Non-adiabatic Laser Induced Spin Coupling Phenomena

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A number of spin resonance properties can be measured in terms of rather novel if not always generally useful non-adiabatic effects. We consider the influence of spin hyperfine coupling upon laser excited optical transitions or upon electron paramagnetic resonance excited electron states.

I. NON-ADIABATIC OR ZEEMAN FIELD SWITCHING

As shown in Figure 1, suppose two coupled ground states, mixed by some internal spin-spin or spin-rotation interaction C, are expressed by the wave functions

$$|1'\rangle = |a|1\rangle + b|2\rangle$$

$$|2'\rangle = -b|1\rangle + a|2\rangle \qquad (1)$$

with state

$$|3'\rangle = |3\rangle$$

remaining a pure state. Mixing coefficients are given by a and b with $a^2 + b^2 = 1$. When allowed external Zeeman or Stark interactions are switched on, which exceed the internal interaction energy C, then states $|1'\rangle$ and $|2'\rangle$ become pure basis states $|1\rangle$ and $|2\rangle$ respectively as $a \to 1$ and $b \to 0$. This problem is solved for four levels explictly in ref. 1 for the case of spin-rotation interaction in $^{13}CH_3F$.

For any non-adiabatic jump in eigensplitting between levels $|1'\rangle$ and $|2'\rangle$, the initial density matrix ρ of the three-level system is transformed to a final matrix ρ', given by

$$\rho' = U^{-1}\rho U \ . \qquad (2)$$

Here

$$U = \begin{vmatrix} a' & -b' & 0 \\ b' & a' & 0 \\ 0 & 0 & 1 \end{vmatrix} \ . \qquad (3)$$

If the final mixing coefficients are a_f and b_f and the initial mixing coefficients are a_i and c_i, therefore,

$$a' = a_f a_i + b_f b_i \quad \textit{and}$$

$$b' = b_i a_f - b_f a_i .$$

Echo formation by the three-level system is shown in Figure 1. The first non-adiabatic Stark field pulse E_B brings the two level transition $|1\rangle \leftrightarrow |3\rangle$ into resonance with continuous laser or microwave radiation, and places the levels into a θ pulse coherent superposition state. The transition $|2\rangle \leftrightarrow |3\rangle$ is forbidden or is far off-resonance if the transition were allowed. Because of non-adiabatic switching at the end of the θ pulse, additional coherent superposition among $|1'\rangle$ and $|2'\rangle$ is provided as the pure states $|1\rangle$ and $|2\rangle$ switch back to states $|1'\rangle$ and $|2'\rangle$. During free precession the net coherence among all three states then operates for the time period $\tau_1 < t < \tau_1 + \tau_d$ where the applied continuous radiation is far off-resonance. This free precession behavior has been analyzed previously

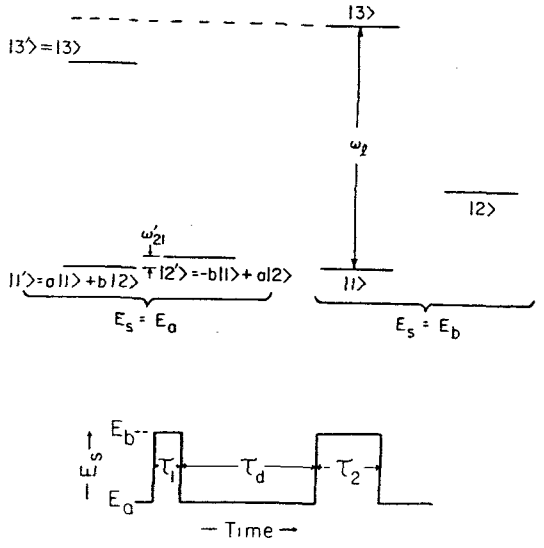

Figure 1. Level scheme (above) and Stark pulse scheme (below) for photon echo production. The laser radiation is constant at frequency ω_l. The ground state levels $|1\rangle$ and $|2\rangle$, making up the ground states of a vibrational transition at ω_l, exhibit a Stark splitting when E_S is applied.

(1). The second θ_2 non-adiabatic pulse imposes reorientation among states $|1\rangle$ and $|3\rangle$ and again does not affect state $|2\rangle$. Again the mixed set of three states couple freely after the θ_2 pulse is removed, and the maximum echo amplitude occurs at time $t_e = \tau_1 + 2\tau_d + \tau_2$.

