PHYSICAL REVIEW VOLUME 107, NUMBER 6 SEPTEMBER 15, 1957

Optical Detection of Magnetic Resonance in Alkali Metal Vapor

WILLIAM E. BELL AND ARNOLD L. BLOOM
Varian Associates, Palo Alto, California
(Received June 10, 1957)

This paper discusses two types of rf magnetic resonance experiments involving optical pumping in alkali vapor which have recently been suggested by Dehmelt. These experiments are, respectively, observation of a change of intensity at resonance of the transmitted pumping light, and observation of high-frequency intensity modulation in a second light beam (the "cross beam") incident at an angle to the first. The method of pumping used here is reviewed, together with some of the special assumptions on which it is based. The function of the light in monitoring population differences is treated as a separate matter from the pumping function; it is shown that the observed changes in transmitted light intensity can be correlated in a simple way with other observables of a spin system, and this leads to a simple explanation of the high-frequency modulation effects. A system of spin-$\frac{1}{2}$ particles subject to optical pumping and monitoring is then treated phenomenologically. The resulting equations have the same form as Bloch's equations except that (1) the time constants must include effects of the incident light, and (2) there is an additional term due to the cross beam which, however, is shown to have no effect on the shape of the resonance.

The apparatus is described, together with experimental conditions under which signals have been observed. Possible applications of the technique include magnetic-field measurements, and studies of atomic constants of alkali metal isotopes.

I. INTRODUCTION

IN a recent paper, Dehmelt[1] described an optical pumping experiment which demonstrated a thermal relaxation time of about 0.2 second for the magnetic moments of sodium atoms in relatively high-pressure argon buffer gas, together with a means of detecting the pumping process with very high signal-to-noise ratio. The detection method was that of monitoring the transmitted light, whose intensity depends upon deviations from the population equilibrium established by the pumping process. Although this paper described only a reorientation process, it was suggested that the method could be applied to magnetic resonance, and in fact this was actually done soon afterwards.[2] More recently, Dehmelt has suggested[3] a novel method for detecting magnetic resonance by the Larmor frequency modulation of a light beam placed at right angles to the magnetic field, an effect which has also been demonstrated recently.[4] The purpose of this paper is to discuss the demonstration experiments of both magnetic resonance phenomena, together with some phenomenological theory capable of predicting with reasonable accuracy the signal intensities and conditions under which signals can be expected. In the concluding remarks a number of possible applications of this experiment is discussed. Many of these applications involve considerable refinement of the apparatus, in particular the development of a light-filtering system and production of a magnetic field whose homogeneity is considerably greater than has ever before been required in experiments of this type. Rather than wait until the apparatus was developed to this point, we felt it to be desirable to publish the work that has been performed up to now.

[1] H. G. Dehmelt, Phys. Rev. **105**, 1487 (1957).
[2] H. G. Dehmelt (private communication).
[3] H. G. Dehmelt, Phys. Rev. **105**, 1924 (1957).
[4] W. Bell and A. Bloom, Bull. Am. Phys. Soc. Ser. II, **2**, 226 (1957).

II. PUMPING PROCESS

Fairly complete descriptions and histories of optical pumping as applicable to these experiments have been given previously by Kastler,[5] Hawkins[6] and by Dehmelt,[1] and the process will be briefly summarized here. The pumping process employs circularly polarized light transmitted along the direction of a magnetic field, producing transitions $\Delta m=+1$, for example, for which the transition probabilities from the various Zeeman sublevels of the ground state are different for some levels than for others. Because of the presence of the relatively high-pressure buffer gas, the optically excited atoms have extremely short relaxation times for disorientation within the Zeeman sublevels of the excited states themselves, and therefore it is likely that considerable disorientation and loss of phase memory occurs for these excited atoms before they are able to reemit their optical energy and return to the ground state.[7] This allows one to make the simplifying assumption that all sublevels of the ground state have an equal probability of being repopulated by the returning atoms. The pumping process can then be described entirely in terms of transition probabilities for optical excitation from the various ground-state sublevels, and, because the lifetime in the optically excited state is short, can be treated macroscopically in terms of an equivalent relaxation process between ground-state sublevels. Dehmelt[1] has indeed shown experimentally the exponential approach to equilibrium characteristic of such processes. In this way we hope to sidestep a problem mentioned by Sagalyn,[8] namely, that the picture of an atom "jumping" between quantum levels is rather naive and a rigorous treatment of optical double-resonance

[5] A. Kastler, Proc. Phys. Soc. (London) **A67**, 853 (1954), J. Opt. Soc. Am. **47**, 460 (1957).
[6] W. B. Hawkins, Phys. Rev. **98**, 478 (1955).
[7] P. L. Bender, thesis, Princeton University, 1956 (unpublished).
[8] P. Sagalyn, Phys. Rev. **94**, 885 (1954).

