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OPTICAL PUMPING AND COLLISIONAL RELAXATION IN THE $^2P_{1/2}$ GROUND STATE OF THALLIUM

H. M. Gibbs and G. G. Churchill
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

and

T. R. Marshall, J. F. Papp, and F. A. Franz*
Department of Physics, Indiana University,† Bloomington, Indiana 47401

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The $^2P_{1/2}$ ground state of thallium has been optically pumped in the presence of various buffer gases. The measured cross sections for the destruction of the electron polarization are small (10^{-19} to 10^{-17} cm^2), verifying the selection rule $M_J \not\leftrightarrow -M_J$ for the adiabatic contributions and demonstrating the strong dependence of the nonadiabatic contributions upon the multiplet energy separation.

The $^2P_{1/2}$ ground state of Tl has been optically pumped. The electron randomization cross sections have been measured to be (at 610°C, in units of 10^{-20} cm^2, and with a ±30% uncertainty) He, 60; Ne, 14; Ar, 110; Kr, 220; Xe, 620; H_2, 380; N_2, 920. Diffusion coefficients of Tl have been measured to be (in units of cm^2/sec at 510°C, at atmospheric pressure, and with a 50% uncertainty) He, 1.7; Ne, 0.79; Ar, 0.35. The cross sections are the smallest yet found for a state with nonzero orbital angular momentum.

In 1966 it was suggested that collisional relaxation might be diminished within the Zeeman sublevels of an energetically isolated $^2P_{1/2}$ state.[1] This was verified in Rb and Cs, where the cross sections (σ's) were found to be 10 to 50 times smaller than geometric σ's.[2] A selection rule $M_J \not\leftrightarrow -M_J$ was derived by assuming an odd total number of electrons, a time-reversal–invariant interaction Hamiltonian, a large energy separation ΔE between the $^2P_{1/2}$ and $^2P_{3/2}$ states, and the neglect of nonadiabatic terms.[2-4] Since the rule $M_J \not\leftrightarrow -M_J$ depends strongly on ΔE (238 cm^{-1} in Rb; 554 in Cs; 7793 in Tl), the $^2P_{1/2}$ relaxation should be much weaker in Tl than in Rb and Cs. But the failure of several laboratories to optically pump Tl (and reported[5] theoretical and preliminary experimental σ's for Cs larger than Gallagher's) weakened Gallagher's experimental demonstration[2] of the rule $M_J \not\leftrightarrow -M_J$. However, the successful optical pumping of Tl and the smallness of the σ's reported here establish the rule $M_J \not\leftrightarrow -M_J$ in the Tl ground state.

Natural Tl consists of Tl^{203} and Tl^{205}, each with nuclear spin $\frac{1}{2}$. An atom in a given sublevel F,M of the $^2P_{1/2}$ state cannot make a transition to another sublevel F,M' without violating either $M_J \not\leftrightarrow -M_J$ or $\Delta M_I = 0$; such is not the case in the $^2P_{3/2}$ state. Small σ's in the $^2P_{1/2}$ state therefore imply that both the selection rules $\Delta M_I = 0$ and $M_J \not\leftrightarrow -M_J$ are operative.

Nuclear spin complicates the analysis by introducing three resolved hyperfine components.[6] Let $L_{FF'}$ be proportional to the incident light intensity absorbable in a transition from the F hyperfine level of the $^2P_{1/2}$ state to the F' level of the $^2S_{1/2}$ excited state. The absorption of circularly polarized light incident along the magnetic field is $A_{cp} = L_{01}n_{00} + L_{10}n_{1\,-1} + L_{11}(n_{1\,-1} + n_{10})$, where n_{FM} is the density of the M sublevel of the F level. If all hyperfine components are equal ($L_{FF'} = L$), then $A_{cp} = L[n - (n_{11} - n_{1\,-1})] = Ln(1 - 2\langle J_z \rangle)$, where $n = n_{11} + n_{10} + n_{1\,-1} + n_{00}$, and $\langle J_z \rangle$ is the electronic polarization. The collisional relaxation of

$\langle J_z\rangle$ was measured in two ways: (a) by observing optical-pumping recovery transients, and (b) by monitoring the amplitude of the absorption signal with and without *rf* saturation.

