5

Hyperfine Structure Measurements in the Metastable 2S State of Hydrogenic Atoms*

P. KUSCH
Columbia University, New York, New York

The typical atomic or molecular beams experiment on the spectroscopy of atoms or molecules at electronically generated frequencies differs from all other spectroscopic experiments in that a transition is detected through an observation of the atoms or molecules that have undergone transition rather than on the radiation that has been absorbed or emitted. In the most common atomic beam spectroscopic experiment an atom or molecule has a differential trajectory through an apparatus depending on whether or not the atom has made a transition at some point along its trajectory. The number of atoms that arrive at some specified point is then a measure of the probability of transition in the atoms. The general methods are well known and will not be further discussed here.

It is, however, possible to perform atomic beam spectroscopic experiments on the metastable state of the hydrogen-like atoms that depend on a wholly different principle for the detection of transitions. Detection of transitions may be accomplished because it is possible in principle and feasible in practice to depopulate certain of the component levels in the metastable $2^2S_{\frac{1}{2}}$ state of the hydrogenic atoms. The process of depopulation always leads to a return of the atom to the ground, $1S$, state with the emission of an energetic photon. In fact, the experiments are possible because of the large excess energy of the metastable state which allows the highly selective detection of atoms in this state as well as the detection of the process of depopulation through the photon energy.

It is at once evident that the extremely precise definition of a beam that is necessary in experiments in which a transition is detected through

* The work described in this paper has been supported in part jointly by the Signal Corps, the Office of Naval Research, and the Air Force Office of Scientific Research.

a differential trajectory is not here necessary. This feature of the experiments to be described has considerable value, for it allows the use of a large beam aperture under circumstances in which a high beam intensity is difficult to achieve. In the case of experiments on He^{3+} the space charge density within the beam may be kept low through the use of the large available aperture. The aperture is, of course, limited in this case also by the requirement that all metastables in the beam are in the same magnetic field while undergoing transitions and that all metastables be subjected to the same perturbing rf fields, often of high frequency.

The classic experiments of Lamb,[1] his co-workers and others on the fine structure of the $n = 2$ state of hydrogen and ionized helium have made use of the possibility of depopulating the metastable state of hydrogen-like atoms. These experiments will not be discussed here. Two rather atypical atomic beam experiments, less familiar than those of Lamb will be described. In the first[2] of them the hyperfine structures of hydrogen and deuterium in the $2S$ state were measured. In the second of them the hyperfine structure of the helium 3 ion in the metastable state was measured by Novick and Commins.[3]

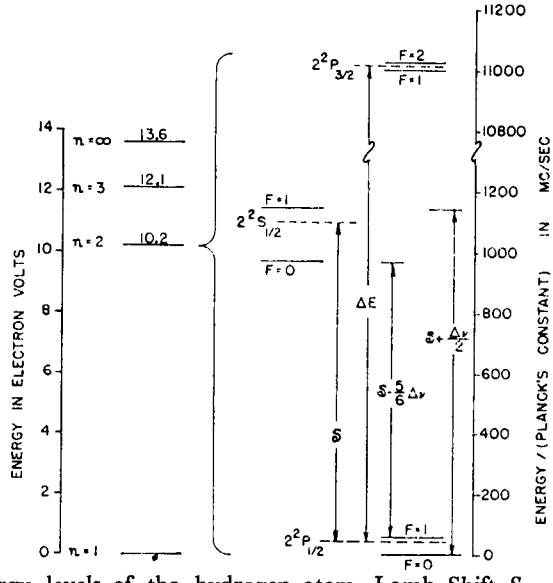

Fig. 1. Energy levels of the hydrogen atom. Lamb Shift $S = 1058$ Mc/sec. $\Delta E = 10{,}968$ Mc/sec. $\Delta\nu = 178$ Mc/sec.

