The Solomon equations

$$\frac{d\langle I_z\rangle}{dt} = -\rho_I\left(\langle I_z\rangle - \langle I_0\rangle\right) - \sigma_{IS}\left(\langle S_z\rangle - \langle S_0\rangle\right) \qquad \cdots[1]$$

$$\frac{d\langle S_z\rangle}{dt} = -\rho_S\left(\langle S_z\rangle - \langle S_0\rangle\right) - \sigma_{SI}\left(\langle I_z\rangle - \langle I_0\rangle\right) \qquad \cdots[2]$$

Steady state NOE

If spin S were saturated ($\langle S_z\rangle = 0$), in the steady state we have:

$$\frac{d\langle I_z\rangle}{dt} = 0 = -\rho_I\left(\langle I_z\rangle - \langle I_0\rangle\right) - \sigma_{IS}\left(\langle S_z\rangle - \langle S_0\rangle\right)$$

$$= -\rho_I\left(\langle I_z\rangle - \langle I_0\rangle\right) + \sigma_{IS}\langle S_0\rangle$$

$$\Rightarrow \frac{\left(\langle I_z\rangle - \langle I_0\rangle\right)}{\langle S_0\rangle} = \frac{\sigma_{IS}}{\rho_I}$$

$$\therefore \frac{\left(\langle I_z\rangle - \langle I_0\rangle\right)}{\langle I_0\rangle}\frac{\langle I_0\rangle}{\langle S_0\rangle} = \frac{\sigma_{IS}}{\rho_I} \Rightarrow \frac{\left(\langle I_z\rangle - \langle I_0\rangle\right)}{\langle I_0\rangle} = \frac{\langle S_0\rangle}{\langle I_0\rangle}\frac{\sigma_{IS}}{\rho_I} = \frac{\gamma_S}{\gamma_I}\frac{\sigma_{IS}}{\rho_I} \qquad \cdots[3]$$

Note that under these conditions, Equation [2] above does not apply, since relaxation processes of the *S* spin are rendered ineffective (‘short circuited’) by saturation.

Equation [3] describes the steady state Overhauser effect, which leads to an enhancement of the signal of spin *I* when spin *S* is saturated, provided these two spins relax each other by mutual dipolar interactions as given by the Solomon equations.

Under motional narrowing (‘extreme narrowing’) conditions, the ratio of cross-relaxation rate σ and auto-relaxation rate ρ is ½. For ^{13}C NMR therefore the nuclear Overhauser effect could result in a relative enhancement by a factor of 2 when protons are saturated. This implies that the observed ^{13}C signal under proton saturation conditions could be upto 3 times the normal ^{13}C signal.

Transient NOE

If we assume $\rho_I = \rho_S$, represent the cross-relaxation rate by σ (= $\sigma_{IS} = \sigma_{SI}$) and invert the *S* spins at time 0, we have from Eqs. [1] and [2]:

$$\frac{d\left(\langle I_z\rangle+\langle S_z\rangle-\langle I_0\rangle-\langle S_0\rangle\right)}{dt} = -\left(\rho+\sigma\right)\left(\langle I_z\rangle+\langle S_z\rangle-\langle I_0\rangle-\langle S_0\rangle\right)$$

$$\frac{d\left(\langle I_z\rangle-\langle S_z\rangle-\langle I_0\rangle+\langle S_0\rangle\right)}{dt} = -\left(\rho-\sigma\right)\left(\langle I_z\rangle-\langle S_z\rangle-\langle I_0\rangle+\langle S_0\rangle\right)$$

Solving these equations with the initial condition as stated gives rise to the following:

$$\left(\langle I_z\rangle+\langle S_z\rangle-\langle I_0\rangle-\langle S_0\rangle\right) = -2\langle S_0\rangle e^{-(\rho+\sigma)t} \qquad \cdots[4]$$

$$\left(\langle I_z\rangle-\langle S_z\rangle-\langle I_0\rangle+\langle S_0\rangle\right) = 2\langle S_0\rangle e^{-(\rho-\sigma)t} \qquad \cdots[5]$$

Adding Eq. [4] and Eq. [5], we have:

$$\langle I_z\rangle-\langle I_0\rangle = \langle S_0\rangle\left(e^{-(\rho-\sigma)t} - e^{-(\rho+\sigma)t}\right) \qquad \cdots[6]$$

On the other hand, subtracting Eq. [5] from Eq. [4], we have:

$$\langle S_z\rangle-\langle S_0\rangle = -\langle S_0\rangle\left(e^{-(\rho-\sigma)t} + e^{-(\rho+\sigma)t}\right) \cdots[7]$$

Eq. [6] indicates a build-up followed by decay (or the opposite), while Eq. [7] describes a monotonic bi-exponential decay.

It may be noted that cross-relaxation rates σ as well as auto-relaxation rates ρ have an inverse sixth power dependence on the distance between the spins *I* and *S*, as well as a square dependence on the product of magnetogyric ratios of the two spins. In the two-spin model treated above, the steady state NOE loses the distance information because the ratio (σ/ρ) is involved. However, the transient experiment retains the distance information because the algebraic sum of the two rates is involved in the exponents. In particular, the initial rate of build-up of the *I* spin transient NOE upon inverting spin *S* corresponds clearly to 2σ.