

V. RADIO-FREQUENCY SPECTROSCOPY

A. MOLECULAR-BEAM RESEARCH

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1. The Fourth Atomic-Beam Apparatus

The fourth atomic-beam apparatus has been completed, and is in operation. A beam has been obtained through the apparatus, and r-f transitions have been observed.

A potassium beam was used to align the apparatus. As a check on the operation of the apparatus and its associated circuits, the nuclear spin of naturally radioactive K^{40} was measured. A value of 4 was obtained for the spin, which is in agreement with the results of Zacharias (1). As K^{40} exists in a concentration of only 1 part in 10^4 parts of K^{39} , the ease with which this experiment was done illustrates the extremely high resolution of this apparatus. The enrichment factor of the double mass spectrograph, described in the Progress Report, October 15, 1949, has been found to be 10^5 , one mass number away from the K^{39} position.

It was hoped that the nuclear spin and magnetic moment of radioactive Cs^{134} could be measured with this apparatus. These data would be valuable as a check on β -decay theory, as well as of interest in regard to shell structure of heavy nuclei. This is particularly true since the nuclear constants of Cs^{133} , Cs^{135} , and Cs^{137} are all known (2). An aliquot of $Cs_2^{134}CO_3$ was obtained from the Isotopes Division of the Atomic Energy Commission. Satisfactory beams of atomic Cs have been obtained in the apparatus by using as a source an oven containing a mixture of Cs_2CO_3 and metallic Na. When the oven is heated to temperatures of the order of $180^\circ C$, the Cs is replaced in the Cs_2CO_3 by the Na, thus producing a beam of free Cs atoms. However, since the Cs^{134} exists only in a concentration of 1 part in 10^5 parts of the isotope Cs^{133} , the apparatus as yet possesses insufficient resolution to resolve the Cs^{134} . This is true because a change of one mass number at the Cs mass number represents less than a third of the fractional change at the K mass number. The mass spectrographic enrichment factor is found to be only 100, one mass number away from the Cs^{133} position, as compared to a value of 10^5 at the K^{39} position.

Consequently, an attempt is being made to improve the mass spectrograph resolution. It has been found that there is a large amount of electrostatic scattering of the ion beam. Glass ports in the apparatus, as well as the

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insulation on the mass spectrograph windings, were found to be acquiring an electric charge and scattering the beam. The glass ports were all replaced with brass, and the mass spectrograph windings were shielded. This resulted in a quite noticeable improvement. However, there still remains a large amount of scattering. Part of this is thought to be due to oil from the diffusion pumps which has condensed in the interior of the apparatus. This is quite possible despite the water-cooled baffles in all the pumps. A large amount of the scattering is found to occur at the collimating slit between the two mass spectrographs, although this slit is well grounded. Experiments are now in progress to determine whether or not this scattering is due to actual condensation of the beam itself on the slit jaws.

T. M. Hahn, Jr.

References

- (1) J. R. Zacharias, Phys. Rev. 61, 270 (1942).
- (2) L. Davis, Jr., D. E. Nagle, and J. R. Zacharias, Phys. Rev. 76, 1068 (1949).

B. NUCLEAR MAGNETIC RESONANCE

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1. Factors Influencing the Positions
of Nuclear Magnetic Resonances

A study is being made of possible shifts in the value of the applied magnetic field H_0 for nuclear magnetic resonance, for a fixed value of radio frequency. The resonance condition is most simply written

$$\omega = \gamma H_{loc} \quad (1)$$

where ω is the angular Larmor frequency of nuclear precession in the constant magnetic field H_{loc} and γ is the nuclear gyromagnetic ratio. The field H_{loc} is not the applied magnetic field but the actual magnetic field seen by the nucleus. It can be thought of as consisting of four components

$$H_{loc} = H_0 + H' + H'' + H''' \quad .$$

H_0 is the "external field" of the magnet. H' is the small diamagnetic field at the nucleus due to the Larmor precession of its atomic electrons

