^{1}H-^{13}C Separate Local Field NMR under Moderately Fast Magic-Angle-Spinning Conditions

1. Basic Physical Observations on the MAS NMR of ^{1}H-^{13}C Systems

The measurement of site-specific ^{1}H-^{13}C dipolar couplings provides a sensitive tool for elucidating structures and motions in solids at a molecular level: Separate-Local-Field (SLF) NMR (Vaughan 1976; Waugh, 1977; Ernst, 1980; Griffin 1982; Schaefer 1983). During recent years, we have been exploring the opportunities opened by the acquisition of such experiments *in the absence of multipulse NMR, under the sole assistance of moderately fast Magic-Angle-Spinning (MAS)*

The reason why SLF provides purely dipolar ^{1}H-^{13}C dipolar information:

multiple-pulse decoupling

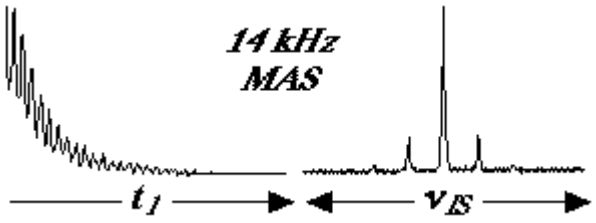
$$\mathcal{H} = \left[\sum_I \nu_{IS}(t) I_z\right] S_z + \sum_{I<J} \nu_{IJ}(t)(3 I_z J_z - \bar{I}\cdot\bar{J})$$

Yet when the 13C-1H dipolar evolution is monitored in the absence of multiple-pulse decoupling rotor echoes and spinning sidebands are also observed.

