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Effect of Spin-Exchange Collisions on the Optical Orientation of Atomic Sodium*

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The effect of spin-exchange collisions on the state populations obtained in an optically pumped Na^{23} vapor is studied in the limit of low light intensity. These state populations and hence the intensity of the rf Zeeman transitions are found theoretically to depend strongly on the spin-exchange cross sections. The various Zeeman rf transitions are found experimentally to be very different in intensity and this is interpreted as being partially due to spin-exchange collisions. From the intensity of the rf transitions in a magnetic field large enough to separate the six Zeeman components and from the observed relaxation time a spin-exchange cross section for two sodium atoms of $\pi S_0^2 = 6\times 10^{-14}$ cm² is found.

INTRODUCTION

THE optical orientation of an atomic sodium vapor has been studied in order to examine the effects of spin-exchange collisions on the relaxation processes and hence on the various state populations in the vapor. Relaxation processes in an optically oriented alkali metal vapor have been studied by Dehmelt[1] and more intensively by Franzen.[2] However, neither of these considered the effects of spin-exchange collisions in detail. Spin-exchange collisions betweena toms have been studied by several people[3–9] but these studies have not been combined with studies of other relaxation processes.

A sodium vapor diffusing in helium buffer gas was oriented in a low-magnetic field by the absorption and the re-emission in a different state of polarization of circularly polarized resonance radiation. As the polarization of the sample increases, the cell becomes more transparent so that the polarization of the sodium vapor can be monitored by observing the transmission of the resonance radiation through the cell.

Suppose that left circularly polarized resonance radiation containing only the D_1 line is passing through a sodium vapor. The relative optical transition probabilities $P_{F,m}$ for the eight sublevels of the ground state are $P_{2,2}:P_{2,1}:P_{2,0}:P_{2,-1}:P_{2,-2}:P_{1,1}:P_{1,0}:P_{1,-1}=0:1:2:3:4:3:2:1$. Because the sodium is diffusing in a helium buffer gas at a pressure of several cm Hg, one can assume, as Dehmelt did, that the atoms in the excited P state are randomly redistributed among the 24 hfs magnetic sublevels due to collisions with the buffer gas before re-emission.[1] This assumption would indicate that the populations $n_{F,m}$ of the ground-state sublevels would be in the limit of low light intensity $n_{2,2}:n_{2,1}:n_{2,0}:n_{2,-1}:n_{2,-2}:n_{1,1}:n_{1,0}:n_{1,-1}=\frac{1}{8}+2\alpha:\frac{1}{8}+\alpha:\frac{1}{8}:\frac{1}{8}-\alpha:\frac{1}{8}-2\alpha:\frac{1}{8}-\alpha:\frac{1}{8}:\frac{1}{8}+\alpha$, where α is determined by the light intensity and the ground-state relaxation time. It has been shown that the sodium vapor, if allowed to come to an equilibrium state controlled by spin collisions, would have ground-state populations given by $n_{2,2}:n_{2,1}:n_{2,0}:n_{2,-1}:n_{2,-2}:n_{1,1}:n_{1,0}:n_{1,-1}:=\frac{1}{8}+2\beta:\frac{1}{8}+\beta:\frac{1}{8}:\frac{1}{8}-\beta:\frac{1}{8}-2\beta:\frac{1}{8}+\beta:\frac{1}{8}:\frac{1}{8}-\beta$, where β is determined by the polarization of the sample.[6,7] Thus when the optical orientation and the spin-exchange mechanisms compete the population difference between two states $F=2$, m, and $F=2$, $m-1$ might be expected to be much larger than the population difference between two states $F=1$, m and $F=1$, $m-1$. This is true because in the $F=2$ state the optical transitions and the spin-exchange collisions both tend to populate heavily the state with the highest m value, whereas in the $F=1$ state the two effects tend to work in opposite directions. The actual populations will, of course, depend on the relaxation time necessary for the sodium spins to be disoriented by collisions with the buffer gas or the cell wall. If this relaxation time is much shorter than the time between collisions of sodium atoms, the populations will be dominated by the optical absorption probabilities. However, if this time is much longer than the time between collisions of sodium atoms, the state populations will be dominated by the spin exchange collisions. When these two times are about the same, interference effects can be expected, as both processes compete in setting up an equilibrium distribution. These effects have been observed and from the analysis of state populations and relaxation times the spin-exchange collision cross section for two sodium atoms has been found to be 6×10^{-14} cm².

