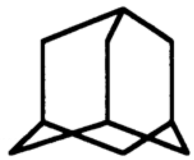
High Resolution Techniques for Multiple Quantum NMR of Coupled Spin-1/2 Solids

Yong Ba

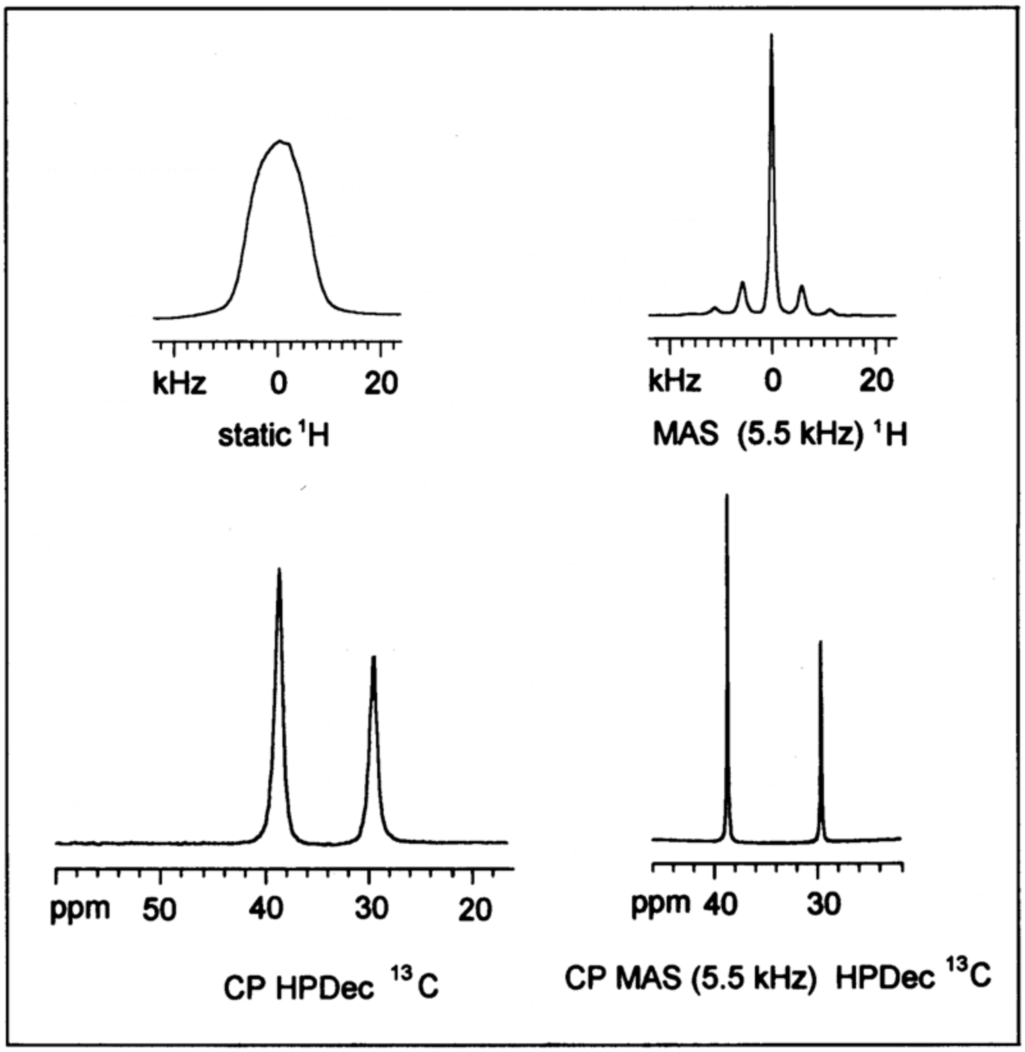
Department of Chemistry and Biochemistry, California State University Los Angeles

Ba, Yong; Veeman, Wiebren S., Multiple-quantum nuclear magnetic resonance spectroscopy of coupled ½ spins in solid. Combination with cross-polarization and magic-angle spinning. Solid State Nucl. Magn. Reson. 3(5), 249 (1994).

