V. RADIO-FREQUENCY SPECTROSCOPY

A. MOLECULAR-BEAM RESEARCH

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1. The Fourth Atomic-Beam Apparatus

The difficulties in the double mass spectrometer have been resolved. After replacing the collimating slit between the mass spectrometer magnets with one which possessed very thin slit jaws, the ion beam was found to decrease slowly enough with time to permit the experiments to be undertaken.

The monel source was loaded with a charge of 5 millicuries of $Cs_2^{134} Co_3$ and a corresponding amount of metallic Na. When this source was heated to 215° C, satisfactory beam intensities were obtained. With the deflection magnets on, and with an obstacle wire in position, the beam intensity was reduced by a factor of 100. This factor times the mass spectroscopic enrichment factor per mass number at mass number 134, still gave a total enrichment of only 10^4. This meant, since the Cs^{134} existed only in 2 parts in 10^5 parts of Cs^{133}, that at the Cs^{134} mass number there would be 5 atoms of Cs^{133} background for every Cs^{134} atom in the beam. Since this factor could not be improved, an attempt was made to observe Cs^{134} transitions.

With the deflecting magnets on, the frequency of transition for Cs^{133} atoms was measured. Since the frequencies of transition of Cs^{133} and Cs^{134} would be in the ratio of $2I_{134} + 1/2I_{133} + 1$, it was possible to look for the Cs^{134} transitions at frequencies corresponding to different assumed values of the spin I. A search for Cs^{134} transitions was made at the frequencies corresponding to all the integral spin values from 0 to 7.

At no value of the spin except 0 was there any indication of transitions but at the frequency corresponding to I = 0 there seemed to be an audible increase in counting rate. It was impossible to obtain satisfactory resonance curves, due to fluctuations in the background. Rough transition curves were obtained, indicating that it was quite probable that transitions were being observed. These curves, combined with the fact that tuning through the resonance seemed to result in repeated audible indication at the same frequency, established with a small degree of uncertainty that the resonance corresponding to I = 0 was being observed.

If these transitions were real, it is possible to assign an upper limit for the value of the nuclear magnetic moment. A simple calculation, based on the width of the observed resonance, enables one to assign an upper limit of $2.5 \cdot 10^{-4}$ nuclear magnetons for the value of the nuclear magnetic moment of Cs^{134}. It is impossible to say that the nuclear spin is equal to zero, for the observed transitions can be explained by merely assuming that the nuclear magnetic moment is small enough for the nuclear moment and

electronic moment to be completely decoupled at the values of magnetic fields used.

Since there is some uncertainty in the above results, and since this uncertainty is due to the very small concentrations of Cs^{134} available, it was decided to attempt to obtain a richer sample of Cs^{134}. The Isotopes Division of the AEC has undertaken to supply us with pile-produced Cs^{134} in approximately 10 times the concentration used in this experiment. This sample will be available early in the summer, and work with the new material will start early in June. At that time a complete report of the work will be prepared. T. M. Hahn, Jr.

B. NUCLEAR MAGNETIC RESONANCE

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1. Optical Detection of Radio-Frequency Resonance in Excited Atomic States

Attention has recently been drawn to the possibility of an optical detection of r-f resonance (1). A further analysis has shown that the effects to be expected on the position of the lines and on the intensities of a Zeeman pattern are exceedingly small (2). The possibility of selectively exciting the magnetic sublevels (3) has led to a method of detection which is described below and which we have used successfully in the case of the excited state $^3P_1$ of mercury.

Polarized radiation of a suitable frequency will excite an atom in a magnetic field to one or more of the sublevels in its first excited state in accordance with the selection rules

$\Delta m = 0$ gives rise to σ-components with the electric vector perpendicular to the field;

$\Delta m = \pm 1$ gives rise to π-components with the electric vector parallel to the field.

The re-emitted resonance radiation will in general be polarized. The degree of this polarization can be altered by the absorption of r-f energy capable of changing the m-value of the atom in its excited state. The field and frequency at which this depolarization occurs can be used to estimate atomic and nuclear moments, as in atomic beam experiments. The main difference is that in atomic beams the structure of the ground state may be analyzed; in the optical experiment, it is an excited state that is involved. New measurements are therefore possible, but due to the generally short lifetimes of excited atoms, broad resonance lines are to be expected.

