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Radio-Frequency Spectra of Hydrogen Deuteride in Strong Magnetic Fields[*]

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Molecular beam observations have been made of the radio-frequency spectra corresponding to reorientations of the deuteron, proton, and rotational magnetic moments in the HD molecule. For HD in the zeroth vibrational and first rotational state, these observations were made in magnetic fields of approximately 1700, 3400, and 4800 gauss. The results are found to be consistent with the theory of heteronuclear diatomic molecules. The direct result of these experiments is the determination of the Hamiltonian interaction constants: $(1-\sigma_{J1})b/\nu_d$ equals 0.773527 ± 0.000016, c_p is 85 600$\pm$18 cps, c_d equals 13 122$\pm$11 cps, d_1 is 17 761$\pm$12 cps, d_2 equals 22 454$\pm$6 cps, and f/H^2 is $(-26.90 \pm 0.40)\times 10^{-6}$ cps gauss^{-2}. From these values of the interaction constants are derived the following physical quantities: the HD rotational magnetic moment ${}^{\mathrm{HD}}{}_0\langle \mu_J/J\rangle_1$ equals 0.663211$\pm$0.000014 nuclear magneton, the quadrupole moment Q of the deuteron is $(2.738\pm 0.014)\times 10^{-27}$ cm^2, the rotational magnetic field H_p' at the proton is 19.879$\pm$0.006 gauss and H_d' at the deuteron is 20.020$\pm$0.028 gauss, the internuclear spacing in the zeroth vibrational and first rotational state is such that ${}^{\mathrm{HD}}{}_0\langle R^{-3}\rangle_1{}^{-\frac{1}{3}}$ equals $(0.74604\pm 0.00010)\times 10^{-8}$ cm, and the dependence of the diamagnetic susceptibility on molecular orientation $(\xi_{\pm 1}-\xi_0)$ is $-(3.56\pm 0.20)\times 10^{-31}$ erg gauss^{-2} molecule^{-1}. Combining these values with Ramsey's theory on zero-point vibration and centrifugal stretching in molecules gives the high-frequency contribution to the molecular susceptibility, ${}^{\mathrm{HD}}{}_0\langle \xi^{\mathrm{hf}}\rangle_1 = (1.675\pm 0.005) \times 10^{-31}$ erg gauss^{-2} molecule^{-1}; the quadrupole moment of the electron distribution relative to the internuclear axis, ${}^{\mathrm{HD}}{}_0\langle Q_e\rangle_1 = (0.324\pm 0.010)\times 10^{-16}$ cm^2; and the high-frequency contribution to the magnetic shielding constant for HD,

$${}^{\mathrm{HD}}{}_0\langle \sigma^{\mathrm{hf}}\rangle_1 = (-0.594\pm 0.030)\times 10^{-5}.$$

I. INTRODUCTION

THE adaptation of an electron-bombardment detection system[1] to molecular beams has made possible a precision study of the radio-frequency spectra of the hydrogen deuteride molecule in the relatively long Harvard molecular beam apparatus.[2] The original HD molecular beam studies were preformed by Kellogg, Rabi, Ramsey, and Zacharias[3] with observations of the proton and deuteron nuclear spectra in the first rotational and zeroth vibrational state in moderately strong magnetic fields. From measurements on the HD rotational spectrum, Ramsey[4] determined the rotational magnetic moment and the diamagnetic interaction parameter, and checked the values of the Hamiltonian interaction constants as determined in the initial experiments. The considerably higher precision of the present results arises from a longer homogeneous field magnet,[2] use of the separated oscillatory field method,[5] the employment of improved frequency-measuring equipment, and the use of an electron-bombardment detector with associated modulation techniques.[1] Also, a ninth-order perturbation calculation[6] has been used to determine the energy levels and aid in the analysis of the measurements. In addition to the energy interactions considered in the original experiments, the interpretation of the results include the magnetic shielding[7] within the molecule and the electron-coupled nuclear spin-spin[8] interaction.

The present investigation includes measurements on the proton nuclear spectrum, the deuteron nuclear spectrum, and the rotational spectrum in the first rotational state of HD in magnetic fields ranging from 1700 to 5000 gauss. From these measurements of transition frequencies, values of the Hamiltonian interaction constants and several related physical quantities are determined.[9] Non-molecular-beam magnetic resonance experiments on gaseous HD have provided little information on these interaction constants because the frequent molecular collisions average together the spectral lines which can be individually observed by the molecular-beam resonance method.

The heteronuclear HD molecule was studied in this experiment because of the significant information which can be inferred from the experimental results. In addition to the considerably higher precision determination of the various HD molecular interaction constants, the present experiment provides an excellent test of the validity of the detailed physical theory[8] of diatomic molecules. In particular, this investigation allows a study of the important question as to whether all the existing interactions have been included in the theory for a heteronuclear molecule.[10] Since HD is the simplest of heteronuclear molecules it serves to test the theory which has successfully been used to interpret the experimental results from measurements on the homonuclear H_2 and D_2 molecules. In fact the HD interaction

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[1] Quinn, Pery, Baker, Lewis, Ramsey, and LaTourrette, Rev. Sci. Instr. **29**, 935 (1958).

[2] Kolsky, Phipps, Ramsey, and Silsbee, Phys. Rev. **87**, 395 (1952).

[3] Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **57**, 677 (1940); hereafter referred to as KRRZ.

[4] N. F. Ramsey, Phys. Rev. **58**, 226 (1940).

[5] N. F. Ramsey, Phys. Rev. **78**, 695 (1950), and *Molecular Beams* (Oxford University Press, New York, 1956), p. 124 ff.

[6] N. F. Ramsey and H. R. Lewis, Phys. Rev. **108**, 1246 (1957).

[7] N. F. Ramsey, Phys. Rev. **78**, 699 (1950).

[8] N. F. Ramsey, Phys. Rev. **85**, 60 (1952), and **91**, 303 (1953).

[9] Cohen, DuMond, Layton, and Rollett, Revs. Modern Phys. **27**, 363 (1955); the values of the fundamental constants in this paper are used throughout.

[10] Quinn, Baker, LaTourrette, and Ramsey, Bull. Am. Phys. Soc. Ser. II, **2**, 200 (1957).

constants and spectra were predicted theoretically using the latter results.

II. APPARATUS AND METHOD

The basic features of the molecular-beam apparatus employed in these experiments are essentially those described previously.[2] In addition to subsequent modifications and improvements,[11–13] an electron-bombardment detector was developed and used for the detection of the noncondensable HD beam. This short-time-constant detection system and associated components have been described elsewhere.[1] The advantages of the electron-bombardment detector over a Stern-Pirani detector are illustrated by the fact that attempts were made over many months to detect the same HD resonances in the same apparatus with a Stern-Pirani detector with no success whatsoever, while the present detector makes observation of the HD resonances relatively easy. A phase modulation of the radio-frequency perturbing field facilitated the resonance observations. This detection arrangement aided the various optimizing adjustments on the apparatus.

With the source at liquid nitrogen temperature, the maximum possible number of molecules contributing to a HD resonance in the first rotational state is 3% of the total HD beam when the effect of the velocity distribution among the molecules is taken into account. An additional decrease of this resonance amplitude occurs in the rotational and deuteron nuclear spectra due to the simultaneous existence of the small rotational and deuteron magnetic moments in the HD molecule with the larger proton moment. Since the force experienced by a molecule in the inhomogeneous fields of the polarizing and analyzing magnets is $F=\mu(\partial H/\partial z)$, the HD configuration of angular moments requires a compromise adjustment of these fields. These deflecting and refocusing fields were adjusted experimentally to a value large enough such that most of the molecules which have the small rotational moment reoriented in the homogeneous field are deflected out of the beam, and small enough so the deflections of the molecules, which may be large because of the contribution from the large proton moment, do not destroy the beam.

The resonance transitions were observed by maintaining the homogeneous C field at a constant value and varying the perturbing oscillator frequency in a slow and uniform sweep as the resonance curve was traced out on a recorder. A 0° to 180° phase modulation[5] was used in conjunction with the separated oscillatory field method for all data taking. The relative initial phases of the separated radio-frequency fields were monitored in accordance with the symmetry of the line shape. In all data taking, each resonance line was swept both directions in frequency to nullify any time-constant distortion.

III. THE HAMILTONIAN

Theoretically, the heteronuclear HD molecule is essentially a 3 angular momentum problem in which the proton spin $\mathbf{i}_p$, deuteron spin $\mathbf{i}_d$, and rotational angular momentum $\mathbf{J}$ interact with an external magnetic field $\mathbf{H}$, with themselves in pairs, as well as in a mutual interaction between all three. The Hamiltonian which describes these interactions for the heteronuclear diatomic HD molecule in an external magnetic field $\mathbf{H}$ is given by

$$\begin{aligned}\mathcal{H}/h= &-[1-\sigma_p(J)]a_p\mathbf{i}_p\cdot\mathbf{H}/H-[1-\sigma_d(J)]a_d\mathbf{i}_d\cdot\mathbf{H}/H\\ &-[1-\sigma_J(J)]b\mathbf{J}\cdot\mathbf{H}/H-c_p\mathbf{i}_p\cdot\mathbf{J}-c_d\mathbf{i}_d\cdot\mathbf{J}\\ &+\frac{5d_1}{(2J-1)(2J+3)}[\tfrac{3}{2}(\mathbf{i}_p\cdot\mathbf{J})(\mathbf{i}_d\cdot\mathbf{J})\\ &+\tfrac{3}{2}(\mathbf{i}_d\cdot\mathbf{J})(\mathbf{i}_p\cdot\mathbf{J})-\mathbf{i}_p\cdot\mathbf{i}_d\mathbf{J}^2]\\ &+\frac{5d_2}{(2J-1)(2J+3)}[3(\mathbf{i}_d\cdot\mathbf{J})^2+\tfrac{3}{2}(\mathbf{i}_d\cdot\mathbf{J})-\mathbf{i}_d^2\mathbf{J}^2]\\ &-\frac{5f}{3(2J-1)(2J+3)}[3(\mathbf{J}\cdot\mathbf{H})^2/H^2-\mathbf{J}^2]\\ &-g+\delta\mathbf{i}_p\cdot\mathbf{i}_d. \qquad (1)\end{aligned}$$

The symbols in Eq. (1) have been defined and discussed previously.[6] In a strong magnetic field, the terms representing the respective interactions of the proton, deuteron, and rotational angular momenta with the external field make the major contribution to the Hamiltonian. The remaining intramolecular interactions have been treated as a perturbation in the evaluation of the energy levels in an m_J, m_p, m_d representation for the HD molecule in the first rotational state $J=1$.