The density matrix $\rho'(t)$ which forms the echo in the mixed state representation is given by

$$\rho'(t) = P(t)^{-1}U^{-1}T(\theta_2)^{-1}$$
$$UP(\tau,_d)^{-1}U^{-1}T(\theta_1)^{-1}$$
$$\propto \rho_0 T(\theta_1) UP(\tau_d) U^{-1}T(\theta_2) UP(t). \quad (4)$$

The initial density matrix at t = 0 is chosen as

$$\rho_0 = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{vmatrix}, \quad (5)$$

and the θ pulse rotation matrix is

$$T(\theta) = \begin{vmatrix} \cos\theta/2 & 0 & \sin\theta/2 \\ 0 & 1 & 0 \\ -\sin\theta/2 & \theta & \cos\theta/2 \end{vmatrix}. \quad (6)$$

The free precession matrix in the frame rotating at ω is

$$\rho(t) = \begin{vmatrix} \exp(i\omega_1't) & 0 & 0 \\ 0 & \exp(i\omega_2't) & 0 \\ 0 & 0 & \exp[i(\omega_3'-\omega)t] \end{vmatrix} \quad (7)$$

where the eigenfrequencies are given by ω_i' (i = 1,2,3) and ω_l is the applied radiation frequency. Any field inhomogeneity is contained in the $\omega_3' - \omega$ term. The echo intensity at time $t > \tau_1 + \tau_2 + \tau_d$ is proportional to

$$S = Tr\{\rho'\mu'\}$$
$$= a^4b^4 + 2a^2b^2\cos\omega_{21}'\tau_d,$$

where the mixed state dipole operator is given by $\mu' = U^{-1}\mu U$, with U defined by Eqn. (3) for $a_i = c_i = 1$, $b_i = 0$, and $a_f, b_f = a, b$. The pure state transition dipole matrix element is given by μ_{31}, and the mixed state matrix elements are $\mu_{31}' = a\mu_{31}$ and $\mu_{32}' = -b\mu_{31}$.

The envelope S displays a beat frequency $\omega_{21}' = C/\hbar$ which corresponds to the splitting between levels $|1\rangle$ and $|2\rangle$ in the absence of applied external fields ($E_S = E_B = 0$ in Figure 1) which remove level degeneracy. Although ω_{21}' may exceed $C/\hbar$ if the fields are applied, the factor ab becomes too small to observe the cosine modulation, particularly if the damping time constant T_2 is very short. This was the case in a previous investigation (1). A slight reduction in echo amplitude, however, indicates a rough measure of C in the absence of B and E fields, compared to the condition when these fields are large and totally lift the degeneracy between levels $|1\rangle$ and $|2\rangle$. Thus a perceptible reduction in the echo can be observed although the cosine beat in S is overdamped by virtue of the condition $T_2 < 2\pi/\omega_{21}'$ as τ_d exceeds T_2. The degeneracy lifting field $E_S = E_B$ acts as a bias field which controls the amount of state

mixing during the time τ_d between pulses θ_1 and θ_2, and time τ_d after the θ_2 pulse.

The superposition created among the states $|1'\rangle$ and $|2'\rangle$ is, of course, brought about because the switching time t_s of the E or B field is short compared to the period $\omega_{21'}/2\pi$. If an appropriate resonance radiation pulse or step function source has Fourier components which exceed hyperfine level splittings, the various levels will be placed in coherent superposition by purely optical means. Hashi and co-workers (2) have reported an experiment in which the hyperfine coupled electron spin levels of $Tm^{2+}:CaF_2$ in the optical ground state are placed in coherent superposition by this principle. A short laser pulse of order nanoseconds in width creates excess spin populations among the Tm^{2+} hyperfine ground states in $Tm^{2+}:SrF_2$. The spin orientation is prepared non-adiabatically, perpendicular to a magnetic field (0-100 gauss) which in turn is normal to the laser beam k vector. By means of the magnetic circular dichroism effect, using cross polarizers to monitor optical Faraday rotation, a probe laser beam is modulated by the precessing spin population in the range of megahertz.

