IV. RADIO-FREQUENCY SPECTROSCOPY

A. MOLECULAR-BEAM RESEARCH

Staff: Professor J. R. Zacharias
Professor B. T. Feld
Dr. D. E. Nagle
L. Davis, Jr.
H. Lew
C. W. Zabel

1. Hyperfine Structures and Nuclear Quadrupole Moments of Cl^{35} and Cl^{37}.

Staff: Professor J. R. Zacharias
Professor B. T. Feld
L. Davis, Jr.
C. W. Zabel

Results. The hyperfine structures of the $^2P_{\frac{3}{2}}$ ground state of Cl^{35} and Cl^{37} have been determined by the atomic beam magnetic resonance method. For both isotopes, $I = J = \frac{3}{2}$, there are four energy levels at zero magnetic field corresponding to F=0, 1, 2, and 3, given by the relation

$$W = a\frac{C}{2} + \frac{b'}{24}C(C+1) + c(C^3 + 4C^2 + \frac{4}{5}C)$$

where $$C = F(F+1) - J(J+1) - I(I+1),$$

and where a is the magnetic dipole, b' the electric quadrupole, and c the magnetic octopole interaction constants. The measurement of the separations between adjacent levels, $a - b' + 153.1c$, $2a - b' + 54.2c$, $3a + b' + 171.3c$, led to the following determination of the interaction constants a, b', and c.

$a_{35}=205.288 \pm 0.030$ Mc $\quad b'_{35}= 55.347 \pm 0.070$ Mc $\quad c_{35}=380 \pm 500$ cps.

$a_{37}=170.686 \pm 0.030$ Mc $\quad b'_{37}= 43.256 \pm 0.070$ Mc $\quad c_{37}=20 \pm 500$ cps.

After including small relativity corrections, the electric quadrupole moments calculated from the ratio of b'/a are

$$Q_{35} = -(7.921 \pm 0.05) \times 10^{-26} \text{ cm}^2$$

$$Q_{37} = -(6.189 \pm 0.05) \times 10^{-26} \text{ cm}^2 .$$

Experiment. The apparatus was the same as used in the K^{40} experiment and was described in the last quarterly report. The energy-level system for an

atom with $J = I = \frac{3}{2}$ is sketched in Fig. IV-1. The arrangement of the inhomogeneous magnetic fields in the apparatus will refocus a beam only if m_J at large fields changes sign as a result of a transition in the region of the homogeneous field. Of the eleven such transitions (indicated by

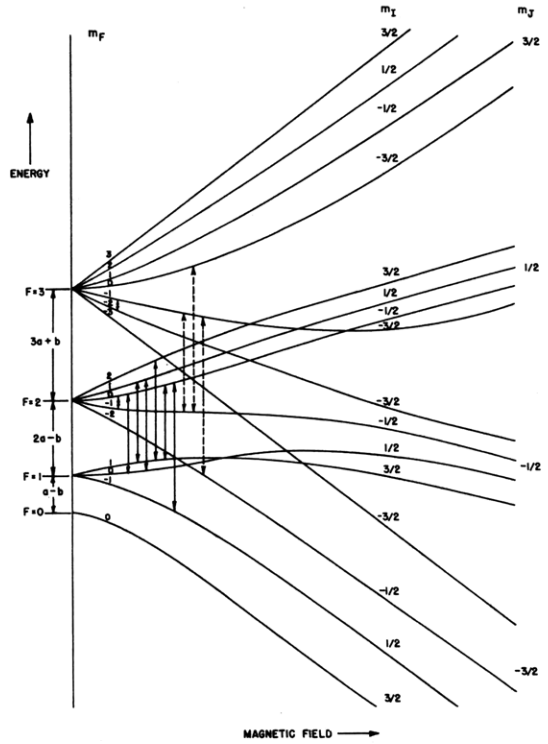

Fig. IV-1. Rough plot of hyperfine structure energy levels of an atom with $J = I = 3/2$. The vertical lines indicate observable transitions in which m_J changes sign.