The quantities in the Hamiltonian which we are most interested in evaluating are the following: b, which gives the molecule's rotational magnetic moment; the spin-rotational interaction constants c_p and c_d, which are a measure of the magnetic fields at the proton and deuteron arising from the molecule's rotational motion; the spin-spin magnetic interaction constant d_1, which gives the internuclear spacing; the quadrupole interaction constant d_2; and the diamagnetic interaction constant f which relates the dependence of the diamagnetic susceptility on molecular orientation. The interaction constants a_p and a_d are accurately known since they are a measure of the proton and deuteron magnetic moments, respectively. The known experimental value[14]

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[11] Harrick, Barnes, Bray, and Ramsey, Phys. Rev. **90**, 260 (1953).

[12] H. R. Lewis, Ph.D. thesis, Harvard University, 1955 (unpublished).

[13] W. E. Quinn, Ph.D. thesis, Harvard University, 1956 (unpublished).

[14] T. F. Wimett, Phys. Rev. **91**, 476 (1953).

TABLE I. Radio-frequencies (cps) at which resonances will occur for changes of orientation of the deuteron spin in HD molecules in the first rotational state ($J=1$) for strong magnetic fields H. Each term of this table must be multiplied by the power of H listed at the top of each column. The value of H should be in kilogauss.

Transition	m_J	m_p	m_d	Zeroth order	First order	Second order $\times H^{-1}$	Third order $\times H^{-2}$	Fourth $\times H^{-3}$	Fifth $\times H^{-4}$	Sixth $\times H^{-5}$	Seventh $\times H^{-6}$	Eighth $\times H^{-7}$	Ninth $\times H^{-8}$
BA/RQ	±1	$\pm\frac{1}{2}$	$0\leftrightarrow\pm1$	$(1-\sigma_{d1})a_d$	$\pm c_d\mp\frac{1}{2}d_1\mp\frac{3}{2}d_2\mp\frac{1}{2}\delta$	$+7560$	±1299	-194	∓169	-19	±18	$+8$	∓1
CB/QP	±1	$\pm\frac{1}{2}$	$0\leftrightarrow\mp1$	$(1-\sigma_{d1})a_d$	$\pm c_d\mp\frac{1}{2}d_1\pm\frac{3}{2}d_2\mp\frac{1}{2}\delta$	$+15\,514$	±3465	-863	∓574	$+122$	±135	-33	∓49
ED/ON	±1	$\mp\frac{1}{2}$	$0\leftrightarrow\pm1$	$(1-\sigma_{d1})a_d$	$\pm c_d\pm\frac{1}{2}d_1\mp\frac{3}{2}d_2\pm\frac{1}{2}\delta$	$+25\,299$	∓3423	-3406	±1696	$+747$	∓840	-101	±405
FE/NM	±1	$\mp\frac{1}{2}$	$0\leftrightarrow\mp1$	$(1-\sigma_{d1})a_d$	$\pm c_d\pm\frac{1}{2}d_1\pm\frac{3}{2}d_2\pm\frac{1}{2}\delta$	-8048	∓2956	$+5781$	∓2581	-430	±783	$+32$	∓295
HG/LK	0	$\pm\frac{1}{2}$	$0\leftrightarrow\pm1$	$(1-\sigma_{d0})a_d$	$\pm d_1\pm3d_2\mp\frac{1}{2}\delta$	-390	±2969	$+3237$	±1458	$+195$	∓78	-36	∓61
IH/KJ	0	$\pm\frac{1}{2}$	$0\leftrightarrow\mp1$	$(1-\sigma_{d0})a_d$	$\pm d_1\mp3d_2\mp\frac{1}{2}\delta$	$+31\,122$	±1696	-6838	∓3324	$+533$	±936	-57	∓644

of the relatively small electron-coupled spin-spin interaction constant δ is used in analyzing our data.

In the rotational state $J=0$, all orientations of the HD molecule are equally probable with the result that the interactions of interest average to zero; the Hamiltonian reduces to the first two and last terms. Consequently, the first rotational state $J=1$ is the case of greatest experimental interest. With the source at liquid nitrogen temperature, approximately 37% of the HD molecules populate the first rotational state while most of the remainder exist in the state $J=0$.

IV. HD TRANSITIONS IN A STRONG MAGNETIC FIELD

In the high-field limit, the selection rules allow 33 transitions between the 18 equally populated HD energy levels of the first rotational state. These form three spectral groups: (1) the proton nuclear spectrum with $\Delta m_J=\Delta m_d=0$, $\Delta m_p=\pm1$ consisting of 9 transitions clustered about the Larmor frequency of the proton; (2) the deuteron nuclear spectrum with 12 transitions in the vicinity of the deuteron Larmor frequency with $\Delta m_J=\Delta m_p=0$, $\Delta m_d=\pm1$; (3) the rotational spectrum consisting of 12 transitions grouped about the Larmor frequency of the rotational magnetic moment with $\Delta m_J=\pm1$, $\Delta m_p=\Delta m_d=0$. The theoretical expressions[6] for the energy levels combined with the selection rules predict the transition frequencies in a magnetic field **H**.

V. HD DEUTERON NUCLEAR SPECTRUM

The deuteron nuclear spectrum consists of the 12 transitions for which $\Delta m_J=\Delta m_p=0$, $\Delta m_d=\pm1$. The expressions for the deuteron transition frequencies are given in Table I. These are given by the separation of the appropriate energy levels of Tables II and III of reference 6. The notation BA signifies the frequency of the transition between the energy levels B and A.

The deuteron spin-rotational interaction constant c_d, the spin-spin interaction constant d_1, and the deuteron quadrupole interaction constant d_2 are determined from observations of the deuteron spectrum. The theoretical expressions for the deuteron transitions, Table I, are combined in such a way that these interaction constants are determined in terms of the transition frequencies, which are the experimental observables. Table I indicates that certain pairs of transitions have odd-order terms which have the same magnitude but different sign, and higher even-order terms which are the same for both. Differences between these paired lines provide 6 linear relations between the desired interaction constants and the transition frequencies with higher odd-order field-dependent terms,

$$2c_d-d_1-3d_2=BA-RQ-\Delta(BA-RQ)+\delta=a_1, \quad (2)$$

$$2c_d-d_1+3d_2=CB-QP-\Delta(CB-QP)+\delta=a_2, \quad (3)$$

$$2c_d+d_1-3d_2=ED-ON-\Delta(ED-ON)-\delta=a_3, \quad (4)$$

$$2cd+d_1+3d_2=FE-NM-\Delta(FE-NM)-\delta=a_4, \quad (5)$$

$$2d_1+6d_2=HG-LK-\Delta(HG-LK)+\delta=a_5, \quad (6)$$

$$2d_1-6d_2=IH-KJ-\Delta(IH-KJ)+\delta=a_6. \quad (7)$$

The quantity $\Delta(BA-RQ)$, for example, is the contribution to the transition frequency difference, $BA-RQ$, from the second- and higher-order perturbation terms listed in Table I. These equations are valid up to the eleventh-order perturbation terms since all even-order term contributions to the quantities Δ vanish.

The method of least squares is applied to this set of 6 linear equations to obtain the desired solutions for the 3 interaction constants,

$$c_d=(a_1+a_2+a_3+a_4)/8, \quad (8)$$

$$d_1=[-a_1-a_2+a_3+a_4+4(a_5+a_6)]/20, \quad (9)$$

$$d_2=[-a_1+a_2-a_3+a_4+4(a_5-a_6)]/60, \quad (10)$$

where the symbols a_n are defined in Eqs. (2)–(7).

The complete 12-line deuteron nuclear spectrum was observed twice in two separate runs. From the nature of the Eqs. (2)–(7), it was advantageous to observe the paired transitions consecutively in order to obtain their resonant frequencies at nearly the same value of the magnetic field. The paired lines are corrected to an intermediate common magnetic field with the assumption that any magnetic field drift is linear in time. The magnetic field in which these resonant frequencies occurred was conveniently monitored by observing the HD deuteron resonance in the rotational state $J=0$,

$$H=\nu_d/[\gamma_d(1-\sigma_d)]. \quad (11)$$

TABLE II. Data used in the evaluation of c_d, d_1, and d_2 from the deuteron nuclear spectrum.