FREE NUCLEAR PRECESSION FOLLOWING NON-ADIABATIC SWITCHING IN SOLIDS

Analogies of non-adiabatic switching in NMR are well known. Eigenstates of coupled protons in solids may be investigated following non-adiabatic B field switching. An early experiment (3) showed that initial dipolar ordered states, produced by adiabatic demagnetization ($B \rightarrow 0$), result in free precession about new axes of quantization following the non-adiabatic switching of magnetic field B = 0 to B = B where $\mu B \sim H_{dipolar}$.

Recently a related experiment, "zero-field NMR," by Weitekamp et al. (4), provides dipolar coupling spectra without the need for single crystals. Initial Zeeman spin ordered orientation among nuclei for $\mu B >> H_{dipolar}$ is suddenly transformed to superposition among dipolar states by switching of B to zero. The resultant oscillations from the initial Zeeman orientation about internal axes of quantization in zero field are Fourier analyzed to give a measure of local fields.

OPTICAL MEASUREMENTS OF ELECTRON SPIN HYPERFINE CROSS-RELAXATION IN CRYSTALS

The paramagnetic spin-spin interaction among neighboring optical ions, characterized as Kramer doublets in the optical ground state has been studied (5) by making use of the optical property of magnetic circular dichroism (MCD). A complete manifold of level crossings involving divalent thulium and divalent holmium ions contained in CaF_2 single crystal can be investigated

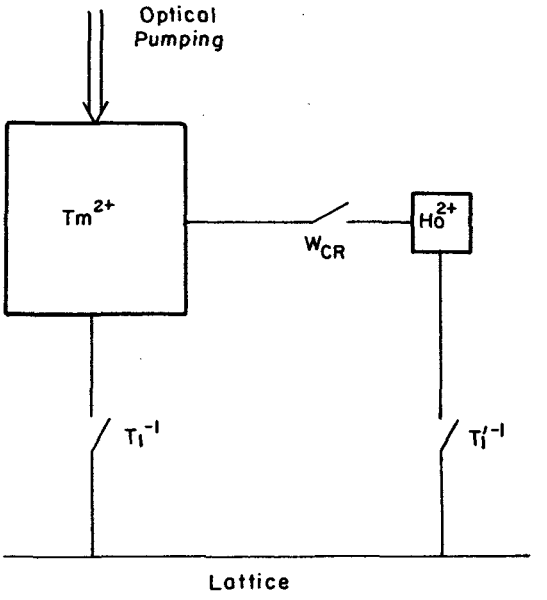

Figure 2. Schematic for hyperfine state cross-relaxation coupling among Tm^{2+} and Ho^{2+} ions in single crystal CaF_2. Optical pumping creates non-equilibrium spin populations among Kramers doublet optical ground states of Tm^{2+} with S = 1/2 for the electron and I_{Tm} = 1/2 for the Tm nucleus. The cross-relaxation rate W_{CR} becomes finite at specific magnetic fields as the levels of Ho^{2+} (S = 1/2, I_{Ho} = 7/2) cross with the Tm^{2+} levels. Spin-lattice relaxation times T_1 and T_1' for each reservoir are indicated.

simply by adjustment of the external dc magnetic field without the need of microwave detection or excitation. Neighboring thulium-thulium or thulium-holmium hyperfine level crossing interactions may be adiabatically or non-adiabatically turned on by adjustment of the dc magnetic fields. The cross-relaxation signal appears as a change in population difference of the thulium optical transtition by a dye laser (see Figure 2). Following the pumping a weak probe beam monitors the thulium spin population recovery towards equilibrium (or changes in population) by the effect of MCD. Direct and higher spin coupling processes are observed.

Evidence of a phonon bottleneck is indicated [6; first noted in ref. (7)] by the onset of Orbach transitions of holmium hyperfine levels that couple to a low lying holmium excited state. The phonons which allow the coupling appear to be created by radiationless phonon transitions in the thulium pumpband, where the phonons have a spectral width which is sufficient to overlap the ground hyperfine and a low lying excited state of holmium at 33 cm^{-1} above the ground state. The inference of this effect, which requires further investigation, is as pointed out above, by observation of non-equilibrium cross-relaxation between matched thulium-holmium hyperfine spin levels, where the thulium spin populations are monitored by differential MCD transmission.

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