TABLE I. Unnormalized relative transition probabilities ($\Delta m=+1$) for D_1 and D_2 light (or their equivalents in the other alkali metals). The pumping rate P_i for any level is obtained by weighting the intensities of the D_1 and D_2 components by the coefficients given below.

F	m	D_1 ($^2S_{\frac{1}{2}}\rightarrow{}^2P_{\frac{1}{2}}$)	D_2 ($^2S_{\frac{1}{2}}\rightarrow{}^2P_{\frac{3}{2}}$)
2	2	0	6
	1	1	5
	0	2	4
	−1	3	3
	−2	4	2
1	1	3	3
	0	2	4
	−1	1	5
$\frac{1}{2}$	$\frac{1}{2}$	0	3
	$-\frac{1}{2}$	2	1

problems has not yet been developed. By treating the optical pumping as a relaxation process, we can avoid the use of any specific model. We merely assert that if a rigorous theory were available it could be used to obtain a time-dependent perturbation solution of the wave equation, perhaps similar to that of Wangsness and Bloch[9] for thermal processes, which would include terms linear in time (relaxation terms) and higher order terms which we have reason to believe are very small. There may also exist relatively large secular terms, giving rise to shifts in resonant frequencies, but we need not be concerned about them here.

The relative transition probabilities for optical excitation from the various F, m sublevels of the $S_{\frac{1}{2}}$ ground state to the $P_{\frac{1}{2}}$ and $P_{\frac{3}{2}}$ excited states can be calculated by a straightforward application of the matrix elements for electric dipole excitation ($\Delta m=+1$) and the Wigner coefficients $(IJm_Im_J|IJFm)$.[10] They have been calculated by Dehmelt[1] for the case $I=\frac{3}{2}$ and are presented here in a somewhat different form in Table I. Table I also lists the case for $I=0$, or for nuclear spin uncoupled from electron spin, which is applicable in strong magnetic fields. If P_i is the pumping rate out of the ith level, and a_i is the population of this level then the net pumping process can be described by the following system of equations:

$$da_i/dt=-a_iP_i+n^{-1}\sum a_jP_j, \qquad (1)$$

$$\sum a_i=A_0, \qquad (2)$$

where n is the number of levels in the $S_{\frac{1}{2}}$ ground state, A_0 is the total population of the sample, and the summation term in Eq. (1) is based on the previously expressed assumption that re-emission from the optically excited state is the same to all sublevels of the ground state. From Eqs. (1) and (2) we arrive at the following result for the equilibrium population difference, without thermal relaxation, between any two states:

$$a_i-a_j=A_0(P_i^{-1}-P_j^{-1})/\sum(P_i^{-1}). \qquad (3)$$

This expression, which is somewhat more general than a similar expression given by Dehmelt, is applicable to any situation where the P_i are known for each of the ground-state sublevels and applies not only for cases of D_1 and D_2 radiation or its equivalent, but for any other radiation which might be present to excite optical transitions. It can also be applied to include the effect of incompletely circularly polarized light and the effect of trapped resonance radiation which is necessarily unpolarized.

It is evident from an inspection of Eq. (3) and Table I that the end result of pumping with pure circularly polarized D_1 light is to place the entire population A_0 in the state $F=2$, $m=2$, except for the effect of thermal relaxation processes. This is true not only in the case of weak magnetic fields but also in strong magnetic fields where I and J are nearly decoupled. In that case the optical pumping process acts directly only on the electronic angular momentum; however, it is interesting to examine the indirect effect on the nuclear moment. This is most easily accomplished by a "circuit diagram" of the type suggested by Bloch[11] for a study of the Overhauser effect. Figure 1 shows the circuit based on the assumption that the chief relaxation mechanism available to the nucleus is the spin-flip exchange generated by the hyperfine coupling with the surrounding electron, and that this relaxation mechanism is strong compared to direct nuclear interactions with extra-atomic surroundings. The "battery" across each pair of electronic levels corresponds to the optical pumping process. It is evident that the effect of the hyperfine relaxation process is to place all the "batteries" in series resulting in an overwhelming alignment in the upper energy state.

