

## II MICROWAVE PHYSICS

### A MICROWAVE SPECTROSCOPY

#### 1 Microwave-Frequency Bridge

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A series of measurements on methyl fluoroform have led to indications of a line at 5.7 mm. Further work on this molecule has been dropped for the time being.

#### 2 Sweep Spectroscope

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Measurements have been made to date on the rotational lines of COS as follows:

	<u>O<sup>16</sup> C<sup>12</sup> S<sup>32</sup></u>	<u>O<sup>16</sup> C<sup>13</sup> S<sup>32</sup></u>	<u>O<sup>16</sup> C<sup>12</sup> S<sup>34</sup></u>
J = 1→2	24,325 92 Mc/sec	24,247 32	—
J = 2→3	36,488 82	—	—
J = 3→4	48,651 64	—	47,462 40
J = 4→5	60,814 08	—	—

Precision Stark measurements have also been made which indicate a dipole moment of 0.739 Debye units.

Precision Stark measurements have also been made on the known H<sub>2</sub>O line at 22,307.90 Mc/sec and the H<sub>2</sub>O line at 22,235.05 Mc/sec and on a D<sub>2</sub>O line discovered in this laboratory at 20,460.36 Mc/sec.

Attempts will be made with these data to establish the identities of these lines, and the dipole moment of these molecules.

Work has been in progress on a cleaned-up version of our square-wave Stark modulation apparatus and we hope to resume these types of measurements.

#### 3 Nuclear Moment of Hydrogen

Staff R B Lawrence

The hydrogen cavity has been completed with the exception of the glass liner, and has been in use for some time. Since, according to the literature, recombination of hydrogen atoms takes place with high probability on metallic surfaces, it is expected that it may be difficult to obtain an adequate atom concentration without the glass liner. The apparatus

has been operated in its present condition but incomplete tests have not so far shown the looked-for absorption

#### 4 Caesium Spectrum

Staff: Professor A G Hill  
M W P Strandberg

Nothing to report

#### 5 Asymmetric Top Molecules

Staff C I Beard

Methyl Isothiocyanate The spectrum of methyl isothiocyanate ( $\text{CH}_3\text{NCS}$ ) has been investigated in collaboration with Dr B P Dailey of Harvard A paper giving the experimental results was presented at the ACS meeting in New York on September 15 1947

By using the Stark modulation scheme developed at Harvard<sup>1 2</sup> the lines listed in Table I were found The ratio of the strongest line in each group  $25264/20216 = 1.2497$ , or the ratio of 5/4, establishes the lower frequency group at 20,000 Mc/sec to be  $J = 3 \rightarrow 4$  transitions and the higher frequency group at 25,000 Mc/sec to be  $J = 4 \rightarrow 5$  transitions The lines exhibit a Stark effect which is intermediate between first and second order, indicating that the molecule is not unduly asymmetric By using Mecke's approximation for nearly symmetric tops, approximate values of the average rotational constants  $\frac{1}{2}(B + C)$  were obtained from the main line in each group 20216 and 25264 Mc/sec To obtain an approximate idea of the angle that the methyl group is bent from the axis of the linear NCS chain, the  $\frac{1}{2}(B + C)$  value was combined with the moment of inertia equations with the following assumed distances  $\text{CS} = 1.57\text{\AA}$ ,  $\text{NC} = 1.21\text{\AA}$ ,  $\text{N-CH}_3 = 1.47\text{\AA}$ ,  $\text{CH} = 1.094\text{\AA}$ , and angle  $\text{HCH} = 112^\circ$  The approximate value of the  $\text{CH}_3\text{-N-C}$  angle comes out as  $150^\circ$ , or the methyl group is bent only  $30^\circ$  from the NCS axis

By using the method and tables of King, Hainer and Cross<sup>3</sup> to calculate the spectrum of the asymmetric molecule, six different lines are calculated for the  $J = 3 \rightarrow 4$  group and six different lines for the  $J = 4 \rightarrow 5$  group of "a"-type transitions corresponding to  $\Delta K = 0$  for the limiting symmetric top No other "a"-type transitions (the dipole moment lying in the axis of the least moment of inertia  $I_A$ ) of  $\Delta J = +1$  and corresponding to  $\Delta K = \pm 1$  (in the limiting symmetric top analogy) can account for the excess number of observed lines since their intensities are zero<sup>4</sup> Of the "a"-type transitions for  $\Delta J = 0$ ,

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1 R H Hughes and E B Wilson, Jr, Phys Rev 71, 562 (1947)