Transition frequency difference	Run	Magnetic field H (gauss)	Transition frequency difference (cps)	Δ (cps)	a_n (cps)
$BA-RQ$	$D1$	3378.622	+76 025	−225	+75 816±28
$BA-RQ$	$D2$	3423.410	+75 964	−219	
$CB-QP$	$D1$	3378.518	−58 350	−598	−58 907±20
$CB-QP$	$D2$	3423.489	−58 369	−583	
$ED-ON$	$D1$	3408.291	+110 802	+564	+111 372±48
$ED-ON$	$D2$	3423.752	+110 902	+560	
$FE-NM$	$D1$	3378.363	−23 837	+557	−23 322±20
$FE-NM$	$D2$	3423.596	−23 818	+541	
$HG-LK$	$D1$	3377.768	−98 803	−535	−99 261±20
$HG-LK$	$D1$	3401.104	−98 794	−535	
$HG-LK$	$D2$	3408.291	−98 716	−533	
$HG-LK$	$D2$	3423.752	−98 772	−528	
$IH-KJ$	$D2$	3422.250	+170 454	−242	+170 260±12
$IH-KJ$	$D1$	3375.335	+170 492	−242	
$IH-KJ$	$D1$	3408.563	+170 436	−242	
$IH-KJ$	$D2$	3423.895	+170 457	−242	

Each observation consisted of a minimum of two resonance curves since each resonance was swept in both frequency directions to minimize the effect of any time-constant distortion. Two frequency determinations were made from each resonance curve: (1) The intersection of two lines drawn tangent to the sides of the resonance curve gave one determination. (2) The mean of the half-amplitude point gave a second determination. The first determination was interpolated between the two frequency markers nearest to the intersection which were generally separated by 100 cps while the second frequency was interpolated between frequency markers near the half-amplitude points which were separated by approximately 350 cps.

The resonant frequencies are determined within an accuracy of ±20 cps from the resonance curves with 350-cps line widths. However, there are two sources of error. During these experiments, the homogeneous magnetic field exhibited a nearly linear downward drift of approximately 0.1 gauss/hour. One hour is about the time required to observe an unknown resonance line and to monitor the field before and after. The second source of error results from the uncertainty in the relative phase between the rf end coils. In the separated field method, the resonance line shape is dependent on this relative phase. Since the correct phase is determined by minimizing the asymmetry of the line, with a low signal-to-noise ratio it is difficult to ascertain the proper relative phase. However, the $J=0$ deuteron resonance lies in the $J=1$ deuteron nuclear spectrum and was used to determine the optimum phase. A Tektronix 545 oscilloscope with a dual beam input was used to reset this same relative phase after retuning for each resonance line

The useful data from the deuteron nuclear spectrum are displayed in Table II. Inserting the averaged a_n values into Eqs. (8)–(10) gives the values for the interaction constants listed in Table VII in the rows designated by the runs $D1$ and $D2$.

VI. HD PROTON NUCLEAR SPECTRUM

The proton nuclear spectrum consists of 9 transitions clustered about the Larmor frequency of the proton as allowed by $\Delta m_J=\Delta m_d=0$, $\Delta m_p=\pm 1$. Table III gives the proton transition frequencies for arbitrarily strong magnetic fields. These frequencies are the separations of the appropriate energy levels of Tables II and III of reference 6.

The proton spin-rotational interaction constant c_p and the spin-spin magnetic interaction constant d_1 are obtained from the measurements on the proton spectrum. Differences between pairs of transitions in Table III such that the even-order terms vanish, provide 4 linear equations between the desired interaction constants and the experimentally observable transition frequencies plus higher odd-order field-dependent terms.

$$2c_p-2d_1=DA-RO-\Delta(DA-RO)+2\delta=k_1, \quad (12)$$

$$2c_p \quad =EB-QN-\Delta(EB-QN) \quad =k_2, \quad (13)$$

$$2c_p+2d_1=FC-PM-\Delta(FC-PM)-2\delta=k_3, \quad (14)$$

$$4d_1=JG-LI-\Delta(JG-LI)+2\delta=k_4. \quad (15)$$

TABLE III. Radio-frequencies (cps) at which resonances will occur for changes of orientation of the proton spin in HD molecules in the first rotational state ($J=1$) for strong magnetic fields H. Each term of this table must be multiplied by the power of H listed at the top of its column. The value of H is in kilogauss.

Transition	m_J	m_p	m_d	Zeroth order	First order	Second order $\times H^{-1}$	Third order $\times H^{-2}$	Fourth $\times H^{-3}$	Fifth $\times H^{-4}$	Sixth $\times H^{-5}$	Seventh $\times H^{-6}$	Eighth $\times H^{-7}$	Ninth $\times H^{-8}$
DA/RO	±1	$-\frac{1}{2}\leftrightarrow+\frac{1}{2}$	±1	$(1-\sigma_{p1})a_p$	$\pm c_d\mp d_1\mp\delta$	+474	±2.01	+0	+0	+0	+0	+0	+0
EB/QN	±1	$-\frac{1}{2}\leftrightarrow+\frac{1}{2}$	0	$(1-\sigma_{p1})a_p$	$\pm c_p$	+18 213	∓4723	−3212	±1866	+766	∓857	−109	±406
FC/PM	±1	$-\frac{1}{2}\leftrightarrow+\frac{1}{2}$	∓1	$(1-\sigma_{p1})a_p$	$\pm c_p\pm d_1\pm\delta$	−5350	∓11 145	+3432	∓142	+214	∓210	−44	±160
JG/LI	0	$-\frac{1}{2}\leftrightarrow+\frac{1}{2}$	±1	$(1-\sigma_{p0})a_p$	$\pm 2d_1\mp\delta$	−14 665	±4666	+3213	∓1866	−766	±858	+109	∓406
KH	0	$-\frac{1}{2}\leftrightarrow+\frac{1}{2}$	0	$(1-\sigma_{p0})a_p$	+0	+16 847	+0	−6862	+0	−429	+0	+88	+0

The quantity $\Delta(DA-RO)$, for example, is the contribution to the transition frequency difference, $DA-RO$, from the second- and higher-order perturbation terms listed in Table III. These equations are valid up to eleventh-order perturbation terms since all even-order term contributions to the quantities Δ vanish.

Applying the method of least squares to the resulting set of 4 linear equations to obtain the desired solutions for the interaction constants c_p and d_1 gives

$$c_p=(k_1+k_2+k_3)/6, \tag{16}$$

$$d_1=(2k_4+k_3-k_1)/12, \tag{17}$$

where the symbols k_n are defined in Eqs. (12)–(15).

The complete 9-line proton nuclear spectrum was observed in three separate runs in a magnetic field of approximately 1700 gauss. The observational procedure was identical to that described in Sec. V. The magnetic field in which these resonances occurred was monitored by observing the HD proton resonance in the rotational state $J=0$,

$$H=\nu_p/[\gamma_p(1-\sigma_p)]. \tag{18}$$

The useful data from the proton nuclear spectrum are given in Table IV. Substituting the values of the quantities k_n into Eqs. (16) and (17) yields the values of the proton spin-rotational interaction constant c_p and the spin-spin interaction constant d_1 listed in Table VII in the rows designated by the runs $P1$, $P2$, and $P3$.

VII. HD ROTATIONAL SPECTRUM ($J=1$)

The 12-line rotational spectrum arises from reorientations of the molecular rotational angular momentum. The energy expressions[6] are subtracted subject to the selection rules $\Delta m_p=\Delta m_d=0$, $\Delta m_J=\pm1$ to obtain the relations for the transition frequencies given in Table V.

In addition to the rotational magnetic moment interaction constant b, the intramolecular interaction constants are determined from the measurements on the rotational spectrum including the diamagnetic interaction constant f. As in the case of the nuclear spectra, taking the difference between certain paired expressions for the transition frequencies eliminates the

TABLE IV. Data used in the evaluation of c_p and d_1 from the proton nuclear spectrum.

Transition difference	Run	Magnetic field H (gauss)	Transition frequency difference (cps)	Δ (cps)	k_n (cps)
$DA-RO$	$P1$	1707.556	+135 610	+2	+135 612
$DA-RO$	$P2$	1701.195	+135 602	+2	+135 604
$DA-RO$	$P3$	1705.283	+135 610	+2	+135 612
$EB-QN$	$P1$	1707.551	+168 393	+2859	+171 252
$EB-QN$	$P2$	1701.247	+168 359	+2886	+171 245
$EB-QN$	$P3$	1705.260	+168 334	+2866	+171 200
$FC-PM$	$P1$	1707.535	+199 154	+7690	+206 844
$FC-PM$	$P2$	1701.312	+199 055	+7747	+206 802
$FC-PM$	$P3$	1705.262	+199 174	+7711	+206 885
$JG-LI$	$P1$	1707.607	+73 748	−2819	+70 929
$JG-LI$	$P2$	1701.152	+73 843	−2838	+71 005
$JG-LI$	$P3$	1705.253	+73 798	−2826	+70 972

TABLE V. Radio-frequencies (cps) at which HD rotational resonances ($J=1$) should occur for a strong magnetic field H. Each term of this table must be multiplied by the power of H listed at the top of its column. The value of H is in kilogauss. For this table it is assumed that $\sigma_{pm}=\sigma_{dm}=\sigma_{im}$.