Although the condition of nearly 100% population in the $F=2$, $m=2$ level may be highly desirable for certain types of experiments, the actual condition using unfiltered light from the usual alkali metal vapor discharge is that the intensities of both lines are very nearly equal.[6] Let us use Q to denote the fractional intensity difference between the two lines:

$$Q=[\mathcal{I}(D_2)-\mathcal{I}(D_1)]/\mathcal{I}(D_2),$$

where $\mathcal{I}$ = intensity. If $|Q|\ll1$, then it can be calculated from Table I and Eq. (3) that the population difference (in weak fields) between any two adjacent levels is about the same for all such combinations and is approximately equal to $QA_0/48$. This indicates that we are actually observing a rather small net population difference, and the fact that signal-to-noise ratios are as high as they are at the present time gives considerable promise for those experiments where an appreciably

[9] R. K. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1953).
[10] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1935).
[11] F. Bloch, Phys. Rev. **102**, 104 (1956).

large population difference (10% or greater) can be achieved.

III. MONITORING PROCESS

Let us now consider the other function of the light—that of monitoring the orientation of the sample. If we observe the intensity of the transmitted light beam relative to a constant input, we can observe the removal of energy from the incident beam. This effect we shall call the "signal" and denote by the symbol $\mathcal{S}$. If we omit the purely geometrical factors which are constant for a given experimental setup, then

$$\mathcal{S}=\sum a_i P_i, \tag{4}$$

a statement which is true regardless of any assumptions which one might make regarding the role of the light in a pumping process. The form of Eq. (4) suggests the trace of an operator product and, indeed, if the a_i are the diagonal elements of a spin density matrix, ρ, then (4) is true even if ρ has nonvanishing off-diagonal elements. However, we can generalize even further and define, for any kind of incident light, a "monitoring operator" $\mathbf{P}$ such that

$$\mathcal{S}=\langle\mathbf{P}\rangle=\mathrm{Tr}(\mathbf{P}\rho), \tag{5}$$

and if the nature of the light is completely specified so that the components of $\mathbf{P}$ are known, then $\mathcal{S}$ becomes an observable of the system ρ. Fano[12] has shown that, for a system described in terms of n states, there are n^2 independent operators including the identity operator. Any monitoring operator, therefore, can be expressed in terms of the identity operator plus familiar observables such as the multipoles and, furthermore, must satisfy the same transformation relationships as these observables.* (The identity operator must be included because $\mathrm{Tr}\mathbf{P}\geq 0$ by definition.) Dehmelt has shown[3] that for pure circularly polarized D_1 light incident on a hypothetical sodium atom of spin $\frac{1}{2}$, the monitoring operator has the form $(1-\mathbf{p}\cdot\boldsymbol{\sigma})$, where $\mathbf{p}$ is the direction defined by the polarization of the light, and the components of $\boldsymbol{\sigma}$ are the Pauli spin operators. Here the corresponding signal is related directly to the magnetic dipole moment of the sample in the direction of the light beam. However, the method is quite general and one can easily devise experiments where the signal gives information about quadrupole or higher moments of the system.[2,13]

In our experiments we have a primary light beam (the z beam), which performs the optical pumping and whose signal gives information about the z component of magnetic moment, M_z. There may be another light beam—the cross beam or x beam—whose signal is related to M_x in exactly the same way that the z beam signal is related to M_z. If there is Larmor precession about the z axis then the x beam will be modulated at the corresponding frequency. This signal will depend directly on M_x and not on dM_x/dt as is the case when the magnetic moment is coupled rf-wise to a detecting coil or cavity; there is therefore no frequency dependence of the type usually encountered in magnetic resonance.

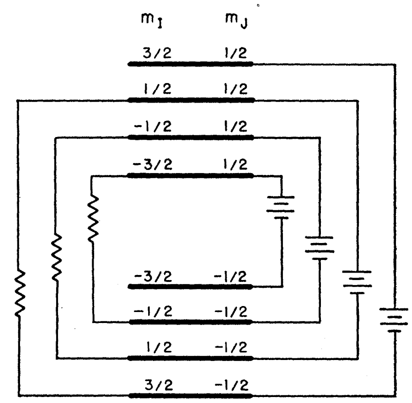

FIG. 1. "Circuit diagram" to describe optical pumping in strong magnetic fields.

Although the x beam is intended for monitoring purposes only, we must inquire about any pumping effects it may have. There are two such effects. First of all, it attempts to set up an orientation in the x direction. This effect is obviously very small unless the x beam is of such intensity that it can produce essentially complete orientation in a fraction of a Larmor cycle. Secondly it acts somewhat to the detriment of the pumping process generated by the z beam. In the representation in which the Hamiltonian is diagonal, the x-beam monitoring operator has large off-diagonal elements and acts equally on pairs of levels. This tends to equalize the populations of the ground state sublevels while shortening their over-all lifetimes. These points are illustrated in the phenomenological description which follows.

