Enhancement of singlet-order at natural abundance in a large spin system via bang-bang optimal control

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Not many experimental architectures allow as elaborate control of quantum dynamics as that of NMR. Several powerful RF optimal control techniques have been developed to efficiently control the spin dynamics for spectroscopy as well as quantum information processing purposes. Generally, the numerical complexity of optimal control techniques scales rapidly with the size of the spin system, thus limiting their applications. In this work, we use bang-bang (BB) optimal control that utilizes a sequence of full power radio frequency (RF) pulses with variable phases separated by variable delays [1, 2]. It relies on one-time matrix exponentiation to build basic unitaries, and hence its complexity scales much slower and therefore is applicable also for fairly large spin systems.

Long-lived singlet-order has gained significant theoretical and experimental interest due to its wide range of applications in NMR [3]. It is very difficult to observe ^{13}C -^{13}C singlet-order at natural abundance of ^{13}C where ^{13}C -^{13}C pair appears with a probability of 0.011% [4]. One way to enhance the singlet-order is through polarization transfer if the singlet-pair is connected to a set of ancillary spins. In this work, we utilize the BB control to directly transfer polarization from nine chemically equivalent ^{1}H spins to the long-lived singlet-order of a pair of naturally abundant, weakly coupled ^{13}C spins of 1,4-Bis (trimethylsilyl) butadiyne. Compared to the standard method [5] not involving polarization transfer, we find an enhancement of singlet-order by about 3.4 times. Also, since the singlet magnetization is contributed by the faster relaxing protons, the recycle delay is halved. Thus effectively we observe a reduction in the overall experimental time by a factor of 23. We also compare the enhancement of singlet-order achieved (1) using BB direct polarization transfer scheme and (2) using INEPT polarization transfer followed by standard singlet sequence [5]. Because of its comparatively high robustness against magnetic field inhomogeneity BB direct polarization transfer scheme performs better than the later. Exploiting the enhanced sensitivity, we investigated the decay of the singlet-order under spin-lock and found it to be three to four times longer lived compared to individual spin-lattice relaxation time constants (T_1) of each carbon. Since T_1 of faster relaxing protons is smaller than singlet-order lifetime, we also discuss the possibility of iterative polarization transfer where singlet-order stores the polarization while protons re-thermalize with the bath for further transfer of polarization.

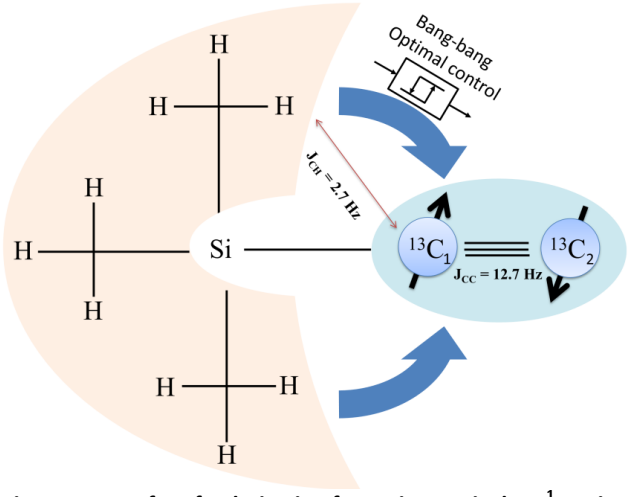

Figure 1. **Transfer of polarization form nine equivalent ^{1}H spins to singlet-order of ^{13}C - ^{13}C spin-pair at natural abundance in 1,4-Bis (trimethylsilyl) butadiyne using bang-bang optimal control. Chemical shift difference between two carbons is 2.32 ppm.**

References:

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