

# Longer-lived Singlets in Chemically Equivalent Systems

Pairs of chemically equivalent (or nearly equivalent) spins have been shown to create disconnected eigenstates which are very long lived, yet accessible by pulse sequences. Here we extend the classes of known molecules with long-lived states to include deuterium substitution, and this significantly broadens the applicability of hyperpolarization.

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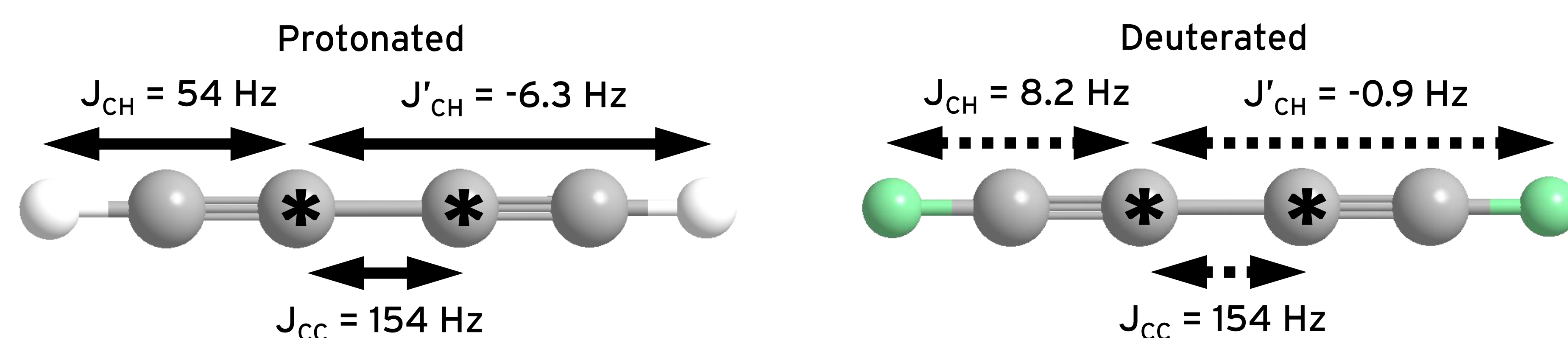
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## Objectives: Duration & Diversity

Chemically equivalent singlet states are stable when  $J_{CC} \gg J_{CX}$ .

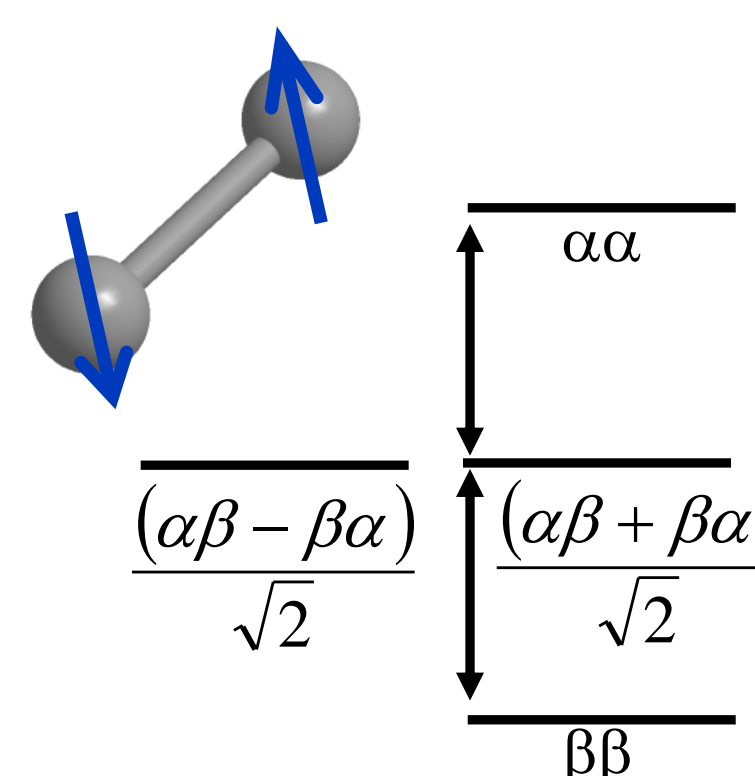
Since  $J_{CD} \ll J_{CH}$ , the singlet state is more nearly an eigenstate and can persist for longer.



