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. Lev
       C. W. Zabel

1. Hyperfine Structures and Nuclear Quadrupole Moments of the Halogens, and Na$_{22}^+$

The second molecular-beam apparatus has been assembled and is nearly ready for preliminary experiments. A chlorine beam will be used to adjust the apparatus; the detection of the remaining halogens will then be attempted with low work-function surface ionization wires.

Work continues on the oven problem for Na$_{22}^+$ in the first molecular-beam.

2. The Generation and Detection of a Beam of Aluminum Atoms

Staff:  H. Lew

Preliminary to the measurement of the nuclear moments of aluminum, work is being carried out on the generation and detection of a beam of aluminum atoms. It has been found possible to detect a beam of aluminum atoms by the familiar surface ionization method. In the case of aluminum, the tungsten ribbon which does the ionizing has to be heated to a much higher temperature than in the case of the alkalis. The temperature is of the order of 2000°C. At this temperature, a large amount of impurity in the tungsten is boiled off. Among the impurities is aluminum itself. Therefore before the ribbon can be used for aluminum detection, prolonged heating to clear it up is necessary.

For the generation of a beam of aluminum atoms, the proper oven material and oven design have not yet been found.

3. The Third Molecular-Beam Apparatus

Staff:  H. Lew

Machine work on the third molecular-beam apparatus is still in progress.
4. Theory of Nuclear Effects in Microwave Spectra

Staff: Professor B. T. Feld
G. Knight

A theory has been developed for the fine structure of the rotational levels of slightly asymmetric top molecules due to nuclear electric quadrupole moments. The wave functions for the asymmetric top were expanded in terms of the symmetric top wave functions and a parameter representing the degree of asymmetry of the molecule. The nuclear quadrupole coupling was evaluated to first order in the asymmetry parameter. The result introduces, in addition to the term usually obtained for symmetric tops, a term involving the difference between the gradients of the electric field with respect to the minor axes.

The results are of the same form as those obtained by Bragg with the difference that the result can be expressed in terms of a simple formula involving the molecular and nuclear constants and the quantum numbers \( J \) and \( K \) of the molecule. The result for \( K \neq \pm 1 \) is:

\[
\left\langle \frac{3 \cos^2 \theta - 1}{r^3} \right\rangle_{J, K} = \frac{J}{2J + 3} \left[ \frac{3K^2}{J(J + 1)} - 1 \right] \frac{\partial^2 \psi}{\partial \eta^2} \\
- b \left[ G(J, K) + G(J, -K) \right] \left[ \frac{\partial^2 \psi}{\partial x^2} - \frac{\partial^2 \psi}{\partial y^2} \right]
\]

where

\[
G(J, K) = \frac{(J + K + 1)(J + K + 2)(J - K - 1)(J - K)}{8(J + 1)(J + 1)(2J + 3)}
\]

and

\[
b = \frac{(A - B)}{[2C - (A + B)]};
\]

A, B, and C are the reciprocal principle moments of inertia.

For the case of \( K = \pm 1 \), the general expressions obtained are no longer valid since these states are degenerate in terms of the representation employed, and the perturbation due to the quadrupole term fails to remove this degeneracy. In this case degenerate perturbation theory has

been applied and similar results obtained. This work was reported at the New England Section Meeting of the American Physical Society held at Harvard on May 29, 1948.

B. MAGNETIC NUCLEAR RESONANCE

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

1. Measurements of Nuclear Magnetic Moments

Staff: H. L. Poss

In previous progress reports, precision measurements were reported in which the deuteron moment and those of the thallium isotopes were compared with the proton moment. Further measurements of this type have been completed for C$^{13}$ and F$^{19}$.

C$^{13}$ is a stable isotope of carbon occurring naturally in an abundance of 1.1 per cent. Its gyromagnetic ratio had been measured previously by molecular-beam methods. The availability of a sample of methyl iodide enriched in C$^{13}$ prompted measurements to be made on it.

A hollow polystyrene coil form was made into which could fit the sealed-off glass tube containing the methyl iodide, a liquid. A second coil was used to obtain a reference proton resonance at 17.9 Mc/sec., the C$^{13}$ resonance then being expected to occur at 4.5 Mc/sec. Each coil was part of a bridge circuit of the type we have described in the last progress report.

