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Collisional Depolarization within Atomic States of Half-Integral J; Thallium $^2P_{1/2}$

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Abstract. Within the semiclassical and adiabatic approximations we derive the following selection rule for collisional depolarization by noble gas atoms: $m_J \not\leftrightarrow -m_J$ within a J-multiplet of an atom with an odd number of electrons. This result suggests the possibility of extending conventional optical pumping techniques to non-S-state atoms. Preliminary results on the optical pumping of the $^2P_{1/2}$ ground state of thallium, however, indicate that typical cross sections for depolarization in Tl-noble-gas-atom collisions are greater than 10^{-17} cm^2, and hence are disappointingly large.

Introduction

In the past, conventional optical pumping techniques utilizing buffer gases and wall coatings have been applied only to vapors of atoms possessing electronic ground states of zero orbital angular momentum ($L = 0$). The effectiveness of the noble gases as buffers in this case is demonstrated by the remarkably small depolarization cross sections of the order of 10^{-22} to 10^{-26} cm^2 that have been measured for alkali atoms in the $^2S_{1/2}$ ground state colliding with He, Ne, or Ar atoms [1]. In contrast, it generally has been assumed that an atom in a state of $L > 0$ should suffer considerable depolarization in a single collision, whether the collision be with a buffer gas atom, or with the walls of the cell. Typical depolarization cross sections of order of magnitude 10^{-14} cm^2, measured for atoms in P_1 and $P_{3/2}$ states colliding with noble gas atoms, support this hypothesis [2, 3]. An increase of ten orders of magnitude in the rate of collisional depolarization precludes the use of buffer gases in the optical pumping of non-S-state atoms. Recently, however, it was suggested that atoms in states of J ($= L + S$) equal to 1/2 could be an exception, and might prove resistant to such relaxation [4]. In the present paper, we derive a selection rule, $m_J \not\leftrightarrow -m_J$, restricting collisionally induced depolarization within a given J-multiplet. We also report an attempt to optically pump the $^2P_{1/2}$ ground state of thallium atoms in the presence of various buffer gases.

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Selection Rule for Collisional Depolarization

In this section we show, within the semiclassical and adiabatic approximations, that the reorientation of electronic angular momentum in an atomic collision involving an odd number of electrons is restricted by the selection rule, $m_J \not\to -m_J$. The derivation is directed towards the depolarization of alkali metal atoms or of thallium-like atoms, in isolated $^2P_{1/2}$ or $^2P_{3/2}$ states, induced by collision with noble gas atoms. The result, however, is of general validity, and is not restricted to P states.

The relative motion of a magnetic atom and a noble gas atom is taken as classical, but not necessarily along a straight line. Nuclear spin is ignored. We use time dependent perturbation theory to describe the mixing of electronic states during a collision. The equations of motion in the interaction representation are

$$i\hbar\,\dot{a}_n(t) = \sum_{n'} \langle n \mid V(t) \mid n' \rangle \exp(i\,\omega_{nn'}t)\, a_{n'}(t)\,, \tag{1}$$

where $\omega_{nn'} = (E_n - E_{n'})/\hbar$, and the $\mid n\rangle$ are the eigenstates of the Hamiltonian, H_0, for the isolated atoms, including spin-orbit interaction and exchange. The perturbation of electronic energy due to the finite nuclear separation at time t is,

$$V(t) = \int d^3 r_1\, d^3 r_2\, \varrho_1(r_1)\, \varrho_2(r_2)\, r_{12}^{-1}\,, \tag{2}$$

where $\varrho_1(r_1)$ and $\varrho_2(r_2)$ are the respective operators of total charge density for the two colliding atoms. This interaction neglects magnetic coupling and interatomic exchange. The selection rule derived in this section depends only on the invariance of $V(t)$ under reversal of *electronic* motion. However, it is useful to realize that because the ground state of a noble gas atom is neutral and spherically symmetric, $V(t)$ does not have matrix elements between two states in which the noble gas atom is unexcited.