The case of the resonance radiation 2537 Å of the even isotopes of mercury is

particularly simple. The line is a $^1S_0 - ^3P_1$ transition (Fig. V-1) and has three Zeeman components. By π-excitation it is possible to raise the atom to the middle upper state. When the atom radiates after about 10^{-7}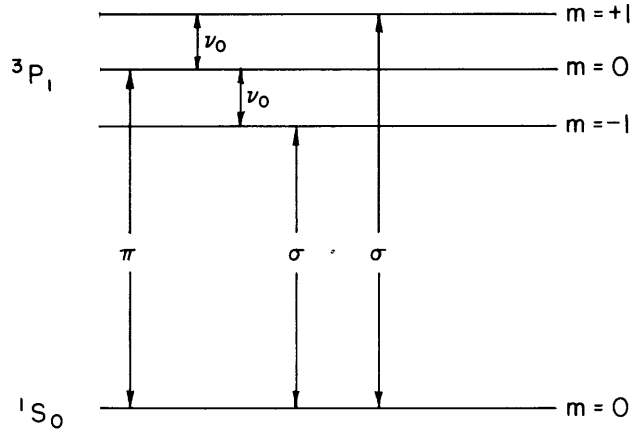 sec, it re-emits only this π-component (unless collisions transfer it to the state m = $\pm$1). When viewed along the magnetic field this component is not visible. If an r-f field of the frequency ν_0 is applied, some induced transitions to the levels m = $\pm$1 will take place and from there the atoms fall back to the ground state emitting σ-components which are visible in the field direction. This effect can be used to detect magnetic resonance in the upper state. In other words, the r-f field, when it reaches the proper frequency ν_0, tends to equalize the populations of the magnetic sublevels. This appears as a change in the degree of polarization of the resonance radiation emitted.

Fig. V-1 The Zeeman pattern of resonance line of Hg.

The problem is then to induce a transition within the life of the excited state. Majorana's formula shows that in our experiment transition probabilities of the order of 1/2 can be achieved when the amplitude of the r-f field H_0 is about 2 gauss.

This experiment has been performed with ordinary mercury, and has completely confirmed our expectations. The work is in an exploratory state, and the results given below are preliminary.

A resonance has been observed for the even isotopes of mercury at the expected field and frequency.

The width of the resonance was found to increase with the amplitude H_0 of the r-f field.

For high values of H_0 a saturation effect was observed, resulting in a dip in the center of the line. This minimum disappears for lower values of H_0.

For small values of H_0 the half-width of the line will yield directly the half-width of the $^3P_1$ level. At 144 Mc, the frequency used, this may be calculated from optical data to be of the order of 1.8 gauss. Comparable line widths were observed.

A resonance has been observed for Hg^{199} under conditions to be expected for its nuclear spin of 1/2. The observed line corresponds to resonance among the levels having F = 3/2. For the conditions of the experiment no line is to be expected for the F = 1/2 levels, and none was found.

The magnet used was a water-cooled air core solenoid run on storage batteries, and capable of producing fields up to about 1000 gauss.

The crystal controlled oscillator operates between 100 and 150 Mc with a power output of about five watts. The r-f field is at right angles to the constant field, and is produced by two coils outside of the resonance lamp.

F. Bitter, J. Brossel, P. Sagalyn

References

(1) F. Bitter: Phys. Rev. 76, 833 (1949).

(2) M. H. L. Pryce: Phys. Rev. 77, 136 (1950).

(3) J. Brossel, A. Kastler: Comptes Rendus, 229, 1213 (1949).

2. Factors Influencing the Positions of Nuclear Magnetic Resonances

Nuclear resonance positions for chemical compounds of several different elements are being observed in an effort to detect effects similar to those observed in fluorine (see last Quarterly Progress Report). Shifts of 1.3 gauss in a field of 5800 gauss have been observed in phosphorus compounds; the resonance occurs in one position when phosphorus exhibits a valency of +3 and in the other for a valency of +5. The origin of these small molecular fields seems to be in a high-frequency, temperature-independent paramagnetism which always is present in polyatomic molecules. Although this paramagnetic term is usually less than the diamagnetic term in the expression for the magnetic susceptibility, its effect at a nucleus in such a molecule could be appreciable. The field dependence of these shifts has been checked in the case of fluorine. The magnitude of the shifts was found linearly proportional to the field strength.