Buffer-gas relaxation of Tl should occur by electron randomization,[7] for which $\langle J_z\rangle$ relaxes by a sum of two exponentials, in general.[8] But for $I=J=\frac{1}{2}$, the transient signal is a single exponential,[8]

$$S=\frac{A_{cp}(0)-A_{cp}(t)}{A_{cp}(0)-A_{cp}(\infty)}\approx\frac{\langle J_z(t)\rangle}{\langle J_z(\infty)\rangle}=1-e^{-t/T}, \qquad (1)$$

$$\frac{1}{T}=\frac{1}{2T_{ER}}=\frac{\sigma_{ER}N_0\bar{v}}{2}\left(\frac{p}{p_0}\right). \qquad (2)$$

σ_{ER} is the electron randomization cross section, N_0 is the density of buffer atoms at the operating temperature and at atmospheric pressure p_0, and $\bar{v}$ is the mean relative velocity of Tl and buffer-gas atoms. σ_{ER} is determined by measuring the recovery time T at a high buffer-gas pressure p, as shown in Fig. 1.

If both the $^2P_{1/2}$ relaxation rate and the $^2P_{3/2}$ depopulation rate are large compared with the $^2P_{1/2}$ pumping rate, the equilibrium polarization, $\langle J_z\rangle_{\rm eq}$, is proportional to the ratio of pumping to relaxation rates. Assuming uniform relaxation at the walls and electron randomization in collisions with buffer gas atoms, one obtains[9,3]

$$\langle J_z\rangle_{\rm eq}=C\{[(r/v_{\rm Tl})+p(GD_0p_0)^{-1}]^{-1}+N_0(p/p_0)\tfrac{1}{2}\sigma_{ER}\bar{v}\}^{-1}, \qquad (3)$$

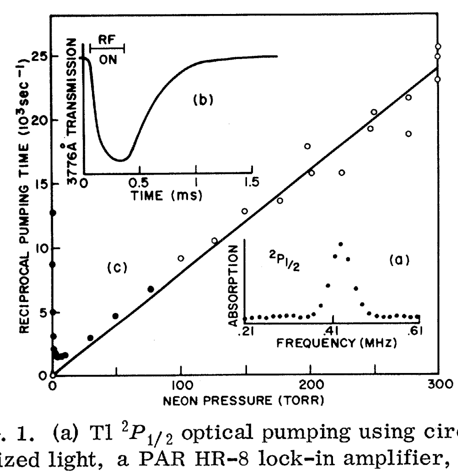

FIG. 1. (a) Tl $^2P_{1/2}$ optical pumping using circularly polarized light, a PAR HR-8 lock-in amplifier, and rf modulation at 1 kHz. The signal peaked for a sidearm temperature of 440°C. (b) Time dependence of the $^2P_{1/2}$ signal with a 5-sec time constant on the waveform eductor. (c) Reciprocal pumping time versus Ne pressure. The cross section is extracted from the slope of the straight line which is a least-squares fit to the open-circle points.

where $G=[(2.4/r)^2+(\pi/L)^2]$. C is proportional to the incident light intensity, r is the cell radius and L its length, $v_{\rm Tl}$ is the mean velocity of Tl atoms, and D_0 is the diffusion coefficient at atmospheric pressure and the cell temperature. The ratio D_0/σ_{ER} was determined by measuring $\langle J_z\rangle_{\rm eq}$ versus buffer pressure; multiplying by the σ_{ER} from the transient experiment gave the diffusion coefficients D_0 listed in the first paragraph. The data for argon are shown in Fig. 2.

In the Bell Telephone Laboratories transient experiment, 3776-Å radiation from a flow lamp[10] impinged upon Tl vapor of 10^{11} to 10^{12} atoms/cm^3 in a 5-cm-long, 3-cm-diam Suprasil quartz cell at 610°C, with the Tl sidearm at 420°C.[11] $\langle J_z(t)\rangle$ was monitored in the $^2P_{1/2}$ ($^2P_{3/2}$) state with a 3776-Å interference filter (Wratten 74, 5350-Å pass), RCA 8575 tube, PAR CR-4 amplifier, and PAR TDH-9 waveform eductor (PAR 160 boxcar and a data averager[11]). Relaxation studies are simplified by observing transients; here the recovery transient was observed after an rf pulse destroyed the polarization [Fig. 1(b)]. The transients were single exponentials, as expected, and were unaffected by a threefold increase in Tl density or decrease in light intensity. The σ_{ER}'s calculated as in Fig. 1(c) and Eq. (2) are listed in the first paragraph; the factor of 2 in Eq. (2) results from the assumption of electron randomization and $I=\frac{1}{2}$.[8] The quoted 30% uncertainty is three times the largest of the standard deviations from the straight-line least-squares fits and should easily include errors from neglecting diffusion, cell-length corrections, etc., in the fits.