The equations of motion may be integrated iteratively in the usual manner.

$$i\hbar\,\dot{a}_n(t) \approx \sum_{n'} \Bigg[\exp(i\,\omega_{nn'}t)\,\langle n \mid V(t) \mid n' \rangle + \sum_k \exp(i\,\omega_{nk}t)\,\langle n \mid V(t) \mid k \rangle \times \int_{-\infty}^{t} dt'\,(i\hbar)^{-1} \exp(i\,\omega_{kn'}t')\,\langle k \mid V(t') \mid n' \rangle + \cdots \Bigg] a_{n'}(-\infty)\,. \tag{3}$$

Partial integration with respect to time everywhere in Eq. (3) yields integrated terms and terms containing $\mathrm{d}V(t)/dt$. In the adiabatic approximation the latter are discarded. The remainder is,

$$i\hbar\,\dot{a}_n(t) \approx \sum_{n'} \exp(i\,\omega_{nn'}t) \Bigg[\langle n \mid V(t) \mid n' \rangle + \sum_k \langle n \mid V(t) \mid k \rangle \langle k \mid V(t) \mid n' \rangle (E_{n'} - E_k)^{-1} + \sum_{k,l} \langle n \mid V(t) \mid k \rangle \langle k \mid V(t) \mid l \rangle \langle l \mid V(t) \mid n' \rangle (E_{n'} - E_k)^{-1} (E_{n'} - E_e)^{-1} + \cdots \Bigg] a_{n'}(-\infty)\,. \tag{4}$$

The terms appearing in the brackets of Eq. (4) are matrix elements of the operators, V, $V\,(E_{n'} - H_0)^{-1}\,V$, etc., between the states $\mid n\rangle$ and $\mid n'\rangle$. If V is purely electro-

static, the operators V, $V\,(E_{n'} - H_0)^{-1}\,V\,\ldots$, are Hermitian and time reversal invariant. As we show in the appendix, matrix elements of such operators vanish between pairs of sublevels that are related by Wigner's operation of time reversal. The entire expression in the brackets therefore vanishes if $|\,n'\rangle$ is $|\,J, m_J\rangle$ and $|\,n\rangle$ is $|\,J, -m_J\rangle$, yielding the selection rule, $m_J \not\to -m_J$. It is important to note that the quantization axis for J may be chosen arbitrarily, *and in particular may be fixed in the laboratory.* This selection rule, which has been derived previously in a somewhat different form by GALLAGHER [5] implies no relaxation for a $^2P_{1/2}$ state, and incomplete randomization of J in a single collision for a $^2P_{3/2}$ state.

Violation of the selection rule can, however, occur through non-adiabatic or non electrostatic effects. In general there will be some nonadiabatic contribution to $i\hbar\,\dot{a}_n(t)$ regardless of how slowly $V(t)$ varies. For example, there may be fourth order terms of Eq. (3) which have the initial state appearing also as an intermediate state. It is clearly not possible then to assert the adiabatic approximation

$$\langle k\,|\,V(t)\,|\,l\rangle \exp(i\,\omega_{kn'}\,t)\,(i\,\hbar)^{-1}\,dt \approx d\,[\langle k\,|\,V(t)\,|\,l\rangle \exp(i\,\omega_{kn'}\,t)\,(E_{n'} - E_k)^{-1}] \qquad (5)$$

because for such a case, $E_k = E_{n'}$. One may, however, separate such terms from the perturbation series, and consider them with other nonadiabatic terms omitted from Eq. 4. By application of the procedure in the appendix, the $m_J \not\to -m_J$ selection rule for the right hand side of Eq. (4) remains valid even if all terms containing some particular intermediate energy are omitted.

It has been suggested that diminished collisional relaxation in a $^2P_{1/2}$ state might be observed in the depolarization of the D_1 resonance lines of *Rb* and Cs induced by alkali-atom-noble-gas-atom collisions [6]; this expectation has been confirmed [5]. The measured cross sections for depolarization within the $^2P_{1/2}$ state show a marked dependence on the energy separation between the $^2P_{1/2}$ and $^2P_{3/2}$ states, ΔE. In Cs, where ΔE is only twice as great as in Rb, typical depolarization cross sections are about a factor of five smaller than in Rb. An inviting speculation is that in the doublet ground state of thallium, where ΔE is 15 times larger than in Cs, extremely small cross sections within the $^2P_{1/2}$ state might be found, perhaps even approaching those of the alkali ground state. In the present experiment we have found that this is not the case; typical Tl-noble-gas collisional depolarization cross sections appear to be greater than 10^{-17} cm^2, and hence are disappointingly large.

