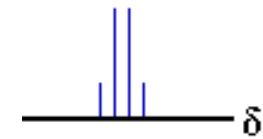
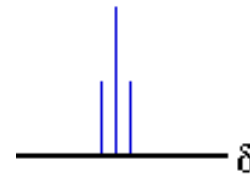
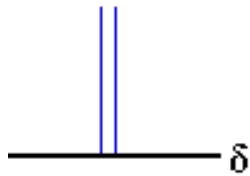
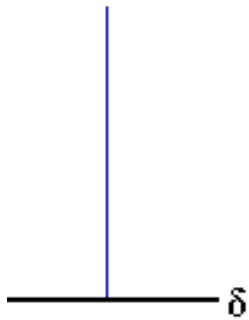
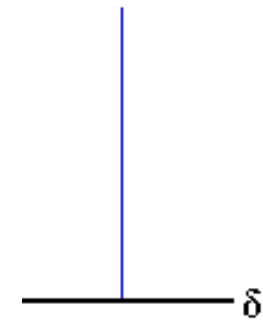


Entkopplung



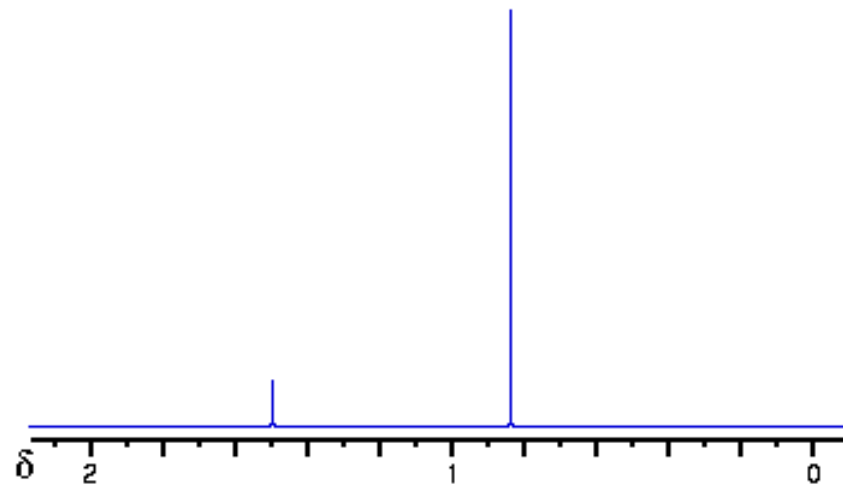
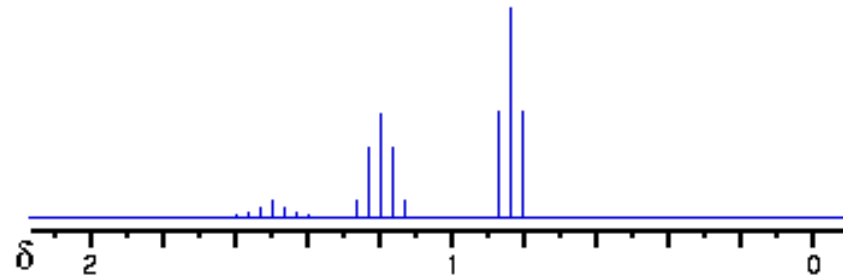
$$1:3:3:1$$
$$1+3+3+1=8 \quad (24)$$