High resolution techniques



Adamantane
$C_{10}H_{16}$



MAS=magic angle sample spinning
CP= cross polarization
HPDec=high power (proton) decoupling

Internal Hamiltonian in rotating solids*

$$H^{r}_{int}(t) = H^{r}_{z}(t) + H^{r}_{zz}(t)$$

chemical shift term

$$H^{r}_{z}(t) = \sum_{i=1}^{N} \gamma_i B_0 I_{iz} \left\{ \sigma_{iso\,i} + \delta_i \left[\frac{1}{2}\left(3\cos^2\Theta - 1\right) \right] \cdot \right.$$
$$\left. \left[\frac{1}{2}\left(3\cos^2\beta_i - 1\right) + \frac{\eta_i}{2}\sin^2\beta_i \cos 2\gamma_i \right] + \delta_i \xi^{(i;\sigma)}(t) \right\},$$

dipolar coupling term

$$H^{r}_{zz}(t) = -\sum_{i<j} \gamma_i \gamma_j \hbar r_{ij}^{-3} \left(3 I_{iz} I_{jz} - \vec{I}_i \cdot \vec{I}_j\right) \cdot$$
$$\left\{ \left[\frac{1}{2}\left(3\cos^2\Theta - 1\right) \right] \left[\frac{1}{2}\left(3\cos^2\beta_{ij} - 1\right) + \frac{\eta_{ij}}{2}\sin^2\beta\cos 2\gamma_{ij} \right] + \xi^{(ij;D)}(t) \right\},$$

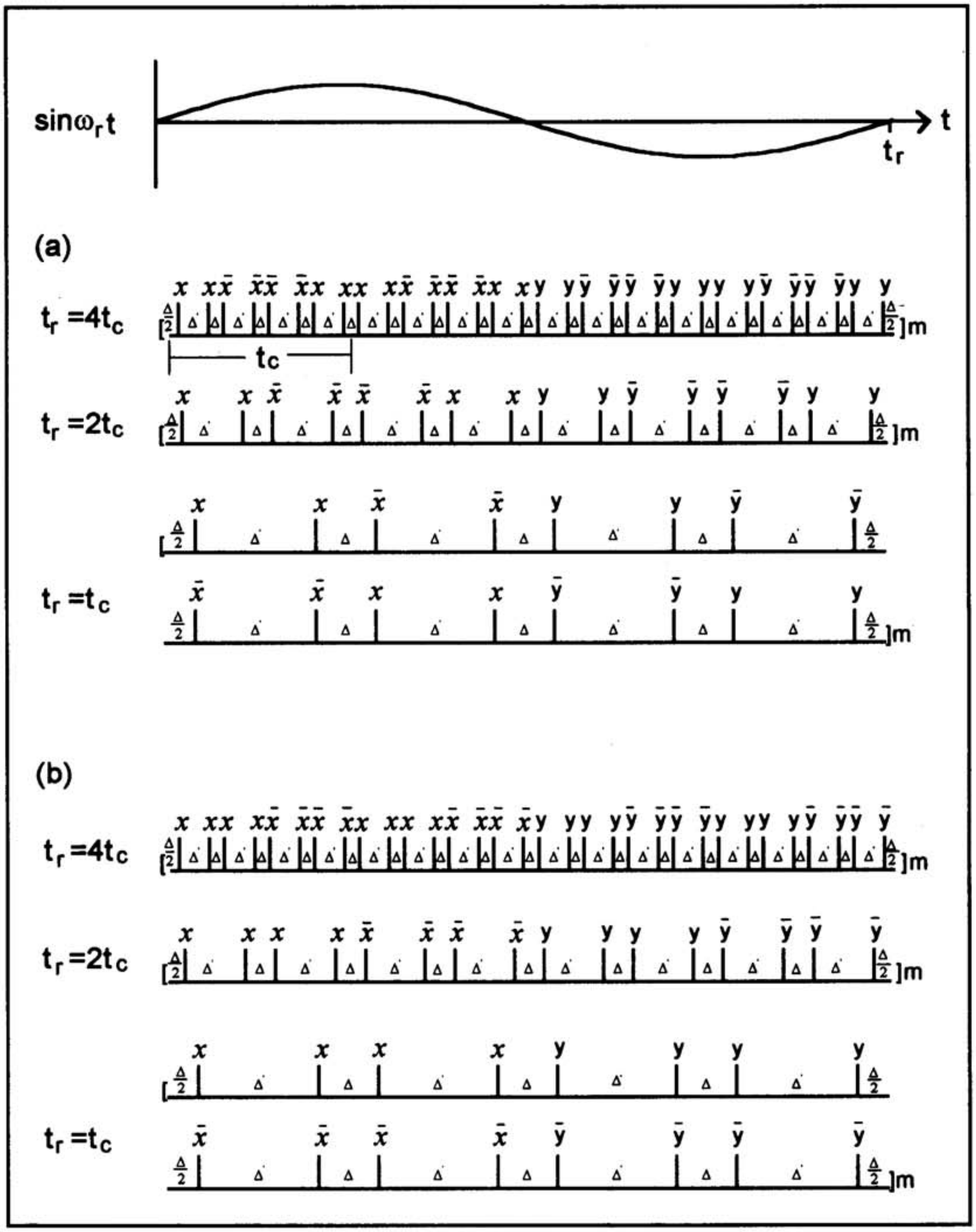
$$\xi(t) = C_1 \cos\omega_r t + S_1 \sin\omega_r t + C_2 \cos 2\omega_r t + S_2 \sin 2\omega_r t,$$

