Spin relaxation time in NMR spectroscopy

2015.05.20.
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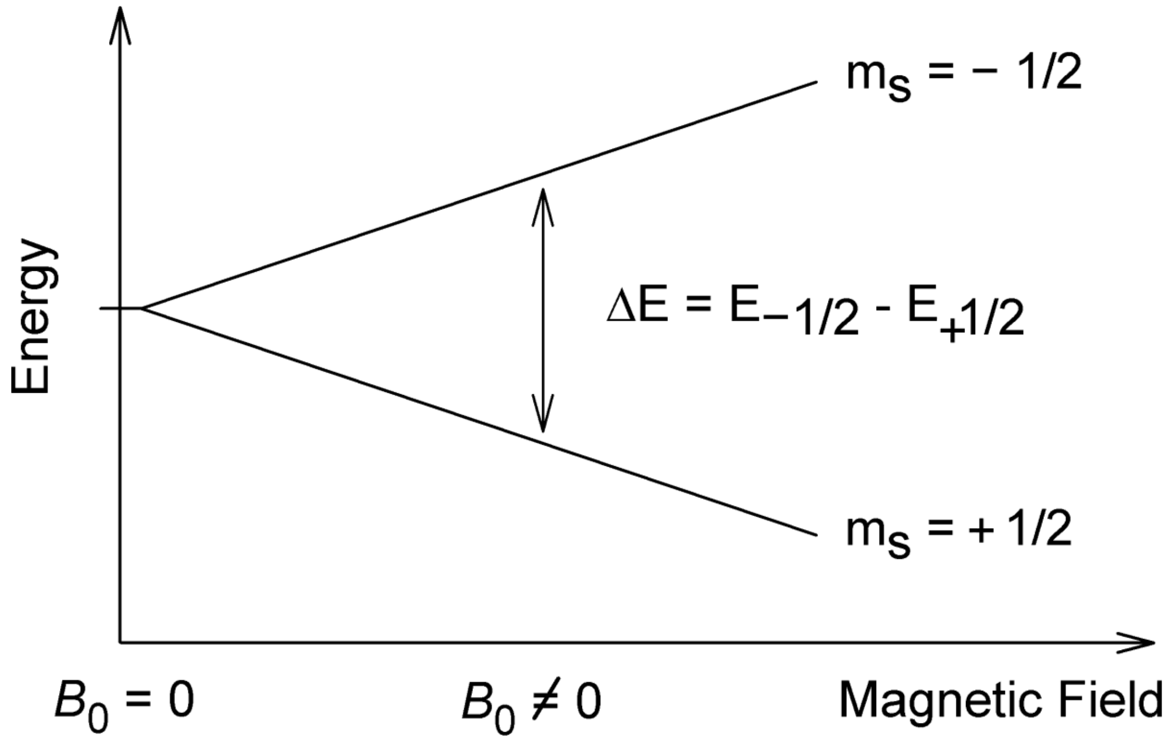
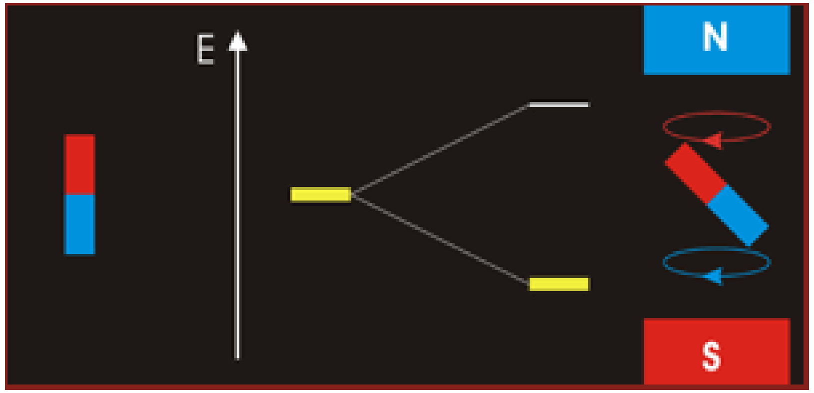
Introduction: NMR spectroscopy





When placed in a magnetic field, NMR active nuclei (such as ^{1}H or ^{13}C) absorb electromagnetic radiation at a frequency characteristic of the isotope. The resonant frequency, energy of the absorption, and the intensity of the signal are proportional to the strength of the magnetic field.