EXPERIMENTAL ARRANGEMENT

The experimental apparatus consists of a GE Na 1 sodium lamp mounted in an oven and powered by a dc current. The light from this lamp was made into a parallel beam by a lens, polarized by a Polaroid circularly polarizing filter, passed through an absorption cell, and focused onto a vacuum photo cell. The absorption cell was mounted in an oven in the uniform magnetic

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field created by a pair of Helmholtz coils. The light beam and the magnetic field were parallel. The absorption cell was heated to a temperature of about 125° to 150°C so that it absorbed about 50% of the light incident on it. Changes in the polarization created by radio-frequency transitions or by reversing the dc magnetic field were monitored by observing the transmitted light intensity with the photocell whose output was amplified and displayed on an oscilloscope. The rf transitions were induced by a General Radio oscillator whose output was fed into a coil around the absorption cell. The absorption cell was a 500-cc flask containing about 3 cm Hg of helium, into which a small amount of sodium had been vacuum distilled. The dc magnetic field was modulated at about 20 cps.

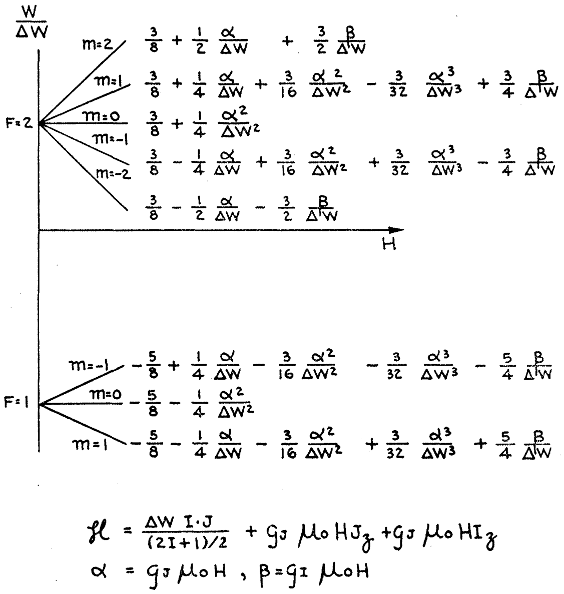

FIG. 1. The energy levels of the ground state of Na^{23}.

THEORY

The energy levels of Na^{23}, which has a $^2S_{\frac{1}{2}}$ ground state and a nuclear spin of $\frac{3}{2}$, are shown in Fig. 1. All six Zeeman transitions ($\Delta F=0$, $\Delta m=\pm1$) were well separated at a field such that their frequency was about 10.5 Mc/sec. These transitions were easily identified from the computed frequencies.

The spin-exchange collisions will be considered in a manner similar to that of Purcell and Field[3] and Wittke and Dicke.[4]

In order to specify the state of a sodium atom in a low magnetic field the quantum numbers $F=I+J$, m_F, $J=\frac{1}{2}$, and $I=\frac{3}{2}$ are necessary. Suppose two sodium atoms in states F_1, m_1 and F_2, m_2 collide and emerge from the collision in states F_1', m_1' and F_2', m_2'. These transitions occur because of the dependence of the scattering cross section on the relative electronic angular momenta of the colliding atoms. The interaction Hamiltonian for such a system is $V(r)P_1+K(r)P_0$, where P_1 and P_0 are the projection operators for total electronic spin angular momenta 1 and 0, respectively. This Hamiltonian assumes that the Na_2 molecule, which is formed when the two sodium atoms collide, is formed in the $^1\Sigma_0$ state [for which $K(r)$ is the effective interatomic potential] or in the $^3\Sigma_1$ state [for which $V(r)$ is the effective interatomic potential]. Because of the different potentials for the singlet and triplet states, the singlet and triplet parts of the wave function will evolve with different relative phases. Thus if $\psi(F_1,m_1;F_2,m_2)$ is the initial wave function for two atoms, one at rest, the other incident upon the first with an energy E, then

$$\psi_f=(P_1+P_0e^{i\varphi})\psi(F_1,m_1;F_2,m_2)$$

will be the final wave function, where φ is the relative phase change. The scattering cross section will be the product of the geometrical area, in which a strong collision (one in which the phase shifts are large) will occur, times the square of the matrix element of $(P_1+P_0e^{i\varphi})$. Thus

$$\sigma=\pi S_0^2|\langle F_1',m_1';F_2',m_2'|P_1+P_0e^{i\varphi}|F_1,m_1;F_2,m_2\rangle|^2,$$

where πS_0^2 is the geometrical area in the cross section, and where an average is taken over φ since $\varphi\gg1$ and since there are many collisions per second.