$$C_1 = \frac{1}{2}\sin 2\Theta \sin\beta \left[\cos\beta(\eta\cos 2\gamma - 3)\cos\alpha - \eta\sin 2\gamma \sin\alpha \right],$$
$$S_1 = \frac{1}{2}\sin 2\Theta \sin\beta \left[\cos\beta(3 - \eta\cos 2\gamma)\sin\alpha - \eta\sin 2\gamma \cos\alpha \right],$$
$$C_2 = \frac{1}{2}\sin^2\Theta \left\{ \left[\frac{3}{2}\sin^2\beta + \frac{\eta}{2}\cos 2\gamma\left(1 + \cos^2\beta\right) \right] \cos 2\alpha - \eta\cos\beta\sin 2\gamma \sin 2\alpha \right\},$$
$$S_2 = \frac{1}{2}\sin^2\Theta \left\{ -\left[\frac{3}{2}\sin^2\beta + \frac{\eta}{2}\cos 2\gamma\left(1 + \cos^2\beta\right) \right] \sin 2\alpha - \eta\cos\beta\sin 2\gamma \cos 2\alpha \right\}.$$

Θ-the angle between the rotation axis and $\vec{B}_0$.
$\Theta = 54.7^{o}$-magic angle.
ω_r-the rotation angular frequency of the rotor.

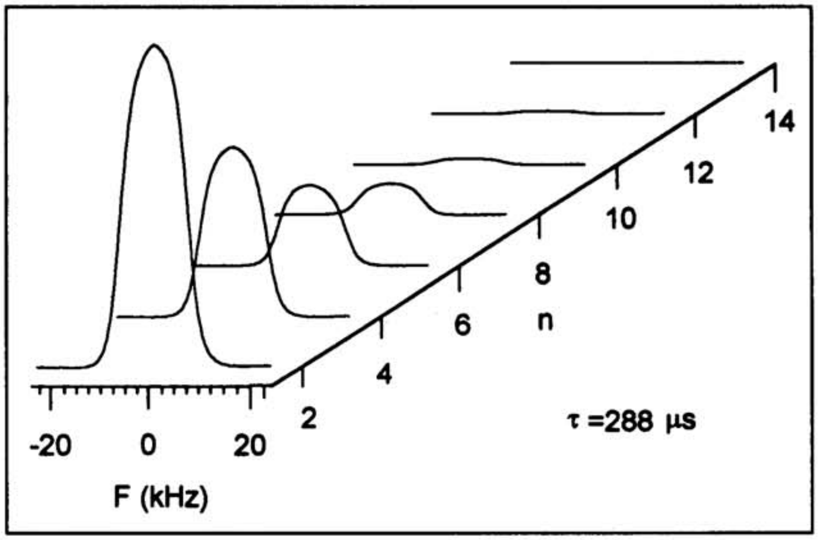
---

*M.M. Maricq and J.S. Waugh, *J. Chem. Phys.* **70**(1979) 3300.

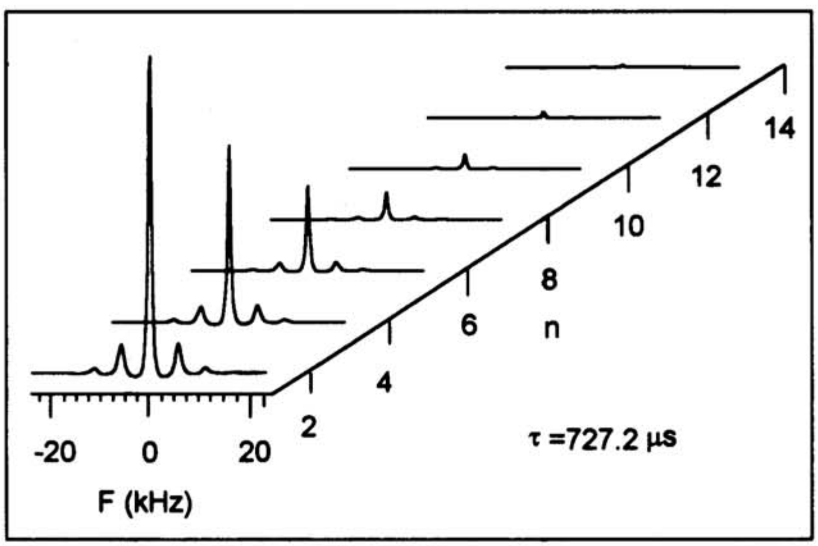


The pulse sequences for exciting MQ coherences in rotating solids

$$\overline{H}_{\xi}^{(0)} = -\frac{1}{2}k\sum_{i<j}\frac{\gamma_i \gamma_j \hbar}{r_{ij}^3} S_1^{(ij;D)}\left(I_{+i}I_{+j} + I_{-i}I_{-j}\right)$$

