THE PRINCIPLES OF DNP WITH STRONG μ-WAVE FIELDS

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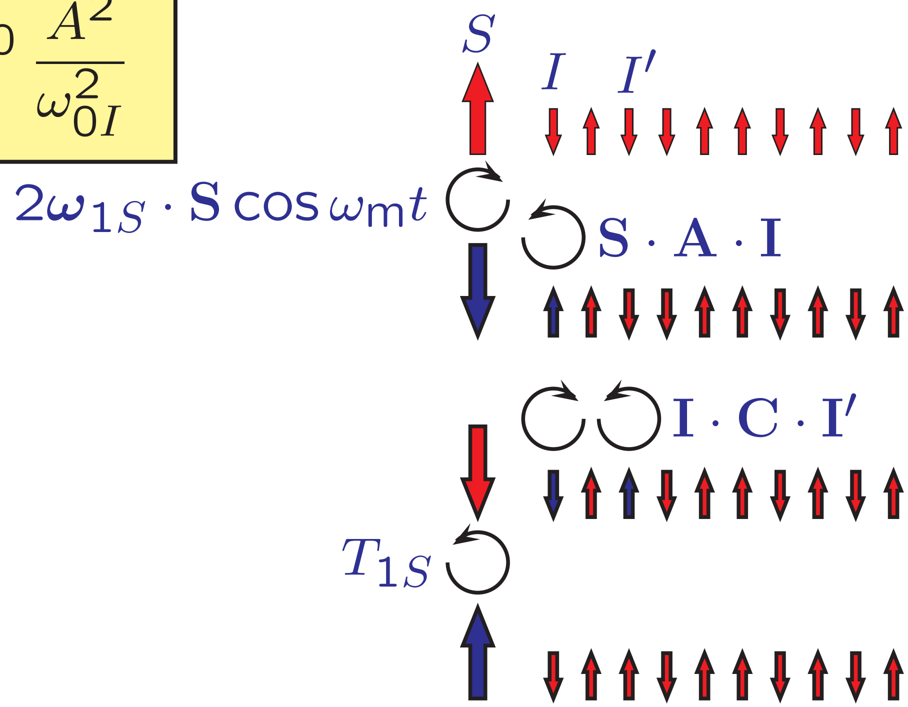
SOLID EFFECT

rate:

$$W^{\pm} = W^0 \, \frac{A^2}{\omega_{0I}^2}$$



energy conservation:

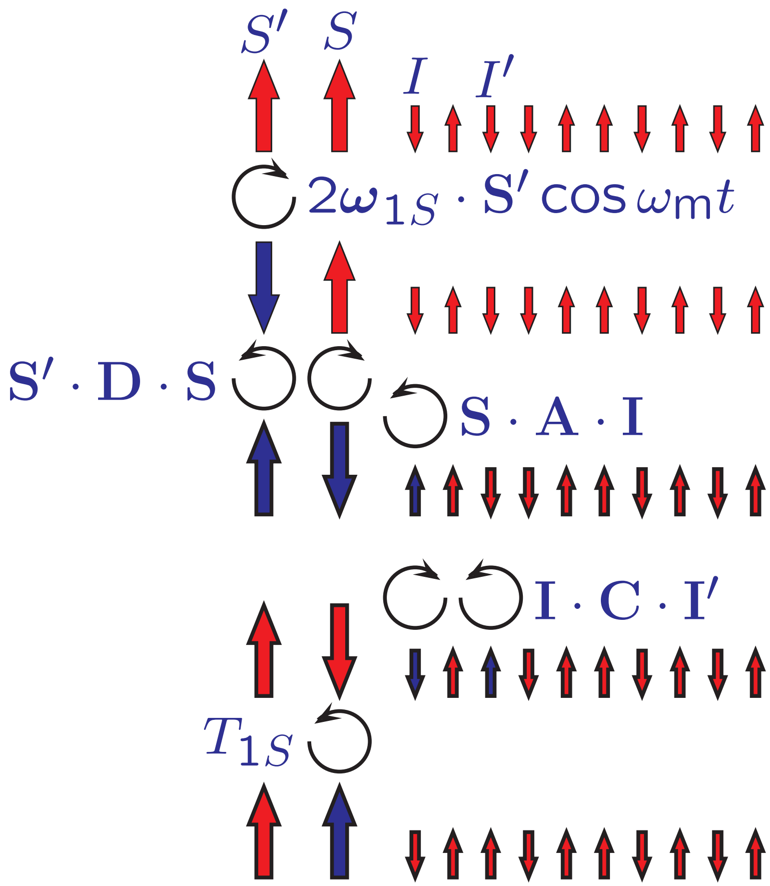
$$\omega_{\mathrm{m}} = \omega_{0S} \pm \omega_{0I}$$

THERMAL MIXING/CROSS EFFECT

rate:

$$W^0 = \omega_{1S}^2 T_{2S}$$

$$\frac{1}{T_{SSI}} = \frac{1}{T_{2S}} \frac{A^2}{\omega_{0I}^2}$$



energy conservation:

$$\omega_m = \omega'_{0S}$$

$$\omega_{0S} - \omega'_{0S} = \pm\omega_{0I}$$

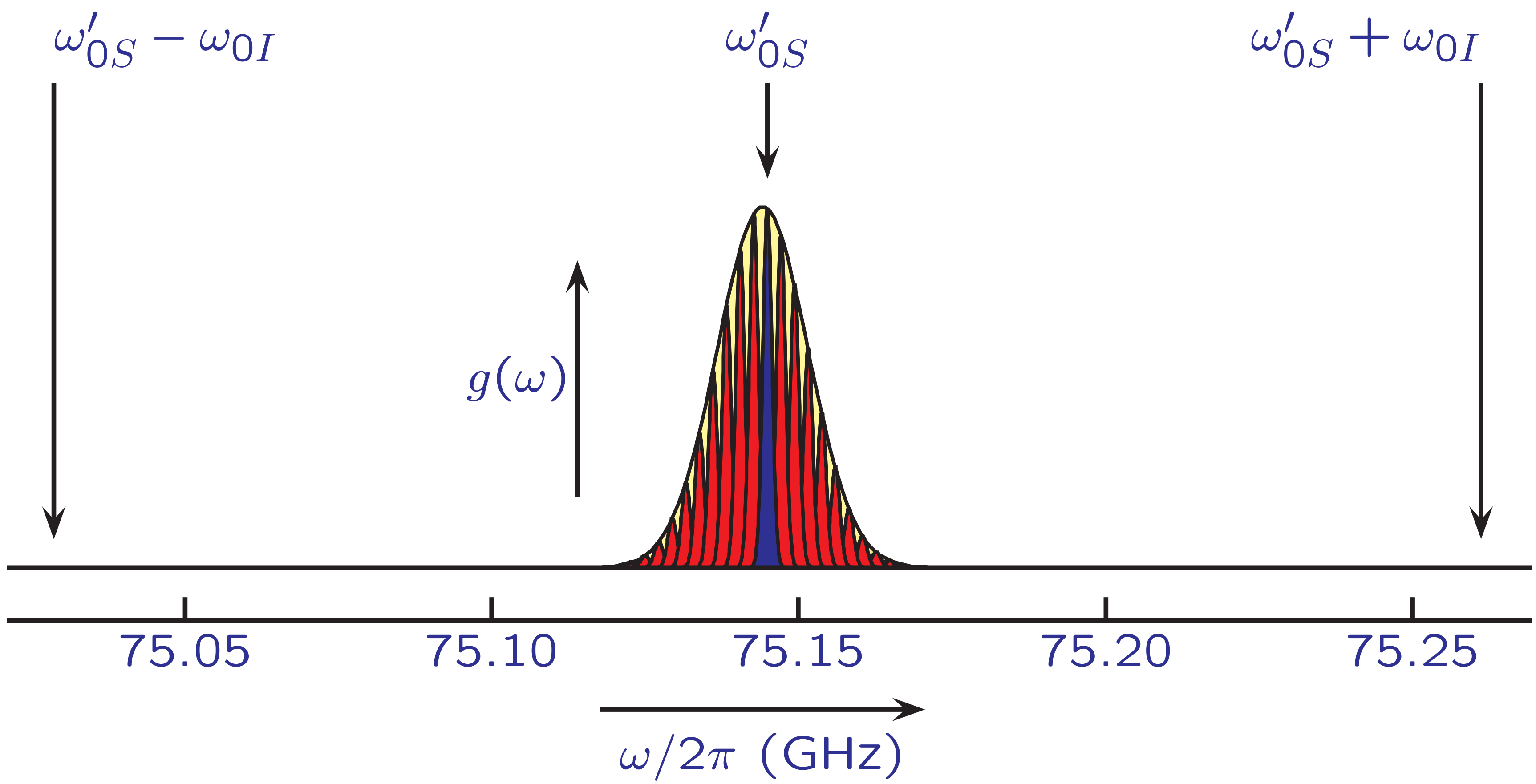
$$W^{\pm} T_{SSI} = \omega_{1S}^2 T_{2S}^2$$