Directly bonded hydrogens typically have  $J_{CH} > J_{CC}$ ; creating an unstable singlet.

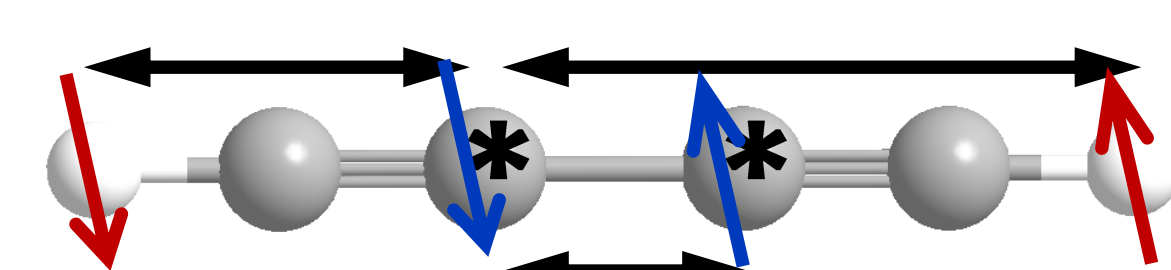
Since  $J_{CD} \ll J_{CH}$ , we can create singlet states between <sup>13</sup>C and directly bonded <sup>2</sup>H. This opens up a much wider array of potential singlet-state supporting molecules.

## Accessing the Singlet State



In a chemically equivalent system, such as parahydrogen (right), the singlet state is disconnected from the MR accessible triplet states and persists almost indefinitely.

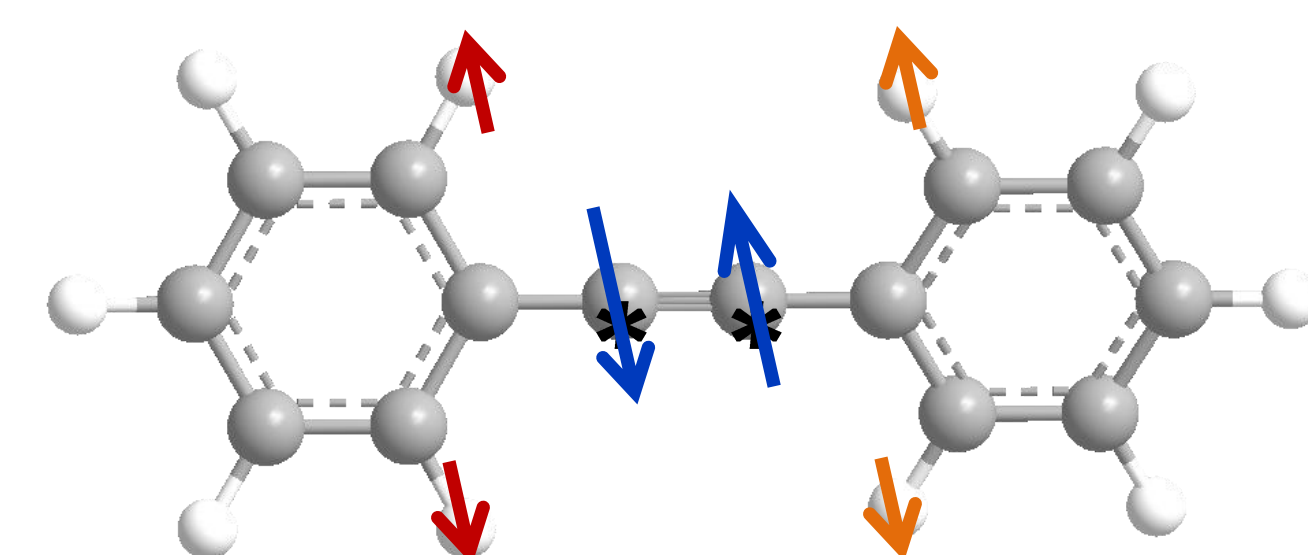
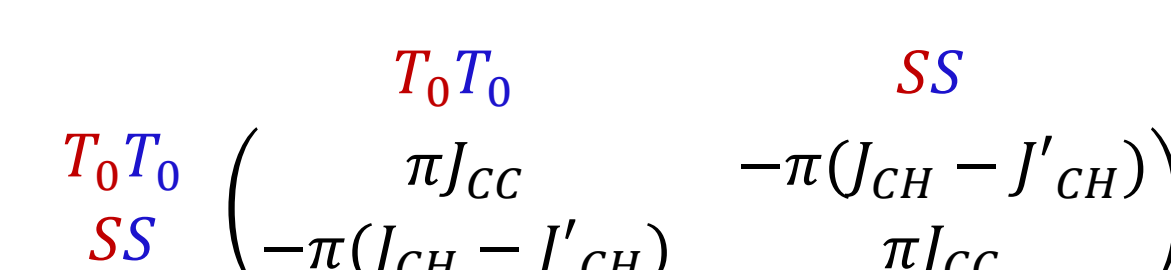
But how can we make singlet states on demand if they're not directly accessible?