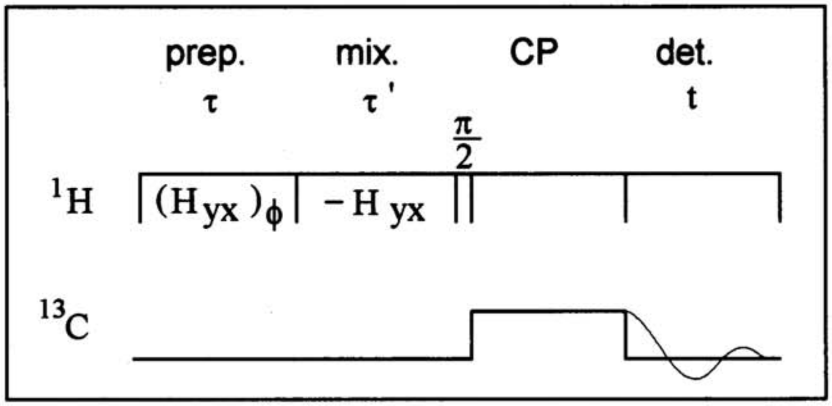


2D proton MQ spectra of static adamantane solid

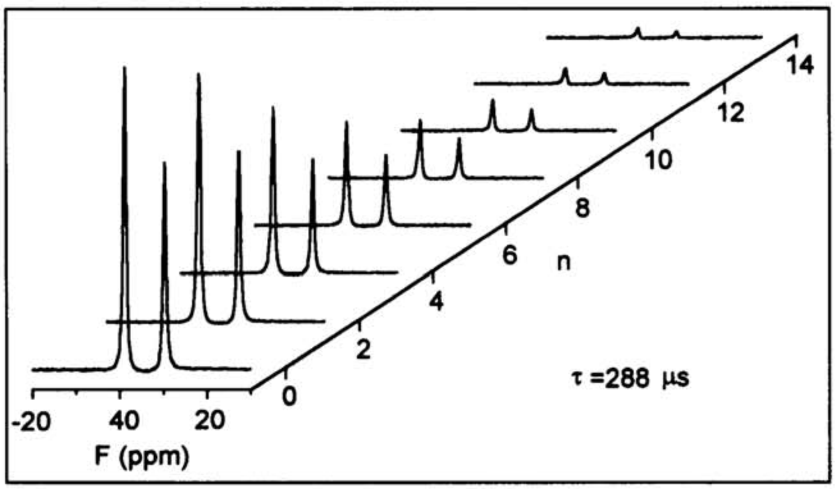


2D proton MQ spectra of rotating (MAS) adamantane solid

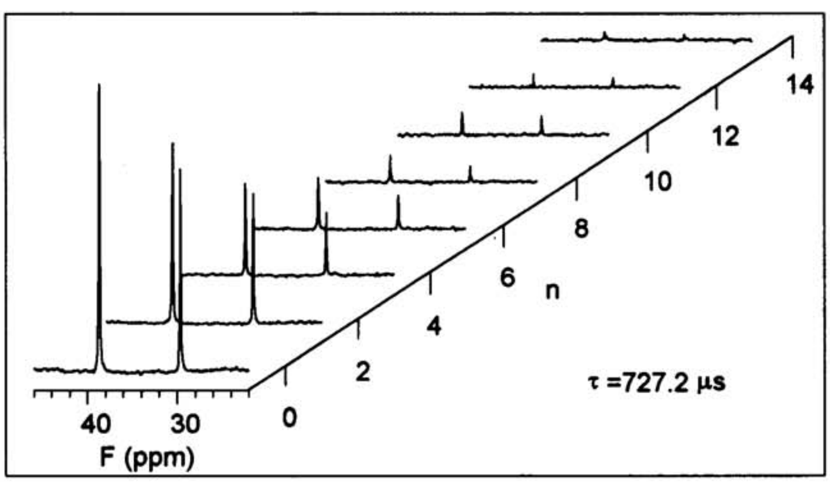
Proton MQ coherences via CP MAS ^{13}C detection



