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HYPERFINE STRUCTURE AND NUCLEAR MOMENTS OF BROMINE-82

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ABSTRACT

The nuclear spin, the magnetic dipole, and the electric quadrupole interaction constants have been measured for 35-hr bromine-82 by the method of atomic beams. The results are $I = 5$, $|a| = 205.04 \pm 0.05$ Mc, $|b| = 870.7 \pm 0.9$ Mc, and $b/a = -4.246 \pm .001$.

The nuclear magnetic and electric quadrupole moments obtained from these values of a and b are $|\mu| = 1.6264 \pm 0.0005$ nm, and $|Q| = 0.76 \pm 0.03$ barn. While only the relative sign of μ and Q is determined, both μ and Q are almost certainly positive. A new method for solving the interaction Hamiltonian with magnetic field, for arbitrary I and J, by using an IBM 650 computer, is described.

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INTRODUCTION

This paper reports the results of a measurement by the method of atomic beams of the spin and hyperfine-interaction constants of bromine-82. The measured hyperfine constants have been used to calculate the nuclear magnetic dipole and electric quadrupole moments of bromine-82. The work reported here is part of a continuing program whose aim is the determination of the nuclear spins and moments of those radioactive halogens amenable to study by the method of atomic beams.

The measurement of the nuclear spins of odd-odd isotopes is of interest, for such spins are not, in general, predictable with certainty by any nuclear model. In addition a direct determination of the ground-state spin of a radioactive nucleus is useful in checking the spin assignments to ground and intermediate states made by the methods of nuclear spectroscopy. A determination of the moments of a series of isotopes where one of the nuclear parameters (in this case the charge) is held constant should aid understanding of the reasons for the deviations of these quantities from the values predicted by different nuclear models.

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1. METHOD

The method employed in this experiment is the atomic-beams "flop-in" technique due to Zacharias.[1] This method has been extensively used in recent years for the study of radioactive species and has been adequately described in recent review articles.[2,3] The electronic ground state of bromine atoms is $^2P_{3/2}$, and with this configuration there are two "flop-in" transitions observable at low field, with normal ordering of the hyperfine levels. These transitions are labeled α and β in the energy-level diagram of Fig. 1, and observation of one or both of these transitions at two or three known low magnetic fields is usually sufficient to establish the spin. A detailed description of the method used to determine the spins of $^2P_{3/2}$ ground-state atoms has been given elsewhere[4] and need not be reproduced here.

In order to appreciate the method used to determine the hyperfine-interaction constants it is necessary to examine the Hamiltonian of the interaction between the electrons and nucleus in the presence of an external magnetic field H. This Hamiltonian can be written as[5]

$$H = a\vec{I} \cdot \vec{J} + b\, Q\widehat{op} - g_J \mu_o \vec{J} \cdot \vec{H} - g_I \mu_o \vec{I} \cdot \vec{H}, \qquad (1)$$

also

$$(\vec{I} \cdot \vec{J}) = 1/2\ [F(F+1) - J(J+1) - I(I+1)]$$

and

$$Qop = \frac{3(\vec{I} \cdot \vec{J})^2 + 3/2\ (\vec{I} \cdot \vec{J}) - I(I+1)\ J(J+1)}{2\ I(2I-1)\ J(2J-1)},$$

where $\vec{F} = \vec{I} + \vec{J}$.

The above Hamiltonian does not include octupole and higher-order interactions or any terms due to nuclear structure effects, and it also presuppos

negligible perturbation by the upper state of the fine structure ($^2P_{1/2}$) and negligible configuration interaction. Here a and b are respectively the nuclear-magnetic-dipole and electric-quadrupole interaction constants. The effective electronic and nuclear magnetic moments have been defined as $+ g_J \mu_o \vec{J}$ and $+ g_I \mu_o \vec{I}$ respectively. With this notation, and with the fact taken into account that the valence-electronic configuration is $4p^5$ (i.e., closed shell minus one), the constants a and b are related to the nuclear gyromagnetic ratio g_I and nuclear quadrupole moment Q by the expressions[6,7]

$$a = \frac{\mu_0^2}{h} \quad g_I \mathcal{F} \frac{2L\,(L+1)}{J\,(J+1)} \quad \langle 1/r^3 \rangle \,, \tag{2a}$$

$$b = \frac{-e^2}{h} \; Q \; \mathcal{R} \; \frac{2L}{2L+3} \quad \langle 1/r^3 \rangle . \tag{2b}$$

Here $\mathcal{F}$ and $\mathcal{R}$ are relativistic correction factors; for bromine $\mathcal{F}$ = (1.0261) and $\mathcal{R}$ = (1.0535).[8] The nuclear gyromagnetic ratio g_I is related to the nuclear moment μ by $g_I = \frac{m}{M} \frac{\mu}{I}$, μ being expressed in nuclear magnetons; m and M are the electron and proton mass respectively; other symbols have their common meanings.

In order to determine μ and Q it is necessary to determine a, b, and $\langle 1/r^3 \rangle$; a and b can be expressed in terms of the zero-field hfs separations by solving the Hamiltonian (1) with H set equal to zero.

For bromine-82, I = 5,[9] and we have

$$\begin{aligned} \Delta\nu\,(13/2,\ 11/2) &= (13/2)a + \frac{351}{540}\,b, \\ \Delta\nu\,(11/2,\ 9/2) &= (11/2)a - \frac{99}{540}\,; \end{aligned} \tag{3}$$

$\langle 1/r^3 \rangle$ can be obtained from the known moments of the stable isotopes.

When one is dealing with a stable isotopic species it may well be that some information is available from optical spectroscopy on the magnitudes of the zero-field hfs splittings, and it may be feasible to make an immediate search for the $\Delta F = \pm 1$ transitions. Unfortunately, this is rarely possible for short-lived radioactive isotopes, where the paucity of material is an additional complication. The procedure adopted here to determine a and b is as follows:

A search is made for the two flop-in transitions α and β at a field high enough so that an appreciable shift of the resonance centers from the linear prediction is induced, but low enough that the search problem is manageable. A perturbation solution of the Hamiltonian (1) is made to second or third order and approximate values of the constants a and b are calculated. These values of a and b are used to predict the positions of the two resonances at a higher field, where the deviations of the levels from linearity are larger still. Once the resonances have been observed at the new field more precise values of a and b can be estimated and the procedure continued. Obviously some judgment must be exercised in the choice of the field increment. One would like to make as large a step as possible, but the size of the step must depend on the precision with which the new resonance positions can be calculated. Thus the uncertainties in a and b at any point in the series, together with the resulting search problem, determine the size of the step that can be made. After a certain point the perturbation solution becomes inadequate and an exact solution of the Hamiltonia becomes necessary. An IBM-650 digital computer has been programmed in two ways to facilitate the calculation of a and b. (The programs are described in some detail in the Appendix.) The first program calculates the transition frequency between an arbitrary pair of levels as a function of the magnetic field H, given the values of a and b. The second program calculates

best value of a and b from any given set of resonance data. These programs have enormously reduced the amount of labor involved in obtaining more and more precise values of a and b. It should be emphasized at this point that the second of the above programs is not restricted by any particular set of levels. Any and all transitions whether they be $\Delta F = 0$ or $\Delta F = \pm 1$ (whether they obey first-order selection rules or not!), can be fitted into the program to contribute their quota to knowledge of the hyperfine constants. Provision is made for feeding in uncertainties arising from the finite width of the resonance, and the uncertainty in the magnetic field. The second routine may also be used for the determination of the absolute sign of a and thus of the nuclear moment. As is explained in detail in the Appendix, the term in g_I in the Hamiltonian enters as a small additive correction to the observed frequencies and fields. Initially g_I is assumed zero, but when a reasonably precise value of a has been found g_I is computed by using Eq. (2a), and the moments and a values of the stable isotope. This value of g_I is then included in the calculation and the calculation iterated until consistency is obtained. Two sets of input data are prepared, one with g_I taken positive, the other with g_I taken negative. The routine makes a least-squares fit to the data for both signs of g_I and compares the fit by the χ^2 test of significance. An acceptable fit is obtained only for the correctly chosen sign of g_I if observations have extended to sufficiently high fields and resolution is adequate.