The answer is to take advantage of a  $J$ -coupling network.

In protonated diacetylene (right) we can write the carbon and proton states in the singlet-triplet basis.

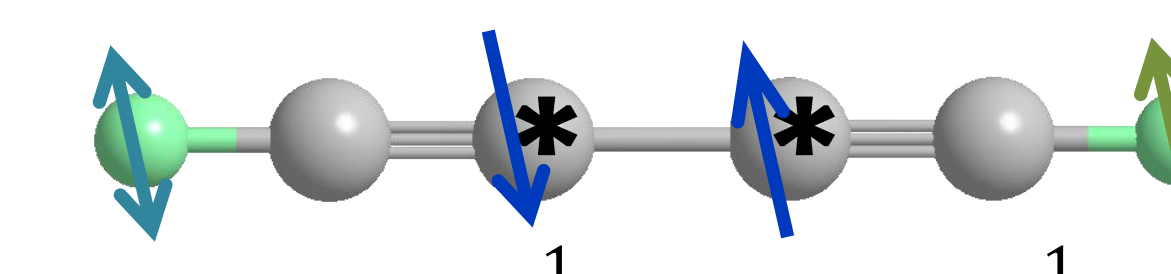
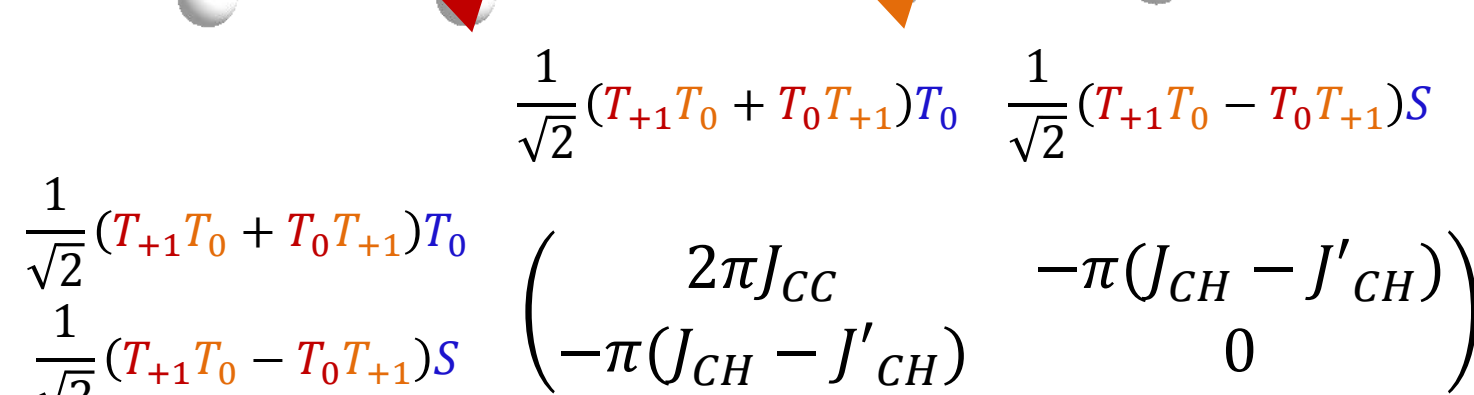
In this basis, we can see that there is a 2-level system where the  $J$ -coupling difference connects the MR accessible triplet to the long lived singlet.



This works in more complicated spin systems as well.