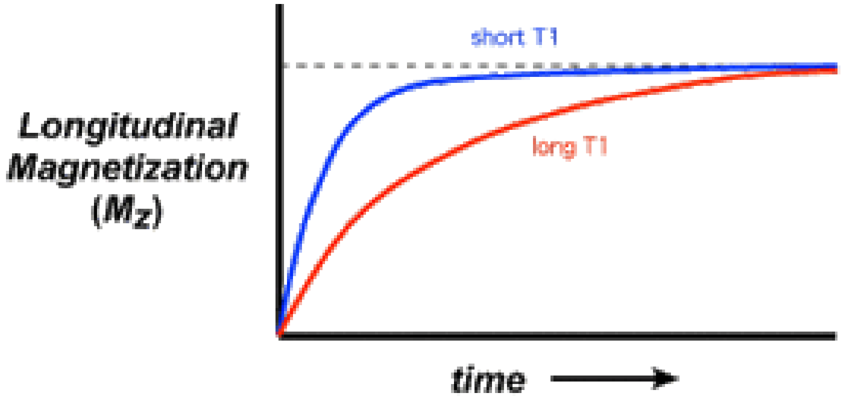
NMR relaxations: T_1 & T_2

In general, signals deteriorate with time, becoming weaker and broader.
Relaxation is the conversion of this non-equilibrium population to a normal population.
In other words, relaxation describes how quickly spins "forget" the direction in which they are oriented.

T_1 (spin-lattice relaxation time)

Relaxation time corresponding to longitudinal(z) component of magnetization.

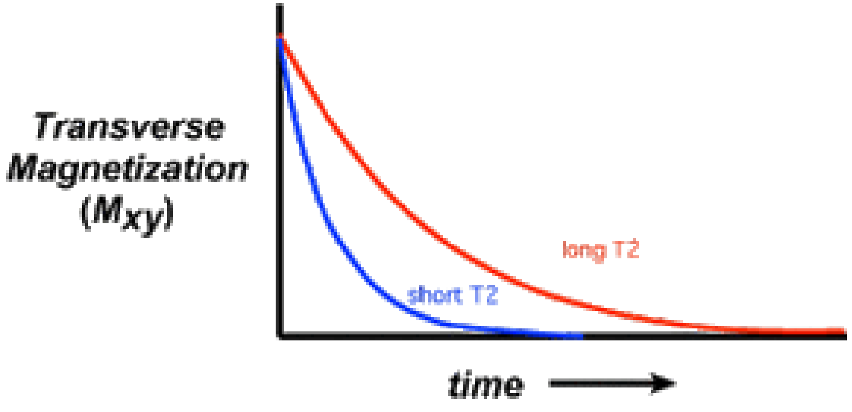
$$\frac{dM_z}{dt} = -\frac{(M_z - M_0)}{T_1}$$



T_2 (spin-spin relaxation time)

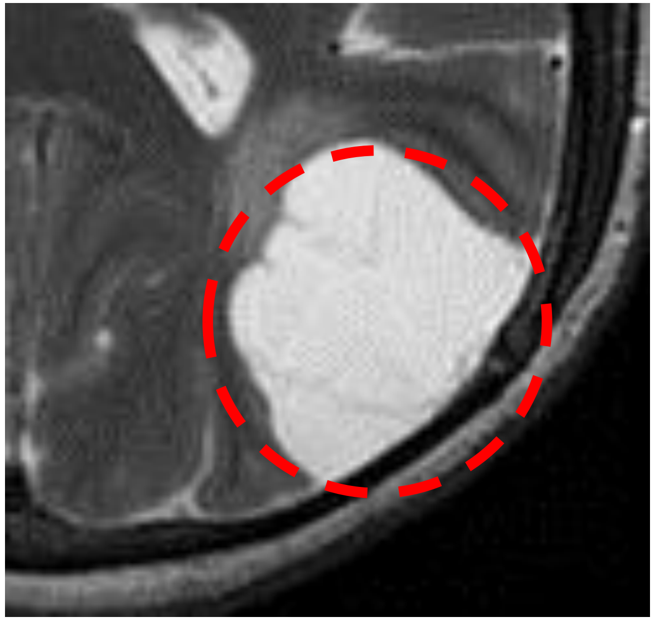
Relaxation time corresponding to transverse(x,y) component of magnetization.

$$\frac{dM_{x,y}}{dt} = -\frac{M_{x,y}}{T_2}$$



NMR relaxations: T_1 & T_2

In case of liquid NMR the relaxation time contains information about the system surrounding the spin, and can provide a feasible probe to liquid sample.



