 368 $\pm$ 80		-(4.30 $\pm$ 1.72)	-(3.25 $\pm$ 1.46)
3507.80 $\pm$ 0.11	$(EF-DE)_{III}$	150 089 $\pm$ 60	-185	-(3.18 $\pm$ 0.32)	-(3.48 $\pm$ 0.35)
3474.20 $\pm$ 0.11	$(GK-BC)_{IV}$	94 302 $\pm$ 75	-189	-(3.49 $\pm$ 0.49)	-(3.51 $\pm$ 0.38)
	$(AB-KL)_{IV}$	58 833 $\pm$ 60		-(3.83 $\pm$ 0.46)	-(3.52 $\pm$ 0.44)
5145.24 $\pm$ 0.16	$(EF-DE)_{V}$	149 687 $\pm$ 70	-86	-(3.48 $\pm$ 0.16)	-(3.61 $\pm$ 0.17)
				-(3.45 $\pm$ 0.50) <sup>b</sup>	-(3.50 $\pm$ 0.30) <sup>a</sup>
					-(3.50 $\pm$ 0.40) <sup>b</sup>

<sup>a</sup> Evaluated from Eq. (46).

<sup>b</sup> Average of 3500 gauss experiments.

compared to the result

$$o^H\langle\chi\rangle_1^{hf} = (0.0990 \pm 0.0010) \times 10^{-6} \text{ erg gauss}^{-2} \text{ mole}^{-1} \quad (45)$$

found<sup>9</sup> before the result of Ramsey's work<sup>9</sup> on zero-point vibration and centrifugal stretching effects was available.

### C. Deuterium Diamagnetic Interaction

The quantity  $(\xi_{\pm 1} - \xi_0)$ , characterizing the dependence of the diamagnetic susceptibility on molecular orientation, is calculated from Eq. (12) using the values of  $f$  obtained from Eqs. (13)–(15) and the data of Table I. A considerable effect on the scattering of the  $(\xi_{\pm 1} - \xi_0)$  values about the average value can be achieved by choosing slightly different values of the parameters  $c$  and  $d$ . When the best values of these parameters obtained from measurements on nuclear spectra [Eqs. (57) and (58)] are used, the  $(\xi_{\pm 1} - \xi_0)$  values calculated from the lines  $AB/KL$  at 1800 gauss are significantly greater than the 5100 gauss value from lines  $DE/EF$ , and the 1800 gauss value using lines  $DE/EF$  is significantly lower than that at 5100 gauss. These various values are tabulated in the first column of  $(\xi_{\pm 1} - \xi_0)$  values in Table V. On the other hand, when the values of the parameters  $c$  and  $d$  evaluated from the present measurements [Eqs. (50) and (56)] are used, an almost fivefold reduction in scattering is obtained [second column of  $(\xi_{\pm 1} - \xi_0)$  values in Table V]. It is also possible to combine Eqs. (13)–(15) to obtain a calculation of  $(\xi_{\pm 1} - \xi_0)$  directly:

$$(\xi_{\pm 1} - \xi_0)(2H_a^2 + H_b^2)/h = (BC - GK - 2C_3) + (KL - AB) + (EF - DE - 4C_3). \quad (46)$$

Here,  $H_a$  is the magnetic field for the measurements on  $AB/KL$  and  $BC/GK$  while  $H_b$  is the field for measurements on  $EF/DE$ . The value of  $C_3$  is very slightly affected by this small difference in field strengths (see Table V). All the values of  $(\xi_{\pm 1} - \xi_0)$  obtained from the present measurements and Eq. (46) above, are listed in Table V. The results based on nuclear and on rotational spectrum values of  $c$  and  $d$  are separately listed.

