Modern methods in experimental physics:
site-directed spin labeling EPR

WS 2014 FU Berlin 04.11.2014

Solution Set 2

Problem 2: Lineshape analysis: continuous wave power saturation technique

a. The EPR (analogous to NMR) signal absorption is obtained by the steady state solution of the Bloch equations in the rotating frame:

$$M_y = \gamma B_1 M_o T_2 \frac{1}{1 + (\gamma B_1)^2 T_1 T_2 + (\gamma \Delta B_0)^2 T_2^2} \tag{1}$$

with $(\gamma\Delta B_0)^2$=$(\Delta\omega)^2$

The first derivative M_y' is:

$$M_y' = -2\gamma B_1 M_o T_2^3 \frac{\Delta\omega}{(1 + (\gamma B_1)^2 T_1 T_2 + (\Delta\omega)^2 T_2^2)^2} \tag{2}$$

The first derivative signal crosses the x axis for $\Delta\omega$=0. To obtain the I_{pp} we calculate the second derivative M_y'':

$$M_y'' = -2\gamma B_1 M_o T_2^3 \frac{(1 + (\gamma B_1)^2 T_1 T_2 + (\Delta\omega)^2 T_2^2) - 4T_2^2(\Delta\omega)^2}{(1 + (\gamma B_1)^2 T_1 T_2 + (\Delta\omega)^2 T_2^2)^3} \tag{3}$$

The M_y'' is equal to zero for:

$$\Delta\omega^2 = \frac{1 + (\gamma B_1)^2 T_1 T_2}{3T_2^2} \tag{4}$$

$$\Delta\omega_{1,2} = \pm \frac{\sqrt{1 + (\gamma B_1)^2 T_1 T_2}}{\sqrt{3} T_2} \tag{5}$$

which corresponds to

$$I_{pp}' = M_y'(\Delta\omega_1) - M_y'(\Delta\omega_2) = -\frac{9\gamma M_0 T_2^2}{4\sqrt{3}} \frac{B_1}{(1 + \gamma^2 B_1^2 T_1 T_2)^{\frac{3}{2}}} = -\frac{9 M_0 T_2^2}{4\sqrt{3}} \frac{\omega_1}{(1 + \omega_1^2 T_1 T_2)^{\frac{3}{2}}} \tag{6}$$

b. The saturation curves I'_{pp} versus ω_1 with the two sets of T_1, T_2 values are given in Fig. 2. The faster relaxing species shows an almost linear increase of the signal intensity with increasing ω_1. The progressive decrease of I'_{pp} observed for the slower relaxing species ($T_1 = 1\mu$s, $T_2 = 0.5\mu$s) is due to saturation (which implies line broadening). The faster the relaxation, the higher the microwave power required to induce saturation (n.b. ω_1 is proportional to the square root of the microwave power). To obtain reliable lineshape analysis in EPR (without distortion induced from saturation), the microwave power must be adjusted to maximize the signal intensity without leaving the linear regime in which the signal intensity is directly proportional to the square root of the incident microwave power.

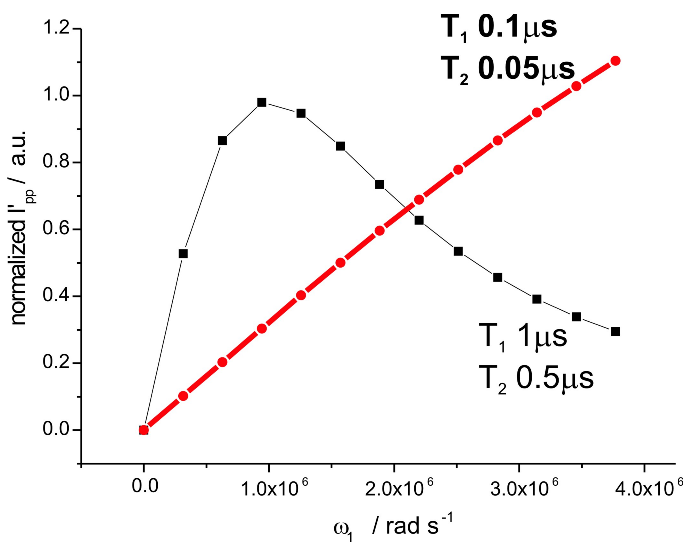

Figure 1: Plot if I'_{pp} versus ω_1 for the two sets of relaxation times.