2 B P Dailey, Phys Rev 72, 84 (1947)

3 G W King, R M Hainer and P C Cross J Chem Physics 11, 27 (1943)

4 P C Cross R M Hainer, and G W King J Chem Physics 12, 210 (1944)

TABLE I  $\text{CH}_3\text{NCS}$  Absorption Lines

Freq Mc/sec	Approx Relative Strength	Freq Mc/sec	Approx Relative Strength	Freq Mc/sec	Approx Relative Strength
19,440	2	24,617	22	29,580	Strong
19,737	1	24,824	5	29,800	Weak
$J = 3 \rightarrow 4$		$J = 4 \rightarrow 5$		$J = 5 \rightarrow 6$	
19,929	1 5	24,910	18		
20,020	1 5	25,029	25		
20,140	3	25,075	5		
20,176	4	25,163	20		
20,216	8	25,195	20		
20,230	2	25,216	20		
20,241	2 5	25,242	20		
20,350	2 5	25,264	97		
20,413	4 5	25,290	55		
20,443	6	25,306	35		
20,481	3	25,333	23		
		25,390	55		
		25,442	32		
		25,480	20		
		25,530	20		
		25,550	52		
		25,580	20		
		25,620	20		

only those between split levels such as  $5_{-4} \rightarrow 5_{-3}$  have an intensity greater than zero, but the frequencies of these lines are too low unless the  $J$  values are very high, and also, the predicted intensities are still weak. Of course "b" and "c"-type transitions are possible but the component of the dipole moment along these axis especially the "c" axes, would be expected to be small so that these lines would be quite weak.

Examination of the  $J = 3 \rightarrow 4$  group and the  $J = 4 \rightarrow 5$  group, however, indicates a twin set of lines in each group. Such a double spectrum could be the result of hindered internal rotation of the methyl group such as occurs in methyl alcohol. The twin spectrum allows a tentative assignment of quantum numbers to be made for a majority of the lines. The pair of lines at the low-frequency end of each group apparently does not belong to the same type of lines ( $\Delta K = 0$ ) as those within each group.

Isothiocyanic Acid To aid in the analysis of the complicated spectrum of  $\text{CH}_3\text{NCS}$ , transitions of the simpler molecules, the acid ( $\text{HNCS}$  and  $\text{HSCN}$ ), were sought and found. This work is reported in a Letter to the Editor of the Journal of Chemical Physics.<sup>1</sup>

1 C. I. Beard and B. P. Dailey "Microwave Spectrum and Structure of Isothiocyanic Acid" October 1947

Table II gives the frequencies of the main absorption lines found for HNCS and its artificially enriched isotopic forms in the region from 19,000 Mc/sec to 30,000 Mc/sec. The

TABLE II The Main Absorption Lines of HNCS Molecules

<u>Molecule</u>	<u>Frequency Mc/sec</u> $\pm 1$ Mc/sec
HNC <sup>12</sup> S <sup>32</sup>	23,464
HNC <sup>13</sup> S <sup>32</sup>	23,389
DNC <sup>12</sup> S <sup>32</sup>	21,897
DNC <sup>13</sup> S <sup>32</sup>	21,839
HNC <sup>12</sup> S <sup>34</sup> (?)	22,915

remainder of the spectrum will be reported upon later.

The acid was prepared by gently warming a mixture of KSCN with H<sub>3</sub>PO<sub>4</sub>. The HNC<sup>13</sup>S was prepared from KSC<sup>13</sup>N obtained by fusing sulphur and KC<sup>13</sup>N containing 17 per cent of C<sup>13</sup>. The deuterium isotopes were made by the same processes merely by substituting D<sub>3</sub>PO<sub>4</sub> for H<sub>3</sub>PO<sub>4</sub>.

In the preliminary analysis of the spectrum the assumption was made that the NCS group is linear and that although the hydrogen atom is at an angle with the NCS group the molecule is very nearly a symmetric top.

The symmetric Stark pattern of one component on each side of the main line supports this assumption and shows that the spectral lines correspond to  $J = 1 \rightarrow 2$  transitions. Using the symmetric top approximation that  $\nu \text{ cm}^{-1} \cong 2C(J + 1)$  the four frequencies of the main lines of the four isotopic molecules enable one to solve for approximate values of the three interatomic distances and the HNC angle neglecting the effect of the zero-point vibrational energy.

The solution for the structure HSCN results in quite unreasonable values of the bond distances and angle. The solution for the structure HNCS, however, yielded  $\text{HN} = 1.2 \pm 0.1 \text{ \AA}$ ,  $\text{NC} = 1.21 \pm 0.01 \text{ \AA}$ ,  $\text{CS} = 1.57 \pm 0.01 \text{ \AA}$ , the angle  $\text{HNC} = 112^\circ \pm 10^\circ$ .