The energy-level diagram of Fig. 1 is an exact solution of the Hamiltonian (1) by the first routine, for a value of b/a differing but slightly from the final result. The contribution from the term in g_I has been neglected in the plotting.

When a and b are known with sufficient precision a search can be made for the direct hyperfine transitions. In this experiment direct transitions between

both of the upper pairs of hyperfine levels have been observed. There is no observable flop-in transition between the lower pair of hyperfine levels.

2. SAMPLE PREPARATION

The active material was obtained from Oak Ridge National Laboratory in units of 1.2 grams of KBr powder, each containing approximately 100 mC of bromine-82. The atomic beam required for this experiment was obtained by dissociating a mixture of natural and active bromine in a discharge tube, and the sample was prepared by using the glass system illustrated in Fig. 2. Each of the four vessels was surrounded by a close-fitting 2-inch-thick lead shield, and the whole assembly was mounted inside a gloved box. The KBr powder was mixed with a predetermined amount of natural KBr (approximately 1.2 grams) to produce a convenient specific activity in the sample, and gently heated in the reaction vessel with manganese dioxide and concentrated sulphuric acid; the liberated bromine was carried over to the first cold trap by a slow stream of helium gas. When the reaction was complete the system to the right of the reaction vessel was evacuated and closed off and the bromine distilled, first to the flask containing P_2O_5 to remove water, and then to the discharge-tube vial. A colorless liquid, thought to be sulphur dioxide, occasionally accompanied the bromine; this was removed quite effectively once the sample was attached to the discharge tube by cooling the vial with dry ice and pumping. The active beam was collected upon brass buttons coated with freshly evaporated silver. The buttons were subsequently counted in small-volume continuous-flow methane beta counters.

3. APPARATUS

As described elsewhere,[4] the present apparatus differs in many constructional details from the more conventional atomic-beams apparatus. In particular, the A, B, and C magnets are mounted externally to the vacuum system, and it is worth pointing out here that the external mounting of the C magnet enables one to control the resonance line width at will. One pole piece of the C magnet can be rotated with respect to the other or can be removed entirely. When the pole pieces are accurately lined up one with the other, the line width of the cesium resonance is approximately 100 kc at low fields and rises to 0.5 Mc at a field of 1500 gauss. With one pole piece removed the width is approximately 0.5 Mc up to fields of 50 gauss or so. Above 50 gauss the width can be as large as several megacycles, and widths intermediate between these extremes can be realized by appropriate adjustment of the pole pieces. This provision has been most useful in reducing the difficulties of a high-field or high-frequency resonance search. The search is made with a broad line, and when a signal is observed the line is narrowed down and a detailed resonance curve traced out.

The rf equipment for a given frequency band consisted of two signal generators, a coaxial switching circuit, and a Hewlett-Packard 524 B frequency counter and its associated equipment. One oscillator was set on the cesium resonance frequency, the other on the bromine resonance frequency, and the rf loop could be rapidly switched between the two oscillators. At frequencies below 500 Mc a General Radio type 805C oscillator and Hewlett-Packard type 608A oscillator were employed to observe bromine resonances; the output of the latter oscillator was amplified by a H.-P. type 460A wide-band amplifier. At frequencies above 500 Mc a H.-P. Type 612 signal generator followed by a traveling-wave tube amplifier provided the rf power. The output of the traveling-wave tube contained a considerable second harmonic component, and

above 1200 Mc considerable power at the second harmonic frequency could be tuned into the loop by stubs. At a later stage an Airborne Instruments power oscillator (Type 124C) was used exclusively to observe high-frequency resonances. The rf could be monitored continuously and was held constant to a small fraction of a resonance line width.

The C field was calibrated by observing the flop-in resonance in a beam of cesium atoms. Adjustment of the C field was made immediately before a button was exposed and was verified at the conclusion of an exposure. If any observable drift of the C field was noted (a rare occurrence) the button was discarded and a new exposure made.

4. EXPERIMENTAL PROCEDURE

The initial exposures were made in the linear Zeeman region to determine the spin. The spin has previously been reported as 5.[9] Both the α and β resonances were observed at five different values of magnetic field up to 417.4 gauss. Figure 3 shows an α resonance observed at a field of 83.83 gauss (ν_{Cs} = 30 Mc) and Fig. 4 a/β resonance observed at a field of 164.03 gauss (ν_{Cs} = 60 Mc). All the resonances observed are consistent with an assignment of 5 for the nuclear spin of bromine 82.[9] In a typical run, for a 10-minute button exposure the full beam counting rate was 2500 cpm, the resonance heights approximately 35 cpm, and the apparatus background (i.e., the button-counting rate with the A and B fields switched on and the stopwire inserted into the path of the beam) was 10 cpm. The dissociation efficiency of the discharge was in a typical instance ~80%. The α and β resonances observed at and below 417.4 gauss permitted calculation of the constants a and b with sufficient accuracy so that a search for the direct hyperfine transitions could be attempted. The searches were made with a broad line which was narrowed down once a resonance had been spotted.

Figure 5 shows the $\Delta M_F = 0$ resonance between the upper pair of hyperfine states at a field of 56.3 gauss (ν_{Cs} = 20 Mc). The line is a little broader than expected from measurements of the cesium resonance line width, probably because the resonance was observed in the fringing field of an rf loop designed for observation of $\Delta M_F = \pm 1$ transitions.

Figure 6 exhibits $\Delta M_F = \pm 1$ resonances between the two hyperfine states F = 11/2, F = 9/2 at a field of 0.95 gauss (ν_{Cs} = 0.3 Mc). The line is broad because there are 17 possible $\Delta M_F = \pm 1$ transitions between these two hyperfine states, all coincident at zero field but partially resolved at 0.95 gauss. In order to increase the precision of measurement of the F = 11/2 → F = 9/2 interval, one of these resonances--the F = 11/2, M_F = -7/2 → F = 9/2, M_F = -5/2 transition--was followed to fields high enough so that it became completely resolved from its partners, the measured g_F value being used for positive identification. The resonance F = 11/2, M_F = -5/2 → F = 9/2, M_F = -5/2 has also been observed at a field of 28.37 gauss (ν_{Cs} = 10 Mc). The frequencies and fields of all transitions that have been observed in bromine-82 are given in Table I together with the uncertainties assigned to the positions of the resonance centers. The uncertainties have been computed by assigning an uncertainty of one third the resonance width at half maximum to both the bromine and cesium resonances and compounding these errors by using Eq. 18 of the Appendix.