A search using a recording output meter revealed a weak resonance in the expected vicinity. It was attributed to C$^{13}$ since there were no other nuclei in the sample which would give resonances in this region.

Measurements were made by recording the C$^{13}$ resonance at a known frequency and then obtaining the proton resonance with the second coil in the same position as that formerly occupied by the C$^{13}$ sample. The magnet field current was kept constant throughout. The C$^{13}$ resonance was traversed by varying the current through a set of auxiliary coils on the magnet. From the calibration of these coils, a small correction could be made for the field difference separating the two resonances.

The result of seven determinations of the ratio of resonant frequencies is

$$\frac{\nu_{C^{13}}}{\nu_H} = 0.25143 \pm 0.00005.$$
The spin of $^1\text{H}$ is known to be $\frac{1}{2}$. Taking $5.5791 \pm 0.0016$ for the gyromagnetic ratio of the proton and applying a small correction for the diamagnetism of the electrons surrounding the carbon nucleus gives the result, in nuclear magnetons,

$$\mu_{\text{C}^{13}} = 0.7016 \pm 0.0004.$$ 

Most of the error results from the uncertainty in the proton gyromagnetic ratio. The value is well within the limit of error of the molecular-beam result,

$$\mu_{\text{C}^{13}} = 0.701 \pm 0.002.$$ 

Fluorine exists in the form of a single isotope of mass number 19. Its high gyromagnetic ratio together with the existence of suitable samples enables its resonance to be observed readily on the oscilloscope. It was decided to apply the resonance-absorption method to the measurement of its moment to see how the results would compare with the observed molecular-beam value.

Hydrofluoric acid was used as a sample. Since it affects glass, it could not be kept in the vials used for other samples. It does not affect polystyrene, however, and was poured directly into the coil forms.

A series of measurements was made in the vicinity of 19 Mc/sec. One sample coil was used. The field was kept constant and the frequency varied so that first the proton resonance was obtained and then the fluorine one. The resonance frequencies are sufficiently close together so that one bridge circuit could be used for both.

Four determinations give for the ratio of resonance frequencies

$$\nu_{\text{F}^{19}}/\nu_{\text{H}^1} = 0.94077 \pm 0.0001.$$ 

The spin of $^1\text{F}$ is known to be $\frac{1}{2}$. Taking into account a small diamagnetic correction and using the previously referred to value of the proton gyromagnetic ratio give the result, in nuclear magnetons,

$$\mu_{\text{F}^{19}} = 2.626 \pm 0.001.$$ 

1. S. Millman and P. Kusch; Phys. Rev. 60, 91 (1941). New values incorporating corrections due to a change in the accepted moment of the electron [see J. Schwinger, Phys. Rev. 73, 416 (1948)] may be computed by using $g_\text{F} = 5.5858$. 

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the error again arising mostly from that in the gyromagnetic ratio of the proton. The result is in good agreement with the molecular-beam value

$$\mu_{F^19} = 2.627 \pm .003$$

A tabular summary of the measurements we have thus far made is given below.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Observed ratio of (g)-factor to that of the proton</th>
<th>Magnetic moment in nuclear magnetons</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H^2)</td>
<td>(.153511 \pm .000003)</td>
<td>(.85645 \pm .00025)</td>
</tr>
<tr>
<td>(Cl^3)</td>
<td>(.25143 \pm .00005)</td>
<td>(.7016 \pm .0004)</td>
</tr>
<tr>
<td>(F^19)</td>
<td>(.94077 \pm .0001)</td>
<td>(2.626 \pm .001)</td>
</tr>
<tr>
<td>(Tl^{203})</td>
<td>(.571499 \pm .00005)</td>
<td>(1.612)</td>
</tr>
<tr>
<td>(Tl^{205})</td>
<td>(.577135 \pm .00005)</td>
<td>(1.628) (\mu_{205}/\mu_{203} = 1.00986)</td>
</tr>
</tbody>
</table>

A full report of this work is to be found in a thesis by H. L. Poss, entitled "Measurements of Nuclear Magnetic Moments", and will appear shortly in the Physical Review.