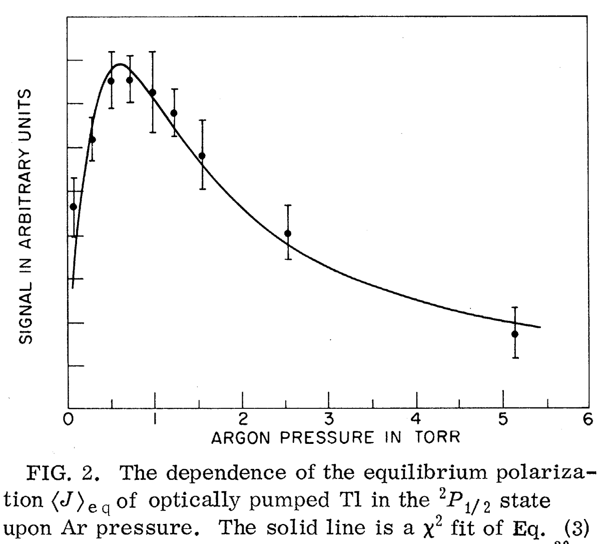

FIG. 2. The dependence of the equilibrium polarization $\langle J\rangle_{\rm eq}$ of optically pumped Tl in the $^2P_{1/2}$ state upon Ar pressure. The solid line is a χ^2 fit of Eq. (3) to the experimental data, assuming $\sigma_{ER}=110\times10^{-20}$ cm^2 and $D_0=0.35$ cm^2/sec.

The evacuated-cell relaxation time was lengthened from 0.1 to 0.5 msec by inserting H_2 for a few minutes.[12] For unpolarized light along the field, $A_{up} = 2L_{01}n_{00} + L_{10}(n_{1\,-1} + n_{11}) + L_{11}(n_{1\,-1} + 2n_{10} + n_{11})$. For equal hyperfine components, $A_{up} = 2Ln$, so the signal vanishes. A weak signal was observed with unpolarized light, but only for low lamp oven power. Under the conditions for optimum circularly polarized signal, no unpolarized signal was seen, supporting the assumption of equal hyperfine components.

Measurement of the recovery time in the ${}^2P_{3/2}$, $F=2$ level yielded $\sigma \equiv (TN_0\bar{v})^{-1} = (24 \pm 12) \times 10^{-16}$ cm^2 for Ne (and 10 to 100 Å^2 for He and Ar). The Tl-Ne depolarization σ is 10^4 times larger in the ${}^2P_{3/2}$ than in the ${}^2P_{1/2}$ state of the same multiplet! The lifetime of the ${}^2P_{3/2}$ metastables was determined by monitoring 5350-Å light from a second lamp when the 3776-Å pumping light was suddenly removed, yielding a quenching σ upper limit of 0.2×10^{-20} cm^2 for Ne and a lower limit of 4 msec for the radiative lifetime.[13] The large σ for ${}^2P_{3/2}$ then results from the fact that J is $\frac{3}{2}$ rather than that the ${}^2P_{3/2}$ state is not the ground state.

The Tl equilibrium polarization $\langle J_z \rangle_{\mathrm{eq}}$ versus buffer-gas pressure was measured at Indiana University. The light source was a 30-mm-diam quartz sphere containing a small amount of Tl buffered by argon at a pressure of 3-4 Torr. The lamp was placed in a stainless steel coil, excited by a 100-W, 14-MHz transmitter, and electrically heated by a noninductive oven. Light intensities were 5 to 10 times that obtained from an Osram lamp. The typical lamp lifetime was 10 h for optimum output and stability. The light traversed a linear polarizer (Polaroid HNP′B) and a stressed quartz plate[14] tuned for circular polarization at 3776 Å. This plate acted as a linear polarizer for 5350-Å light. No interference filters were used before the cell; the presence of 5350-Å light provided an escape route for atoms collecting in the ${}^2P_{3/2}$ state. The optical pumping cell was a quartz cylinder 12 cm long and 6 cm in diameter, connected by a 12-mm tube to a bakable gas-handling manifold and vacuum system. The cell was electrically heated by coaxial heater elements arranged to keep the cell about 60°C hotter than a small Tl reservoir. The transmitted light was collimated by a lens, passed through a 3776-Å pass interference filter to reduce noise, and monitored by an RCA 934 phototube. Zeeman resonances were observed by modulating the rf power, sweeping the static field, and observing the resultant signal on a PAR HR-8 lock-in amplifier. The strength of the unresolved Zeeman resonance was taken to be proportional to $\langle J_z \rangle_{\mathrm{eq}}$, a good approximation where only one hyperfine state ($F=1$) is involved. The static magnetic field was 1 G, and the sweeping field about 0.1 G.