W. C. Dickinson

3. Liquid Nitrogen Magnet

The small iron magnet designed to be cooled by liquid nitrogen has been used at room temperature to give resonances in oil. With the coils in series, 3.0 amp give 1000 gauss and the field is homogeneous to one gauss over a sample 5 mm in diameter by 5 mm in length. The resistance of each coil is 0.8 ohm at room temperature and is 0.1 ohm at nitrogen temperature. Saturation becomes evident at 8000 or 9000 gauss; the maximum field obtained was 12,000 gauss for a current of 41 amp. Thus at room temperature we can obtain 1000 gauss for 15 watts. At the temperature of liquid nitrogen we can obtain 1000 gauss for 5 watts, 6500 gauss for 70 watts, and 12,000 gauss for 340 watts. The initial cooling of the magnet and its container (a large glass dewar) takes some 10 to 12 liters of liquid nitrogen.

N. I. Adams III

4. Simplified Circuit for Nuclear Magnetic Resonance Experiments

After trying several different types of null circuits in an effort to find one which yields satisfactory control of line shape and at the same time gives optimum signal-to-noise ratio, the bridged-T (Fig. V-2) circuit was arrived at. Similar circuits have been used at the Brookhaven Laboratory and by R. H. Spencer of the University of Connecticut.
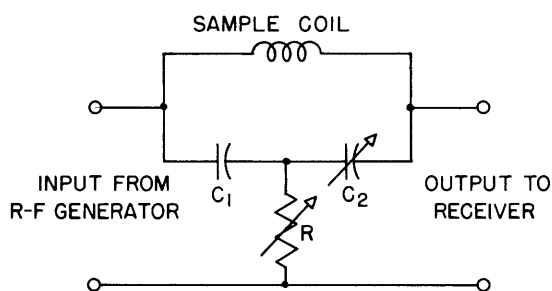
This type of null circuit has the advantage of eliminating bulky half-wave lines or r-f transformers which were previously used. Also the entire circuit can be built into one box small enough to be located easily in the magnetic field. Stray capacitance problems and microphonics are easily eliminated in this circuit because of its minimum of leads and components. Analysis shows that the signal-to-noise power ratio at the sample coil is reduced by a factor of two for the symmetrical bridged-T, but will approach unity if C_1 is made larger than C_2 (Fig. V-2). In any of the bridge circuits used previously this factor is generally greater than two.

Fig. V-2 Nuclear resonance circuit.

One such circuit was assembled and tested at 4.5 Mc. A balance of 80 db was obtained with ease and showed no tendency to drift. A proton-resonance was obtained and line shape was easily and smoothly changed from the absorption type to the dispersion type as displayed on an oscilloscope.

T. F. Wimett

C. MICROWAVE SPECTROSCOPY

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J. R. Eshbach	J. G. Ingersoll	M. T. Weiss
	H. R. Johnson	

1. Intensity Measurements and Line Shapes of Formaldehyde

We have made a precision measurement of the pressure broadening of the $17_{3,15} \rightarrow 17_{3,14}$ line of formaldehyde at 24068.31 Mc/sec in the 10-70μ pressure region. The results of this measurement and knowledge of the structure parameters of formaldehyde permit an absolute calculation of the microwave absorption coefficients for this molecule by use of the Van Vleck-Weisskopf formula (1).

