Substituting (B2) into (B4), we obtain the dispersion law

$$\omega^2=(\omega_0+\omega_e a^2k^2)(\omega_0+\omega_e a^2k^2+4\pi\gamma M). \quad \text{(B5)}$$

When $k=0$, this is the usual $(BH)^{\frac{1}{2}}$ resonance condition; combining (B2), (B4), (B5), we find that $R(k)$ is given by

$$R(k)=-[(\omega_0+\omega_e a^2k^2)/(\omega_0+\omega_e a^2k^2+4\pi\gamma M)]. \quad \text{(B6)}$$

Following Sec. III, we apply a uniform transverse rf field ($h_0 \cos\omega t$, $h_0 \sin\omega t$, 0) and calculate the amplitude coefficients. With the additional rf driving field, the equations of motion become

$$\begin{aligned}\partial S^x/\partial t&=-\omega_e a^2(\partial^2 S^y/\partial s^2)+\omega_0 S^y-\gamma S h_0 \cos\omega t,\\ \partial S^y/\partial t&=\omega_e a^2(\partial^2 S^x/\partial x^2)-\omega_0 S^x \qquad \text{(B7)}\\ &\qquad +\gamma S h_0 \sin\omega t+\gamma S H_k{}^x.\end{aligned}$$

The boundary conditions are the same as those in Sec. III and, consequently, the eigenmodes are the same. We now define $\Psi_p{}^x$ and $\Psi_p{}^y$ by

$$\Psi_p{}^y=\alpha \sin k_p x+\beta \cos k_p x, \quad \Psi_p{}^x=R(k_p)\Psi_p{}^y. \quad \text{(B8)}$$

Then, we try solutions of the form

$$S^x=\cos\omega t \textstyle\sum_p \beta_p{}^x\Psi_p{}^x, \quad S^y=\sin\omega t \sum_p \beta_p{}^y\Psi_p{}^y. \quad \text{(B9)}$$

From (B7) and (B9) we obtain the following coupled equations for the amplitude coefficients $\beta_p{}^x$ and $\beta_p{}^y$:

$$\begin{aligned}\gamma S h_0&=\sum_p [(\omega_0+\omega_e a^2k_p{}^2)\beta_p{}^y+\omega R(k_p)\beta_p{}^x]\Psi_p{}^y,\\ \gamma S h_0&=\sum_p [\omega\beta_p{}^y+(\omega_0+\omega_e a^2k_p{}^2 \qquad \text{(B10)}\\ &\qquad +4\pi\gamma M)R(k_p)\beta_p{}^x]\Psi_p{}^y.\end{aligned}$$

The ratio $\beta_p{}^x/\beta_p{}^y$ is then found to be

$$\frac{\beta_p{}^x}{\beta_p{}^y}=\frac{\omega-\omega_0-\omega_e a^2k_p{}^2}{R(k_p)(\omega-\omega_0-\omega_e a^2k_p{}^2-4\pi\gamma M)}. \quad \text{(B11)}$$

The power absorbed per mode is now easily seen to be

$$P=(2\hbar\gamma^2 S h^{+2})\sum_p \frac{[1+R^2(k_p)]g^2(k_p)S(\omega-\omega_p)}{k_p{}^2 L Q(k_p)}, \quad \text{(B12)}$$

where ω_p is given by (B5). We see that the absorption per mode in the parallel use is only $\frac{1}{2}[1+R^2(k_p)]$ of that in the perpendicular case.

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Spin Relaxation and Line Width in Alkali Metal Vapors

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Relaxation constants T_1 and T_2 have been computed for experiments involving optical pumping and optical detection in alkali metal vapor. The calculations have been performed for several possible spin relaxation mechanisms; namely, magnetic dipole, electric quadrupole, spin exchange, and the optical pumping process itself. For all of these mechanisms a reorientation experiment will approximately predict a spin resonance line width (equivalent to the statement $T_1 \approx T_2$ for spin-$\frac{1}{2}$ particles.) However, a spin reorientation experiment of the type originally performed by Dehmelt, employing circularly polarized light, gives approximate results because of the nonexponential character of the reorientation. A more suitable experiment is one employing hyperfine population differences and unpolarized light.