The energy level system of hydrogen is shown in Fig. 1. The system is essentially the same for ionized helium 3. For He^3 the energy scale on the left is to be increased by a factor of four, so that the $n = 2$ state

lies about 40.8 volts above the $n = 1$ state in He^+. The Lamb shift is 14,042 Mc/sec. The fine structure separation in He^+ is about 176,000 Mc/sec. The spins of both H^1 and He^3 are $\frac{1}{2}$ but since the nuclear magnetic moment of the proton is positive and that of He^3 is negative, the hfs is normal in the first case and inverted in the second. The hyperfine structure of the ground state of hydrogen is, of course, accessible to study and the hfs splittings of all three isotopes of hydrogen in the $1S$ state have been measured[4] with great precision. The hyperfine splitting of the ground state of the He^3 ion has not been measured nor has a scheme for making the measurement been proposed that appears to offer a substantial chance of success. The lifetime of the P states is very short (about 1.6×10^{-9} sec for H and less for He^+) but, in the absence of perturbing fields, that of the $2S$ state is relatively long, of the order of one-tenth second for H and 2×10^{-3} sec for He^+. In the experiments that we shall discuss, the velocities of the atoms or ions in the beam are in the range from 4×10^5 to 5×10^6 cm/sec. The distance that a metastable particle may travel without significant decay is thus of the order of many meters, much greater than the length of a beam that is necessary for precise spectroscopic observation.

An electrostatic field mixes the $2P$ state into the $2S$ state and the lifetime of the latter is reduced. The application of a moderate electric field for a relatively short time may completely quench the metastable population, that is, return it to the ground state. So effective is the quenching that an electric field is used as a beam flag to determine the total metastable population in a beam. The process of quenching produces new photons but the aperture of the detector presented to these photons is small. This effect of a field also introduces the hazard of accidental quenching of the metastable population by random fields. More importantly, a mixing of the $2S$ and P states by an electric field gives rise to a shift in the hyperfine structure splitting of the $2S$ state. For these reasons all experiments have included careful precautions to exclude uncontrolled electrostatic fields, especially in that portion of the trajectory in which line frequencies are determined.

The motional electric field, $\boldsymbol{E} = (\boldsymbol{v}/c) \times \boldsymbol{H}$, serves the same purpose as an electrostatic field and its effect increases with $\boldsymbol{E}$ but also with diminishing separation between a component of the $2S$ state and one of a P state. Consider the Zeeman splitting of the hyperfine structure of hydrogen in the $2S$ state shown in Fig. 2. At a field of 575 gauss the level $m_J = \frac{1}{2}$ of the $P_{\frac{1}{2}}$ state crosses the $m_J = -\frac{1}{2}$ level (the β levels) of the $2S$ state. An atom with a velocity of 5×10^5 cm/sec in either one of the β levels has a decay length of about 0.5 mm in a field of 575 gauss perpendicular to the velocity vector while an atom in either one of the

levels $m_J = \frac{1}{2}$ (the α levels) has a decay length of about 87 cm. It is apparent that this highly differential behavior may produce a beam of neutral metastable atoms in which the population is entirely in the α levels.

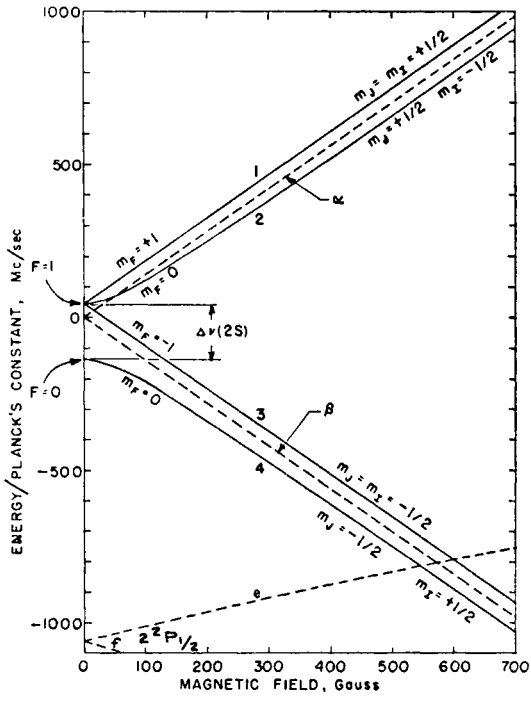

Fig. 2. Zeeman splitting of the hyperfine structure of the $2S$ state of hydrogen. The dashed lines show the energy level, when hfs is ignored.

The width of a resonance line corresponding to a transition between the component levels of the $2S$ state is determined entirely by the usual transit time relationship provided that the lifetime of the metastable atom or ion is large compared to the time interval in which the atom is subjected to the radiation field. The width of a resonance line for transitions between a level of the $2S$ state and one of the P state is determined by the lifetime of the P state and is 100 Mc/sec and 1600 Mc/sec for H and He^+ respectively.