Since only one set of measurements was made at 5100 gauss, the best value of  $(\xi_{\pm 1} - \xi_0)$  is taken to be the average of the four 3500 gauss values calculated using rotational spectrum results for  $c$  and  $d$ . The result is that

$$(\xi_{\pm 1} - \xi_0) = -(3.50 \pm 0.40) \times 10^{-31} \text{ erg gauss}^{-2} \text{ molecule}^{-1}, \quad (47)$$

which is not significantly different from that obtained with the nuclear spectrum results for  $c$  and  $d$  (see Table V).

### D. Quadrupole Moment of the Deuterium Electron Distribution

To calculate  $o^D\langle Q_e \rangle_1$  from Eq. (17) it is first necessary to determine the high-frequency part of the diamagnetic susceptibility per molecule  $o^D\langle \xi \rangle_1^{hf}$  from the value per mole  $o^D\langle \chi \rangle_1^{hf}$ . Using the value of Eq. (43), one finds

$$o^D\langle \xi \rangle_1^{hf} = (1.623 \pm 0.006) \times 10^{-31} \text{ erg gauss}^{-2} \text{ molecule}^{-1}. \quad (48)$$

When this is used in Eq. (17) together with the value of  $(\xi_{\pm 1} - \xi_0)$  from Eq. (47), one obtains

$$o^D\langle Q_e \rangle_1 = (0.318 \pm 0.030) \times 10^{-16} \text{ cm}^2 \quad (49)$$

for the quadrupole moment of the electron distribution in the deuterium molecule in the first rotational state.

### E. Evaluation of $c$ and $d$ for Deuterium

The data displayed in Table I show that measurements which can be used in Eqs. (18)–(21) for evaluation of  $c$  and  $d$  were obtained during three periods of operation. Table V displays the useful data and the respective field ( $H$ ) and third-order correction term ( $C_3$ ) values.

From the data IV and Eq. (20),

$$c = \frac{1}{4} \{ (GK - BC) - (AB - KL) + 2C_3 \} = 8773 \pm 34 \text{ cps}. \quad (50)$$

If this value of  $c$  is used with data II and Eq. (18),

$$d = (1/9) \{ (EF - DE) + (AB - KL) + 2c - 4C_3 \} = 25 246 \pm 23 \text{ cps}. \quad (51)$$

A satisfying check of these values can be obtained if use is made of data III. The 30-gauss difference in field existing between measurements III and IV has only a small effect on the transition frequency differences of interest (note the very minor change in  $C_3$  occasioned by this field difference). From the  $EF-DE$  measurements III, the  $GK-BC$  and  $AB-KL$  measurements IV, and Eqs. (18) and (19), one finds

$$2c+9d=244\,765\pm 135 \text{ cps,} \quad (52)$$

$$-2c+9d=209\,670\pm 120 \text{ cps.} \quad (53)$$

Note that the  $EF-DE$  and  $AB-KL$  measurements II yield

$$-2c+9d=209\,665\pm 140 \text{ cps,} \quad (54)$$

in excellent agreement with Eq. (53). Using the average of Eqs. (53) and (54) with Eq. (52) yields

$$c=8774\pm 64 \text{ cps,} \quad (55)$$

$$d=25\,246\pm 14 \text{ cps.} \quad (56)$$

The values of Eqs. (50) and (56) offer an interesting comparison with the values

$$c=8788\pm 40 \text{ cps,} \quad (57)$$

$$d=25\,237\pm 10 \text{ cps,} \quad (58)$$

previously found<sup>7</sup> by the authors and N. J. Harrick from measurements on the deuterium nuclear spectrum.

#### VIII. ANALYSIS OF EXPERIMENTAL HYDROGEN ROTATIONAL SPECTRUM IN THE SECOND ROTATIONAL STATE

The four transition frequencies which are to be expected in the rotational spectrum of the second rotational state are spaced symmetrically about the re-orientation frequency  $b$  of the rotational magnetic moment alone [see Eq. (25)] except for the negligibly small shielding correction. The splitting to be expected due to the diamagnetic interaction can be calculated from the known value<sup>3</sup> of  $(\xi_{\pm 1}-\xi_0)$  for the first rotational state. In a field of 2000 gauss, the splitting away from the frequency  $b$  would amount to  $79\pm 4$  cps. Such a small splitting would not be resolved by the present apparatus, but it was thought that some broadening of the resonance would appear.