$Ca(HCO_2)_2$

relatively isolated ^{13}C-^{1}H pair

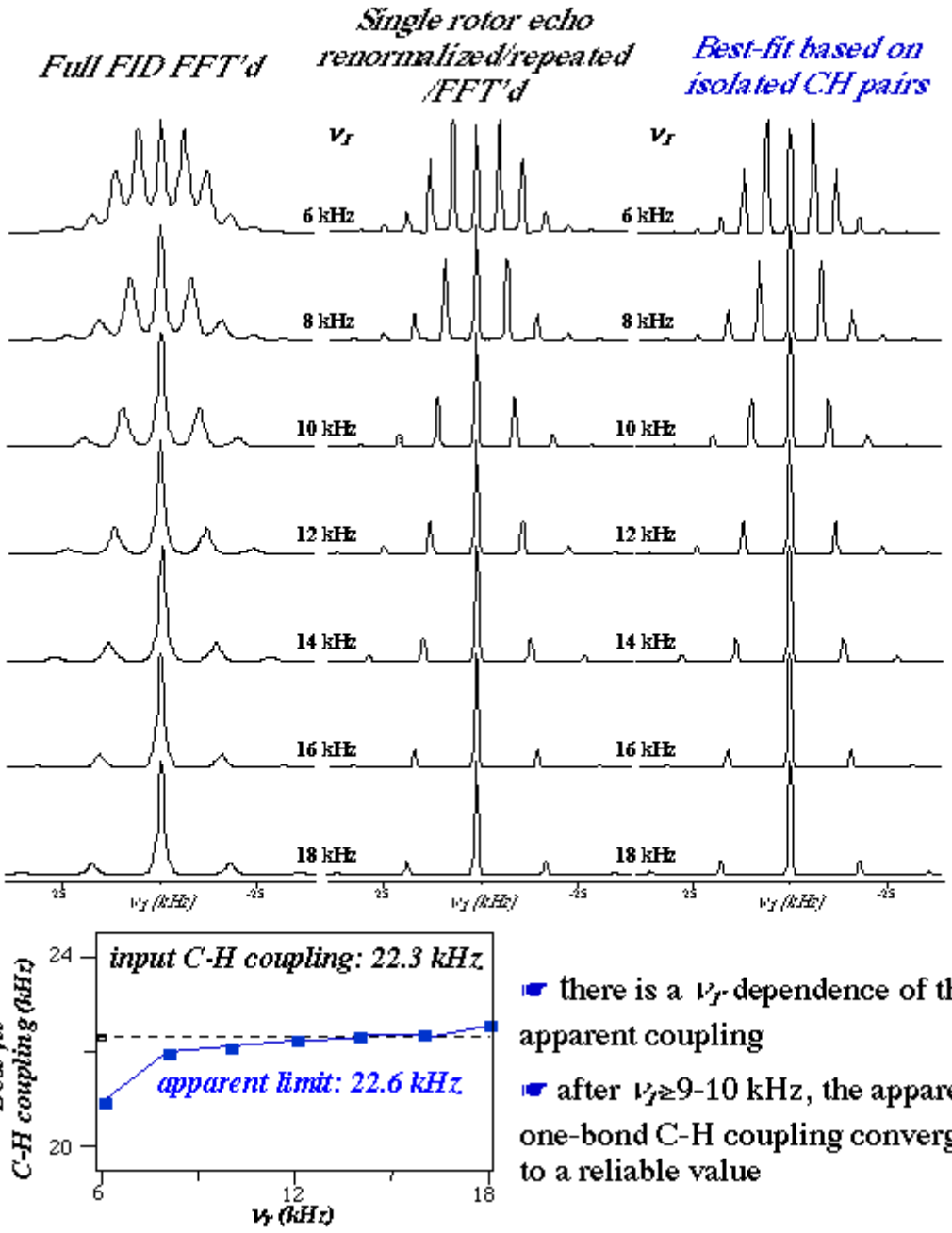
SLF data; site@167.1ppm



We investigate to what extend do these sidebands represent the actual, ideal ^{1}H-^{13}C expected dipolar evolution

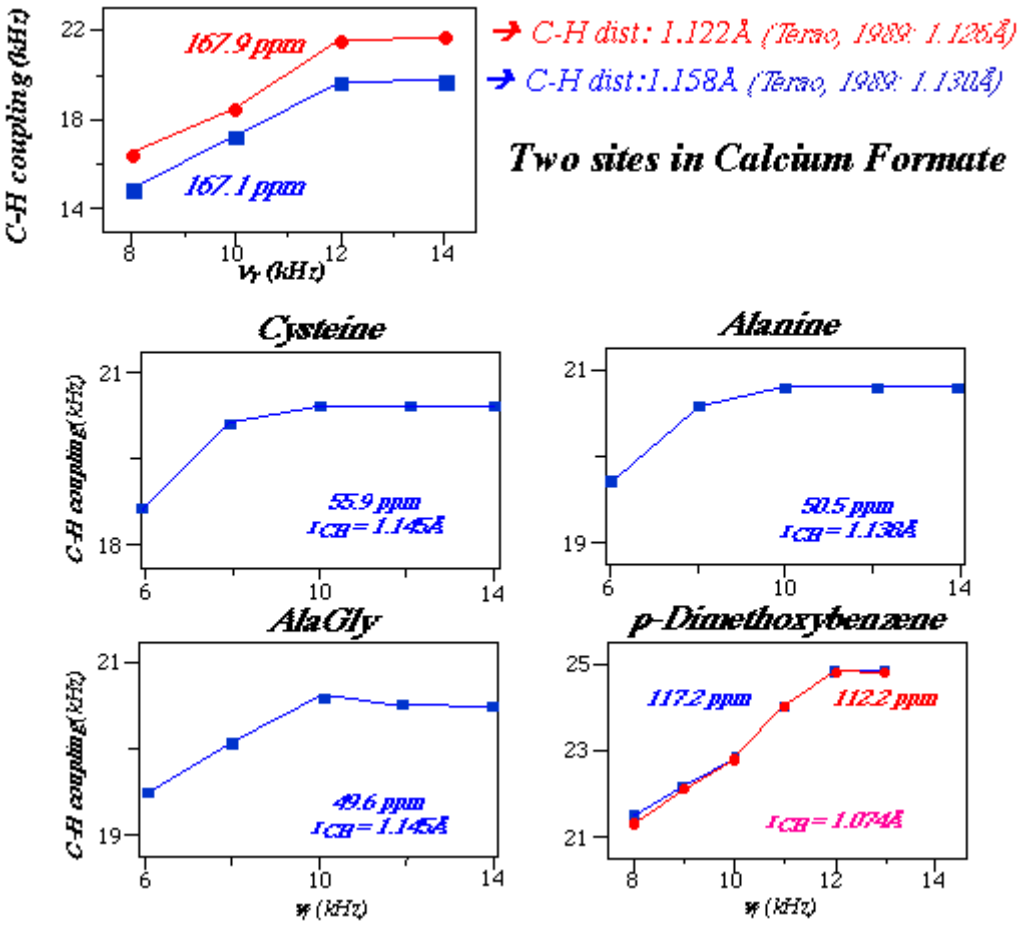
Patterns predicted from a 6-spin full-density-matrix simulation