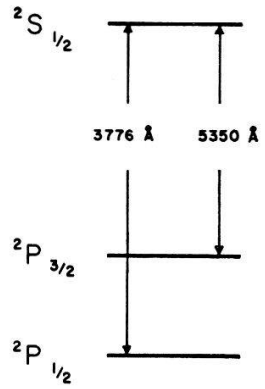

Figure 1

Thallium energy levels of interest in the Optical pumping process.

Optical Pumping of Thallium

The Tl energy levels of interest are shown in Figure 1. The nuclear spin of Tl is 1/2. In a weak magnetic field, the $^2P_{1/2}$ ground state splits into four $|F, m_F\rangle$ sublevels. The goal of the optical pumping process is to preferentially populate the sublevel $|1, +1\rangle$. Pumping is performed by passing circularly polarized 3776 Å light through the vapor. The relative absorption probabilities of the sublevels $|0, 0\rangle$, $|1, -1\rangle$, $|1, 0\rangle$, $|1, +1\rangle$ are 1:2:1:0. Of the atoms that are raised to the $^2S_{1/2}$ excited state, about half decay to $^2P_{3/2}$, and about half to $^2P_{1/2}$ [7]. Linearly polarized 5350 Å light is passed through the vapor in order to depopulate the $^2P_{3/2}$ level. In order to derive equations for the anticipated equilibrium polarization, we have made the following approximations:

1. We assume the use of a broad line light source possessing equal intensity in all hyperfine components of the 3776 Å and 5350 Å lines, and of an optically thin absorption cell. The pumping rate from each sublevel is given by the sublevel population multiplied by the product of the relative absorption probability and a pumping rate constant, A, proportional to the incident light intensity and the absolute absorption cross section.

2. There is no collisionally induced mixing within the $^2S_{1/2}$ excited state; that is, atoms decay from the particular sublevel to which they were excited. The measurements of alkali ground state depolarization cross sections make this assumption reasonable.

3. Collisionally induced transitions between the $^2P_{1/2}$ and $^2P_{3/2}$ ground states are negligible. The probability of such transitions decreases rapidly with increasing energy separation, ΔE, between the states. For Cs, typical cross sections for this process are of the order of 10^{-21} cm^2 [8]. Since ΔE in the ground state of Tl is more than an order of magnitude larger than ΔE in the excited state of Cs, such transitions should be negligible in our experiment.

4. Depolarization within $^2P_{3/2}$ should be described by a "normal" cross section of the order of 10^{-14} cm^2. We assume complete collisionally induced mixing throughout all sublevels of this state. Pumping out of $^2P_{3/2}$ is described by a pumping rate parameter, $A!$.

5. It is not possible at present to calculate the relative probabilities connecting the sublevels of the $^2P_{1/2}$ state through relaxation. We assume for simplicity a model of "uniform relaxation", in which any sublevel can relax to any other sublevel with equal probability. Ground state relaxation between sublevels is described by a rate constant, $(1/\tau)$.

Under these assumptions, the equilibrium populations $n(F, m_F)$ of the $|F, m_F\rangle$ ground state sublevels are:

$$\begin{aligned} n\,(1, -1) &= \alpha\,(\alpha + 2/3)\,\gamma^{-1} \\ n\,(1, 0) &= n(0, 0) = \alpha\,(\alpha + 11/6)\,\gamma^{-1} \\ n\,(1, +1) &= \alpha^2 + 3\,\alpha + 35/18)\,\gamma^{-1} \end{aligned} \tag{6}$$

where

$$\alpha = (\tau A)^{-1}$$
$$\beta = A/A'$$
$$\gamma = 4\,\alpha^2\,(1+\beta) + (22 + 15\,\beta)\,\alpha/3 + 35/18\,. \tag{7}$$