The relative population of the second rotational state is only 0.1 percent at 78°K, whereas it increases to 7 percent at 200°K, and to 12 percent at 300°K. Since the width of the resonance pattern also increases with increasing temperature,<sup>5</sup> a temperature close to 200°K was taken as a compromise (195°K, the temperature of a dry ice-acetone mixture). The average over-all height of the resonances was about 4 percent of the total beam.

##### A. Hydrogen Rotational Magnetic Moment

It is interesting to note whether any indication of the diamagnetic splitting appears. As mentioned above,

such splitting might cause a broadening of the resonance. No actual splitting was observed; the widths of the central peak of the resonances at the zero mark (zero deflection when switching phase 180°) are included with the data in Table II.

The theoretically expected line width has been given by Ramsey<sup>6</sup>

$$(\Delta\nu=0.64(3RT/M)^{1/2}/L. \quad (59)$$

$L$  is the path length of the molecules in the homogeneous magnetic field. The application of this equation to the 0-180° phase-shifting pattern supposes that the in-phase and out-of-phase patterns correspond exactly in frequency. Since this may not actually be the case in practice, the equation is used here only to obtain the following expression for ratios of line widths. At the same temperature, one has

$$\Delta\nu(\text{H}_2)/\Delta\nu(\text{D}_2)=[M(\text{D}_2)/M(\text{H}_2)]^{1/2}=1.44. \quad (60)$$

By comparison, the ratios of the average measured line widths are (excepting the first value for  $\nu_D$  in each case, which are probably due to the source oven's not having warmed up to 195° from the 78° temperature used during alignment of the apparatus):

data of 1-24-52

$$\Delta\nu(\text{H}_2)/\Delta\nu(\text{D}_2)=570/400=1.420, \quad (61)$$

data of 2-4-52

$$\Delta\nu(\text{H}_2)/\Delta\nu(\text{D}_2)=584/418=1.396.$$

The agreement with the value of Eq. (60) is very good, certainly well within the error incurred in reading the line widths from the plots. Thus there is no evidence for a broadening of the resonance.

Since by Eq. (25) above, the average of the unresolved resonance frequencies is  $b''$ , it is assumed that the observed single resonance represents that frequency. Examination of Table II shows that the drift of the magnetic field, indicated by the wandering of either resonance frequency during a run, is less than the experimental error of the resonances themselves. Accordingly, the line positions have not been corrected for drift; instead, the ratio  $b''/\nu_D=(1-\sigma_{22})(\mu_{RH}/J)/(1-\sigma_D)\mu_D$  has been evaluated from each  $\nu_D$  value and the  $b''$  values immediately following and preceding it. In this manner, one obtains six ratios from the measurements of each data. The numerical average of the twelve ratios is almost exactly the mid-point of the two extreme values, and is taken to be the best value:

$$b''/\nu_D=1.029014\pm 0.000030. \quad (62)$$

The corresponding value obtained from Eq. (27) for  $\sigma^H\langle\mu_R/J\rangle_2$  in units of nuclear magnetons is

$$\sigma^H\langle\mu_R/J\rangle_2=0.882265\pm 0.000035 \text{ nuclear magneton.} \quad (63)$$

The value of  $\sigma_D$  used here is given by Eq. (34) and the negligibly small difference between  $b$  and  $b''$  is omitted.



TABLE VI. Experimental results and derived quantities.

