Linewidths in DAS (Homonuclear Dipole-Dipole Interaction)

In this section, the contribution of the homonuclear dipole-dipole interaction to dynamic-angle spinning spectra will be discussed. Remember, the form of the static homonuclear dipolar Hamiltonian from equation 2.48.

$$H_D = -\sum_{j \neq i} \hbar \omega_{D_{ij}} \tfrac{1}{2}\left(3 I_{i,0} I_{j,0} - I_i \cdot I_j\right) d^{(2)}_{0,0}\left(\beta^D_{ij}\right) \tag{3.34}$$

Under rapid spinning conditions, this may be expressed below.

$$\begin{aligned} H_D &= -\hbar \sum_{j \neq i} \omega_{D_{ij}} \tfrac{1}{2}\left(3 I_{i,0} I_{j,0} - I_i \cdot I_j\right) \sum_{m=-2}^{2} D^{(2)}_{m0}\left(\omega_r t + \phi_r, \theta, 0\right) D^{(2)}_{0,m}\left(\alpha^D_{ij}, \beta^D_{ij}, \gamma^D_{ij}\right) \\ &= -\hbar\, d^{(2)}_{00}(\theta) \sum_{j \neq i} \omega_{D_{ij}} \tfrac{1}{2}\left(3 I_{i,0} I_{j,0} - I_i \cdot I_j\right) d^{(2)}_{0,0}\left(\beta^D_{ij}\right) \end{aligned} \tag{3.35}$$

This Hamiltonian will allow the coherence, which until this point has been assumed to be between −1 and +1, to evolve into higher order bilinear coherences. The homonuclear dipolar contribution to the isotropic linewidth in a DAS spectrum arises since the storage pulses used during a hop cannot store bilinear terms. Also, the reduced Wigner matrix element $d^{(2)}_{00}(\theta)$ indicates that the spinning merely scales the entire interaction, under the time independent approximation (and under high speed magic-angle spinning, all dipolar couplings are scaled to zero). Since the sign of $P_2\left[\cos\left(\theta_i\right)\right]$ is reversed (see equation 3.7) following a hop from the DAS angle θ_1 to θ_2, and if the density matrix describing the system was the same before and after the hop, all dipolar contributions to the isotropic spectrum would be refocused at the DAS echo top. Unfortunately, the density matrix is not the same before and after the hop and the homonuclear dipolar interaction continues to dephase in the isotropic t_1 time domain, rather than refocus. An approximation which describes the dipolar dephasing of a static on-resonance homonuclear bath of spins is a Gaussian decay

$$S(t) = \exp\left(-M_2 t^2 / 2\right), \tag{3.36}$$

where M_2 is the second moment as defined by Van Vleck[87]. Under fast spinning VAS conditions, the effective dipolar coupling is scaled by $P_2\left[\cos\left(\theta_i\right)\right]$ and therefore the effective second moment is $M_2 P_2^2\left[\cos\left(\theta\right)\right]$. The signal function for an on-resonance spin would then be

$$S(t) = \exp\left(-M_2 P_2^2\left(\cos\theta\right)t^2/2\right). \tag{3.37}$$

Figure 3.14 shows the dipolar linewidth of both ^{23}Na and ^{87}Rb nuclei in sodium oxalate and rubidium perchlorate respectively under rapid VAS conditions. The linewidth was measured from the homogeneously broadened isotropic spectrum collected by Fourier transforming the echo tops at $t_2 = t_1$ of a 90˚ - t_1 - 180˚ - t_2 experiment (where the dwell time in t_1 was equal to the rotor period). The curves in both cases correspond to the function $\left|C_D P_2\left[\cos\left(\theta\right)\right]\right|$. where C_D is the static homogeneous linewidth. Notice that the linewidth goes nearly to zero at the magic angle (54.74˚) in both cases. This indicates that, at a spinning speed of approximately 6 kHz, the homonuclear dipolar coupling is well described by equation 3.35 and 3.37.

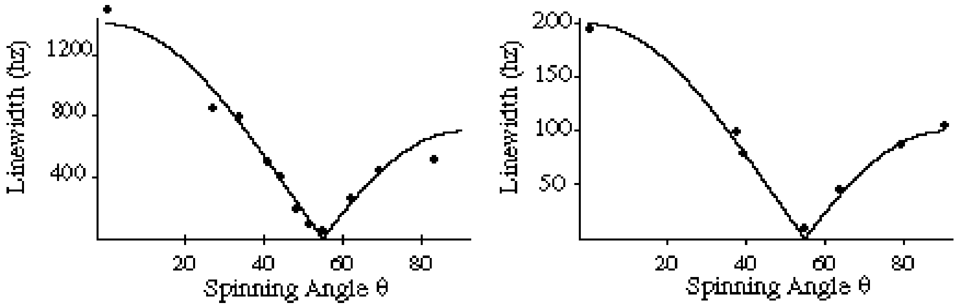

Figure 3.14 Homonuclear Dipolar Linewidth versus Spinning Angle. The left set corresponds to $Na_2C_2O_4$ ^{23}Na linewidth as a function of angle where the static linewidth is 1400 Hz. The right set corresponds to $RbClO_4$ ^{87}Rb linewidth as a function of angle where the static linewidth is 195 Hz.