Indirect detection of proton MQ coherences via ^{13}C signal

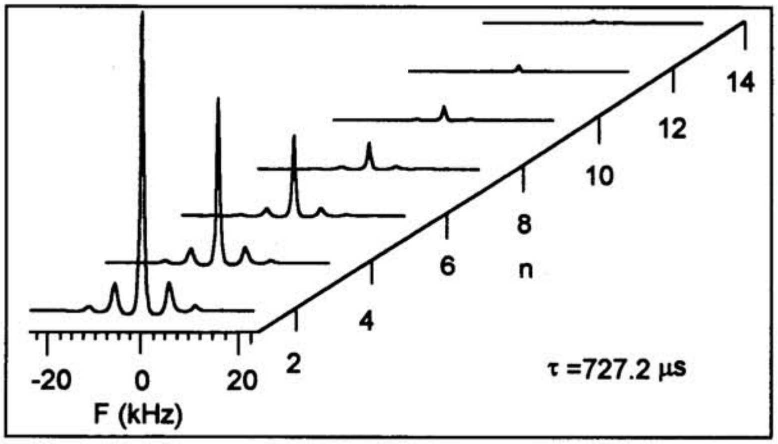


Adamantane proton MQ coherences via CP (static) ^{13}C detection

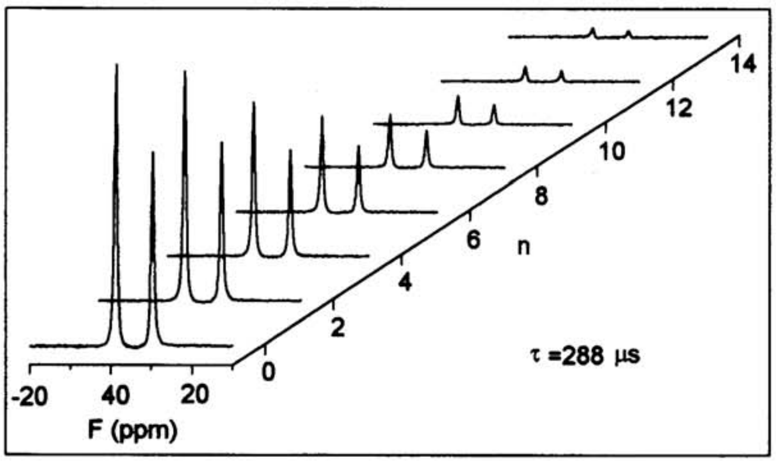


Adamantane proton MQ coherences via CP MAS ^{13}C detection

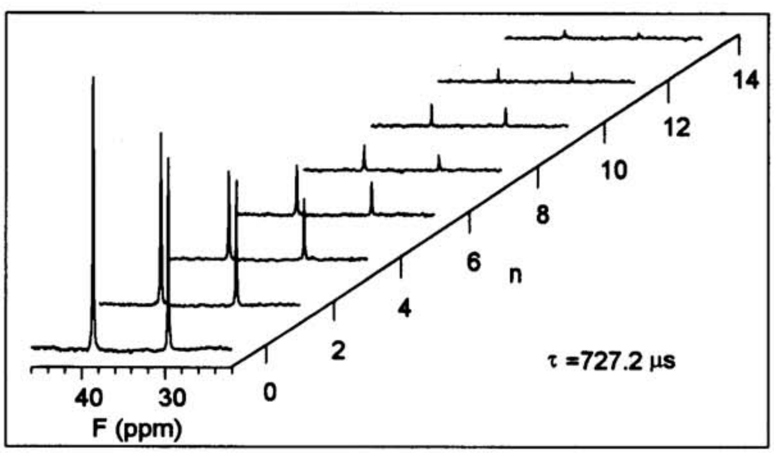
High resolution MQ NMR



2D proton MQ spectra of adamantane solid with **MAS**



Adamantane proton MQ coherences via **CP (static)** **HPDec** **^{13}C detection**