vertical lines in the figure) which obey the selection rules, $\Delta F = \pm 1, 0$; $\Delta m_F = \pm 1, 0$, nine have been observed: two low-frequency lines with $\Delta F = 0$, $\Delta m_F = \pm 1$, six lines between $F = 1$ and $F = 2$, and one line between $F = 2$ and $F = 3$. There is no transition possible between the $F = 0$ and $F = 1$ levels which satisfy the requirement that m_J change sign. The transition was observed, however, by adjusting the A and B inhomogeneous fields to refocus atoms which made the transition $m_J = +\frac{1}{2} \leftrightarrow m_J = -\frac{1}{2}$, and superimposing two oscillating fields in the transition region. The frequency of the first field was adjusted to induce transitions between $F = 1$ and $F = 2$ ($F = 1$, $m_F = 0 \leftrightarrow F = 2$, $m_F = 1$). The refocused beam intensity so obtained was diminished when the frequency of the second oscillating field corresponded to the $F = 0$, $m_F = 0 \leftrightarrow F = 1$, $m_F = 1$ transition. The decrease in beam intensity arises from the competition between the transitions from the $F = 1$, $m_F = 1$ to either $F = 2, m_F = 1$ or $F = 0, m_F = 0$, the latter state not being refocused in the second inhomogeneous field because its m_J value at large fields is $- 3/2$.

In order to facilitate the search for an identification of transition frequencies, the secular determinant involving the energy of the states,

the applied field, and the interaction constants was solved numerically for the energy for various values of the parameters. The form of the curves obtained is sketched in Fig. IV-1.

The quadrupole moment was determined by the use of relations given by Casimir for the interaction constants a and b'. Both relations depend upon the average value of $1/r^3$ where r is the radius vector to the electronic charge. By eliminating the $(1/r^3)$ term, the quadrupole moment is determined, for the halogens, by the relation

$$Q = -\frac{b'}{a}\frac{8}{3} g_I \left(\frac{\mu_o}{e^2}\right)^2 \frac{m}{M_p} \cdot \frac{F}{R}$$

where F/R is a small relativistic correction.

A paper is in preparation for publication.

2. Hyperfine Structure of Na^{22}

Staff: L. Davis, Jr.

The use of small quantities of Na^{22} (about 10^{-9} moles) has caused considerable trouble in oven design. As was reported previously (Progress Report, January 15, 1948), the beam intensity from the reaction of NaCl on calcium was proceeding too slowly. It was found by detecting the radioactive Na^{22} in cleansing solutions, that the Na or NaCl was to some extent left in the calcium chips, but had mostly diffused into the walls of the oven. It required etching away a thin film of oven material with acid to remove the activity. Moreover, considerable "contamination" of the beam by Na^{23} from the calcium was encountered.

To be free of the latter difficulty as well as to run at lower temperatures and hence to some extent decrease the diffusion (amalgamation) into the walls of the oven, a new method of obtaining sodium vapor was sought. The most satisfactory reaction for our purpose seems to be NaN_3 (sodium azide) heated to about 300°C forming free sodium and gaseous nitrogen which is pumped away under vacuum. The azide is stable in water or air so that this presents a method of obtaining minute quantities of free sodium in a vacuum without handling in an inert atmosphere.

By trying several oven materials and reducing the oven surface area, it was found that although many metals amalgamate with sodium in such small quantities, monel metal seemed almost free from this difficulty. Fused quartz was found to be reduced by the hot sodium vapor and it is assumed that this trouble would be encountered in any of the refractory oxide materials.

The use of an electron multiplier as a detector led to rather poor results, as an efficiency of 1 per cent or less was encountered. It

is believed that this was due to surface contamination from solder when refired. A new multiplier was tried and found to have an efficiency of 15 per cent.

3. Equipment Problems

Staff: Dr. D. E. Nagle
H. Lew

In the Quarterly Progress Report of January 15, 1948, it was reported that, according to rough tests, an electron multiplier constructed of beryllium copper detected between 50 and 100 per cent of the particles in an incident beam of potassium ions of 3600-ev energy. More careful tests since have shown that only 15 per cent are detected.

Work continues on the design and assembly of a second molecular-beam apparatus for precise measurements on hyperfine structure of the hydrogens. The castings for the third molecular-beam apparatus have been made and the machine work on them is about to begin.