IV. PHENOMENOLOGICAL EQUATIONS

We shall describe the behavior of the spin system in terms of phenomenological equations for a system of particles of spin $\frac{1}{2}$, with the hope that it will be a fairly good approximation for the resonance behavior of the more complex system which actually exists. In general, this approximation can be expected to hold under operating conditions such that only population differences between the two levels directly concerned in the resonance need be considered.

[12] U. Fano, Revs. Modern Phys. **29**, 74 (1957).

* *Note added in proof.*—This statement is true if the line width of the incident light is broad compared to the level splittings. More generally, however, it is valid only if the light contains frequency and polarization components corresponding to *all* the optical transitions implied by the transformed monitoring operator.

[13] Strictly speaking, optical monitoring gives direct information only about population of spin states, and indirect information about electromagnetic moments only if the moments are already known to be associated with the spin. Thus, for example, the strength of the signal bears no direct relationship to the magnitude of the magnetic moment of the atom.

The phenomenological behavior can be thought of as being composed of two parts—the magnetic and thermal relaxation parts common to all spin systems, and the part due to optical pumping. For the magnetic and thermal description we shall use Bloch's equations[14] with the Boltzmann population factor set equal to one, since its effect is obviously small compared to effects of optical pumping. For the optical effects consider only two Zeeman levels, α and β; then Eqs. (1) and (2) can be rewritten in the following form for the z light alone:

$$(dM_z/dt)_{\text{pumping}}=(\mathfrak{M}_0-M_z)P_z, \qquad (6a)$$

where[15]

$$P_z=\tfrac{1}{2}(P_\alpha+P_\beta),$$
$$M_z=a_\alpha-a_\beta, \qquad (6b)$$
$$\mathfrak{M}_0=A_0(P_\beta-P_\alpha)/(P_\beta+P_\alpha).$$

A similar relation holds for the x beam alone:

$$(dM_x/dt)_{\text{pumping}}=(\mathfrak{M}_0'-M_x)P_x. \qquad (6c)$$

(If the two light beams have the same spectral quality, then $\mathfrak{M}_0=\mathfrak{M}_0'$ and P_x/P_z is merely the ratio of intensities of the two beams.) In addition we need equations describing the effect of the j light on M_i, where $i\neq j$:

$$dM_i/dt+M_iP_j=0. \qquad (6d)$$

By combining the Bloch equations with Eqs. (6) we arrive at our phenomenological equations of motion of the macroscopic moment:

$$dM_x/dt+\gamma[\mathbf{H}\times\mathbf{M}]_x+M_x/S_2=M_0'/S_2, \qquad (7a)$$
$$dM_y/dt+\gamma[\mathbf{H}\times\mathbf{M}]_y+M_y/S_2=0, \qquad (7b)$$
$$dM_z/dt+\gamma[\mathbf{H}\times\mathbf{M}]_z+M_z/S_1=M_0/S_1, \qquad (7c)$$

where we define

$$S_1=(P_x+P_z+T_1^{-1})^{-1},$$
$$S_2=(P_x+P_z+T_2^{-1})^{-1},$$
$$M_0'=\mathfrak{M}_0'P_xS_2, \quad M_0=\mathfrak{M}_0P_zS_1. \qquad (8)$$

We can neglect the term on the right-hand side of Eq. (7a) (this will be justified later), and in that case Eqs. (7) become identical to the Bloch equations if we substitute S_1, S_2 for T_1, T_2 of Bloch's equations. The observed signals in the phototubes are given by expressions like Eq. (4) which, when rewritten using the definitions of (6) and (8), become

$$\mathcal{S}_x=A_0P_x-\mathfrak{M}_0'M_xP_x/A_0, \qquad (9a)$$
$$\mathcal{S}_z=A_0P_z-\mathfrak{M}_0M_zP_z/A_0. \qquad (9b)$$

On substituting into Eq. (7) and setting the derivatives equal to zero, we obtain the slow-passage signals:

$$\mathcal{S}_x=A_0P_x-\frac{\gamma H_1S_2[1+(S_2\Delta\omega)^2]^{\frac{1}{2}}M_0P_x\mathfrak{M}_0'/A_0}{1+(S_2\Delta\omega)^2+\gamma^2H_1^2S_1S_2}\times\cos(\omega t+\varphi), \qquad (10a)$$

$$\mathcal{S}_z=A_0P_z-\frac{[1+(S_2\Delta\omega)^2]M_0P_z\mathfrak{M}_0/A_0}{1+(S_2\Delta\omega)^2+\gamma^2H_1^2S_1S_2}, \qquad (10b)$$

where H_1 is a rotating rf field and all other terms not defined elsewhere are as defined originally by Bloch.[14] The phase term φ can also be determined from Bloch's original equations.