(and found essentially independent of the actual molecular geometry)

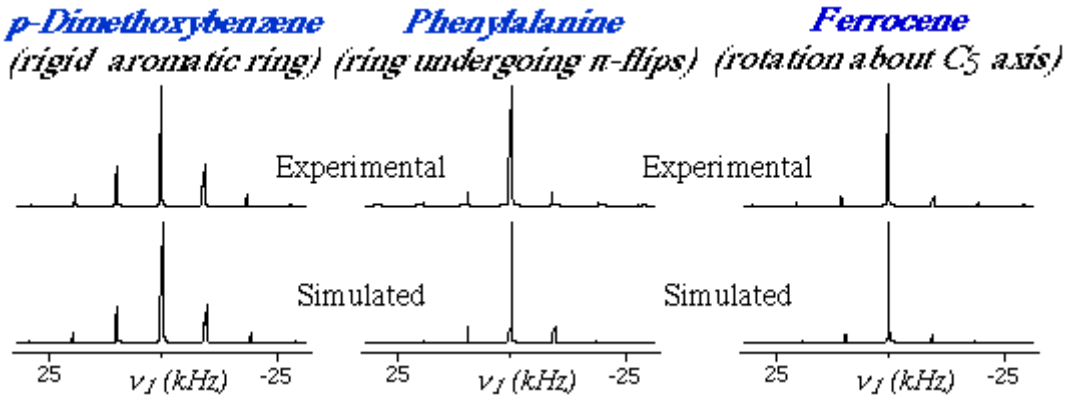


- there is a ν_1-dependence of the apparent coupling
- after $\nu_1 \geq 9$-10 kHz, the apparent one-bond C-H coupling converges to a reliable value

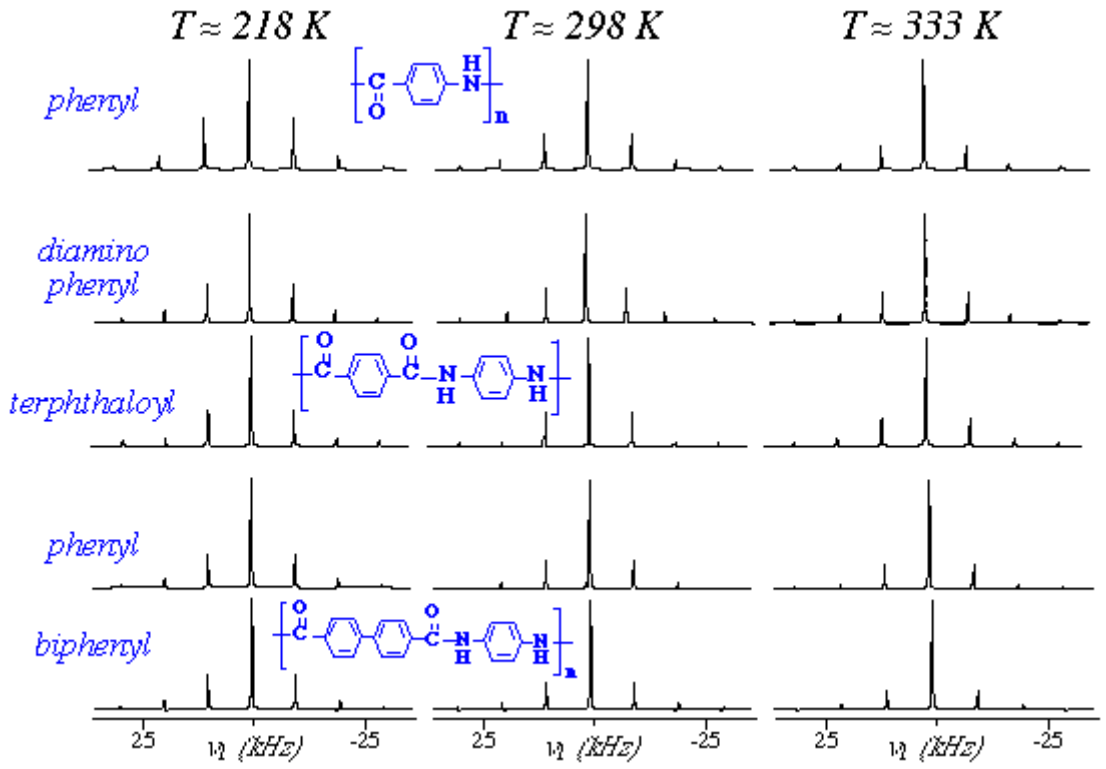
This is also the experimentally-observed behavior whenever analyzing methine groups