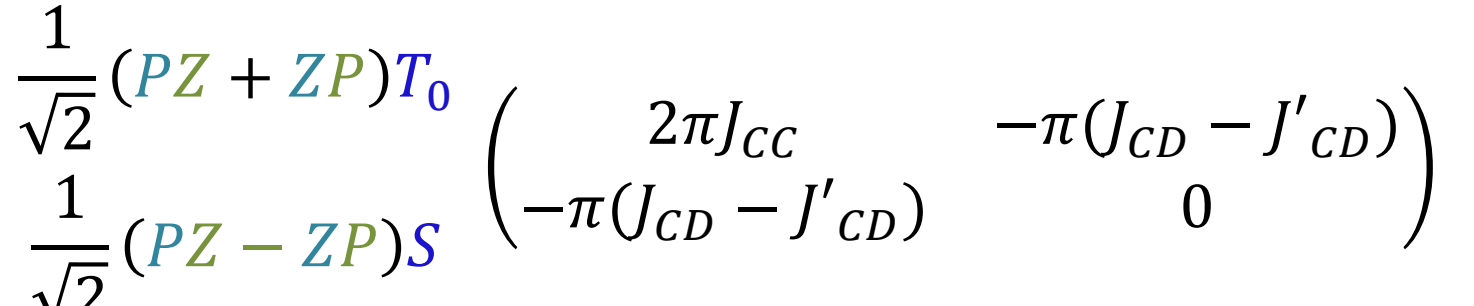
Here, we write the two closest ring protons in the singlet-triplet basis.

This combined basis again forms a 2-level system where the difference in out-of-pair  $J$ -couplings drive the triplet to singlet transition.

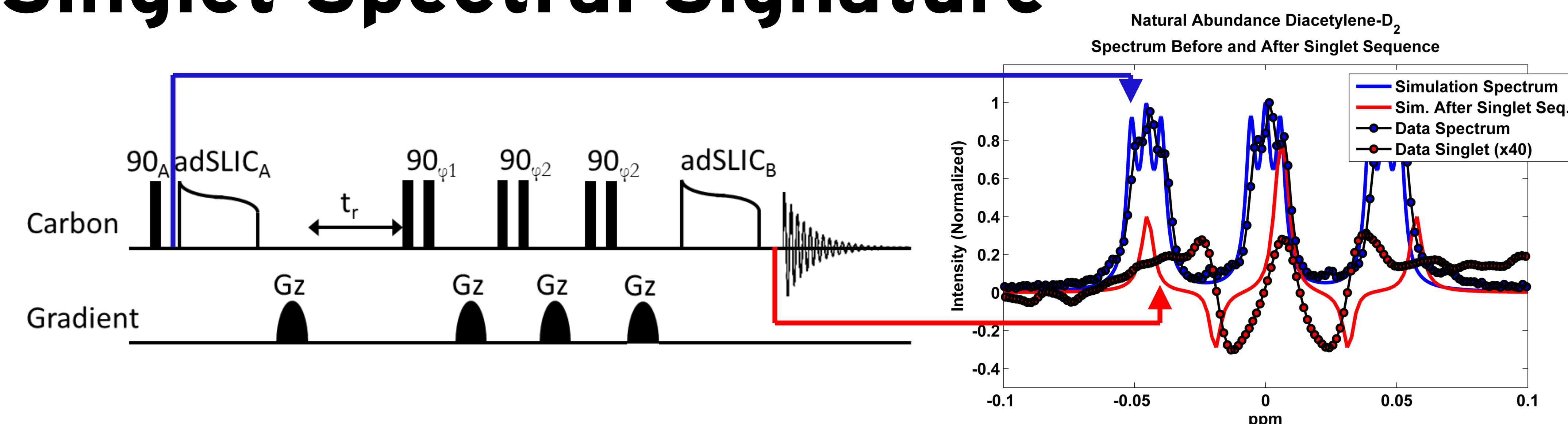


The spin-1 case is very similar to the above, with the  $|+1\rangle$ ,  $|0\rangle$ , and  $|-1\rangle$  states (P, Z, M) taking the role of the proton triplet.

We can again use the out-of-pair  $J$ -couplings to drive the triplet to singlet transition.