Transition	m_J	m_p	m_d	Zeroth order	First order	Dia-magnetism	Second order $\times H^{-1}$	Third $\times H^{-2}$	Fourth $\times H^{-3}$	Fifth $\times H^{-4}$	Sixth $\times H^{-5}$	Seventh $\times H^{-6}$	Eighth $\times H^{-7}$	Ninth $\times H^{-8}$
GA/RL	$0\leftrightarrow\pm1$	$\pm\frac{1}{2}$	±1	$(1-\sigma_{J1})b+(\sigma_{i0}-\sigma_{i1})(\frac{1}{2}a_p+a_d)$	$\pm\frac{1}{2}c_p\pm c_d\mp\frac{3}{2}d_1\mp\frac{3}{2}d_2$	$\pm f$	−8 034	∓1297	+194	±169	+19	∓18	−8	±1
HB/QK	$0\leftrightarrow\pm1$	$\pm\frac{1}{2}$	0	$(1-\sigma_{J1})b+(\sigma_{i0}-\sigma_{i1})(\frac{1}{2}a_p)$	$\pm\frac{1}{2}c_p\quad\pm3d_2$	$\pm f$	−15 984	±374	+3626	±1796	+234	∓114	−52	∓60
IC/PJ	$0\leftrightarrow\pm1$	$\pm\frac{1}{2}$	∓1	$(1-\sigma_{J1})b+(\sigma_{i0}-\sigma_{i1})(\frac{1}{2}a_p-a_d)$	$\pm\frac{1}{2}c_p\mp c_d\pm\frac{3}{2}d_1\mp\frac{3}{2}d_2$	$\pm f$	−375	∓1395	−2350	∓954	+645	±687	−76	∓355
JD/OI	$0\leftrightarrow\pm1$	$\mp\frac{1}{2}$	±1	$(1-\sigma_{J1})b+(\sigma_{i0}-\sigma_{i1})(-\frac{1}{2}a_p+a_d)$	$\mp\frac{1}{2}c_p\pm c_d\pm\frac{3}{2}d_1\mp\frac{3}{2}d_2$	$\pm f$	−23 173	±3371	+3407	∓1696	−747	±840	+101	∓404
KE/NH	$0\leftrightarrow\pm1$	$\mp\frac{1}{2}$	0	$(1-\sigma_{J1})b+(\sigma_{i0}-\sigma_{i1})(-\frac{1}{2}a_p)$	$\mp\ c_p\quad\pm3d_2$	$\pm f$	−17 349	±5097	−25	∓69	−962	±744	+146	∓465
LF/MG	$0\leftrightarrow\pm1$	$\mp\frac{1}{2}$	∓1	$(1-\sigma_{J1})b+(\sigma_{i0}-\sigma_{i1})(-\frac{1}{2}a_p-a_d)$	$\mp\frac{1}{2}c_p\mp c_d\mp\frac{3}{2}d_1\mp\frac{3}{2}d_2$	$\pm f$	−9 690	±5084	−2570	±1054	−336	±39	+77	∓109

even-order perturbation terms. This procedure gives 6 linear equations which relate the 5 intramolecular interaction constants to transition frequency differences:

$$\begin{aligned} c_p+2c_d-3d_1-3d_2+2f& \\ &=GA-RL-\Delta(GA-RL)=b_1, &(19)\\ c_p\qquad\quad +6d_2+2f& \\ &=HB-QK-\Delta(HB-QK)=b_2, &(20)\\ c_p-2c_d+3d_1-3d_2+2f& \\ &=IC-PJ-\Delta(IC-PJ)=b_3, &(21)\\ c_p+2c_d+3d_1-3d_2+2f& \\ &=JD-OI-\Delta(JD-OI)=b_4, &(22)\\ -c_p\qquad\quad +6d_2+2f& \\ &=KE-NH-\Delta(KE-NH)=b_5, &(23)\\ -c_p-2c_d-3d_1-3d_2+2f& \\ &=LF-MG-\Delta(LF-MG)=b_6. &(24)\end{aligned}$$

The quantity $\Delta(GA-RL)$, for example, is the contribution to the transition frequency difference, $GA-RL$, from the higher-order perturbation terms listed in Table V.

Application of the method of least squares to those equations results in the solutions

$$c_p=(b_1+b_2+b_3-b_4-b_5-b_6)/6, \tag{25}$$

$$c_d=(b_1-b_3+b_4-b_6)/8, \tag{26}$$

$$d_1=(-b_1+b_3+b_4-b_6)/12, \tag{27}$$

$$d_2=(-b_1+2b_2-b_3-b_4+2b_5-b_6)/36, \tag{28}$$

$$f=(b_1+b_2+b_3+b_4+b_5+b_6)/12. \tag{29}$$

In order to determine the rotational magnetic moment interaction constant b, certain paired transitions are summed in such a way that the odd-order perturbation contributions vanish. The magnetic field is eliminated from the zero-order terms by dividing each transition sum by the observed deuteron resonance frequency $\nu_d=(1-\sigma_d)a_d$ which is obtained from the molecules in the $J=0$ state and used to monitor the magnetic field. From Table V,

$$\begin{aligned}(1-\sigma_{J1})b_{GA+RL}/\nu_d=&[GA+RL-\Delta(GA+RL)]/2\nu_d\\ &-(\sigma_{i0}-\sigma_{i1})(\mu_p+\mu_d)/(1-\sigma_d)\mu_d, &(30)\\ (1-\sigma_{J1})b_{LF+MG}/\nu_d=&[LF+MG-\Delta(LF+MG)]/2\nu_d\\ &+(\sigma_{i0}-\sigma_{i1})(\mu_p+\mu_d)/(1-\sigma_d)\mu_d, &(31)\\ (1-\sigma_{J1})b_{JD+OI}/\nu_d=&[JD+OI-\Delta(JD+OI)]/2\nu_d\\ &+(\sigma_{i0}-\sigma_{i1})(\mu_p-\mu_d)/(1-\sigma_d)\mu_d, &(32)\\ (1-\sigma_{J1})b_{IC+PJ}/\nu_d=&[IC+PJ-\Delta(IC+PJ)]/2\nu_d\\ &-(\sigma_{i0}-\sigma_{i1})(\mu_p-\mu_d)/(1-\sigma_d)\mu_d, &(33)\\ (1-\sigma_{J1})b_{HB+QK}/\nu_d=&[HB+QK-\Delta(HB+QK)]/2\nu_d\\ &-(\sigma_{i0}-\sigma_{i1})\mu_p/(1-\sigma_d)\mu_d, &(34)\\ (1-\sigma_{J1})b_{KE+NH}/\nu_d=&[KE+NH-\Delta(KE+NH)]/2\nu_d\\ &+(\sigma_{i0}-\sigma_{i1})\mu_p/(1-\sigma_d)\mu_d. &(35)\end{aligned}$$

The quantity $\Delta(GA+RL)$, for example, is the contribution to the sum of transition frequencies, $GA+RL$, from the second- and higher-order perturbation terms listed in Table V.

The terms involving the quantity $(\sigma_{i0}-\sigma_{i(\pm1)})/(1-\sigma_d)$

TABLE VI. Data used in the evaluation of $(1-\sigma_{J1})b/\nu_d$, c_d, c_p, d_1, d_2, and f from the rotational spectrum.

Transitions involved	Run	ν_d (cps)	$\frac{1}{2}\times$transition frequency sum (cps)	$(1-\sigma_{J1})b/\nu_d$	Transition frequency difference (cps)	b_n (cps)
GA RL	*R*1	2 248 422	1 736 906	0.7735242	125 052	125 269
LF MG	*R*1	2 248 524	1 736 400		−97 469	−98 343
KE NH	*R*1	2 248 957	1 734 577	0.7735236	−220 078	−220 939
HB QK	*R*1	2 248 829	1 734 968		−49 680	−49 769
JD OI	*R*1	2 248 816	1 732 848	0.7735212	61 227	60 681
IC PJ	*R*1	2 248 656	1 739 224		179 118	179 366
GA RL	*R*2	2 237 050	1 728 073	0.7735186	125 050	125 269
LF MG	*R*2	2 236 891	1 727 372		−97 484	−98 368
KE NH	*R*2	2 236 409	1 724 818	0.7735174	−220 042	−220 913
HB QK	*R*2	2 236 487	1 725 392		−49 649	−49 739
JD OI	*R*2	2 236 598	1 723 380	0.7735239	61 241	60 689
IC PJ	*R*2	2 236 752	1 730 008		179 094	179 345
GA RL	*R*3	3 176 433	2 455 479	0.7735498	124 487	124 596
LF MG	*R*3	3 176 576	2 455 223		−98 624	−99 058
KE NH	*R*3	3 176 858	2 453 779	0.7735427	−221 128	−221 559
HB QK	*R*3	3 176 749	2 454 193		−50 479	−50 517
JD OI	*R*3	3 177 169	2 452 873	0.7735090	60 368	60 089
IC PJ	*R*3	3 177 013	2 457 308		178 696	178 817
GA RL	*R*4	3 175 952	2 455 081	0.7735344	124 500	124 609
LF MG	*R*4	3 176 120	2 454 796		−98 717	−99 151
KE NH	*R*4	3 176 380	2 453 471	0.7735374	−221 144	−221 576
HB QK	*R*4	3 176 250	2 453 699		−50 400	−50 438
JD OI	*R*4	3 176 884	2 452 618	0.7735322	60 322	60 043
IC PJ	*R*4	3 176 568	2 457 146		178 631	178 752
GA RL	*R*5	3 175 706	2 454 912	0.7735399	124 561	124 670
LF MG	*R*5	3 175 882	2 454 626		−98 640	−99 074
KE NH	*R*5	3 176 275	2 453 397	0.7735439	−221 176	−221 608
HB QK	*R*5	3 176 070	2 453 592		−50 354	−50 392
JD OI	*R*5	3 176 871	2 452 698	0.7735362	60 315	60 036
IC PJ	*R*5	3 176 598	2 457 104		178 543	178 664
GA RL	*R*6	1 107 744	852 170	0.7735210	124 911	125 775
LF MG	*R*6	1 107 508	850 406		−94 148	−97 945
IC PJ	*R*6	1 107 468	855 989	0.7735262	178 654	179 810
JD OI	*R*6	1 107 488	843 651		63 126	61 130
QK HB	*R*6	1 107 488	847 994	0.7735118	−48 599	−49 284
NH KE	*R*6	1 107 447	846 302		−216 907	−220 490
GA RL	*R*7	1 107 543	851 957	0.7734657	124 818	125 682
LF MG	*R*7	1 107 548	850 371		−94 058	−97 855
IC PJ	*R*7	1 107 598	856 026	0.7734583	178 553	179 708
JD OI	*R*7	1 107 674	843 710		62 969	60 974
QK HB	*R*7	1 107 670	848 078	0.7734676	−48 567	−49 252
NH KE	*R*7	1 107 550	846 344		−216 827	−220 410

TABLE VII. Values of Hamiltonian interaction constants as determined from the HD radio-frequency spectra in strong magnetic fields.