We searched for magnetic resonance between the $F = 1$, $m_F = \pm 1{,}0$ hyperfine sublevels of the $^2P_{1/2}$ ground state, using the light transmission monitoring method of DEHMELT [9]. In the present case, the absorption coefficient, K, for σ^+ 3776 Å light is,

$$K = [2\,n\,(1,-1) + 2\,n\,(1,0)]\,. \tag{8}$$

In the partially polarized state of the vapor,

$$K_{pol} = 2\,\alpha\,(2\alpha + 5/2)\,\gamma^{-1}\,. \tag{9}$$

If we sweep with saturation through the unresolved $F = 1$, $\Delta m_F = \pm 1$ resonances, the absorption coefficient, K_{res}, at the center of the resonance, is

$$K_{res} \cong \lim_{\tau \to 0} K_{pol} = (1+\beta)^{-1}\,. \tag{10}$$

Defining the resonance signal, S, as the relative change of light absorption as the pass through resonance is made, we obtain

$$S = (K_{pol} - K_{res})/K_{pol} = 1 - \gamma\,[2\alpha\,(2\alpha + 5/2)\,(1+\beta)]^{-1}\,. \tag{11}$$

In our experiment, the ratio A/A' $(= \beta)$ was approximately 1/2. In Figure 2 we plot the expected resonance signal as a function of $(1/\tau A)$, the ratio of the relaxation rate to the pumping rate. For comparison, we include in the same figure a similar calcula-

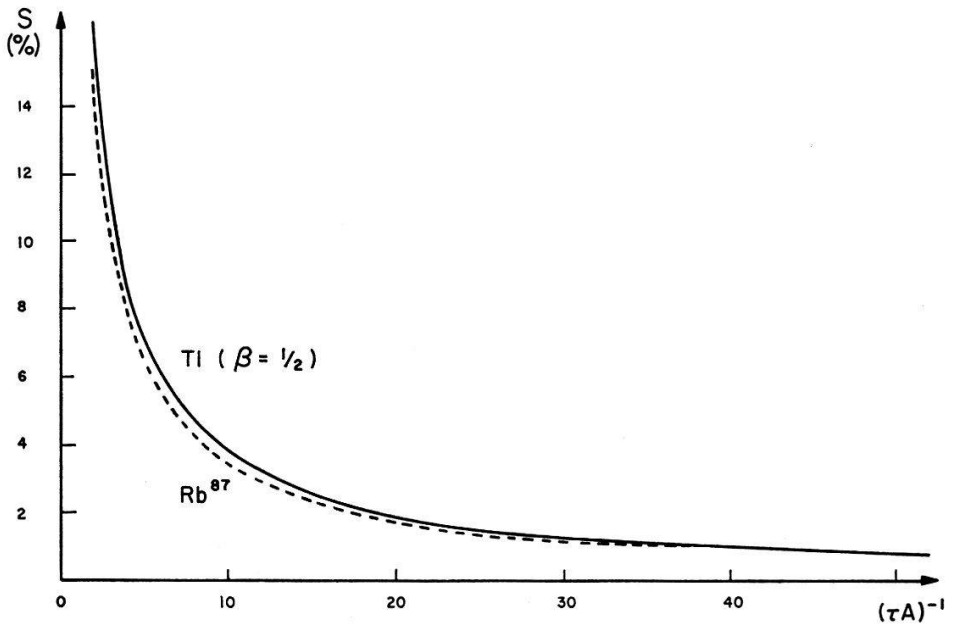

Figure 2

Expected strengths of resonance signals as a function of the ratio of relaxation rate to pumping rate for thallium vapor ($I = 1/2$), and for an alkali metal vapor ($I = 3/2$). S and β are defined in the text.

tion (assuming uniform relaxation) for a nuclear spin 3/2 alkali atom. It is evident that for a given value of $1/\tau A$ the signal in a Tl pumping experiment should be virtually the same as that obtained in alkali optical pumping.

A search for Tl resonances in a variety of buffer gases (Ne, Ar, N_2), and over a wide range of buffer gas pressures (0.05 to 10 Torr) proved negative. Evidently the collisional depolarization cross sections within the $^2P_{1/2}$ state are too large to be determined by the present apparatus. We are able, however, to set a lower bound on the cross sections in the following way. We take the relaxation time, τ, of Tl in the $^2P_{1/2}$ state to be given by

$$(1/\tau) = N_0(p/p_0)\,\sigma\, v_{rel} + [(R/v_{\mathrm{Tl}}) + (p\, R^2/D_0\, p_0\, \pi^2)]^{-1}\,. \tag{12}$$

N_0 is 1×10^{19} atoms/cm^3 (at 450 °C), p_0 is 760 Torr, p is the actual buffer gas pressure, v_{rel} is the mean relative velocity of Tl and buffer gas atoms. v_{Tl} is the mean velocity of Tl atoms, D_0 is the diffusion coefficient of Tl in the buffer gas, R is the radius of the cell, and σ is the depolarization cross section. Equation [12] is similar to an expression commonly used to describe the relaxation of an optically pumped alkali metal vapor [10]. It has been modified to insure that in the limit of low buffer pressure, the relaxation time approaches a limiting value equal to the average time between collisions of a Tl atom with the walls.

