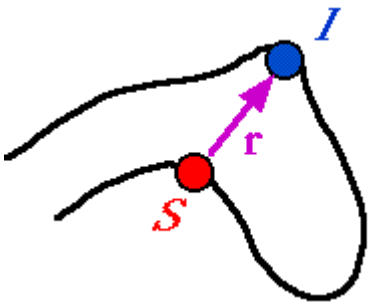
4. DISTANCE MEASUREMENTS IN SOLIDS: THE DEAR NMR EXPERIMENT

We have recently introduced a new approach for determining internuclear distances in solids by means of NMR. This method can reveal the structure of complex chemical systems without the single-crystal limitations faced by diffraction techniques.

Solids NMR measures distances by relying on dipolar interactions:

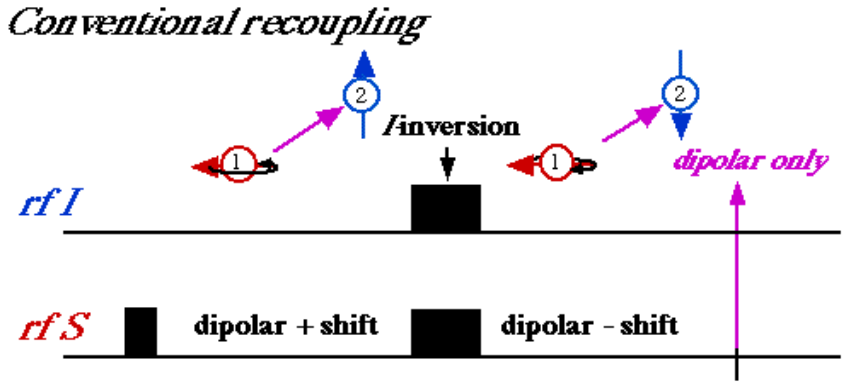


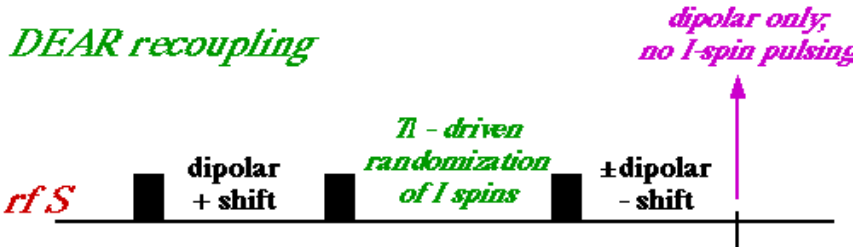
Dipolar interaction α r^{-3}

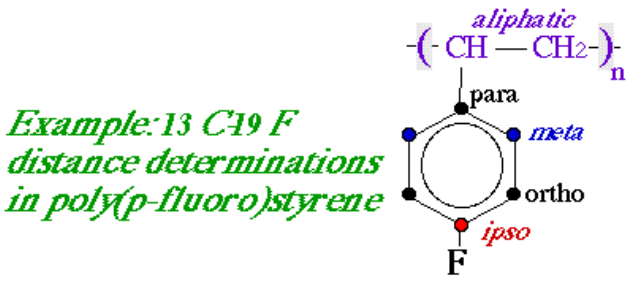
Methods developed so far for determining these dipolar couplings require irradiation of both the *I* and *S* spins. This complicates their application to the analysis of organic & biological systems where a third irradiation source for proton decoupling becomes necessary, as well as to spin pairs involving quadrupolar nuclei which are of difficult or impossible manipulation.

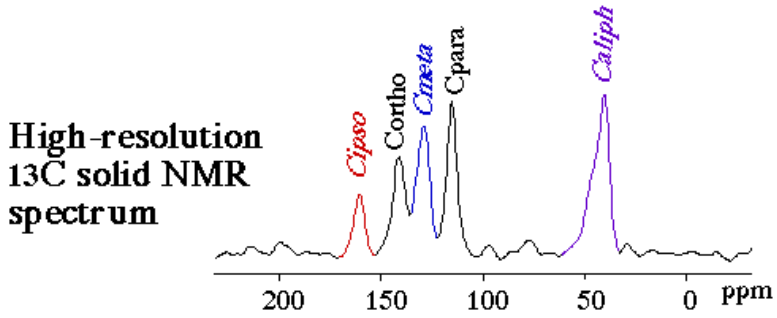
We have developed an alternative distance measurement approach, Dipolar Exchange-Assisted Recoupling (DEAR), that by avoiding the irradiation of one of the spins in the pair does not suffer from any of these complications.

DEAR exploits the fact that natural relaxation processes induce on one of the members of the spin pair (e.g., *I*), transitions that are closely analogous to those induced by coherent irradiation. The rate at which this relaxation occurs is given by $(T^I)^{-1}$

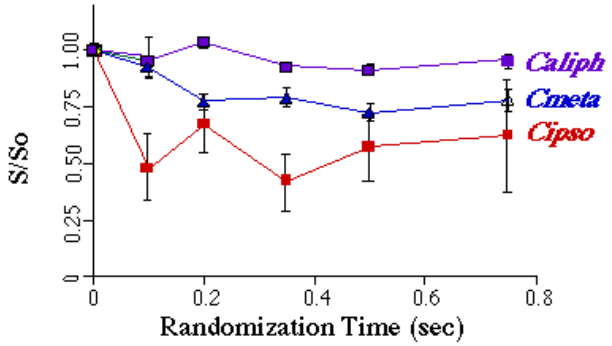








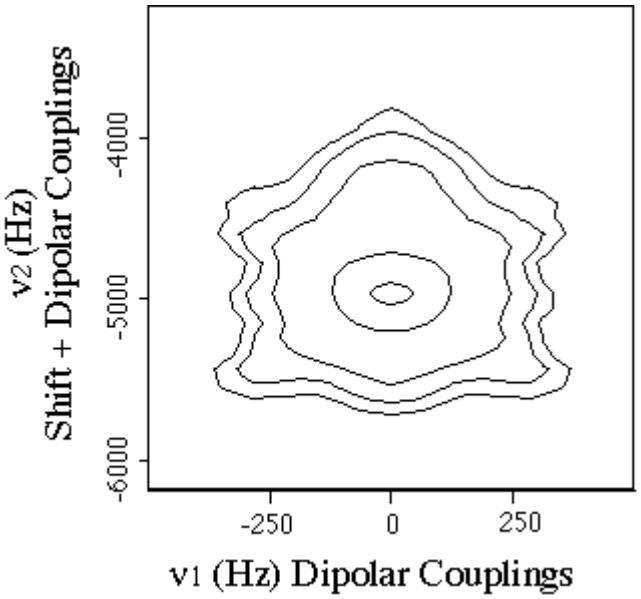
DEAR decay curves:



The rate and extent of the decays unambiguously map the internuclear distances

By correlating chemical shift and dipolar interactions, 2D NMR versions of DEAR may allow one to find relative orientations between molecular groups.

Example: ^{13}C-^{14}N pairs in DL-alanine



The shape of this contour plot depends on the Euler angles relating the chemical shift and dipolar tensors

Furthermore, by endowing these 2D NMR experiments with an additional high-resolution dimension, their application to the analysis of multi-site systems becomes feasible