The NC and CS distances are intermediate between the values for double and triple bonds. The probable resonating structures are  $\text{H} - \overset{+}{\text{N}} = \overset{-}{\text{C}} = \overset{-}{\text{S}}$ ,  $\text{H} - \overset{+}{\text{N}} \equiv \overset{-}{\text{C}} - \overset{-}{\text{S}}$ , and  $\text{H} - \overset{+}{\text{N}} - \overset{-}{\text{C}} \equiv \overset{-}{\text{S}}$ . The CS distance is the same as in COS and CS<sub>2</sub>. The NCS distances compare well with those obtained by Goubeau and Gott<sup>1</sup> by interpretation of Raman spectra of  $\text{NC} = 1.21 \text{ \AA}$  and  $\text{CS} = 1.575 \text{ \AA}$ . The HN distance is larger than the  $1.01 \text{ \AA}$  value in N<sub>3</sub>H and in NH<sub>3</sub>. The HN distance and HNC angle were the least accurately determinable from the equations, because differences reduced the number of significant figures. Calculations using the more accurate approximation  $\nu \text{ cm}^{-1} \cong (B + C)(J + 1)$  are now being made to improve

1 J. Goubeau and O. Gott, Ber. 73B, 127 (1940).

the accuracy of these values

The spectral analysis thus indicates that the vapor is principally isothiocyanic acid (HNCS); thiocyanic acid (HSCN) if it exists in the vapor, cannot be present by more than 5 per cent Goubeau and Gott<sup>1</sup> and Gallais and Voigt<sup>2</sup> also conclude that HNCS is the predominant form The position and intensity of the very weak line at 22,915 Mc/sec indicate that it may be the HNCS<sup>34</sup> line due to the natural 4 per cent abundance of S<sup>34</sup>

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B MOLECULAR BEAM RESEARCH

Staff Professor J R Zacharias  
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D E Nagle  
C W Zabel

1 Hyperfine Structure of Hydrogen

Staff R S Julian  
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Summary The study of the r-f spectrum of atomic hydrogen which was discussed in the last report, has been essentially completed The value obtained for the hyperfine splitting  $\Delta\nu_H$  is  $1420.47 \pm 0.05$  Mc Atomic deuterium has been measured and  $\Delta\nu_D$  found to be  $327.381 \pm 0.005$  Mc While both of these values differ from the values  $\Delta\nu_H = 1416.9 \pm 3$  Mc and  $\Delta\nu_D = 326.55 \pm 2$  Mc predicted by the Fermi formula<sup>3</sup>, the ratio  $\Delta\nu_D/\Delta\nu_H = 0.230474 \pm 0.0001$  (measured) agrees with the ratio  $0.230450 \pm 0.0007$  obtained through this formula from the ratio of the magnetic moments of the deuteron and proton<sup>4</sup> The measured values of  $\Delta\nu$  are in agreement with the latest results obtained at Columbia University

Theoretical Considerations The  $^2S_{1/2}$  atomic ground state of deuterium ( $l = 0, J = S = \frac{1}{2}, i = 1$ ) is split into two levels by the interaction of the magnetic dipole moment of the deuteron with that of the electron These levels are separated in energy by  $h\Delta\nu$  The electric quadrupole moment of the deuteron has no effect because of the symmetry of the atomic state

In an external magnetic field B these two levels which are characterized by values of total angular momentum quantum number  $F = 1 + \frac{1}{2} = 3/2$  and  $F = 1 - \frac{1}{2} = \frac{1}{2}$ , are split into the six levels given in Table I and Fig 1 Here x is a measure of the coupling between the atomic electron and the applied field in units of the coupling between the electron and the field of the deuteron

$$x = \frac{(\mathcal{E}_1 - \mathcal{E}_1) \mu_0 B}{h\Delta\nu}$$

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1 Goubeau and Gott loc cit

2 F Gallais and D Voigt Compt rend., 210 104 (1940)

3 E Fermi Zeits f Phys., 60 320 (1930)

4 W Arnold and A Roberts Phys Rev., 71, 878 (1947)

TABLE I Energy Levels of Deuterium

$F$	$m_F$	$\frac{W}{h\Delta\nu}$
$\frac{3}{2}$	$+\frac{3}{2}$	$\frac{1}{3} + \frac{1}{2}x + \frac{3}{2} \frac{\epsilon_1}{\epsilon_j - \epsilon_1} x$
$\frac{3}{2}$	$+\frac{1}{2}$	$-\frac{1}{6} + \frac{1}{2} (1 + \frac{2}{3}x + x^2)^{\frac{1}{2}} + \frac{1}{2} \frac{\epsilon_1}{\epsilon_j - \epsilon_1} x$
$\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{6} + \frac{1}{2} (1 - \frac{2}{3}x + x^2)^{\frac{1}{2}} - \frac{1}{2} \frac{\epsilon_1}{\epsilon_j - \epsilon_1} x$
$\frac{3}{2}$	$-\frac{3}{2}$	$\frac{1}{3} + \frac{1}{2}x - \frac{3}{2} \frac{\epsilon_1}{\epsilon_j - \epsilon_1} x$
$\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{6} - \frac{1}{2} (1 + \frac{2}{3}x + x^2)^{\frac{1}{2}} + \frac{1}{2} \frac{\epsilon_1}{\epsilon_j - \epsilon_1} x$
$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{6} - \frac{1}{2} (1 - \frac{2}{3}x + x^2)^{\frac{1}{2}} - \frac{1}{2} \frac{\epsilon_1}{\epsilon_j - \epsilon_1} x$