T2- weighted image of brain tumor, showing the tumor region having intrinsically long T2 as bright part.

PHYSICAL REVIEW VOLUME 73, NUMBER 7 APRIL 1, 1948

Relaxation Effects in Nuclear Magnetic Resonance Absorption*

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(Received December 29, 1947)

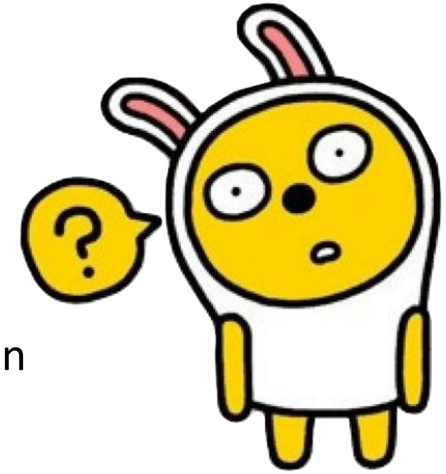
N. Bloenbergen, E. M. Purcell, R. V. Pound, *Phys. Rev.* **73**, 679 (1948)

$$\frac{1}{T_1} = K[\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}]$$

$$\frac{1}{T_2} = \frac{K}{2}[3\tau_c + \frac{5\tau_c}{1+\omega_0^2\tau_c^2} + \frac{2\tau_c}{1+4\omega_0^2\tau_c^2}]$$

τ_c : correlation time of the molecular tumbling motion

ω_0: Larmor frequency



Bloch equations & solution

The equation of motion for magnetic dipole in the magnetic field :

$$\frac{d\vec{M}}{dt} = \gamma_N(\vec{M} \times \vec{H})$$

Incorporating the decay terms :

$$\begin{cases} \dfrac{dM_x}{dt} = \gamma_N(\vec{M} \times \vec{H})_x - \dfrac{M_x}{T_2} \\ \dfrac{dM_y}{dt} = \gamma_N(\vec{M} \times \vec{H})_y - \dfrac{M_y}{T_2} \\ \dfrac{dM_z}{dt} = \gamma_N(\vec{M} \times \vec{H})_z - \dfrac{M_z - M_0}{T_2} \end{cases}$$

If $\vec{H} = H_0\hat{z}$ ($\omega_0 = \gamma_N H_0$):

$$\begin{cases} \dfrac{dM_x}{dt} = \omega_0 M_y - \dfrac{M_x}{T_2} \\ \dfrac{dM_y}{dt} = -\omega_0 M_x - \dfrac{M_y}{T_2} \\ \dfrac{dM_z}{dt} = -\dfrac{M_z - M_0}{T_2} \end{cases}$$

Bloch equations & solution

Let the rotating wave H_1 :

$$\overrightarrow{H_1} = H_1(\hat{\imath}\cos\omega t - \hat{\jmath}\sin\omega t)$$

It is better to solve the equation in new coordinate system (rotating along z-axis):

$$\begin{cases} \vec{M} = \hat{\imath}'u + \hat{\jmath}'v + \hat{k}'M_z \\ \vec{H_1}' = \hat{\imath}'H_1 \\ \omega' = -\omega\hat{k} \end{cases}$$

$$\frac{du}{dt} = (\omega_0 - \omega)v - \frac{u}{T_2}$$

$$\frac{dv}{dt} = -(\omega_0 - \omega)u + \gamma_N H_1 M_z - \frac{v}{T_2}$$

$$\frac{dM_z}{dt} = -\gamma_N H_1 v - \frac{(M_z - M_0)}{T_1}$$

Bloch equations & solution

The solution of the equation:

$$u = M_0 \frac{\gamma_N H_1 T_2^2\,(\omega_0 - \omega)}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma_N^2 H_1^2 T_1 T_2}$$

$$v = M_0 \frac{\gamma_N H_1 T_2}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma_N^2 H_1^2 T_1 T_2}$$

$$M_z = M_0 \frac{1 + T_2^2(\omega_0 - \omega)^2}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma_N^2 H_1^2 T_1 T_2}$$