Table I

Observed resonances in Br^{82}

Resonance type	Resonance frequency (Mc)	Cesium frequency (Mc)	Magnetic field (gauss)	Compounded uncertainty (Mc)	Weighti factor (ω)
α	1.25	1	2.86	.06	259
α	6.26	5	14.24	.06	251
β	3.54	5	14.24	.05	340
α	12.81	10	28.37	.07	192
β	7.19	10	28.37	.05	474
α	6.31	5	14.24	.06	325
α	41.13	30	83.83	.11	83
β	22.15	30	83.83	.08	163
α	90.30	60	164.02	.24	18
α	90.25	60	164.02	.11	81
β	173.05	164	417.38	.52	3.6
β	173.05	164	417.38	.66	2.3
α	304.70	164	417.38	.43	5.6
β	46.95	60	164.02	.07	224
(13/2, -9/2)↔(11/2, -9/2)	727.50	20	56.31	.21	22
(11/2, -7/2)↔(9/2, -5/2)	1281.50	2	5.71	.18	57
(11/2, -7/2)↔(9/2, -5/2)	1273.10	5	14.24	.16	41
"	1281.60	2	5.71	.14	72
"	1281.60	2	5.71	.10	100
"	1273.03	5	14.24	.10	110
(11/2, -5/2)↔(9/2, -5/2)	1265.91	10	28.37	.10	100

5. RESULTS AND DISCUSSION

As explained in the Appendix, the hyperfine constants were evaluated by using an IBM digital computer. The machine calculation gives

$$a = 205.04 \pm .01 \text{ Mc}, \quad b = -870.66 \pm .18 \text{ Mc}.$$

In order to allow for unknown systematic sources of error that might be present, we adopt the values

$$a = 205.04 \pm .05 \text{ Mc}, \quad b = -870.7 \pm .9 \text{ Mc}.$$

The values of χ^2 with g_I assumed positive and negative are

$$\chi^2 (g_I > 0) = 3.5,$$
$$\chi^2 (g_I < 0) = 6.4.$$

In theory the value of χ^2 for the correct choice of sign of g_I should be equal to the number of observations, minus two--i.e. nineteen--for about 50% probability of being correct. The small values of χ^2 above result from our unwillingness, in the absence of a theory of the resonance line shape, to split the resonance lines by more than a factor of three, despite the fact that purely statistical arguments suggest that this would be justified (see Sec. 6). A value of $g_J(\text{Br}) = -1.3338 \pm .0003$, obtained from the measurements by King and Jaccarino on stable bromine, has been used in the data reduction.[10] The effect of the uncertainty in g_J upon the final values of a and b was obtained by reducing the data with a slightly different value of g_J. The effect on the uncertainty in a and b is negligible.

In order to check the internal consistency of the data the α and β resonances ($\Delta F = 0$, $\Delta m = \pm 1$) and the $\Delta F = \pm 1$ resonances were run separately through the IBM program. The results are:

Resonance group	a (Mc)	b (Mc)
All α, β	205.28 ± .31	-871.63 ± 1.98
All $\Delta F = \pm 1$	205.038 ± .007	-870.66 ± .18

The uncertainties quoted are those resulting directly from the calculation; g_I has been assumed positive. The internal consistency of the data is well demonstrated.

No measurement appears to have been made of the magnetic interaction constant $a_{1/2}$ in the $P_{1/2}$ state of stable bromine. It is therefore difficult to say with certainty what the effect of configuration interaction is upon the present measurement of $a_{3/2}$ in Br^{82}. The effect, however, is probably quite small, and has not been included as a correction. In addition, corrections to $a_{3/2}$ due to the finite size of the nuclear-charge distribution[11] and magnetic-moment distribution[12] are negligible for atoms in pure $^2P_{3/2}$ ground states and can be neglected. Perturbations of the $^2P_{3/2}$ ground state by admixture of the $^2P_{1/2}$ state do not affect the results significantly to the accuracy stated here. In any event, these considerations do not affect the value of μ_I for Br^{82} obtained below.

6. MAGNETIC MOMENT

We have, from Eq. (2),

$$\frac{a_{3/2}(Br^{82})}{a_{3/2}(Br^{s})} = \frac{\mu^{82}}{\mu^{s}} \frac{I^{s}}{I^{82}} , \qquad (4)$$

where μ^s is the nuclear magnetic moment and I^s the nuclear spin of the stable bromine isotope Br^s. Using the results of King and Jaccarino[10] for the $a_{3/2}$ values of Br^{79} and Br^{81}, together with the nuclear moments of

the same isotopes measured by Walchli,[13] we find for both comparison isotopes

$$\mu^{82} = \pm 1.6264 \quad (5) \text{ nuclear magnetons } (Br^{79}),$$

$$\mu^{82} = \pm 1.6264 \quad (4) \text{ nuclear magnetons } (Br^{81}).$$

The difference between the two values of χ^2 listed above is not sufficient to permit a definite statement as to the sign of the magnetic moment of Br^{82}. However, if the weighting factors ω_i entering into the calculation of χ^2 (see Appendix II, Eq. (17)) are increased by a factor of 6, then $\chi^2 (g_I > 0) = 21$ and $\chi^2 (g_I < 0) = 38.5$. This is equivalent to splitting the resonance lines by the factor $3\sqrt{6} = 7.3$ instead of 3. The corresponding values of χ^2 indicate that it is 30 times as probable that g_I is positive rather than negative. However, for the reason stated in Sec. 5, we prefer not to rely heavily upon this statistical argument. Figure 7 shows a plot, for the α and β resonances, to the difference between the observed and calculated resonance frequencies with g_I taken positive and negative, together with the experimental uncertainties obtained by splitting the resonance lines by a factor 3. Quite clearly the sign of g_I is not unambiguously determined. While a measurement of the sign must await improvement of the C-field magnet, there are two reasons for believing that the sign is positive:

(a) The magnetic moment of Rb^{82} has been measured to be + 1.50 nm.[15] The spin of Rb^{82} is 5, the same as Br^{82}, and one might expect nuclei differing by pairs of neutrons and protons to have comparable magnetic moments.

(b) The magnetic moment calculated for Br^{82} on the basis of a simple jj coupling model is positive. The magnetic moment of an odd-odd nucleus, based on a single-particle description, is given by the expression[16]

$$\mu = 1/2 \left[(g_p + g_n)I + (g_p - g_n) \frac{j_p (j_p + 1) - j_n (j_n + 1)}{(I + 1)} \right] , \qquad (5)$$

where g_p and g_n are the g factors of the odd neutron and proton, j_p and j_n are the proton and neutron angular momenta, and I the nuclear spin. If the mean of the nuclear moments of Br^{79} and Br^{81} (2.188 nm) and the observed spins of 3/2 are used to define an effective g_p for the proton part of the core of Br^{82}, we find $g_p = 1.459$. An effective g_n for the neutron part of the core can be obtained from the known spins and moments of the neighboring odd-A odd-N nuclei ${}_{34}Se^{77}_{43}$, ${}_{36}Se^{79}_{45}$ and ${}_{36}Kr^{83}_{47}$. By setting I = 5 and making use of Eq. (5), the following results are obtained.

Isotope	Spin	Configuration	g_n	$\mu(Br^{82})_{calc}$ (nm)	$\mu(Br^{82})_{obs}$ (nm)
Se^{77}	1/2	$p_{1/2}$	1.068	6.42	1.63
Se^{79}	7/2	$(g_{9/2})^7_{7/2}$	-.291	1.17	
Kr^{83}	9/2	$g_{9/2}$	-.215	0.18	

It is thus likely that the neutron part of Br^{82} does not couple to J = 9/2; coupling to J = 7/2 is a possibility. With the assignment $(g_{9/2})^7_{7/2}$, Nordheim's weak rule[17] applies and predicts for Br^{82} a nuclear spin of 5 or less. It is significant that for all reasonable choices of the neutron configuration the calculated magnetic moment is positive, and it is this that lends weight to the conclusion of the previous paragraph--i.e. that μ is positive.