Adamantane proton MQ coherences via **CP MAS** **HPDec** **^{13}C detection**

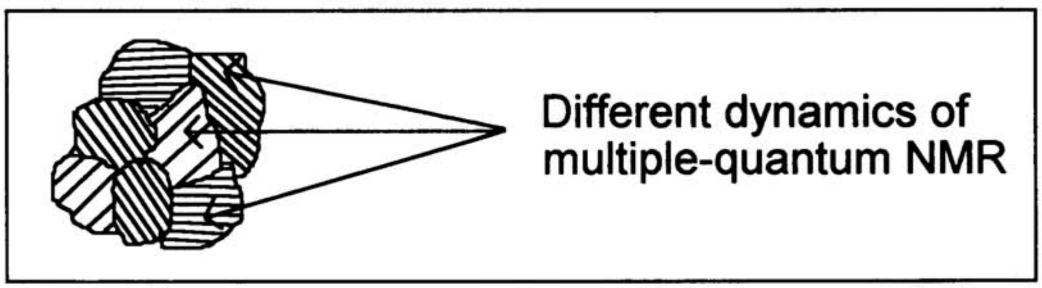
The study of heterogeneous solids

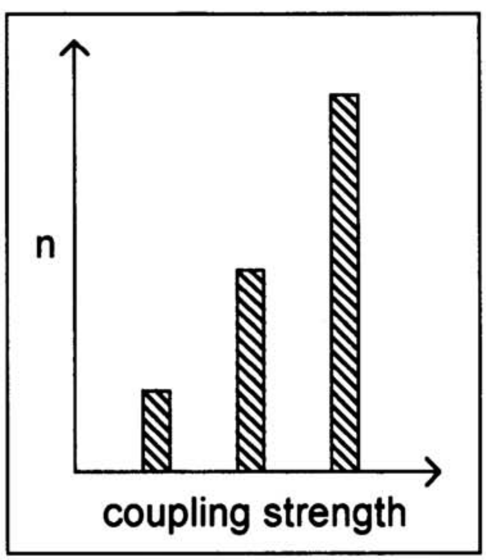
Dynamics

$$H_{yx} = -\frac{1}{2}\sum_{i<j} D_{ij}\left(I_{i+}I_{j+} + I_{i-}I_{j-}\right)$$

$$D_{ij} = -\frac{\gamma_i \gamma_j \hbar}{2r_{ij}^3}\left(1 - 3\cos^2\theta_{ij}\right)$$

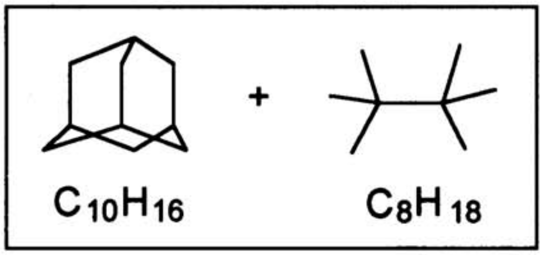
(1) The coupled spin numbers
(2) The internuclear displacements
(3) The molecular motion
(4) The length of MQ pulse sequence compared to the inverse of the line width of the dipolar interaction