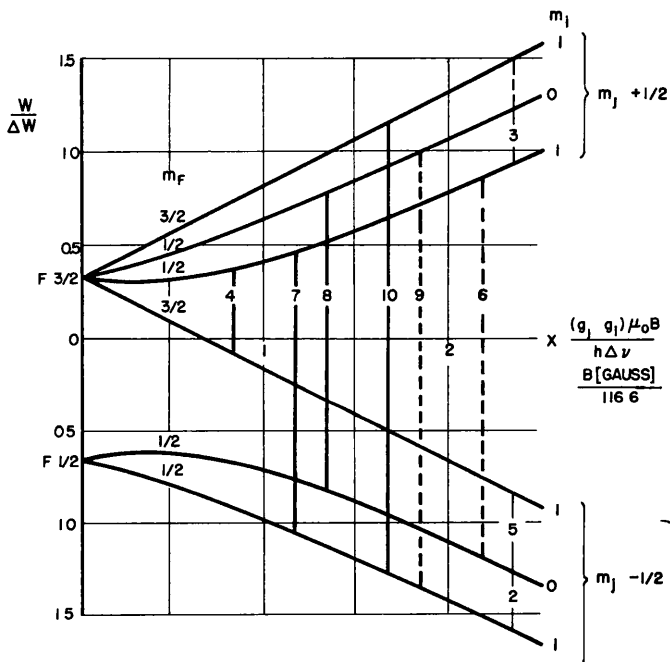


Figure 1 Atomic deuterium energy levels  $\frac{2}{1}S_{\frac{1}{2}}$  ground state splitting in a magnetic field

where  $g_j (= 2 \text{ Bohr magnetons})$  and  $g_1 (= - 00046 \text{ Bohr magneton})$  are the negative gyromagnetic ratios of the electron and of the deuteron,  $\mu_0 (= 927 \times 10^{-20} \text{ erg gauss}^{-1})$  is the value of the Bohr magneton,  $h (= 6.62 \times 10^{-27} \text{ erg sec})$  is Planck's constant,  $B$  is the applied field in gauss and  $\Delta\nu$  is the hyperfine separation in cycles per second

Possible transitions among these levels give rise to ten r-f spectral lines numbered in order of increasing frequency in Fig 1. Of these ten lines only numbers 4 and 10, and the unresolved pair 7 and 8 are observed in the present experiment because of peculiarities of the experimental arrangement

Considerations corresponding to the above for hydrogen were discussed in the last progress report

**Apparatus** The apparatus has been described in detail in the progress reports of October 15, 1946, January 15, 1947 and July 15 1947

The present arrangement differs from the last description only in that wider (3-mil) source and collimator slits are in use and that an improved source giving 60 per cent atoms instead of the previous 25 per cent is installed. The increased intensity accompanying these changes has considerably increased the precision obtainable with the apparatus

**Method** The experimental procedure for deuterium differs from that described for hydrogen in the July 15 report only in the details of obtaining  $\Delta\nu$  from the observed curves of beam intensity vs frequency

For deuterium the line arising from transitions 7 and 8 of Fig 1 is sharp at low magnetic fields ( $x \ll 1$ ) because it approaches field independence, while the other two lines (4 and 10), as well as all lines thus far observed for hydrogen, are broadened by the inhomogeneity of the magnetic field  $B$ . This effect is clearly shown by the typical set of experimental deuterium curves given in Fig 2. The value of  $\Delta\nu$  for deuterium is

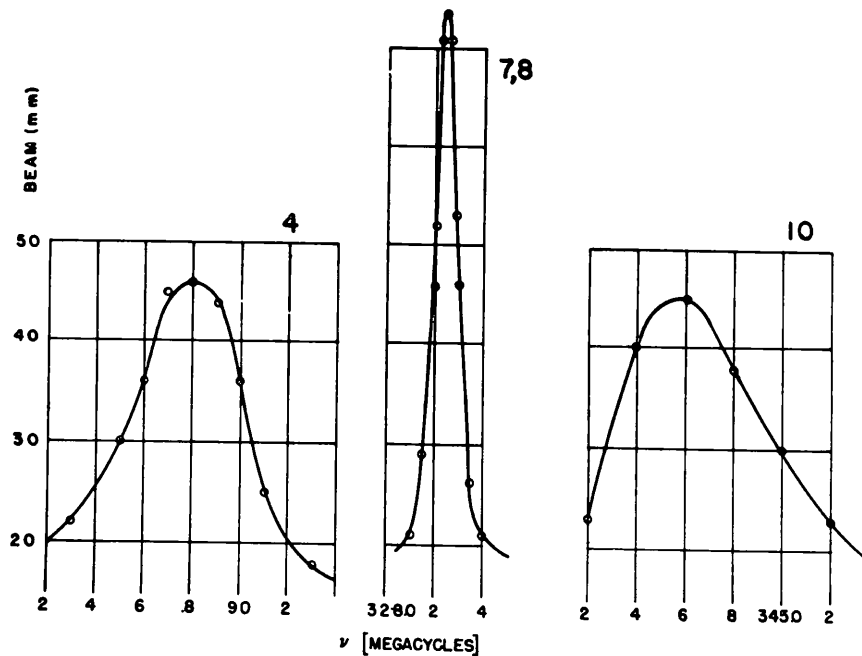


Figure 2 Deuterium resonance curves

obtained from the observed resonance 7, 8 by subtracting only a small correction (quadratic in  $x$ ) calculated from the value of  $x$  obtained from the broader curves 4 and 10

