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The Molecular Beam Magnetic Resonance Method. The Radiofrequency Spectra of Atoms and Molecules*†

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THE MOLECULAR BEAM MAGNETIC RESONANCE METHOD

1. General Considerations

A NEW method known as the "Magnetic Resonance Method" which makes possible accurate spectroscopy in the low frequency range ordinarily known as the "radiofrequency" range

* This article was prepared in 1941 and has not been revised to take into account the possible applicability to the method of higher frequencies and other useful instrumental techniques developed during the war years. Other ingenious magnetic resonance methods, recently published, have been applied to the measurement of the proton moment and of the h.f.s. separation of caesium atoms in the ground state.

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was announced in 1938 by Rabi, Zacharias, Millman, and Kusch (R6, R5). This method reverses the ordinary procedures of spectroscopy and instead of analyzing the radiation emitted by atoms or molecules analyzes the energy changes produced by the radiation in the atomic system itself. Recognition of the energy changes is accomplished by means of a molecular beam apparatus. The experiment was first announced as a new method for the determination of nuclear magnetic moments, but it was immediately apparent that its scope was not limited to the measurement of these quantities only. It is the purpose of this article to summarize the more important of those successes which the method has to date achieved.

Historically the molecular ray approach toward

the solution of problems in atomic and nuclear physics received its first success in the classic experiment of Stern and Gerlach (S4, G1) which gave experimental proof of the space quantization of atoms in a magnetic field. An atom in a magnetic field, which we may take in the z direction, experiences a change of energy $\Delta W = -\mu_z H$ where μ_z is the magnetic moment in the direction of the field. The force acting on this atom in the z direction is then

$$F_z = (-\partial W/\partial z) = \mu_z (\partial H/\partial z)$$

for constant μ_z . If, moreover, the field is of such a nature that

$$\partial H/\partial z \neq 0,$$

while

$$\partial H/\partial y = \partial H/\partial x = 0,$$

this will be the only magnetic force acting on the atom. Thus if an atom with velocity, v , in the x direction is shot through such a field of length l , it will suffer a deflection, d , given by

$$d = \frac{1}{2} a t^2 = \frac{1}{2} \frac{F_z}{m} t^2 = \frac{\mu_z}{4E} \frac{\partial H}{\partial z} l^2,$$

where E is the translational energy of the atom of velocity v . Although the atom will be accelerated only while in the field, in general it will have a total deflection which is partly acquired while it is in the field and partly after it has left the field. The deflection formula as given above must, of course, be modified to take account of this fact, but after this is done it turns out that the only change is to substitute a factor "G" for l^2 , where G is simply a function depending upon the geometry of the apparatus. In actuality, the atoms passing through the field have a rather broad distribution of velocities and this must also be taken into account in experiments of this type. If the deflection, d , is measured, μ_z may be found.

Stern and Gerlach performed a molecular ray deflection experiment on a beam of silver atoms. Classically the values of μ_z and hence the values of d should form a continuous range. According to quantum mechanics only certain orientations of μ are allowed, and spectroscopic evidence indicated that for the silver atom only two possible orientations exist. The Stern-Gerlach experiment shows that the beam of silver atoms is

split into two parts in the magnetic field, i.e., that the values of μ_z are only two in number. Furthermore, the magnitude of the deflections which produced the splitting was such as to show that the magnetic moment μ_z is 1 Bohr magneton ($eh/4\pi mc$). This pioneering work was followed by a series of determinations of atomic magnetic moments by various investigators.

The range of the molecular beam deflection method was further extended by Stern, Estermann, and Frisch (F5, E3) in their experiments on the proton magnetic moment. They demonstrated the possibility of measuring magnetic moments of the order of a nuclear magneton ($eh/4\pi Mc$), that is, of the order of 1/1800 of a Bohr magneton. They worked with a low temperature beam of hydrogen molecules sent through a strong magnetic field of high gradient. The hydrogen molecule has no net electronic magnetic moment, and under the conditions of their experiment the magnetic moment arises only from the contribution of the two nuclear magnetic moments and a magnetic moment coming from the molecular rotation. They evaluated the rotational moment from experiments on pure parahydrogen which has no nuclear magnetic moment and found the rotational magnetic moment to be of the order of 0.9 nuclear magneton per rotational quantum number. Further deflection experiments performed on orthohydrogen, when ordinary hydrogen was used for the beam, could then be corrected for the contribution to the moment coming from the rotation. Their experiments revealed the unexpected result that the magnitude of the proton moment is not 1 but of the order of 2.5 nuclear magnetons.

Another important contribution was made by Breit and Rabi (B4) who suggested a method whereby molecular beam experiments could be used to determine nuclear spins. In the Stern-Gerlach type of experiment where high fields are used the beam is split into $2J+1$ components, where $J\hbar$ is the electronic angular momentum of the atom. If the nucleus possesses angular momentum $i\hbar$ and a magnetic moment, each of these $2J+1$ components consists of $2i+1$ individual components which are all superposed in the strong field. Breit and Rabi pointed out that if the inhomogeneous field is not too large the

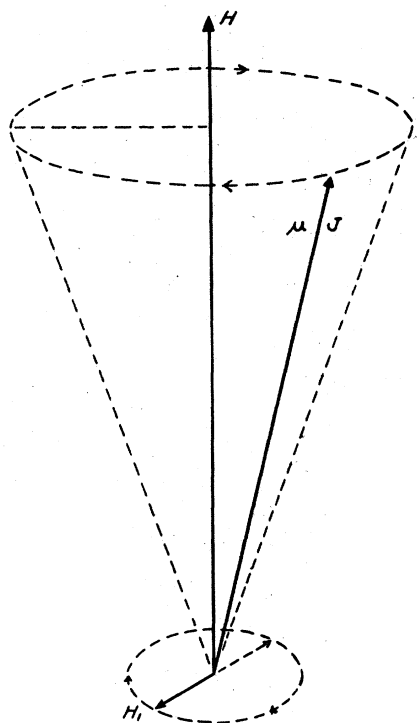


FIG. 1. Simple vector representation of a system possessing angular momentum and magnetic moment in the same direction under the influence of a large fixed magnetic field H and a small rotating field H_1 .

coupling of the electrons to the nucleus will not be destroyed and that under these conditions the beam should be split into $(2J+1)(2i+1)$ components. If J is known, the nuclear spin may then be determined by counting components. The suggestion was followed with an experiment by Rabi and Cohen (R3) to show that the nuclear spin of Na is $\frac{3}{2}$.

This method was immediately superseded by a powerful modification suggested by Rabi and first utilized in an experiment by Cohen (C1, M4, F2, M2, M6, M3) which made it possible to measure h.f.s. separations of the ground state of atoms as well as their nuclear spins. The method was applicable even in cases where the h.f.s. was too small to be observed spectroscopically. Further modification of the method provided the means for determining whether the h.f.s. was regular or inverted (R1, K3). Although the h.f.s. of a state was measured with a precision of about 1 percent, it was not possible, except in the case of the hydrogens, to calculate the

nuclear magnetic moments with anything approaching this accuracy, since such calculations require the knowledge of wave functions of the atomic state. With the exception of the magnetic resonance method, the applications of the procedures of molecular beams to the determination of atomic and nuclear moments and also to problems such as gas kinetics, diffraction of molecules from crystal surfaces, and the measurement of electric dipole moments has been beautifully set forth in two books by Fraser (F3, F4).

The resonance method was then introduced. This method, in addition to the previously developed artifices of molecular ray techniques, utilized the fact that an angular momentum and its associated magnetic moment will suffer a reorientation in a rotating magnetic field if the frequency of rotation of the field is equal to the Larmor frequency of precession of the angular momentum. These reorientation processes, or non-adiabatic transitions, as they were called, had been discussed (G4, M1) by Güttinger and by Majorana, and in particular for the general case of the rotating field by Rabi (R2).

The principle on which the method is based applies not merely to nuclear magnetic moments but rather to any system which possesses angular momentum and a magnetic moment. It is possible to give a rather simple qualitative picture of the reorientation process in terms of the classical model of a rotating gyroscope of angular momentum $J\hbar$ and possessed of a magnetic moment μ . Such a system is represented in Fig. 1, where for simplicity the angular momentum and the magnetic moment are shown in the same direction. The vector J will then precess about H with the Larmor frequency $\nu = \mu H / J\hbar$. Now suppose a small rotating field H_1 is applied to the system in such a manner that initially it is perpendicular to both H and J , and also such that its angular velocity of rotation is in the same direction as the angular velocity of the Larmor precession. This is the situation represented in Fig. 1, and inspection of that figure shows that the torque on J produced by the addition of the field H_1 is in such a direction as to increase the angle between H and J . If H_1 rotates with the frequency ν , this effect is cumulative, and the change in angle between J and H can be made large. It is apparent that

if the frequency of revolution, f , of H_1 about H is markedly different from ν , the net effect will be small, since the added torque will rapidly get out of phase with the precession. The smaller the ratio H_1/H , the sharper the effect will be in its dependence on the exact agreement between the frequency of precession ν and the frequency f . Furthermore, if the sense of rotation of H_1 is opposite to that of the precession, the added torque will tend to open the angle during one-half of the period of precession, to close it during the other half, and the net effect will be small. This latter fact is of prime importance in the determination of the signs of magnetic moments. For if the direction of μ had been opposite to that of J (negative magnetic moment), the sense of the precession would have been in a direction opposite to that indicated in Fig. 1, requiring a reversal of the sense of rotation of H_1 .

Any method (G2) which enables one to detect the change in orientation of the angular momentum with respect to H for a given applied rotation frequency provides the information $f = \nu$, and one can therefore utilize this process to measure the precession frequency and therefore the gyromagnetic ratio, $g = \mu/J$, if H is also known.

The precise form of the initial conditions previously described is not important and we may consider H_1 initially at any angle ϕ with the plane determined by J and H but still perpendicular to H . In fact, according to quantum mechanics, we must consider the initial conditions of an ensemble of systems with a definite projection of J in the direction of H as uniformly distributed over ϕ . This only means that some systems will increase and other systems decrease their projections in the direction H . Since most of the systems in which one is interested have small angular momenta ($< 10\hbar$), the classical considerations given above have to be reconsidered from the point of view of quantum mechanics. The reorientation process is more accurately described as one in which the system having angular momentum $J\hbar$ and magnetic moment μ , originally in some state with magnetic quantum number m , makes a transition to another magnetic level, m' . An exact solution for the transition probability for the case where

H_1 rotates and is arbitrary in magnitude has been given by Rabi (R2). He considers a system of magnetic moment $\mu = g\mu_0 J$, where J is the total angular momentum due to all causes and μ_0 is the Bohr magneton. If g is positive, the total moment is negative, as in the spinning electron. If g is negative, the moment is positive. In a magnetic field H the system precesses with the Larmor frequency $\nu = g\mu_0 H/h$. For the particular case of $J = \frac{1}{2}$, Rabi's formula is

$$P_{(1,-1)} = \frac{\sin^2 \theta}{1 + q^2 - 2q \cos \theta} \times \sin^2 \pi t f (1 + q^2 - 2q \cos \theta)^{\frac{1}{2}}. \quad (1)$$

Here $P_{(1,-1)}$ is the probability that the system, originally in the state $m = \frac{1}{2}$ is found in the state $m = -\frac{1}{2}$ after a time t spent in a magnetic field of magnitude $(H^2 + H_1^2)^{\frac{1}{2}}$, where H_1 rotates with frequency f ; $q = \nu/f$ and is to be taken as positive if the rotation of H_1 is in the same sense as the precession, and negative if in the opposite sense, and $\tan \theta = H_1/H$.

If the experimental conditions are so arranged that $H_1/H \ll 1$, this formula becomes

$$P_{(1,-1)} = \frac{\theta^2}{(1-q)^2 + q\theta^2} \sin^2 \pi t f [(1-q)^2 + q\theta^2]^{\frac{1}{2}}. \quad (2)$$

It follows from the last equation and from the definition of q that, if the rotation of H_1 is in the same sense as the Larmor precession, and if the respective frequencies are in resonance, then $q = +1$, and the probability that the system will suffer a reorientation of its magnetic moment with respect to the field direction is $P_{(1,-1)} = \sin^2 \pi t f \theta^2$, which can be made as close to unity as one pleases by experimentally choosing the correct values for t and θ . Moreover, if one were to leave everything unchanged except the direction of rotation of H_1 (or of the Larmor precession, by reversing the direction of H), the transition probability would become

$$P_{(1,-1)} = \frac{\theta^2}{4 - \theta^2} \sin^2 \pi t f (4 - \theta^2)^{\frac{1}{2}},$$

a quantity much less than unity. Hence from this qualitative difference, and a knowledge of the sense of rotation one can infer the sign of the moment.

Although the above formulae are derived for a spin of $\frac{1}{2}$, it is of course true that many systems exist with spins greater than $\frac{1}{2}$. For these higher spins the general formula given by Majorana (G4, M1) applies, i.e.,

$$P_{(a, m, m')} = (\cos \alpha/2)^{4J} \\ \times (J+m)!(J+m')!(J-m)!(J-m')! \\ \times \left[\sum_{\lambda=0}^{2J} \frac{(-1)^\lambda (\tan \alpha/2)^{2\lambda-m+m'}}{(\lambda-m+m')!(J+m-\lambda)!(J-m'-\lambda)!} \right]^2$$

In this equation α is defined through the relation $\sin^2 \frac{1}{2}\alpha = P_{(1, -1)}$, where $P_{(1, -1)}$ is obtained with the use of Eq. (1) for a system with a spin of $\frac{1}{2}$ which has the same μ/J and which is situated in the same magnetic field as the system under consideration. Any term in the summation containing factorials of negative numbers is to be omitted.

It is to be noted, however, that the Majorana formula need only be used when quantitative information is sought concerning the distribution of the reoriented molecules in state m among the other states, m' . For purposes of measuring the Larmor precession frequency of a nucleus one need only make use of the idea that when $f = \nu$ a maximum number of reorientations will take place.