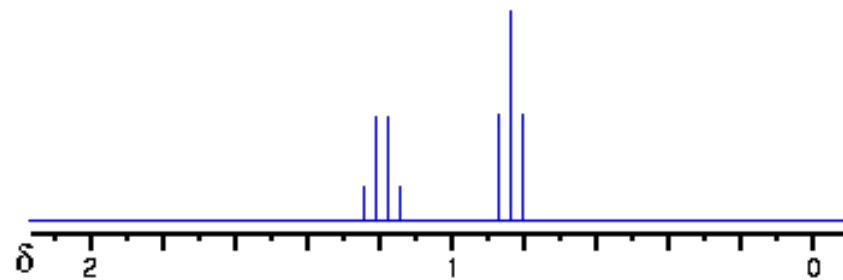
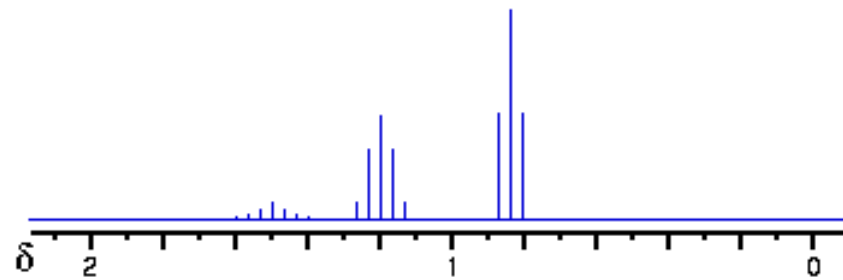
Entkopplung



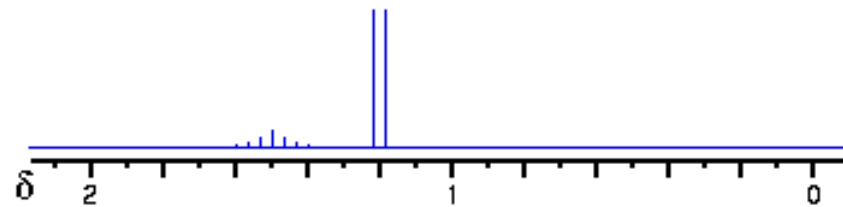
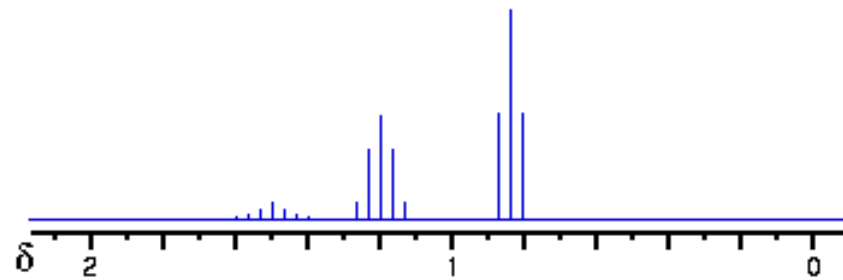
1:6:15:20:15:6:1



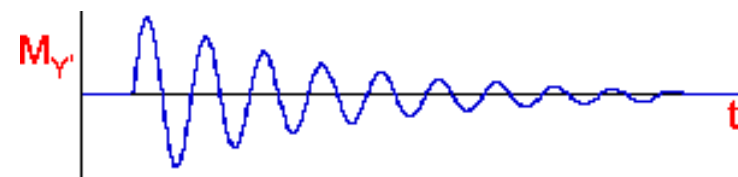
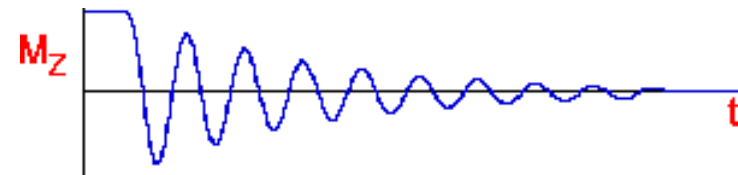
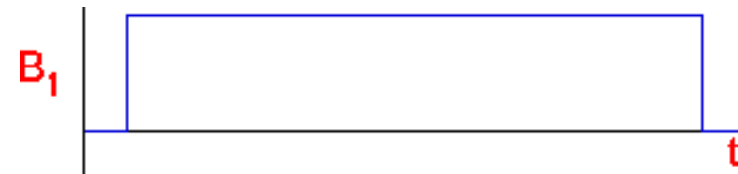
Entkopplung