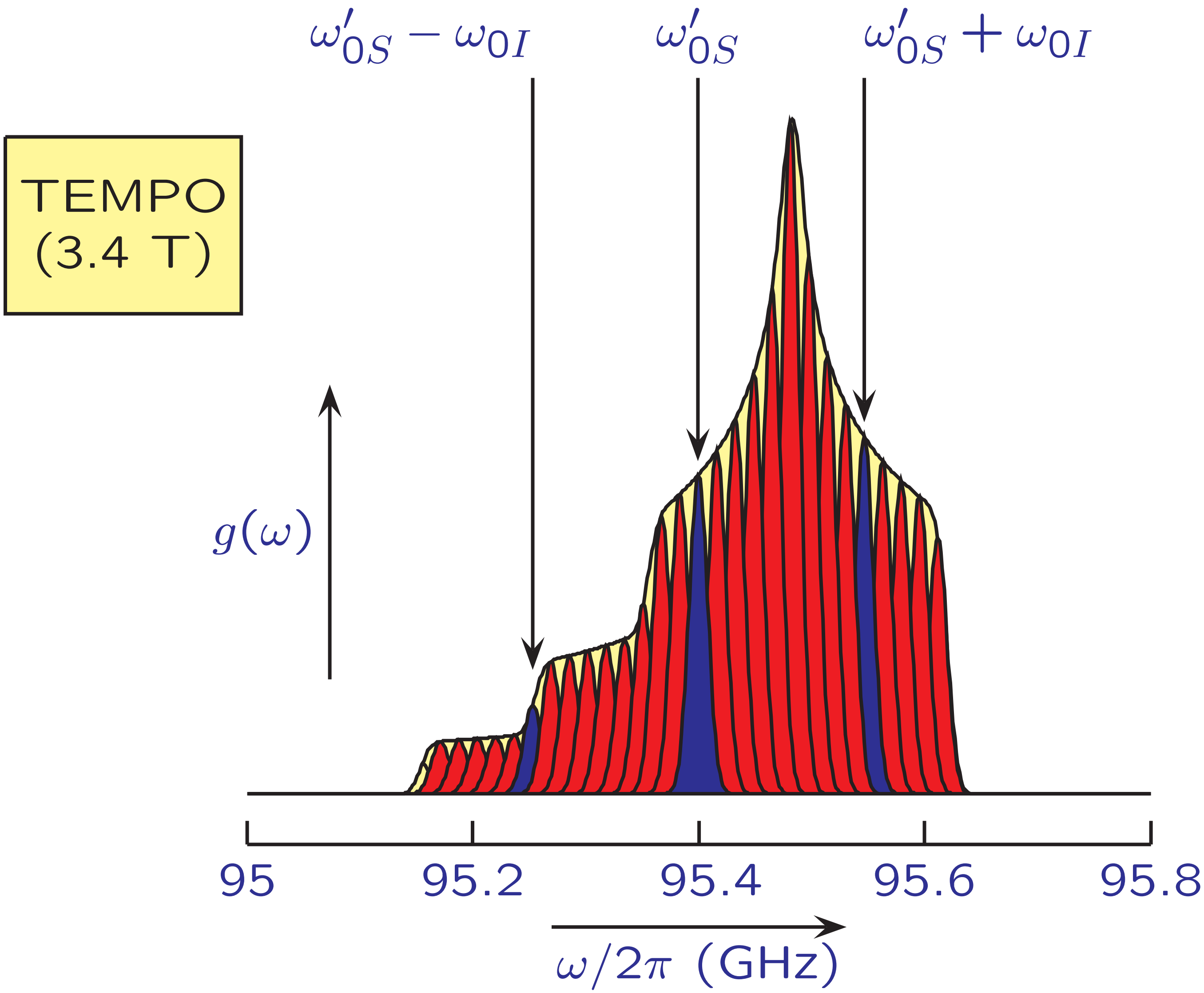
> 1 → solid effect

< 1 → thermal mixing/cross effect

$Ca(OH)_2{:}O_2^-$
(2.73 T)