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in H_0 . This effect may be thought of as a shielding of the nucleus by the outer electrons. It should not be confused with the ordinary diamagnetic effects which result in a general diminution of field strength and need not be considered further. H'' is the additional magnetization field due to any paramagnetic ions that might be added to the sample for the purpose of shortening the thermal relaxation time of the nuclei. H''' is any other small field that might be a function of the chemical composition of the sample containing the nuclei. Each of these fields will now be more closely considered.

a. H_0

Referring to Eq. (1), since ω can be measured with much greater accuracy than can H_0 it is preferable and also convenient to compare the value of ω with that of some standard nucleus (usually the light hydrogen nucleus) in the same external magnetic field. It is necessary however to insure that the external field H_0 seen by the two types of nuclei is the same. This is best accomplished by using one sample containing both types of nuclei (1).

b. H'

This shielding field cannot be experimentally determined since there is no way of stripping the atom of its extranuclear electrons. However it can be shown by a simple calculation to be

$$H' = \frac{eH_0}{3mc^2} \int_0^{\infty} \frac{\rho'(r)}{r} dr \quad . \quad (2)$$

$\rho'(r) dr$ is the charge lying between r and $r + dr$, where r is the distance from the nucleus outward. The expression under the integral is just the potential at the nucleus of the negative distribution of charge due to the outer electrons and is of course negative. In general, it can be most accurately determined using the Hartree atomic model. This has been done by the author for those atoms which have been treated by the Hartree method (about 25). If H' is then plotted vs. atomic number Z a smooth curve can be drawn and values of H' for other atoms found by interpolation. To correct a measured ratio for this effect the factor

$$\frac{1 - \left(\frac{H'}{H_0}\right)_{\text{hydrogen}}}{1 - \left(\frac{H'}{H_0}\right)_{\text{nucleus}}}$$

must be multiplied with the experimentally determined value of γ/γ_p .

c. H''

It has been assumed by workers in this field that if both types of nuclei were in the same sample, they would see the same field H'' due to added paramagnetic ions and hence its effect would cancel in a measurement. Or, if only one type of nucleus was contained in the sample it was assumed that by using a spherically shaped sample the field H'' would be zero due to the fact that the demagnetization field $(4\pi/3)M$ should be equal and opposite to the "cavity" field in which the nucleus is situated. However it has been found in the present study that both of these assumptions are untenable. It is found that the shift in resonance due to paramagnetic ions depends both in magnitude and sense on the resonating nucleus and also on the chemical compound in which it is contained. It depends linearly on concentration of the paramagnetic ions as expected. Also shifts have been observed on the addition of paramagnetic ions to spherically shaped samples. A fuller exposition of these findings will be made in a future report.

d. H'''

Most unexpectedly, it has been found that the nuclear resonance frequency depends on the chemical compound which contains the nucleus. This effect has never been observed or predicted previously for liquids, the assumption being made that the time average of all internal magnetic fields (excluding those of added paramagnetic ions) was zero. Shifts in nuclear resonances have been observed (2) in metals but can be qualitatively explained by the paramagnetic effect of the conduction electrons in the vicinities of the metal nuclei.

Figure V-1 is the trace of two nuclear resonances, both due to the fluorine nucleus, as the magnetic field H_0 (~ 7000 gauss) is slowly increased. The sample contained a mixture of BeF_2 and SbF_3 in aqueous solution. No paramagnetic ions were present. When the two compounds are mixed together the fluorine nucleus in BeF_2 resonates at an applied field which is (0.82 ± 0.03) gauss higher than for the fluorine nucleus in SbF_3 . However when the resonances are observed in separate samples of BeF_2 and SbF_3 they are separated by (0.99 ± 0.03) gauss. Figure V-2 shows more completely the dependence of resonance field on the chemical compound containing the fluorine. SbF_3 gives a resonance at the lowest applied field of those compounds observed so far. An interesting fact is, that although the resonances in HF and SbF_3 are separated by 0.83 gauss, a 50-50 mixture of the two gives