The observation of the above field-insensitive line makes possible the greater accuracy specified for deuterium. Present plans are to arrange a component of r-f magnetic field parallel to the fixed field so that such a field-insensitive line may be observed for hydrogen also

Results Seven sets of resonance curves for deuterium similar to those of Fig 2 have been recorded. The resulting data are presented in Table II. The result of  $\Delta\nu_0 = 327.381 \pm 0.005$  Mc is obtained as the equally weighted average of runs Nos 3, 4, 6, and 7, which runs are felt to be more reliable than the other three

TABLE II Atomic Deuterium Hyperfine Structure Measurements of Transition Frequencies

Run No.	Resonant Frequencies (Mc)			Calculated Values	
	$\nu_4$	$\nu_{7,8}$	$\nu_{10}$	$x$	$\Delta\nu$
1		330 160	359 8		327 39
2	89 96	373 70	472 32	5760	327 32
3	8 84	328 246	344 55	0769	327 385
4	12 18	328 954	350 80	1041	327 378
5	16 34	330 09		1367	327 38
6	15 48	329 838		1301	327 380
7	15 48	329 839		1301	327 380

## 2 Mass Spectrograph

Staff L Davis Jr

A mass spectrograph for attachment to the present molecular beam apparatus has been designed and is under construction. This device incorporates a surface ionization detector as an ion source and will be used for investigating the alkali metal isotopes



II B 3 Second Molecular Beam Resonance Apparatus

Staff C W Zabel

The second molecular beam apparatus is nearly completed. One of the two 5-ft cast bronze tubes which will contain the magnets has been tested for vacuum tightness and was found to be very satisfactory. On the basis of this test, it was decided not to dip the casting in tin. The machining of the tubes has been completed. The concrete support for them has been constructed, and the apparatus is ready to be assembled.

## II. C LOW-PRESSURE GAS DISCHARGES

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Microwave Breakdown Characteristics The measurement of breakdown voltages under the influence of a microwave electric field  $E$  has resulted in a method of measuring ionization coefficients at very low values of  $E/p$  ( $p$  = pressure) by an experimental method which is considerably simpler than the d-c Townsend experiment used classically. The breakdown condition is that the ionization rate be sufficient to replace diffusion losses, this condition is easily expressed mathematically as a simple boundary-value problem. Variation of either tube size or pressure leads to the ionization coefficient curve plotted against the variable  $E/p$ , and these two methods of getting the same curve have checked each other. Check with classical d-c experiments is difficult, because d-c curves covered the high  $E/p$  range, whereas our work covers the low range. They appear to extrapolate together in some cases, but not in others. Purity of gas, which is still in question, may be the reason for this disagreement.

In order to reach higher  $E/p$  and to provide a further check on theory a cavity designed to provide a d-c field as well as a microwave field on the gas has been used. Ionization rate vs  $E/p$  curves show much more ionization than should be present in the light of present theory. This discrepancy was attributed to secondary emission from the end walls (which were glass, not metal). Secondary emission has been put into the boundary-value problem, as well as the additional d-c field. It has been shown theoretically that the pure microwave breakdown is practically unaffected, but with the d-c field present the multiplication of the secondary electrons yields an apparent increase in ionization, this is in agreement with observations. The theory becomes complicated by these additional factors, and the details are not yet completely worked out. An experimental check on the secondary emission hypothesis has been made by introducing alcohol vapor into the gas; alcohol is a well-known agent that quenches secondary emission from positive-ion bombardment. The result with metal end plates is quite conclusive that secondary emission effects are the cause of the fictitious ionization but the glass end-plate result is still doubtful.

A parallel-plate cavity with copper walls is being constructed in such a way that a constant field can be applied between the plates in addition to a high frequency field. Breakdown voltages will be measured as a function of both the constant and the alternating field at various pressures of the filling gas. It is hoped that the copper cavity will give additional information on whether or not a secondary effect from the walls is complicating the experiment.

Dielectric Constant of an Ionized Medium Classical theory predicts that the real part of the dielectric constant of an ionized medium should depart from that of empty space by a factor linearly proportional to the electron density. In two experiments however, a radical departure from linearity has been observed at high electron densities. A possible ex-

planation may lie in the effect of the local fields of the positive ions and electrons. A theory is being worked out to include the effects of the positive ions and has predicted results qualitatively in agreement with those observed. This theory is being re-examined to check the range of validity of certain approximations and to extend the theory to cover effects of the local fields of the electrons.