7. QUADRUPOLE MOMENT

The uncorrected quadrupole moment Q_e can be calculated from Eq. (2) Section I. We find

$$Q_e = 8/3 \left(\frac{\mu_0}{e}\right)^2 \frac{m}{M} \left(\frac{\mu}{I}\right) \left(\frac{F}{Q}\right) \frac{b}{a} . \tag{6}$$

Introducing the measured values of a for the stable isotopes[10] Br^{79} and Br^{81}, and the values of μ listed by Walchli,[13] we find in both cases $Q_{exp} = 0.730$ barn. In order to obtain the true nuclear quadrupole moment Q_t a correction factor C such that $Q_t = CQ_e$ is introduced. This factor, first introduced by Sternheimer, allows for the changed interaction of the valence electron with the inner core of electrons in the presence of the polarizing field due to the nuclear quadrupole moment. The constant C has been calculated for bromine by Sternheimer[18] but with the neglect of certain antishielding corrections.[19] C is 1.040, but in view of the uncertainty associated with the exact value of C we have chosen to assign an uncertainty to Q_t equal to the value of the correction itself. Thus

$$Q_t\ (Br^{82}) = 0.76 \pm .03 \text{ barn.}$$

If μ is positive, the sign of the quadrupole moment is also positive.

Q can be calculated by an alternative procedure by making use of the fine-structure separation δ to obtain a value of $\langle 1/r^3 \rangle$; δ is related to $\langle 1/r^3 \rangle$ by the expression[20]

$$\delta = \frac{\mu_0}{hc}^2 \hat{Z} (2L + 1) H \left\langle \frac{1}{r^3} \right\rangle . \tag{7}$$

Here δ is 3685 cm^{-1}, $\hat{Z}$ is the effective value of the nuclear charge, and $\Xi(Z_i)$ is a relativistic correction factor tabulated by Kopfermann.[8] Barnes and Smith have shown $Z_i = Z - n$ approximately, n being the radial quantum number of the

valence electron.[21] For bromine n = 4 and Z_i = 31, and the value of Q_e obtained by using $\langle 1/r^3 \rangle$ from Eq. (7) is 0.69 barns and the corrected quadrupole moment Qt = 0.72 barn. The uncertainty in this value of Q_t arises both from the uncertainty in Z_i and the uncertainty in the Sternheimer correction. An examination of the results of Barnes and Smith and a comparison with some similar calculations by Koster[22] indicates that Z_i is probably known to about 5%. Thus we have finally $Q_t = 0.72 \pm 0.06$ barn.

The agreement between these two methods of calculation is satisfactory.

8. HYPERFINE SEPARATIONS

The hyperfine separations in Br^{82} are easily calculated from Eq. (3). The results are

$$\Delta\nu\,(13/2,\ 11/2) = 766.82 \pm .60 \text{ Mc.}$$

$$\Delta\nu\,(11/2,\ 9/2) = 1287.32 \pm .43 \text{ Mc.}$$

$$\Delta\nu\,(9/2,\ 7/2) = 1488.6 \pm 1.1 \text{ Mc.}$$

The authors wish to thank Mr. Larry Cohen for much help with the taking of data and Mr. Douglas MacDonald, who coordinated the machine shop work. The Health Chemistry Division and the Chemistry Department at Lawrence Radiation Laboratory gave invaluable assistance and advice during the performance of this work.

APPENDIX

I. IBM Program for Calculation of Transition Frequencies for Given a and b Values

As noted in the text, two IBM 650 routines have been used in this work. The first computes the eigenvalues of the Hamiltonian for the hyperfine structure in a magnetic field as a function of the field. Dipole and quadrupole terms are the only interaction terms included, and it is assumed that configuration perturbations of the electronic states are absent. The answers are presented in dimensionless form as a table of dimensionless frequencies versus ρ, the dimensionless field, starting from $\rho = 0$ to an indefinite value of ρ. The increments of ρ can be chosen at will. The input information is I, the spin of the nucleus; J, the electronic angular momentum; F_1, M_1, F_2, M_2, the total angular momenta and magnetic quantum numbers of the two levels involved; ξ, the ratio of the quadrupole to dipole interaction constants; and $\Delta\rho$, the increment in ρ. The output is the dimensionless frequency ν, this frequency divided by ρ, the two term values, and the derivative of the frequency with respect to ρ.

The Hamiltonian can be written

$$\mathcal{H} = \vec{I} \cdot \vec{J} + \frac{\xi}{2I(2I-1)J(2J-1)} \left[3(\vec{I}\cdot\vec{J})^2 + 3/2\,(\vec{I}\cdot\vec{J}) - I(I+1)J(J+1)\right]$$

$$+ \rho J_Z - g_I \frac{\mu_0 H}{\hbar a} F_Z \,. \tag{8}$$

This Hamiltonian is in units of a, which is itself in units of frequency and

$$\rho = (-g_J + g_I) \frac{\mu_0 H}{\hbar a} \quad \text{and} \quad |g_I| \ll |g_J| \,.$$

If the energies of Eq. (8), neglecting the term in g_I, are X_{FM} then the true energies (including the nuclear term) are X'_{FM}, where

$$X'_{FM} = X_{FM} - \frac{g_I \mu_0 H}{ha} M. \tag{9}$$

If X_1 is the term value for Level 1 and x_2 that for Level 2 of the routine, then

$$\nu' = \nu - \left(\frac{g_I \ \mu_0 H \ (M_1 - M_2)}{ha} \right) ,$$

where ν is the frequency computed by the routine that neglects the contribution from g_I, and ν' the true frequency.

The matrix elements employed by the routine are taken from Condon and Shortley. They are

$$\begin{aligned}
&(FM \ |I \cdot J| \ FM) = 1/2 \ \{ F(F+1) - I(I+1) - J(J+1) \} = a_p . \\
&(FM \ | \text{Quadrupole operator} \ |FM) = b_p . \\
&(FM \ | J_Z | \ FM) = \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} \cdot M = c_p , \\
&(FM \ | J_Z | \ F+1, \ M)^2 = \frac{(F+1-I+J)(F+1+I-J)(I+J+2+F)(I+J-F)(F+I-M)(F+I+M)}{16 \ (F+1)^2 \ (2F+1)(2F+3)} = d_p
\end{aligned} \tag{10}$$

The diagonal elements of the Hamiltonian are $A_p = a_p + b_p \zeta + \rho c_p$, and the square of the elements one off the diagonal (the only nonvanishing ones) are equal to $\rho^2 d_p$. No others exist.

The term p = 1 for the diagonal elements corresponds to the lowest F value for the given M submatrix; p = 1 for the off-diagonal elements corresponds to the lowest row of the matrix and the next to the last column. It is understood that the lowest row is assigned the lowest F value. Let $||H||$ be the submatrix to be solved. Then we require the solution of the secular determinant

$$D = \| H - X_i \| = 0 , \tag{11}$$

where X_i are the eigenvalues.

Let D_1 be the 1×1 determinant consisting of the lower right-hand corner of the matrix, D_2 be the 2×2 determinant that includes the two lowest diagonal elements and associated off-diagonal element, etc. The pth determinant constructed in this way is given by the recursion relation

$$D_p = (A_{p-1} - X) D_{p-1} - \rho^2 d_{p-1} D_{p-2} , \tag{12}$$

where $D_0 = 1$, $D_{-1} = 0$.

This may be differentiated with respect to X, giving

$$\frac{\partial D}{\partial X} = (A_{p-1} - X) \frac{\partial D_{p-1}}{\partial X} - \rho^2 d_{p-1} \frac{\partial D_{p-2}}{\partial X} - D_{p-1} . \tag{13}$$

By recurring both relations together to the value $\rho = n$, the matrix dimension, Newton's method can be used to obtain a root.