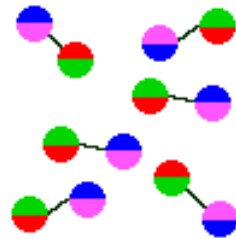
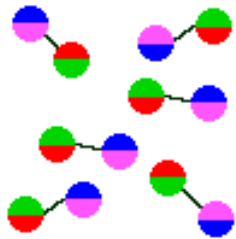
Entkopplung



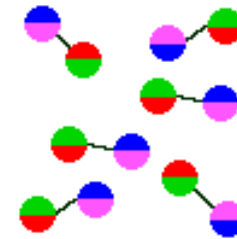
Entkopplung



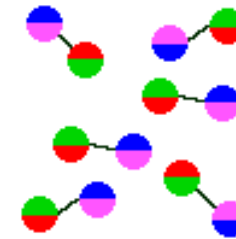
Kern-Overhauser-Effekt (NOE)



T_{1CC}



T_{1HH}



T_{1CH}

Kern-Overhauser-Effekt (NOE)

Solomon-
Gleichungen:

$$\frac{dM_z(H)}{dt} = -\frac{\cancel{M_z(H)} - M_0(H)}{T_{1HH}} - \frac{M_z(C) - M_0(C)}{T_{1CH}}$$

$$\frac{dM_z(C)}{dt} = -\frac{M_z(C) - M_0(C)}{T_{1CC}} - \frac{\cancel{M_z(H)} - M_0(H)}{T_{1CH}}$$

$M_z(H) = 0$:

$$\frac{dM_z(H)}{dt} = -\frac{0 - M_0(H)}{T_{1HH}} - \frac{M_z(C) - M_0(C)}{T_{1CH}}$$

$$\frac{dM_z(C)}{dt} = -\frac{M_z(C) - M_0(C)}{T_{1CC}} - \frac{0 - M_0(H)}{T_{1CH}}$$

Kern-Overhauser-Effekt (NOE)

$$M_z(H) = 0:$$

$$\frac{dM_z(H)}{dt} = -\frac{0 - M_0(H)}{T_{1HH}} - \frac{M_z(C) - M_0(C)}{T_{1CH}}$$

$$\frac{dM_z(C)}{dt} = -\frac{M_z(C) - M_0(C)}{T_{1CC}} - \frac{0 - M_0(H)}{T_{1CH}}$$

$$d M_z(C)/dt = 0$$

$$\frac{dM_z(H)}{dt} = +\frac{M_0(H)}{T_{1HH}} - \frac{M_z(C) - M_0(C)}{T_{1CH}}$$

$$0 = -\frac{M_z(C) - M_0(C)}{T_{1CC}} + \frac{M_0(H)}{T_{1CH}}$$

Kern-Overhauser-Effekt (NOE)

$$d M_z(C) / dt = 0$$

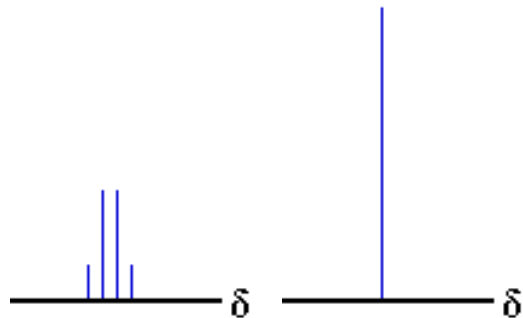
$$\frac{dM_z(H)}{dt} = + \frac{M_0(H)}{T_{1HH}} - \frac{M_z(C) - M_0(C)}{T_{1CH}}$$

$$0 = - \frac{M_z(C) - M_0(C)}{T_{1CC}} + \frac{M_0(H)}{T_{1CH}}$$



$$M_z(C) = M_0(C) + \frac{M_0(H) T_{1CC}}{T_{1CH}}$$

1:3:3:1
1+3+3+1=8 (24)