A transition may be induced between the $2S$ state and the P state by application of an oscillating electric field of appropriate frequency and amplitude. Atoms or ions that have made the transition to the $2P$ state decay almost immediately to the $1S$ state so that this is a mechanism for depopulating but not repopulating the $2S$ state. For both hydro-

gen and helium the hyperfine structure separation is, very roughly, the same as the width of the line connecting the $2S$ and P state. The application of a field of a frequency corresponding to the energy difference between one of the hyperfine levels of the $2S$ state and the P state will not, therefore, depopulate only a single one of the hyperfine levels. Nevertheless, it is possible by this mechanism to achieve a significant differential depopulation of the two hfs levels.

With these general statements in mind, we will now discuss the experiments on the hydrogens and on ionized helium 3 in more detail.

Hydrogen

A schematic diagram of the experiment on atomic hydrogen and deuterium is shown in Fig. 3. Molecular hydrogen is thermally dissociated at a temperature of about 2800°K to produce a beam of atomic hydrogen. The dissociation is nearly complete at this temperature. It would be possible to produce atomic hydrogen by use of a conventional Wood's discharge tube as well. The beam traverses a region in which it is bombarded by electrons with an energy of about 13 volts. This serves to excite a fraction of the atoms to the $2S$ state. An approximate calculation of Lamb and Retherford indicates a yield of about one in forty million for the production of the atoms in the $2S$ state under the conditions of the present experiment. Since the momentum of the electron is perpendicular to that of the hydrogen atom there is a recoil dilution, that is, there is a range of recoil angle for any particular velocity and the range itself will depend on the atomic velocity. The subsequent aperture will selectively accept metastable atoms in a

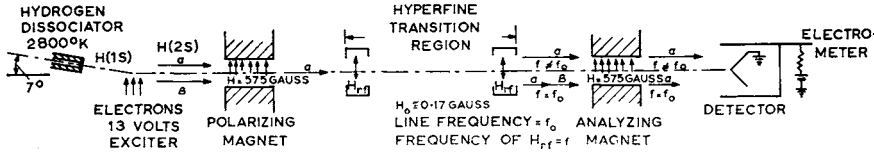

Fig. 3. A schematic diagram of the experimental arrangements used in measuring the hfs of H and D in the $2S$ state.

velocity range more restricted than that of the thermally produced atoms. An adjustment of the angle at which the thermal atoms enter the exciter allows an experimental choice of the velocity range of the metastable atoms.

The atoms in the $2S$ state are now distributed among the several hfs levels. If the atoms traverse a magnetic field of about 575 gauss, those in the β states are very strongly quenched, that is, they return to the

ground state with the emission of a photon. The atoms in the α states are only weakly quenched. The atoms that leave the polarizing field are thus predominantly in the α states. In practice the electron bombardment occurs within the polarizing field which then serves the additional purpose of aiding in the collimation of electrons.

The beam now traverses an extended region of space that contains the circuits in which the rf transitions are induced. Those transitions are observable which correspond to a transition from an α state to a β state. By reference to Fig. 2 it is seen that the observable transitions $(F, m; F', m')$ are (1, 1; 0, 0), (1, 0; 1, -1) and (1, 0; 0, 0). The first two of these have a frequency with a linear dependence on field and require for their stimulation an oscillating magnetic field perpendicular to the static field, H_0. The last of these transitions has only a quadratic dependence on field and requires for its stimulation an oscillating field parallel to H_0. By an adjustment of the relative directions of H_{rf} and H_0 both polarizations of H_{rf} occur simultaneously. With H_0 about 0.17 gauss, the frequency of the line (1, 0; 0, 0) exceeds the zero field hfs splitting by about 640 cycles per second. The frequency is thus nearly field independent. A measurement of the frequency of the line (1, 1; 0, 0) allows the determination of the field to a good accuracy. The small correction necessary to derive the zero field hyperfine structure separation from the frequency of the nearly field independent line can then be determined. It should be noted that a line (actually a pair of unresolved lines with a frequency separation of 200 cycles/sec at 0.17 gauss), with only a quadratic dependence of frequency on H_0 may be observed in deuterium and from the frequency of this line the zero field hfs splitting may be deduced after auxiliary lines have been observed to find the magnetic field. Since the hfs splitting in D is considerably smaller than in H, the quadratic term in the line frequency is greater and its determination is subject to greater inherent uncertainties.