The increment in X is given by

$$\Delta X = \frac{-Dn}{\partial Dn / \partial X} . \tag{14}$$

Other derivatives may be easily found. For example,

$$\frac{\partial D_p}{\partial \rho} = (A_{p-1} - X) \frac{\partial D_{p-1}}{\partial \rho} + C_p D_{p-1} - \rho^2 dp + \frac{\partial D_{p-2}}{\partial \rho} - 2\rho d_{p-1} D_{p-2} \tag{15}$$

This derivation is useful for estimating errors caused by the uncertainty in the field. The advantage of this method of decomposition is that it can be performed rapidly by the computer. They are one-dimensional recursion formulae that are made to terminate at $d_p = 0$. The routine is an open routine independent of the matrix dimension. One of the major problems is that of root identification. However, only one root is required from a given submatrix and the root is easily identified at $\rho = 0$. By incrementing ρ using the previous root as a trial root, the eigenvalue is followed

adiabatically with ρ. The M noncrossing rule prevents the failure of Newton's method caused by doubled roots. There are accidental degeneracies between M levels for $\rho = 0$ for certain critical ξ values, but they can be easily treated.

II. IBM Program for Calculation of Best Values of a and b from Experimental Data.

The second routine takes sets of observational data in the form of magnetic fields and frequencies for arbitrary hyperfine transitions for given but arbitrary I and J, and reduces the data by means of a least-squares fit to yield the magnetic dipole and electric quadrupole constants a and b. It yields the errors in a and b (Δa and Δb) and the χ^2 for the optimum fit as well as the best-fitting term values for each observational point. This routine operates with true magnetic fields and frequencies, and in order to appreciate the methods of solution employed it is necessary to write the Hamiltonian (1) in dimensional form. We have

$$\mathcal{H} = a\vec{I} \cdot \vec{J} + b\, Q\hat{o}\hat{p} + (-g_J + g_I)\, \frac{\mu_0 H_{Obs}}{h}\, J_z - g_I\, \frac{\mu_0 H_{Obs}}{h}\, F_z. \qquad (16)$$

The routine computes the eigenvalues and their various derivatives, using the first three terms on the right only; the last term enters as an additive correction. Rough preliminary values of a and b are required before the input cards are cut, but at the point where this routine is employed these values are always at hand from the previously described routine. The determinants to be solved are the same as those of Appendix I subject to the condition that

$$N = \sum_i (f^i - x^i_1 + x^i_2)^2 \quad \omega_i \tag{17}$$

be a minimum. The i sum is over the data sets. N, of course, is equal to χ^2, f^i is the observed center frequency of the ith resonance, and the statistical weight ω_i is given by

$$\omega_i = \frac{1}{(\Delta f^i)^2 + \left(\frac{\partial f^i}{\partial H}\right)^2 \cdot \Delta H^2}, \tag{18}$$

where Δf^i is some fraction of the width of the observed line, ΔH is the uncertainty in the magnetic field, and $\frac{\partial f^i}{\partial H}$ can be estimated from the first routine.

The method of finding the minimum of N has been described elsewhere[23] and is only briefly described here.

The following linear equations in δa and δb are set up:

$$\begin{aligned} \frac{\partial^2 N}{\partial a^2}\,\delta a + \frac{\partial^2 N}{\partial a \partial b}\,\delta b &= \frac{\partial N}{\partial a}, \\ \frac{\partial^2 N}{\partial a \partial b}\,\delta a + \frac{\partial^2 N}{\partial b^2}\,\delta b &= \frac{\partial N}{\partial b}, \end{aligned} \tag{19}$$

where the derivatives are treated as constants and calculated for the given a and b values. The new a, b values $(a_1 b_1)$ are computed from

$$a_1 = a - \delta a,$$

$$b_1 = b - \delta b,$$

and the process is iterated. The variances in a and b are given by

$$(\overline{\delta a})^2 = \frac{\partial^2 N/\partial b^2}{\Delta} ,$$

$$(\overline{\delta b})^2 = \frac{\partial^2 N/\partial a^2}{\Delta} ,$$

where Δ is the determinant of Eq. (19). For our purposes the usual $\frac{\chi^2}{n-m}$ factor has been omitted.

In order to calculate x_1 and x_2 it is necessary to solve the determinant, Eq. (11). Recursion relations between the various subdeterminants D_p, D_{p-1}, etc. are set up. Typical relations are

$$D_p = (A_p - X)\, D_{p-1} - E_{p-1}\, D_{p-2} ,$$

$$\frac{\partial D_p}{\partial x} = (A_p - X) \frac{\partial D_{p-1}}{\partial x} - E_{p-1} \frac{\partial D_{p-2}}{\partial x} - D_{p-1} , \tag{20}$$

$$\frac{\partial D_p}{\partial a} = (A_p - X) \frac{\partial D_{p-1}}{\partial a} - E_{p-1} \frac{\partial D_{p-2}}{\partial a} + a_p D_{p-1} ,$$

and the others required are easily found. The recursion relations are repeated n times and each equation (except the first) has terms depending upon some previous one, so that the recursion process is employed on all simultaneously. The roots of $D_N(a, b, x) = 0$ are the eigenvalues of the Hamiltonian and they are found by using Newton's method.

The correction to x, δx is given by

$$\delta x = \frac{D_n}{\partial D_n/\partial x} , \tag{21}$$

and the new x is $x - \delta x$. When the root and all derivatives of the type of Eq. (20) have been found, the derivatives of the type

$$\frac{\partial x}{\partial a} , \quad \frac{\partial^2 x}{\partial a \partial b} \quad \frac{\partial^2 x}{\partial a^2}$$

are calculated, and it is these that are used in setting up Eq. (19).

REFERENCES

1. J. R. Zacharias, Phys. Rev. 61, 270 (1942).
2. W. A. Nierenberg, Annual Review of Nuclear Science (Annual Reviews, Inc., Stanford, 1957) Vol. 7 p. 349.
3. K. F. Smith, Progr. Nuclear Phys. 6, 52 (1957).
4. H. L. Garvin, T. M. Green, and E. Lipworth, Phys. Rev. 111, 534 (1958).
5. N. F. Ramsey, Molecular Beams (Oxford. London 1956) Chap. 9.
6. H. B. G. Casimir, On the Interaction Between Atomic Nuclei and Electrons (Teylers Tweede Genootschap, Haarlem, 1936), p. 57, 58.
7. Davis, Feld, Zabel, and Zacharias, Phys. Rev. 76, 1076 (1949). Note that the difference in sign between the expressions for a and b above and those in Ref. 7 is due to our having defined the electronic and nuclear moments as $+ g_J \mu_0 \vec{J}$ and $+ g_I \mu_0 \vec{I}$. Usually a minus sign is placed in front of each term, but the definition used here seems preferable because it is logical.
8. H. Kopfermann, Nuclear Moments (Academic Press, Inc., New York, 1958), p. 445 and 448.
9. This value of I = 5 has been reported earlier: Garvin, Green, and Lipworth, Bull. Am. Phys. Soc. II 2, 344 (1957).
10. J. G. King and V. Jaccarino, Phys. Rev. 94, 1610 (1954).
11. M. F. Crawford and A. L. Schawlow, Phys. Rev. 76, 1310 (1949).
12. A. Bohr and V. F. Weisskopf, Phys. Rev. 77, 94 (1950).
13. H. E. Walchli, A. Table of Nuclear Moment Data, Oak Ridge National Laboratory Report ORNL-1469 (Suppl. 2), Feb. 1955. See also ORNL-1775, Oct. 1954, by the same author.
14. R. A. Fisher, Statistical Methods for Research Workers (Oliver and Boyd, London, 1948).