Run	Magnetic field H (gauss)	$(1-\sigma_{J1})b/\nu_d$	c_p (cps)	c_d (cps)	d_1 (cps)	d_2 (cps)	f/H^2 (cps) gauss^{-2}
$D1$	3378			13 120	17 757	−22 458	
$D2$	3424						
$R1$	3440	0.7735230	85 578	13 116	17 760	−22 455	-26.30×10^{-6}
$R2$	3422	0.7735200	85 578	13 123	17 761	−22 451	-26.45×10^{-6}
$R3$	4860	0.7735338	85 571	13 116	17 781	−22 461	-26.92×10^{-6}
$R4$	4860	0.7735347	85 601	13 131	17 778	−22 452	-27.38×10^{-6}
$R5$	4859	0.7735400	85 598	13 140	17 759	−22 453	-27.19×10^{-6}
$R6$	1694	0.7735197	85 601	13 130	17 759	−22 453	
$R7$	1695		85 572	13 100	17 737	−22 440	
$P1$	1708		85 618		17 757		
$P2$	1701		85 608		17 767		
$P3$	1705		85 622		17 766		
Average value		0.773527±0.000016	85 600±18	13 122±11	17 761±12	−22 454±6	$(-26.90\pm0.40)\times10^{-6}$
Theoretically predicted value		0.77347±0.00007	85 650	13 148	17 767	−22 448	-27.6×10^{-6}

arise from nuclear shielding and are not accurately known. However, averaging pair values of $(1-\sigma_{J1})b/\nu_d$ obtained independently from different transition frequency sums cancels these unwanted terms.

The considerations and procedures discussed in Sec. V apply equally well to the measurements on the rotational spectrum. As discussed in Sec. II, observation of the HD rotational spectrum is difficult because of the small rotational moment coexisting with the appreciably larger proton moment. The difficulty is clearly illustrated by the observation that the intensity of the *GA* and *RL* rotational resonance lines, where the contributing molecules have all three magnetic moments aligned, are approximately one-fourth the intensity of the *OI* and *JD* rotational lines, where the rotational and deuteron moments are aligned opposite to the proton moment.

The 12-line rotational spectrum was observed at three different magnetic field strengths of about 1700, 3400, and 4800 gauss. The resonance transitions paired in Eqs. (30)–(35) were observed consecutively and corrected to a common intermediate magnetic field under the assumption that any magnetic field drift was linear in time. The data from the rotational measurements used in evaluating the intramolecular interaction constants are given in Table VI. Utilizing Eqs. (25)–(29) and (30)–(35), the interaction constants are determined and listed in Table VII in the rows designated by *R*'s. The data from the rotational spectrum which are used in determining the rotational magnetic moment interaction constant b are listed in Table VI along with the experimental values of $(1-\sigma_{J1})b/\nu_d$.

VIII. ANALYSIS OF RESULTS

The values determined for the Hamiltonian interaction constants from the respective runs are listed in Table VII. In the averaging, the deuteron results are weighted doubly since they are the averaged results of two runs. The weighted average is obtained by averaging the respective results from the same spectra at approximately identical magnetic fields, followed by an average of these quantities weighted inversely as their deviations. These results agree with the earlier results of KRRZ[3,4] to well within the large experimental error of the early experiments. Table VII also compares these results for the HD interaction constants with the values predicted theoretically from precision measurements[2,11,15,16] on the homonuclear molecules H_2 and D_2. The agreement between the present determinations and the predicted values verify the theory[6,8] for hetero- and homonuclear diatomic molecules. Table VIII gives the HD interaction constants and derived quantities.

A. HD Rotational Magnetic Moment

Since the electronic state of the HD molecule is ${}^1\Sigma$, the nonrotating molecule does not possess an electronic magnetic dipole moment. However, the rotation of the molecule induces a rotational magnetic moment due to

TABLE VIII. Experimental results and derived quantities for HD.

Quantity	Result
$(1-\sigma_{J1})b/\nu_d$	$+0.773527\pm0.000016$
$c_p={}^{\mathrm{HD}}{}_0\langle 2\mu_p H_p'/h\rangle_1$	85 600±18 cps
$c_d={}^{\mathrm{HD}}{}_0\langle \mu_d H_d'/h\rangle_1$	13 122±11 cps
$d_1={}^{\mathrm{HD}}{}_0\langle 4\mu_p\mu_d/5hR^3\rangle_1$	17 761±12 cps
$d_2={}^{\mathrm{HD}}{}_0\langle e^2qQ/2h\rangle_1$	−22 454±6 cps
$f/H^2={}^{\mathrm{HD}}{}_0\langle(\xi_{\pm1}-\xi_0)/2h\rangle_1$	$-(26.90\pm0.40)\times10^{-6}$ cps gauss^{-2}
${}^{\mathrm{HD}}{}_0\langle\mu_J/J\rangle_1$	$+0.663211\pm0.000014$ nm
${}^{\mathrm{HD}}{}_0\langle\mu_J/J\rangle_1\mu_{\mathrm{HD}}'/{}^{\mathrm{H}}{}_0\langle\mu_J/J\rangle_1\mu_{\mathrm{H}_2}'$	1.00139 ± 0.00009
${}^{\mathrm{D}}{}_0\langle\mu_J/J\rangle_1\mu_{\mathrm{D}_2}'/{}^{\mathrm{HD}}{}_0\langle\mu_J/J\rangle_1\mu_{\mathrm{HD}}'$	1.00135 ± 0.00013
Q	$(2.738\pm0.019)\times10^{-27}$ cm^2
${}^{\mathrm{HD}}{}_0\langle H_p'\rangle_1$	19.879 ± 0.006 gauss
${}^{\mathrm{HD}}{}_0\langle H_d'\rangle_1$	20.020 ± 0.028 gauss
${}^{\mathrm{HD}}{}_0\langle R^{-3}\rangle_1{}^{-\frac{1}{3}}$	$(0.74604\pm0.00010)\times10^{-8}$ cm
${}^{\mathrm{HD}}{}_0\langle aR_e\rangle_1$	1.33 ± 0.60
${}^{\mathrm{HD}}{}_0\langle\sigma^{\mathrm{hf}}\rangle_1$	$(-0.594\pm0.030)\times10^{-5}$
${}^{\mathrm{HD}}{}_0\langle\sigma\rangle_1$	$(2.622\pm0.032)\times10^{-5}$
$d\ln\xi^{\mathrm{hf}}/d\ln R$	3.80 ± 0.12
${}^{\mathrm{HD}}{}_0\langle\xi^{\mathrm{hf}}\rangle_1$	$(1.675\pm0.005)\times10^{-31}$ erg gauss^{-2} molecule^{-1}
${}^{\mathrm{HD}}{}_0\langle\xi_{\pm1}-\xi_0\rangle_1$	$(-3.56\pm0.10)\times10^{-31}$ erg gauss^{-2} molecule^{-1}
${}^{\mathrm{HD}}{}_0\langle Q_e\rangle_1$	$(0.324\pm0.020)\times10^{-16}$ cm^2

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[15] N. J. Harrick and N. F. Ramsey, Phys. Rev. **88**, 228 (1952).

[16] Barnes, Bray, and Ramsey, Phys. Rev. **94**, 893 (1954).

the circulating protons and electrons. This rotational magnetic moment is obtained from the definition[6] of the Hamiltonian interaction constant b,

$$b=\mu_J H/Jh, \tag{36}$$

through the use of the experimentally measured quantity $(1-\sigma_{J1})b/\nu_d$,

$$^{\mathrm{HD}}{}_0\langle\mu_J/J\rangle_1=\frac{1-\sigma_d}{1-\sigma_{J1}}\mu_d[(1-\sigma_{J1})b/\nu_d]. \tag{37}$$

Using the best value of $(1-\sigma_{J1})b/\nu_d$ from Table VIII and neglecting the small unknown quantity σ_{J1} gives[9]

$$^{\mathrm{HD}}{}_0\langle\mu_J/J\rangle_1=+0.663211\pm0.000014\text{ nm}. \tag{38}$$

Here use has been made of the value

$$\sigma_d=(2.62\pm0.04)\times10^{-5}$$

found from the theory of Ramsey[17] and measurements on the H_2 and D_2 nuclear spectra.[11]

A theoretical value of the HD rotational magnetic moment can be calculated from the expression[17]

$$\begin{aligned} ^X{}_0\langle\mu_J/J\rangle_1=(M/2\mu_X')[1+4\,{}^X{}_0\langle(D^2-d^2)/R^2\rangle_1 \\ -16(mc^2/e^2)R_e^{-3}F_e\,{}^X{}_0\langle(R/R_e)^{l-2}\rangle_1], \end{aligned} \tag{39}$$

where $Z_1=Z_2=1$ has been substituted in Eq. (8) of reference 17. If the permanent electric dipole moment of HD is assumed to be negligible, the quantity $(D^2-d^2)/R^2$ can be neglected. The quantity $^X{}_0\langle(R/R_e)^{l-2}\rangle_1$ is calculated from Eq. (21) of reference 17 after determination of the exponent in Eq. (66). The quantity F_e is obtained from the two simultaneous equations which result when the measured values of the rotational magnetic moments[11,15,16] of the isotropic H_2 and D_2 molecules are inserted[9] in Eq. (39),

$$F_e=+34.892\pm0.070\text{ nm cm}^4. \tag{40}$$

The parameter R_e is determined in Eq. (62). The insertion of the numerical values for the parameters in Eq. (39) gives

$$(^{\mathrm{HD}}{}_0\langle\mu_J/J\rangle_1)_{\mathrm{theor}}=0.66316\pm0.00007\text{ nm}, \tag{41}$$

in agreement with the experimental value of Eq. (38).