INTRODUCTION

THE recent observation of long spin reorientation times in alkali metal vapors in buffer gases,[1] or with buffering wall coatings[2,3] has prompted considerable speculation as to the existence of correspondingly narrow line widths and application to magnetic field and frequency measurements. Implicit in this is the assumption that conditions in the alkali vapor are analogous to those of nuclear magnetic resonance of spin-$\frac{1}{2}$ nuclei in a nonviscous fluid, for which one has equal times ($T_1=T_2$). However, the alkali vapor differs from an ensemble of spin-$\frac{1}{2}$ particles in two important respects; first, because of the strong hyperfine coupling, and secondly, because of the special nature of the observables measured by optical detection. Thus, for example, the quantity measured by the optical detection of hyperfine population differences using unpolarized light[4] is not simply related to classical dynamical variables such as magnetic dipole moment, electric quadrupole moment, etc.

The observed values of reorientation times in alkali vapor, in the limit of vanishing light intensity, are of the

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[1] H. G. Dehmelt, Phys. Rev. **105**, 1487 (1957).

[2] H. G. Robinson, E. S. Ensberg, and H. G. Dehmelt, Bull. Am. Phys. Soc. Ser. II, **3**, 9 (1958).

[3] W. Franzen, Phys. Rev. **115**, 850 (1959).

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order of 0.1 second.[1–3] If $T_2 = T_1$, then the resonance line widths should be of the order of 3 cps, however published values of line widths, for both Zeeman[5] and hyperfine[6–8] transitions, are about 10 times as great. It seemed worthwhile, therefore, to investigate the relaxation theoretically in enough detail to take the facts of the above paragraph into account and to see if one could account for the observation $T_2 \ll T_1$ without having to make *ad hoc* assumptions about sources of inhomogeneous line broadening.[9] As it turns out, the theory does not predict large differences between T_1 and T_2. More recently, Bender[10] has observed line widths of a few cycles per second for Zeeman resonances in very weak magnetic fields, where all the resonances are superimposed and the signal-to-noise ratio is higher. The conclusions of the present study, although not strictly valid in very weak fields, are nevertheless supported by Bender's results for Zeeman transitions. For hyperfine resonances the situation is less clear. The existence of large secular perturbations giving rise to pressure shifts[6,8] suggests that there may also exist statistical effects, contributing to line broadening, of a sort not considered here.

METHOD

The calculation is for alkali atoms of nuclear spin $\frac{3}{2}$ and strong hyperfine coupling, with the following simplifying assumptions:

1. The thermal energy kT is very large compared to the hyperfine constant so that, in the absence of optical pumping, all ground-state sublevel populations are assumed equal.
2. The applied magnetic field is weak enough so that F, m_F are approximately good quantum numbers but strong enough so that there are no overlapping resonance lines. This condition can be satisfied for all stable alkali isotopes of spin $\frac{3}{2}$ with fields of one gauss or less.
3. The relaxation is assumed to be of the "classical" type,[11] in which the spin is perturbed by an isotropic, fluctuating perturbation field whose Fourier components have uniform intensity from $\omega = 0$ to the correlation frequency $\omega = \omega_c$. We assume ω_c much greater than the hyperfine frequency, although the treatment can be easily modified to suit other situations.

Bloch[12] has given a treatment of relaxation which is applicable to the present problem. However, the relaxation parameters $\Gamma_{gg'}{}^{p}$ which he employs are used here only in the case $g = g'$, in which case they merely represent transition probabilities due to the relaxation process. Furthermore we may take $e^{hp/kT} = 0$, where this term occurs in his equations. Because of this we can adopt a simpler notation and merely write $W_{ab} = \epsilon |H_{ab}'|^2$ for the relaxation transition probabilities between levels a and b. H_{ab}' is the matrix element of the relaxation part of the Hamiltonian connecting states a and b, and ϵ is a constant which we will choose to be unity.