$c_{D-rot}$	8773±34 cps
$d_{D-rot}$	25 246±14 cps
$b_D'/(1-\sigma_D)a_D$	0.516550±0.000016
$b_H'/(1-\sigma_D)a_D$	1.029014±0.000030
${}_0^D\langle\mu_R/J\rangle_1$	0.442884±0.000052 nm
${}_0^H\langle\mu_R/J\rangle_1$	0.88291±0.00007 nm <sup>a</sup>
${}_0^H\langle\mu_R/J\rangle_2$	0.882265±0.000035 nm
${}_0^D\langle\mu_R/J\rangle_1(M_d/M_p)/{}_0^H\langle\mu_R/J\rangle_1$	1.00274±0.00011
${}_0^H\langle\mu_R/J\rangle_2/{}_0^H\langle\mu_R/J\rangle_1$	0.99927±0.00009
$d \ln \xi^{hf}/d \ln R=l$	3.72 <sup>+0.06</sup> (from H <sub>2</sub> and D <sub>2</sub> ); 3.80±0.12 (from H <sub>2</sub> J=1 and -0.12 J=2); 3.76±0.10 (average)
${}_0^D\langle\chi\rangle_1^{hf}$	(0.0978±0.0003)×10 <sup>-6</sup> erg gauss <sup>-2</sup> mole <sup>-1</sup>
${}_0^H\langle\chi\rangle_1^{hf}$	(0.1036±0.0005)×10 <sup>-6</sup> erg gauss <sup>-2</sup> mole <sup>-1</sup>
${}_0^H\langle\chi\rangle_2^{hf}$	(0.1049±0.0008)×10 <sup>-6</sup> erg gauss <sup>-2</sup> mole <sup>-1</sup>
${}_0^D\langle\xi\rangle_1^{hf}$	(1.623±0.006)×10 <sup>-31</sup> erg gauss <sup>-2</sup> molecule <sup>-1</sup>
${}_0^H\langle\xi\rangle_1^{hf}$	(1.719±0.009)×10 <sup>-31</sup> erg gauss <sup>-2</sup> molecule <sup>-1</sup>
${}_0^D\langle\xi_{\pm 1}-\xi_0\rangle$	-(3.50±0.40)×10 <sup>-31</sup> erg gauss <sup>-2</sup> molecule <sup>-1</sup>
${}_0^D\langle Q_e\rangle_1$	(0.318±0.030)×10 <sup>-16</sup> cm <sup>2</sup>
${}_0^H\langle Q_e\rangle_1$	(0.333±0.019)×10 <sup>-16</sup> cm <sup>2</sup>
${}_0^H\langle Q_e\rangle_1^{theor}$	(0.345±0.010)×10 <sup>-16</sup> cm <sup>2</sup>

<sup>a</sup> See reference 3.

It is of interest to compare the value of  ${}_0^H\langle\mu_R/J\rangle_2$  given above with the value of  ${}_0^H\langle\mu_R/J\rangle_1$  given by Eq. (35). Different centrifugal stretching in the two cases accounts for the difference between these values. Direct application of this difference is made in the next section.

### B. Hydrogen Molecular Susceptibility

The value of the parameter  $l$  characterizing the dependence of the high-frequency matrix elements of the electron angular momentum on inter-nuclear spacing has been calculated [see Eq. (39)] by comparing the rotational magnetic moments of H<sub>2</sub> and D<sub>2</sub> in the first rotational state. A second, and independent, determination of this parameter can be made by comparing the rotational magnetic moments of H<sub>2</sub> in the first and second rotational states. When the values of Eqs. (35) and (63) are substituted in Eq. (29), one obtains

$${}_0^H\langle(R/R_e)^{l-2}\rangle_1/{}_0^H\langle(R/R_e)^{l-2}\rangle_2 = 1 - (0.005478 \pm 0.00038). \quad (64)$$