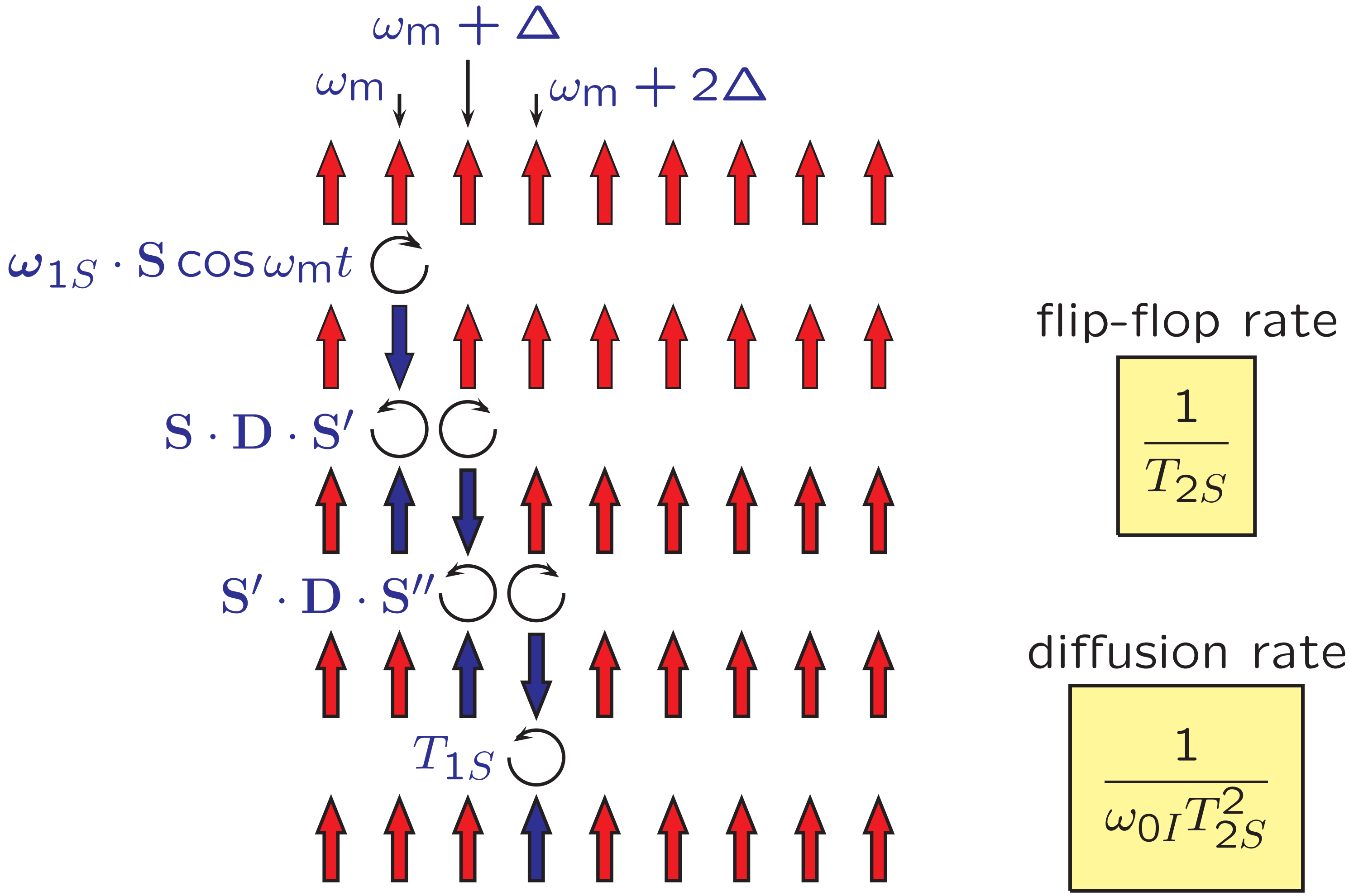
narrow ESR line → solid effect





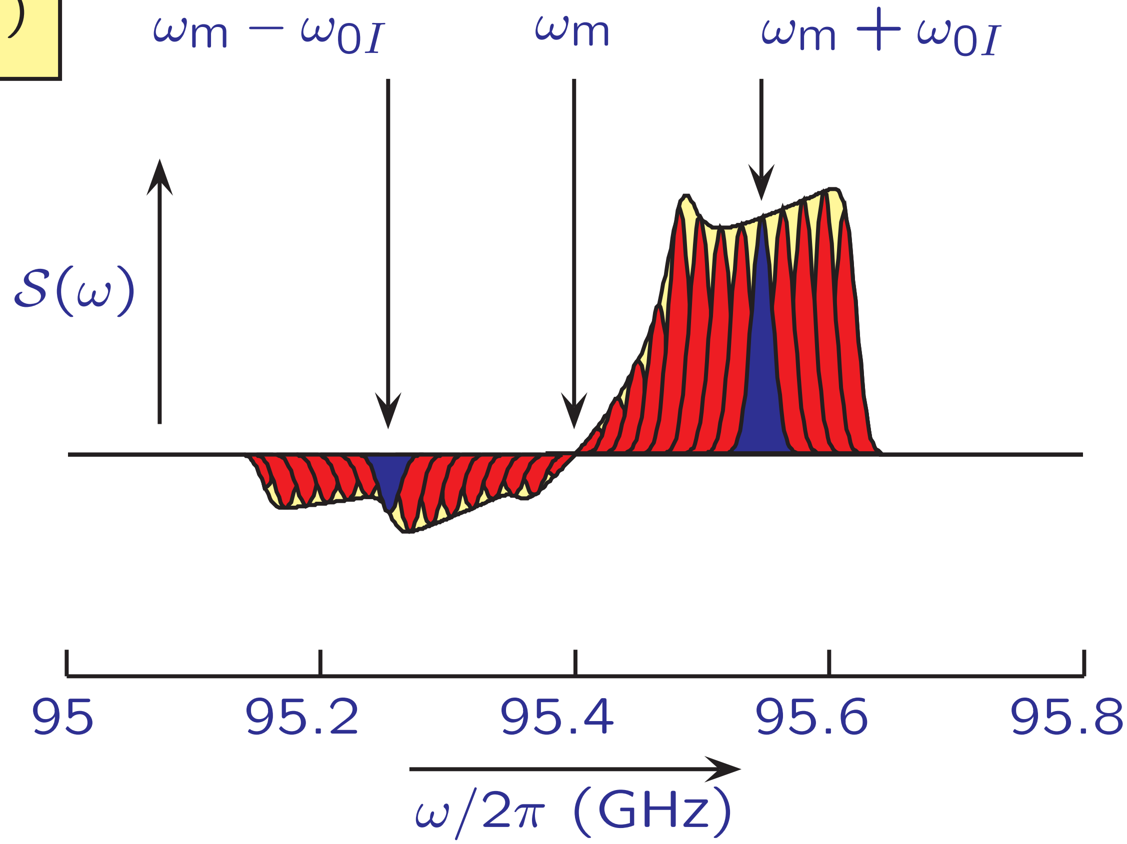
broad ESR line → **thermal mixing**
cross effect
differential solid effect

SPECTRAL DIFFUSION



$$\frac{\partial P_I}{\partial t} \propto \mathcal{S}(\omega_{\mathrm{m}} + \omega_{0I}) - \mathcal{S}(\omega_{\mathrm{m}} - \omega_{0I})$$

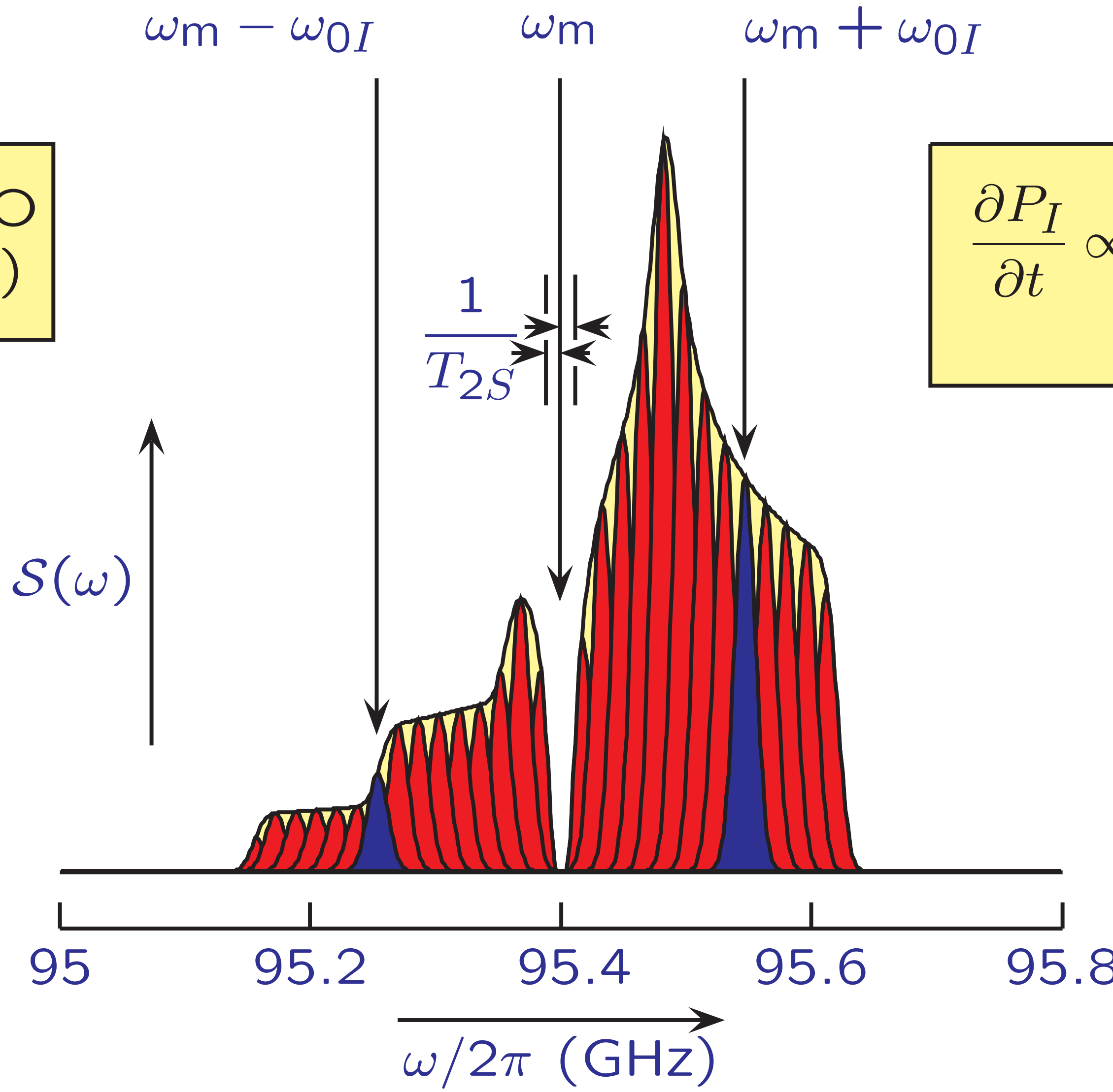
TEMPO
(3.4 T)