$$M_0(H) T_{1CC} / T_{1CH} \approx 2 M_0(C)$$

Kern-Overhauser-Effekt (NOE)

$$M_z(C) = M_0(C) + \frac{M_0(H) T_{1CC}}{T_{1CH}}$$

$$NOF(C) = [M_z(C) - M_0(C)] / M_0(C)$$

$$NOF(C) = \left[\frac{M_0(C) + M_0(H)(T_{1CC} / T_{1CH}) - M_0(C)}{M_0(C)} \right] = \left[\frac{M_0(H)T_{1CC}}{M_0(C)T_{1CH}} \right]$$

Kern-Overhauser-Effekt (NOE)

$$M_0(C) = k\gamma_C S(S+1)$$

$$M_0(H) = k\gamma_H I(I+1)$$

$$NOF(C) = \left[\frac{M_0(H)T_{1CC}}{M_0(C)T_{1CH}} \right] = \left[\frac{k\gamma_H I(I+1)S(S+1)}{k\gamma_C S(S+1)2I(I+1)} \right]$$

$$NOF(C)_{\max} = \left[\frac{\gamma_H}{2\gamma_C} \right]$$

$$NOE(C)_{\max} = 1 + \left[\frac{\gamma_H}{2\gamma_C} \right]$$

Kern-Overhauser-Effekt (NOE)

$$NOF(C) = \left[\frac{M_0(H)T_{1CC}}{M_0(C)T_{1CH}} \right]$$

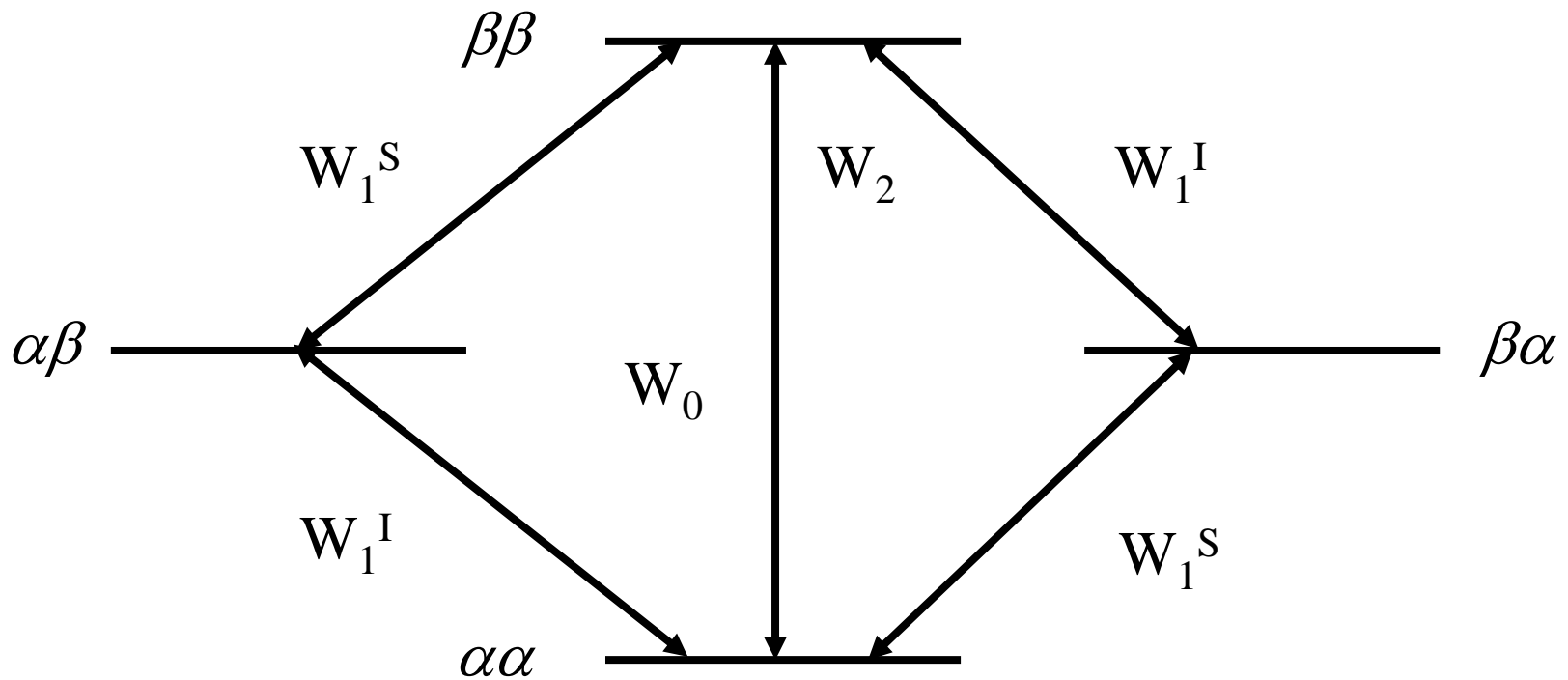
$$\frac{1}{T_1^{II}} = \frac{1}{20} b_{ij}^2 [J(\omega_I - \omega_S) + 3J(\omega_I) + 6J(\omega_I + \omega_S)]$$