A principal parameter in the Van Vleck-Weisskopf formula is the half-width at half intensity, $\Delta \nu$. This quantity is simply related to the mean time between
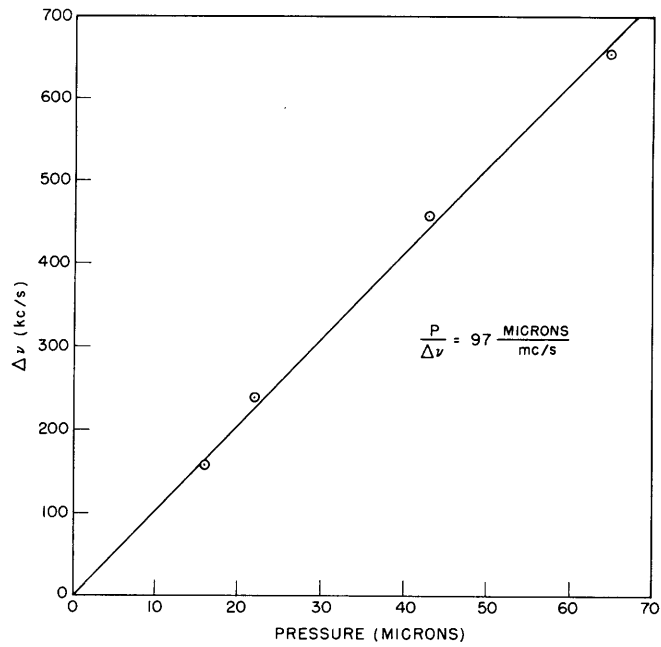
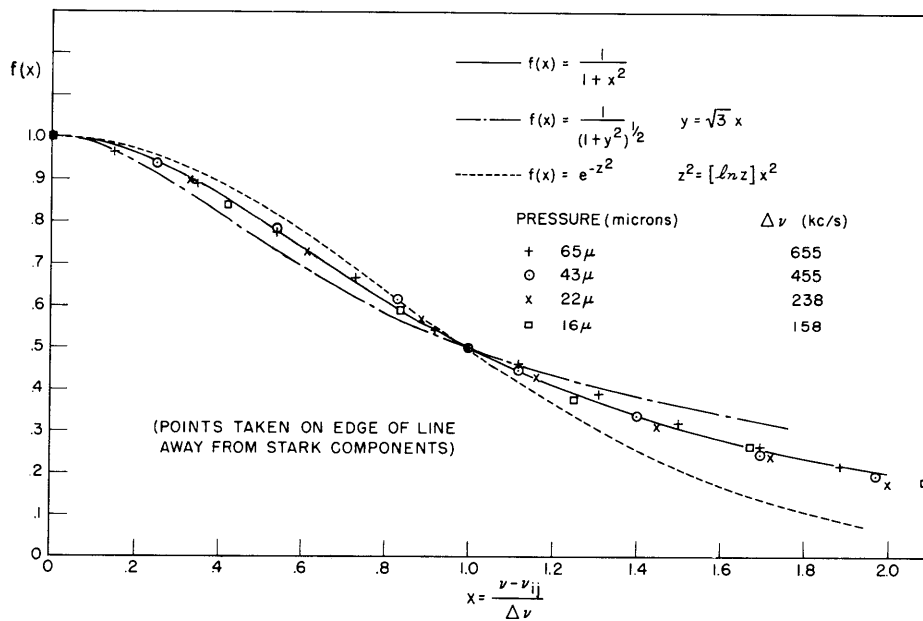Fig. V-3 Pressure broadening of formaldehyde line.

Fig. V-4 Line shape of $17_{3,15} \rightarrow 17_{3,14}$ H_2CO line at 24068.31 Mc/sec.

radiation-disturbing collisions, which, as remarked by Van Vleck (2), is not necessarily the mean time between momentum-transferring collisions. Since all other quantities in the formula are known and since $\Delta\nu$ is proportional to the pressure, it turns out that the only unknown factor is $P/\Delta\nu$, which we have measured experimentally.

Our experimental results are displayed in Fig. V-3. The slope of the curve is $P/\Delta\nu = 97\ \mu/Mc/sec$. This measured value is about two and one-half times greater than the estimated value used in calculating the previously reported absorption coefficients (3). Since an additional factor of 3 was inadvertently omitted from the previous calculations, those values should be multiplied by a net factor of 7.28.

The line width measurements were made with a slow sweep recording spectrograph and are considered to be accurate to 15 kc/sec. Because of the large intensity of the line studied ($\alpha = 3.2 \times 10^{-5}\ cm^{-1}$) and the use of a very narrow band receiver, the recordings were practically noise free and afforded the opportunity for an interesting comparison of line shape with that predicted by the Van Vleck-Weisskopf formula. Assuming a square law crystal response and a shape factor given by the above-mentioned formula, the response of the system should be $1/(1 + x^2)$, where x is the departure from resonance expressed as a fraction of $\Delta\nu$. Each of the curves corresponding to the four pressures of Fig. V-3 was analyzed and the results are shown in Fig. V-4. The agreement is excellent, especially in the outer skirts. The curves $1/(1 + 3x^2)^{1/2}$ and $e^{-(\ln 2)x^2}$ are also shown for comparison.