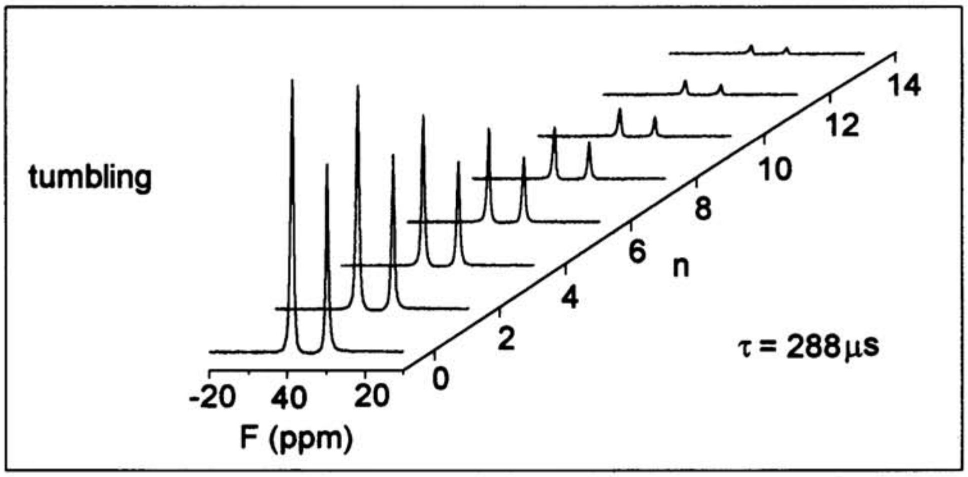


Multiple-quantum filtering

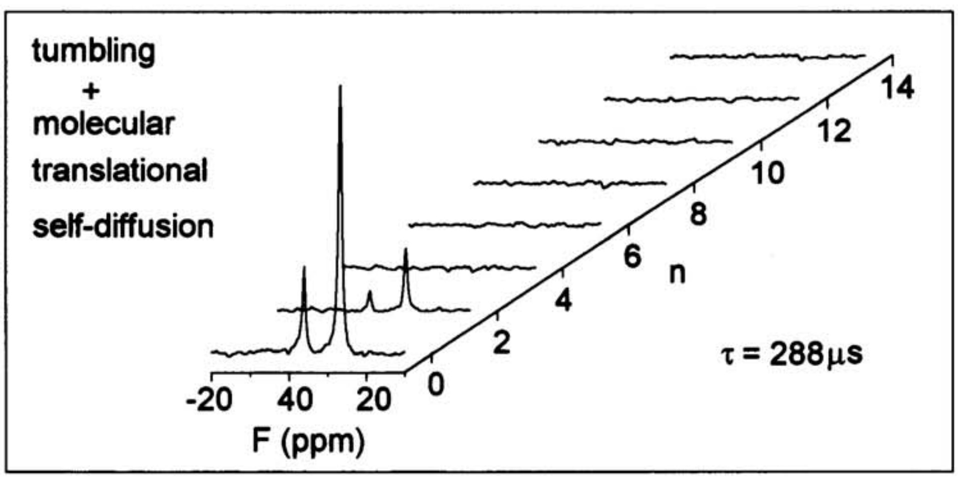
Molecular mixture



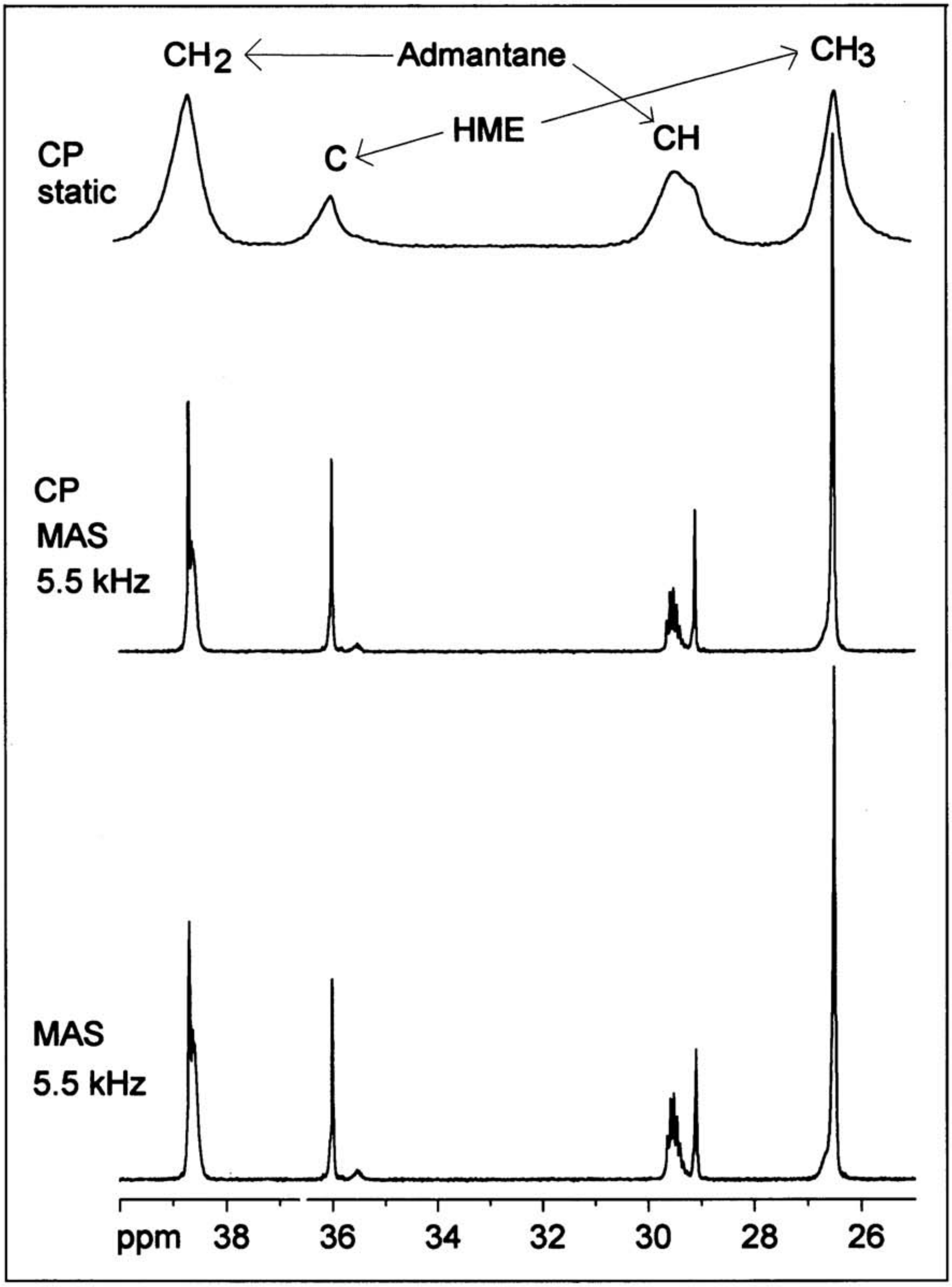
adamantane+hexamethylethane (HME) by melt