15. Hubbs, Nierenberg, Shugart, Silsbee, and Sunderland, Phys. Rev. 107, 723 (1957).

16. R. J. Blin-Stoyle, Theories of Nuclear Moments (Oxford University Press, London, 1957), p. 66.

17. L. W. Nordheim, Revs, Modern Phys. 23, 322 (1951).

18. R. Sternheimer, Phys. Rev. 86, 316 (1952).

19. R. Sternheimer, Phys. Rev. 95, 736 (1954).

20. H. B. G. Casimir, On the Interaction Between Atomic Nuclei and Electrons (Teylers Tweede Genootschrap, Haarlem, 1936), p. 55.

21. R. G. Barnes and W. V. Smith, Phys. Rev. 93, 95 (1954).

22. G. F. Koster, Phys. Rev. 86, 148 (1952).

23. W. A. Nierenberg, A Method for Minimizing a Function of n Variables, University of California Radiation Laboratory Report UCRL-3816, June 1957.

FIGURE LEGENDS

Fig. 1. Hyperfine-structure levels of bromine-82 as a function of magnetic field, calculated by using an IBM 650 computer and the program described in the text. The value of b/a used is -- 4.24. The magnetic field ρ is in units of $g_J \frac{\mu_0 H}{ha}$.

Fig. 2. Glassware used in the extraction of bromine from pile-activated KBr.

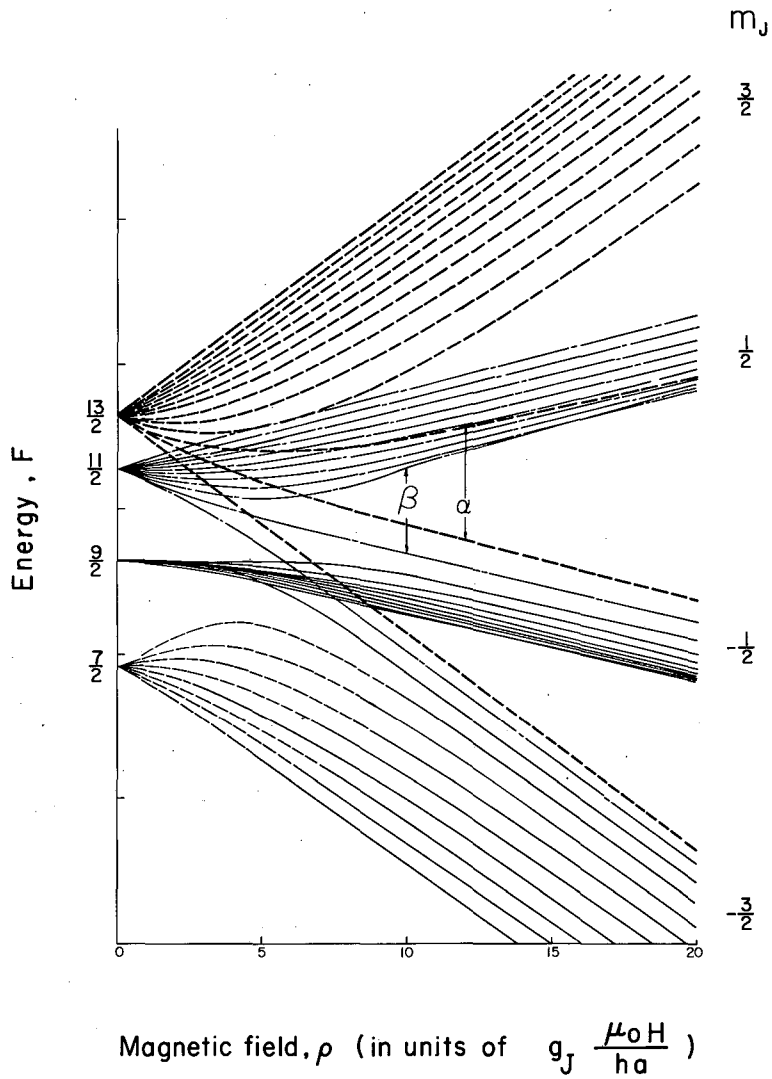
Fig. 3. A 5(α) resonance (13/2, -9/2) $\longleftrightarrow$ (13/2, -11/2) observed at a field of 83.83 gauss. Note the substantial shift of the resonance center from the linear Zeeman prediction.

Fig. 4. A 5(β) resonance (11/2, -7/2) $\longleftrightarrow$ (11/2, -9/2). observed at a magnetic field of 164.02 gauss.

Fig. 5. The transition (13/2, -9/2) $\longleftrightarrow$ (11/2, -9/2) between the upper pair of hyperfine levels observed at a field of 56.31 gauss.

Fig. 6. Superposition of $\Delta m_F = \pm 1$ transitions observed between the F = 11/2 and F = 9/2 hyperfine levels. The resonance shown is a superposition of 17 partially resolved transitions. Individual resonances were resolved at higher fields.

Fig. 7. A plot, for the α and β resonances, of the difference between the observed frequencies and the calculated frequencies, the latter calculated with the best-fitting values of a and b. The two curves are these differences with g_I assumed positive and negative respectively. The horizontal bars are the experimental uncertainties. The horizontal scale is in order of increasing resonance frequency. It will be noted that though the curve for $g_I > 0$ lies always within the experimental limits, the curve with $g_I < 0$ does not lie sufficiently far outside these limits to warrant a definite statement as to the sign of the nuclear moment


m_J
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$\frac{1}{2}$
$-\frac{1}{2}$
$-\frac{3}{2}$
$\frac{13}{2}$
$\frac{11}{2}$
$\frac{9}{2}$
$\frac{7}{2}$
Energy , F
β
α
0
5
10
15
20
Magnetic field, ρ (in units of $g_J \frac{\mu_0 H}{ha}$)
MU-17271