IV. B. MAGNETIC NUCLEAR RESONANCE

Staff: Professor F. Bitter
N. L. Alpert
C. G. Lehr
H. L. Poss

1. Deuteron-Proton Magnetic Moment Ratio

Staff: Professor F. Bitter
N. L. Alpert
H. L. Poss
Dr. D. E. Nagle

The measured result recently reported by us[1]

$$\frac{\mu_D}{\mu_H} = 0.307021 \pm .000005$$

is not quite identical with that reported by F. Bloch, E. C. Levinthal, and M. E. Packard[2]

$$\frac{\mu_D}{\mu_H} = 0.3070126 \pm .000002 ,$$

but is probably significantly different from the value calculated from the ratio of the hyperfine structure constants reported by D. E. Nagle, R. S. Julian and J. R. Zacharias[3]

$$\frac{\mu_D}{\mu_H} = \frac{4}{3}\left(\frac{m_H}{m_D}\right)^3 \frac{\Delta\nu_o}{\Delta\nu_H} \qquad (1)$$

$$= 0.30705 \pm .00001 .$$

In view of the great interest in checking the validity of Eq. (1), preparations are being made to improve the accuracy of the observations. The requirements are:

a. Constancy and uniformity of field.
b. Sharp and symmetrical resonance lines.

---

1. Phys. Rev. 72, 1271 (1947).
2. Phys. Rev. 72, 1125 (1947).
3. Phys. Rev. 72, 971 (1947).

By means of submarine storage batteries to supply the exciting current for the magnet, and small auxiliary coils carrying a few milliamperes to produce slow uniform changes in field, it has been possible to make observations on lines for which $\Delta\nu/\nu \sim 10^{-5}$. It has so far been difficult to maintain balance conditions in the bridge circuit sufficiently constant to make use of these narrow lines. Further work on this matter is in progress, as well as the design of new pole faces to give even more uniform fields and consequently narrower lines.

Our measurements of magnetic moment ratios assume that the average field at a proton is the same as the average field at a deuteron. As a preliminary to testing this point a series of measurements in applied fields ranging from 1000 to 7000 gauss were made on protons in different substances. Two substances were placed in the same external field, and a search made for double or broadened lines. The following substances were investigated: water, oil, glycerine, liquid H_2, and liquid HD. In no case was there any evidence of a difference in the resonance condition for protons in different molecules.

2. Rotational States in Solids

Staff: N. L. Alpert

An apparatus has been constructed for the study of nuclear magnetic resonance phenomena at low temperatures. This was designed to fit inside of a one-foot long glass dewar flask with an I.D. of about $3\frac{1}{4}$ in. at the top which narrows down to about $1\frac{1}{2}$ in. for the bottom five inches, so that it fits between the poles of our electromagnet.

The apparatus works on the principle of a variable heat leak from the heavy copper pot at the bottom, containing the sample and r-f coil, to the cold reservoir in the wide part of the dewar, filled, for example, with liquid nitrogen. The heat leak is controlled by a heater wound on a thin-walled brass tube connecting the pot reservoir. Although the apparatus is designed primarily for use from 80°K to 300°K, it has been made air-tight so that it may be adapted for use at lower temperatures.

Work with this apparatus has so far been principally in two directions: first, to prepare an r-f coil which satisfies both the r-f and the mechanical requirements; secondly, to obtain a temperature calibration. For the latter, thermocouples were initially used. However, it was necessary to replace these with resistance thermometers because of spurious thermal e.m.f.'s introduced at the glass-to-metal seals used to bring leads through the cover. Each resistance thermometer consists of about 26 feet of No. 38 copper wire.

The first investigation which is being undertaken with this apparatus is a more detailed study of some of the substances which show more

than one phase in the solid state, and for which preliminary results were previously obtained. These include HCl, HBr, HI, CH_4, CH_3D, KDP, and NH_4Cl. Previous experience with samples of the hydrogen halides and deuterated methane indicated the necessity of greater purification before attempting to condense the gases. Considerably better samples have recently been prepared by Dr. C. S. Pearsall and his staff.

3. Circuit Improvement

Staff: C. G. Lehr

A positioning mechanism[1] for the r-f coil containing the sample has been built and attached to the magnet. By turning two handwheels, which drive a horizontal rack and pinion and a vertical screw, the sample can be moved conveniently to any point in the air gap of the magnet. Incorporated in the positioning mechanism is a shielded duralumin box in which are contained a tuning capacitor and two coupling capacitors. The two coaxial cables, which form a part of the r-f bridge, are attached permanently to this box. A General Radio coaxial connector in the underside of the box fits into a second General Radio connector in the shield around the r-f coil. By separating these connectors the r-f coil can be changed easily, even when this coil is enclosed in a low-temperature cryostat.