In order to understand the state populations, the equations for the rate of change of $n_{F,m}$ must be considered. Let $P_{F,m}$ be the optical transition probability from the ground state and let T_1 be the relaxation time for the system to reach equilibrium due to spin disorienting collisions of the sodium with the buffer gas and the cell walls. Then

$$dn_{F,m}/dt=-AP_{F,m}n_{F,m}+\tfrac{1}{8}A\sum_{F,m}P_{F,m}n_{F,m}-\frac{(n_{F,m}-\frac{1}{8})}{T_1}-\pi S_0^2\bar{v}\Big[\sum_{F',m',F'',m'',F''',m'''}n_{F,m}n_{F',m'}\times|\langle F''',m''';F'',m''|P_1+e^{i\varphi}P_0|F,m;F',m'\rangle|^2_{\text{av over }\varphi}-\sum_{F',m',F'',m'',F''',m'''}n_{F''',m'''}n_{F'',m''}\times|\langle F,m;F',m'|P_1+e^{i\varphi}P_0|F''',m''';F'',m''\rangle|^2_{\text{av over }\varphi}\Big],$$

where A depends on the light intensity and $\bar{v}$ is the average velocity of a sodium atom. Although these equations are very complicated, steady-state solutions to them have been found for the case where A is small and only first-order terms in A are considered, and where $P_{F,m}$ are the transition probabilities for D_1

TABLE I. The state populations of Na. The notation is

$$\alpha=A\frac{(64/T_1^2+44/T_1T_2+7.6/T_2^2)}{(8/T_1+2.78/T_2)(32/T_1^2+16.5/T_1T_2)},$$

$$\beta=A\frac{(32/T_1^2+27.6/T_1T_2+3.8/T_2^2)}{(8/T_1+2.78/T_2)(32/T_1^2+16.5/T_1T_2)},\text{ and}$$

$$\delta=-A\frac{(32/T_1^2+5.4/T_1T_2-3.8/T_2^2)}{(8/T_1+2.78/T_2)(32/T_1^2+16.5/T_1T_2)},$$

where $T_2=1/n\bar{v}\pi S_0^2$. These equations are valid only in the case of low light intensity.

F	m	Population
	2	$\frac{1}{8}+\alpha$
	1	$\frac{1}{8}+\beta$
2	0	$\frac{1}{8}$
	-1	$\frac{1}{8}-\beta$
	-2	$\frac{1}{8}-\alpha$
	-1	$\frac{1}{8}-\delta$
1	0	$\frac{1}{8}$
	1	$\frac{1}{8}+\delta$

radiation only. These solutions are shown in Table I. From these solutions the relative intensity of the various rf transitions can be found. From these solutions one can, also, easily calculate the change in absorption divided by the initial rate of change of absorption if the dc magnetic field is reversed as described by Dehmelt.[1] Each of these will depend on T_1 and $\pi S_0^2\bar{v}$ but not on the light intensity A. Thus by measuring each of these quantities both T_1 and πS_0^2 can be obtained.

RESULTS

In this experiment both the D_1 and D_2 lines of the sodium resonance radiation from the lamp were incident on the absorption cell. The D_1 line from the lamp was about 15% more intense than the D_2 line. Due to the fact that the D_2 line is absorbed twice as fast as the D_1 line, this ratio varies throughout the absorption cell.

TABLE II. The relative intensity of the rf Zeeman transitions in a Na^{23} vapor. The transitions among the $F=2$ sublevels all correspond to an increase in the absorption of the sample and hence a decrease in the transmitted light at resonance. The transitions among the $F=1$ sublevels correspond to a decrease in the absorption of the sample and hence an increase in the transmitted light. The interpretation of this effect is that in the $F=2$ level, the least absorbing sublevels are more heavily populated than the more absorbing levels, and hence rf transitions which tend to equalize the state populations result in an increase in absorption where as in the $F=1$ level the spin-exchange collisions cause the most heavily absorbing sublevels to be more populated than the less absorbing sublevels and so the rf transitions cause a decrease in the absorption of the sample. This inversion is not related to that reported by Franken and Colgrove [Phys. Rev. **119**, 680 (1960)]. The relative intensities were measured at the lowest light intensity, at which all six transitions could easily be distinguished, and no extrapolation was used.

Transition	Relative intensity
2, 2–2, 1	1.6
2, 1–2, 0	1.8
2, 0–2, −1	1.8
2, −1–2, −2	1.6
1, 1–1, 0	0.4
1, 0–1, −1	0.4

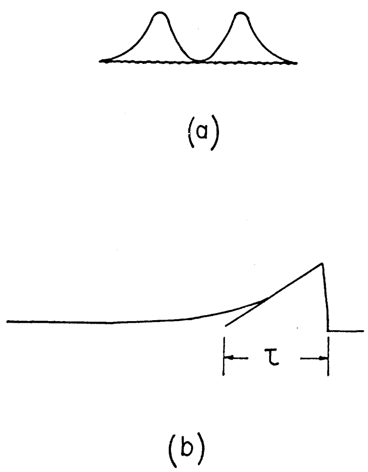

FIG. 2. (a) A typical rf transition. The dc magnetic field is being modulated at about 20 cps. The frequency is approximately 10.5 Mc/sec. (b) A typical signal upon reversing the dc magnetic field. τ represents the change in the absorption divided by the initial rate of change of the absorption, i.e.,

$$\tau=\frac{(\sum P_{F,m}n_{F,m})_{\text{after rev.}}-(\sum P_{F,m}n_{F,m})_{\text{before}}}{(\sum P_{F,m}dn_{F,m}/dt)_{t=0}}.$$