Ambipolar Diffusion The ambipolar diffusion experiment has been repeated using purer gases. The data still indicate an unusually low value of  $D_a$ , the ambipolar diffusion constant. In addition the following anomaly has been noted; the value of  $D_a$  does not vary as  $1/p$  as theory indicates it should (See Fig 1)

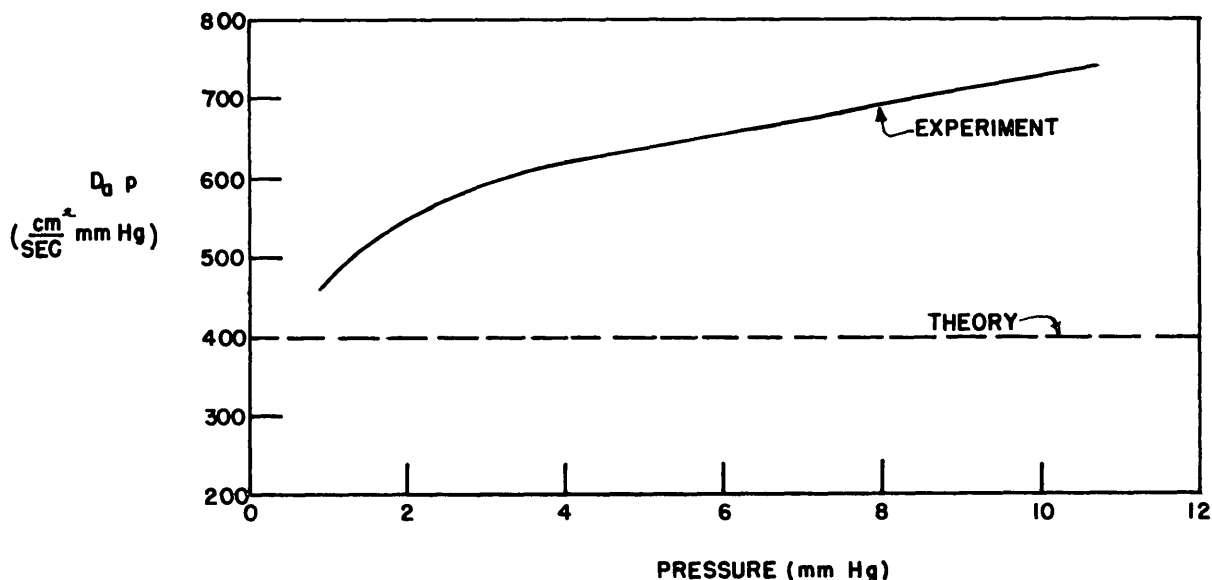


Figure 1 Ambipolar diffusion in helium

These experiments involve electron and ion densities in the transition range between ambipolar diffusion and free diffusion (we apply the term "field-controlled diffusion" to this range). Under these conditions the diffusion is ambipolar at the center of the tube but changes to field-controlled diffusion near the walls. The distance from the walls at which the change occurs depends upon pressure. Theory indicates that in a cylindrical container of 1 cm radius and 2 cm length containing an average density of  $10^{10}$  electrons/cm<sup>3</sup>, the transition point is only 1 mm from the walls at 1 mm Hg pressure and decreases with increasing pressure. Therefore for all practical purposes one may assume that the diffusion is ambipolar throughout the bottle.

Microwave Radioactivity Counter. Work is continuing on the microwave gas discharge counter along the following lines. Extensive data are being collected on the discharge and counting characteristics, varying all possible parameters, to determine the most useful gas fillings, voltage and power operational characteristics. Considerable effort is being directed toward simplifying the associated electronic equipment and a number of different counter cavities have been built in an attempt to arrive at the most satisfactory counter design.

## II D LOW-TEMPERATURE RESEARCH

### 1 Helium Liquefiers

Staff: R P Cavileer

During this quarterly period approximately 17 runs have been made with the two Collins Helium Cryostats This included the experimental work for three doctor's theses Performance of both liquefiers is below the level originally obtained, and investigations are under way to remedy this situation

### 2 Superconductivity at Microwave Frequencies

Staff: Professor J C Slater  
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W B Nowak

Work on the superconductivity of lead has been brought to a conclusion, and a technical report will soon be issued.

The properties of superconducting tin cavities are now being investigated with the use of techniques similar to those previously employed with lead and described in earlier progress reports Preliminary results have been obtained on two tin cavities. The Q increases by about a factor of 10 in going down from room temperature to 15°K, and then levels off At 3.7°K it takes a sudden jump and at 2°K. has increased by another factor of 30 These results were obtained on some 99.97 per cent chemically pure tin Further tests are planned on other cavities made from the same type of tin and from Hilger tin

A quantity of indium is at hand and a number of indium cavities will be made and tested

The transition temperatures of both tin and indium are below 4°K and can be reached by pumping on liquid helium. This allows much finer temperature measurement and control than was possible in the case of lead It is hoped that we shall be able to determine accurately the slope of the transition curve.