Equations (8) and (10) clearly indicate the competition between the pumping action of the z light and the degrading effects of the thermal relaxation and the x beam. They also show the way in which the optical pumping broadens the line. If we vary the intensity of the x beam, and hence P_x, keeping all other quantities constant, the maximum high-frequency signal $|\mathcal{S}_x-A_0P_x|$ occurs when

$$P_x^2=(P_z+T_1^{-1})(P_z+T_2^{-1}). \qquad (11)$$

In practice, where P_z is large compared to the thermal relaxation rates, this indicates that both light beams should have about the same amplitude. In that case the observed z-beam signal has twice the width and half the amplitude that would be expected from the signal observed when the z beam is used alone.

We now return to the question of the term on the right-hand side of Eq. (7a), and show why we have been justified in neglecting it.[16] Let us specialize Eq. (7) to the case of a dc magnetic field $H_z=H_0$ and an alternating rf field $H_x=2H_1\cos\omega t$. The "x beam" may lie anywhere in the xy plane although we shall continue to denote it by the subscript x. Let us define $F=M_x+iM_y$, then the phenomenological equations become

$$dF/dt+i\gamma H_0F+F/S_2-i\gamma H_1M_z(e^{i\omega t}+e^{-i\omega t})=M_0'e^{i\epsilon}/S_2, \qquad (12a)$$

$$dM_z/dt+M_z/S_1-\tfrac{1}{2}i\gamma H_1(F-F^*)(e^{i\omega t}+e^{-i\omega t})=M_0/S_1, \qquad (12b)$$

where the phase term $e^{i\epsilon}$ indicates the direction of the x beam. We now analyze F and M_z in terms of Fourier coefficients,

$$F=\sum_{n=-\infty}^{\infty}f_ne^{in\omega t}, \quad M_z=\sum_{n=-\infty}^{\infty}m_ne^{in\omega t}. \qquad (13)$$

If we substitute Eq. (13) into (12) we can equate those terms with like values of $e^{in\omega t}$, since the equalities must hold at all times. As a result we obtain recursion

[14] F. Bloch, Phys. Rev. **70**, 460 (1946).

[15] We use symbols like M_z which normally represent magnetic moment only for the sake of familiarity, since here they really represent population differences only. See reference 13.

[16] The following treatment is similar to one suggested by E. T. Jaynes (unpublished work).

formulas of the following form:

$$(in\omega+S_2^{-1}+i\gamma H_0)f_n-i\gamma H_1(m_{n-1}+m_{n+1}) = M_0'S_2^{-1}\delta_{n0}e^{i\epsilon}, \quad (14a)$$

$$(in\omega+S_1^{-1})m_n-\tfrac{1}{2}i\gamma H_1(f_{n+1}+f_{n-1}-f_{-n+1}^*-f_{-n-1}^*) = M_0S_1^{-1}\delta_{n0}. \quad (14b)$$

Similar, but somewhat simpler equations are obtained if a rotating rf field is used instead of the alternating one.

For our purposes, the most interesting point about Eqs. (14) is that the second inhomogeneous term, $P_zM_0\delta_{n0}$, defines the terms m_{even} and f_{odd} but not their converses. The first inhomogeneous term $P_xM_0\delta_{n0}e^{i\epsilon}$, on the other hand, defines the terms m_{odd} and f_{even}. There is no mechanism within the framework of these equations whereby the two sets of terms can interact. Thus the first inhomogeneous term can produce signals in the modulation of the x beam with frequency components 0, $2\omega_0$, $4\omega_0$, etc., but cannot affect the term at the Larmor frequency itself. Therefore, if the output of the phototube monitoring the x beam is tuned so as to accept only frequencies of the order of ω_0 and not other frequencies, then the perturbation of the x beam cannot change the shape of the resonance in any way. Similar considerations hold for observing the z-beam signal at low frequencies. On the other hand, if one were to attempt detection under conditions of very weak external magnetic fields, then it might be difficult to filter out the unwanted terms and some perturbation in the detected signals might be observed.

V. EXPERIMENTS

A block diagram of the relatively simple experimental apparatus is shown in Fig. 2. The part of the apparatus which employs the beam parallel to H_0, together with associated sweep or field-reversal coils (not shown in the figure), is similar to that used by Dehmelt.[1] The cross beam and its associated electronic apparatus is the new part of the experiment. Although the word "sodium" is used in the figure, identical experiments have been performed with potassium and presumably could also be done in rubidium and cesium. It is possible to observe signals in the cross beam if this beam is originally unpolarized but an analyzer is placed in front of the photocell so that the photocell sees only one component of circular polarization. This occurs because each component of circular polarization in the unpolarized cross beam is modulated merely by the presence of a precessing orientation, although the modulations are 180° out of phase and therefore cannot be detected in the unpolarized light beam. Detection of the precession by this method is not as useful as by that using polarized light, since the unused component of polarization depumps the sample.