$$\frac{1}{T_1^{IS}} = \frac{1}{20} b_{ij}^2 [-J(\omega_I - \omega_S) + 6J(\omega_I + \omega_S)]$$

Kern-Overhauser-Effekt (NOE)

1. Der intermolekulare Abstand ist kurz (100 pm).
2. Die Relaxation beruht auf reiner DD-Wechselwirkung.
3. Die Probe befindet sich im Bereich des ‚extreme narrowing limit‘.

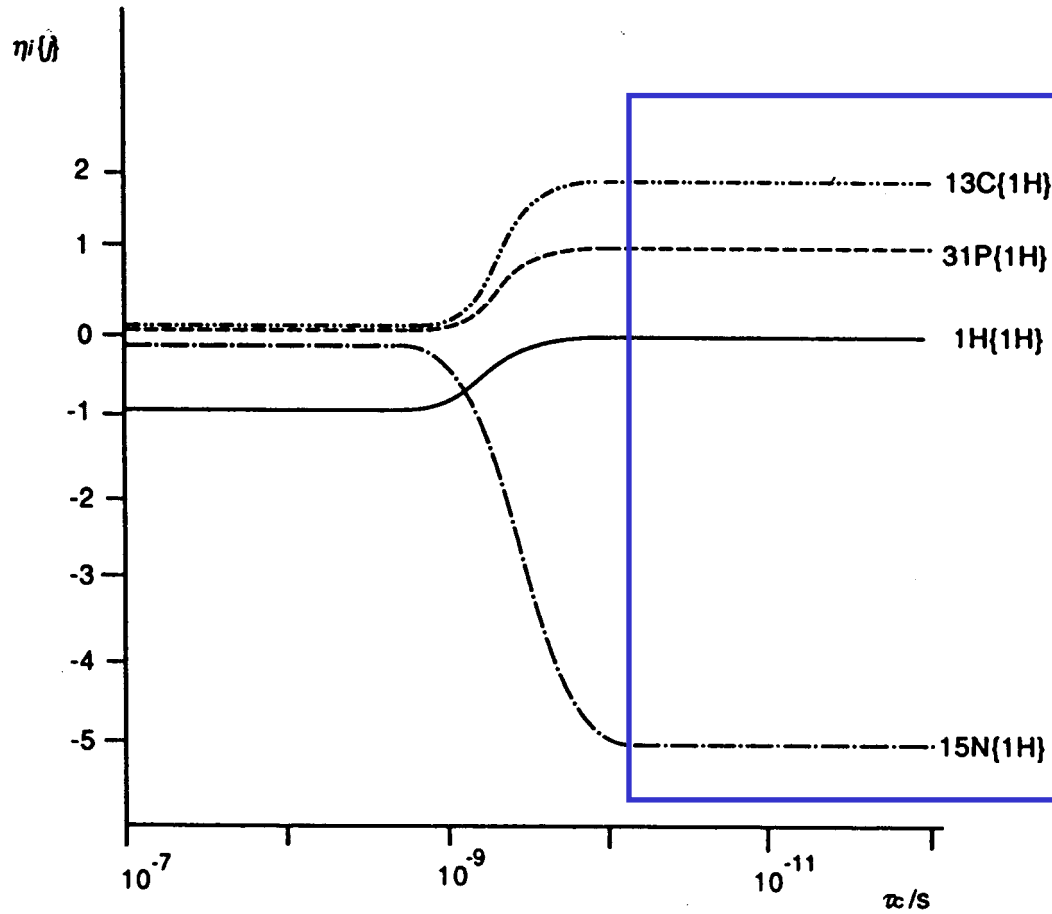
Kern-Overhauser-Effekt (NOE)