All the components of the r-f bridge which do not have to be placed in the magnet gap are mounted on panels and assembled in a single rack. To prevent microphonics, all circuit components were mounted and wired as rigidly as possible. National drive units, which have a gear ratio of 20:1 and a minimum of backlash, are used to drive the variable capacitors which balance the bridge. A special differential capacitor[1] with variable plate spacing was constructed to compensate in part for restriction in the range of amplitude balance caused by the output resistance of the signal generator.

These improvements have been found very satisfactory, particularly with regard to the ease of adjustment and flexibility of the apparatus.

A new pre-amplifier for the bridge detector was built. This pre-amplifier is made up of a grounded-grid triode and a cathode follower. Rough measurements show that the over-all noise figure of the detector was improved by a factor of two or more. A new noise diode is being constructed for more rapid and accurate measurements of noise figures.

---

1. The mechanical design of the positioning mechanism and differential capacitor was done by E. C. Ingraham.

IV. C. PARAMAGNETIC AND FERROMAGNETIC RESONANCE ABSORPTION AT MICROWAVE FREQUENCIES

Staff: Professor A. F. Kip
R. D. Arnold
E. Lebow

(1) Improved equipment for measuring the d-c magnetic field used in these experiments has been constructed. A small, rotating search coil, driven by an 1800-rpm synchronous motor, is placed in the magnetic field and the generated 30-cps voltage is applied to an oscilloscope whose sweep frequency is 60 cycles, synchronized to the line. In series with the search coil is the output of a Leeds and Northrup student potentiometer which has a constant-amplitude, 3000-cps signal applied to its input. The arrangement is shown in Fig. IV-2. Schematic screen patterns for conditions of balance and unbalance are shown in Fig. IV-3. At balance the potentiometer reading is proportional to the magnetic field strength. The device is calibrated by placing the search coil in a known magnetic field. Resetability of $\frac{1}{2}$ per cent full scale is easily obtained.

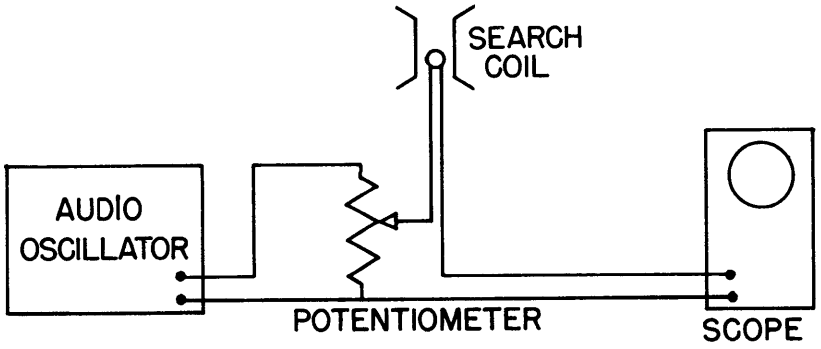

Fig. IV-2. Equipment for measuring magnetic field.