The line width of the resonance between states a and b is given in terms of the inverse parameter $(T_2)_{ab}$ by Bloch's[12] equation (3.8) which, simplified, becomes

$$1/(T_2)_{ab} = \sum_k \left(|H_{ka}'|^2 + |H_{kb}'|^2 \right) - 2H_{aa}'H_{bb}', \qquad (1)$$

where k includes all of the magnetic and hyperfine sublevels of the ground ${}^2S_{\frac{1}{2}}$ state of the atom.

For the calculation of reorientation effects we use Eq. (2.44) of Bloch, but with all off-diagonal elements of the density matrix equal to zero, since resonance effects are not involved in reorientation experiments. We define the following terms: ρ_i is the time-dependent population of state i, ρ_{i0} is the steady-state or equilibrium population, and $\chi_i = \rho_i - \rho_{i0}$. Then Bloch's general equation (2.44) can be simplified for our purposes to the following system of equations:

$$d\chi_i/dt = -2 \sum_k |H_{ki}'|^2 (\chi_i - \chi_k). \qquad (2)$$

Now, the quantity observed in an optical detection experiment as proportional to the intensity of transmitted light is a linear combination of the ρ_i's and can be expressed by a "monitoring operator"[13] Q and corresponding observed signal S such that

$$S = \mathrm{Tr}\,(Q\rho). \qquad (3)$$

In a given experimental situation, Q is uncertain to within an additive multiple of the unit operator, equivalent to selection of the "base line" of the indicator output. We shall choose Q so that

$$\mathrm{Tr}\,(Q\rho_0) = 0; \qquad (4)$$

then

$$S = \mathrm{Tr}\,(Q\chi) = \sum c_i \chi_i, \qquad (5)$$

the c's being constants. By properly weighting and summing the individual equations in (2) we can write,

$$(d/dt)\left(\sum c_i \chi_i\right) = \sum c_i' \chi_i. \qquad (6)$$

For certain fortunate choices of Q and H', and consequently of the c_i's, we may have

$$c_i'/c_i = \text{constant for all } i; \qquad (7)$$

in this case Eq. (6) reduces simply to

$$dS/dt = -S/T_1, \qquad (8)$$

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[5] T. L. Skillman and P. L. Bender, J. Geophys. Research **63**, 513 (1958).

[6] M. Arditi, J. phys. radium **19**, 873 (1958).

[7] E. C. Beaty, P. L. Bender, and A. R. Chi, Phys. Rev. **112**, 450 (1958).

[8] P. L. Bender, E. C. Beaty, and A. R. Chi, Phys. Rev. Letters **1**, 311 (1958).

[9] Doppler broadening represents such a possible mechanism for the hyperfine lines, though not for the Zeeman lines. However, for buffer pressures of 1 cm Hg or above, its effect should be small.

[10] P. L. Bender, Proceedings of the Ann Arbor Conference on Optical Pumping, June, 1959 (University of Michigan, Ann Arbor, 1959), page 111.

[11] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

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[13] W. E. Bell and A. L. Bloom, Phys. Rev. **107**, 1559 (1957).

with T_1 a unique relaxation time for this particular experiment. However if (7) does not hold, there is no unique time constant and the relaxation is not only nonexponential but depends in detail on the initial population distribution.

The calculations outlined above have been carried out with four observables for each of three thermal relaxation mechanisms as well as relaxation by the incident light itself. The observables are the following: (a) The line width parameter T_2 of the Zeeman resonance $F=2$, $m_F=2\rightarrow F=2$, $m_F=1$. (b) The T_2 of the field-independent hyperfine resonance $F=2$, $m_F=0\rightarrow F=1$, $m_F=0$. (c) The relaxation time T_1 for reorientation and optical detection by circularly polarized light[1] propagated parallel to the magnetic field and with equal intensity in both hyperfine components. This is precisely the experiment performed by Franzen,[3] in which the light is shut off for varying periods of time and the depolarization due to thermal relaxation is observed. The signal is given by

$$S_m=2\chi_{2,2}+\chi_{2,1}-\chi_{2,-1}-2\chi_{2,-2}-\chi_{1,1}+\chi_{1,-1}. \qquad (9)$$