Such well-behaved dependence finds immediate applications towards the analysis of *molecular motions in organic solids*

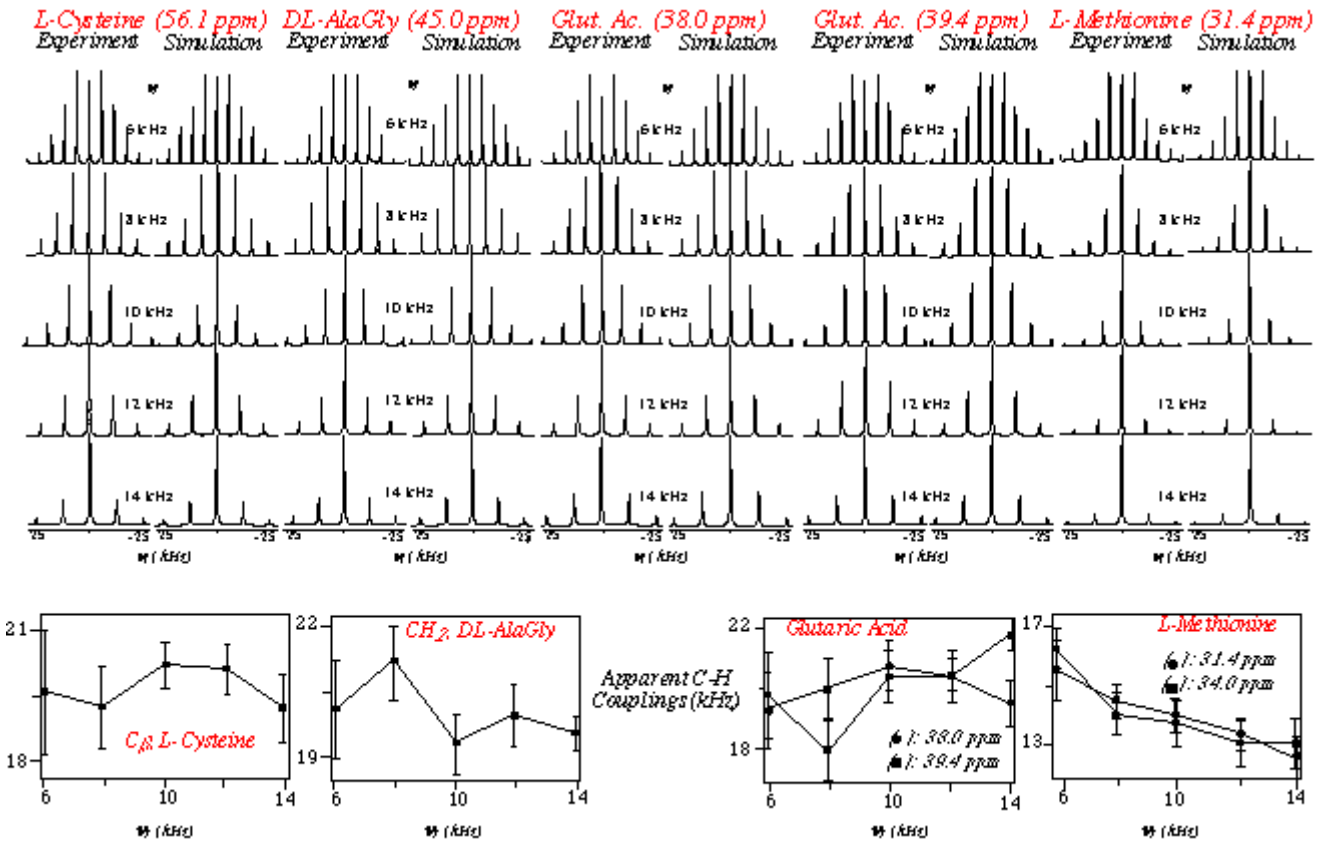


We exploit this potential to analyze a variety of motions in semicrystalline polymers. For instance in the case of aromatic polyamides



Will the same "trick" work as well for methylene groups, subject to strong intramoiety ^{1}H-^{1}H homonuclear dipolar couplings? Density matrix calculations reveal that the isolated heteronuclear pair assumption is still valid, even if the exact behavior is now semiquantitative

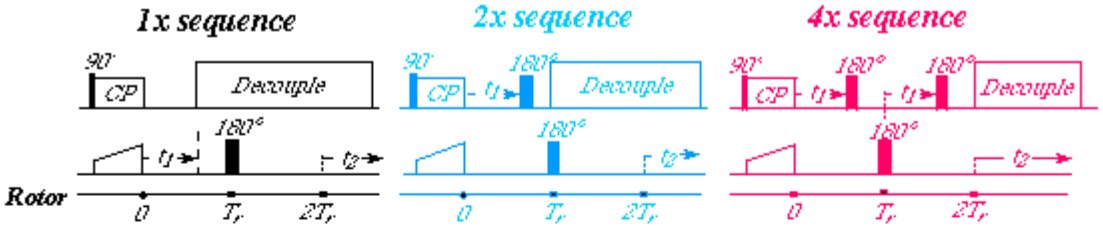
Some experimental spectra and their simulations based on solely ^{1}H-^{13}C heteronuclear couplings:



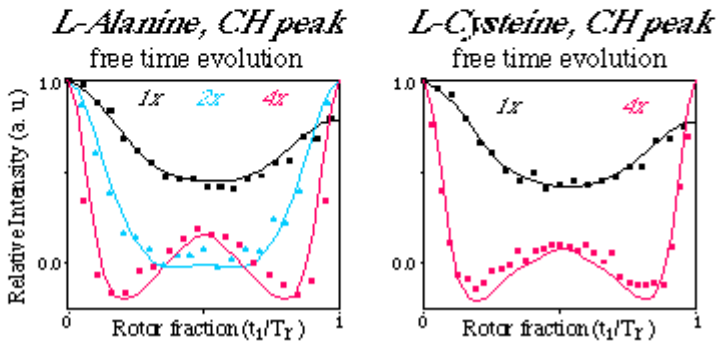
2. Extensions and Spectral Editing Applications in Organic Systems

A problem with these moderately-fast MAS SLF experiments is that as spinning rates increase, spectra become dominated by increasingly uninformative centerbands

Some alternatives for amplifying the effective dipolar/(spinning rate) ratio (Hong et al, 1987)

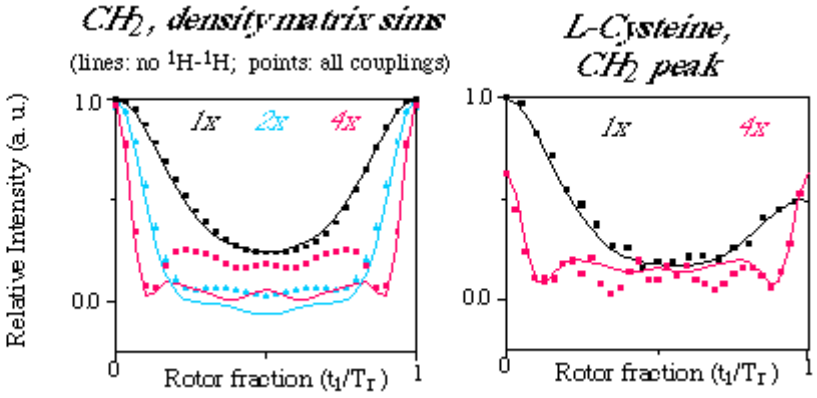


Experiments (points) agree well with the scaled expectations (lines) arising from purely heteronuclear dipolar evolutions, in spite of the absence of multiple-pulse decoupling.
$\nu_r = 14$ kHz
$r_{CH} = 1.12 \pm 0.01$ Å