$$\frac{R_{II}}{R_{IS}} \approx \frac{-J(\omega_I - \omega_S) + 6J(\omega_I + \omega_S)}{J(\omega_I - \omega_S) + 3J(\omega_I) + 6J(\omega_I + \omega_S)}$$

$$\frac{R_{II}}{R_{IS}} \approx \frac{-J(\omega_0) + 6J(\omega_2)}{J(\omega_0) + 3J(\omega_1) + 6J(\omega_2)}$$

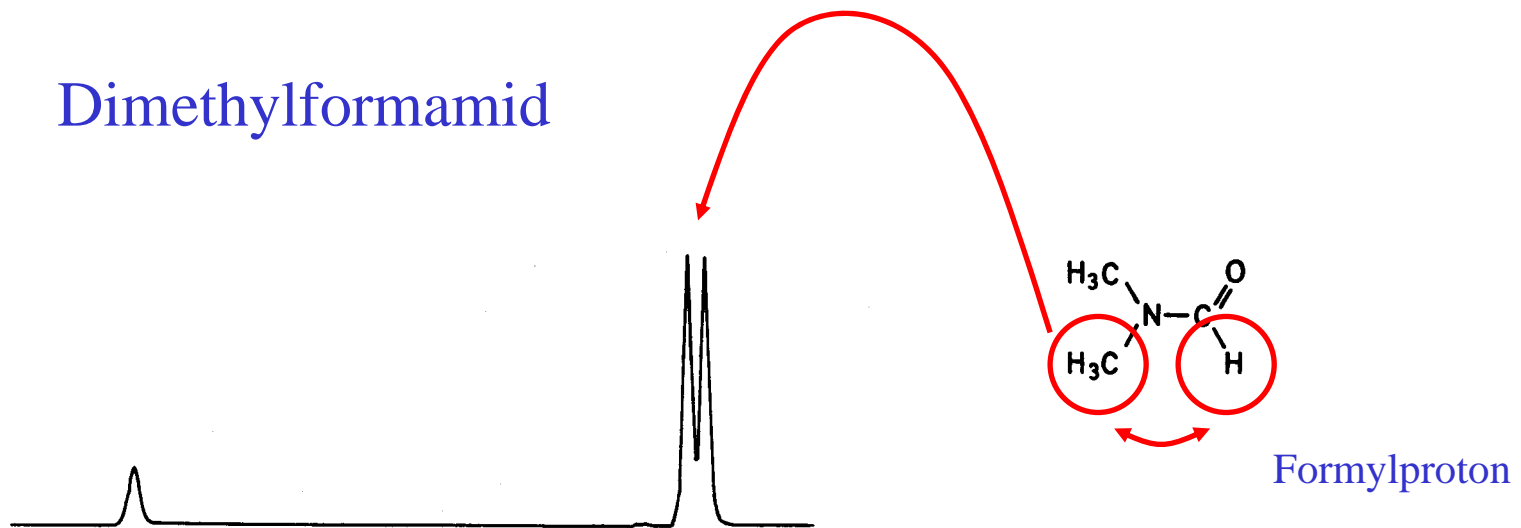
Kern-Overhauser-Effekt (NOE)