The theoretical value of this expression is given by Eq. (30) and comparison of the right sides of Eqs. (64) and (30) shows that

$$l = 3.80 \pm 0.12. \quad (65)$$

The values of  $B_e$  and  $\omega_e$  are due to Herzberg.<sup>13,14</sup>

Combining the value of Eq. (65) with Eq. (21) of reference 9 yields

$$\begin{aligned} {}_0^H\langle(R/R_e)^l\rangle_1/{}_0^H\langle(R/R_e)^{l-2}\rangle_1 &= 1.1394 \pm 0.0080, \\ {}_0^H\langle(R/R_e)^l\rangle_2/{}_0^H\langle(R/R_e)^{l-2}\rangle_2 &= 1.1444 \pm 0.0080. \end{aligned} \quad (66)$$

The value of  $R_e$  has been determined [Eq. (42)], so that direct substitution of these various values in Eq. (28)

(where  $J=J'$ ) yields

$$\begin{aligned} {}_0^H\langle\chi\rangle_1^{hf} &= (0.0139 \pm 0.0008) \\ &\quad \times 10^{-6} \text{ erg gauss}^{-2} \text{ mole}^{-1}, \\ {}_0^H\langle\chi\rangle_2^{hf} &= (0.1049 \pm 0.0008) \\ &\quad \times 10^{-6} \text{ erg gauss}^{-2} \text{ mole}^{-1}, \end{aligned} \quad (67)$$

by using  $l=3.80 \pm 0.12$ . The value of  ${}_0^H\langle\chi\rangle_1^{hf}$  should be compared with that obtained via the evaluation of  $l$  from the D<sub>2</sub> results [Eq. (44)] and with the earlier value [Eq. (45)].

### C. Quadrupole Moment of the Hydrogen Electron Distribution

Equation (17) can be applied directly to the case of H<sub>2</sub> in the zeroth vibrational and first rotational states. The value of  $(\xi_{\pm 1}-\xi_0)$  has been given by Harrick and Ramsey<sup>3</sup> as  $-(3.66 \pm 0.20) \times 10^{-31}$  erg gauss<sup>-2</sup> molecule<sup>-1</sup>, and the value of  ${}_0^H\langle\xi\rangle_1^{hf}$  is obtained from Eq. (67) by division by  $L$ . When these values are substituted in Eq. (17) one finds

$${}_0^H\langle Q_e\rangle_1 = (0.333 \pm 0.019) \times 10^{-16} \text{ cm}^2 \quad (68)$$

for the quadrupole moment of the electron distribution in molecular hydrogen. The value computed from the theory of James and Coolidge<sup>15</sup> is  ${}_0^H\langle Q_e\rangle_1^{theor} = (0.345 \pm 0.010) \times 10^{-16} \text{ cm}^2$ .

## IX. SUMMARY OF RESULTS

The experimental results and their theoretical implications are summarized in Table VI. In the calculations, the values for the fundamental constants were taken to be those of DuMond and Cohen.<sup>16</sup>

One of the most interesting of the direct results, as

<sup>14</sup> G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950).

<sup>15</sup> H. M. James and A. S. Coolidge, *Astrophys. J.* **87**, 447 (1938).  
<sup>16</sup> J. W. M. DuMond and E. R. Cohen, *Phys. Rev.* **82**, 555 (1951).

shown in the eighth row of Table VI, is that the ratio for  $H_2$  and  $D_2$  of the rotational magnetic moments is not exactly equal to the inverse ratio of the nuclear masses but departs from exact equality by 0.27 percent. Similarly, in row nine of Table VI, the rotational magnetic moment in the second rotational state of hydrogen is not exactly double that in the first but is less than double by 0.07 percent. These discrepancies from the simplest theoretical predictions can successfully be attributed to differences in the zero point vibration and the centrifugal stretching for the molecule. Under such

an assumption,  $d \ln \xi^{hf} / d \ln R$  can be calculated independently from each of the above two observed discrepancies. The resulting values agree to within experimental error and average to  $3.76 \pm 0.10$ .

With the above value for  $d \ln \xi^{hf} / d \ln R$ , the zero point vibration correction can be suitably made in the calculation of the high-frequency term of the diamagnetic susceptibility. The resulting values are given in Table VI along with the best values for the quadrupole moments of the electron distribution that can be inferred from them.