2. Studies of Phase Transitions by Means of Magnetic Nuclear Resonance Phenomena

Staff: N. L. Alpert

During the past quarter considerable data have been obtained on the line width of the proton resonance in solids at low temperatures. Attention was concentrated on those substances which show more than one phase in the solid state. The resultant data, of which the graphs for \(HCl\) and \(HBr\) are illustrative (Figs. IV-1 and IV-2), enable us to interpret the mechanism of these well-known phase transitions.

In order to clarify the interpretation of the results, we shall discuss briefly the factors which affect the resonance line width for the cases studied. Under the conditions of the experiment, the line width is determined by the magnetic interaction between nuclei. Since in general the neighbors of a magnetic nucleus are themselves magnetic, they will contribute to a local magnetic field \(B_{loc}\) at the nucleus in question, which field will add to, or subtract from, the applied d-c field, \(H_o\).
Fig. IV-1. Line width vs. temperature for the proton resonance in HCl.

Fig. IV-2. Line width vs. temperature for the proton resonance in HBr.

In both cases the transition temperatures separating the two or more solid phases and the melting points are indicated.
That is, we may say that the magnetic field at a nucleus is $H_0 + H_{loc}$ and that the resonance condition is then

$$\omega = \gamma(H_0 + H_{loc})$$

where $\omega$ is the resonant angular frequency and $\gamma$ the nuclear gyromagnetic ratio. A simple calculation shows that these internuclear fields may be of the order of several gauss. The result is thus a dispersion of the magnetic fields at the various nuclei about the applied $H_0$, the average field at the nuclei still being $H_0$. From the resultant broadening of the Zeeman levels, $\Delta E = \hbar \gamma H_{loc}$, we may define a time $T_2$ on the basis of the uncertainty principle of quantum mechanics: $T_2 = \hbar/\Delta E = 1/|\gamma| H_{loc}$. Since this broadening is due to interactions between nuclei, $T_2$ is called the spin-spin relaxation time. It should be noted that $H_{loc}$ represents a deviation of the magnetic field from an average $H_0$. Therefore, gradients in the magnetic field due to the inhomogeneity of the magnet serve also to broaden the line.

Most solids are found to fit well with this extremely elementary picture, giving resonance line widths of five or more gauss. In fact, for many cases the line width may be accurately estimated by computing the mean square local magnetic field, summing over contributions from all neighbors. However, in the case of most liquids and gases and a few solids, line widths of a small fraction of a gauss are found. The key to these narrow resonances is the lattice motion, which we have so far neglected. Qualitatively the resonance line width is reduced by an averaging out of the inter-nuclear fields due to the motion of the lattice which carries the nuclei. This is particularly obvious in the extreme case of a nucleus residing in a freely rotating molecule, since rotational periods are much smaller than times associated with the nuclear resonance. In most cases of interest all orientations are equally probable. As a consequence, the internuclear fields essentially average out to zero, resulting in an extremely narrow line. Actually in the case of water a line width of $10^{-4}$ gauss is predicted. In practice it is impossible to observe this "true" line width since it would require, at a working field of 7000 gauss, a homogeneity of almost one part in $10^8$ over the sample. Thus the line width in most liquids is determined entirely by the homogeneity of the magnet.

A theory of line widths and relaxation times by Bloembergen, Purcell, and Pound\textsuperscript{1} approximates this description of the lattice motion by means of a single parameter $\gamma_c$. This so-called correlation time is

\textsuperscript{1} N. Bleombergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).
essentially the average time for a molecule to change its position or orientation appreciably. It is very closely related to the "characteristic relaxation time" introduced by Debye in his theory of polar molecules.\(^1\)

The effect of \(\tau_0\) on \(T_2\) and on the line width may be seen as follows:

Let us denote by \(T_2\)" the spin-spin relaxation time in the limiting case of the rigid lattice. Thus, for this case, \(T_2\)" represents the average time a nucleus spends in a particular Zeeman energy state (or orientation). Now if \(\gamma_0 \gg T_2\)", the slow variation of the internuclear fields during the "lifetime" of a nuclear orientation will have a negligible effect on the spin-spin interaction. Therefore we have

Case I: \(\tau_0 \gg T_2\)"

\[
T_2 = T_2; \\
\Delta H = \frac{1}{\gamma T_2\text{"}}
\]

If on the contrary \(\tau_0 \ll T_2\)"", considerable averaging out of the internuclear fields occurs during a normal nuclear level "lifetime". As a result the spin-spin interaction is greatly reduced and the relaxation time increased accordingly. In this case it may be shown that, in general, the relaxation time varies inversely as the correlation time.