Fig. 1

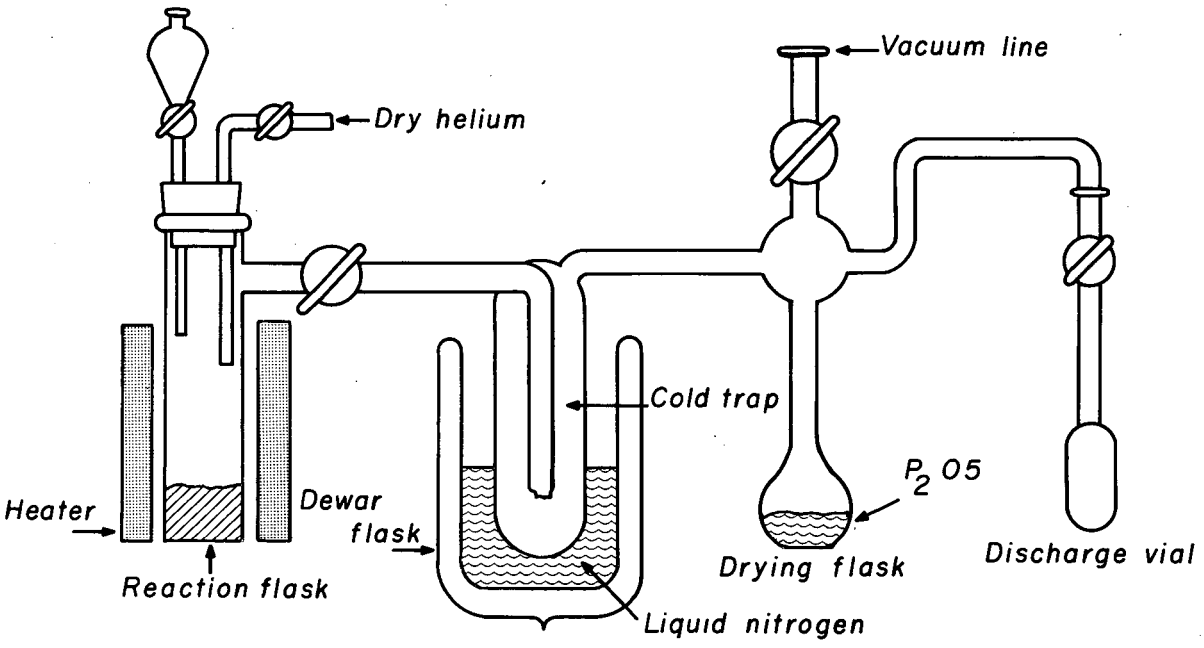

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Fig. 2

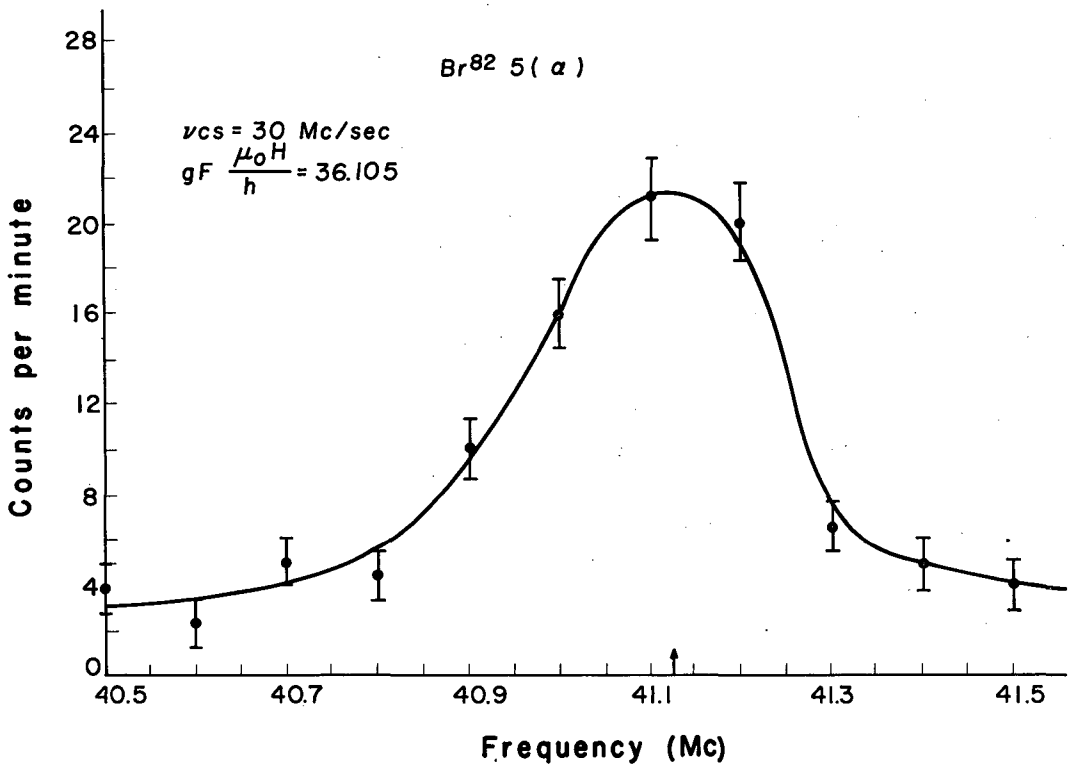

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Fig. 3

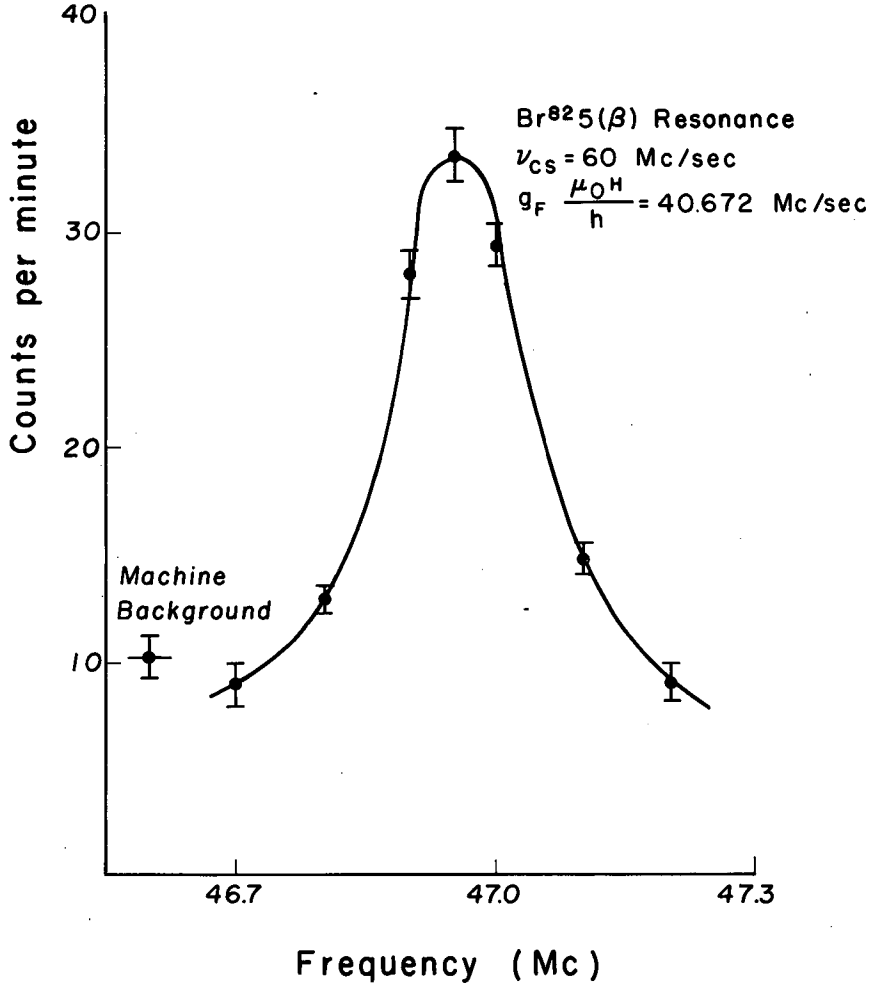

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Fig. 4

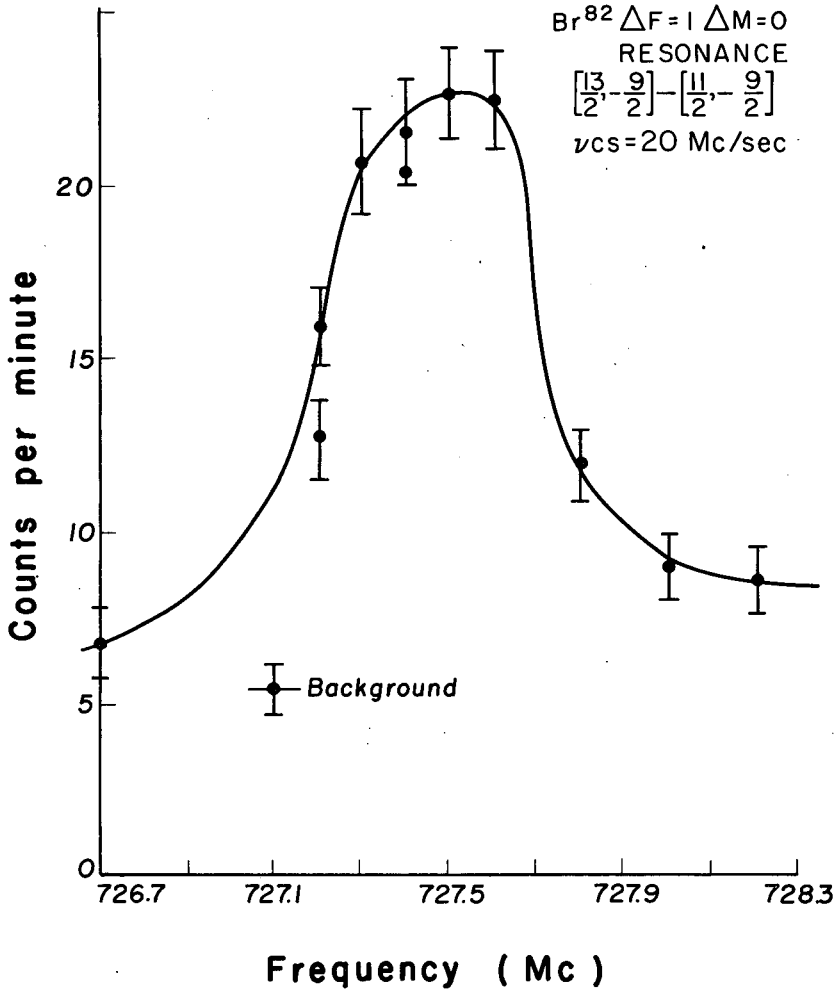