Use is made of the method of separated oscillating magnetic fields, first suggested by Ramsey,[5] to induce transitions among the hfs levels. The method has several advantages over other schemes that have been employed but will not be further described here.

After the beam has passed through the transition region it again passes through a field, produced by the analyzing magnet, of about 575 gauss. If no transitions have occurred between the α and β states in the transition region, the flux of metastable atoms through the field is constant. If, however, a transition has occurred, the atoms in the β state are quenched. The flux of metastable atoms is reduced and photons are emitted within the analyzing field. Detection of transitions can be achieved either by a measurement of the flux of metastable atoms

that arrive at the detector beyond the analyzing magnet or by a measurement of the photons produced in the magnet. In practice the first of the two methods was used. A metastable atom may eject an electron from a metal surface and the electron current is measured by conventional methods. There is an inevitable flux of photons to the metal surface that also produces an electron current. Since the metastable atoms may be completely quenched by the interposition of an electrostatic field along the beam trajectory, it is possible to make a good determination of the photon background.

A resonance curve observed for the line in D with only a quadratic dependence on field is shown in Fig. 4. The typical Ramsey pattern is noted, where, however, the auxiliary maxima are not damped as rapidly as in Ramsey's theoretical curve since the velocity distribution of the metastable atoms in which transitions have been observed is considerably sharper than a Maxwellian distribution. The width of the central maximum of a typical resonance curve was 5.5 kc/sec for H and 4.8 kc/sec for D.

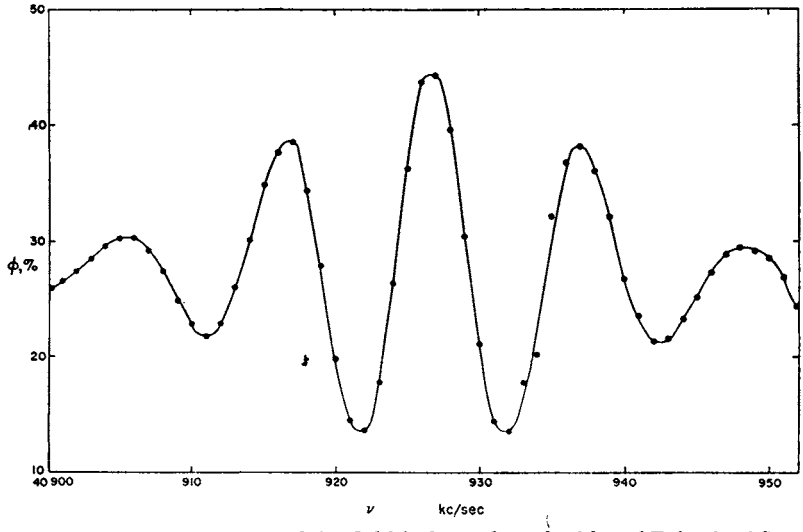

Fig. 4. A resonance curve of the field independent doublet of D in the $2S$ state showing several subsidiary maxima in the Ramsey pattern. The ordinate φ describes the decrease in the flux of metastable atoms.

The experiments yield the following results for the zero field hfs splittings in the $2S$ state of H and D:

$$\Delta\nu\ (2S;\mathrm{H}) = 177\ 556.86 \pm 0.05 \text{ kc/sec, and}$$
$$\Delta\nu\ (2S;\mathrm{D}) = 40\ 924.439 \pm 0.020 \text{ kc/sec.}$$

The ratio of the hyperfine splittings in the $2S$ and the $1S$ states, $R = \Delta\nu\,(2S)/\Delta\nu\,(1S)$, is, to the first order $\frac{1}{8}$. A relativistic treatment of the hfs by Breit[6] gives

$$R_{\text{theor}} = (\tfrac{1}{8})[1+(\tfrac{5}{8})\alpha^2+0(\alpha^4)].$$

The present results when combined with previous determinations of $\Delta\nu\,(1S)$ yield:

$$\Delta R = R_{\text{exp}} - R_{\text{theor}} = (\tfrac{1}{8})(13\pm 3)\times 10^{-7} \text{ for H and}$$
$$(\tfrac{1}{8})(9\pm 6)\times 10^{-7} \text{ for D.}$$

The existence of a real difference in ΔR for H and D has not been established.