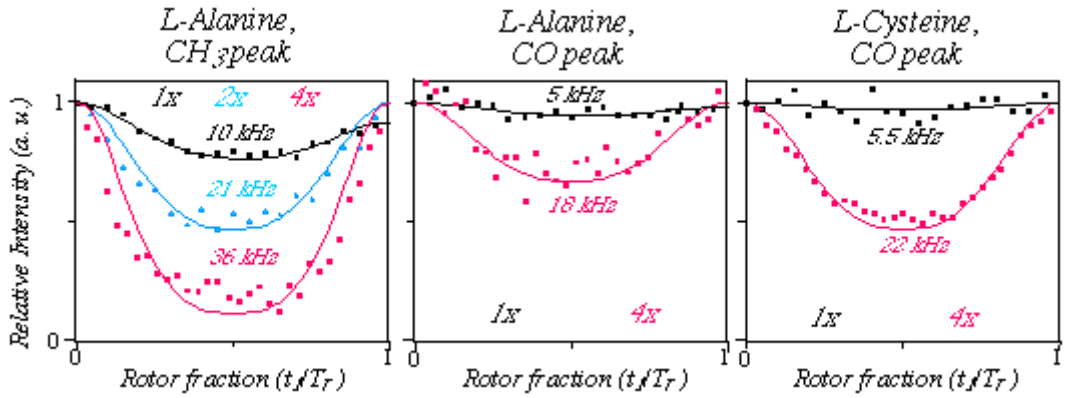


When extending these principles to methylenes, agreement with experiment is again acceptable at moderately fast spinning rates:

Experiments and full density matrix simulations (points) vs scaled expectations (lines) arising from purely heteronuclear dipolar evolutions. ($r_{CH} = 1.14$ Å)