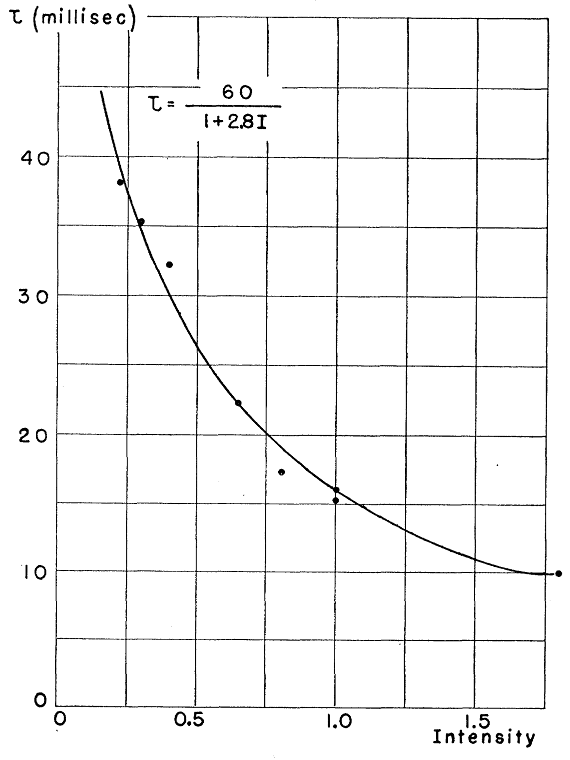

FIG. 3. The values of τ as a function of light intensity. The solid curve represents the curve $\tau=60/(1+2.8I)$ which was used to extrapolate the values of τ to zero light intensity.

The absorption probabilities used in the calculations of the state populations were those for the D_1 line only, even though both the D_1 and D_2 lines were present, and the value of the light intensity was assumed to be equal to the difference between that of the D_1 line and that of the D_2 line. This is valid in the limit of low light intensity because if both D lines are present in equal intensity and if the redistribution in the excited state is complete, as has been assumed, then no orientation is obtained.[1] This difference of the intensity of the lines varies through the cell, of course. The ratio of the intensity of the various rf transitions does not depend on the light intensity nor does the change in absorption divided by the initial rate of change of the absorption upon reversing the dc magnetic field. These were thus the quantities used to deduce T_1 and $\pi S_0^2\bar{v}$.

The relative intensity of the various rf transitions is given in Table II. A typical rf transition as observed is shown in Fig. 2(a).

The change in absorption divided by the initial rate of change of the absorption upon reversing the dc magnetic field as a function of light intensity is shown in Fig. 3 and a typical signal is shown in Fig. 2(b).

The intensity of the rf transitions is taken to be proportional to the difference in populations between the various states as given in Table I. From the measured intensities one can obtain the value of $T_1 n\bar{v}\pi S_0^2=7$, where n is the number of sodium atoms per cc. From the measured decay time upon field reversal and using the fact that $T_1 n\bar{v}\pi S_0^2=7$ one can obtain $T_1=109$ msec and $1/n\bar{v}\pi S_0^2=15.5$ msec. The average velocity of sodium atoms at 160°C is 0.7×10^5 cm/sec. The value of n is difficult to obtain. It was taken to be about 2×10^{10} atoms/cc from vapor pressure measurements. This could be quite inaccurate, however. This yields a value of $\pi S_0^2=6\times10^{-14}$ cm^2 for the spin-exchange cross section.

The error in the determination of the spin-exchange cross section by this method is not easy to evaluate. A very serious error may be introduced by a lack of good vapor-pressure data for sodium at these temperatures. Another error may occur in the extrapolation of the relaxation time or the intensity of rf transitions to zero light intensity. Another serious source of error may be the fact that at 500°K the hyperfine structure of the sodium in the absorption of the D lines is still present.[10] This means that the light intensity will not be the same for both F levels throughout the cell. This may possibly alter the results. Probably even with all these sources of error the spin-exchange cross section obtained is accurate to within a factor of 3.

It is hoped that a systematic study of relaxation mechanisms along these lines will yield improved values for the spin-exchange cross sections and for the relaxation times in alkali metal vapors.

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[10] J. W. Chamberlain, D. M. Hunten, and J. E. Mack, J. Atm. and Terrestrial Phys. 12, 153 (1957).