From Figure 2, we see that the resonance signal is proportional to the relaxation time, τ, if $1/\tau A$ is large For a given pump rate, there is thus a minimum relaxation time, τ_M, that yields an experimentally detectable signal, where τ_M is dependent on the sensitivity of the apparatus. If no resonances are seen, then the actual relaxation time is shorter than τ_M. We utilize this fact in Eq. (12) to obtain Eq. (13).

$$\sigma \geq (p_0/p\, N_0\, v_{rel})\,\{\tau_M^{-1} - [R/v_{\mathrm{Tl}} + R^2\, p/\pi^2\, D_0\, p_0]^{-1}\}\,. \tag{13}$$

There exists an optimum pressure for which the bound on σ as set by Eq. (13) has a maximum value. In our experiment, this pressure was about 0.15 Torr. For this reason, especially careful measurements were made in the range 0.05 to 1.0 Torr.

The optical pumping apparatus was of sufficient sensitivity to permit measurement of Rb Zeeman resonances, with a sensitivity of 200:1, in an uncoated cell containing 0.35 Torr or Ar as a buffer gas. Inserting the known value of the diffusion coefficient for Rb in Ar [11] into Eq. (12), we obtain for this cell a Rb relaxation time of 2.8 msec. By measuring the ratio of Tl and Rb pumping rates to be 1:25, we estimate that in the Tl experiment, τ_M should be 0.35 msec. With $v_{\mathrm{Tl}} = 3\times 10^4$ cm/sec, $v_{rel} = 7.3\times 10^4$ cm/sec (Tl-Ar), and $D_0 \approx 0.8$ cm^2/sec, we find $\sigma > 1\times 10^{-17}$ cm^2. An extension of this experiment, in which considerable greater sensitivity will be available, is planned.

Appendix
Time Reversal Symmetry

We denote Wigner's time-reversal operator by T. With the standard phase conventions,

$$T\mid J, M_J\rangle = (-1)^{J+M_J}\mid J, -M_J\rangle\,. \tag{A1}$$

If 0 is a time-reversal-invariant operator, and a any state, we have

$$\langle a \mid 0 \mid T\,a\rangle = \langle T\,a \mid 0 \mid T^2\,a\rangle^* \tag{A2}$$

from the antiunitarity of T. For a system of odd total number of electrons, $T^2 = -1$, so that

$$\langle a \mid 0 \mid T\,a\rangle = -\langle T\,a \mid 0 \mid a\rangle^* . \tag{A3}$$

If 0 is also Hermitian, we conclude that

$$\langle a \mid 0 \mid T\,a\rangle = -\langle a \mid 0 \mid T\,a\rangle = 0 . \tag{A4}$$

A symmetric multiple product of Hermitian operators, such as ABA, is also Hermitian. Eq. (4) states that the expression

$$\langle a \mid A \mid n\rangle \langle n \mid B \mid l\rangle \langle l \mid A \mid T\,a\rangle \tag{A5}$$

vanishes when summed over all 1 and n, assuming A and B are time reversal invariant. By a procedure similar to that carried out in Eqs. (2) through (4), the expression (A5) is equal to

$$-\langle a \mid A \mid T\,l\rangle \langle T\,l \mid B \mid T\,n\rangle \langle T\,n \mid A \mid T\,a\rangle \tag{A6}$$

so the vanishing of the sum may be considered to result from pairwise cancellation of terms. Similarly, we see that an expression such as

$$\sum_{nl} \langle a \mid v \mid n\rangle \langle n \mid V \mid l\rangle \langle l \mid V \mid T\,a\rangle [E_0 - E_n]^{-1} [E_0 - E_e]^{-1}$$

vanishes when the indices n and 1 are each extended over the sublevels of two energy levels E_n and E_1.

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