Case II: \(\tau_0 \ll T_2\)"

\[
T_2 \propto \frac{1}{\tau_0} \\
\Delta H \propto \tau_0
\]

Thus it becomes apparent that the line width is a sensitive function of the correlation time. It is this fact that makes this method useful in the study of the class of phase transitions considered, since these may possibly be explained in terms of a change in molecular activity.

There are two conflicting theories to explain the transitions in question. One theory, put forward by Pauling\(^2\) and Fowler\(^3\), associates the transition temperatures with a change from rotational oscillations of the molecules or ionic groups below the critical temperature to a phase in which most of the molecules are freely rotating. The second theory, developed by Frenkel\(^4\) and Landau\(^5\) assumes that the transition is from

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an ordered to a disordered state. In this theory there is assumed a
preferred orientation, occupied by a majority of the molecules, below
the transition, while above the transition the molecules occupy with
equal probability one of two, or more, equilibrium orientations. It
should be noted that both below and above the transitions the molecules
flip between equilibrium orientations.

An investigation of orders of magnitude involved indicates the
following: The line width is a measure of $\gamma_c$ in the range from about
10 $\mu$sec, the magnitude of $T_2^*$, down to about 0.1 $\mu$sec, as limited
by the homogeneity of the magnet. For the case of rotating molecules, one
should expect characteristic times of $10^{-10}$ seconds or less, while for
normal solids one should expect characteristic times of a microsecond or
more, a difference of at least $10^4$.

The expected effect of phase transitions may now be discussed on
the basis of the expected values of $T_2^*$ and $\gamma_c$. For the case of a
rotational transformation the line should be broad, typical of most
solids, below the transition; upon reaching the transition, where free
rotation becomes predominant, one should expect a rapid decrease, over
the range of the transition to a narrow line limited in width only by
magnet inhomogeneity. However, in the case of an order-disorder transi-
tion, there may be little or no change in $\gamma_c$ at the transition tempe-
tature. That is, if a moderate change, or zero change in line width occurs
at the transition, this must be identified with the order-disorder
mechanism. On the contrary, if a rapid change to a very narrow line
occurs at the transition, the rotational transformation mechanism may be
indicated, although the order-disorder mechanism is not completely ruled
out on the basis of this evidence alone.

Complete curves of line width versus temperature have recently
been obtained for HCl, HBr, HI, $H_2S$, and $H_2Se$. All of these were found to
have the same fundamental characteristics as shown in Figs. IV-1 and IV-2
for HCl and HBr. Therefore, in these cases the phase transitions cannot
possibly be associated with the onset of molecular rotation but satisfy,
instead, the conditions of an order-disorder transformation. Preliminary
results for $NH_4Cl$, $NH_4Br$, $NH_4I$, and $KH_2PO_4$ indicate that transitions in
these solids also fall in the same classification. In those cases
studied in detail, a narrow line, limited only by the magnetic field, was
found in a temperature range of roughly 20$^\circ$K below the melting point.
This indicates extraordinary activity in these solids, but since this
does not set in at the transition, the Pauling-Fowler interpretation is
still out of the question for these cases.
In a few cases, reported in the July 15 and October 15, 1947, Quarterly Progress Reports, results indicate the plausibility of a rotational transformation, although the order-disorder mechanism is not absolutely eliminated for these transitions. These exceptional solids are CH$_4$ and CH$_3$D, as well as natural rubber, for which internal rotation is shown to be reasonable but is not unquestionably proved.

These experiments were carried on in a cryostat constructed especially for this purpose. The temperature of the sample is controlled by means of a variable heat leak. Temperatures from 80° to 160°K can be obtained by using liquid nitrogen as a low-temperature reservoir; from 150° to 180°K by using pumped liquid ethylene; and from 170° to 260°K by using liquid ethylene boiling under atmospheric pressure. The samples which were not available commercially were prepared by Dr. C. S. Pearsall of this Laboratory and his staff.