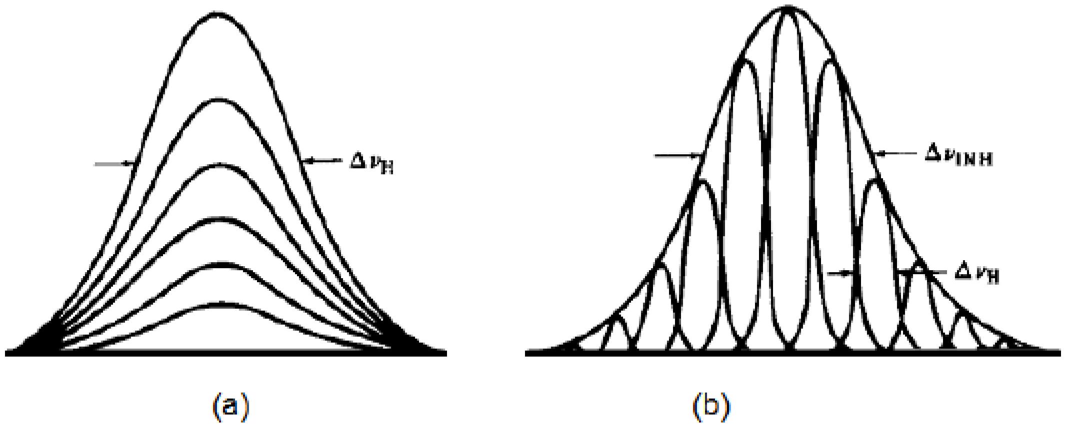
$$\begin{aligned} M_x &= u\cos\omega t + v\sin\omega t \\ &= H_1\left(\chi(\omega)e^{-i\omega t} + \chi^*(\omega)e^{+i\omega t}\right) \\ &= 2H_1\chi'(\omega)\cos\omega t + 2H_1\chi''(\omega)\sin\omega t \end{aligned}$$

$$\chi'(\omega) = \frac{1}{2}\chi_0\omega_0 \frac{T_2^2(\omega_0 - \omega)}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma_N^2 H_1^2 T_1 T_2}$$

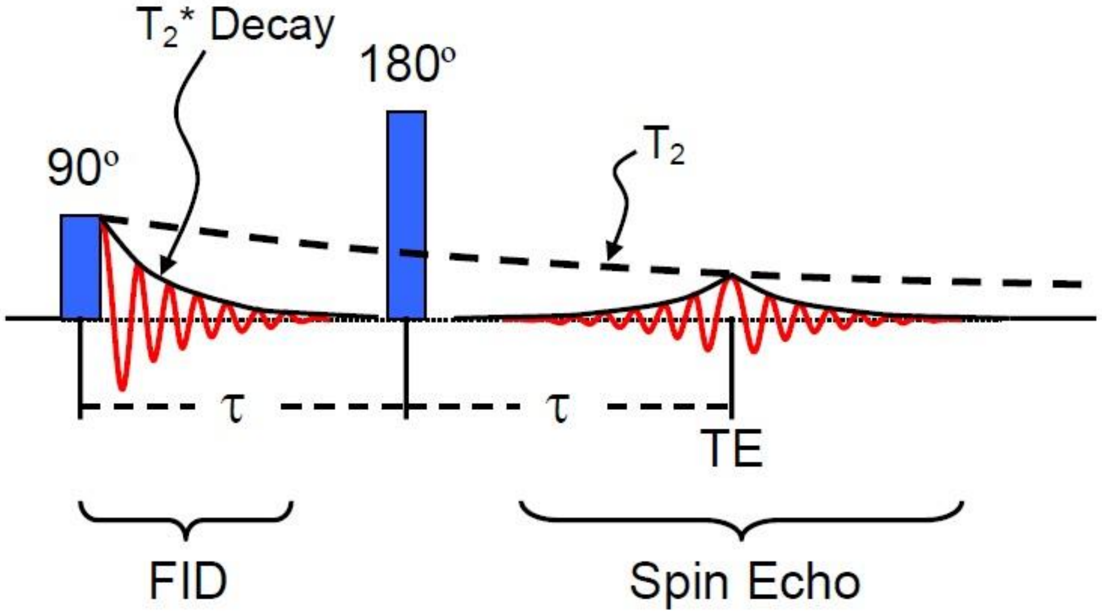
$$\chi''(\omega) = \frac{1}{2}\chi_0\omega_0 \frac{T_2}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma_N^2 H_1^2 T_1 T_2}$$