We consider that the determination of line intensities by the above method was limited by the accuracy of the pressure measurements. The pressure was measured with a McLeod gauge and no corrections were attempted for possible deviations from the perfect gas law at room temperature. A room temperature of 300°K was assumed in the calculations.   R. B. Lawrance, J. R. Eshbach

References

(1) J. H. Van Vleck, V. F. Weisskopf: Rev. Mod. Phys. 17, 227 (1945).
(2) J. H. Van Vleck: Phys. Rev. 71, 416 (1947).
(3) Quarterly Progress Report, Research Laboratory of Electronics, M. I. T., p. 35, Jan. 15, 1950.

2. Precision Stark Measurements

Precise Stark-effect measurements to refine previous work (Technical Report No. 59, Research Laboratory of Electronics) have been carried out with the molecule carbonyl sulfide, OCS. The measurements of the perturbation of the rotational absorption fre--quency due to an external, uniform, electric field yields a value for the electric dipole moment of the molecule if the electric field strength is known. The determination of

the electric field depends upon an exact knowledge of the absorption cell geometry, and the voltage applied to an insulated electrode. Mr. Ingraham constructed a waveguide with a flat, insulated electrode along one wall. The electrode is mechanically stable, and the separation between it and the opposite wall of the guide has been determined. This measurement was made using a strain gauge designed by Mr. Atchley. The guide dimensions so determined were also corrected for flexure of the walls when the guide is evacuated. The accuracy is such that the mean square separation may be determined to 2 parts in 1000.

The Stark effect for the $J = 0 \rightarrow 1$ and $J = 1 \rightarrow 2$ transitions were measured with this guide. The applied potential for the $J = 1 \rightarrow 2$ transition was a zero-based square wave, while for the $J = 0 \rightarrow 1$ transition a direct potential with a small square wave superimposed on it was used. The magnitude of the peak potential for the $J = 1 \rightarrow 2$ transition was determined by comparison with a d-c source by means of a direct coupled oscilloscope. The d-c potential in turn was measured with an accurate (0.05 percent) resistor divider and type-K L-N potentiometer. The average potential applied to the Stark electrode for the $J = 0 \rightarrow 1$ transition was determined directly by use of the resistance divider and the type K potentiometer. The mean square potential may then be calculated if a rough value is known for the small superimposed square wave potential.

A further correction due to field inhomogeneities due to the guide geometry may be applied to the field calculated from these potentials and the previously determined spacings.

The values of the dipole moment so determined for a series of runs on both the $J = 0 \rightarrow 1$ and $1 \rightarrow 2$ transitions may be given as

$$\mu_{0 \rightarrow 1} = 0.707 \pm 0.0035 \text{ Debye at 1500 volts applied}$$

$$\mu_{1 \rightarrow 2} = 0.714 \pm 0.0035 \text{ Debye at 650 volts applied}$$

$$\mu_{1 \rightarrow 2} = 0.711 \pm 0.0035 \text{ Debye at 1350 volts applied}$$

$$\mu_{OCS} = 0.711 \pm 0.0035 \text{ Debye}$$

The $J = 0 \rightarrow 1$ transition of OCS occurs at the frequency $\nu = 12,162.97$ Mc/sec. Absorption lines were discernible for the isotopes $O^{16}C^{12}S^{34}$ and $O^{16}C^{13}S^{32}$, and for the first vibrational state a_1 $(O^{16}C^{12}S^{32})$. Theory predicts that the second degenerate vibrational state a_2 (1 − doublet) should not exist for a state with $J = 0$. There has been some conjecture over this matter and hence a search was made for this absorption. If the state existed, its intensity should be greater than the a_1 and $O^{16}C^{13}S^{32}$ absorption. No a_2 was to be found while a_1 and $O^{16}C^{13}S^{32}$ were readily discernible, hence we are forced to the conclusion that the theory is correct!

R. E. Hillger, R. B. Lawrance

3. Sulphur

The microwave absorption spectrum of HDS has been resolved and twelve absorption lines have been accurately measured (including S^{34} isotopic HDS) for values of J ranging from one to twelve. Calculations are proceeding to determine the centrifugal distortion corrections and the values of the physical constants a, b and c of this molecule.

R. E. Hillger