weak μ-wave field: $\omega_{1S} T_{2S} < 1$

fast spectral diffusion: $\frac{1}{\omega_{0I} T_{2S}^2} > \frac{1}{T_{1S}}$ → **thermal mixing**

TEMPO
(3.4 T)



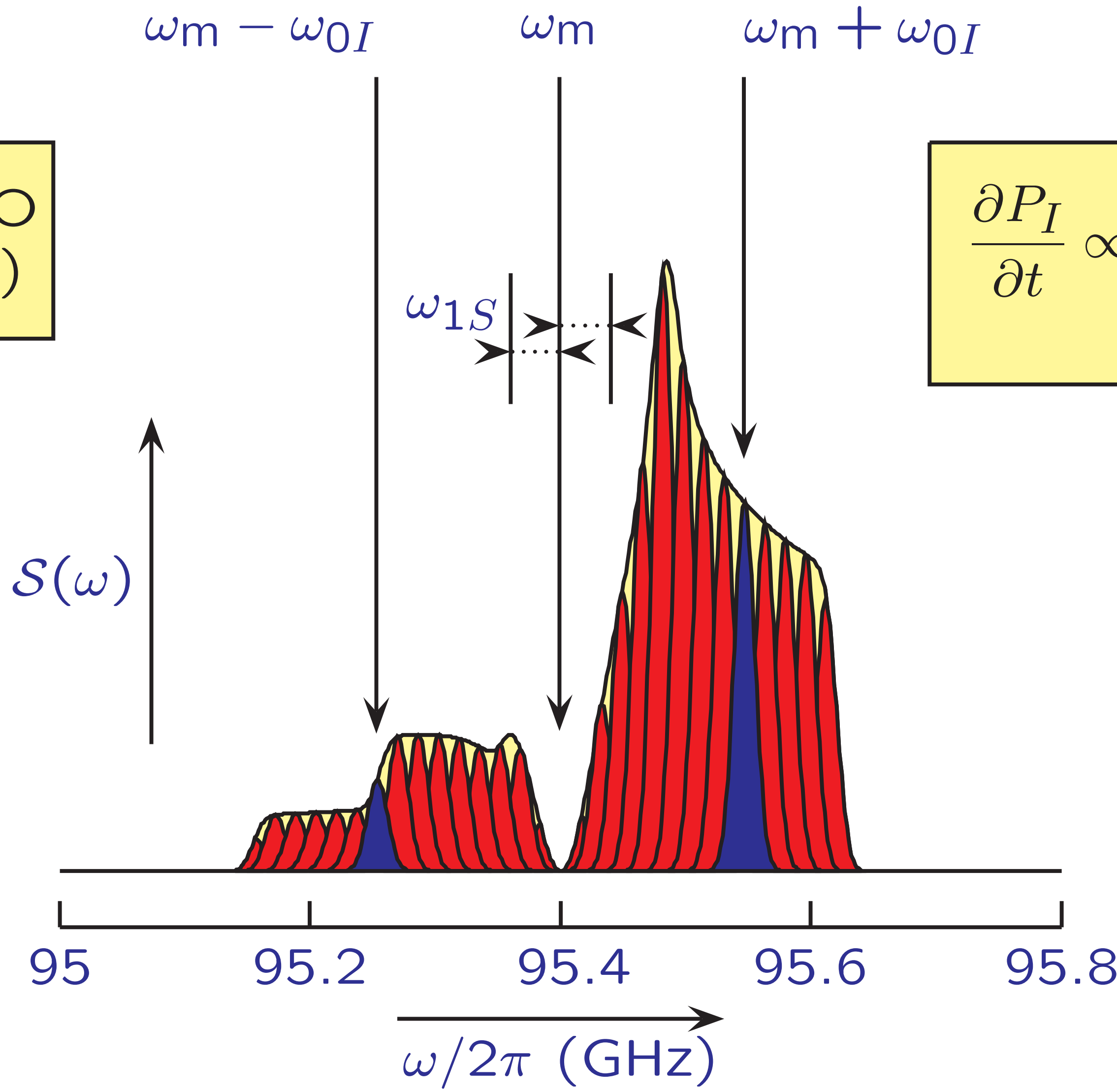
$$\frac{\partial P_I}{\partial t} \propto \mathcal{S}(\omega_m + \omega_{0I}) - \mathcal{S}(\omega_m - \omega_{0I})$$

weak μ-wave field: $\omega_{1S}T_{2S} < 1$

fast spectral diffusion: $\frac{1}{\omega_{0I}T_{2S}^2} < \frac{1}{T_{1S}}$ → **cross effect**

