ABSTRACT

The CP/MAS spectra of spins-1/2 directly bonded to a quadrupolar nucleus (for example, ^{13}C coupled to ^{14}N) often show fine structure, due to dipolar coupling. As the magnetic field is increased, splittings decrease and disappear. For the ^{13}C - ^{14}N system, spectra appear as doublets with an intensity ration of 1:2. The mechanism for this is well-understood. Internuclear dipolar coupling, normally averaged out by spinning, appears because the ^{14}N nucleus is not quantized exactly along the static magnetic field - the molecule-fixed quadrupolar interaction is not negligible compared to the lab-frame Zeeman interaction. Sample spinning cannot remove dipolar coupling if the quantization direction depends on molecular orientation.

While the principle is clear, a fully-detailed theory is lacking. Perturbation theory or average Hamiltonian theory work well if the quadrupolar interaction is small, or is very large, with respect to Zeeman term. However, there is little available that permits the calculation of the full spinning sideband spectra for all strengths of the quadrupolar interaction.

In this paper, the spin system is solved exactly, by full matrix diagonalization, for a given orientation. This involves a careful analysis of the definition of quantization. Floquet theory is adopted to handle sample spinning – the time-dependent Hamiltonian is replaced by an expanded time-independent "Floquet" Hamiltonian. Due to the time-dependent quantization direction resulting from quadrupolar coupling, off-diagonal blocks must be computed by numerical Fourier transformation. Once the Floquet matrix is set up, and dephasing of coherences accounted, the result is a comprehensive means of simulating spectra, valid for all ranges of parameters.