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only one resonance located halfway between the positions where the two resonances would occur if in separate samples. Increasing the relative amount of SbF_3 shifts the resulting resonance toward the position of the resonance

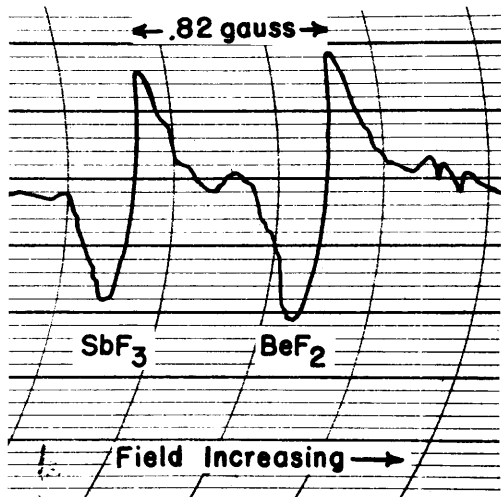


Fig. V-1 Both resonances are due to F^{19} in a single sample containing an aqueous solution of SbF_3 and BeF_2 . The resonance frequency ≈ 28 megacycles and the magnetic field is slowly varied in the region of 7000 gauss.

in pure SbF_3 . It has not yet been determined whether the shift of resonance is proportional in magnitude to the magnetic field used. The shifts observed

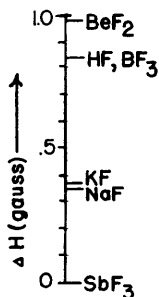


Fig. V-2 Dependence of fluorine resonance field on chemical compound. Resonance in SbF_3 arbitrarily taken as origin.

for $H_0 \approx 7000$ gauss constitute an effect of about 0.01 percent. The diamagnetic correction H'/H_0 for fluorine is equal to 0.046 percent. It will be slightly dependent on the ionic form of the fluorine atom in the solution but the difference $\Delta H'/H_0$ between the negative fluorine ion and the neutral atom is only about 0.0008 percent. (Both F and F^- have been treated by the Hartree method.) Therefore another cause must be found for the observed shifts.

Various explanations for these shifts are now being considered and will be more fully reported in the near future.

W. C. Dickinson

References

- (1) W. C. Dickinson and T. F. Wimett, Phys. Rev. 75, 1769 (1949).
- (2) W. D. Knight, Phys. Rev. 76, 1259 (1949).

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2. Deuteron-Proton Moment Ratio

In the process of adjusting field uniformity of the Helmholtz coils to be used in this measurement, proton resonance line widths of about 0.01 gauss in a field of 1000 gauss have been obtained and reproduced on successive days without readjustment of the field coils. The resonances were obtained in an oil sample of approximately 1 cm³ in volume. Difficulties have been encountered in observing such narrow lines because of frequency and field fluctuations caused by temperature drifts in the r-f generator and field coils, and by contact troubles in the field current supply circuit. Crystal-controlled oscillators are being assembled with crystal ovens in order to control frequency drift, and the contact troubles are being eliminated. With these factors under control, it is expected that more precise field adjustments will lead to still narrower line widths.

T. F. Wimett

C. MICROWAVE SPECTROSCOPY

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Dr. R. B. Lawrance	H. R. Johnson
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M. T. Weiss

1. Formaldehyde

The accompanying table gives all of the presently known absorption frequencies of H₂C¹²O and H₂C¹³O, together with approximate values of the absorption coefficient.