It is of interest to compare the rotational magnetic moments of HD with those of H_2 and D_2:

$$\frac{^{\mathrm{HD}}{}_0\langle\mu_J/J\rangle_1\mu_{\mathrm{HD}}'}{^{\mathrm{H}}{}_0\langle\mu_J/J\rangle_1\mu_{\mathrm{H}_2}'}=1.00139\pm0.00009, \tag{42}$$

$$\frac{^{\mathrm{D}}{}_0\langle\mu_J/J\rangle_1\mu_{\mathrm{D}_2}'}{^{\mathrm{HD}}{}_0\langle\mu_J/J\rangle_1\mu_{\mathrm{HD}}'}=1.00135\pm0.00013. \tag{43}$$

These product ratios of rotational magnetic moments and reduced masses μ_X' show that the rotational magnetic moments of H_2, D_2, and HD are not inversely proportional to the reduced nuclear masses as would be expected on a simple theory. These results are in agreement with the previous comparison[16] of the rotational magnetic moments of H_2 and D_2. A small portion of this variation 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 reduced nuclear mass ratio and the reduced atomic mass ratio. However, even if reduced atomic masses are used, Eqs. (42) and (43) give 1.00130 and 1.00117, respectively. This deviation from the simple theory is attributed[17] to the effects of zero-point vibrations and centrifugal stretchings in the molecules as indicated in Eq. (39).

B. Quadrupole Moment of the Deuteron

To obtain the deuteron quadrupole moment Q from the quadrupole interaction constant d_2 requires the gradient of the electric field along the internuclear axis, since by definition[6]

$$d_2=-eqQ/10h, \tag{44}$$

with $q=\partial^2V^e/\partial z_0{}^2$. Newell[18] has calculated the electric field gradient for HD and finds

$$q'=q/2e=0.1745a_0{}^{-3}, \tag{45}$$

with an error of ±0.7%. Here

$$q=\partial^2V^e/\partial z_0{}^2=(1.1338\pm0.0066)\times10^{15}\text{ statvolts cm}^{-2}. \tag{46}$$

From the best value of d_2, Table VIII, and Eqs. (44)–(46)

$$Q=(-10h/eq)d_2=(2.738\pm0.019)\times10^{-27}\text{ cm}^2. \tag{47}$$

The stated error results from the uncertainty in the calculated q, which is known only to an accuracy of 1 part in 200 compared to the experimental accuracy of 1 part in 6000 for the product qQ.

This result for the deuteron quadrupole moment is in excellent agreement with the result obtained from D_2 measurements,[2] though the latter is slightly more difficult to evaluate since for a homogeneous diatomic molecule the quadrupole interaction cannot be distinguished from the spin-rotational interaction.

C. Rotational Magnetic Fields at the Nuclei in HD

The magnetic fields at the position of the deuteron and proton produced by the rotational motion of the molecule can be determined from the spin-rotational interaction constants c_d and c_p, respectively. These interaction parameters are defined[6] by

$$c_i=\mu_iH_i'/i_ih, \tag{48}$$

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[17] N. F. Ramsey, Phys. Rev. 87, 1075 (1952).

[18] G. F. Newell, Phys. Rev. 78, 711 (1950).

where H_i' is the magnetic field in question. However, Ramsey[19] has shown there is also a contribution, c_{iA}, to the spin-rotational interaction of a nucleus in a molecule analogous to the spin-orbital interaction in an atom such that

$$c_i = c_{iW} + c_{iA}. \tag{49}$$

This nuclear acceleration contribution is given by[19]

$$\begin{aligned} {}^{\mathrm{HD}}{}_0\langle c_{iA}\rangle_1 = {} & 2\pi\gamma_i e(\hbar c/e^2)(\mu_{\mathrm{HD}}'/M_i)(1-e/2M_i c_i\gamma_i) \\ & \times\{B_e\omega_e + B_e^2[-(aR_e)^2-(aR_e)+5]\}. \end{aligned} \tag{50}$$

Substitution of numerical quantities, including the values of the molecular constants from Herzberg,[20] yields

$${}^{\mathrm{HD}}{}_0\langle c_{dA}\rangle_1 = 37 \text{ cps}, \tag{51}$$

$${}^{\mathrm{HD}}{}_0\langle c_{pA}\rangle_1 = 957 \text{ cps}. \tag{52}$$

After subtracting the acceleration contribution from c_i, the best values for the quantities c_{iW} are obtained as

$$c_{dW} = 13\,085 \pm 11, \tag{53}$$

$$c_{pW} = 84\,643 \pm 18. \tag{54}$$

These values may be substituted into Eq. (48) to determine the rotational magnetic fields at the respective nuclei in the zeroth vibrational and first rotational state of the HD molecule,

$${}^{\mathrm{HD}}{}_0\langle H_d'\rangle_1 = (h/\mu_d)c_{dW} = (20.020 \pm 0.028) \text{ gauss}, \tag{55}$$

$${}^{\mathrm{HD}}{}_0\langle H_p'\rangle_1 = (h/2\mu_p)c_{pW} = (19.879 \pm 0.006) \text{ gauss}. \tag{56}$$

The difference between these two values is possibly due to the different masses of the proton and deuteron and to their consequently different vibrational velocities. It might be noted that if the above nuclear acceleration correction is ignored, the values of ${}^{\mathrm{HD}}{}_0\langle H_d'\rangle_1$ and ${}^{\mathrm{HD}}{}_0\langle H_p'\rangle_1$ are in closer agreement, being 20.077 and 20.104 gauss, respectively.

D. HD Internuclear Distance

The interaction constant d_1,

$$d_1 = (4/5h)\mu_p\mu_d R_e^{-3}\,{}^{\mathrm{HD}}{}_0\langle (R/R_e)^{-3}\rangle_1 - \mathfrak{d}_0, \tag{57}$$

corresponds[6] to the direct spin-spin magnetic interaction between the two nuclei with a small contribution from the tensor portion of the electron-coupled spin-spin interaction.[21] R is the internuclear distance, R_e is the equilibrium internuclear-spacing for a nonvibrating and nonrotating molecule, and $\mathfrak{d}_0 = \mathfrak{d}_{\rho\rho}$ is the diagonal component along the internuclear line ρ of the traceless second-rank tensor for the electron-coupled nuclear spin-spin interaction.[21] Numerical calculations[21] of the latter interaction for HD indicate that this tensor portion contributes less than 1 cps out of the observed[14] 43 cps for the electron-coupled nuclear spin-spin interaction constant. Therefore, the contribution of a nonmagnetic interaction to d_1, Eq. (57), is the order of 0.2 cps which is negligible.

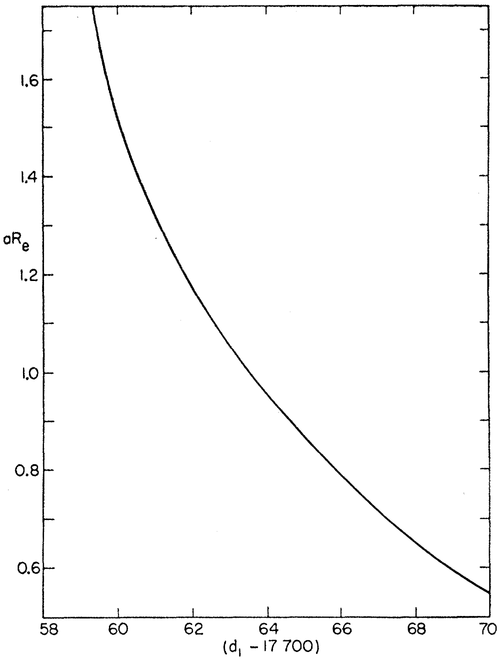

FIG. 1. aR_e as a function of d_1.

From Eq. (57), the reciprocal cube of the internuclear distance in the zeroth vibrational and first rotational state is obtained,

$$\begin{aligned} & R_e^{-3}\,{}^{\mathrm{HD}}{}_0\langle (R/R_e)^{-3}\rangle_1 \\ & \qquad = (2.4083 \pm 0.0009) \times 10^{24} \text{ cm}^{-3}, \end{aligned} \tag{58}$$

or, taking the cube root, the internuclear distance is

$$({}^{\mathrm{HD}}{}_0\langle 1/R^3\rangle_1)^{-\frac{1}{3}} = (0.74604 \pm 0.00010) \times 10^{-8} \text{ cm}. \tag{59}$$

The interaction constant d_1 can be used to evaluate the quantity aR_e, where R_e is the equilibrium internuclear spacing for a molecule in the absence of rotation and zero-point vibration and a determines the asymmetry in the Morse potential.[22] Ramsey[17] has expressed the spin-spin magnetic interaction in terms of the parameter aR_e,

$$\begin{aligned} (5h/4)d_1 = {} & \mu_p\mu_d[8\pi^2 c\mu_{\mathrm{HD}}'B_{00}/h]^{\frac{3}{2}} \\ & \times\{1+\tfrac{3}{2}B_e/\omega_e + (B_e/\omega_e)^2[(9/4)(aR_e)^2 \\ & -(17/2)(aR_e)+99/8-12J(J+1)]\}. \end{aligned} \tag{60}$$

This quadratic equation for aR_e with the insertion of Herzberg's values of the numerical constants and our value of d_1 gives

$${}^{\mathrm{HD}}{}_0\langle aR_e\rangle_1 = 1.33 \pm 0.60. \tag{61}$$

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[19] N. F. Ramsey, Phys. Rev. **90**, 232 (1953).