It has been pointed out by Dehmelt[2] and can be seen from the analysis of Secs. II and III, that the two beams in the cross-beam experiment could be replaced

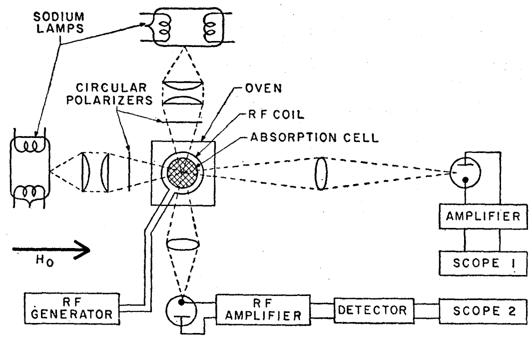

FIG. 2. Schematic diagram of apparatus. Sweep coils, coaxial with H_0, are not shown.

by a single beam oriented at about 45° to the dc magnetic field. Such an arrangement would have a reduced signal-to-noise ratio and the experiment has not been attempted.

The samples used in these experiments were made from one-liter Pyrex flasks which, in some cases, were glazed with a thin layer of fused potassium fluoborate (KBF_4) to keep the alkali metal from discoloring the glass.[17] The flasks were sealed off with the metal deposited as a thin layer in the neck and with spectroscopic-grade argon at a pressure (at room temperature) of about 30 mm Hg. The optimum operating temperatures for the absorption cells appeared to be about 140°C for sodium and 65°C for potassium. In both cases these correspond to equilibrium vapor pressures of about 2×10^{-6} mm Hg for the metals concerned. The mean free path of a photon at the center of the optical resonance is, according to a calculation by Hawkins,[6] about 0.1 cm at these pressures. The actual mean free path appeared to be about 15 cm. The reasons for the discrepancy are not entirely clear but probably include the following as contributing factors: (1) broadening of the absorption line by the buffer gas, over and above the usual Doppler broadening, thus reducing the absorption cross section per atom; (2) a relatively small evaporating surface area of the metal; and (3) the possible existence of part of the vapor in diatomic form. No differences in behavior have been observed between glazed or unglazed cells, nor have any aging effects been observed.

One of the advantages of the cross-beam method of detecting magnetic resonance in alkali vapor is the fact that the observed signal is at the Larmor frequency (in this case 360 kc/sec) and not at dc or a relatively low sweep frequency where the photocell detection is subject to interference from microphonics and extraneous sources of variable light. We have been able to observe the cross-beam signal not only in the presence of light from 60-cycle fluorescent lamps, which completely obliterates the z-beam signal, but we have even detected the signal when the discharge lamps themselves were excited from 60-cycle ac. Figure 3 shows

[17] This process was kindly suggested by Mr. P. E. Dittman of Corning Glass Works.

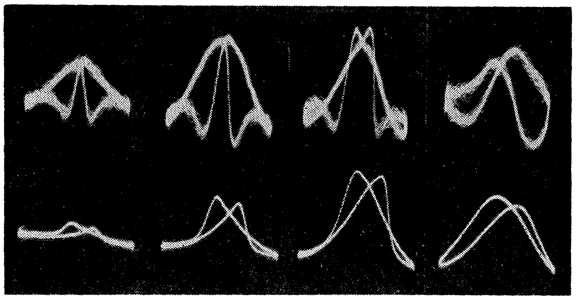

FIG. 3. Oscilloscope traces of resonance signals from cross beam (above) and z beam (below) as a function of rf field intensity (increasing left to right). The light beam geometries were such that $P_x \approx P_z \approx 10^{-2}$ sec.

typical oscilloscope signals employing a 60-cycle sweep modulation, from both the x-beam and z-beam signals. The first two sets of traces indicate that, as the rf level is increased, the cross-beam signal increases at a rate faster than the z-beam signal. This is to be expected from the form of Bloch's equations, which predict a quadratic dependence of $(M_0 - M_z)$ and a linear dependence of $M_{x,y}$ on weak rf. There is an indication of structure in the pictures third from the left, corresponding to "optimum" rf. The actual hyperfine structure to be expected from sodium if line widths were infinitely narrow is shown in Fig. 4. Although field homogeneity is not yet sufficient to resolve individual lines there is a definite indication that there is resolution of the two over-all structures corresponding to $F=2$ and $F=1$. This is further substantiated by the fact that this type of structure is not observed in the potassium samples, where the hyperfine structure does not split itself into two groups this way. These observations, together with measurements of resonance position as a function of frequency, indicate that the line width of the observed resonances is of the order of 1000 cps. It is believed that this width is caused almost entirely by field inhomogeneity. The principal contributors to the inhomogeneity are the ferromagnetic components of the lamps and the photocells, which in