Here the subscripts refer to F, m_F, respectively, and $S_m=0$ if all populations are equal. (d) The T_1 for a reorientation experiment similar to (c) except that the incident light is unpolarized and is filtered so that it can excite atoms out of the $F=1$ state but not out of the $F=2$ state.[8] The signal is given by

$$S_H=3(\chi_{2,2}+\chi_{2,1}+\chi_{2,0}+\chi_{2,-1}+\chi_{2,-2})\\ -5(\chi_{1,1}+\chi_{1,0}+\chi_{1,-1}). \qquad (10)$$

The relaxation mechanisms are the following:

(i) Magnetic dipole relaxation. This is most likely the principle contribution to the thermal relaxation process. Besides usual direct collision effects, it includes the perturbation of the hyperfine coupling that occurs during a collision. The matrix elements H_{ik}' are simply the matrix elements for angular momentum operators, which are well known in the literature.[14] Numerical constants are chosen so that hypothetical alkali atoms of spin $\frac{1}{2}$ in the same environment would have unit relaxation times ($T_1=T_2$).

(ii) Electric quadrupole. The possible importance of this mechanism is not known. Nuclear spins in noble gases are known to have extremely long relaxation times even if the nuclei possess a quadrupole moment[15]; however, the situation may be different in alkali atoms with their valence electron, even if most of the collisions are with noble gas atoms. The quadrupole matrix elements are also well known.[14] Numerical constants used here are arbitrary, since one cannot perform these experiments with a bare nucleus.

(iii) Electron spin exchange, normalized so that $T_1=1$ for spin-$\frac{1}{2}$ particles. We have in mind here the mechanism described in detail by Wittke and Dicke,[16] in which the exchange energy during a collision is so large and so dependent on collision parameters that there is no correlation between initial and final states (except conservation of total angular momentum). The matrix elements are the same as in (i) except that diagonal elements and elements connecting states of the same m value are zero. The treatment used here requires that the equilibrium populations be equal, which implies the presence of a large "sink" of unpolarized spins. This is not a usual condition in alkali vapor experiments and we have not investigated the effect of exchange within an already polarized system.[17]

(iv) The incident light itself as a relaxation agent. We assume here an alkali sample with buffer gas, so that there is complete disorientation in the excited state[1] and no correlation between absorption and emission even if the atom returns to the same ground-state sublevel from which it came. Thus in applying Eq. (1), the interference term $2H_{aa}'H_{bb}'$ is zero and $\sum_k H_{ki}'$ is merely the rate of photon absorption in state i. Equation (2) must be replaced by the "pumping equation,"[13]

$$d\rho_i/dt=-\rho_iP_i+\tfrac{1}{8}\sum_j\rho_jP_j, \qquad (11)$$

where $P_i=\sum_k H_{ki}'$. The monitoring operators must be chosen so that $\mathrm{Tr}\,(Q\rho)=0$ when the system is completely "pumped" instead of for equal populations. For circularly polarized light, pumping the population into the $F=2$, $m_F=2$ level, the signal is

$$S_m'=\chi_{2,1}+2\chi_{2,0}+3\chi_{2,-1}+4\chi_{2,-2}\\ +3\chi_{1,1}+2\chi_{1,0}+\chi_{1,-1}. \qquad (12)$$

For hyperfine filtered light it is

$$S_H'=\chi_{1,1}+\chi_{1,0}+\chi_{1,-1}. \qquad (13)$$

TABLE I. Relaxation times for various experiments and relaxation mechanisms. Those cases where there is no unique relaxation time are denoted by letters and the corresponding signal equations are given in Table II. "Line width" in the table refers to the type of measurement; the quantity given in T_2.

Experiment	Magnetic dipole	Electric quadrupole	Spin exchange	Light
Zeeman line width	2/5	16/11	1/2	1[a]
0 → 0 line width	1/3	2	1/2	1[b]
Spin reorientation	(a)	(b)	(c)	(d)[a]
Hyperfine reorientation	1/4	2	(e)	8/5[b]

[a] Circularly polarized light.
[b] Hyperfine filtered light.

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[14] E. Feenberg and G. E. Pake, *Notes on the Quantum Theory of Angular Momentum* (Addison-Wesley Publishing Company, Cambridge, 1953) and (Stanford University Press, Stanford, 1959).

