

Second Order Effects, Overtone NMR, and their Application to Overtone Rotary Recoupling of ^{14}N - ^{13}C Spin Pairs under Magic-Angle-Spinning

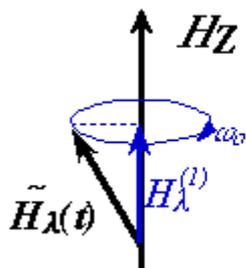
1. The NMR Interactions

NMR is defined by a series of interactions, each of them described in turn by a quantum mechanical Hamiltonian. These interactions describe internal fields such as the chemical shielding, the dipolar and J couplings between spins, and (for spins higher than 1/2) the quadrupolar couplings; they also need to describe external couplings such as those arising from the the external Zeeman magnetic field, and couplings arising between spins and the oscillating rf irradiation usually involved in NMR experiments:

THE NMR INTERACTIONS

$$H_Z(\text{dominant}), H_Q, H_D, H_J, H_{CS}, H_{RF}$$

Although the external couplings are needed for the realization of condensed phase NMR experiments, it is in the internal couplings that the chemical and structural information usually lies.



ZEEMAN TRUNCATION

Because of the conditions under which NMR signals are acquired, one doesn't really detect the internal interactions *but their effects in the presence of a dominating external magnetic field*. This strong, dominant coupling truncates the internal interactions, a process which can be visualized as resulting from the time dependencies that H_{CS} , H_D , H_J , H_Q acquire in the usual NMR rotating frame.

TO FIRST ORDER AND IN THE ROTATING FRAME:

$$H_\lambda^{(1)} = C_\lambda \times \text{Spatial (2nd-rank anisotropy)} \times \text{Spin } (S_z)$$

This linear approximation provides an excellent description of the NMR interactions, as long as all internal couplings $H_i \ll H_Q$. This is invariably the case, unless a strong interaction such as the quadrupolar coupling is involved.

When quadrupolar couplings are involved, a second order correction might be needed.

In Average Hamiltonian Theory this is given by the Hamiltonian>

$$H_{\lambda\lambda'}^{(2)} = \frac{-\omega_0}{4\pi} \int_0^{2\pi/\omega_0} dt \int_0^t [\tilde{H}_\lambda(t), \tilde{H}_{\lambda'}(t')] dt'$$

These terms are proportional to $C_\lambda C_{\lambda'}/\omega_0$ and mostly inconsequential except when $\lambda = Q$

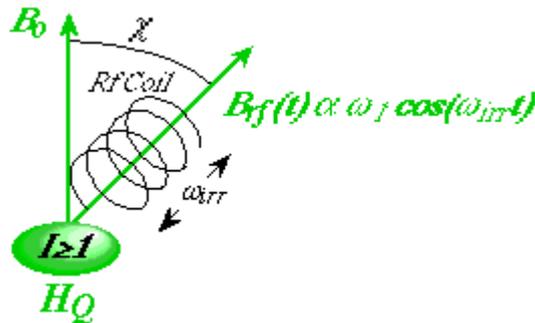
**INTERNAL
SECOND
ORDER
EFFECTS**

- $\lambda = \lambda' = Q$: Second order quadrupole effects
- $\lambda = Q, \lambda' = D$: Quadrupole-dipole effects (e.g., residual ^{13}C - ^{14}N splittings @ MAS)
- $\lambda = Q, \lambda' = CS$: Second order quadrupole-shielding effects

2. Overtone NMR

This study is concerned with the second order effects arising when irradiating a quadrupolar nucleus, between the external H_{RF} and the internal H_Q interactions.

Irradiation of a quadrupolar nucleus inside a moderate magnetic field



Multiple correlations are then found for $w_{irr} = n\omega_0, n = 0, 1, 2, \dots$

For $\omega_{irr} \approx 2\omega_0$

$$H_{Q,RF}^{(2)} = \frac{\sqrt{6}\chi_Q\omega_1}{\omega_0} \left[\left(R_{2-1}^Q \cos \chi + R_{2-2}^Q \sin \chi \right) I_+^2 + \left(R_{21}^Q \cos \chi + R_{22}^Q \sin \chi \right) I_-^2 + \dots \right]$$

This is actually equivalent to the **overtone excitation Hamiltonian**, first described in the context of NMR by Bloom, Tycko, Opella & coworkers in 1987.