Although Rabi's theory requires H_1 to rotate in a plane perpendicular to H , no experiments have been performed which make use of a rotating field. In practice it is more convenient to use an oscillating field for H_1 . Although for this case the situation is not quite as clear as for the rotating field, Bloch and Siegert (B3) have shown that the transition probability is approximately the same for weak oscillating fields near the resonance frequency, and the formulae for $P_{(1, -1)}$ remain the same except that θ is to be replaced by $\theta/2$. The oscillating field may be considered as the superposition of two fields rotating with the same frequency but in opposite directions and with amplitudes one half the oscillating amplitude and it is this fact which accounts for the replacement of θ by $\theta/2$. The reorientation is produced by the component which rotates in the same sense as the precession. The other component has no effect on the system. There is one unfortunate result which apparently accompanies the substitution of an

oscillating field for a rotating one, namely that it becomes impossible to determine the sign of the moment, since it is impossible to tell which of the two rotating fields is producing the transitions. However, it has been pointed out (M5) that in the actual experimental set-ups a rotating field of known direction is produced by certain end effects of the oscillating field and that this field may be used in the determination of the sign. A discussion of this effect will be reserved until the details of the apparatus have been described.

The above description has been given for a simple system containing only one angular momentum vector with its associated magnetic moment which interacts with an applied external field. More generally it is necessary to consider complicated systems containing two or more coupled angular momenta which interact with each other as well as with the external field. For this case it is simpler to view the resonance reorientations as taking place when the frequency of the oscillating field is in resonance with the frequency given by the Bohr relation

$$h\nu_{nm} = W_n - W_m, \quad (3)$$

where W_n and W_m represent the energies of two states of the whole molecular system in the magnetic field. The selection rule which governs these transitions in the cases which we will discuss is $\Delta m = \pm 1$ where m is the magnetic quantum number of the system. It may be pointed out here that the method detects not only transitions from state m to n , but also the reverse transit on n to m . One of these corresponds to absorption of radiation and the other to stimulated emission. As Einstein has pointed out, these processes are equally probable. This description in the absence of interactions within the system is equivalent to the earlier description because the energy difference between successive states of spin quantization are then all equal to $\mu H/J$, whence the Larmor frequency is the same as the frequency given by Eq. (3).

2. Experimental Arrangement

The experimental recognition of these transitions can be accomplished with the aid of the type of molecular beam apparatus which is described below. The essential features of such an apparatus are those which deal with the produc-

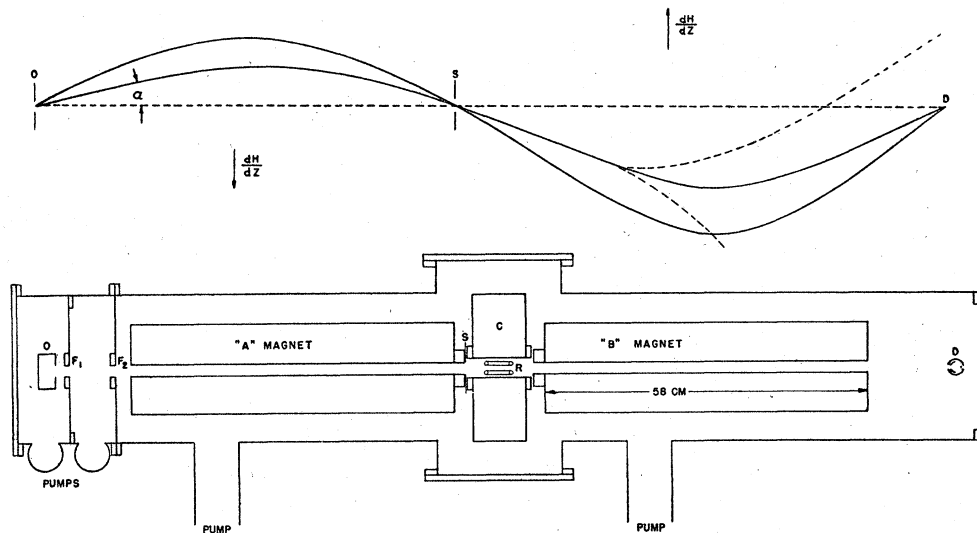


FIG. 2. Schematic diagram of a molecular beam apparatus and of some molecular paths. The two solid curves in the upper part of the figure indicate the paths of two molecules having different moments and velocities and whose moments are not changed during passage through the apparatus. The two dotted curves in the region of the *B* magnet indicate the possible changes in path for one of these molecules if its component of magnetic moment has been either increased or decreased in the region of the *C* field. The motion in the *z* direction has in each of the curves been greatly exaggerated.

tion and detection of a beam of molecules, the provision of suitable experimental conditions for reorientations to take place, and the recognition of such reorientations.

Figure 2 shows the arrangement of magnetic fields and slits in such an apparatus. Molecules effuse from a source slit at *O* into a highly evacuated chamber. A very small fraction of these molecules will pass through the collimating slit *S* and reach the detector at *D*. In the absence of any inhomogeneous magnetic deflecting fields the molecules traverse straight-line paths *OSD* and form the so-called "direct" beam.

The source frequently takes the form of a small oven made of some suitable material and equipped with knife-edge slits. This oven is then maintained at a temperature such that the vapor pressure of its contents is a few tenths of a mm of mercury. The molecules emerge in all directions from such a source, but with an intensity distribution which is proportional to $\cos \alpha$ (the angle α is shown in Fig. 2). Since it is necessary to use narrow collimating slits, a few hundredths of a mm wide at most, the number of molecules which go to form the beam is only an extremely small fraction of the total number of molecules leaving the source. Some disposition must, of course, be

made of the non-beam-forming molecules, and the ordinary procedure is either to freeze them out on the walls of the apparatus, or if this is not feasible, e.g., in the case of the permanent gases, to use fast pumps to eliminate them. Some such procedure is necessary in order to keep the pressure in the apparatus sufficiently low so that a substantial fraction of the molecules of the beam do not suffer scattering by other molecules. The slits *F*₁ and *F*₂ do not serve to limit the beam in any way since they are ordinarily from five to ten times as wide as the source and collimating slits. They do, however, serve to isolate the main portion of the apparatus from the relatively high pressures ($\sim 10^{-5}$ mm Hg) which may prevail in the oven chamber.

The "intensity of the beam," which may be defined as the number of molecules arriving at unit area of the detector per second, depends on a number of factors. Subject to the restriction that the beam be collision-free, the intensity is proportional to the source pressure and the useful area of the source, and is inversely proportional to the square of the distance from the source. Consequently when large intensities are needed it is advantageous to work with beams as short as possible. While the intensity may be increased by

increasing the source pressure, there is a limitation on the gain that may be obtained in this manner, for the source pressure may not be increased beyond the point where the mean free path of the molecules becomes comparable with the width of the source slit. Otherwise collisions at the slit will give rise to a "cloud" in front of the slit which will act as a virtual source of much greater width than the actual source. Since the intensity is proportional to the source area, and since it is usually necessary to work with narrow beams, the slits are made as long as other features of the apparatus, notably the inhomogeneous fields, will permit and as narrow as is consistent with reasonable intensity and ease of adjustment. Slits less than 0.01 mm wide are seldom used, and for this slit width diffraction effects are negligible, since the deBroglie wave-length associated with the moving molecules is of the order of one angstrom unit or less.

The use of such narrow slits renders it necessary that the source and collimator be accurately parallel. This may most easily be accomplished by making both slits parallel to a plumb line through the intermediary of the cross hair of a telemicroscope. Horizontal setting of the slits by means of a level would at first seem a feasible method, but the spreading of the beam in the gravitational field of the earth makes this procedure impractical.* Whenever possible, final adjustment of the slits to parallelism is brought about by means of the molecular beam itself. A most satisfactory device for accomplishing this has been described (M6).

Returning now to a consideration of Fig. 2, suppose the *A* and *B* magnets are excited and produce inhomogeneous fields whose gradients $(\partial H/\partial z)_A$ and $(\partial H/\partial z)_B$ are in the directions indicated by the arrows. A molecule with magnetic moment μ will be deflected in the direction of the gradient if μ_z , the projection of μ in the field direction, is positive, and in the opposite direction if μ_z is negative. The molecules for which $\alpha = 0$ will therefore, unless their moment is very small or their velocity very great, be thrown to one side or the other by the *A* field and miss the collimating slit. However, molecules which leave

the oven in a direction other than OS may now pass through the slit. In general, for a molecule having any value of μ_z and speed v it is possible to find an initial direction for the velocity of the molecule at the source such that it will pass through the collimating slit. Such paths are indicated by the solid line of the diagram. If d_A denotes the deflection at the detector from the line OSD suffered by the molecule due to the *A* field alone, it may be expressed by $d_A = \mu_z(\partial H/\partial z)_A G_A/4E$, where G_A is a factor which depends on the geometry of the apparatus. If no change in μ_z occurs in passing from the *A* to the *B* field region, then, since the directions of the gradients of the two fields are opposed, the deflection $d_B = \mu_z(\partial H/\partial z)_B G_B/4E$ produced by the *B* field will be opposite in direction to the deflection produced by the *A* field. Thus if $d_A = d_B$ the molecules are returned to the detector in the manner indicated and form a "refocused" beam. This focusing is independent of the velocity distribution of the molecules and only requires that $(\partial H/\partial z)_A G_A = (\partial H/\partial z)_B G_B$, a condition which may be easily satisfied. It is found experimentally that when the fields *A* and *B* are properly adjusted the number of molecules reaching the detector is almost the same with the magnets *A* and *B* on as with them off.

The magnet *C* produces the homogeneous field *H*. In addition there is situated in this region a pair of parallel wires carrying an oscillating current which produces an oscillating field perpendicular to *H*. If the reorientation which we have described changes the value of μ_z , the conditions for deflecting the molecules back to *D* by means of the *B* field no longer prevail. The molecule will follow one dotted-line path or the other depending upon whether μ_z has become more positive or changed sign. In either case the molecule will miss the detector and a decrease in the detector reading will result. We thus have a means of knowing when the reorientation effect occurs.

As a numerical example we shall consider an apparatus having the following dimensions: the source and collimating slits are each 0.01 mm wide, the *A* field is 25 cm long and begins 10 cm from the source slit, the *B* field is 30 cm long and begins 52 cm from the source, the collimating slit is 37 cm from the source, and the distance of the detector from the oven is 92 cm. Under these

* However, at least one experiment makes use of this deflection of a horizontally collimated beam in the earth's gravitational field. See O. Stern, Phys. Rev. 51, 852 (1937).

conditions the ratio of the geometrical factors $G_A/G_B=1.11$, and for focusing the reciprocal of this ratio is required for the corresponding gradients. Assume a gradient in the A field of 5×10^8 gauss/cm. Then if the beam is composed of molecules effusing from a room temperature source with a Maxwellian distribution and having $J=\frac{1}{2}$ and $\mu=1$ nuclear magneton, and if all these molecular moments suffer a reorientation in the region between the A and B fields, the intensity at the position of the detector will drop to about 10 percent of the value it would have if no such reorientation took place. The deflection from the refocused position of molecules having the most probable velocity will be 0.05 mm. It is because of this small deflection that it is necessary to work with narrow beams.

The inhomogeneous fields are ordinarily produced by iron electromagnets wound with a few turns of heavy water-cooled copper through which large currents may be sent from banks of heavy-duty storage batteries connected in parallel. A cross section of the pole faces of such a magnet is shown in Fig. 3. The effective boundaries of the gap are formed by portions of two circular cylinders whose intersections are separated by a distance $2a$. The iron faces of the gap are then the magnetic equipotentials corresponding to the field produced by two parallel wires carrying currents in opposite directions and whose centers coincide with the intersections of these

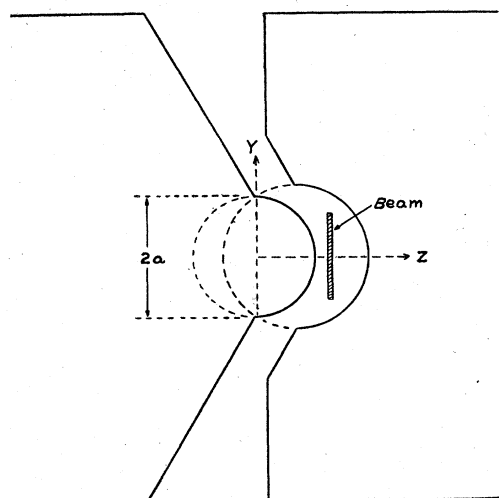


FIG. 3. Cross section of pole pieces of magnets producing inhomogeneous fields.

cylindrical surfaces. We may therefore assume, for purposes of rough calculations, that the field distribution in the gap is the same as that produced by the currents flowing in such wires.

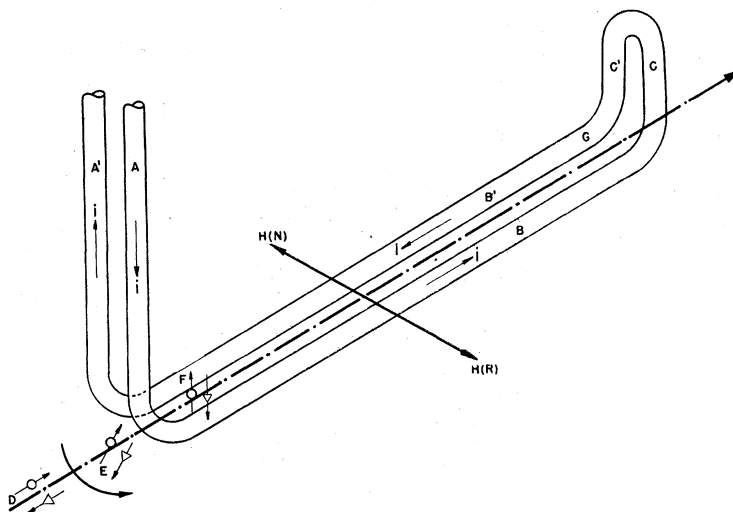
The properties of such a field and its gradient may readily be calculated (R4, M11), and are found to be ideal for these experiments. At $z=1.2a$ the gradient is nearly constant over the region $y=+0.7a$ to $y=-0.7a$, and for this position of the beam the ratio of gradient to field is about $1/a$. An Armco iron field with a 1 mm gap and wound with 4 turns will give a field in the gap of about 10,000 gauss for a current of 200 amp. With an " a " value of about $\frac{1}{8}$ cm gradients of 80,000 gauss/cm are easily obtainable.

The magnet C producing the homogeneous magnetic field may be a single yoke magnet of Armco iron. This magnet is carefully annealed in a hydrogen atmosphere and the pole faces and spacers are surface-ground and lapped to produce a gap of constant width of about 0.6 cm.