It is also planned to investigate the behavior of normal conductors in the temperature range of 2 to 300°K in order to obtain more data on the divergence between a-c and d-c conductivities at low temperatures

### 3 Magnetic Nuclear Resonance Experiments

Staff Professor F Bitter  
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H L Poss

Rotational States in Solids Further exploratory application of nuclear magnetic resonance absorption to the study of the solid state has led to new results in investigations of deuterated methane ( $\text{CH}_3\text{D}$ ), hydrogen chloride, rubber, and single crystals of Rochelle salt, ammonium dihydrogen phosphate (ADP) and potassium dihydrogen phosphate (KDP)

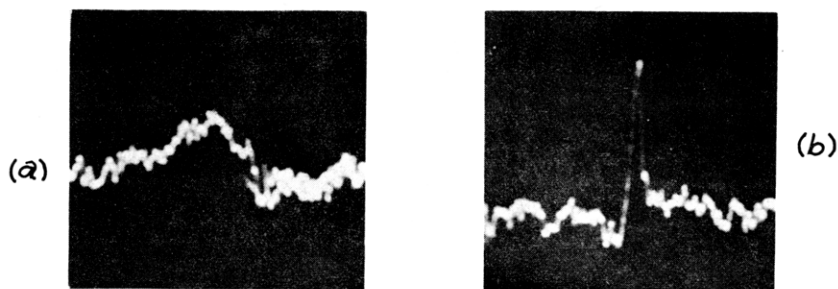


Figure 1. (a) Proton resonance in deuterated methane at a temperature just below the upper transition.  
 (b) The same resonance just above the same transition temperature.

Although normal methane ( $\text{CH}_4$ ) shows a  $\lambda$ -point transition in the solid at  $20.4^\circ\text{K}$ , the deuterated methane, in contrast, has two  $\lambda$ -point transitions in the solid state, at  $15.5^\circ\text{K}$  and at  $22.6^\circ\text{K}$ . In earlier experiments<sup>1</sup> a narrow resonance in methane above its  $\lambda$ -point and a broad resonance below this temperature were reported and interpreted as a transition from free molecular rotation to hindered rotation. This indicated that one of the transitions in deuterated methane might also be identified with a rotational transformation. A behavior of the proton resonance analogous to that found in solid methane was observed in deuterated methane just above liquid hydrogen temperature ( $20.4^\circ\text{K}$ ). Below this transition a resonance of the order of 5 gauss in width was observed, while above the transition line widths of the order of 0.5 gauss were found. (See Fig. 1). That is, deuterated methane apparently undergoes a transition from free to hindered rotations at the upper  $\lambda$ -point.

Hydrogen chloride exhibits a transition of the first order at  $98.4^\circ\text{K}$  which has been alternately interpreted either as a transition from hindered to free molecular rotation, or as a transition between ordered and disordered arrays of dipoles.<sup>2</sup> These experiments eliminate the former explanation in favor of the latter. Following the proton resonance from about  $80^\circ\text{K}$  to the melting point of hydrogen chloride at  $159^\circ\text{K}$  a line width of roughly 10 gauss was observed. There was no appreciable change in this width at the transition point. A narrow line was observed only after the sample had melted. Further studies are contemplated for hydrogen iodide and hydrogen bromide which, although similar to hydrogen chloride, undergo multiple transitions in the solid state.

In the case of natural rubber, samples of pale crepe, unloaded and unvulcanized and a vulcanized sample, unloaded, gave proton resonance widths of 0.3 gauss at a resonant frequency of 30.5 Mc/sec and at room temperature. Such narrow resonances have been identified with molecular rotation in liquids and in a few solids (e.g.  $\text{CH}_4$ ). In view of the chain-like structure of the rubber molecule the interpretation of the narrow lines cannot be so direct. The effect is probably due to internal rotation of parts of the chain; i.e., hydrogen bonds, side methyl groups, or radicals.

The pale crepe natural rubber, unvulcanized and unloaded, was studied over a temperature range from  $24^\circ\text{C}$  to  $-75^\circ\text{C}$ . Contrary to what might be expected, there was little

1. F. Bitter, N. L. Alpert, H. L. Poss, C. G. Lehr, and S. T. Lin, *Phys. Rev.*, **71**, 738(1947).  
 2. L. Tisza, *Phys. Rev.* **72**, 161 (1947).

or no apparent hindering of the internal free rotations at lower temperatures. That is, no change in the width or damping properties of the resonance was noted in the above temperature range. However, there was a drastic change in the amplitude of the resonance which decreased by about a factor of 10 over this range. The greatest change in amplitude occurred in the temperature interval from 24°C to 0°C. At liquid nitrogen temperature the narrow resonance was not visible. This behavior might indicate that at the lower temperatures there is a decrease in the number of atoms which are rotating and as a result fewer nuclei find themselves in high-frequency fields which essentially average out to zero.

The observation that this effect occurred gradually over the entire temperature range and was not yet complete at -75°C is surprising in view of dynamic Young's Modulus measurements<sup>1</sup> on this same material by A. W. Nolle of the M I T. Acoustics Laboratory. Nolle found a relatively rapid transition in this quantity near -50°C. Also, the transition of rubber to its rigid form is generally assumed to be complete by -70°C.