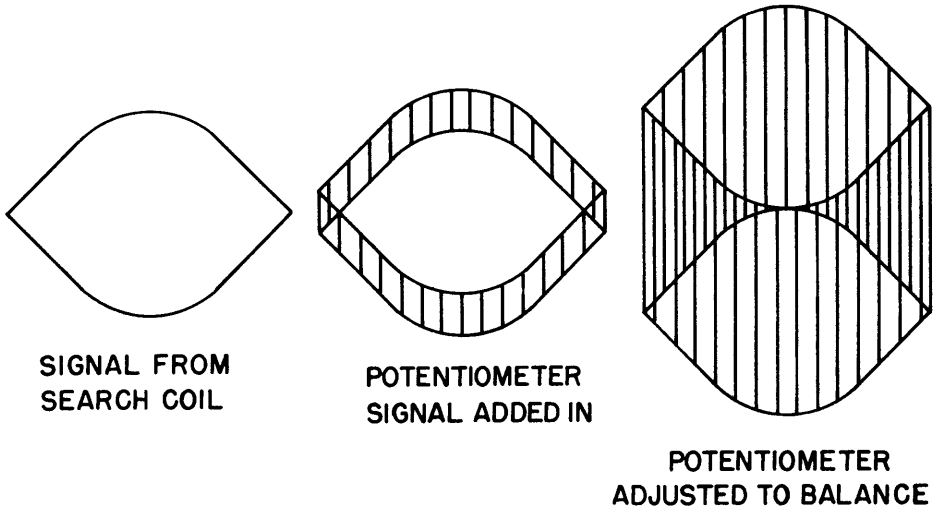

Fig. IV-3. Scope patterns in field measurement.

(2) A 10-cm set-up for resonance absorption measurements is being constructed.

(3) Further absorption measurements on the iron crystal described in the preceding progress report have been made at 3 cm. When a certain area of the crystal surface is used, a third absorption peak is observed in addition to the two mentioned in the preceding progress report. (That report is in error in stating that the second peak occurs at the 011 and $0\bar{1}1$ orientations; it should be 010 and 001.) The third peak is probably due to strains localized on a certain part of the crystal surface.

IV. D. MICROWAVE SPECTROSCOPY

Staff: Professor A. G. Hill
Professor G. G. Harvey
Dr. R. L. Kyhl
Dr. M. W. P. Strandberg
R. E. Hillger
J. G. Ingersoll
R. B. Lawrance
C. C. Loomis
G. H. Pettingill
M. Weiss
T. Wentink, Jr.

1. Microwave-Frequency Bridge

Staff: Dr. M. W. P. Strandberg
J. G. Ingersoll

With the bridge adopted to sweep technique between 48200 and 56300 Mc/sec the $J = 6 \rightarrow 7$ transitions for $COSe^{78}$, $COSe^{80}$, and $COSe^{82}$, and the $J = 5 \rightarrow 6$ transitions for $COSe^{78}$ and $COSe^{80}$ were detected and measured. The data are sufficient to consider the work on rotational distortion of these isotopic molecules complete. The variation in the centrifigual distortion coefficient with isotope change is outside experimental error.

Work in the 5-mm region to detect rotational absorptions in D_2O was started, and is being continued. No lines in D_2O have been found yet, but the $^3 2,2;0 \rightarrow {}^3 2,1;1$ transition in HDO at 6 mm was found and measured. Positive identification of this transition was made from the Stark spectrum obtained in another of our sweep spectroscopes.

2. Sweep Spectrometers

Staff: Dr. M. W. P. Strandberg
T. Wentink, Jr.
R. E. Hillger
M. Weiss

Considerable time was spent in further construction on a new 1-cm spectroscope and the absorption cell intended for wide-range temperature work. Preliminary tests on the new spectroscope will begin shortly. The high-temperature absorption cell was used in search for transitions in COSe and HgCl. Despite present negative results this work will be continued.

The study of HDO was resumed. The Stark effect of the 6-mm line reported above (Sec.1) was measured. Another HDO line at 2.92 cm was found and its Stark effect was measured. The Stark patterns confirm the prediction of these lines by King, Hainer, and Cross[1]. We have started on a paper which will summarize our work on this molecule.

---

1. G. W. King, R. M. Hainer and P. C. Cross, "Expected Microwave Absorption Coefficients of Water and Related Molecules", Phys. Rev. 71, 433 (1947).

The large absorption coefficients of the HDO lines at 10279.69 Mc/sec, 22307.67 Mc/sec, and 50236.44 Mc/sec ($\pm$ .05 Mc/sec) make them convenient frequency markers for calibration purposes in microwave spectroscopy.

Forty-three lines between 19000 and 27000 Mc/sec have been measured in pyridine (C_5H_5N), the first heterocyclic compound studied in the microwave region. It was hoped that this molecule, an asymmetric top, would closely approximate a symmetric top, but the extreme complexity of the observed spectrum and the Stark effect indicated a high degree of asymmetry ($\kappa \cong 0.8$). Tentative line assignment must await our further work at 9.2 mm for verification. Until more data are obtained, no precise calculation of moments of inertia and the molecular structure is possible.