Although the gradients of the two inhomogeneous fields must be in opposite directions for refocusing to be possible, it is essential that all three magnetic fields be in the same direction and that the three magnets be close together to prevent reorientations of the molecules in regions of weak, rapidly-changing field between the magnets. To diminish these reorientations further iron slabs are attached to the ends of the inhomogeneous magnets. These slabs increase the value of the field in the gaps between the magnets and make the changes of field more gradual. This arrangement insures a fairly strong field along that portion of the path of the beam where changes in the over-all moment of the molecule affects its refocusing, i.e., from the beginning of the A field to the end of the B field, and thus limits transitions between the quantum states to the region of the oscillating field where they may be controlled and studied.

The oscillating field R may be produced by a high frequency current flowing through two copper tubes bent in the form of a "hairpin" as shown in Fig. 4. These tubes are inserted in the gap of the C magnet so that the high frequency field is approximately perpendicular to the homogeneous field. The beam traverses the path between the legs of this hairpin as shown by the dotted line. The resultant field in this region is

FIG. 4. Perspective sketch of "hairpin" shape copper tubes carrying radiofrequency current.



therefore oscillatory in character and vibrates with a frequency equal to the frequency of the current in the tubes. The tubes are supported by heavy copper tubing through which electrical and water connections may be made outside the apparatus and are supplied with current by coupling a loop in series with them to the tank circuit of an oscillator. The frequencies used in the various experiments have ranged from 0.3 to 1100 megacycles.

Since the value of the magnetic moment of any nucleus is calculated from a known magnetic field and an observed frequency, it is essential that these quantities be known to a high degree of precision. The frequency of the oscillating field may be easily determined to better than 0.01 percent by measuring the frequency of the oscillator with a commercial crystal-controlled heterodyne frequency meter. A calibration of the homogeneous magnetic field of the *C* magnet in terms of the current through the exciting coils may be made in the usual way by measuring the ballistic deflection of a galvanometer when a flip coil is pulled from the field. However, in the example of an atomic spectrum to be given later, a method of field measurement will be described which is much more accurate and better suited to these experiments.

There are in use at the present time three types of detector of the molecular beam which are capable of measuring small changes of intensity: the Pirani gauge (F5, E3, K4, E1), the ionization

gauge (D1, J2, H5), and the surface ionization detector (T1). Each of these detectors is limited in its application, and only one, the surface ionization gauge, is useful in the measurement of extremely small intensities. Both the Pirani and the ionization gauges are slow in response to the beam. The former is of use only in the detection of beams of the light permanent gases, and the latter, up to the present, has been used only for the heavier elements. The surface ionization detector has been applied to the detection of beams of the alkali metals, of indium, barium, and gallium, and of molecules containing one of the alkalis. All three detectors give a linear response to beam intensity.

The Pirani and ionization gauges are similar in that both are manometers which measure the change in pressure produced by the entrance of the beam through a small slit into an otherwise closed chamber. The effect in the case of the Pirani is to increase the heat conduction from a warm nickel ribbon to the walls of the chamber enclosing it. If the nickel ribbon forms one arm of a balanced Wheatstone bridge, the change in resistance of the ribbon, because of its change in temperature, will produce a galvanometer deflection which is proportional to the beam intensity. In the ionization gauge, electrons are accelerated from a hot filament to a positively charged grid. Collisions of these electrons with the atoms or molecules in the chamber produce positive ions which are collected by a negatively charged plate.

The change in this positive ion current when the beam enters the gauge can then be measured, and will be proportional to the change in pressure.

The difficulty with this type of detector is that very small pressure changes must be measured in the presence of comparatively large background pressures. On admission of the beam into such a manometer the pressure builds up until an equilibrium value, p_e , is attained such that as many molecules leave the chamber per second as enter it. If there is no scattering of the molecules of the beam between source and detector, and if the detector is at the same temperature as the source, this final pressure is given by $p_e = pa/\pi r^2$ where r is the distance from source to detector, p is the pressure in the source, and a is the area of the source slit. Thus for a beam length of 92 cm, a source pressure of 1 mm of Hg, and a source slit 0.01 mm wide and 2 mm high, the change in pressure in the manometer produced by entry of the full beam is of the order of 10^{-8} mm Hg. If this pressure change is to be measured to 1 percent, one is faced with the problem of reading pressure changes of the order of 10^{-10} mm Hg in the presence of a background pressure of the order of 10^{-7} mm Hg.

The change in pressure in the manometer produced by the beam may be increased by a factor K by providing the entrance to the chamber with a canal-shaped opening. If this canal is aligned with its length along the beam direction, it will offer no resistance to the passage of the beam molecules into the gauge whereas it will offer resistance to the exit of these same molecules after they have acquired random motions in the manometer chamber. K values as large as 50 have been successfully used with Pirani gauges.

Unfortunately these manometers suffer from the disadvantage that an appreciable time must be allowed for the chamber to fill and empty, and this time lag is also increased by the same factor, K . Since the manometers are always possessed of zero drift and some unsteadiness, it has been the custom in the Columbia laboratory to take six readings of the intensity, and then to average these readings to obtain a single observation. Thus with a time lag of 30 seconds a single observation will take 5 minutes, which is unpleasantly long.

Because the background pressure itself fluctu-

ates by about 10 percent, a single manometer uncompensated for these fluctuations would be worthless for the detection of weak beams. It is customary to build two manometers as nearly alike as possible, and then mount them with one facing the beam and the other facing away from the beam. The electrical connections are then made in such a manner that the background pressure fluctuations balance out.

For those molecules for which it is suitable, by far the most satisfactory detector in use at present is the surface ionization detector. In this method of detection a thin tungsten filament is placed in the path of the molecular beam. The impinging neutral atoms or molecules re-evaporate from the tungsten as positive ions, each having given up an electron to the surface. The fraction of atoms that re-evaporate as positive ions is very close to unity if the tungsten surface is kept sufficiently hot and if the difference between its work function and the ionization potential of the atom or molecule is appreciably greater than kT . The ions are collected by a plate which surrounds the filament and which is kept at a potential of about -10 volt with respect to the filament. For the length of apparatus and slit widths described earlier the ion current has to be amplified. This is achieved by connecting the collector to the control grid of an FP 54 vacuum tube. The insertion of a high resistance (about $4 \times 10^{10} \omega$) in the grid circuit converts the collector current into an appreciable grid potential which causes an increase in the plate current of the tube. With the normal tube plate current balanced out, the change in this current is a direct measure of the number of atoms or molecules impinging on the tungsten surface.

The work function of a pure tungsten surface is sufficiently high (4.5 ev) to detect beams of Cs, Rb, and K atoms, since their respective ionization potentials are less than 4.5 ev, but not high enough to detect Na or Li atoms whose ionization potentials are 5.1 ev and 5.4 ev, respectively. However, when the tungsten is heated in an atmosphere of oxygen of about 1-mm pressure, it may be made to acquire a stable oxide coat which serves to increase the work function of the surface. In this manner Na, Li, In, and Ga atoms were detected. When this procedure is applied to detect Ba atoms, with ionization potential of only

5.2 eV, it fails. This may be explained by the circumstance that Ba atoms require a relatively high surface temperature (about 1800°K or greater) for re-evaporation and that oxide coats are known to be unstable at high temperatures. The proper filament temperatures are about 1200°K for Cs, Rb, and K, 1300°K for Na, 1350°K for Ga and In, and 1400°K for Li. It is, however, possible to detect a barium beam with a pure tungsten filament kept at a temperature of 1800°K or higher. The mechanism of this detection is not quite clear (H3, G3).

The surface ionization method of detection has many significant advantages over the two detectors previously described. The surface detector is very sensitive. It will detect an ion current of about 10^{-15} ampere, or about 6000 atoms per second. For a detector area of 5×10^{-4} cm² this implies a beam intensity of 12×10^6 atoms per cm² per sec., which is equivalent to a beam pressure of the order of 10^{-14} mm of mercury. This is a much smaller number than the minimum detectable by the pressure gauges. Moreover, the detection is independent of pressure fluctuation in the chamber, since the ionization potential of any residual gas is well above the detectable limit. The effect of poor vacuum in the apparatus is merely to scatter some of the molecules and decrease the beam intensity. Any unsteadiness thus resulting is caused by fluctuations in the number of molecules arriving at the detector. Finally, one must not overlook the ease and speed with which measurements are made with this detector. A complete resonance curve may be obtained in ten minutes or less. This in turn makes the data more reliable, since changes in experimental conditions are less likely to occur in short time intervals than in long periods.

The chief limitation on this method is the fact that only a few atoms have low enough ionization potentials to be detected in this manner. However, in the nuclear moment work to be described, it was possible to observe resonance curves of other nuclei such as H, Be, F, and Al by studying them in molecules having an alkali atom as one of the constituents. The presence of the alkali serves to give the molecule a low ionization potential. It is found experimentally that all alkali containing molecules can be detected in the same manner as the respective alkali atoms.

Thus molecules containing K, Rb, or Cs can be detected with a pure tungsten surface, while molecules having either Na or Li as a constituent require an oxide coat on the tungsten for the detection. It is found, however, that the filament temperature required to detect alkali-containing molecules is in general slightly higher than that needed for the detection of the corresponding alkali atom.

As an example of the power of this method of detection we may cite the fact that Li⁶ resonance curves were observed for Li₂ molecules. In this experiment when Li was heated in the oven, the emergent beam was predominantly atomic and the atoms were completely thrown out by the strong deflecting fields. Only about 0.6 percent of the beam was in the form of Li₂ and of this 0.6 percent only 4 percent failed to reach the detector when the Li⁶ nucleus was reoriented in the oscillating field region. Thus the whole depth of the Li⁶ resonance curve represented about one part in 4000 of the total beam.

Using an apparatus especially designed for high intensity Zacharias (Z1) has been able to experiment with the atomic radio frequency spectrum of K⁴⁰ in its natural abundance (one part in 8000). His results could not have been obtained without the use of the surface ionization detector.

TYPICAL RADIOFREQUENCY SPECTRA

In order to clarify the procedure and to illustrate the power of the method, examples of its application will be given which serve to bring out the methods by which information has been obtained as to nuclear magnetic moments, nuclear spins, rotational magnetic moments, electric quadrupole moments, molecular interaction energies, and hyperfine structure separations.

1. Resolved Molecular Spectra. Nuclear

The radiofrequency spectrum of the deuterium molecule, a portion of which is shown in Fig. 5, provides an ideal example of a completely resolved molecular spectrum. The experiment (K1) was performed on deuterium molecules emerging from a source maintained at the temperature of liquid nitrogen.

The nuclei of the D₂ molecule have spins of 1 and obey the Bose statistics. The lowest rota-

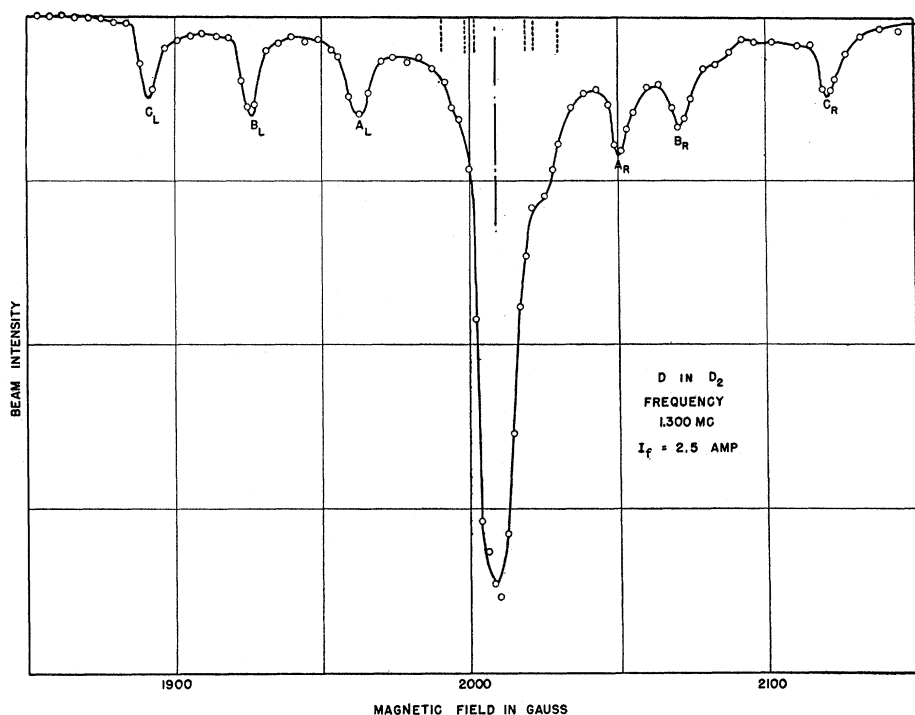


FIG. 5. Portion of radiofrequency spectrum of the deuterium molecule. The deep central resonance curve arises from reorientation of molecules for which $J=0$, $I=2$. The other six resonance curves are associated with reorientations of molecules for which $J=1$, $I=1$. The symbols A_R , A_L , etc. when used in conjunction with Table III enable one to identify the transition that corresponds to any one of these resonance minima.

tional state of this homonuclear molecule, $J=0$, is therefore a state in which the wave function of the nuclear spins is symmetrical and the total spin angular momentum, I , is either 0 or 2. For the next higher rotational state, $J=1$, the wave function for the two nuclear spins is anti-symmetrical and the total spin angular momentum is 1. For the state $J=2$, the wave function is again symmetrical and I is either 0 or 2. Thus the even rotational states are populated only with ortho- D_2 molecules, and the odd rotational states only with para- D_2 . At liquid nitrogen temperatures almost all the D_2 molecules are in these first three rotational states, and they are therefore all we need consider. The relative concentration of the molecules in the states of given J and I is shown in Table I. The concentrations are calculated on the assumption of an ortho-para ratio of 2 to 1, which is the normal high temperature equilibrium ratio for D_2 . The fraction of the molecules in a given rotational state which have a given value of I will then be given by $(2I+1)/\Sigma(2I+1)$.

Thus 9.3 percent of the molecules of the beam will have $J=0$ and $I=0$. Consequently these molecules will have no magnetic moment and will be completely inert in the apparatus.

The molecules with $J=0$, and $I=2$, will comprise 46.7 percent of the beam. But a molecule with rotational angular momentum equal to zero is one in which the internuclear axis is oriented in every direction with equal probability independent of the nuclear spin orientation. Since these molecules are in the $^1\Sigma$ state there is no resultant electronic moment and all interactions between each nucleus and the rest of the molecule become independent of the orientation of the nucleus in the external magnetic field. Furthermore, the magnetic interaction of the two nuclear moments averages out to zero because the mutual energy of two dipoles averaged over all possible orientations of the line joining them is zero. Therefore each of the two nuclei in the molecule has a definite energy in the external magnetic field depending on its own orientation and independent of the orientation of the other nucleus.