As indicated in the Progress Report, October 15, 1949, the great accuracy and large number of these measured frequencies affords an excellent opportunity for evaluating the frequency shifts due to centrifugal distortion. For the $\Delta J = 0$, $\Delta K = 0$ transitions of a non-rigid asymmetric top molecule with small asymmetry parameter δ , the distortion correction ν_d can be shown to be the following:

$$\nu_d \equiv \nu_c - \nu_t$$

$$\nu_d = \nu_c \left[(X_j + X_{jk}K) J(J+1) + (X_k + X_{kk}K)K^2 \right]$$

where ν_t is measured "true" frequency, ν_c is calculated rigid-rotor frequency,

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 ABSORPTION FREQUENCIES OF $\text{H}_2\text{C}^{12}\text{O}$ AND $\text{H}_2\text{C}^{13}\text{O}$
 WITH APPROXIMATE VALUES OF ABSORPTION COEFFICIENT

Freq. (Mc/s)	$\text{H}_2\text{C}^{12}\text{O}$ (Pure)	
	Transition	Abs. Coeff. (cm^{-1})
7,362.60	$22_{4,19} \rightarrow 22_{4,18}$	4.7×10^{-8}
7,892.03	$14_{3,12} \rightarrow 14_{3,11}$	9.6×10^{-7}
8,884.87	$7_{2,6} \rightarrow 7_{2,5}$	1.0×10^{-6}
10,366.51	$23_{4,20} \rightarrow 23_{4,19}$	7.1×10^{-8}
11,753.13	$15_{3,13} \rightarrow 15_{3,12}$	1.7×10^{-6}
14,361.54	$24_{4,21} \rightarrow 24_{4,20}$	1.0×10^{-7}
14,488.65	$2_{1,2} \rightarrow 2_{1,1}$	9.0×10^{-6}
14,726.74	$8_{2,7} \rightarrow 8_{2,6}$	2.2×10^{-6}
17,027.60	$16_{3,14} \rightarrow 16_{3,13}$	2.8×10^{-6}
19,595.23	$25_{4,22} \rightarrow 25_{4,21}$	1.4×10^{-7}
22,965.71	$9_{2,8} \rightarrow 9_{2,7}$	4.3×10^{-6}
24,068.31	$17_{3,15} \rightarrow 17_{3,14}$	4.4×10^{-6}
26,358.82	$26_{4,23} \rightarrow 26_{4,22}$	1.8×10^{-7}
28,974.85	$3_{1,3} \rightarrow 3_{1,2}$	2.5×10^{-5}
48,284.60	$4_{1,4} \rightarrow 4_{1,3}$	5.0×10^{-5}
72,409.35	$5_{1,5} \rightarrow 5_{1,4}$	8.7×10^{-5}
72,838.14	$0_{0,0} \rightarrow 1_{0,1}$	9.8×10^{-5}
	$\text{H}_2\text{C}^{13}\text{O}$ (Pure)	
13,778.86	$2_{1,2} \rightarrow 2_{1,1}$	8.0×10^{-6}
14,592.44	$16_{3,14} \rightarrow 16_{3,13}$	2.0×10^{-6}
20,649.30	$17_{3,15} \rightarrow 17_{3,14}$	3.0×10^{-6}
20,736.30	$9_{2,8} \rightarrow 9_{2,7}$	3.0×10^{-6}
27,555.73	$3_{1,3} \rightarrow 3_{1,2}$	1.5×10^{-5}
28,582.40	$18_{3,16} \rightarrow 18_{3,15}$	5.0×10^{-6}

v_d is distortion correction, and $X_j \dots X_{kk}$ are four constants to be determined.

The fitting process involves adjusting the four constants $X_j \dots X_{kk}$ and the three rotational constants a, b, c . Certain simplifications and converging processes are available and have been exploited, but final results require many computations to eight significant figures. Since these final results are now nearly completed it does not seem worthwhile to give the earlier approximate values in detail, except to mention that their agreement with the general Wilson-Howard theory is quite good. This agreement is of some importance since the present method is entirely independent theoretically and is based on accurate experiments.

Work is continuing on the isotopic formaldehydes, the higher-frequency lines of ordinary formaldehyde, more accurate Stark-effect measurements, and on the vibrational states. The study should eventually result in a rather exhaustive paper.