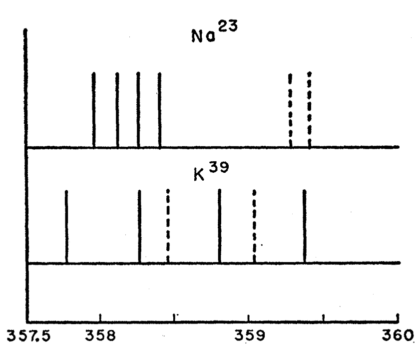

FIG. 4. Theoretical resonance spectrum for Na and K in a field H_0 of 0.513 gauss. Solid lines are $F=2$; dashed lines are $F=1$.

the present optical system are necessarily close to the absorption cell.

Of particular interest in Fig. 3 is the signal-to-noise ratio which can be obtained even under conditions of unfiltered light. The z-beam signals, shown on the bottom, were taken with no band-width limiting in the photocell amplifier or oscilloscope except for the natural band width of the amplifier itself, which was about 30 kc/sec. The x-beam traces, showing a somewhat poorer signal-to-noise ratio, were taken through a band pass of about 1000 cps following the diode detector. The reasons for the poorer signal-to-noise ratio in the cross beam are probably the following: (1) smaller effective volume of the absorption cell (the intersection of the two beams), and (2) a poor impedance match between the photocell and its load, which consisted of a tuned circuit whose resonant impedance was about 2000 ohms. On the basis of impedance matching alone it is calculated that the cross-beam signal-to-noise ratio should be reduced a factor of 10 from that of the z beam, which is in reasonable agreement with experiment.

An interesting variant of the cross-beam experiment is produced by connecting the output of the rf amplifier of the cross-beam photocell to the rf coil itself. This provides an oscillator whose frequency of oscillation is determined by the peak of the resonance curve, presumably in this case some average of the Larmor frequencies of the hyperfine lines. It can be easily demonstrated in the laboratory that the oscillation frequency of this system is determined by and follows variations in the magnetic field.

VI. POSSIBLE APPLICATIONS

The most obvious application of this experimental method is to the precise measurements of weak magnetic fields. An interesting factor in its usefulness is the fact that the intensity of the observed optical signals is independent of the value of the magnetic field, provided only that the field is small compared to the hyperfine structure constant so that optical transition probabilities are approximately constant as a function of magnetic field, and not so small as to be comparable to the line width. The existing apparatus has been used quite satisfactorily for this purpose and it is believed that one can do even better by proper design and filtering of the light. Considerable improvement can also be achieved as magnetic-field homogeneity over the sample is brought under control. When the line structure is well resolved it will be possible to make an accurate measurement of g factors of the various alkali metals by comparing the resonant frequencies of the metals between themselves and with protons in the same magnetic field. Because the resonance frequency depends on the g factor to first order in weak fields, and because the lines are so narrow, it is believed that the g factors can be measured to an order of magnitude greater accuracy than has been possible up to now. The hyperfine splittings will also give information regarding the hyperfine structure constant and magnetic moments of the nuclei; however, it is not likely that these measurements can be made to any greater accuracy than by existing methods.

VII. ACKNOWLEDGMENTS

We are indebted to Professor Dehmelt for suggesting this work and for his assistance, and to Mr. H. R. Lawler for constructing most of the apparatus. The absorption cells were prepared by Mr. E. Hodges.

PHYSICAL REVIEW VOLUME 107, NUMBER 6 SEPTEMBER 15, 1957

Electronic Polarizabilities of Ions*

R. M. STERNHEIMER
Brookhaven National Laboratory, Upton, New York, and Enrico Fermi Institute for Nuclear Studies,† University of Chicago, Chicago, Illinois
(Received June 6, 1957)

The dipole polarizability α_d and the quadrupole polarizability α_q have been calculated for several ions by solving the Schrödinger equation satisfied by the first-order perturbation of the wave functions of the electrons of the core. The results for α_d of the helium-like ions are in good agreement with those obtained previously by an analytic method. The calculated quadrupole polarizability α_q of the alkali ions increases very rapidly with increasing Z, from 0.056 A^5 for Na^+ to 7.80 A^5 for Cs^+.