In a DAS experiment, the signal of an on-resonance spin can be expressed as the product of two Gaussian decays at two different angles.

$$\begin{aligned} S(t_1) &= \exp\left(-M_2 P_2^2(\cos\theta_1)\left(\tfrac{t_1}{k+1}\right)^2 \Big/ 2\right)\exp\left(-M_2 P_2^2(\cos\theta_1)\left(\tfrac{kt_1}{k+1}\right)^2 \Big/ 2\right) \\ &= \exp\left(-M_2^{eff} t_1^2/2\right) \end{aligned} \tag{3.38}$$

For the DAS angle pairs, θ_1 and θ_2, the value of $P_2[\cos(\theta)]$ can be expressed in terms of k where $P_2[\cos(\theta_1)] = \sqrt{k/5}$ and $P_2[\cos(\theta_2)] = -\sqrt{1/5k}$. This yields an effective second moment for the isotropic line in the DAS experiment of $M_2^{eff} = 2kM_2/5(k+1)^2$ giving a linewidth of approximately $\sqrt{2kM_2}/\sqrt{5}(k+1)$. The narrowest line in a conventional DAS experiment should therefore arise when the $k = 5$ angle pair, 0˚ - 63.43˚, is used and should be about 75% of the linewidth for a $k = 1$ experiment.

For the isotropic linewidth measurements, samples of sodium oxalate, $Na_2C_2O_4$ and rubidium perchlorate, $RbClO_4$, were obtained from commercial sources while the deuterated boric acid, D_3BO_3, was made by exchanging the protons in H_3BO_3 in D_2O, both commercially obtained. The experiments were performed at 11.7T (^{87}Rb frequency 163.623 MHz, ^{23}Na frequency 132.201 MHz, ^{11}B frequency 160.446 MHz) with the same probe as before. The pulse sequence used for DAS was the original sequence. The selective 90˚ times were between 4 and 8 μs and the recycle delays were between 1 and 4 s. The spinning speeds were between 5.0 and 7.0 kHz which effectively removed all spinning sidebands from these spectra. The spectral widths were set to 10 kHz and between 256 and 1024 scans were acquired for each of 60 t_1 points at each k value.

The dipolar linewidths for $Na_2C_2O_4$, $RbClO_4$ and D_3BO_3 are shown in figure 3.15 for a range of k values from 0.8 to 5. It is always true that the linewidth at $k = 5$ is about 20% less than at $k = 1$, in agreement with the theory presented earlier. The solid curves through these data points are the best fit using the function

$$\Delta\omega_{isotropic} = \Delta\omega_{T_2} + \frac{\sqrt{2kM_2}}{\sqrt{5}(k+1)} \qquad 3.39$$

where M_2 is the second moment due to homonuclear dipolar interactions in a static sample and $\Delta\omega_{T_2}$ is the intrinsic linewidth due to field inhomogeneity and T_2 relaxation.

The values for M_2 extracted in this manner are very similar the those extracted from static CPMG experiments. This further confirms that the $k = 5$ angle pair is the best angle pair to perform the DAS experiment.

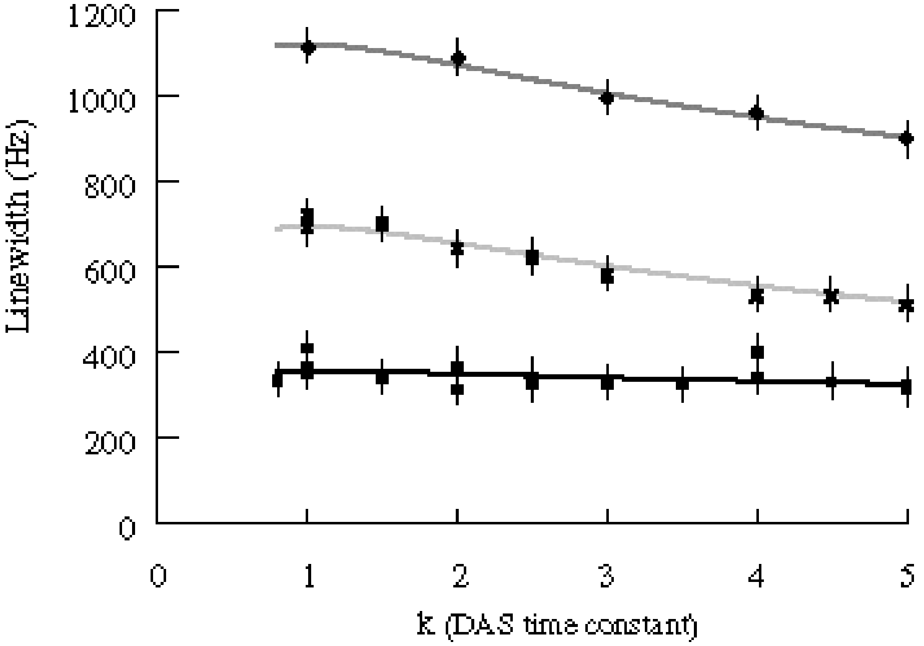

Figure 3.15 Dynamic-Angle Spinning Linewidths as a function of *k*. The solid circles are for D_3BO_3, the crosses are for $Na_2C_2O_4$ and the solid boxes are for $RbClO_4$. The lines through each set of points are the best fit with the linewidth function given by equation 3.39.