Gallagher has compared the ΔE dependence of the Rb, Cs, and Tl σ's with the predicted inverse-square dependence for nonadiabatic contributions; see Fig. 3.[15] The Rb and Cs σ's were measured at 300°C and the Tl at 880°C, but Gallagher has shown that the nonadiabatic contributions are independent of temperature.[16] The near $(\Delta E)^{-2}$ dependence is striking and is strong evidence that

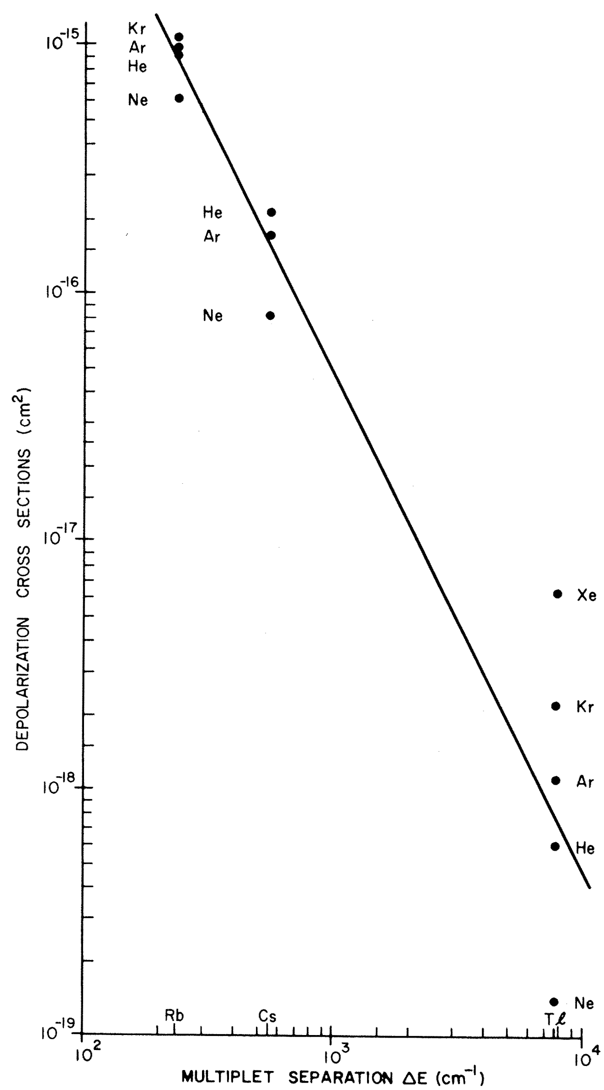

FIG. 3. Dependence of ${}^2P_{1/2}$ cross sections upon ΔE. Rb and Cs data are from Ref. 2. The straight line is the theoretically predicted $(\Delta E)^{-2}$ dependence; see Ref. 15.

the adiabatic selection rule $M_J \not\to -M_J$ is valid and that the residual nonadiabatic terms behave as predicted. The $(\Delta E)^{-2}$ dependence could be tested further by optically pumping In and Ga.

Since the selection rule $M_J \not\to -M_J$ is so effective in the Tl $^2P_{1/2}$ state, it would be worthwhile to check it in the Tl $^2P_{3/2}$ state where its validity is much less certain.[4]

A possible significant application of Tl pumping would be a 21-GHz maser. If the relaxation by the heavier noble gases results from the formation of molecular complexes rather than from simple binary collisions, the σ for relaxation between hyperfine levels should be smaller than the σ's reported here.[17] It might then be possible to obtain overpopulations sufficient for maser oscillation.[18]

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