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[16] J. P. Wittke and R. H. Dicke, Phys. Rev. **103**, 620 (1956).

[17] L. W. Anderson, F. M. Pipkin and J. C. Baird, Phys. Rev. **116**, 87 (1959).

TABLE II. Signal equations for the cases specified in Table I. From the definitions, it is possible to replace χ by ρ wherever it appears in Eqs. (a) through (d), but not in Eq. (e). $\dot{S} \equiv dS/dt$.

$$\dot{S}_m = -\tfrac{5}{2} S_m + 4(\chi_{1,1} - \chi_{1,-1}). \tag{a}$$

$$\dot{S}_m = -\tfrac{7}{16} S_m - \tfrac{1}{2}(\chi_{1,1} - \chi_{1,-1}). \tag{b}$$

$$\dot{S}_m = -\tfrac{5}{2} S_m + \tfrac{3}{2}(\chi_{2,1} - \chi_{2,-1}) + \tfrac{5}{2}(\chi_{1,1} - \chi_{1,-1}). \tag{c}$$

$$\dot{S}_m' = \chi_{2,1} + \chi_{1,-1} - 3(\chi_{2,-1} + \chi_{1,1}) - 8\chi_{2,-2}. \tag{d}$$

$$\begin{aligned} \dot{S}_H = & -12(\chi_{2,2} + \chi_{2,-2}) - 6(\chi_{2,1} + \chi_{2,-1}) - 4\chi_{2,0} \\ & + 14(\chi_{1,1} + \chi_{1,-1}) + 12\chi_{1,0}. \end{aligned} \tag{e}$$

RESULTS

Table I lists those combinations of experiments and interactions for which measurable relaxation times T_1 or T_2 exist, and Table II gives the equations corresponding to Eq. (6) for the other cases.

The lack of a unique relaxation time under any conditions for the Dehmelt spin reorientation experiment is of interest because this is the experiment that has been performed extensively to estimate line widths. The worst situation is that of the incident light as a relaxation agent, Eq. (d). This has been solved on a computer by Franzen and Emslie[18] for certain initial conditions, and the nonexponential character can be seen in their published curves. For the other cases involving spin reorientation, it may be possible to infer approximate values of T_1 under certain conditions. These situations, Eqs. (a), (b), and (c), differ from a purely exponential decay only in the presence of terms representing population differences which may be small in a thoroughly "pumped" sample. Thus, in an experiment such as that of Franzen, if only the initial slope of the decay is used, the result may well be a usable relaxation constant. The values of T_1 derived in this way are 2/5, 16/7, and 2/5 for magnetic, quadrupole, and spin exchange relaxation, respectively.

CONCLUSIONS

The naive assumption $T_1 \approx T_2$ is shown to be justified in a rough sort of way. However, the Dehmelt[1] type of reorientation experiment is not as well suited to measurement of T_1 as a hyperfine reorientation experiment. This type of experiment has not, to our knowledge, been performed. It differs from the Dehmelt experiment only in the substitution of hyperfine-filtered light for circularly polarized light. Such light is easily available for rubidium[8] and cesium,[7] and with some difficulty for sodium[4,19], and potassium. The hyperfine reorientation should be a relatively foolproof experiment, from the standpoint of experimental difficulties, and will give a unique relaxation time for all cases except spin exchange. Spin-exchange parameters can, however, often be inferred from other experiments, such as exchange with another species of alkali atom not directly involved in the optical pumping process.

With regard to spin reorientation, *if only the initial slope of the decay is used*, then meaningful results are obtainable in Franzen's experiment, and presumably also in Dehmelt's original experiment where T_1 is an extrapolated value taken in the limit of zero light intensity. What is questionable, however, is the value of the initial slope at a *given* light intensity. In a given experimental setup this will probably bear the simple inverse relationship postulated by Dehmelt, but its exact value must depend in some detail on the manner in which the spin reversal was produced.

ACKNOWLEDGMENT

We are indebted to P. L. Bender for valuable discussions on relaxation mechanisms and measurements in alkali metal vapor.

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