[20] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), second edition, p. 532.

[21] N. F. Ramsey, Phys. Rev. **91**, 303 (1953).

[22] P. M. Morse, Phys. Rev. **34**, 57 (1929).

The rather large uncertainty arises because of the rapid decrease of aR_e with d_1 as shown in Fig. 1. This determination of aR_e with its rather large uncertainty is in agreement with the value $aR_e=1.608$ which was determined[18] by making the Morse potential agree with the leading terms of the Dunham power series expansion[23] of the potential.

The quantity R_e is also calculated from the experimentally determined spin-spin magnetic interaction constant, Eq. (57), where ${}^{\mathrm{HD}}{}_0\langle (R/R_e)^{-3}\rangle_1$ is obtained from Eq. (21) of reference 17,

$$R_e=(0.7415\pm 0.0004)\times 10^{-8}\ \mathrm{cm}. \tag{62}$$

This is in good agreement with the value of $R_e=0.7414\times 10^{-8}$ cm as calculated from Herzberg's constants[20] determined from band spectra.

E. HD Molecular Susceptibility

The high-frequency term of the HD molecular susceptibility in the zeroth vibrational and first rotational state can be related to the rotational magnetic moment [Eq. (14) of reference 17],

$$\begin{aligned}{}^{\mathrm{HD}}{}_0\langle \xi^{\mathrm{hf}}\rangle_1 &= (e^2/12mc^2)R_e^2\ {}^{\mathrm{HD}}{}_0\langle (R/R_e)^{l}\rangle_1/{}^{\mathrm{HD}}{}_0\langle (R/R_e)^{l-2}\rangle_1\\ &\quad\times[1-(2\mu_{\mathrm{HD}}'/M)\ {}^{\mathrm{HD}}{}_0\langle \mu_J/J\rangle_1].\end{aligned} \tag{63}$$

This relation is based on the assumption introduced by Newell[18] that the high-frequency terms in the theory of diatomic molecules vary with internuclear spacing R as R^n. The quantity ${}^{\mathrm{HD}}{}_0\langle (R/R_e)_l\rangle_1/{}^{\mathrm{HD}}{}_0\langle (R/R_e)_l{}^{-2}\rangle_1$ can be calculated from Eq. (21) of reference 17 after determination of the exponent l. This exponent is determined from the relation

$$\begin{aligned}&{}^{\mathrm{H}}{}_0\langle (R/R_e)^{l-2}\rangle_1/{}^{\mathrm{HD}}{}_0\langle (R/R_e)^{l-2}\rangle_1\\ &\qquad=1+\frac{1-(\mu_{\mathrm{H}_2}'/\mu_{\mathrm{HD}}')\ {}^{\mathrm{H}}{}_0\langle \mu_J/J\rangle_1/{}^{\mathrm{HD}}{}_0\langle \mu_J/J\rangle_1}{(M/2\mu_{\mathrm{HD}}')\ {}^{\mathrm{HD}}{}_0\langle \mu_J/J\rangle_1-1},\end{aligned} \tag{64}$$

which is a specific case of Eq. (23) of reference 17. Utilizing the measurements[15] of the H_2 rotational moment with our HD measurements yields the experimental value

$$\begin{aligned}&({}^{\mathrm{HD}}{}_0\langle (R/R_e)^{l-2}\rangle_1/{}^{\mathrm{H}}{}_0\langle (R/R_e)^{l-2}\rangle_1)-1\\ &\qquad=-0.0104_{-0.0020}{}^{+0.0010},\end{aligned} \tag{65}$$

where the asymmetry in the probable error arises from the uncertainty in the extent to which the electron contributes to the moment of inertia. This result combined with the theoretical plot[6] of the left-hand side of Eq. (65) *versus* the exponent $(l-2)$ determines the value

$$l=3.80_{-0.12}{}^{+0.06}, \tag{66}$$

which is in good agreement with previous determinations.[16] R_e in Eq. (63) has been calculated from the experimentally determined spin-spin magnetic interaction constant in Eq. (62). Substitution of these parameter values into Eq. (63) yields the high-frequency term of the HD molecular susceptibility in the zeroth vibrational and first rotational state,

$$\begin{aligned}{}^{\mathrm{HD}}{}_0\langle \xi^{\mathrm{hf}}\rangle_1&=(1.675\pm 0.005)\\ &\quad\times 10^{-31}\ \mathrm{erg\ gauss^{-2}\ molecule^{-1}},\end{aligned} \tag{67}$$

or in terms of molar susceptibility

$$\begin{aligned}{}^{\mathrm{HD}}{}_0\langle \chi^{\mathrm{hf}}\rangle_1&=(0.1009\pm 0.0003)\\ &\quad\times 10^{-6}\ \mathrm{erg\ gauss^{-2}\ mole^{-1}}.\end{aligned} \tag{68}$$

F. HD Diamagnetic Interaction

For molecules in the first rotational state, the diamagnetic interaction parameter f is related[6] to the diamagnetic susceptibilities $\xi_{\pm 1}$ and ξ_0 by

$$\xi_{\pm 1}-\xi_0=2hf/H^2, \tag{69}$$

where the subscripts ± 1 and 0 refer to the value of the rotational magnetic quantum number m_J in the state $J=1$. Since f increases as the square of the magnetic field, the susceptibility dependence upon orientation is best determined by experiments in strong magnetic fields. This dependence of the diamagnetic susceptibility on molecular orientation is calculated using the best average value of f/H^2 from the 3400- and 4800-gauss measurements on the rotational spectrum in Table VIII.

$$\begin{aligned}\xi_{\pm 1}-\xi_0&=-(3.56\pm 0.10)\\ &\quad\times 10^{-31}\ \mathrm{erg\ gauss^{-2}\ molecule^{-1}}.\end{aligned} \tag{70}$$

G. Quadrupole Moment of the HD Electron Distribution

Ramsey[24] has shown that $(\xi_{\pm 1}-\xi_0)$ and ξ^{hf} can be combined to give a measure of the quadrupole moment of the electron distribution in a molecule. For the HD molecule in the first rotational and zeroth vibrational state, this quadrupole moment is given by

$${}^{\mathrm{HD}}{}_0\langle Q_e\rangle_1=-(20mc^2/e^2)[(\xi_{\pm 1}-\xi_0)-\tfrac{3}{2}\ {}^{\mathrm{HD}}{}_0\langle \xi^{\mathrm{hf}}\rangle_1], \tag{71}$$

relative to the internuclear axis. Utilizing the values of the parameters determined in Eqs. (67) and (70) gives

$${}^{\mathrm{HD}}{}_0\langle Q_e\rangle_1=(0.324\pm 0.010)\times 10^{-16}\ \mathrm{cm}^2. \tag{72}$$

The mean square distance ${}^{\mathrm{HD}}{}_0\langle r^2\rangle_1$ of an electron from the centroid[17] of the electron distribution of the HD molecule is given[17,25] by

$$\begin{aligned}{}^{\mathrm{HD}}{}_0\langle r^2\rangle_1&=\tfrac{1}{2}\ {}^{\mathrm{HD}}{}_0\langle \textstyle\sum_k r_\kappa{}^2\rangle_1=(3mc^2/e^2)\\ &\quad\times[{}^{\mathrm{HD}}{}_0\langle \xi^{\mathrm{hf}}\rangle_1-\chi/L],\end{aligned} \tag{73}$$

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[23] J. L. Dunham, Phys. Rev. **41**, 713, 721 (1932), and **49**, 797 (1936).

[24] N. F. Ramsey, Phys. Rev. **78**, 221 (1950).

[25] N. F. Ramsey, Science **117**, 470 (1953).

where χ is the ordinary diamagnetic susceptibility. The complete diamagnetic susceptibility has not been determined for the HD molecule. However, Havens[26] has measured the diamagnetic susceptibility of H_2:

$$(\chi)_{H_2} = -4.0051 \pm 0.0016 \times 10^{-6} \text{ erg/gauss}^2. \quad (74)$$

For the purpose of illustrating the nature of the calculation that can validly be made when HD susceptibility data exist, the somewhat inconsistent assumption will be made below that the susceptibility of the HD molecule is not appreciably different from that for H_2. With this assumption, Eq. (73) can be evaluated using the value of ${}^{HD}{}_0\langle \xi^{hf} \rangle_1$ from Eq. (67) and this H_2 value for χ,

$${}^{HD}{}_0\langle r^2 \rangle_1 = (0.7256 \pm 0.0025) \times 10^{-16} \text{ cm}^2. \quad (75)$$

This value of ${}^{HD}{}_0\langle r^2 \rangle_1$ and the value of Q_e, combined with the symmetry result that $\langle x_0^2 \rangle = \langle y_0^2 \rangle$, give the principal second moments of the electron distribution:

$$\begin{aligned} {}^{HD}{}_0\langle z_0^2 \rangle_1 &= \tfrac{1}{3}[{}^{HD}{}_0\langle r^2 \rangle_1 + Q_e/N] \\ &= (0.3165 \pm 0.0095) \times 10^{-16} \text{ cm}^2, \\ {}^{HD}{}_0\langle x_0^2 \rangle_1 = {}^{HD}{}_0\langle y_0^2 \rangle_1 &= \tfrac{1}{6}[2\ {}^{HD}{}_0\langle r^2 \rangle_1 - Q_e/N] \\ &= (0.1879 \pm 0.0056) \times 10^{-16} \text{ cm}^2. \quad (76) \end{aligned}$$

One should note that the results given in Eqs. (75) and (76) are chiefly illustrative since they involve the assumption that $\chi_{HD} \approx \chi_{H_2}$, since HD diamagnetic susceptibility is not known.