R. B. Lawrance

2. Oxygen

Two improvements have been attempted on the method of measurement described in the Progress Report, October 15, 1949.

The first was an arrangement for continuous monitoring of the square-wave Zeeman field. Such an arrangement is desirable for two reasons. First, it gives directly the shape of the time-variation of the field (which in general is different from that of the magnetizing current on account of hysteresis effects). It is important that the shape should be approximately square in order that sufficient energy be thrown into the audio signal superimposed upon the r-f by the action of the field. Second, the magnetic field should be zero for half the cycle. Otherwise a spurious line-broadening results. Hence it is necessary to send a reverse current through the magnetizing coils in order to counteract the residual flux in the core. The exact adjustment of the reverse current could best be made by a continuous monitoring arrangement.

A non-linear transformer employing an easily saturable permalloy core was used for monitoring. The arrangement was not very successful. However it was found that the "wave-shape" was sufficiently close to square for all practical purposes and that the adjustment of the reverse current with d-c operation was accurate enough. The continuous monitoring arrangement was accordingly abandoned.

The other improvement that was tried was a slow variation of the frequency of the stabilized oscillator which was effected by changing the

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temperature of the stabilizing cavity. While such a slow sweep system is definitely feasible, it is not certain that it will result in any definite economy of time as compared with point-by-point measurement.

The actual measurements have not been sufficiently extended to deserve reporting.

B. V. Gokhale

3. Tellurium

The search for absorption lines of HDTe has been temporarily discontinued. The small moments of inertia of the molecule, its high degree of asymmetry and the effects of zero point vibrations make prediction of rotational absorption very difficult. No lines were found in the available microwave spectrum attributable to HDTe , and the chemical instability of the compound makes it exceedingly unlikely that it existed at all in the absorption cell.

4. Sulphur

The two impurity lines mentioned in the Progress Report, October 15, 1949, have definitely been identified as belonging to the compound HDS^{32} . Since then, six additional lines have been found, four for HDS^{32} and two for HDS^{34} . All are $\Delta J = 0$ transitions covering a range of J from 2 to 12. Work continues to fill the gaps in this range and to devise a formula predicting centrifugal distortion corrections for any value of J . Isotope shift will be studied for the sulphur isotopes 32, 33, 34, 35 and 36 which, in conjunction with the centrifugal distortion correction, will enable a structural check of the molecule to be made.

Magnets are being constructed to fit X-band guide and produce fields of the order of 5000 gauss in order to study the Zeeman effect of the HDS^{33} stable molecule and the HDS^{35} radioactive molecule. An attempt will be made to measure the nuclear magnetic moments of the S^{33} and S^{35} and to correlate these with the observed quadrupole moment.

R. E. Hillger

5. Methyl Stannane

The search for the spectrum of methyl stannane CH_3Sn has been temporarily halted while the chemical sample is checked in the infra-red spectroscopy. While this test is being made the tripler system has been adjusted for the purpose of measuring the spin and quadrupole moment of antimony and bismuth. The molecules to be used are SbD_3 and BiD_3 .

C. C. Loomis

6. Nuclear Spin of B^{10}

The nuclear spin of 3 for B^{10} was deduced by Gordy, Ring and Burg (1) from microwave observation of the quadrupole hyperfine structure of the $J = 1 \rightarrow 2$ rotational transition of borine carbonyl $H_3B^{10}CO$. The spectrum of this transition is, however, quite complicated because of the K splitting of both the $J = 1$ and $J = 2$ levels of the molecule, thus requiring a best-fit type of interpretation of the observed structure for an exact spin determination. It was therefore felt desirable to observe the much simpler spectrum of the $J = 0 \rightarrow 1$ transition of $H_3B^{10}CO$ to obtain conclusive evidence of the B^{10} spin.