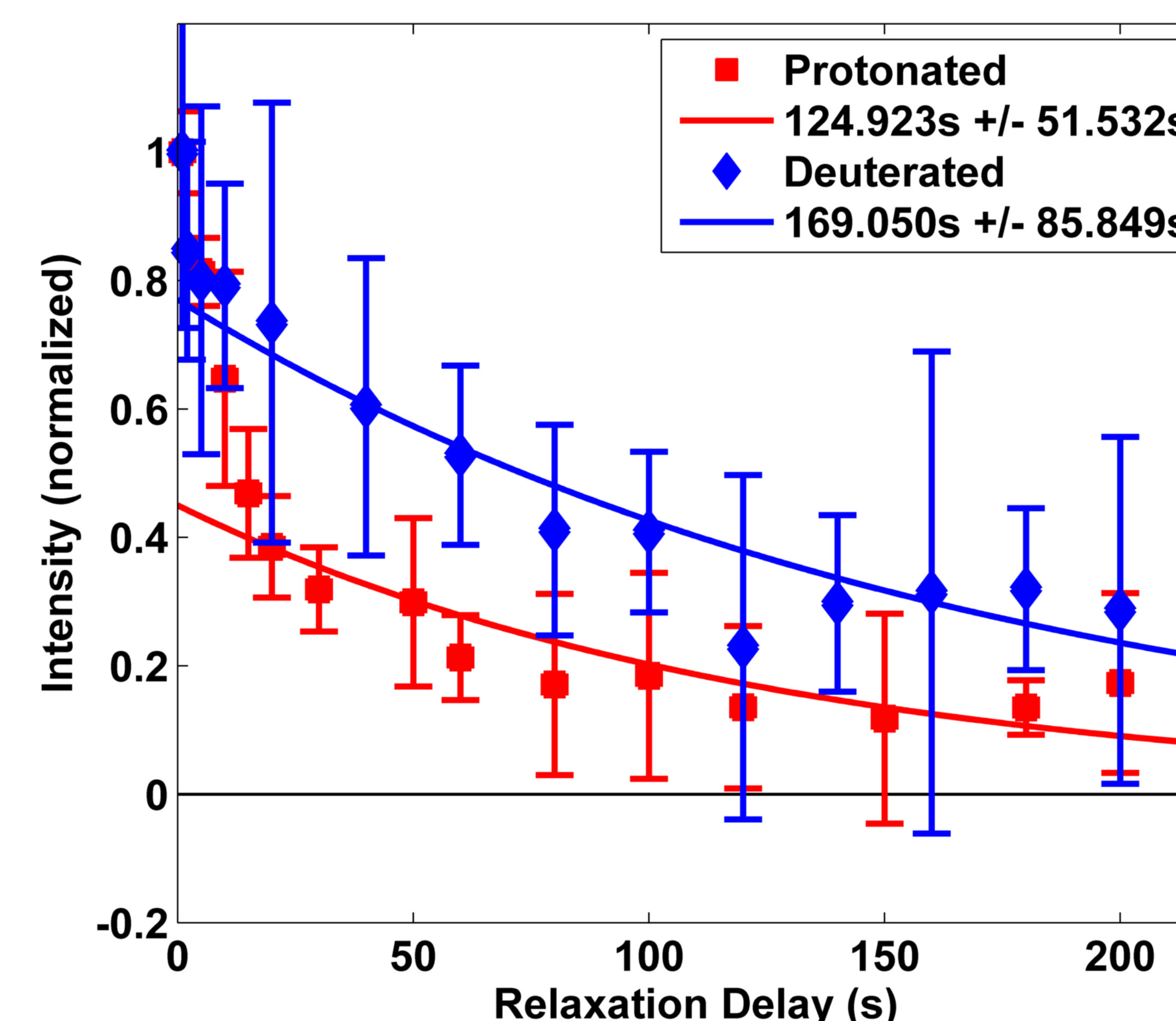


## Singlet Spectral Signature



## <sup>1</sup>H vs <sup>2</sup>H Diacetylene

Diacetylene-H<sub>2</sub>/D<sub>2</sub> Singlet Lifetime Comparison



Exponential fits show that the lifetime for the deuterated diacetylene is substantially longer than its protonated counterpart.