We thus have an example of a simple system of angular momentum and associated magnetic moment without any molecular interaction. These are exactly the circumstances under which the reorientations will occur if the Larmor frequency of precession

$$\nu = \mu H / I h \quad (4)$$

and the frequency of the oscillating field are in resonance, and under which the rigorous theory for the transition probabilities in the oscillating field applies.

The reorientations of these molecules for which $J=0, I=2$, give rise to the deep central resonance curve of Fig. 5. The position of the minimum, the depth, half-width, and asymmetry of this resonance curve are of physical interest.

In these experiments the procedure was to keep the frequency of the oscillating field constant and vary the frequency of the Larmor precession by varying the field H . The minimum of the curve corresponds to the condition $\nu = f$. The magnitude of $g = |\mu|/I$ may then be immediately calculated from Eq. (4). This equation gives the value of μ in units of ergs/gauss. If μ is to be expressed in units of the nuclear magneton, $eh/4\pi Mc$, where M is the proton mass, and if g is to be defined as the ratio of the magnetic moment in nuclear magnetons to the spin I , Eq. (4) may be rearranged to read, for the condition $\nu = f$,

$$g = \frac{4\pi}{e/Mc} \frac{f}{H} = 1.3120 \times 10^{-3} \frac{f}{H} \quad (5)$$

The specific charge of the proton in electromagnetic units, e/Mc , is obtained directly from the Faraday which has the value 9650.6 e.m.u. per gram equivalent on the physical scale. On the same scale the atomic weight of H is 1.00813. After correcting for the mass of the electron the quantity e/Mc becomes 9578.0 e.m.u. per gram. It may be noted here that the ratio of f to H only fixes the value of g . The spin must also be known before the magnetic moment can be calculated. Inserting the values $f=1300$ megacycles and $H=1992$ gauss obtained from the curve of Fig. 5 one obtains $g=0.855$ and hence, since the spin is one, $\mu=0.855$ nuclear magneton.

The depth of the central resonance minimum is in good agreement with the predictions of the

theory. In what has been said so far, it has been tacitly assumed that if the transition probability $P_{(1,-1)}$ is close to unity for any molecule of the beam, it is also one for all the molecules. That this cannot be true may be seen from the following considerations. The molecules of the beam emerge from the source with a velocity distribution which is approximately determined by their Maxwellian distribution in the source itself. But the formula for the transition probability at resonance contains the factor $\sin^2 \pi f t \theta$, where t is the length of time the molecules are in the oscillating field. Hence, if experimental conditions are so arranged that this factor is 1 for, say, the most probable velocity of the molecules, it will not be 1 for any other velocity. The faster molecules will not be in the oscillating field long enough, and the slower molecules will be in the field too long. The net effect of the velocity distribution is to so modify the transition probability that only about 75 percent of the systems are reoriented. Recalling that the central minimum of Fig. 5 is caused by the reorientations of only those molecules for which $J=0, I=2$, and that these molecules form only 47 percent of the beam, it is seen that the beam intensity at the position of the minimum should be decreased by 75 percent of 47 percent, or 35 percent, in excellent agreement with the experimental results.

The observed half-width (width at half depth) of the resonance curve is also in reasonable accord with the theory. The expression for $P_{(1,-1)}$ for small values of θ shows that if θ is still sufficiently large to make the argument in the \sin^2 factor equal several times π , the average of this factor over the velocity distributions will not deviate much from 0.5 as H and therefore ν , departs from its resonance value. In this case the factor $\theta^2 / [(1-q)^2 + q\theta^2]$ determines the shape of the resonance curve and the half-width of the curve is approximately $\Delta f = 2\theta f$ in frequency or $\Delta H = H_1$ in gauss units if H_1 is the magnitude of

TABLE I. Relative concentration of para-D₂ and ortho-D₂ molecules.

J	Total spin	Stat. wt.	Rel. conc.
0	0, 2	6	0.559
1	1	9	0.328
2	0, 2	30	0.105
3	1	21	0.004

the oscillating field. In this region, therefore, decreasing H_1 decreases the half-width of the resonance curve proportionately. However, as θ is decreased to the point where it is no longer correct to say that the average of the \sin^2 factor is 0.5, we must use the entire expression for $P_{(1,-1)}$ to calculate the half-width. This has been done by Torrey (T2), taking into consideration the velocity distribution. He shows that the best transition probability and narrowest resonance curve is obtained when $\nu t \theta = 0.6$ where t is the time spent in the oscillating field by a molecule moving with the most probable velocity. A further decrease in H_1 not only serves to decrease the transition probability but also widens the resonance curve slightly. When the optimum value of H_1 is used, the half-width of the curve is given by $t \delta \nu = 1.07$ where $\delta \nu$ is the width in frequency at half-intensity. If the curves are much broader than this it is an indication either that the curve contains fine structure or that the magnitude of the oscillating field is too large.

It will be noted that the central resonance minimum of Fig. 5 is not symmetrical about the field value for minimum intensity; that there is a broadening of the curve toward the high field side. This asymmetry arises from certain end effects produced by the oscillating field and may be used for the determination of the sign of the moment (M5). Consider now the magnetic field H_1 produced by the oscillating current in the wires shown in Fig. 4. When the direction of the current in the wires is as indicated by the arrows, the directions of the field at representative points along the beam path is that shown by the circled arrows. At D the contribution to the oscillating field is chiefly from the sections A and A' , and the field direction here is approximately that of the beam axis, whereas in the greater portion of the beam path in the oscillating field, from F to G , the field is vertical. With respect to the moving molecule the field has therefore turned in the sense indicated by the arc of the circle, the plane of which is vertical and at right angles to the strong homogeneous field. When the current in the wires has reversed, the field directions are as shown by the triangled arrows. Again the field has turned in the same sense as before. Similar considerations show that

the turning sense of the lines of force at the detector end of the oscillating field is the same as the one just described for the source end. Thus with respect to the moving molecule the perturbing field is strictly oscillatory only in the region from F to G , while at the end regions the field is a superposition of oscillation and rotation. Furthermore the sense of the rotation is known.

If we assume for calculations of orders of magnitude that the turning of the field through an angle of 90° takes place in a distance about twice that between the axes of B and B' , then for molecules having thermal velocities of the order of 10^5 cm/sec. it is equivalent to a rotational frequency Δf , of 3×10^4 cycles per second. Since the oscillating field can be resolved into two component fields, one rotating in the same direction as the end rotation just described and the other in the opposite sense, the effective perturbing field at the end regions rotates with a frequency $f + \Delta f$ if the Larmor precession is in the same sense as this end rotation, and with a frequency $f - \Delta f$ if the precession is in the opposite sense. A resonance curve plotting intensity against value of strong homogeneous field, H , will show a principal minimum at the position H_0 given by $\nu = \mu H_0 / I h$ and an additional minimum (which may or may not be resolved from the principal minimum) at a field value given either by $H_0 + \Delta H = (f + \Delta f) I h / \mu$ or by $H_0 - \Delta H = (f - \Delta f) I h / \mu$. Since the sense of the Larmor precession depends only on the direction of H and on the sign of the magnetic moment we may determine the sign of μ by a mere glance at a resonance curve obtained for a known H direction, or better still by observing two curves corresponding to opposite field directions. No quantitative consideration as to the shape of the asymmetry need be given for the sign determination. A more detailed calculation of this asymmetry has been given by Stevenson (S5).

The asymmetry in this case is such as to assign a positive value to the deuteron moment, in agreement with the sign obtained by a different method (R1, K3).

The magnetic resonance method has been applied by Alvarez and Bloch (A1) to the determination of the magnetic moment of the neutron. Here again one deals with a system which interacts only with the external field, and

hence only one resonance minimum is to be expected. While it is entirely possible in principle to perform a resonance experiment on a beam of neutrons in the type of apparatus described above, it is impractical to obtain a sufficiently narrow and intense neutron beam for this purpose. In consequence, except for the use of the oscillating field, an entirely different experimental set-up was employed. Reference to their original paper should be made for the details of the apparatus and for a description of their method of detecting the reorientations. Their final result, obtained after counting some 200 million neutrons is $|\mu_N| = 1.935 \pm 0.02$ nuclear magnetons. The sign of the magnetic moment of the neutron was found to be negative by Powers (P1).

We turn now to a discussion of the other six minima of Fig. 5. These minima arise from reorientations of the deuteron moment in those molecules which have $J=1$, $I=1$, and which comprise 33 percent of the beam (see Table I). When the rotational quantum number is not zero, the various interactions between the molecular constituents are no longer zero and the energy of a nucleus in the external magnetic field depends not only on its own orientation but also on the orientation of the other nucleus and on the orientation of the rotational angular momentum of the molecule. Since in a strong magnetic field there are $2J+1$ possible orientations of J , and for each of these there are $2I+1$ possible orientations of I , there are altogether 9 energy states of these molecules.

Transitions from a state with $J=1$ to one for which $J \neq 1$ cannot occur in these experiments because, if for no other reason, such a transition involves an energy change for which the frequency as determined from Eq. (3) is far greater than the frequencies employed in these experiments. There are, however, twelve possible transitions between the nine energy levels into which the state is split by the various interactions. These transitions give rise to two six-line spectra: the so-called "nuclear spectrum" characterized by $\Delta m_J = 0$, $\Delta m_I = \pm 1$, wherein the nuclei only suffer reorientation, and the "rotational" spectrum for which $\Delta m_J = \pm 1$, $\Delta m_I = 0$. It is the six-line nuclear spectrum shown in Fig. 5 which is now the subject of

discussion; the rotational spectrum will be considered later. Each of the nine levels will contain 3.7 percent of the beam molecules. Since, as mentioned previously, transitions from level a to level b are counted as well as those from level b to level a , each of the six minima of the nuclear spectrum should be 7.4 percent of the total beam intensity if the effect of the velocity distribution is neglected, and about 5 percent of the total intensity if the velocity distribution is included.

There is one startling feature of this six-line D_2 spectrum, namely the large energy separations of the lines. In order to bring out this point it is necessary to consider briefly the results obtained from the analysis of that portion of the spectrum of ortho- H_2 molecules in the state $J=1$, $I=1$ which arises from reorientations of the nuclei. The situation for the para- D_2 molecules having $J=1$, $I=1$ is exactly the same, except for intensity considerations, as that for these ortho- H_2 molecules. The six-line nuclear spectrum for H_2 molecules in this state is shown in Fig. 6. It is found that it is possible to account very accurately for the separations of these lines, for the asymmetry of these separations, and for the variation of these separations with field on the assumption that the only interactions which need be considered are: (1) the interaction with the external magnetic field, (2) the interaction of the two nuclear magnets with each other (the "spin-spin" magnetic interaction), and (3) the magnetic interaction between the nuclear spins and the molecular rotation (the spin-orbit interaction). The data enable one to evaluate the interaction constants (K_1). The value of the spin orbit constant $H'(H_2)$, which is essentially the magnetic field at the position of the nucleus produced by the rotation of the molecule, is found to be 27.2 gauss. The value of the spin-spin interaction constant $H''(H_2)$, is 34.1 gauss. Since this constant is defined by the relation $H''(H_2) = \langle \mu_P / r^3 \rangle_{av}$ where μ_P is the magnetic moment of the proton, and $\langle r^{-3} \rangle_{av}$ is the average value of the reciprocal of the cube of the effective internuclear distance of H_2 , we may also calculate it from direct measurements of μ_P and the results for r^{-3} obtained from band spectra analysis. The values of $H''(H_2)$ obtained by the two methods are in excellent agreement.

If one makes the assumption that only these

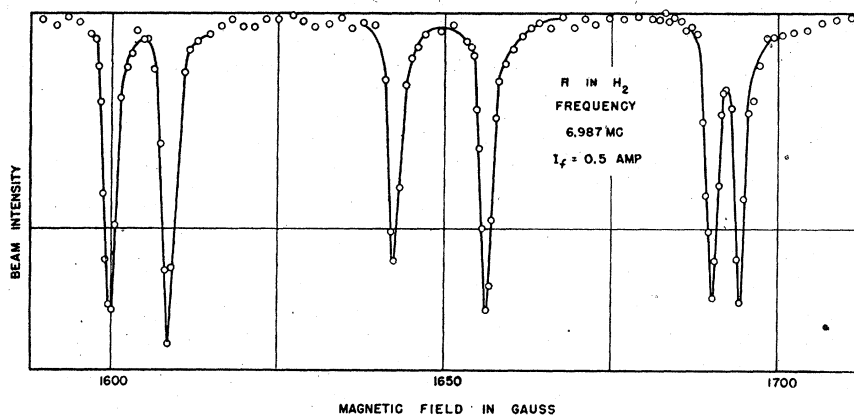


FIG. 6. Portion of radio-frequency spectrum of ortho- H_2 molecules in the state $J=1, I=1$. The resonance curves arise from the reorientation of the resultant nuclear spin.

same types of interaction are necessary to account for the spectrum of D_2 , one is led to exactly the same expressions for the energy levels for D_2 in the state $J=1, I=1$ as for H_2 in the state $J=1, I=1$ except that, of course, the values of H' and H'' are different. However, the value of $H'(D_2)$ should be one-half the value of $H'(H_2)$ since the angular velocity of rotation of the D_2 molecule is half as great as that for H_2 and the internuclear distances are so nearly the same for the two molecules. This last assumption can be made with some confidence since it has been shown experimentally that the ratio of the rotational magnetic moments of the two molecules is 2:1 within the experimental error of 0.2 percent. Similarly the value of the spin-spin constant, $H''(D_2) = \langle \mu_D / r^3 \rangle_{av}$ for D_2 can be obtained since μ_D / μ_P and μ_P / r^3 are both known.

With these assumptions it is possible to predict completely the nuclear spectrum of D_2 . The positions of the predicted minima are indicated by the dotted vertical lines in Fig. 5. The agreement with the experimental positions of the minima is wholly unsatisfactory.

A theory which will account for the positions of the deuterium nuclear lines, which is consistent with the results obtained from the H_2 spectrum, and what is more important, is consistent with results obtained from an analysis of the spectrum generated by the reorientations of the deuteron in the molecule HD , can be constructed if, in addition to the interactions previously listed, it is assumed that the deuteron has an electric quadrupole moment (K2). A nuclear electric quadrupole moment will exist if the nuclear charge distribution departs from

spherical symmetry. A quadrupole moment is taken as positive if the charge is elongated along the axis of spin, and negative if the opposite is true. The way in which a nuclear quadrupole moment manifests itself is through the fact that its energy in an external electric field depends not only on its position, but also on its orientation with respect to the gradient of the field. In an atom this field arises from the electronic charge distribution. In a molecule the field arises from the other nuclei as well as from the electrons.