$$\frac{dE}{dt} = 2\omega H_1^2\chi''(\omega) = H_1^2\chi_0\omega\omega_0 \frac{T_2}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma_N^2 H_1^2 T_1 T_2}$$

Inhomogeneous broadening: T2*

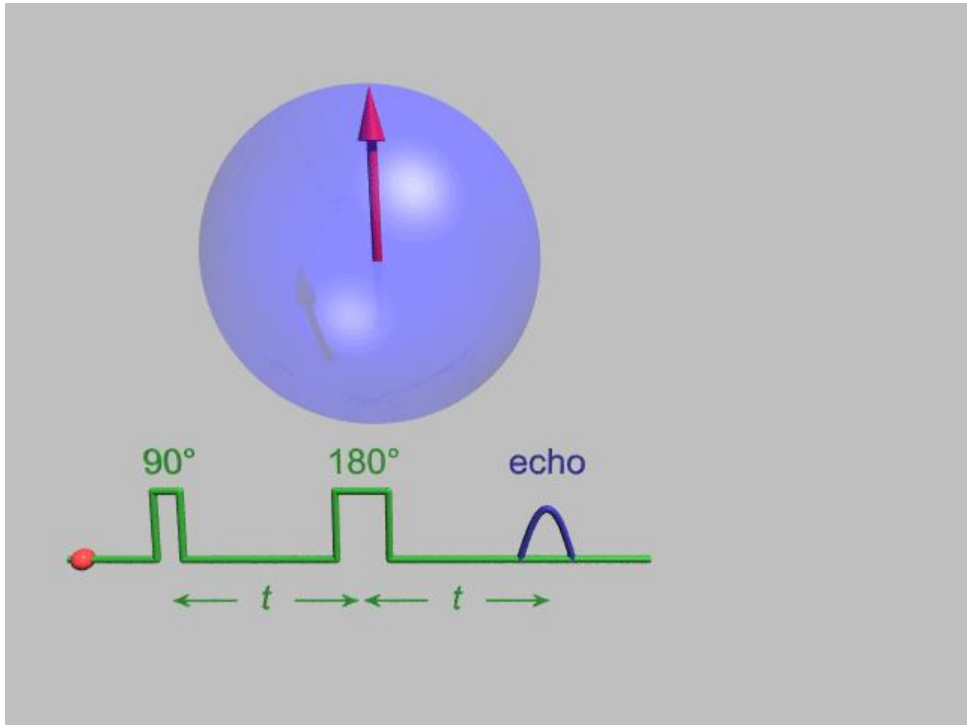


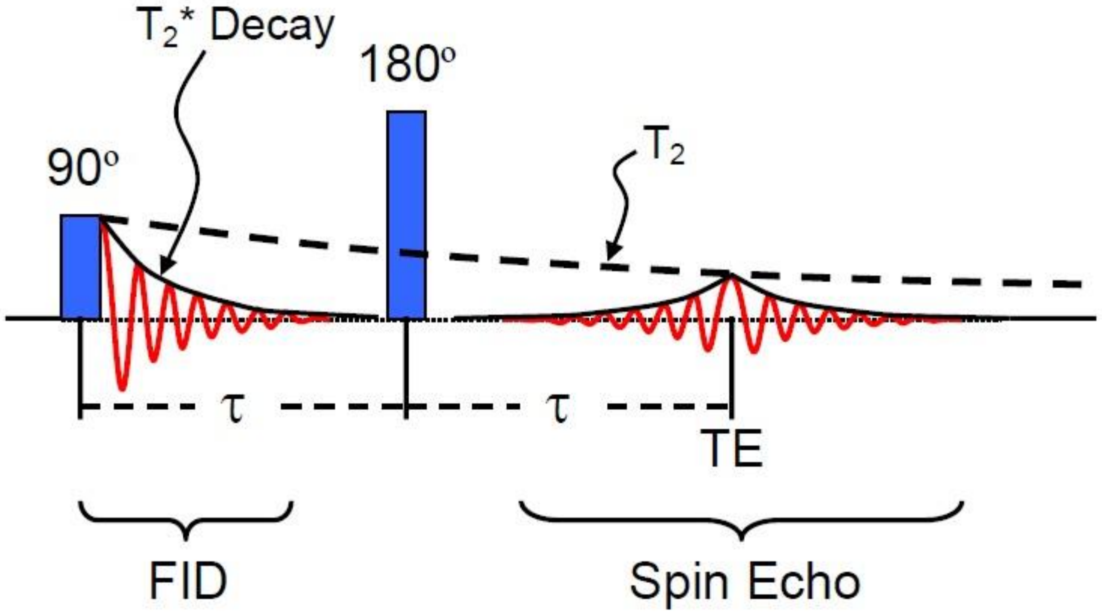
Homogeneous (a) and inhomogeneous (b) band shapes having inhomogeneous width $\Delta\nu_{INH}$ and homogeneous width $\Delta\nu_{H}$



$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_{inhom}} = \frac{1}{T_2} + \gamma \Delta B_0$$

Removing the effect of inhomogeneous broadening: spin-echo experiment





Photon echo – the optical ver. of spin echo

PHYSICAL REVIEW
LETTERS

VOLUME 13 | 9 NOVEMBER 1964 | NUMBER 19

OBSERVATION OF A PHOTON ECHO*

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(Received 2 September 1964)

N. A. Kurnit, I. D. Abella, S. R. Hartmann, *Phys. Rev. Lett.* **13**, 567 (1964)

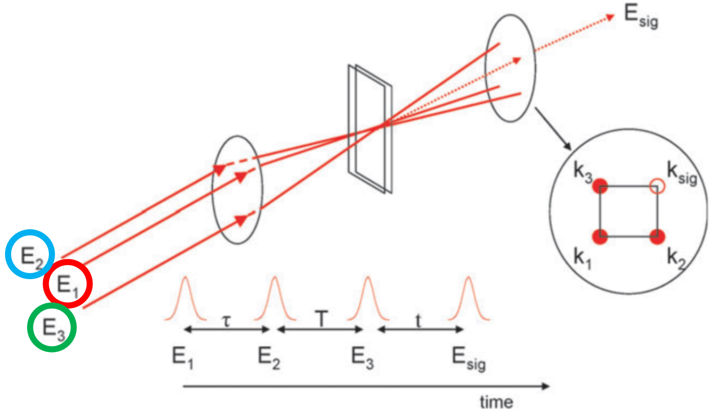

Fig. 3 Diagrammatic representation of the beam orientations used in generating photon echo 2D-IR spectra.[13]

For example, consider the peaks labelled D′ at an excitation frequency (pump frequency) of 2084 cm^{-1} in Fig. 1. In this case, using photon echo terminology, the first interaction with the laser field will excite the ν = 0–1 ($|00\rangle$–$|s\rangle$) coherent superposition state, which oscillates at the frequency of the symmetric vibrational mode of RDC (2084 cm^{-1}). The second pulse then creates a population state in the $|s\rangle$ state before the third pulse excites a coherence between the $|s\rangle$ and $|2s\rangle$ states. Thus the echo pulse has a frequency corresponding to the $|s\rangle$ to $|2s\rangle$ transition and the peak on the detection (probe) axis is shifted from the diagonal by the anharmonicity of the symmetric transition of RDC. In this case the phase relationship of the second coherence to the first results in the positive sign of the peak. Similar pathways can be described for each of the other lines with similar close relationships to the double resonance description.[4,13,16]