The energy of interaction between a nuclear quadrupole moment and molecular electric fields for a symmetric top molecule is given by (2)

$$E = -eqQ \left[1 - \frac{3K^2}{J(J+1)} \right] \frac{\left[\frac{3}{4} C(C+1) - I(I+1) J(J+1) \right]}{2I(2I-1)(2J-1)(2J+3)}$$

where the symbols are defined in Ref. 2. The rotational quantum number $J = 0$ level is not split by the quadrupole effect while the $J = 1$ level splits into three $\vec{F} = \vec{I} + \vec{J}$ levels each of which in turn is split into two K (quantum number for angular momentum about the symmetry axis) levels as shown in the accompanying energy level diagram. Because of the selection rule $\Delta K = 0$ only three transitions can take place since the $K = 1$ levels, though perturbed, do not partake of $K = 0$ character.

The theoretical quadrupole hyperfine structures for a B^{10} spin of 1, 2 and 3 are shown in Fig. V-4. The relative intensities are calculated from formulas developed for atomic fine structure (3) by the following association of quantum numbers: $L \rightarrow J$, $S \rightarrow I$, $J \rightarrow F$.

The ratio of the frequency separation of the low and the high frequency line from the center line should be 0.666, 0.555, 0.350 or 0.257 for a B^{10} spin of 1, 2, 3 or 4 respectively. Thus by measuring the separation ratio one can with certainty determine the B^{10} spin.

A previous attempt (4) to resolve the hyperfine structure of the $J = 0 \rightarrow 1$ transition

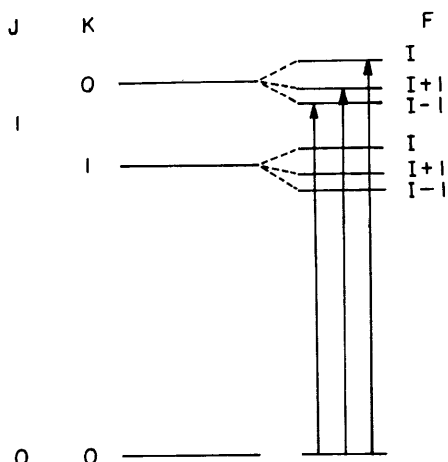


Fig. V-3 Energy level diagram with quadrupole splitting.

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of $\text{H}_3\text{B}^{10}\text{C}^{18}\text{O}$ failed because of sample decomposition at low pressures. In the present investigation, the waveguide absorption cell was kept at dry ice temperature, and by increased sensitivity in the detection system it was possible to resolve the three hyperfine components with the sample at a pressure of about 3μ .

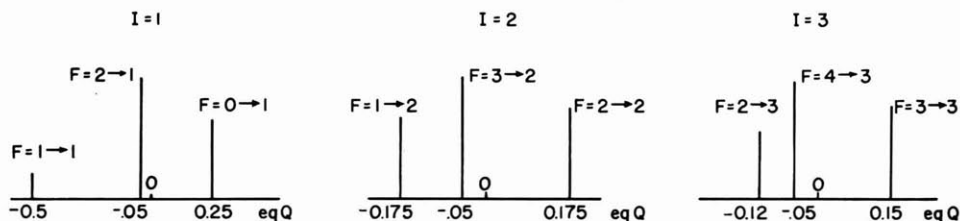


Fig. V-4 Quadrupole hyperfine structure for various spins.

The spectroscope used was described in the Progress Report, October 15, 1949. Fig. V-5(a) shows a photograph of the three observed lines while Fig. V-5(b) shows the degree of resolution of the two low frequency lines. It must be remembered that the oscilloscope sweep is somewhat non-linear. Accurate frequency measurements were made by the method described by Strandberg, Wentink and Kyhl (5).