On the assumption that there are these three types of interaction to consider, i.e., spin-orbit, with interaction constant H' , spin-spin with interaction constant H'' , and electric quadrupole with interaction constant H''' , expressions for the nine energy levels of para- D_2 in a strong field have been derived. These expressions have been calculated to the third order perturbation and are listed in Table II. H' and S_D are first-order perturbation terms, C_2 and C_2' are second-order terms, and C_3 is the third-order term. The definitions of the quantities are as follows: $\alpha = \mu_R / \mu_D$ is the ratio of the rotational magnetic moment of the D_2 molecule in the first rotational state to the magnetic moment of the deuteron,

$$\begin{aligned} S_D &= (H'' + H''')/5; \\ C_2 &= [(H' + 3S_D)^2 + 18S_D^2]/(1 - \alpha)H, \\ C_2' &= (H' - 3S_D)^2/(1 - \alpha)H; \\ C_3 &= (H' + 3S_D)^2(H' - 9S_D)/(1 - \alpha)^2H^2. \end{aligned}$$

The details of the derivation of the expressions for these energy levels, together with a complete discussion of the experimental data and results may be found in reference (K2).

These energy expressions are then differenced with the restriction $\Delta m_J = 0$, $\Delta m_I = \pm 1$, and the resulting differences set equal to hf_0 , where f_0 is the fixed frequency of the oscillating field with which the experiment is conducted. Solving for H the expressions for the magnetic fields at which the resonance minima will occur are obtained. These expressions are listed in Table III, wherein we have substituted H_0 for hf_0/μ_D .

The asymmetry in the positions of the six minima about the central minimum can be used to identify the experimental lines with the field values given in Table III; and when this is done, the correspondence is as given by the symbols A_R , A_L , etc. of the curve and the table. (This identification is better made from the data taken at higher field values than those of Fig. 5.) If now the symbols A_R , A_L , etc. are used to designate the experimental field values at which the resonances occur, it is seen that, if the third-order perturbations are neglected, the following set of equations may be obtained:

$$\begin{aligned} 2(3S_D - H') &= A_R - A_L = 89 \text{ gauss,} \\ 2(3S_D + H') &= B_R - B_L = 146 \text{ gauss,} \\ 2(6S_D) &= C_R - C_L = 232 \text{ gauss.} \end{aligned}$$

From these equations values of S_D and H' may immediately be found. More exact determinations made at higher frequencies and including the slight correction arising from the third-order terms give the values

$$H' = 14.00 \text{ gauss and } S_D = 19.62 \text{ gauss.}$$

Since the quantity S_D is defined as $(H'' + H''')/5$, the experiments with D_2 are incapable of providing a determination of either H'' or H''' separately. However, the value of H'' may be

TABLE II. Energy expressions for para- D_2 molecules in a strong magnetic field.

m_J	m_I	Energy
1	1	$-\mu_D(H + \alpha H + H' - S_D)$
1	0	$-\mu_D(+\alpha H + 2S_D - C_2')$
1	-1	$-\mu_D(-H + \alpha H - H' - S_D - C_2 + C_3)$
0	1	$-\mu_D(H + 2S_D + C_2')$
0	0	$-\mu_D(-4S_D - 2C_3)$
0	-1	$-\mu_D(-H + 2S_D - C_2')$
-1	1	$-\mu_D(H - \alpha H - H' - S_D + C_2 + C_3)$
-1	0	$-\mu_D(-\alpha H + 2S_D + C_2')$
-1	-1	$-\mu_D(-H - \alpha H + H' - S_D)$

deduced from the experiment on H_2 as discussed above and is found to be 10.5 gauss. This gives the value 87.6 gauss for H''' . Detailed consideration of the results shows that H''' is positive. This same interaction constant, H''' , may be obtained from experiments on the rotational spectra (R7) of D_2 and HD arising from the transitions $\Delta m_J = \pm 1$ with $\Delta m_I = 0$ and from the nuclear spectrum (K2) of HD. Furthermore, in HD the interaction constants H'' and H''' can be separately evaluated from the data and hence the value of H''' does not depend on the subtraction of a calculated quantity H'' as in D_2 . If the results of all these experiments are included the value of H''' is found to be 87.2 gauss.

In the detailed theory the definition of H''' is $e^2q'Q/2\mu_D$ where Q is the electric quadrupole moment of the nucleus and $-2eq'$ is the gradient of the electric field produced by the other charges of the molecule at the position of the nucleus. Nordsieck (N1) has calculated the quantity q' and gives its value as $1.193 \times 10^{24} \text{ cm}^{-3}$. Thus, since the experiment gives H''' , the value of Q may be found. It is $2.73 \times 10^{-27} \text{ cm}^2$ and is positive.

2. Resolved Molecular Spectra. Rotational

In addition to the types of transition discussed above, there are also the transitions associated with $\Delta m_J = \pm 1$, $\Delta m_I = 0$ which give rise to radio-frequency spectra from which the same constants H' , H'' , and H''' may be found and which also provide a determination of the rotational magnetic moments of H_2 , HD, and D_2 .

Ramsey (R7) has measured these rotational moments for the first rotational state and finds $\mu_R(H_2) = 0.879$, $\mu_R(HD) = 0.660$, $\mu_R(D_2) = 0.441$. The analysis of the spectra proceeds along lines

TABLE III. Expressions for magnetic field values at which para- D_2 resonances will occur.

m_J	m_I	Magnetic field in gauss	Line designation
1	0 \leftrightarrow 1	$H_0 - H' + 3S_D - C_2' + 0 + 0$	A_R
1	-1 \leftrightarrow 0	$H_0 - H' - 3S_D + C_2' - C_2 + C_3$	B_L
0	0 \leftrightarrow 1	$H_0 + 0 - 6S_D - C_2' + 0 - 2C_3$	C_L
0	-1 \leftrightarrow 0	$H_0 + 0 + 6S_D - C_2' + 0 + 2C_3$	C_R
-1	0 \leftrightarrow 1	$H_0 + H' + 3S_D + C_2' - C_2 - C_3$	B_R
-1	-1 \leftrightarrow 0	$H_0 + H' - 3S_D - C_2' - 0 + 0$	A_L

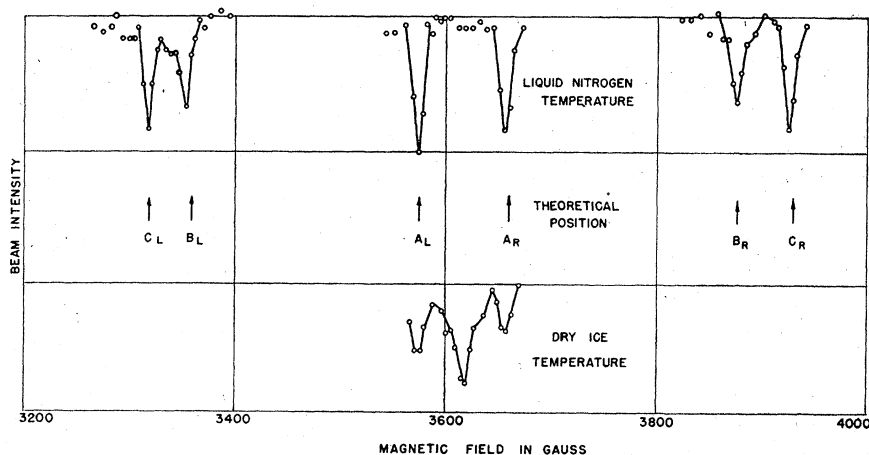


FIG. 7. The radiofrequency spectrum of H_2 corresponding to transitions in which the rotational angular momentum J changes its orientation. The oscillator frequency in this experiment was kept at 2.4198 megacycles per second. The amplitude of the perturbing field H_1 was about 10 gauss.

entirely similar to that given previously for D_2 except that for this case the energy expressions, of which examples have been given in Table II, are to be differenced for constant m_l . If one forms these differences, he immediately discovers that there is no single resonance minimum for the state $J=1$ which can be used for the direct determination of μ_R . However, if H_0 is now used to designate the value of the external field defined by $H_0 = hf_0/\mu_R$, and if only the first-order perturbations are included, it turns out that the actual minima should be displaced symmetrically about H_0 . Thus the value of the field at the center of the pattern may be used to obtain an approximate value for μ_R . If the higher order perturbations are included, together with a small diamagnetic correction, the rotational magnetic moments are found as given above. Actually the minima are not symmetrically located about the position H_0 . There is a slight shift which may be accounted for by the second-order perturbation, and this small asymmetry may be used to show that the signs of the moments are positive.

The rotational magnetic moment of a molecule arises from the circulation of charge in the rotating molecule. Frisch and Stern (F5, E3), who made the first determination of the rotational magnetic moment of the H_2 molecule in the state $J=1$ by means of a magnetic deflection experiment, point out that their result, $\mu_R \approx 0.9$ nuclear magneton, is in disagreement with the assumption of an H_2 molecule rotating as a rigid body. The rigid body model gives an

electronic contribution which is far too large and predicts a negative sign for the moment. The observed magnetic moment is such that one might picture the electronic cloud as almost stationary with the two nuclei rotating inside it. A theoretical calculation of this effect was given by Wick (W1), who also showed that the rotational moment should be proportional to J . This calculation has been extended by Ramsey to show that the moments should be in the inverse ratio of their reduced masses. This is in excellent agreement with his experimental results, given above.

The proportionality of the moments to J has received confirmation from the results on H_2 . If the temperature of the source is raised from that of liquid nitrogen to that of dry ice, the rotational state $J=2$ of H_2 is appreciably populated. Since $J=2$ is a para state in H_2 , the resultant nuclear spin, I , is zero, and consequently there is no interaction between the rotation and the nuclear spin. Thus for H_2 at dry ice temperature another minimum should appear in addition to the six minima arising from the transitions between the nine levels of H_2 in the state $J=1$. The upper curve of Fig. 7 taken at a frequency of 2.4198 megacycles and with the source at liquid nitrogen temperature shows the six lines expected from the state $J=1$. When the source was maintained at dry ice temperatures the lower curve was obtained showing a line midway between A_L and A_R . (The B and C lines are not shown on the lower curve.) The g value corresponding to this minimum is 0.879, and since

this line must be caused by changes of m_J for the state $J=2$, the rotational magnetic moment of this state must be 1.757 or just twice the moment for the state $J=1$.

3. Nuclear g 's from Unresolved Molecular Spectra

The complete resolution of molecular radio-frequency spectra is not essential for the determination of nuclear g values. The only restriction that is imposed on molecules used for such purposes is that their ground state be $^1\Sigma$, i.e., one characterized by zero electronic angular momentum. If the molecules are not in the $^1\Sigma$ state, the interaction of the nuclear spin with the electronic angular momentum is of the order of magnitude of its interaction with the applied field H . Moreover the electronic moment is so much larger than the nuclear moment that the deflections in the A and B fields will be almost entirely caused by this electronic moment and the apparatus will accordingly be insensitive to changes in nuclear orientation. This does not mean that the method will necessarily fail when applied to systems having electronic angular momentum. In fact, resonance experiments on the alkali atoms which have an electronic angular momentum of $\hbar/2$ have met with notable success. The considerations merely indicate that such systems are not the most desirable ones for the investigation of nuclear magnetic moments.

The majority of nuclear g values so far found by the resonance method have been obtained from molecules which yield resonance curves formed by the superposition of many lines. The particular molecular constituent to which the resonance curve corresponds may be identified by finding the resonance minimum common to two molecules containing the same nucleus. For example, if resonance curves are taken for LiCl, LiF, and NaF, the g values common to LiCl and LiF are those of the lithium isotopes, while the g value common to LiF and NaF is that of fluorine.

Figure 8 shows a proton resonance curve (M9) obtained with the molecule KOH. This curve was obtained in a different manner from the ones previously discussed in that the magnetic field was held constant and the oscillator fre-

quency varied. The magnetic moment of the molecule is of course a resultant of the magnetic moments of the nuclei and that due to the rotation, and for the oven temperatures required to produce a vapor pressure of a few tenths of a mm of Hg (600°C), the rotational quantum levels having large J 's are well populated. Experiment shows that despite these large J 's the chief contribution to the moment comes from the hydrogen nucleus. When this molecule passes through the strong homogeneous field, the coupling between the nuclei and between any nucleus and the rotation is broken down, and the individual components precess about the field with their respective Larmor frequencies.

Utilizing the method of measurement of magnetic field described later the experiments with beams of KOH molecules yielded the most precise determination of the proton moment yet made. The effect of the other moments in the molecule is merely to broaden the resonance curve. The half-width of the curve shown in Fig. 8 is only three times as great as one would expect if there were no interactions between the nuclear moments and between the nucleus and the rotation. Viewed classically this broadening arises from the contribution of the other constituents of the molecule to the magnetic field at the H nucleus. This contribution depends on the relative orientations of the constituents as well as on the strength of the rotational magnetic

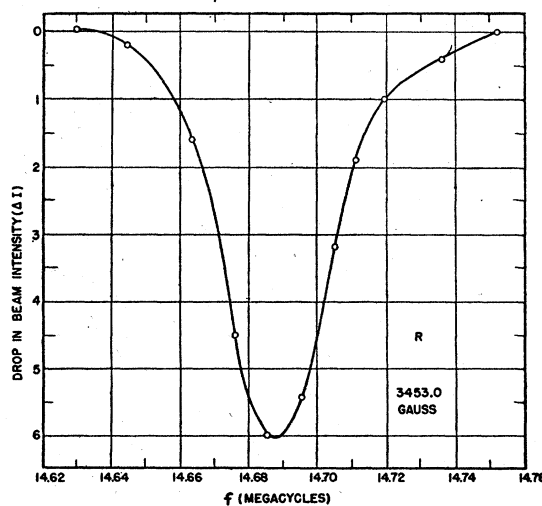


FIG. 8. Proton resonance curve in KOH.

dipole moment of the molecule. A simple consideration shows that such broadening does not disturb the symmetry of the resonance curve.

We will arrive at the same result if we consider the broadening from the point of view of energy levels and the Bohr frequency relationship. The proton moment with a spin of $\frac{1}{2}$ can take up two orientations in a magnetic field. If there were no other interactions in the molecule we would get two discrete energy levels. The presence of the other constituents in the molecule will serve to split each level into a closely spaced multiplet. Transitions between the two multiplets will no longer correspond to a single frequency. For the case under consideration the interaction energies are very small and the transition frequencies do not deviate much from the frequency corresponding to two single levels.