The invaluable discussions with Professor L. Tisza on the theoretical background of this problem are gratefully acknowledged.

A detailed report of this research is to be submitted in the near future for publication in the Physical Review.

3. Circuit Improvement
Staff: L. G. Lehr

A summary of this work is contained in the last progress report. A complete report is available in a master's thesis in the Department of Electrical Engineering entitled, "Equipment for the Measurement of Nuclear Magnetic Resonances".

C. PARAMAGNETIC AND FERROMAGNETIC RESONANCE ABSORPTION
Staff: Professor A. F. Kip
R. D. Arnold
E. Lebow

Experimental apparatus for use in the 1-cm and 3-cm wavelength regions has been improved with the view of making possible more accurate resonance half-width determinations. The problem of relating the magnetic field for apparent resonance maximum, as measured by reflection of power from a cavity containing a sample, to the field for true maximum absorption of the sample alone is being studied. The difference between these two quantities becomes important under some conditions when the absorption curve is broad. A number of paramagnetic salts have been tested, including some tests to extend measurements to 10-cm wavelengths.
A sample of annealed permalloy has been tested (with one test run at liquid N\textsubscript{2} temperature) for the purpose of further investigating the anomalous value of the $g$ factor which has been obtained for various iron samples in other laboratories. Some details are given below.

**Measurements at 10-cm Wavelength.** Work in this frequency range on paramagnetic salts has been so far limited to the study of powders. This has been due to limitations on sensitivity caused by the large size of a simple 10-cm resonant cavity as compared to the size of the usually available single crystals. Modification of cavity design will allow small single crystals to be studied at 10 cm at a later date. Measurements on CuSO\textsubscript{4} 5H\textsubscript{2}O powder give results which are consistent with our earlier results at 3 cm. Chromic potassium alum and ferric alum powders have also been tested at 10 cm, but useful interpretations of the results will be possible only when single crystal measurements can be made.

**Permalloy.** A sample of annealed permalloy (loaned to us by the Bell Telephone Laboratories) is now being tested. Since permalloy has essentially no anisotropy, determination of the $g$ factor is somewhat simpler than in the case of the single crystal of iron which we have previously tested. The frequency for resonance absorption in iron, according to the equation of Kittel, is proportional to $(BH)^{\frac{3}{2}}$. Since the proper value to use for $B$ is somewhat uncertain, we are testing the sample at both 1 and 3 cm, in order that $B$ may be eliminated from the equation. Difficulty in the exact evaluation of $g$ has been encountered due to the rather large width of the resonance of the sample. This difficulty is being resolved and it is believed that an accurate evaluation of the $g$ factor will soon be available.

**D. MICROWAVE SPECTROSCOPY**

Professor A. G. Hill  
Professor G. G. Harvey  
Dr. Y. Beers  
Dr. R. L. Kyhl  
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R. E. Hillger  
J. G. Ingersoll  
R. B. Lawrence  
C. C. Loomis  
M. Weiss

The study of molecular absorption in the microwave region has already covered a wide area of problems. Techniques for observing the absorption have been studied and developed, but the main effort has been directed to a study of the use of absorption data. Various types of absorptions and molecules have been studied so that a working familiarity with the broad field of microwave spectroscopy has been developed.
In order to put the work continuing at present in proper perspective, it is well to review some past work done at this Laboratory.

The ammonia inversion, or vibration, absorption has been studied in conjunction with others in the field. Precise frequencies were measured for some 30 transitions to serve as frequency standards in the 1 - 1.5 cm region. The nuclear quadrupole interaction was also studied and has been reported.

The oxygen band of absorption at 5 mm has been investigated at high pressures and this research is being written for publication in the near future. This absorption is due to electron spin-rotational orbit interaction.

Pure rotational absorption in linear molecules has been studied in the case of OCS and OCSe. The OCS work has been published as RLE Technical Report No. 59, and the report on OCSe work is in preparation. The OCSe analysis has shown that in addition to molecular structure, the nuclear spin, and quadrupole information, absorption measurements may be used to deduce vibration frequencies, isotopic abundances, dipole moments, and variation of dipole moments with vibrational state, quadratic and cubic vibration potential force constants, and as yet to a limited degree, the mass of atoms themselves.