TEMPO
(3.4 T)

$$\frac{\partial P_I}{\partial t} \propto \mathcal{S}(\omega_m + \omega_{0I}) - \mathcal{S}(\omega_m - \omega_{0I})$$



strong μ-wave field: $\omega_{1S}T_{2S} > 1$ → **differential solid effect**

VERY STRONG μ-WAVE FIELD

$\omega_{1S} \approx \omega_{0I}$

laboratory frame

$$\mathcal{H} = \omega_{0S} S_z + 2\omega_{1S} S_x \cos \omega_{\mathrm{m}} t - \omega_{0I} I_z + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}$$

rotating frame

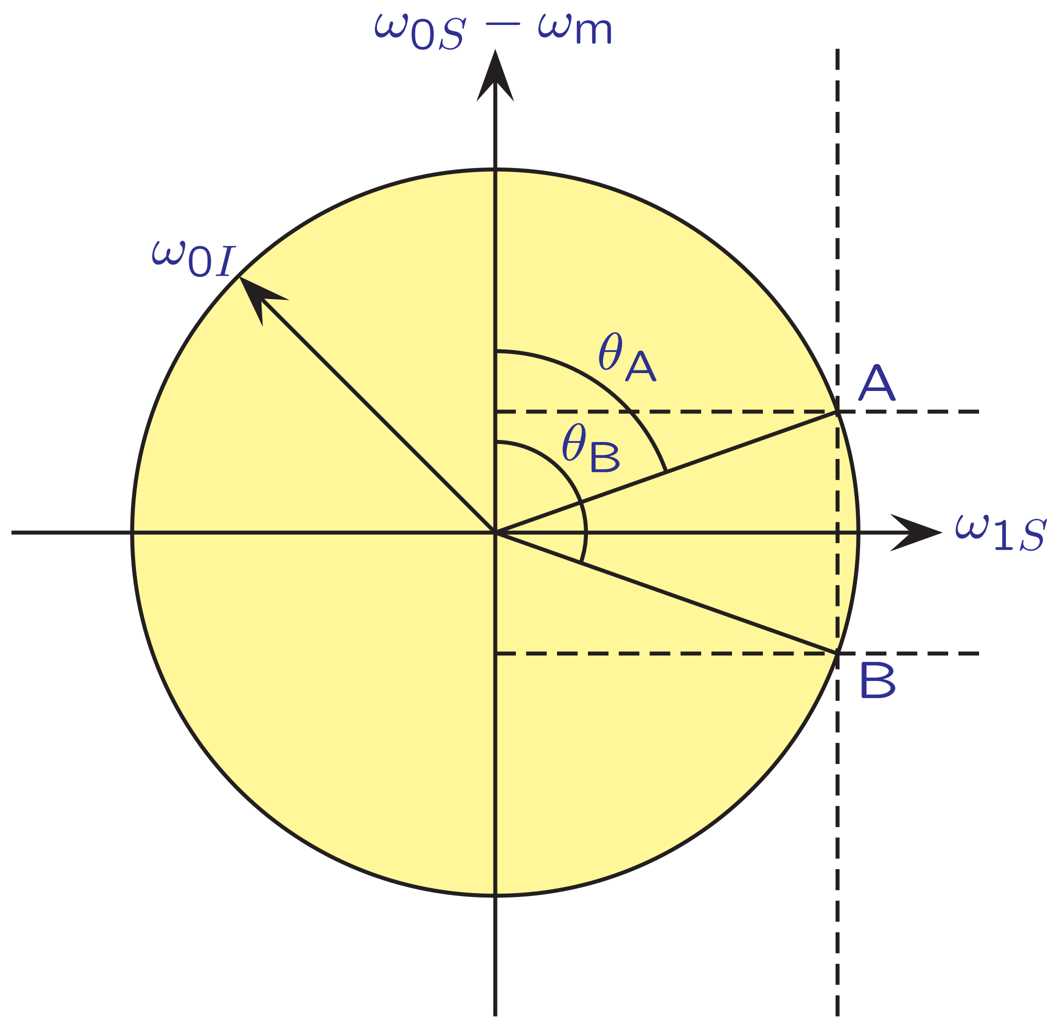
$$\mathcal{H} = (\omega_{0S} - \omega_{\mathrm{m}}) S_z + \omega_{1S} S_{x'} - \omega_{0I} I_z + \mathbf{S} \cdot \mathbf{A}' \cdot \mathbf{I}$$

matching condition

$$\sqrt{(\omega_{0S} - \omega_{\mathrm{m}})^2 + \omega_{1S}^2} = \omega_{0I}$$

transition rate

$$W^{\pm} \propto \left| \tfrac{1}{4} A_{zx} \right|^2 \sin^2 \theta_{\mathrm{A,B}}$$