The effects of nuclear structure that give rise to the hyperfine anomaly in the ground state of H and D are not expected to have a differential effect in the $1S$ and $2S$ states and hence to have an effect on R. However, quantum-electrodynamic effects of the order of α^3 may give rise to observable deviations in R. Mittleman[7] has calculated the α^3 corrections to the hfs of the hydrogens. He finds an effect of the same sign as the experimental effect but 1.55 times as great as that observed for hydrogen. The discrepancy is, of course, greater for deuterium. The source of the discrepancy is unknown.

Helium

From the point of view of the information to be derived from the experiment, it would be quite as valuable to study the hfs of He^{3+} in the $1S$ state as in the $2S$ state. The electronic wave functions are known in each case and deviations from hfs intervals calculated on the basis of a simple model would yield information about the structure of the He^3 nucleus. However, it has so far been possible to study the hfs of He^{3+} only in the $2S$ state precisely because it is metastable.

It is possible to conceive of an experiment to study the hyperfine structure of the helium 3 ion in the metastable $2S$ state similar to the one described for the hydrogens. There are, however, several complications that occur because of the charge on the helium ion. The crossing of the $m_J = -\frac{1}{2}$ levels of the $2S$ state and the $m_J = \frac{1}{2}$ levels of the $2^2P_{\frac{1}{2}}$ state occurs at about 7000 gauss. It is necessary to arrange magnetic fields along the trajectory that will attain this value at two points and a low and constant value over an extended transition region. It appeared to be a formidable task to achieve a configuration of fields with these properties which would allow the ions in a beam of large aperture to follow sufficiently well defined trajectories to yield a useful intensity at

the end of the trajectory. A second difficulty arises from the fact that the detection of the metastable atoms by the method used in the case of hydrogen suffers from the defect that ions in the ground state as well as in the metastable state can eject electrons from a metal surface.

A different procedure has, therefore, been adopted.[3] A schematic representation of the experimental arrangements is shown in Fig. 5. The ions, He^{3+}, are produced by electron bombardment in an ion source. The ions in the $1S$ state predominate but there is a useful population in the $2S$ state. They are removed from the source by a low draw-out voltage and are then accelerated to the full beam energy which has, in this experiment, been in the range from 5 to 40 ev. Electrostatic focussing lenses are used as shown.

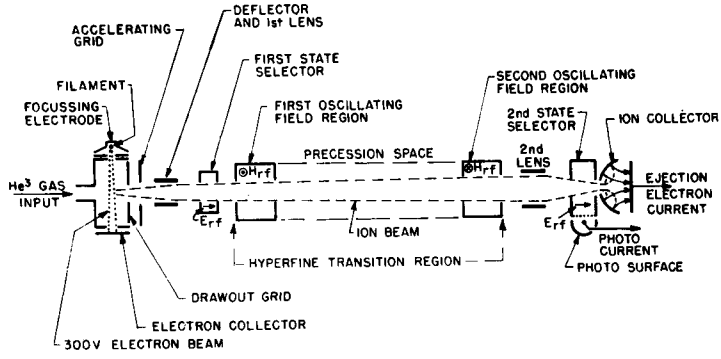

Fig. 5. A schematic diagram of the apparatus used in the measurement of the hfs of He^{3+} in the $2S$ state.

The details of the hfs and Zeeman levels of the $2S$ and $2^2P_{\frac{1}{2}}$ states are shown in Fig. 6. If the lines that connect the $2S$ and the P levels were of small width it would be possible completely to depopulate one of the F levels of the $2S$ state by inducing transitions in the microwave range from the F level to be depopulated to the P state. Since, however, the width of the $^2P_{\frac{1}{2}}$ state is about 1600 Mc/sec and since the hfs splitting is only about 1083 Mc/sec, it is impossible to depopulate completely a single one of the F levels. Nevertheless, by a suitable choice of frequency and power it is possible to achieve a useful excess population in either one of the two F levels. In practice the $F = 1$ level has been depopulated. In the first state selector shown in Fig. 5 the metastable ions are subjected to an electric field with a frequency of 13,350 Mc/sec. As the ions leave the selector there are more than twice as many ions in the $F = 0$ state as in each of the three $F = 1$ substates. When the ions pass through the second state selector there is a further preferential

depopulation of the $F = 1$ state. Here, as elsewhere, the preferential depopulation occurs at the expense of a reduction in the flux of metastable ions in the $F = 0$ state as well. Photons are produced in both state selectors; the yield in the first selector is independent of transitions that may occur between hfs levels at a subsequent point in the trajectory.