It should be mentioned that in calculating magnetic moments from the observed field and frequency of a resonance minimum a correction arising from the diamagnetism of the atoms must be introduced. This correction, although negligible for hydrogen, increases with atomic number and may be as large as $\frac{3}{4}$ of one percent for nuclei of large Z . The Larmor rotation of the electrons in the molecule produces a magnetic field at the nucleus which opposes the external field. The real field acting on the nucleus is less than the applied field so that the value of f/H which we take from the observed resonance minima is too small. The chief contribution to the correction field at the nucleus comes from the electrons of the atom of this nucleus. This contribution is given by the integral

$$\int 2\pi\rho\omega r \sin^3\theta dr d\theta = \bar{H},$$

where ρ is the charge density and ω is the Larmor frequency, $eH/2mc$. Since for a single electron the expression \bar{H} can be written in the form

$$\bar{H} = \omega \frac{e}{c} \left(\frac{l}{r}\right) \frac{\int \sin^3\theta d\theta}{\int \sin\theta d\theta} = \frac{2}{3} \omega \frac{e}{c} \left(\frac{l}{r}\right) = \frac{e^2 H}{3mc^2} \left(\frac{l}{r}\right).$$

For an electron of quantum number n the value of (l/r) is $Z/a_0 n^2$ if we neglect penetration and

screening, where Z is the atomic number and a_0 is the Bohr radius. Since there are $2n^2$ electrons for each n , the contribution to the field at the nucleus is approximately

$$\frac{2Ze^2H}{3mc^2a_0} \times (\text{number of electron shells}).$$

A calculation by Dr. W. E. Lamb, Jr., with the use of the Fermi-Thomas atom model gives as the expression for the correction to the field

$$\bar{H} = 0.320 \times 10^{-4} Z^{4/3} H.$$

This correction is to be subtracted from the measured value of H . It thus serves to increase the magnitude of the nuclear moment.

4. Atomic Radiofrequency Spectra (K7, M8)

Because of the existence of nuclear spin the ground states of many atoms consist of a set of closely spaced energy levels. Each level of this hyperfine structure multiplet corresponds to a value of the total angular momentum of the atom. The spacings are caused chiefly by the feeble interactions of the magnetic and electric fields of the electrons with the nuclear magnetic moment and the electrical quadrupole moments, respectively. Since the magnitudes of these interactions depend on the angle between the angular momentum of the nucleus and that of the electronic configuration, the states of different total angular momentum, F , will differ in energy.

Left to themselves, the atoms would radiate this energy in the form of electromagnetic radiation of frequency given by the Bohr formula [Eq. (3)] and settle down to their lowest energy state. This radiation has the character of magnetic dipole radiation.

The region of frequency in which these radiations are emitted lies approximately between 1.5×10^8 and 1.2×10^{10} sec.⁻¹. Because of these low frequencies the lifetime of a hyperfine structure level is very long and the intensity of spontaneous emission very feeble. Direct observation of this radiation would be very difficult. However, it is possible to illuminate the atom with electromagnetic radiation of the correct frequency and of such intensities as to cause it to absorb, or, by the Einstein process of stimu-

lated emission, to emit a quantum of this frequency in the reasonably short time of about 10^{-4} second. If such a process is detected it offers a direct method of measuring hyperfine structure. Such a method has many important advantages over existing optical methods. Firstly, the results are simple to interpret since we are concerned with only one atomic energy level; secondly, the accuracy is very high because only the measurement of the frequency of a radio wave is involved; thirdly, it is possible to measure extremely small energy separations. It is, of course, clear that similar considerations apply to all metastable states which have sufficiently long lifetimes.

Under appropriate conditions the emission or absorption of a quantum of energy is accompanied by a change in the effective magnetic moment of the atom, and hence the change may be detected by the same methods as described above. The radiation is provided by the oscillating field.

The discussion given here will be limited to the case for which the electronic angular momentum, J , is equal to $\frac{1}{2}$. If J is greater than $\frac{1}{2}$ the situation is more complicated. Furthermore with $J = \frac{1}{2}$ there can be no quadrupole interaction energy and we may then assume that the h.f.s. is caused solely by the magnetic interaction of the nuclear moment with the external electrons. The atomic systems to which the resonance method has been applied and which fulfill this requirement include all the alkali metals and indium.

The levels which compose an h.f.s. doublet are, by the rules of quantum mechanics, characterized by total angular momenta $F = i + \frac{1}{2}$ and $i - \frac{1}{2}$, where i is the nuclear angular momentum. Transitions between the two levels are governed by the selection rules for magnetic dipole radiation, $\Delta F = 0, \pm 1$; $\Delta m = 0, \pm 1$, where m is the magnetic quantum number in a magnetic field the energies of these levels as a function of the field are given by the formulae (B4):

$$W_{i+\frac{1}{2}, m} = -\frac{\Delta W}{2(2i+1)} + g_i \mu_0 H m + \frac{\Delta W}{2} \left(1 + \frac{4m}{2i+1} x + x^2 \right)^{\frac{1}{2}}, \quad (6)$$

for $F = i + \frac{1}{2}$; $m = i - \frac{1}{2}, i - \frac{3}{2}, \dots - (i - \frac{1}{2})$;

$$W_{i+\frac{1}{2}, \pm(i+\frac{1}{2})} = -\frac{\Delta W}{2(2i+1)} \pm g_i \mu_0 H (i + \frac{1}{2}) + \frac{\Delta W}{2} (1 \pm x), \quad (7)$$

for $F = i + \frac{1}{2}$, $m = \pm(i + \frac{1}{2})$;

$$W_{i-\frac{1}{2}, m} = -\frac{\Delta W}{2(2i+1)} + g_i \mu_0 H m - \frac{\Delta W}{2} \left(1 + \frac{4m}{2i+1} x + x^2 \right)^{\frac{1}{2}}, \quad (8)$$

for $F = i - \frac{1}{2}$; $m = i - \frac{1}{2}, i - \frac{3}{2}, \dots - (i - \frac{1}{2})$, where the parameter x is defined by

$$x = (g_j - g_i) \mu_0 H / \Delta W$$

and $\Delta W = h\Delta\nu$ is the energy difference between the two F states $i + \frac{1}{2}$ and $i - \frac{1}{2}$ in zero magnetic field. This also defines the symbol $\Delta\nu$ which we shall have frequent occasion to use.

In these equations the customary usage has been followed and the g factors have been defined as the negative ratio of the magnetic moment, expressed in units of μ_0 , the Bohr magneton, to the angular momentum expressed in units of $h/2\pi$. Thus, for example, the g_j values of the ground states of all the alkali atoms are positive, while the g_i values of the alkali atoms are negative, since the moments are positive. For the alkalis $g_j = 2$.

Figure 9 exhibits graphically the behavior of the ratio $W_{F,m}/\Delta W$ as a function of the parameter x for a nuclear spin of $\frac{3}{2}$. The solid lines correspond to the levels arising from the state $F = 2$, and the dotted lines to the levels arising from the state $F = 1$.

By taking the differences of the energies of the states between which transitions are allowed and dividing by h the frequencies of the lines as a function of the field are obtained.

It is important to realize that whereas the transitions are induced in the region of the oscillating field, the existence of these transitions will only be recognized if, as a result of the transition, the magnetic moment of the atom in the B field is different from its magnetic moment in the A field. The dependence of the magnetic

moment of the atom on field may be found, since $\mu_{F,m} = -\partial W_{F,m}/\partial H$. A plot showing the atomic moment as a function of x is shown in Fig. 10, again for the case $i = \frac{3}{2}$. The full lines and the dotted lines have the same significance as before. Although in some cases a strong field, such as one characterized by $x = 3$, may be advantageous for the use in the C magnet it is not in general desirable in the deflecting magnets, since the change in magnetic moment resulting from a transition will be negligible at such large fields, unless as a result of the transition the sign of the moment in the B field has changed.

In the absence of an applied magnetic field, Eqs. (6)–(8) show that all the magnetic levels belonging to a given value of F coalesce, and therefore under this condition the transition $\Delta F = 1$ will result in a single line of frequency $\Delta = \Delta W/h$. In a magnetic field the Zeeman effect of this line will be observed. When the departure from zero magnetic field is only a few hundredths of a gauss, the splitting of each of the F levels is sufficiently great to observe a completely resolved pattern of Zeeman lines instead of the single line of frequency $\Delta\nu$.

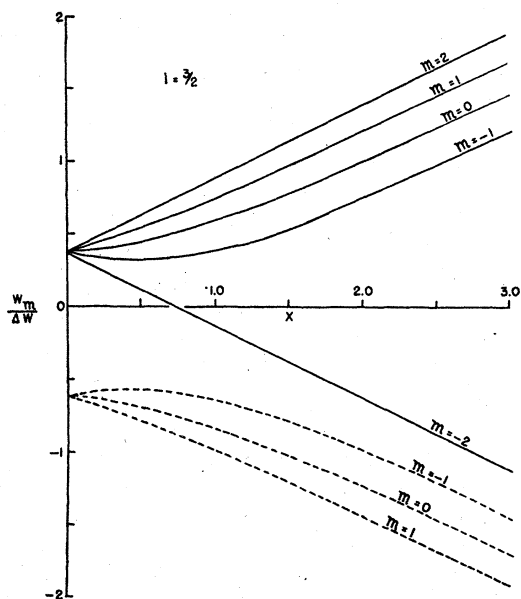


FIG. 9. Variation of energy levels with magnetic field of an atom in a ${}^2S_{1/2}$ state for a nuclear spin of $\frac{3}{2}$. The solid and dotted lines correspond to the levels arising from the states $F=2$ and $F=1$, respectively. The parameter X is proportioned to $H/\Delta W$, where ΔW is the energy difference between states $F=2$ and $F=1$ at zero magnetic field.

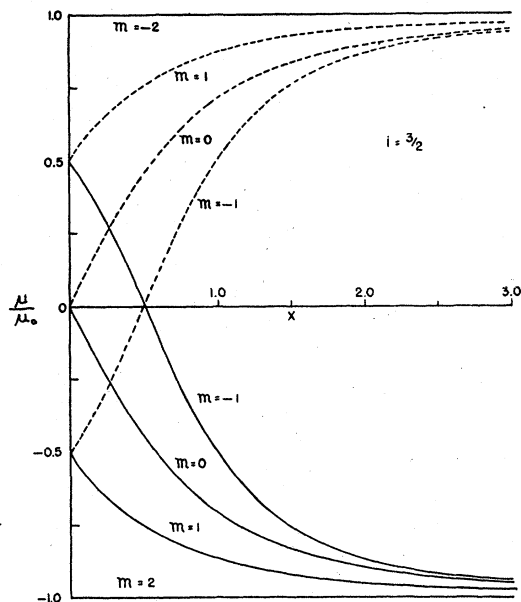


FIG. 10. Dependence of the magnetic moment in magnetic field for an atom in a ${}^2S_{1/2}$ state with a nuclear spin of $\frac{3}{2}$. As in Fig. 9 the solid lines refer to m levels of the state $F=2$ and the dotted lines to $F=1$ levels.

Figure 11 exhibits the Zeeman pattern taken in a field of 0.05 gauss of the $|\Delta F| = 1$ of K^{39} which has a nuclear spin of $\frac{3}{2}$. The lines are characterized by the selection rule $\Delta m = \pm 1$ and are caused by transitions produced by the component of the oscillating field perpendicular to the constant field H . Lines arising from transitions for which $\Delta m = 0$ are caused by the component of the oscillating field which is parallel to H . These lines are missing in this pattern because the oscillating field was very feeble, and since the oscillating field was predominantly at right angles to the fixed field, the component of the oscillating field parallel to H was insufficient to give rise to such transitions. While these transitions have been observed for larger oscillating fields, the broader resonance curves so obtained impair the resolution. If still larger oscillating fields are used, the whole pattern has the appearance of one broad resonance curve. With different field direction arrangements it is of course possible to make the $\Delta m = 0$ transitions more pronounced than those that are accompanied by a change in the magnetic quantum number of unity.

In weak fields where $x \ll 1$, it is permissible to neglect the terms in g_i and x^2 in Eqs. (6)–(8).

Under these conditions the equations show that the frequency corresponding to the center of gravity of such a pattern as that of Fig. 11 is the frequency $\Delta\nu$. Each of the two central lines of Fig. 11 actually comprises a very close doublet whose frequency separation, $2g_i\mu_0H/h$ is too small to be observed. Thus, instead of the six lines which might be expected from cursory perusal of the energy level diagram, only four are experimentally observed. It is to be noted that this method for the determination of $\Delta\nu$ requires no knowledge of the magnetic field H other than that it is small.

The method outlined above for the determination of $\Delta\nu$ is perfectly general, but it has not always proved easy to use because of experimental difficulties which arose with the use of very high radiofrequencies. In the case of K^{39} the h.f.s. separation is about 460 megacycles, a frequency which lies in a region then easily realized in the laboratory with existing commercial vacuum tubes (e.g., Western Electric 316A). On the other hand, the zero field h.f.s. separation of Na^{23} , for example, is about 1770 megacycles, and the production and accurate measurement of such frequencies was considered quite difficult at the time these experiments were performed.

Two methods will now be presented which lead to precise measurement of large $\Delta\nu$'s without the use of very high frequencies. Reference to Fig. 9 shows that for large values of x the energy levels split into two groups whose components are approximately parallel. Thus it appears that the frequencies of the lines arising from transitions between two adjacent levels of a given group are rather insensitive to x if x is large (i.e., for large H). In fact the difference in energies of such levels depends primarily on $\Delta\nu$ and i and only slightly on H and g_i . Since H can easily be determined to 1 percent, uncertainty in its value produces a negligible effect on the value of $\Delta\nu$. Similarly, if the uncertainty in g_i (obtained, say, from nuclear resonance curves) does not exceed 1 percent, it will not affect the value of $\Delta\nu$. If the frequency of the doublet lines arising from

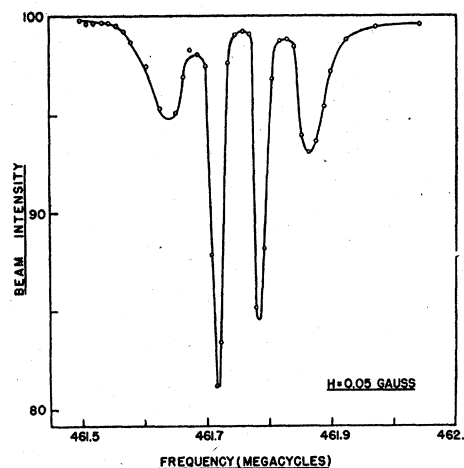


Fig. 11. Zeeman pattern of the line $|\Delta F|=1$ for the K^{39} atom in a magnetic field of about 0.05 gauss. The resonance curves correspond to lines characterized by $|\Delta m|=1$.

transitions such as $(F, m) \rightarrow (F, m')$ are observed at the same value of H and hence of x for both F values and the same m and m' , $\Delta\nu$ may be obtained without the knowledge of g_i . That the average frequency of such a doublet does not depend on g_i may be verified by inspection of Table IV which gives the expressions for the frequencies of these lines in the special case $i = \frac{3}{2}$.