VERY STRONG μ-WAVE FIELD

$\omega_{1S} \approx \omega_{0I}$

transition rate

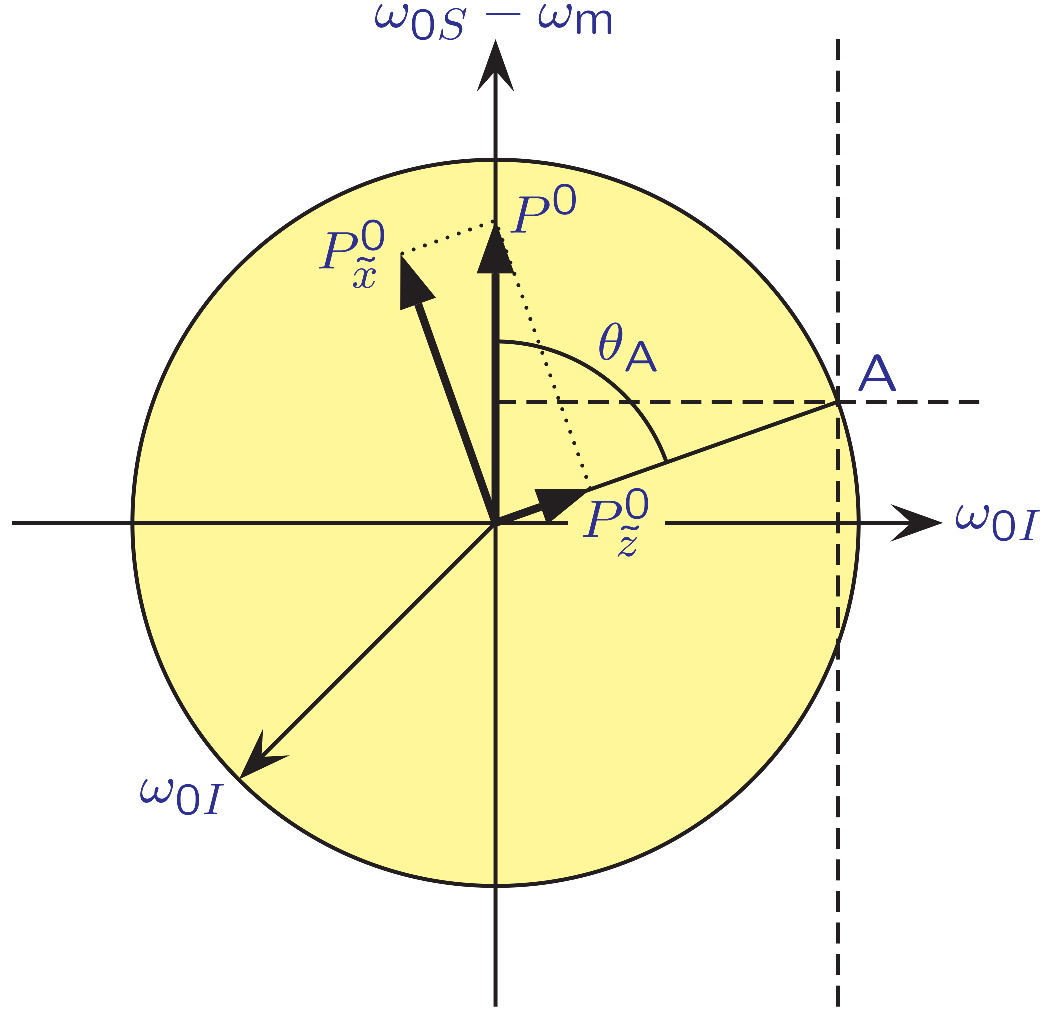
$$W^{\pm} \propto \left|\frac{1}{4}A_{zx}\right|^2 \sin^2\theta_{A,B}$$

transferred polarization

$$P^0_{\tilde{z}} = P^0 \cos\theta_{A,B}$$

fast transfer of low polarization

rotate P^0 ?