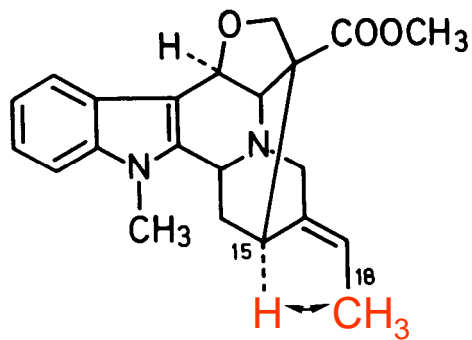
$$NOF(C)_{\max} = \left[\frac{\gamma_H}{2\gamma_C} \right]$$

$$J \propto \frac{\tau_c}{(1 + \omega^2 \tau_c^2)}$$

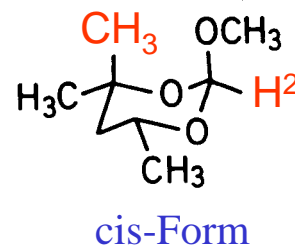
Kern-Overhauser-Effekt (NOE)



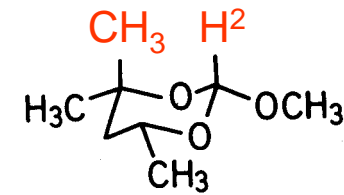
Kern-Overhauser-Effekt (NOE)



Ethyliden-Seitenkette des
Alkaloids Dehydro-voachalotin



cis-Form



trans-Form

2-Methoxy-4,4,6-trimethyl-1,3-dioxan

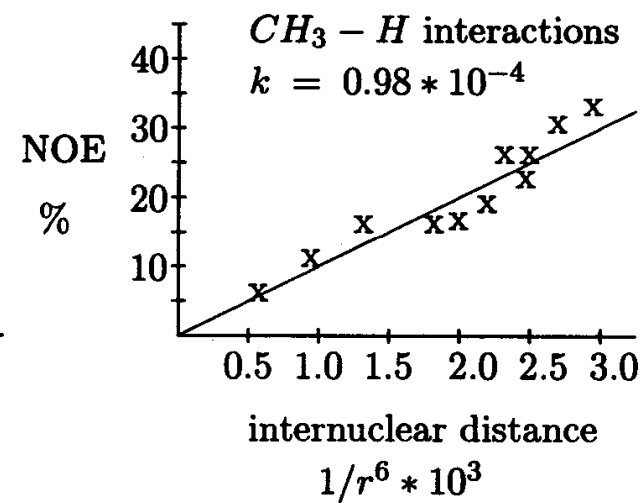
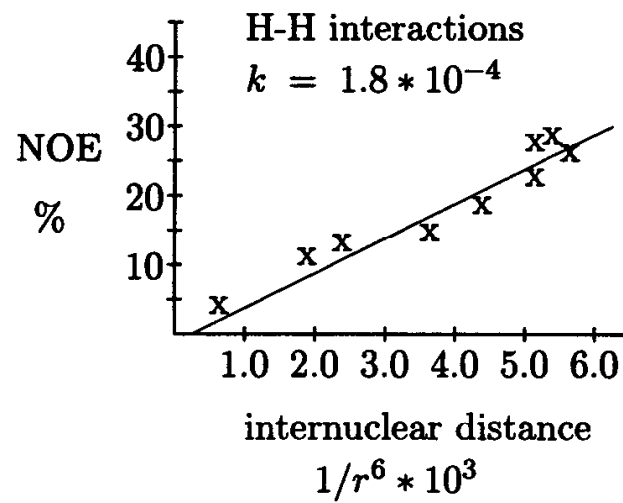
Kern-Overhauser-Effekt (NOE)

$$\text{NOE}(^1\text{H})=1/2 \quad \text{für} \quad r(\text{AB}) < r^0(\text{AB})$$

$$\text{NOE}(^1\text{H})=kr(\text{AB})^{-6} \quad \text{für} \quad r(\text{AB}) > r^0(\text{AB})$$