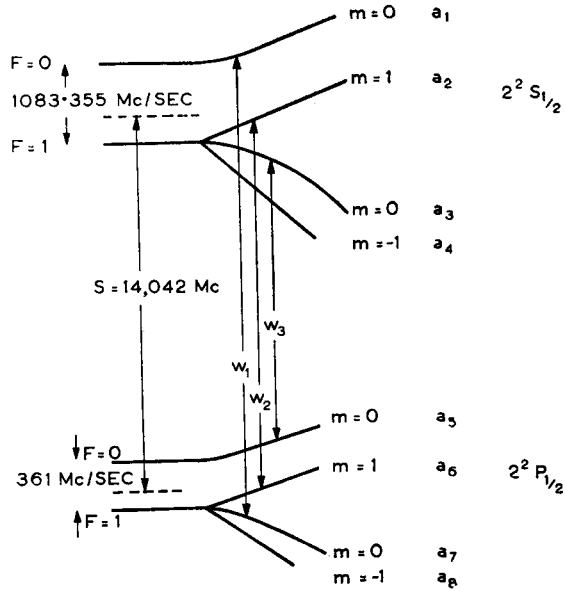

Fig. 6. The Zeeman splitting of the $2^2S_{\frac{1}{2}}$ and $2^2P_{\frac{1}{2}}$ states of He^{3+}. For pictorial purposes the energy intervals are not drawn to scale.

If an oscillating magnetic field of appropriate frequency, amplitude and polarization is applied in the hyperfine transition region or over some portion of it as in the Ramsey method, a transition from the $F = 0$ state to one of the substates of the $F = 1$ state (say the $m = 0$ level) occurs. The population of the $F = 1$, $m = 0$ and $F = 0$, $m = 0$ levels may be almost completely reversed. The complete reversal is possible because the beam is very closely monoenergetic as compared to the case of a beam in which the source of energy of the atoms is thermal where there is a large range of energy of the atoms.

When the beam now enters the second state selector, more transitions to the $2^2P_{\frac{1}{2}}$ state are induced than were induced when no hyperfine transitions occurred. The yield of photons in the selector is thus increased and the flux of metastable ions leaving the selector is decreased. A measurement of either the photon production in the selector or of the

flux of metastable ions beyond the selector yields a measure of the transition probability among the hfs levels in the transition region. The photo-detection method was abandoned after initial experiments because of the low signal strength resulting from a poor photo-yield and unfavorable geometry.

The metastable ion detection depends on the differential electron yield when metastable and normal ions impinge on a metal surface. Evidently the differential yield is essential to the detection of transitions since the total ion flux is invariant with respect to the occurrence of transitions among the hfs levels of the $2S$ state. For the ions in the $1S$ and $2S$ states the electron yield per ion is 0.2 and 0.5 respectively. A large electron background occurs because of the great relative abundance of ions in the $1S$ state. Modulation of the electric field oscillating at 13,350 Mc/sec in the first state selector modulates the metastable component of the beam and hence the electron current. Conventional techniques may then be employed to achieve a high ratio of the signal induced by the rf in the transition region to noise.

It is interesting to note some of the details of the experimental arrangements. The apparatus was designed to avoid several specific hazards principally related to the occurrence of stray electric fields. These might cause an instability in the ion current through the random charging and discharging of layers of organic contaminants on metal surfaces near the beam. They might also cause quenching of metastable ions. Finally, they might serve to mix the $2S$ and $2P$ states in the transition region with a consequent shift of the hfs separation from its true value for the $2S$ state. No organic material was used in the construction of the vacuum envelope and the components contained by it. The envelope was constructed of stainless steel and apertures were sealed with copper or gold gaskets. The system was bakeable and equipped with mercury diffusion pumps. The stability of operation was excellent and a comparison of its operation after it had been baked and its operation when the baking procedure was omitted indicated the value of the procedures which were rather unorthodox in atomic beam practice.