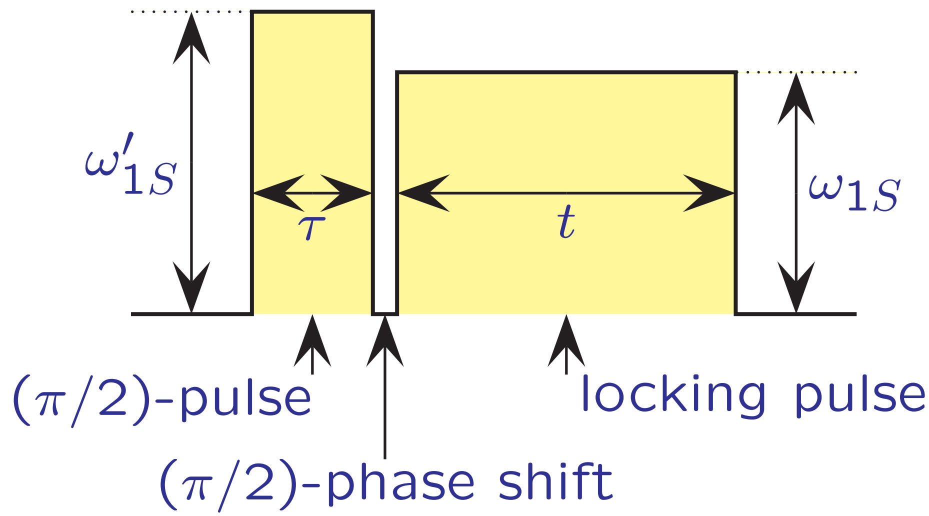
NOVEL

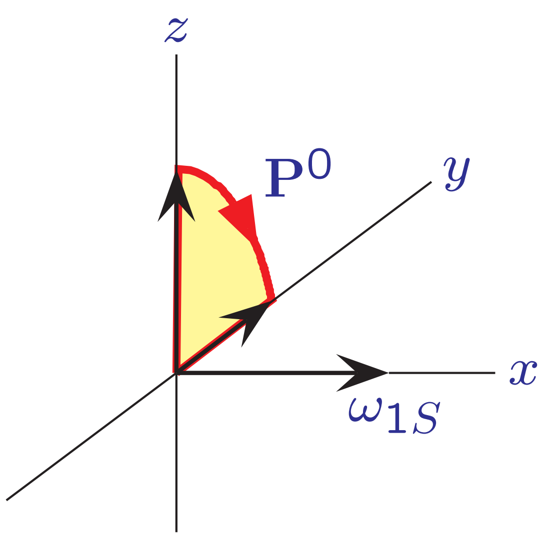
orient $\mathbf{P}^0 \parallel y$-axis

orient $\boldsymbol{\omega}_{1S} \parallel y$-axis

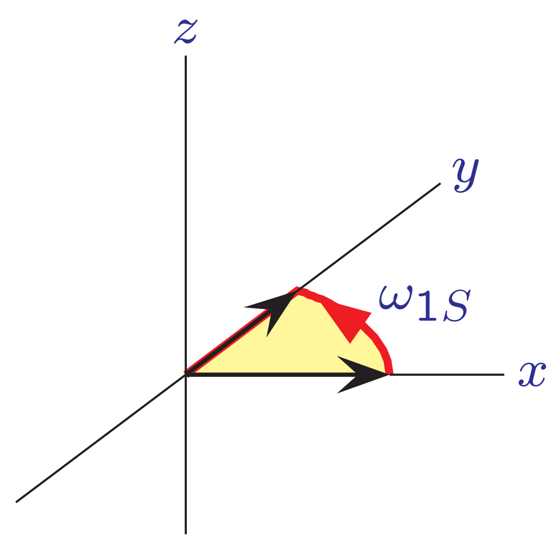
match $\omega_{1S} = \omega_{0I}$

full P^0, max rate





$\frac{\pi}{2}$ -pulse



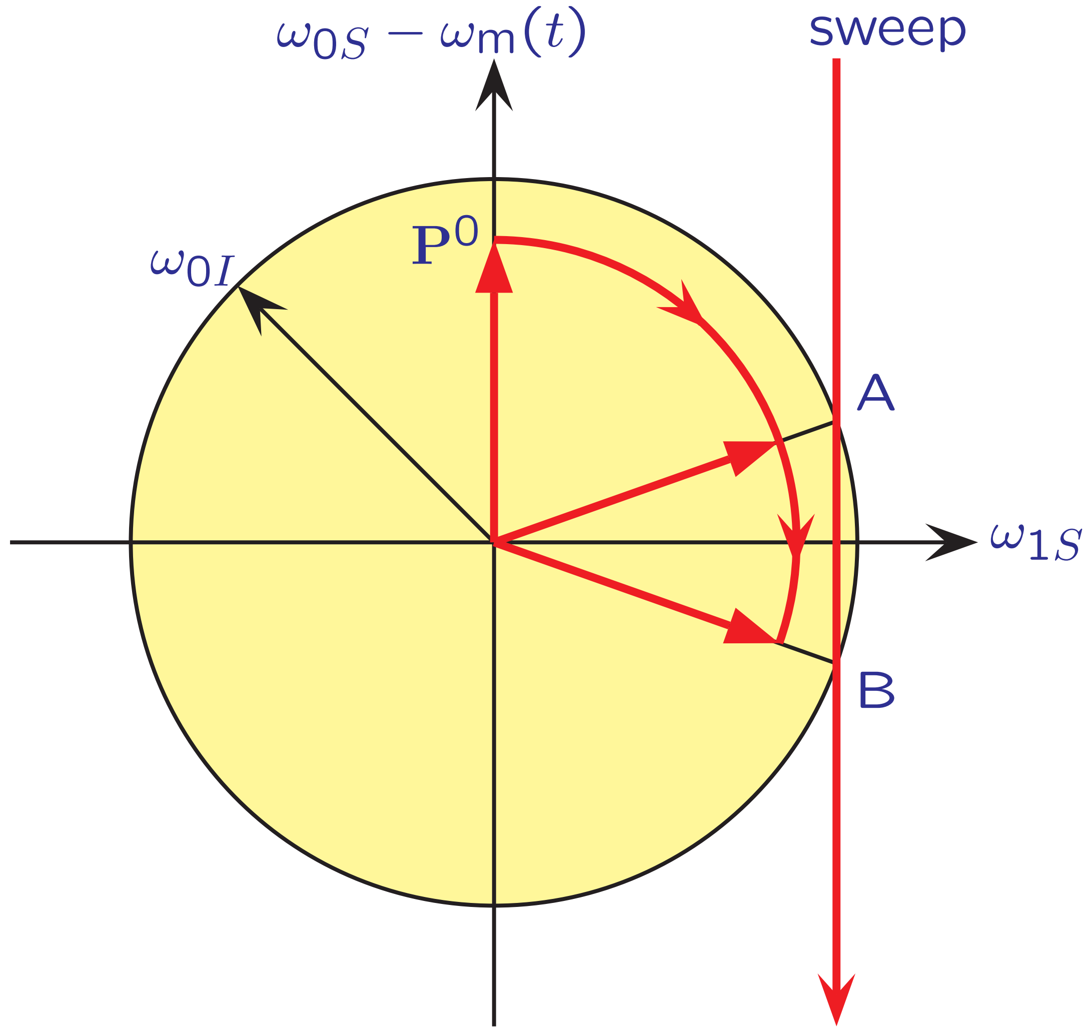
$\frac{\pi}{2}$ -phase shift

ISE (Integrated Solid Effect)

sweep ω_{m} or $\mathbf{B}_0$
adiabatic sweep:
$\mathbf{P}^0 \parallel$ effective field

full P^0, max rate

NOTE:
coherent transfer
= non-linear



Summary

narrow ESR line	$< \omega_{0I}$	**well-resolved solid effect**
broad ESR line	$> \omega_{0I}$	
weak μ-wave field	$\omega_{1S} T_{2S} < 1$	
fast spectral diffusion	$\dfrac{1}{\omega_{0I} T_{2S}^2} > \dfrac{1}{T_{1S}}$	**thermal mixing**
slow spectral diffusion	$\dfrac{1}{\omega_{0I} T_{2S}^2} < \dfrac{1}{T_{1S}}$	**cross effect**
strong μ-field	$\omega_{1S} T_{2S} > 1$	**differential solid effect**
very strong μ-wave field	$\omega_{1S} \approx \omega_{0I}$	**NOVEL ISE**