### Pressure Shift in Helium $\lambda 5875^*$

JOHN R. HOLMES AND LEON PAPE

*Department of Physics, University of Southern California, Los Angeles, California*

(Received February 8, 1954)

Using a Fabry-Perot interferometer, pressure shift in  $\lambda 5875(2\ ^3P-3\ ^3D)$  of  $He^4$  was looked for over a pressure range from  $5 \times 10^{-2}$  to 20 mm. A mean shift of  $0.0074\text{ cm}^{-1}$  toward lower frequency at the higher pressure was found. As this is within the experimental error, it is concluded that over the above pressure range, pressure shift is not likely to falsify isotope shift measurements in the helium spectrum significantly.

#### INTRODUCTION

PRESSURE shifts in the helium spectrum have been reported by Hopfield<sup>1</sup> in the vacuum ultraviolet and by Fred, Tompkins, Brody, and Hamermesh<sup>2</sup> in the visible as observed during a study of isotope shift in helium lines. Since they<sup>2</sup> indicated that their observation of pressure shift was only qualitative and could be regarded as accounting partly for certain discrepancies in their isotope-shift data taken with high-pressure and low-pressure sources, it seemed worth while to make a quantitative direct study of the effect.

#### EXPERIMENTAL

As Fred *et al.* had reported much the largest effect in  $\lambda 5875(2\ ^3P-3\ ^3D)$ , ascribing a pressure shift in this line of  $0.0232\text{ cm}^{-1}$  for  $He^4$  and  $-0.0285\text{ cm}^{-1}$  for  $He^3$  between the low-pressure and the high-pressure source they used, it seemed appropriate to confine our measurements initially to  $\lambda 5875$ . The line was excited in an electrodeless discharge coupled to a 10-megacycle oscillator operated at low power to increase sharpness. The discharge was observed side-on in a flattened section of the tube 1 mm thick and was completely immersed in liquid nitrogen. The optical arrangement consisted of a Fabry-Perot interferometer mounted externally in series with a medium Hilger quartz spectrograph. The general method was to photograph

the interferometer pattern with a low pressure of  $He^4$  in the discharge tube, shift the photographic plate sideways slightly more than the slit width, take an exposure with a higher pressure of  $He^4$ , shift the photographic plate sideways again, and repeat the exposure at the low pressure. Comparison of the first and last exposures provides a check on any drifting of the patterns during the exposures and comparison of the middle pattern with the others should detect a pressure shift.

For the low-pressure exposures a pressure of  $5 \times 10^{-2}$  mm was used and for the high-pressure 20 mm, as this seemed to be about the greatest pressure range over which the discharge operated satisfactorily and gave reasonably sharp lines. As the tubes used by Fred *et al.* were sealed-off tubes initially filled to 0.3 mm and 5 mm, respectively, our pressure range was deemed adequate to detect and measure the effect described.

$\lambda 5875$  has a resolved fine structure component which is separated from the principal component by about  $1.0\text{ cm}^{-1}$ .<sup>3</sup> In order to reduce distortion in the wings of the line fringes an etalon spacer was chosen (1.245 cm) to position the fine structure between the third and fourth succeeding orders. This gives an order separation of  $0.4016\text{ cm}^{-1}$ .

The interferometer patterns were densitometered on a Zeiss microdensitometer and the traces corrected for nonuniform intensity distribution across the slit.

<sup>3</sup> Brochard, Chabbal, Chantrel, and Jacquinet, J. phys. radium **13**, 433 (1952).

\* Supported partly by the U. S. Office of Naval Research.

<sup>1</sup> J. J. Hopfield, *Astrophys. J.* **72**, 133 (1930).

<sup>2</sup> Fred, Tompkins, Brody, and Hamermesh, *Phys. Rev.* **82**, 406 (1951).