In Fig. 7 is shown the typical Ramsey pattern observed for the transition $F = 0$, $m = 0$, to $F = 1$, $m = 0$. The pattern was observed by use of a photodetector. In Fig. 5 the oscillating fields in the two cavities are shown as out of phase by 180°. The purpose of the phase difference is to reduce the possibility of a Stark shift in the hfs splitting by the oscillating electric field which must accompany the oscillating magnetic field. Because of the phase difference in the two cavities a minimum on the resonance curve is observed at the transition

frequency. The auxiliary maxima are very well defined, as compared to the more common case of a beam with a Maxwellian velocity distribution because the beam is very nearly monoenergetic. The resonance curve is shown for two beam energies and the increase of the spacing for the higher energy is precisely as expected.

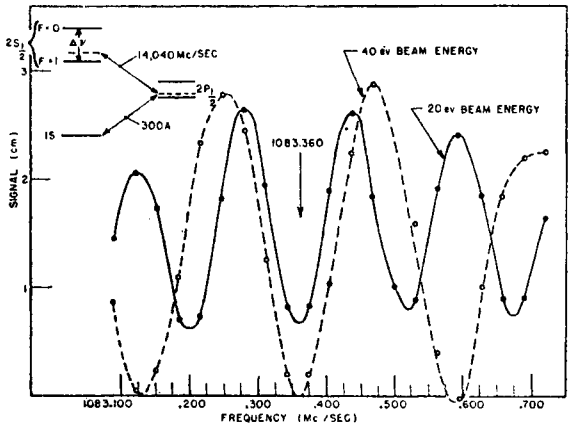

Fig. 7. The observed resonance curve for the transition $F = 0$, $m = 0 \rightarrow F = 1$, $m = 0$ in the $2S$ state of He^{3+}.

A large body of data has been acquired in which the possible effects of a large number of perturbing factors have been investigated. It is found that:

$$\Delta\nu_{\text{exp}}(2S, He^{3+}) = 1083.35499 \pm 0.00020 \text{ Mc/sec.}$$

The quantity is of interest for comparison with the value that is theoretically predicted[3] on the basis of the assumption that the He^3 nucleus is a point magnetic dipole. The predicted value is:

$$\Delta\nu_{p}(2S, He^{3+}) = 1083.557 \pm 0.010 \text{ Mc/sec.}$$

The uncertainty in the predicted value arises principally from the uncertainty in the fine structure constant, α. The discrepancy between the two results is 182 ± 22 parts per million; it exceeds the uncertainty in both experiment and theory within the assumptions of the theory. The discrepancy presumably arises from nuclear structure effects such as those that lead to the hyperfine structure anomaly of hydrogen and deuterium. Nuclear interaction currents and unevaluated higher-order radiative corrections will also contribute to the discrepancy. At the present time no detailed calculation of these effects has been made.

REFERENCES

[1] A general review of the field is given by W. E. Lamb, Jr., *Reports on Progress in Physics*, XIV, 19 (1951), The Physical Society, London.
[2] J. W. Heberle, H. A. Reich, and P. Kusch, *Phys. Rev.* **101**, 612 (1956); H. A. Reich, J. W. Heberle, and P. Kusch, *Phys. Rev.* **104**, 1585 (1956).
[3] R. Novick and E. Commins, *Phys. Rev.* **103**, 1897 (1956). A good many of the details of the experiment are described in the Quarterly Progress Report, Columbia Radiation Laboratory, Columbia University, February 28, 1955 to September 15, 1957. I am indebted to Professor Novick and Dr. Commins for access to unpublished data and for many discussions of the experiment.
[4] P. Kusch, *Phys. Rev.* **100**, 1188 (1955); A. G. Prodell and P. Kusch, *Phys. Rev.* **106**, 87 (1957).
[5] An extended discussion is given in N. F. Ramsey, "Molecular Beams," Section V.4, Oxford University Press, Oxford, 1956.
[6] G. Breit, *Phys. Rev.* **35**, 1447 (1930).
[7] M. H. Mittleman, *Phys. Rev.* **107**, 1170 (1957).