I. INTRODUCTION

THE electronic polarizabilities of a number of ions have been calculated previously by means of a numerical solution of the Schrödinger equation satisfied by the perturbation of the wave functions of the electrons of the core.[1] For the unperturbed wave functions, the Hartree or Hartree-Fock wave functions of the core were used. The calculated results for the dipole polarizability α_d were shown to be in reasonable agreement with the experimental data. The purpose of this paper is to give the results of additional calculations of the dipole polarizability α_d of the helium-like ions and of the quadrupole polarizability α_q of several helium-like and alkali ions.

II. DIPOLE POLARIZABILITY

The method of calculation of α_d was the same as that used in I. Thus, for the helium-like ions, which involve only the $1s\to p$ excitation, α_d is given by

$$\alpha_d=(8/3)\int_0^\infty u'_0u'_{1,0\to1}r\,dr, \tag{1}$$

where u'_0 is r times the radial $1s$ function, normalized according to: $\int_0^\infty (u'_0)^2dr=1$; $u'_{1,0\to1}$ is r times the radial part of the $1s\to p$ perturbation, and is determined by

$$\left(-\frac{d^2}{dr^2}+\frac{2}{r^2}+V_0-E_0\right)u'_{1,0\to1}=u'_0r. \tag{2}$$

In Eq. (2), V_0 is the spherical potential and E_0 is the unperturbed $1s$ eigenvalue. Actually the function,

$$P\equiv V_0-E_0=(1/u'_0)(d^2u'_0/dr^2), \tag{3}$$

is obtained directly from the second derivative of u'_0, as shown by Eq. (53) of I. We note that Eq. (1) gives α_d in units a_H^3 (a_H=Bohr radius) and must be multiplied by $(0.529)^3=0.148$ to obtain α_d in units A^3.

For the helium-like ions, values of α_d have been presented in Table II of I. In obtaining these values, $u'_{1,0\to1}$ was not derived by numerical solution of the Schrödinger Eq. (2), but was obtained analytically in the following manner. One notes that for a hydrogenic wave function u'_0,

$$u'_0=2Z^{\frac{3}{2}}r\exp(-Zr), \tag{4}$$

with atomic number Z, the perturbation is given by

$$u'_{1,0\to1}=Z^{-\frac{1}{2}}r^2(1+\tfrac{1}{2}Zr)\exp(-Zr). \tag{5}$$

The zero-order wave functions u'_0 for the helium-like ions which were used in I and in the present work are the wave functions obtained by Löwdin,[2] which are of the following form:

$$u'_0=c_1[2Z_1^{\frac{3}{2}}r\exp(-Z_1r)]+c_2[2Z_2^{\frac{3}{2}}r\exp(-Z_2r)], \tag{6}$$

where Z_1 and Z_2 are two effective values of the atomic number; c_1 and c_2 are coefficients. In the work of I we assumed that $u'_{1,0\to1}$ is given to a good approximation by a linear combination of the functions (5), corresponding to Z_1 and Z_2, i.e., we took [see Eq. (71) of I]:

$$u'_{1,0\to1}=c_1[Z_1^{-\frac{1}{2}}r^2(1+\tfrac{1}{2}Z_1r)\exp(-Z_1r)]+c_2[Z_2^{-\frac{1}{2}}r^2(1+\tfrac{1}{2}Z_2r)\exp(-Z_2r)]. \tag{7}$$

* The work done at Brookhaven National Laboratory was carried out under the auspices of the U. S. Atomic Energy Commission.
† Supported by the Office of Naval Research.
[1] R. M. Sternheimer, Phys. Rev. 96, 951 (1954). This paper will be referred to as I.
[2] P. O. Löwdin, Phys. Rev. 90, 120 (1953).

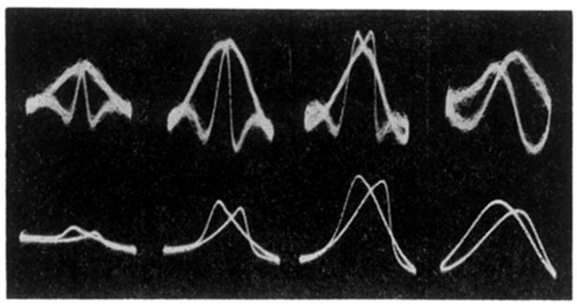

FIG. 3. Oscilloscope traces of resonance signals from cross beam (above) and z beam (below) as a function of rf field intensity (increasing left to right). The light beam geometries were such that $P_x \approx P_z \approx 10^{-2}$ sec.