A single sample of carbon-loaded natural rubber, unvulcanized, was investigated. The resulting resonance was more rapidly damped and slightly wider than for the unloaded sample, indicating the more hindered nature of the internal rotations in the loaded rubber. In addition, one unloaded sample and one carbon-loaded sample of buna-N synthetic rubber showed broad resonances greater than 5 gauss in width. It may be remarked in this connection that the mechanical relaxation phenomena in buna-N rubbers are appreciably slower than those in natural rubber.

Another case which has been interpreted as internal rotation, rather than rotation of the entire molecule, is in liquid ethylene ( $C_2H_4$ ). In view of the structure of the ethylene molecule and other evidence against molecular rotation, the only reasonable interpretation of the resulting narrow resonance seems to be the presence of internal rotations.

Broad proton resonances only were found in investigations of Rochelle salt, ADP, and KDP along each of their crystal axes. Although some workers have explained  $\lambda$ -point transitions in these crystals on the basis of rotations, the above results are in agreement with the more generally accepted theory of displacive transformations. This mechanism is one in which the unit cell of the crystal suffers a small uniform distortion when a symmetry element is either added or eliminated.

Nuclear Resonances in Thallium. During the time in which the M I T cyclotron magnet was available to us, nuclear magnetic resonances due to the isotopes of thallium ( $Tl^{203}$  and  $Tl^{205}$ ) were observed.

Two r-f coils were wound on a glass coil form containing a saturated solution of thallium acetate, the most soluble of the thallium compounds available. Each coil was part of a circuit of the type described by us previously (April 15, 1947 Quarterly Progress Report, p. 26-27).

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1 Private communication.

With proton resonances being observed in one circuit at about 30.5 Mc/sec, thallium resonances occurred for the same magnetic field in the other circuit in the vicinity of 17.5 Mc/sec. An electronic switch was used to display the output of the receiver in each circuit on the same oscilloscope. Measurements of the resonant frequencies of  $Tl^{205}$  and  $H^1$  gave the result

$$\nu_{Tl^{205}}/\nu_{H^1} = 0.577135 \pm 0.0005$$

This information has been reported in a Letter to the Editor of the Physical Review.<sup>1</sup>

The magnetic moment of  $Tl^{205}$  was computed from the above ratio after making a correction to take into account the fact that the magnetic field at a nucleus is less than the applied field because of the Larmor precession of its atomic electrons. The correction used is one given by Rabi and his collaborators.<sup>2</sup> The previously published spectroscopic value of the moment is about 10 per cent too small. We were able to confirm roughly the spectroscopic value of the ratio of the moments of  $Tl^{203}$  and  $Tl^{205}$ . Using this ratio to compute the moment of  $Tl^{203}$ , we get

$$\mu_{Tl^{205}} = 1.628 \mu_N$$

$$\mu_{Tl^{203}} = 1.613 \mu_N$$

where  $\mu_N$  = nuclear magneton.

The measurement on  $Tl^{205}$  marks the heaviest nucleus whose magnetic moment has been measured by other than spectroscopic means.

New Equipment The design of a new r-f bridge circuit for the measurements of nuclear resonances is almost complete, and the construction of some of the components is under way.

The new apparatus will be essentially the same as that already in use, but an attempt is being made to effect the following improvements:

1. Increased ease and precision of bridge balance
2. Increased convenience in checking separately the sensitivity of each arm of the bridge
3. Reduction of the effects of stray pickup
4. Reduction of the effects of mechanical vibration

Work on the air-core magnet to give 65,000 gauss, and on an 8-in iron-core magnet is continuing.

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1. To be published in the October 1 issue  
 2. Phys. Rev. 55, 1176 (1939).

## II E PARAMAGNETISM AND FERROMAGNETISM AT MICROWAVE FREQUENCIES

Staff: Professor A F Kip  
R D Arnold

Equipment for measuring absorption of microwave energy in paramagnetic and ferromagnetic materials placed in a steady magnetic field has been set up and is in operation. The magnetic material is placed in a resonant cavity ( $\sim 3.2$  cm) which is located between the pole pieces of a magnet and is coupled to the end of a waveguide. Changes in the power reflected from the cavity back into the guide are observed as the magnetic field is varied. The reflected power is simply related to the Q of the cavity and therefore to the absorption in the cavity.

Resonance (an absorption peak at a certain value of magnetic field) has been observed in  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (single crystal) and in a single crystal of iron. There seems to be an anisotropy (magnetic field for resonance different for different crystal orientations) in the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , verification awaits the construction of a holder to rotate the crystal without removing it from the cavity. There also appears to be a slight anisotropy in the iron crystal, but it is difficult to determine because the apparent shift is small compared to the width of the resonance. Experiments will be run at liquid nitrogen temperature with the idea of reducing the width of the resonance. All measurements so far have been at room temperature.

Dr Kittel and Dr Luttinger have prepared a paper, entitled, "Crystalline Stark Splitting and Microwave Resonance Absorption in Paramagnetic Salts", which will be published as an RLE technical report.