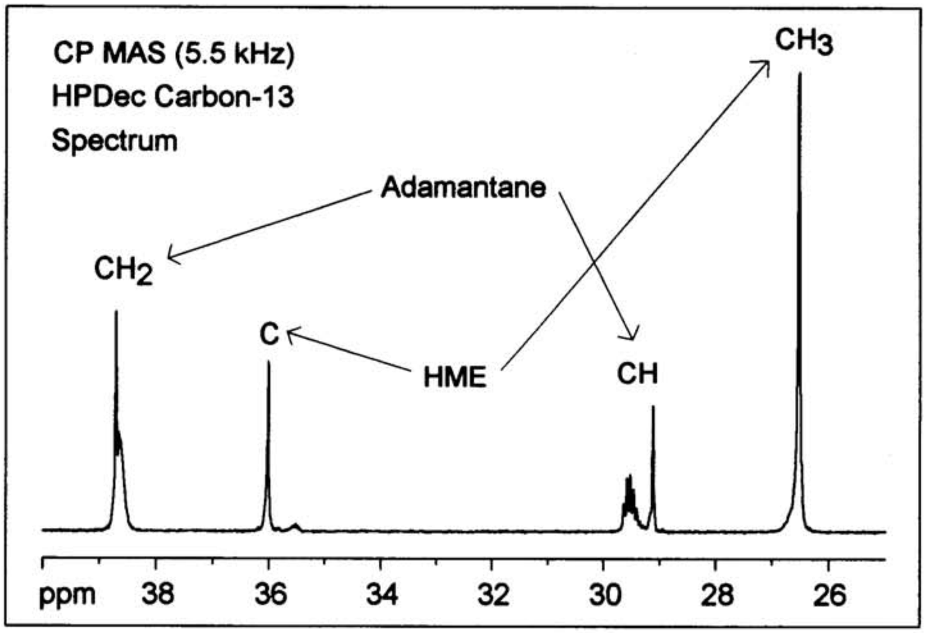
[1]H adamantane MQ coherences via CP HPDec carbon-13 detection

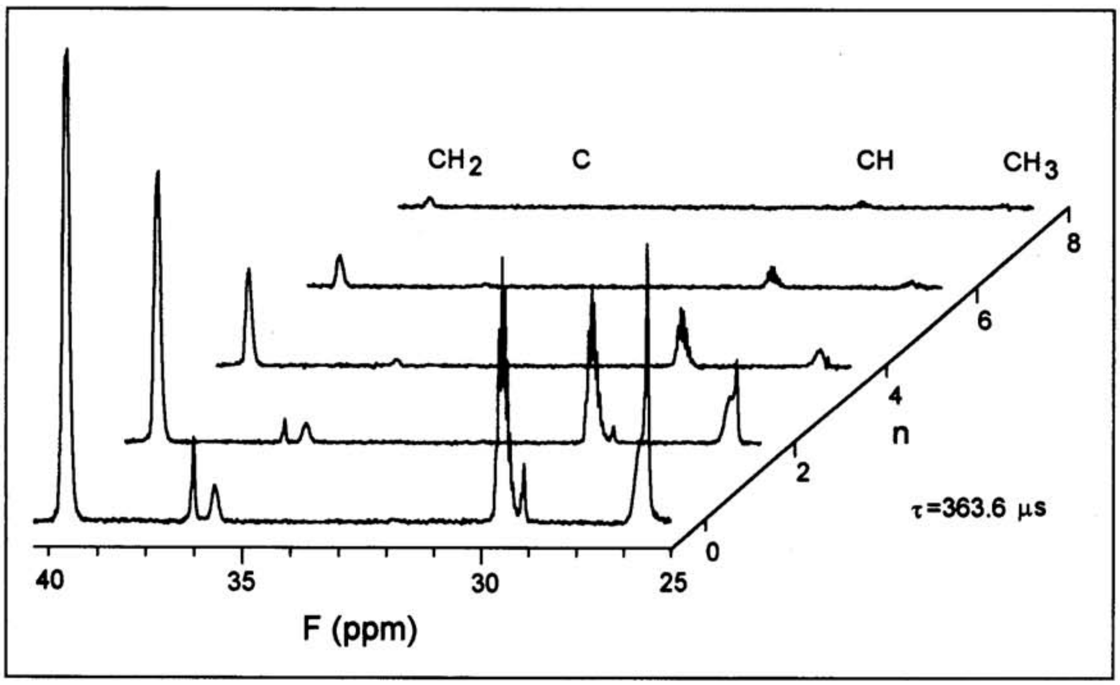


[1]H HME MQ coherences via CP HPDec carbon-13 detection



Proton decoupled ^{13}C spectra
of the mixture of adamantane and HME by melt





CP MAS (5.5 kHz) HPDec ^{13}C detected proton MC coherences

Adamantane/HME=52.3/47.7
Phase 1: adamantane/HME=21.3/78.7
Phase 2: adamantane/HME=86.5/13.5