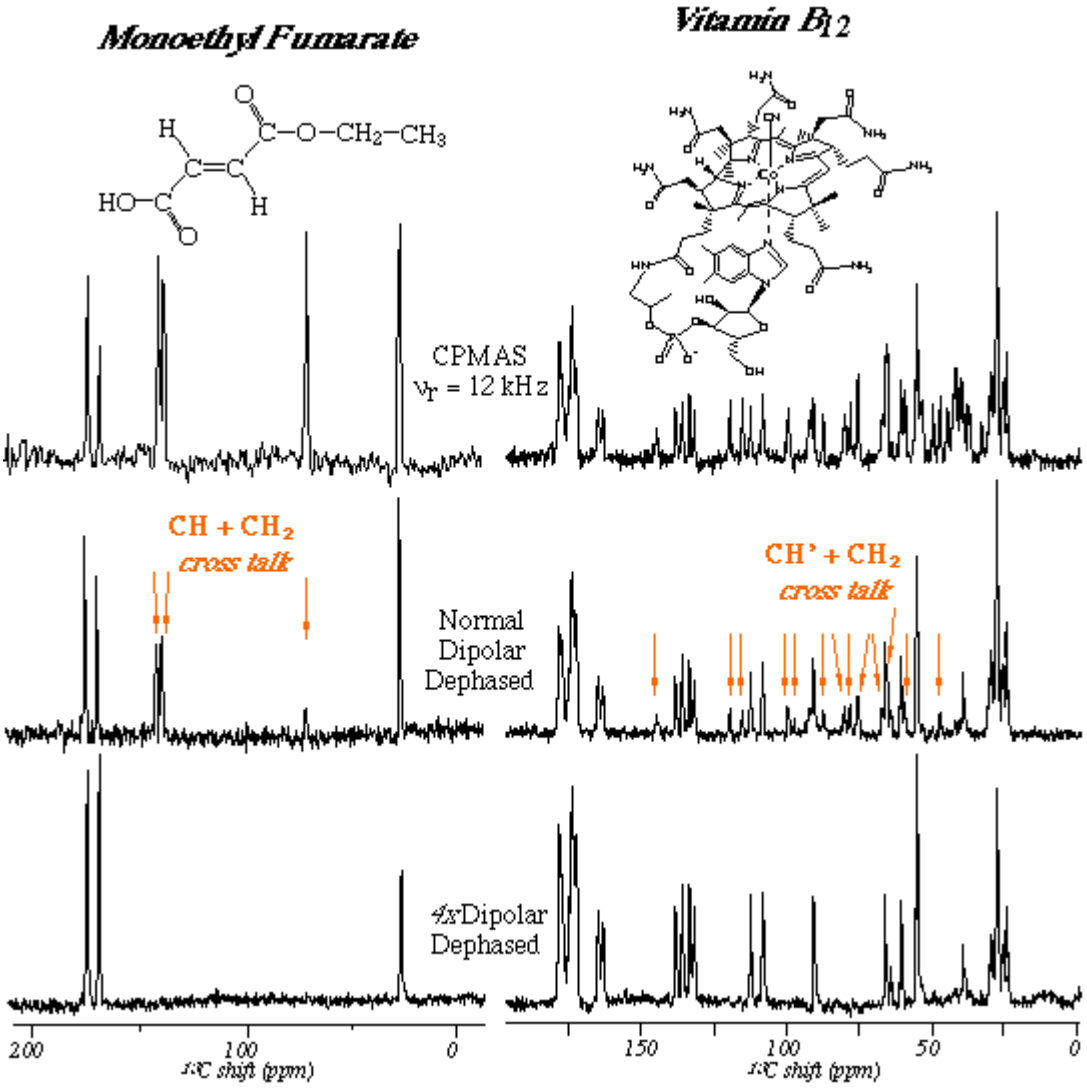


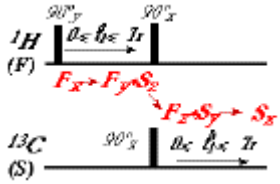
Even methyls and quaternary carbons can be distinguished in this fashion according the their amplified dipolar evolution behavior:



These considerations have immediate implications in spectral editing. For instance when it comes to carrying out dipolar dephasing at moderately fast spinning rates

(Opella & Frey, 1979)



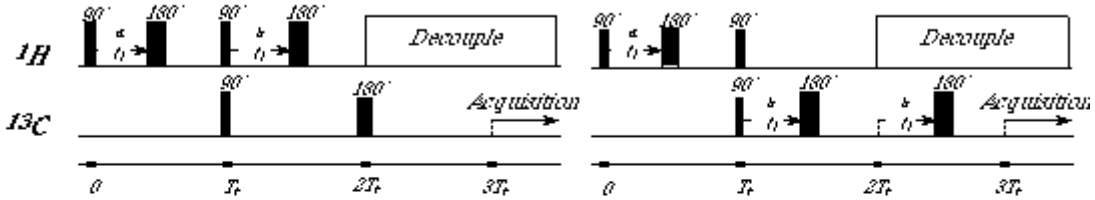


Another possibility opened up by these behavior involves carrying spectral editing in solids based on **INEPT-like transfer sequences**

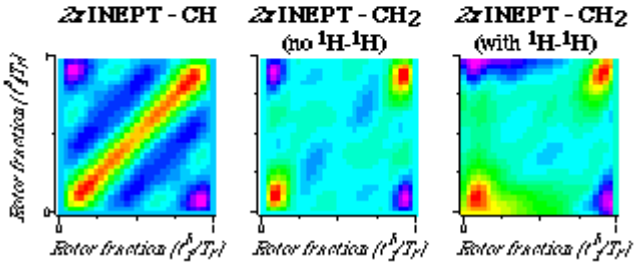
We observe a wide range of conditions where S/N is good, and methylenes can easily be distinguished from methines

Conditions that we assay to test these ideas

We operate at ν_r = 12-14 kHz and implement a 2x amplification of couplings



Calculated INEPT transfer function maps



By setting up these pulse sequences with $t_f = T_f/2$, we end up with a robust and sensitive way for identifying methylenes peaks