NUCLEAR SPIN SINGLET STATE RELAXATION MECHANISMS FROM EXPERIMENT AND MOLECULAR DYNAMICS SIMULATIONS

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Nuclear spins states have been shown to exceed spin-lattice relaxation times several fold, with impressive demonstrations of singlet lifetimes of more than an hour in organic molecules in solution. Over the years, several relaxation mechanisms have been identified, including dipolar coupling, chemical shift anisotropy, paramagnetic relaxation, spin rotation and spin-internal motion, and the scalar relaxation of the second kind. While in principle, many of the mechanisms are well understood, estimating their size can be difficult. Furthermore, multiple experimental examples have been found that decidedly defy expectations.

We present here work on directly estimating singlet relaxation mechanisms from molecular dynamics simulations. Here we show calculations for intermolecular mechanisms and find good agreement with experiment. It is particularly surprising to see that such mechanisms as intermolecular coupling to ^{35}Cl and ^{37}Cl nuclear spins (of the chloroform solvent) could be rate limiting for singlet states. In addition, we also show work on ^{31}P spin singlets, and compare their lifetimes to those from molecular dynamics trajectories and ab initio calculations of chemical shift anisotropy tensors, which show good agreement.

Calculations of this sort may help in the design of particularly long-lived singlet states, or could be used to identify new probes for dynamics.