Work on very asymmetric molecules as H₂O and HDO has also shown that even in these complicated molecules, measurements of the dipole moment, change of dipole moment with rotational state, and in HDO even the HOD angle for each rotational state may all be measured with facility. This work will also be published as an RLE report.

Work has also been done on the problem of observing absorptions at high temperature, to allow observation of substances that are solids at room temperature, and also the rotational absorption of molecules in highly excited vibrational states. Although this work was delayed for some time, it is expected to yield results in the near future.

Work in rotational absorption due to nearly symmetric tops such as pyridine is being continued to allow the analysis of a rather complicated absorption scheme with a complex molecule. Such a study will provide a yardstick with which to measure the analytic ability of microwave spectroscopy.

Some studies of system sensitivity have been made and it appears that absorption coefficients $\alpha'$ of the order of $10^{-8}$ cm$^{-1}$ may be measured with ease, and that with more difficulty, i.e., observation times of the order of 1 second, $\alpha'$s of $10^{-10}$ cm$^{-1}$ may be measured. This is very close to the theoretical limit of sensitivity.

1. The reduction in power in an electromagnetic wave in passing through an absorbing gas a distance $\ell$ is given as

$$ P = P_0 e^{-\alpha' \ell} $$
Work is continuing on the problem of expanding the scope of microwave absorption measurements. This work has been discussed in the previous progress report and continues. The cavity system being assembled is designed to allow absorption studies to be made with small samples of gas, for example, containing radioactive nuclei. Since the sample is so compact, studies of the absorption in gases in a strong magnetic field, i.e., the Zeeman effect, will also be pursued with this apparatus.

Finally, considerable progress has been made in extending the useful frequency range over which absorptions may be studied. A system using as a power source the third harmonic energy produced in a non-linear silicon crystal which is driven with 1-cm klystron power has been completed. This system at present can detect absorption in the 60,000 to 90,000 Mc/sec region and it will allow us to observe rotational spectrum of light molecules, and to extend considerably the region over which absorption data on heavier molecules may be taken. A search has been made for the \( J = 0 \) to \( 1 \) transition in the rotation spectrum of formaldehyde \((\text{H}_2\text{CO})\). This was thought to provide a convenient first molecule for the 60,000 to 90,000 Mc/sec system. The molecule behaves almost like a linear rotor, and the infrared vibration spectrum has been resolved so that the transition in question is accurately predicted to fall at 72,900 Mc/sec. Two strong lines were observed at 72,470 Mc/sec and 72,810 Mc/sec. Commercial paraformaldehyde was used as the source of formaldehyde vapor. The two lines can hardly be explained by a doubling of the line being sought. Tests are continuing.

A signal of useful amplitude has been obtained to 86,000 Mc/sec by quadrupling from 21,500 Mc/sec, using the tripling components. This offers hope that intense lines may be observable soon in the 90,000 to 120,000 Mc/sec range.

Work on atomic absorption spectra is also continuing in the cesium and hydrogen measurements. Until we obtain results, we shall emphasize the experimental rather than interpretational features of the problem.

Several runs have been attempted in order to measure the hydrogen hyperfine structure, but apparatus difficulties have prevented the obtaining of results so far. Steps are being taken to remedy the troubles (mainly with an FM receiver) and a clean run should be possible very soon.

The yield of atomic hydrogen from the r-f arc source has been measured, by using the heating effect when recombination takes place on a platinum foil inside the cavity. At the time of the measurements it was found that slightly over 30 per cent of the molecules were dissociated; since that time, there is reason to believe that this yield has been doubled. It was observed that electrolytic zinc apparently does not recombine atomic hydrogen drastically, a fact which may be of use to other experimenters.
Work on caesium hyperfine absorption spectrum recently has been resumed after a lapse of several months. There are, however, no new results to report. The principal problem continues to be the construction of leak-proof cavities. Cavities of two different designs are being built; one containing a vacuum-tight quartz container; the other with a mica window with a water-cooled cement joint. Some improvement has been made in the circuits for stabilizing oscillators. A study of fluctuations in the apparatus has also been made.