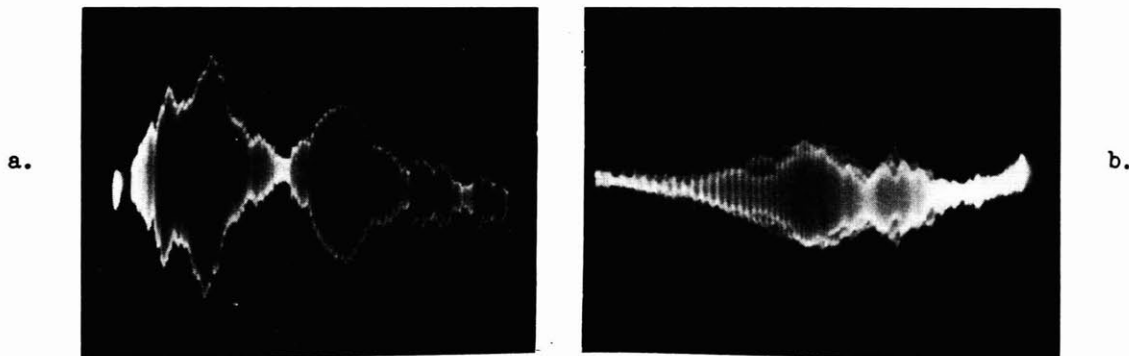


Fig. V-5 Observed $J = 0 \rightarrow 1$ transition.

The observed data is shown in Fig. V-6 and gives a ratio of frequency differences of 0.345 ± 0.015 . This value conclusively determines the B^{10} spin as being 3 since it agrees so well with the theoretical value of 0.350 for this spin value. The quadrupole coupling, eqQ , for this molecule is calculated to be $+3.44 \pm 0.1$ Mc.

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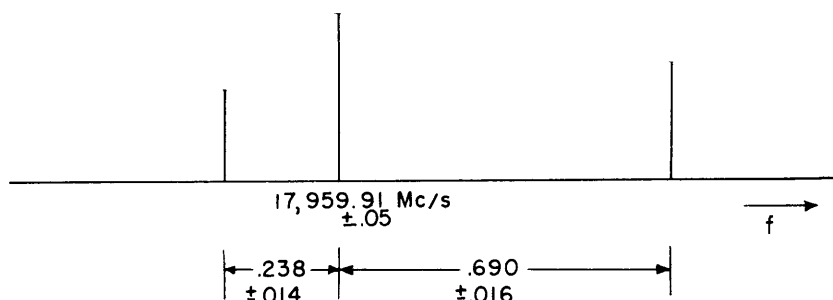


Fig. V-6 Observed data.

We would like to acknowledge the use of a sample of diborane kindly supplied by Dr. L. B. McCarty of the General Electric Company and thank Miss M. T. Westergaard for her assistance in the chemical preparation of the borine carbonyl.

M. Weiss

References

- (1) W. Gordy, H. Ring and A. Burg, Phys. Rev. 74, 1191 (1948).
- (2) J. Bardeen and C. H. Townes, Phys. Rev. 73, 97 (1948).
- (3) H. E. White, "Introduction to Atomic Spectra", p. 206, McGraw-Hill (1934).
- (4) M. Strandberg, C. Pearsall and M. T. Weiss, J. Chem. Phys. 17, 429 (1949).
- (5) M. Strandberg, T. Wentink and R. Kyhl, Phys. Rev. 75, 270 (1949).

7. Apparatus

The slow sweep spectrograph is operating although some difficulties have yet to be satisfactorily worked out. Previously-reported lines of the OCS spectrum have been detected and at present these lines are being used to check the sensitivity of the instrument. The first work planned is an examination of the structure of the OCS⁷⁷, 2 + 3 line, and a search for the weak 2 + 3 lines of OCS_e in the first excited state of the ν_3 vibration.

J. R. Eshbach

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VI. THE LINEAR-ACCELERATOR PROGRAM

Since the Progress Report, October 15, 1949, the linear-accelerator program has been transferred to the Laboratory for Nuclear Science and Engineering. Future progress of this project will be published in the monthly progress reports of that laboratory.

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