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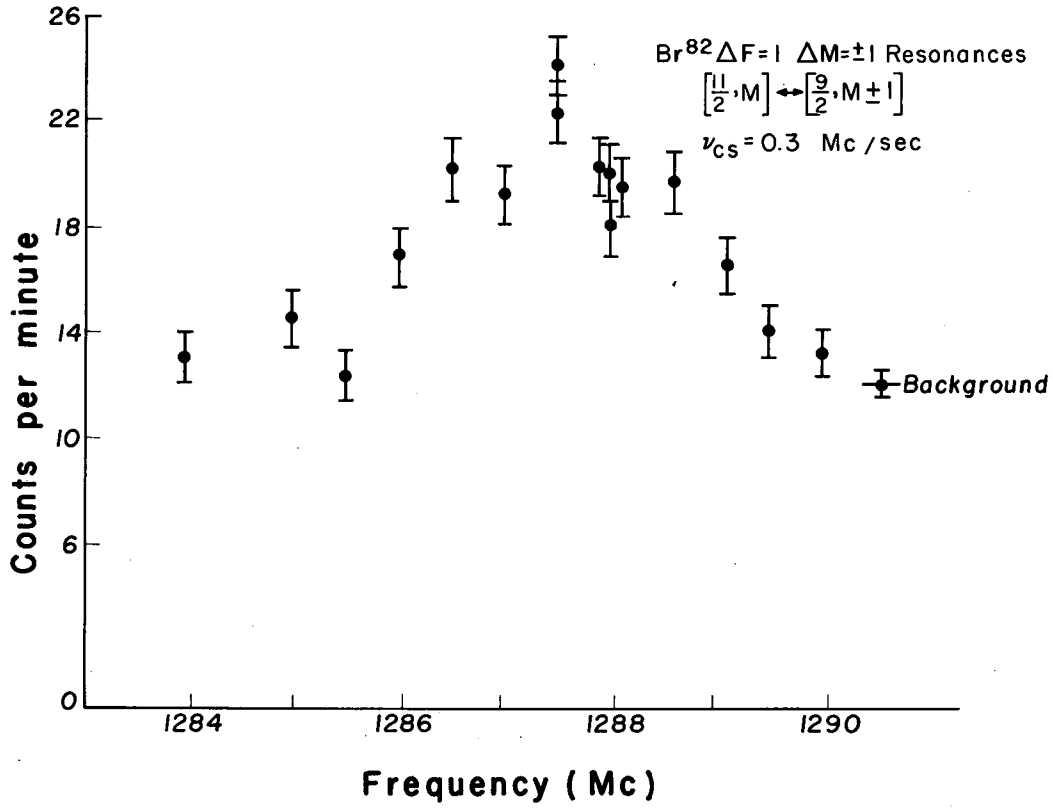
Fig. 5



MU-17268

Fig. 6

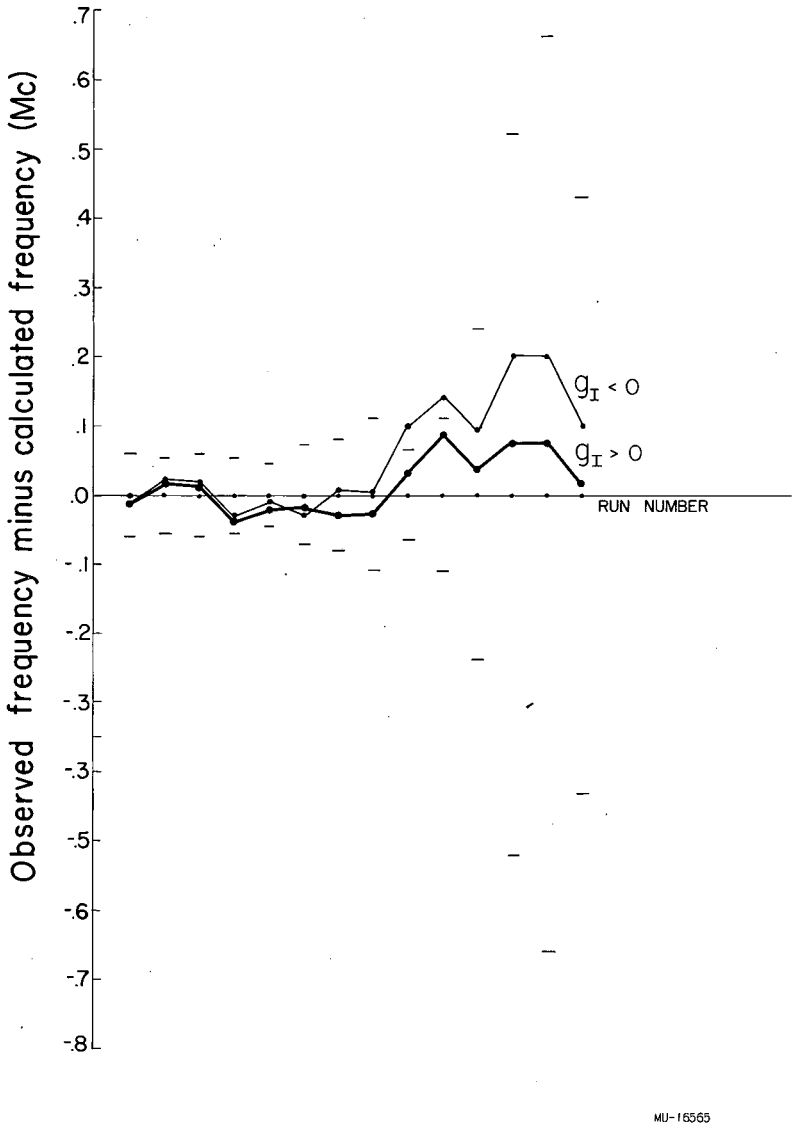

Observed frequency minus calculated frequency (Mc)
.7
.6
.5
.4
.3
.2
.1
.0
-.1
-.2
-.3
-.3
-.5
-.6
-.7
-.8
$g_I < 0$
$g_I > 0$
RUN NUMBER
MU-16565

Fig. 7

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