Furthermore a simple expansion of the expressions for these frequencies for $x^2 \gg 1$ shows that aside from the factor $g_i\mu_0H$, which is fairly small even for the highest fields used in these experiments, they all tend toward the frequency $\Delta\nu/4$ as x increases. In the general case the frequencies tend toward $\Delta\nu/(2i+1)$. This means that it is possible to measure $\Delta\nu$ with the use of frequencies which lie in the region $\Delta\nu/(2i+1)$.

As a matter of fact, if all the transitions are observed, it is not necessary to know either g_i or H . It may be seen by reference to Table IV that the sum of the mean frequencies of all the doublets added to the sum of the frequencies of the single lines is identically equal to $\Delta\nu$ for a constant value of x . This is true not only for the case $i = \frac{3}{2}$, but for any atomic system described by Eqs. (6)–(8). Thus

$$\Delta\nu = \nu(i + \frac{1}{2}, i + \frac{1}{2} \leftrightarrow i + \frac{1}{2}, i - \frac{1}{2}) + \nu(i + \frac{1}{2}, -i - \frac{1}{2} \leftrightarrow i - \frac{1}{2}, -i + \frac{1}{2})$$

$$+ \frac{1}{2} \sum_{m=i-\frac{1}{2}}^{-i+\frac{3}{2}} [\nu(i + \frac{1}{2}, m \leftrightarrow i + \frac{1}{2}, m - 1) + \nu(i - \frac{1}{2}, m \leftrightarrow i - \frac{1}{2}, m - 1)]$$

TABLE IV. Expressions for transition frequencies for atoms in a magnetic field. $J = \frac{1}{2}$, $i = \frac{3}{2}$.

Transitions	Expression for frequencies
$(2, 2) \leftrightarrow (2, 1)$	$\frac{1}{2}\Delta\nu [(1+x) - (1+x+x^2)^{\frac{1}{2}}] + g_i\mu_0 H/h$
$(2, 1) \leftrightarrow (2, 0)$ $(1, 1) \leftrightarrow (1, 0)$	$\frac{3}{2}\Delta\nu [(1+x+x^2)^{\frac{1}{2}} - (1+x^2)^{\frac{1}{2}}] + g_i\mu_0 H/h$ $\frac{3}{2}\Delta\nu [(1+x+x^2)^{\frac{1}{2}} - (1+x^2)^{\frac{1}{2}}] - g_i\mu_0 H/h$
$(2, 0) \leftrightarrow (2, -1)$ $(1, 0) \leftrightarrow (1, -1)$	$\frac{3}{2}\Delta\nu [(1+x^2)^{\frac{1}{2}} - (1-x+x^2)^{\frac{1}{2}}] + g_i\mu_0 H/h$ $\frac{3}{2}\Delta\nu [(1+x^2)^{\frac{1}{2}} - (1-x+x^2)^{\frac{1}{2}}] - g_i\mu_0 H/h$
$(2, -2) \leftrightarrow (1, -1)$	$\frac{1}{2}\Delta\nu [(1-x+x^2)^{\frac{1}{2}} + (1-x)] - g_i\mu_0 H/h$

where, for example, the term $\nu(i + \frac{1}{2}, i + \frac{1}{2} \leftrightarrow i + \frac{1}{2}, i - \frac{1}{2})$ means the frequency of the line characterized by the transition $F = i + \frac{1}{2}$, $m = i + \frac{1}{2} \leftrightarrow F = i + \frac{1}{2}$, $m = i - \frac{1}{2}$. This expression for $\Delta\nu$ is valid for any value of the nuclear spin other than $\frac{1}{2}$. Only the first two terms apply in the case of $I = \frac{1}{2}$.

All three of these methods have been used in the case of K^{39} with identical results for the h.f.s. of the ground state.

If the field is known the value of g_i can be found from the frequency separation of the members of each pair of lines. Such a determination will not be very accurate since one is measuring the rather small frequency difference, $2g_i\mu_0 H/h$, between two lines whose total frequency is large compared to this difference. With the molecular beam magnetic resonance method for determining nuclear g values, the quantity $g_i\mu_0 H/h$ is measured directly as a first-order effect and can, therefore, be determined much more precisely.

If the factor $2i+1$ does not offer a sufficient reduction in frequency, the $\Delta\nu$ can be determined by observing the frequency of two lines at the same field, since such data would yield two equations for the two unknowns x and $\Delta\nu$. For such a procedure to be sufficiently sensitive one has to choose two lines whose frequencies vary with field at a different rate, e.g., the lines $(2, -2) \leftrightarrow (2, -1)$ and $(2, 1) \leftrightarrow (2, 2)$ in the region of $x=0.5$. In this way the h.f.s. of the ground state of Rb^{87} and Cs^{133} were satisfactorily measured with a precision comparable to that obtained by observing a transition between the two F levels at zero field.

MEASUREMENT OF MAGNETIC FIELD

Once the $\Delta\nu$ of the ground state of an alkali atom and the nuclear spin are known, a measurement of the frequency of certain of the lines can be utilized in the precise calibration of the mag-

netic field (M9), for the expressions for the frequencies may then be solved for x and therefore for the field H . Here again, the term $g_i\mu_0 H_0$ is only a small correction term. However, not all lines are satisfactory for this purpose. One must choose a line whose frequency varies markedly with x , e.g., the line arising from a transition such as $(2, -1) \leftrightarrow (2, -2)$ of Fig. 9. This line would be satisfactory in all regions of x up to the limit of the oscillator frequency. The transition $(2, -2) \leftrightarrow (1, -1)$ can be used for field measurement only in the region of x up to 1.5 or 2, and the transition $(F, 0) \leftrightarrow (F, 1)$ can be used only for low values of x . Since the $\Delta\nu$'s of the alkali atoms differ widely in magnitude, we have here a method of calibrating fields in any region up to about 5000 gauss even if the range of available oscillator frequencies is limited.

For precise calibration of a field at which a nuclear resonance curve is observed it is essential that the atomic transitions be observed at the same field setting as that used for the nuclear resonance work. This eliminates the error introduced by the lack of reproducibility of field for the same current in the exciting coils.

Because of the effect of the stray field of the A and B magnets on the C magnet, it is necessary to arrange experimental conditions in such a way that one can proceed from an observation of an atomic transition to the study of a nuclear resonance curve without any change in the value of the inhomogeneous fields. This requirement appears at first sight impossible to fulfill since the detection of nuclear reorientations generally requires large field gradients, while such gradients will tend to remove the alkali atoms completely from the beam. Thus while most nuclear resonance curves were obtained using gradients of about 10^5 gauss/cm, the radiofrequency spectra of the alkali atoms were studied with gradients of about 500 gauss/cm. However, if one observes the resonance curve of a nucleus with a large g , and further chooses particular atomic states, it is possible to overcome this apparent difficulty and observe a nuclear and atomic transition for the same setting of the deflecting fields. The study of a proton resonance curve does not require very high gradients since the g value is large and a reorientation in the nucleus results in a relatively large moment change. Moreover, reducing the

field gradient to the point where the depth of the resonance curve begins to decrease because of the decrease in deflecting power does not affect the width of the resonance curve. If now advantage is taken of the fact that some states of an alkali atom have zero magnetic moment at certain values of magnetic field it becomes feasible to observe atomic and nuclear transitions in rapid succession without any changes in the apparatus conditions other than the switching of oscillators. In the moment diagram shown in Fig. 10 atoms in the states $(2, -1)$ and $(1, -1)$ have no magnetic moment at $x = \frac{1}{2}$. Thus if the deflecting fields are set at the zero moment value, atoms of the states just mentioned will reach the detector undeflected. If, however, a transition to state $m = -2$ or to the state $m = 0$ has taken place, the moment of the atom in the second deflecting field will be appreciably different from zero and the atom will not reach the detector.

Use has been made of these "zero moments" in early atomic beam experiments (C1, M4, F2, M2, M6, M3) to determine the nuclear spins of the alkali atoms. In the case of Na^{23} a zero moment position occurs at 316 gauss. In Rb^{85} there are two such positions, one at 361 gauss and another at 722 gauss. In Cs^{133} there are zero moment positions at 821, 1642, and 2463 gauss, respectively. The proton resonance curve exhibited in Fig. 8 was obtained with the deflecting fields* set at the second zero moment position of Cs^{133} . The line used for this calibration was the one characterized by the transition $(4, -2) \leftrightarrow (4, -1)$.

The procedure just outlined for accurate calibration of magnetic fields requires that the atomic beam which yields the field calibration be detected at about the same time as the molecular beam yielding the nuclear resonance curve. In some cases this is automatically fulfilled. For example, when NaOH is inserted in a silver oven and heated to a temperature of 650°C about $\frac{2}{3}$ of the molecules dissociate yielding an atomic beam of Na , which can be used for field calibration. The remaining third is in the molecular NaOH form which can be used for obtaining a proton resonance curve. For other cases ovens have been constructed containing two separate chambers

which merge only in the region of the slit. It is, of course, necessary to choose substances that have the requisite vapor pressure at approximately the same temperature. KOH at 600°C has about the same vapor pressure as Cs or Rb provided that the alkali metals are not inserted into the oven in their pure form, but are generated in the oven from a mixture of calcium shavings and the alkali chloride.

PRECISION

A nuclear gyromagnetic ratio is determined from the measurement of a magnetic field and an oscillator frequency. For a resonance curve free from any molecular interaction the minimum of the curve represents the condition for which the oscillator frequency is the same as the Larmor precession frequency. The frequency of an oscillator can easily be measured with a precision of 0.01 percent and the limiting factor in the accuracy with which a nuclear g can be determined is the measurement of magnetic field. If atomic transitions are used to calibrate the magnet it is possible to determine fields in terms of the known gyromagnetic ratio of the electron and the frequency of the observed atomic line with a precision of about 0.03 percent. The precision with which the zero field hyperfine structure of the ground state of the alkalis can be measured is about the same as the precision with which the heterodyne frequency meter (General Radio Type 620A) can be read, which is slightly better than 0.01 percent. In almost all of the atomic transitions the half-widths of the lines are not wide enough to affect the precision.

When one nuclear g is accurately known, it is then possible to measure any other g with a high degree of accuracy by observing the two respective resonance curves at the same settings of magnetic field. The limitation on the precision of such measurements arises from the fact that in most cases molecular interactions tend to widen the resonance curve considerably. For wide curves it is not only difficult to locate the minimum but it is also not certain that the minimum represents the condition for which the oscillator frequency matches the precession frequency of the nucleus, since the nature of the molecular interaction is not clearly understood.

* It is important not to confuse the magnitude of the deflecting fields with that of the homogeneous field.

RESULTS

Tables V and VI list the results for nuclear magnetic moments and h.f.s. separations obtained by the molecular beam magnetic resonance method. In Table V the observed g values listed in column two do not include any diamagnetic corrections. These corrections are given separately in column five and serve to increase the magnitudes of the moments. In Table VI column three gives the results for the splitting of the ground state of the atoms in wave numbers, wherein we have used for c the value 2.99776×10^{10} cm/sec. It is obvious that these tables are not to be considered as complete tabulations of the results of all work on h.f.s. and nuclear moments. Only those results obtained by the resonance method are listed here. For a more complete compilation the reader is referred to the article by Bethe and Bacher (B2) in *The Reviews of Modern Physics*. These authors also give a table of nuclear spins together with a resume of the literature up to that time.

Hydrogen (K1, K2, R7, M9)

The nuclear gyromagnetic ratio of H^1 has been determined from the measurement of its Larmor precession frequency in the molecules HD, KOH, and NaOH. It has also been evaluated from the magnitude of the dipole interaction of the two proton moments in the hydrogen molecule. The values all agree to within their experimental errors. The most precise determination of the proton moment comes from the experiments on the alkali hydroxides. The g value so found is 5.5791 ± 0.0016 . Since the nuclear spin is $\frac{1}{2}$, the moment is 2.7896 nuclear magnetons. This moment is the most accurately known of any so far determined.

Nuclear g values for the deuteron come from experiments on the molecules HD and D_2 . The ratio μ_P/μ_D has been carefully determined and is found to be 3.2570 ± 0.001 . Combining this with the value of the proton moment gives 0.8565 nuclear magnetons for the deuteron moment.

From a study of the radiofrequency spectra arising from transitions corresponding to reorientations of the rotational angular momentum in H_2 , HD, and D_2 , Ramsey has determined the rotational magnetic moments of these molecules

TABLE V. Nuclear moments measured by the molecular beam magnetic resonance method.

Nucleus	Observed g value	Spin i	Moment	Diamagnetic correction (%)
H ¹	5.5791 ± 0.0016	1/2	+2.7896	0
H ²	0.8565 ± 0.0004	1	+0.8565	0
Li ⁶	0.8213 ± 0.0005	1	+0.8213	0.01
Li ⁷	2.1688 ± 0.0010	3/2	+3.2532	0.01
Be ⁹	0.784 ± 0.003	3/2*	-1.176	0.02
B ¹⁰	0.598 ± 0.003	1*	+0.598	0.03
B ¹¹	1.791 ± 0.005	3/2*	+2.686	0.03
C ¹³	1.402 ± 0.004	1/2*	+0.701	0.03
N ¹⁴	0.403 ± 0.002	1	+0.403	0.04
N ¹⁵	0.560 ± 0.006	1/2	0.280	0.04
F ¹⁹	5.250 ± 0.005	1/2	+2.625	0.06
Na ²³	1.4765 ± 0.0015	3/2	+2.215	0.08
Al ²⁷	1.452 ± 0.004	5/2	+3.630	0.10
Cl ³⁵	0.547 ± 0.002	5/2*	+1.368	0.14
Cl ³⁷	0.454 ± 0.002	5/2*	+1.136	0.14
K ³⁹	0.260 ± 0.001	3/2	+0.391	0.16
K ⁴⁰		4	-1.290	0.16
K ⁴¹	0.143 ± 0.001	3/2	+0.215	0.16
Kr ⁸³	$0.2148 \dagger$	9/2*	-0.967 †	0.38
Rb ⁸⁵	0.536 ± 0.003	5/2	+1.340	0.39
Rb ⁸⁷	1.822 ± 0.006	3/2	+2.733	0.39
In ¹¹³	1.22 ± 0.01	9/2	+5.49	0.58
In ¹¹⁵	1.22 ± 0.01	9/2	+5.50	0.58
Cs ¹³³	0.731 ± 0.002	7/2	+2.558	0.67
Ba ¹³⁵	0.554 ± 0.002	3/2	+0.831	0.68
Ba ¹³⁷	0.619 ± 0.002	3/2	+0.929	0.68

* Nuclear spins uncertain.