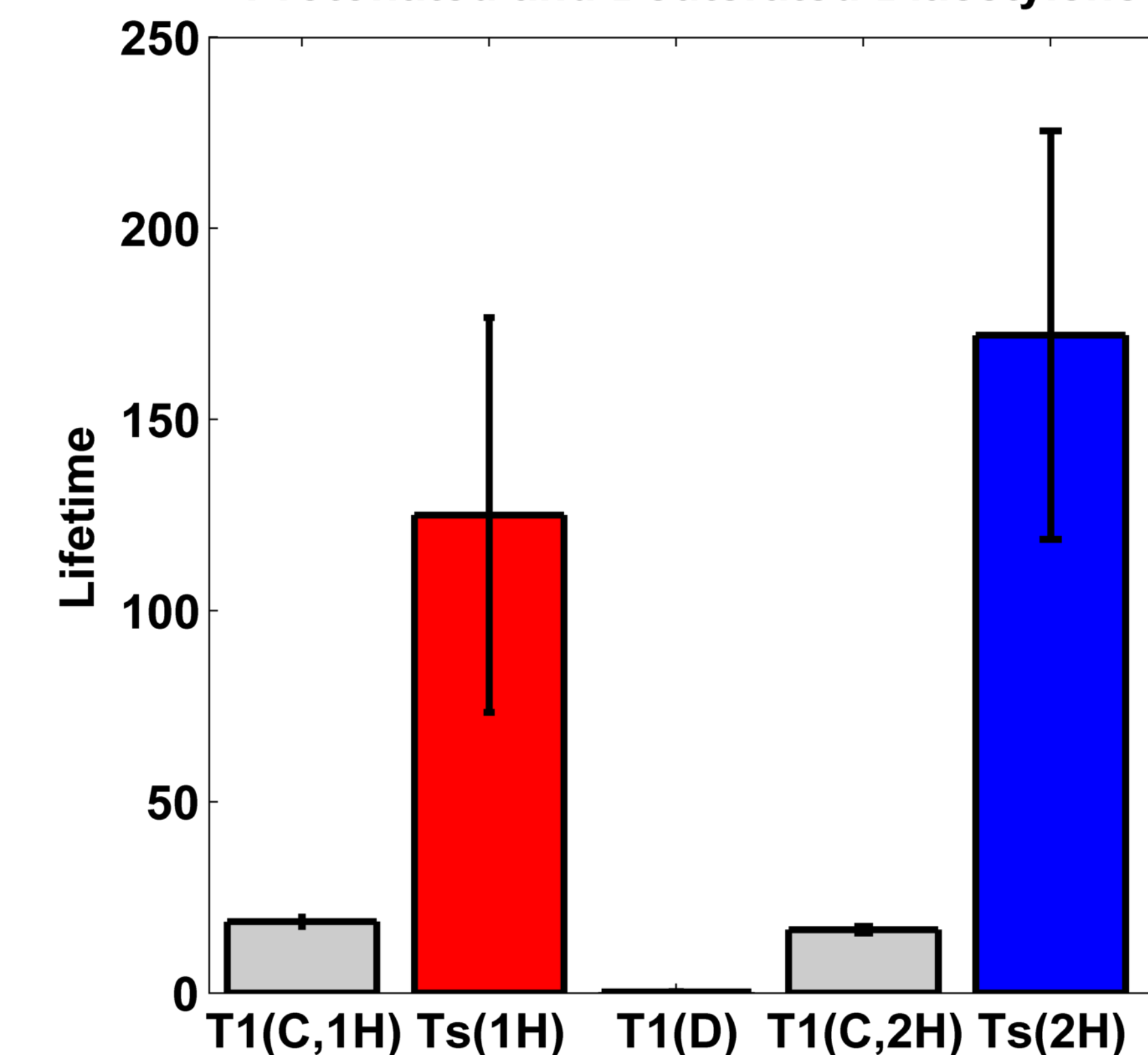
The first 10s of data is excluded, as it likely includes the rapid decay of the triplet state.

## Future directions

Reducing the coupling strength through deuteration successfully increased the lifetime of the diacetylene singlet.

This indicates that replacing directly bonded protons with deuterium may generate long lived singlet states. This increases the array of compounds that can support the singlet state.

T<sub>1</sub> Lifetime and Singlet Lifetimes for Protonated and Deuterated Diacetylene



Lifetimes on the protonated (1H) and deuterated (2H) diacetylene. Deuteration extends the singlet lifetime relative to the carbon T<sub>1</sub> lifetime

## Want More?

Animations & references @ [people.duke.edu/~kec30/deuteratedsinglet.html](http://people.duke.edu/~kec30/deuteratedsinglet.html)