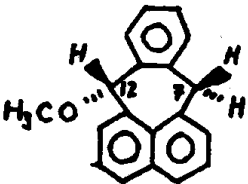
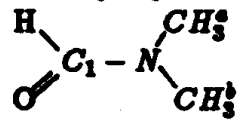
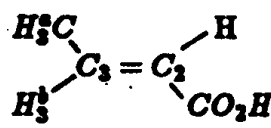
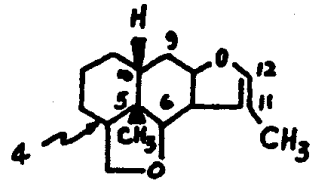
mit $r^0 \approx 190 \text{ pm}$

Kern-Overhauser-Effekt (NOE)

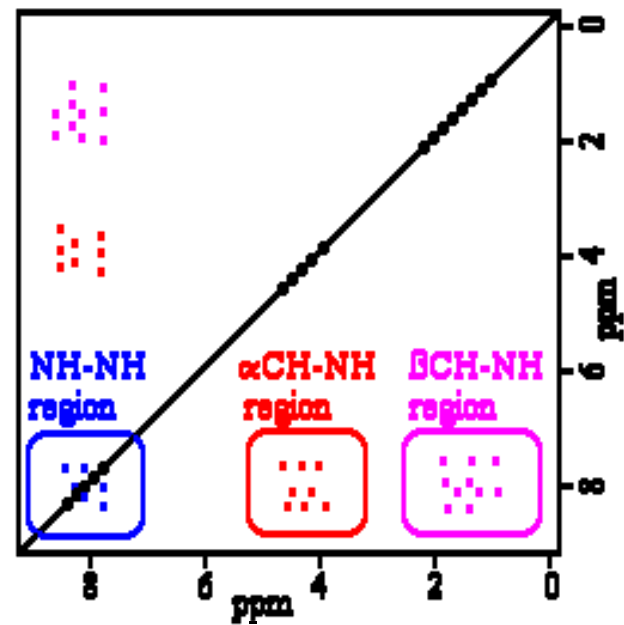
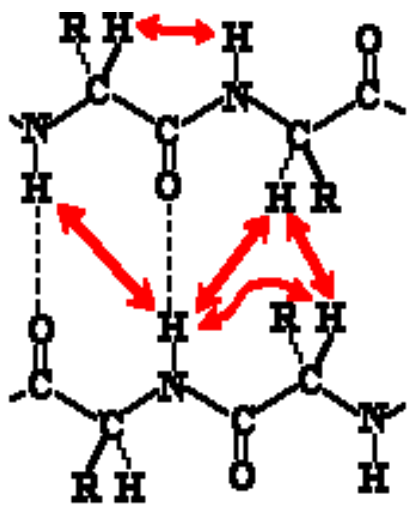


Kern-Overhauser-Effekt (NOE)

Table 6.1

Molecule	Irradiated Group	Observed Group	Percent NOE	Bond Distance $R_{AX}(A)$
	$C_7 - H$ (axial)	$C_{12} - H$	28	2.40
	CH_3^a	$C_1 - H$	28	2.69
	CH_3^a	C_2H	17	2.90
	$C_{11} - CH_3$	$C_{12} - H$	17	2.88
	$C_{11} - CH_3$	$C_6 - H$	6	3.56
	$C_5 - CH_3$	$C_6 - H$	23	2.74

Kern-Overhauser-Effekt (NOE)



Kern-Overhauser-Effekt (NOE)