Since the present limit of sensitivity in the sweep spectroscopes depends largely on existing signal-to-noise ratio in the detecting systems, a preliminary study of noise and noise-reduction in a 3-cm system was started. A noise-reduction system was proposed and tested, with only partial success. At 3 cm a large part of the noise seems to be due to i-f amplifiers and crystals, and not the klystron tubes. At 1 cm the klystron tubes contribute much more noise near the oscillating frequency. The results indicate that a much broader program in studying noise at 1 cm is necessary.

3. Cavity Spectroscope

Staff: Dr. R. L. Kyhl
C. C. Loomis

A cavity system is being constructed at 1 cm. The principal reason for this work is to attempt to detect microwave spectra of extremely small samples, such as radioactive materials. We should like to determine the spin of Co^{60}, for example. Rough preliminary estimates make it doubtful whether the required sensitivity will be obtained, but the problem is sufficiently important to justify an attempt. The chief innovation will be to sweep the cavity mechanically so that the scope presentation will be similar to that of present sweep spectroscopes. The oscillator will be locked to the cavity with a Pound stabilizer. The electronic circuits will be flexible to allow various detection methods to be used. This should provide additional information for the analysis of spectroscope sensitivity.

A mechanical design for the cavity is being completed and the electronic components are partially built and assembled.

4. Five-Mm Sweep Spectroscope

Staff: Dr. R. L. Kyhl

A sweep spectroscope for search at 5 mm has been completed and is in operation. It uses an absorption cell of 9.5 meters of 1" x $\frac{1}{2}$" guide.

Specially designed doubler and mixer plumbing provide for ease of operation over a wide frequency range. The system is not equipped with Stark modulation at present.

Heterodyne detection is used with one crystal serving both as mixer and as doubler for the local oscillator. A 30-Mc/sec i-f amplifier is used. In addition a 15-Mc/sec channel operating on the fundamental frequencies of the signal and local oscillator provides automatic frequency control of the local oscillator.

The sensitivity of the system was checked on the HDO line at 50200 Mc/sec and is estimated to be at least 5×10^{-6} cm^{-1}.

A search has been made for lines in the spectrum of $POCl_3$ in the range of 46000 Mc/sec to 51000 Mc/sec, but without success.

5. Three-Mm Sweep Spectroscope

Staff: Dr. R. L. Kyhl
G. H. Pettingill

Components are being constructed to convert the new 5-mm sweep spectroscope for 3-mm operation as well. A 10-Mc AFC channel is being added and a tripler and tripler mixer have been built. They are to be used with home-made crystals which are to be provided by C. S. Pearsall. The crystal contact will be adjusted in the system for optimum tripling efficiency.

6. Hyperfine Splitting of Atomic Hydrogen

Staff: R. B. Lawrance

The cavity and all auxiliary apparatus have been completed, and searching for absorption in the vicinity of 1420 Mc has been begun. Effects due to the presence of small residual concentrations of free electrons and protons mask the sought-for absorption due to nuclear reorientation, however, and steps are being taken to prevent all such charged particles from entering the cavity.

Work has been done on several collateral instrumental problems of some interest. In the more standard field of microwave spectroscopy with waveguide absorption cells the use of a single oscillator tube with a single-sideband superheterodyne circuit has been investigated and demonstrated to be practical, although limitations are inherent. At the other end of the frequency spectrum a very selective audio amplifier has been built. This amplifier uses the standard null-network feedback principle, (Fig. IV-4.) but the network itself has the new and useful property of being tunable by a single well-bypassed resistor.

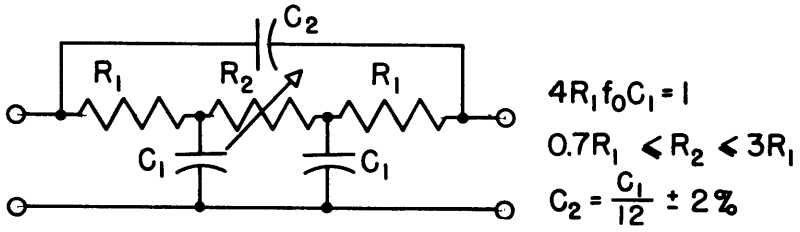

Fig. IV-4. Null network.

As a rejection filter, attenuation of the order of 60 db is obtainable at any frequency within ± 15 per cent of the design frequency f_o. In the selective feedback amplifiers the ease of tuning makes cascade stages simple and practical.