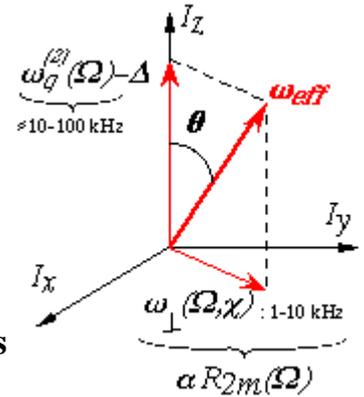
For the case of an $I = 1$ nucleus like ^{14}N :

$$H_{\text{nut}} = \begin{bmatrix} \omega_q^{(1)} + \omega_q^{(2)} - \Delta & 0 & \epsilon (R_{21}^Q \cos \chi + R_{22}^Q \sin \chi) \\ 0 & -2\omega_q^{(1)} & 0 \\ \epsilon (R_{21}^Q \cos \chi + R_{22}^Q \sin \chi) & 0 & \omega_q^{(1)} - \omega_q^{(2)} + \Delta \end{bmatrix}$$

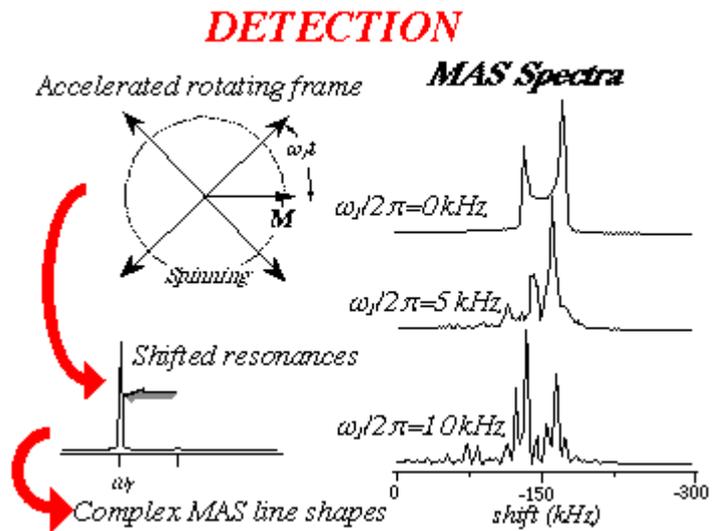
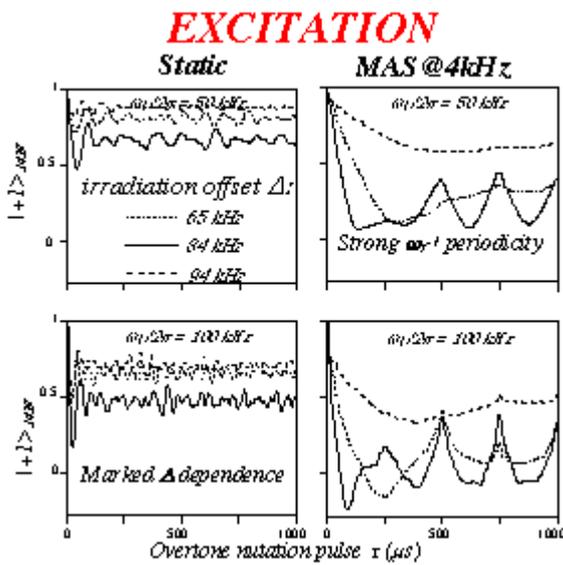
$(\epsilon = \sqrt{6} \omega_{FQ} / \omega_d)$

This irradiation affects solely the $I_z = |\pm 1\rangle$ eigenstates:
A fictitious spin-1/2 subspace where first order quadrupole effects are irrelevant

Still, this overtone excitation & observation over a powdered sample results in a small fraction of the total available signal (1-5%) because of the small effective irradiation and detection coupling strengths.



Some basic features of overtone excitation and detection processes



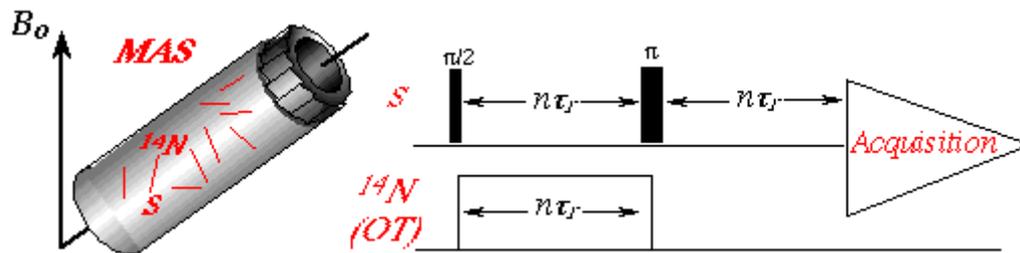
3. Overtone Rotary Recoupling (ORR)

Although direct overtone detection is impractical, the marked rotor dependence of the overtone excitation can be exploited for the efficient dipolar recoupling of nearby (S) nuclei undergoing MAS:

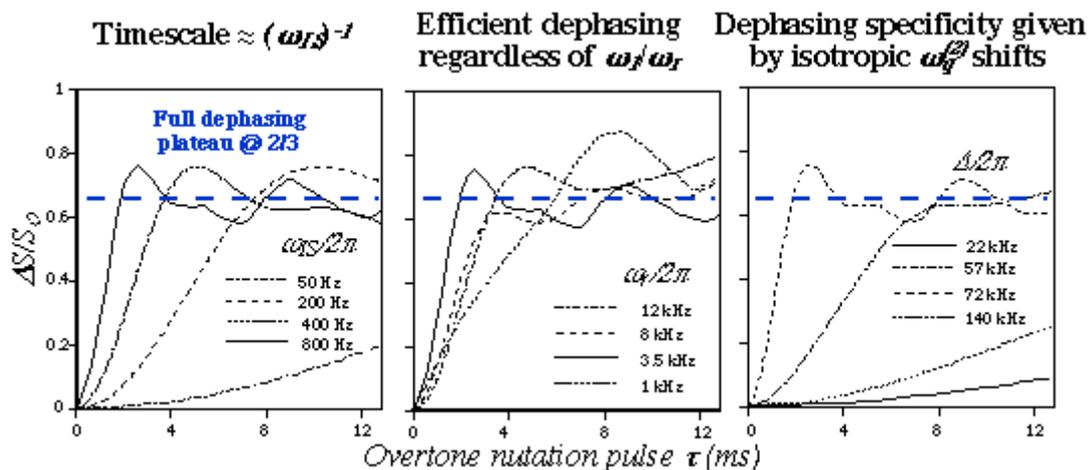
$$H_D(S-^{14}N) = \text{Dipolar anisotropy}(t) \times S_z \times ^{14}N_z(t)$$

@MAS: both periodic modulo ω_r^{-1}

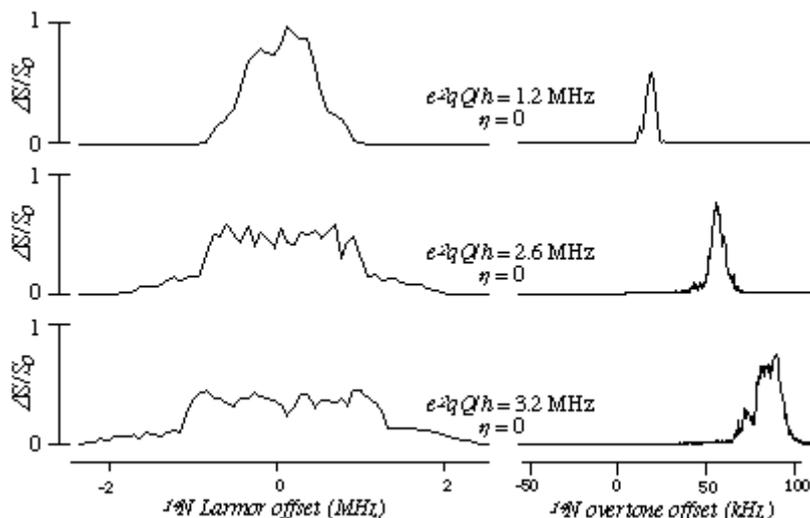
net coupling $\neq 0$ over each rotor period



An exact analysis of the ORR recoupling can be carried out in a straightforward manner on the basis of Bessel functions. Some of the characteristics then resulting for the ORR recoupling curves

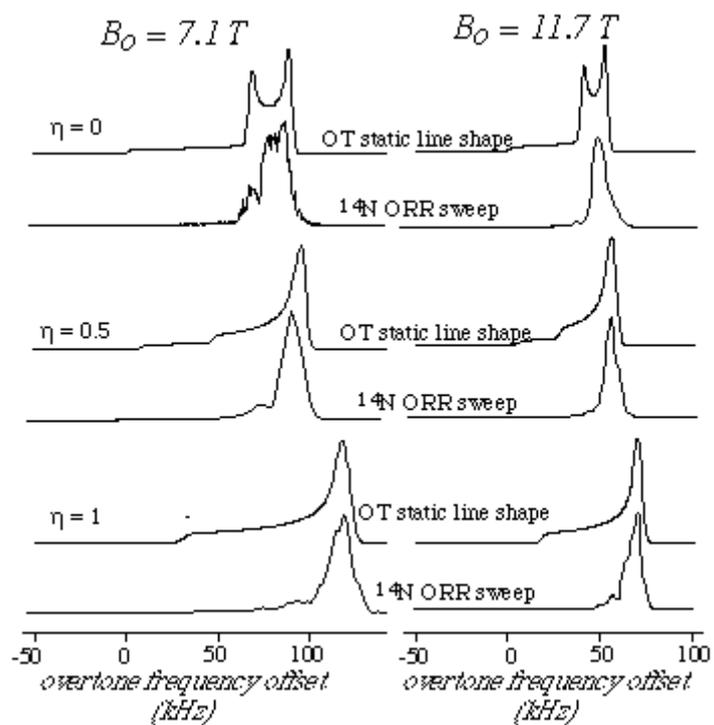


At full dephasing conditions, the relative efficiencies of Larmor vs. Overtone recoupling (i.e., TRAPDOR vs. ORR experiments) depend on the strength of the quadrupolar coupling:



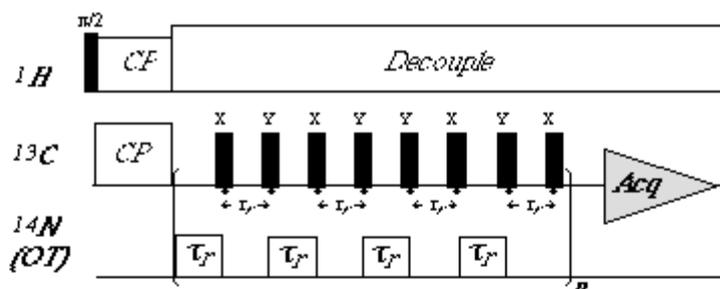
ORR's offset sensitivity then enables a mapping of ^{14}N second-order lineshapes:

INDIRECTLY DETECTED OVERTONE SPECTROSCOPY

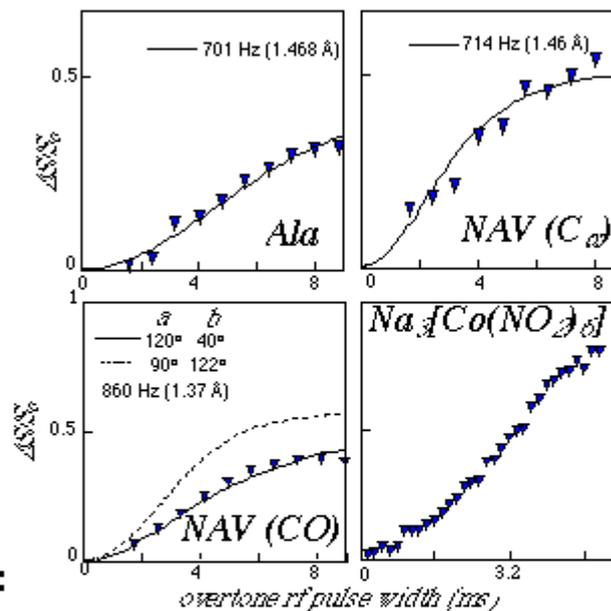


4. ORR NMR: Experimental Results and Interpretations

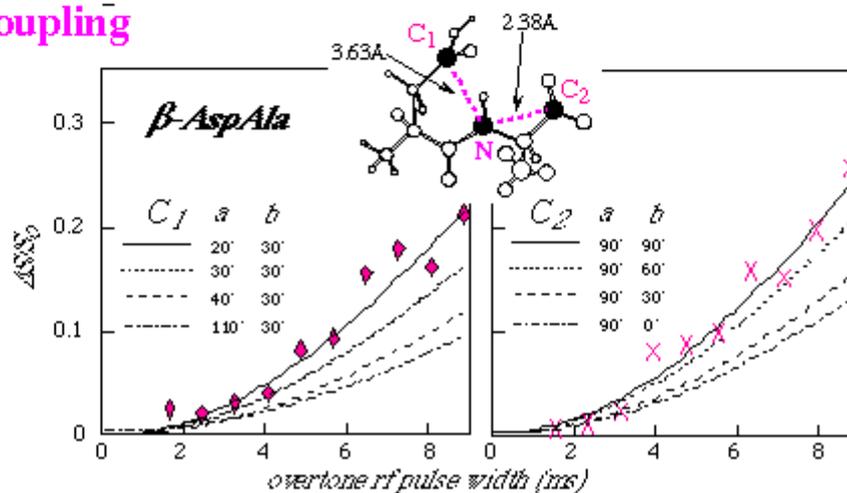
Tests on
natural
abundance
 ^{13}C - ^{14}N



Directly bonded
spin pairs
(optimized offsets)



Remote spin pairs:
specific ^{14}N -amide
recoupling



VARIABLE-OFFSET ORR: HIGH RESOLUTION S-14N 2D CORRELATIONS

ORR with dephasing fixed at 8ms ($\approx \omega_{IS}^{-1}$); offset Δ swept in 2 kHz steps

Experimental — Single-pair simulations —