H. Magnetic Shielding Constant of HD

When an external magnetic field H is applied to a molecule, the electrons acquire an induced diamagnetic circulation which produces at the position of the nucleus a magnetic field $-\sigma H$ which partially cancels the initially applied field, where σ is the magnetic shielding constant. The average over-all molecular orientations of this magnetic shielding parameter can be expressed[27] as

$$\sigma = \sigma^L + \sigma^{hf}, \quad (77)$$

where σ^L is essentially the Lamb[28] diamagnetic correction and σ^{hf} is the high-frequency contribution[27] corresponding to the second-order paramagnetism. For the diatomic HD molecule σ^{hf} can be determined from the corrected spin-rotational interaction constant through the relation [Eq. (15) of reference 17]

$$\begin{aligned} {}^{HD}{}_0\langle \sigma^{hf} \rangle_1 = &-(e^2/6mc^2) R_e^2 \mu_{NM}^{-1} \\ &\times {}^{HD}{}_0\langle (R/R_e)^m \rangle_1 / {}^{HD}{}_0\langle (R/R_e)^{m-2} \rangle_1 \\ &\times \{ 2\mu_{NM} R_e^{-3}\ {}^{HD}{}_0\langle (R/R_e)^{-3} \rangle_1 \\ &\qquad - (2\pi\mu_{HD}'/M\gamma_i)\ {}^{HD}{}_0\langle c_{iW} \rangle_1 \}. \quad (78) \end{aligned}$$

The ratio ${}^{HD}{}_0\langle (R/R_e)^m \rangle_1 / {}^{HD}{}_0\langle (R/R_e)^{m-2} \rangle_1$ can be calculated from Eq. (21) of reference 17 after determination of the exponent m. This exponent is determined by a comparison of theoretical and experimental values of ${}^{H}{}_0\langle (R/R_e)^{m-2} \rangle_1 / {}^{HD}{}_0\langle (R/R_e)^{m-2} \rangle_1$. The relation[17]

$$\begin{aligned} {}^{H}{}_0\langle (R/R_e)^{m-2} \rangle_1 / {}^{HD}{}_0\langle (R/R_e)^{m-2} \rangle_1 = 1 - &\frac{1 - {}^{H}{}_0\langle (R/R_e)^{-3} \rangle_1 / {}^{HD}{}_0\langle (R/R_e)^{-3} \rangle_1}{1 - [2\mu_{NM} R_e^{-3}\ {}^{HD}{}_0\langle (R/R_e)^{-3} \rangle_1 \gamma_{iHD} M / 2\pi\mu_{HD}' c_{iHD} \rangle^{-1}} \\ &+ \frac{1 - (\mu_{H_2}' c_{iH_2} \gamma_{iHD} / \mu_{HD}' c_{iHD} \gamma_{iH_2})}{[2\mu_{NM} R_e^{-3}\ {}^{HD}{}_0\langle (R/R_e)^{-3} \rangle_1 \gamma_{iHD} M / 2\pi\mu_{HD}' c_{iHD}] - 1} \quad (79) \end{aligned}$$

provides an experimental determination of the desired ratio. This relation is based on the assumption that the entire difference between the spin-rotational interaction constants c_i for H_2 and HD is due to the differences in rotational angular velocities, in nuclear magnetic moments, in zero-point vibrations, in centrifugal stretching, and in nuclear acceleration effects, and that the electronic contribution to the fields at the nuclei varies with internuclear spacing as $(R/R_e)^m$. Inserting the results from Eqs. (53), (54), and (58) for the HD parameters with previous H_2 results[11] in Eq. (79) yields the experimental value

$${}^{HD}{}_0\langle (R/R_e)^{m-2} \rangle_1 / {}^{H}{}_0\langle (R/R_e)^{m-2} \rangle_1 = 1.001 \pm 0.003. \quad (80)$$

This theoretical plot[6] of the left-hand member of Eq. (79) *versus* m then determines m to be either between -2.6 and -0.7 or between -0.4 and 2.4. The ambiguity and the large uncertainty arise from the fact that the theoretical curve [6] passes through a maximum at $m=2$. By a previous argument[11] based on the variation of c_i with R it is probable that $m > -1$. Therefore,

$$m = +1.7_{-2.0}^{+0.7}. \quad (81)$$

Disregarding the rather large uncertainty, this value is in good agreement with m determined[11] from

$${}^{D}{}_0\langle (R/R_e)^{m-2} \rangle_1 / {}^{H}{}_0\langle (R/R_e)^{m-2} \rangle_1.$$

Using the results of Eqs. (53), (54), (58), (62), and (81) in Eq. (78) gives the high-frequency contribution to the magnetic shielding constants,

$${}^{HD}{}_0\langle \sigma_d^{hf} \rangle_1 = (-0.591 \pm 0.030) \times 10^{-5}, \quad (82)$$

$${}^{HD}{}_0\langle \sigma_p^{hf} \rangle_1 = (-0.596 \pm 0.030) \times 10^{-5}. \quad (83)$$

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[26] G. G. Havens, Phys. Rev. 43, 992 (1933).

[27] G. F. Newell, Phys. Rev. 80, 476 (1950).

[28] W. E. Lamb, Phys. Rev. 60, 817 (1941).

Newell[27] has calculated the spherically symmetrical contribution σ^L to the magnetic shielding constant for H_2. Extrapolating his result to HD through considerations based on the relative internuclear distances for the two molecules combined with an average of Eqs. (82) and (83) yields the following average shielding constant for the HD molecule:

$$\begin{aligned} {}^{\mathrm{HD}}{}_0\langle\sigma\rangle_1 &= (e^2/3mc^2)\, {}^{\mathrm{HD}}{}_0\langle \textstyle\sum_k r_k^{-1}\rangle_1 - {}^{\mathrm{HD}}{}_0\langle\sigma^{\mathrm{hf}}\rangle_1 \\ &= (3.216\pm0.010)\times10^{-5} \\ &\qquad - (0.594\pm0.030)\times10^{-5} \\ &= (2.622\pm0.032)\times10^{-5}. \end{aligned} \tag{84}$$

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Infrared and Optical Masers

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The extension of maser techniques to the infrared and optical region is considered. It is shown that by using a resonant cavity of centimeter dimensions, having many resonant modes, maser oscillation at these wavelengths can be achieved by pumping with reasonable amounts of incoherent light. For wavelengths much shorter than those of the ultraviolet region, maser-type amplification appears to be quite impractical. Although use of a multimode cavity is suggested, a single mode may be selected by making only the end walls highly reflecting, and defining a suitably small angular aperture. Then extremely monochromatic and coherent light is produced. The design principles are illustrated by reference to a system using potassium vapor.

INTRODUCTION

AMPLIFIERS and oscillators using atomic and molecular processes, as do the various varieties of masers,[1–4] may in principle be extended far beyond the range of frequencies which have been generated electronically, and into the infrared, the optical region, or beyond. Such techniques give the attractive promise of coherent amplification at these high frequencies and of generation of very monochromatic radiation. In the infrared region in particular, the generation of reasonably intense and monochromatic radiation would allow the possibility of spectroscopy at very much higher resolution than is now possible. As one attempts to extend maser operation towards very short wavelengths, a number of new aspects and problems arise, which require a quantitative reorientation of theoretical discussions and considerable modification of the experimental techniques used. Our purpose is to discuss theoretical aspects of maser-like devices for wavelengths considerably shorter than one centimeter, to examine the short-wavelength limit for practical devices of this type, and to outline design considerations for an example of a maser oscillator for producing radiation in the infrared region. In the general discussion, roughly reasonable values of design parameters will be used. They will be justified later by more detailed examination of one particular atomic system.

CHARACTERISTICS OF MASERS FOR MICROWAVE FREQUENCIES

For comparison, we shall consider first the characteristics of masers operating in the normal microwave range. Here an unstable ensemble of atomic or molecular systems is introduced into a cavity which would normally have one resonant mode near the frequency which corresponds to radiative transitions of these systems. In some cases, such an ensemble may be located in a wave guide rather than in a cavity but again there would be characteristically one or a very few modes of propagation allowed by the wave guide in the frequency range of interest. The condition of oscillation for n atomic systems excited with random phase and located in a cavity of appropriate frequency may be written (see references 1 and 2)

$$n \geq hV\Delta\nu/(4\pi\mu^2 Q_c), \tag{1}$$

where n is more precisely the difference n_1-n_2 in number of systems in the upper and lower states, V is the volume of the cavity, $\Delta\nu$ is the half-width of the atomic resonance at half-maximum intensity, assuming a Lorentzian line shape, μ is the matrix element involved in the transition, and Q_c is the quality factor of the cavity.

The energy emitted by such a maser oscillator is usually in an extremely monochromatic wave, since the energy produced by stimulated emission is very much larger than that due to spontaneous emission or to the normal background of thermal radiation. The frequency range over which appreciable energy is distributed is given approximately by[1]

$$\delta\nu = 4\pi kT(\Delta\nu)^2/P, \tag{2}$$

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