† Unpublished preliminary result. See discussion in text.

TABLE VI. Hyperfine structure separations of the alkali and indium atoms in the ground state, as measured by the magnetic resonance method.

Atom	$\Delta\nu$	
	sec. ⁻¹ × 10 ⁻⁶	cm ⁻¹
Li ⁶	228.22 ± 0.01	0.007613
Li ⁷	803.54 ± 0.04	0.026805
Na ²³	1771.75 ± 0.07	0.059102
K ³⁹	461.75 ± 0.02	0.015403
K ⁴⁰	1285.7 ± 0.1	0.042887
K ⁴¹	254.02 ± 0.02	0.008474
Rb ⁸⁵	3035.7 ± 0.2	0.10127
Rb ⁸⁷	6834.1 ± 1.0	0.22797
In ¹¹³	11387 ± 4	0.3799
In ¹¹⁵	11413 ± 3	0.3807
Cs ¹³³	9192.6 ± 0.5	0.30665

in the first rotational state and finds for their values 0.879 ± 0.007 , 0.660 ± 0.005 , and 0.441 ± 0.003 nuclear magneton, respectively. He also evaluates the high frequency contribution to the diamagnetic susceptibility of H_2 , and the dependence upon orientation of the diamagnetic susceptibility of the hydrogen molecule in the first rotational state.

From the analysis of the radiofrequency spectra of the molecules HD and D_2 certain molecular

interaction constants are obtained. The most important of these is the interaction of the electric quadrupole moment of the deuteron with the inhomogeneous electric field of the molecule. This leads to a value of the quadrupole moment of 2.73×10^{-27} cm².

The existence of this quadrupole moment implies that the ground state of the deuteron is not an *S* state but may be a mixture of ³S₁ and ³D₁. On this basis Rarita and Schwinger (R8) derive an expression for calculating the neutron moment from the observed values of μ_P/μ_D . This value of μ_N is -1.911 ± 0.001 wherein the precision measure includes only experimental errors in the determination of μ_P and μ_D . The value of μ_N obtained from a simple subtraction $\mu_D - \mu_P$ is -1.933 ± 0.001 . These results are to be compared with the value -1.935 ± 0.02 obtained by Alvarez and Bloch (A1) for the moment of the free neutron. The uncertainty in the latter experiment is thus too great to yield an experimental check on the theoretical predictions.

Lithium (R6, R5, K7)

Nuclear resonance curves of the isotopes of lithium have been observed in the molecules LiF, LiCl, LiBr, LiI, and Li₂. The resonance curves are generally deep and narrow. The observed nuclear gyromagnetic ratios are 0.8213 ± 0.0005 and 2.1688 ± 0.0010 for Li⁶ and Li⁷, respectively. The spin of Li⁶ is 1 and that of Li⁷ is $\frac{3}{2}$. The nuclear moments are then 0.8213 and 3.2532 nuclear magnetons. The ratio of the moments has been accurately determined by observing the two resonance curves at a fixed field. The result for the ratio $\mu_{(Li^7)}/\mu_{(Li^6)}$ is 3.9601 ± 0.0015 .

The $\Delta\nu$ of the ground state of the Li⁶ atom has been determined by studying the Zeeman lines in fields of 0.25 to 1.5 gauss. The $\Delta\nu$ of Li⁷ was obtained both by the direct observation of the Zeeman lines in a field of 0.15 gauss and by studying the lines characterized by the transition $\Delta F=0$, $\Delta m = \pm 1$ at fields of about 3500 gauss. Both methods yield identical values for the h.f.s. of Li⁷. The measured $\Delta\nu$'s are $(228.22 \pm 0.01) \times 10^6$ and $(803.54 \pm 0.04) \times 10^6$ sec.⁻¹ for Li⁶ and Li⁷, respectively. The ratio of the moments μ_7/μ_6 as

obtained from the relation

$$\frac{\mu_7}{\mu_6} = \frac{[2i/(2i+1)]_7 \Delta\nu_7}{[2i/(2i+1)]_6 \Delta\nu_6}$$

is 3.9610 ± 0.0004 . The excellent agreement of this result with that given above for the directly measured ratio may be taken as confirmation of the belief that the h.f.s. is caused solely by the magnetic interaction of the nuclear moment with the external electrons.

Beryllium (K8)

The nuclear resonance curves of Be⁹ were obtained from the molecules (NaF·BeF₂) and (KF·BeF₂). The observed *g* value is 0.784 ± 0.003 . The nuclear moment was found to be negative. No experimental results are available concerning the spin of this nucleus. Theoretical predictions (R9) coupled with the observed negative sign of the moment make it highly probable that the spin is $\frac{3}{2}$, and if we assume this value the magnetic moment becomes -1.76 .

Boron (M10)

The nuclear *g* values of the boron isotopes have been measured by observing the resonance curves in the alkali tetraborates and metaborates. The gyromagnetic ratios are found to be 0.598 ± 0.003 for B¹⁰ and 1.791 ± 0.005 for B¹¹. The spins of these nuclei have not been measured. The theoretical predictions (R9, F1, S1) are 1 for B¹⁰ and $\frac{3}{2}$ for B¹¹. If these values are assumed, the magnetic moments become 0.598 and 2.686, respectively.

Carbon (H3)

The results of the experiment with the less abundant isotope of carbon has recently been published by Hay. The resonance curves were observed with the use of the molecules KCN and NaCN, wherein the concentration of the C¹³ constituents had been enriched. The measured *g* value is 1.402 ± 0.004 . The spin of C¹³ is not definitely known. Although experiments with alternate intensities of band spectra (T3) indicate that a spin of $\frac{3}{2}$ is more probable than that of $\frac{1}{2}$, simple theoretical predictions (R9) together with the experimental results of Hay make a spin

of $\frac{1}{2}$ much more probable than that of $\frac{3}{2}$. If we assume a nuclear spin of $\frac{1}{2}$ the magnetic moment is 0.701.

Nitrogen (K9, Z2)

The resonance curves for N^{14} were observed with the use of the N_2 , LiCN, NaCN, and KCN molecules, while those of N^{15} were obtained with the use of an enriched sample of N_2 gas. The results with N^{15} were not sufficiently conclusive to determine the sign of the moment. The observed g values are 0.403 ± 0.002 and 0.560 ± 0.006 for N^{14} and N^{15} , respectively. The nuclear spin of N^{14} is known to be 1 while that of N^{15} is $\frac{1}{2}$ (W2, K5). The magnetic moments are then 0.403 and 0.280, respectively.

Fluorine (R6, R5)

The molecules LiF, NaF, and KF give fluorine resonance curves. The NaF molecules offer a particularly good source for narrow and deep fluorine resonance minima. The observed result for the g value is 5.250 ± 0.005 . Since the spin of this nucleus is $\frac{1}{2}$, the magnetic moment is 2.625.

Sodium (M8, K9)

The nuclear resonance curves of Na have been studied with the use of the molecules NaF, NaCN, and Na_2 . The contrast between the resonance curves observed in these three cases is most startling. In NaF the curve is very broad and shallow with a maximum observed drop in intensity at the resonance minimum of 4 percent. In NaCN the resonance curves are considerably narrower while the drop in intensity at the minimum is as much as 9 percent. In Na_2 the curves are very narrow, comparing very favorably with observed hydrogen or lithium resonance curves. Drops in intensity as large as 55 percent have been observed. The differences are caused by the different molecular interactions that exist in the three molecules. The observed g value for Na, however, is the same for each of the three sources and has the value 1.4765 ± 0.0015 . Using the known nuclear spin of $\frac{3}{2}$ the moment becomes 2.215 n.m.

The hyperfine separation of the ground state of the sodium atom was obtained in fields of about 5000 gauss from the lines characterized by the

transitions $\Delta F=0$, $\Delta m = \pm 1$. The result for this is $(1771.75 \pm 0.07) \times 10^6 \text{ sec.}^{-1}$.

Aluminum (M7)

Nuclear resonance curves of aluminum were observed with the molecules $NaCl \cdot AlCl_3$ and $KCl \cdot AlCl_3$. The observed g value is 1.452 ± 0.004 . When this result is compared with that calculated by means of the Goudsmidt formula from observed h.f.s. work of Jackson and Kuhn (J1) and of Heyden and Ritchl (H4) for various assumed values of nuclear spin it lends added support for a spin value of $5/2$. The moment is then 3.630.

Chlorine (K6, S3)

The resonance curves of the isotopes of chlorine were observed with the use of molecular beams of LiCl and RbCl. The g values found were 0.547 and 0.454 for Cl^{35} and Cl^{37} , respectively. Band spectra results give a spin of $5/2$ for each of these nuclei (E2, S2). Assuming these spin values, but bearing in mind that band spectra results for spins as high as $5/2$ are not conclusive, the moments become 1.368 and 1.136, respectively.

Potassium (Z1, K9)

The nuclear resonance curve of K^{39} has been observed with the use of the molecular beam of K_2 . The observed nuclear g is 0.260 ± 0.001 . This value together with the known value of the spin $\frac{3}{2}$ yields a moment of 0.391 for K^{39} . No similar nuclear resonance curves have been observed for the less abundant isotopes of potassium.

The atomic radiofrequency spectra have been studied for each of the three isotopes. The case of K^{39} has been amply discussed in the preceding pages. The $\Delta\nu$ of the ground state was found to be $(461.75 \pm 0.02) \times 10^6 \text{ sec.}^{-1}$. The h.f.s. separation of K^{41} was obtained from the Zeeman pattern in fields of 0.15 to 0.5 gauss. The result is $(254.02 \pm 0.02) \times 10^6 \text{ sec.}^{-1}$. Since the spin of K^{41} is the same as that of K^{39} we may use the ratio of the h.f.s. values of the two isotopes and the measured value of the moment of K^{39} to obtain the magnetic moment of K^{41} . Its value is found to be 0.215.

The radiofrequency spectrum of the K^{40} atoms has been studied by Zacharias (Z1) in various

magnetic fields. He has succeeded in determining the nuclear spin which he finds to be 4, in measuring the $\Delta\nu$ of the ground state with a precision comparable to that obtained for K^{39} and K^{41} , and in showing conclusively that the moment is negative. All of his work was done with K^{40} in its natural abundance which is about one part in 8000. The value of the $\Delta\nu$ is $(1285.65 \pm 0.1) \times 10^6 \text{ sec.}^{-1}$. Again the moment of K^{40} can be calculated from that of K^{39} by using the known spins and the measured values of the $\Delta\nu$ of the ground state. The result is -1.290 .

Krypton

A resonance curve has been obtained for krypton by Retherford and Kellogg (unpublished). The g value found is assigned to Kr^{88} and is 0.2148. The spin is uncertain but is probably $9/2$. The moment is negative.

Rubidium (M8, K6)

The nuclear resonance curves of the rubidium isotopes have been studied with the use of the Rb_2 molecules. The curves are quite broad and do not permit an accurate determination of the nuclear g values. The results are 0.536 ± 0.003 and 1.822 ± 0.006 for the g values of Rb^{85} and Rb^{87} . Using the known spins the moments become 1.340 and 2.733, respectively. These give a value of 2.038 ± 0.010 for the ratio μ_{87}/μ_{85} . The $\Delta\nu$'s of the ground state of these atoms have been obtained by studying the frequencies of the lines characterized by the transitions $\Delta F=0$, $\Delta m = \pm 1$ in strong magnetic fields. The results are $(3035.7 \pm 0.2) \times 10^6 \text{ sec.}^{-1}$ and $(6834.1 \pm 1.0) \times 10^6 \text{ sec.}^{-1}$ for the h.f.s. values of Rb^{85} and Rb^{87} , respectively. These results together with the spins yield the value 2.0261 ± 0.0003 for the ratio of magnetic moments. Thus within the experimental error this ratio is in agreement with that derived from the ratio of the measured nuclear moments.

Indium (H1, H2)

In the radiofrequency spectra of the ground state of the indium atoms lines characterized by the transition $\Delta F=0$, $\Delta m = \pm 1$ were observed for In^{113} as well as for In^{115} . The results show that the nuclear spin of In^{113} is $9/2$, the same as that of In^{115} . The ratio of the h.f.s. separation of the

ground state of In^{115} to that of In^{113} was found to be 1.00224 ± 0.00010 . This is also the ratio of the magnetic moments of the two isotopes. For In^{115} the h.f.s. value is $(11413 \pm 3) \times 10^6 \text{ cycles/sec.}$ and the nuclear moment is 5.49 ± 0.04 nuclear magnetrons. The moments of both isotopes are positive.

Caesium (K9)

The resonance curves of caesium have been observed in the molecules CsF , $CsCl$, and Cs_2 . The g value is found to be 0.731 ± 0.002 . From this value and from the known spin of $7/2$ we get for the moment 2.558. The hyperfine structure of the ground state has been measured by studying the lines characterized by transition $\Delta F=0$, $\Delta m = \pm 1$ in fields of about 1300 gauss. The result for the $\Delta\nu$ is $(9192.6 \pm 0.5) \times 10^6 \text{ sec.}^{-1}$.

Barium (H3)

The resonance curves of the odd isotopes of barium were observed by Hay using atomic barium. Since the electronic moment is zero, there is no interaction of the nucleus with the electronic configuration as is true in the case of the alkalis. The resonance curves are narrow, as one would expect. The observed g values are 0.554 ± 0.002 and 0.619 ± 0.002 for Ba^{135} and Ba^{137} . Spectroscopic results (B1) point strongly toward a spin of $\frac{3}{2}$ for each of these isotopes, giving the values 0.831 and 0.929 for the magnetic moments of these nuclei.

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