

## Pseudopure state of a twelve-spin system

Jae-Seung Lee and A. K. Khitrin

Department of Chemistry, Kent State University, Kent, Ohio 44242-0001

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Pseudopure states of a system of twelve interacting spins are experimentally demonstrated. The system is a cluster of dipolar-coupled nuclear spins of fully labeled  $^{13}\text{C}_6$ -benzene in a liquid crystalline matrix. At present, this is the largest and the most complex composite system where individual quantum states have been addressed. © 2005 American Institute of Physics.

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Clusters of coupled nuclear spins are, at present, the largest and the most complex quantum systems where individual quantum states can be addressed and coherently manipulated. At thermal equilibrium, nuclear spin systems are in highly mixed states, which means that an individual system can be, with some probability, in any of many possible quantum states. The idea of state initialization by creating a so-called pseudopure state was originally proposed for nuclear magnetic resonance (NMR)-based quantum computing.<sup>1,2</sup> In a pseudopure state, populations of all but one state are made equal. As a result, the spin density matrix is a sum of a maximally mixed background, which is proportional to the unity matrix, and a deviation part, which is proportional to a density matrix of a pure state. The unity matrix does not contribute to observables and is not changed by unitary transformations. Therefore, the behavior of a system in a pseudopure state is exactly the same as it would be at zero spin temperature.

Pseudopure states have been used in NMR implementations of quantum computing algorithms,<sup>1-5</sup> quantum simulations,<sup>6,7</sup> and demonstrations of quantum mechanisms of amplified detection<sup>8</sup> and measurement.<sup>9</sup> The largest spin system where a pseudopure state has been constructed to date is a seven-spin (seven-qubit) cluster which was used to implement the quantum factoring algorithm with liquid-state NMR.<sup>10</sup> A six-qubit pseudopure state has been demonstrated as a benchmark in another seven-spin system.<sup>11</sup> With conventional approaches using qubit-selective or transition-selective<sup>12</sup> pulses to equalize populations, there are two major limitations on the system's size: spectral resolution and the length of the pulse sequence. Both the number of allowed transitions and the length of the pulse sequence grow exponentially with the system's size. With multifrequency irradiation, it is possible to cause fast and efficient simultaneous evolution of all populations to desired values,<sup>13</sup> but this technique also requires a well-resolved spectrum.

Recently, we proposed a method of creating pseudopure states, which does not require an equilibrium spectrum to be resolved.<sup>14</sup> It is based on multiple-quantum dynamics with filtering of the highest-order multiple-quantum coherence. This method has been used to prepare a pseudopure state in a cluster of seven dipolar-coupled nuclear spins: single-labeled  $^{13}\text{C}$ -benzene in liquid-crystalline solvent.<sup>9</sup> In the present work we extend this technique and introduce a

double-filtering method using both phase cycling and an array of evolution times to create pseudopure states in a system consisting of two types of nuclear spins. The twelve-spin cluster used in this work is fully labeled  $^{13}\text{C}_6$ -benzene in a liquid-crystalline matrix. It is a complex system of dipolar-coupled spins with  $2^{12}=4096$  quantum states.

Experiments were performed using a Varian Unity/Inova 500 MHz NMR spectrometer. The sample contained 5% of fully labeled  $^{13}\text{C}_6$ -benzene (Aldrich) dissolved in liquid-crystalline solvent MLC-6815 (EMD Chemical). In this system, each benzene molecule contains twelve nuclear spins, six  $^{13}\text{C}$  and six protons, coupled by residual dipole-dipole interactions. All intermolecular spin-spin interactions are averaged out by fast molecular motions. The system is an ensemble of noninteracting spin clusters, where each benzene molecule contains twelve coupled nuclear spins.

The  $^1\text{H}$  thermal equilibrium spectrum of  $^{13}\text{C}_6$ -benzene in MLC-6815 is shown in Fig. 1. It consists of a broad ( $\sim 20$  kHz) spectrum of liquid crystal and, on top of its left slope, a poorly resolved spectrum of  $^{13}\text{C}_6$ -benzene with a width of about 5 kHz. The two sharp peaks in Fig. 1 are due to impurities. The proton signal from the liquid crystal can be eliminated with a two-frequency saturation. According to the Provotorov's saturation theory,<sup>15</sup> off-resonance saturation results in a stationary state with nonzero Zeeman and dipolar temperatures. If saturation is performed at two different frequencies, the only stationary solution gives infinite spin tem-

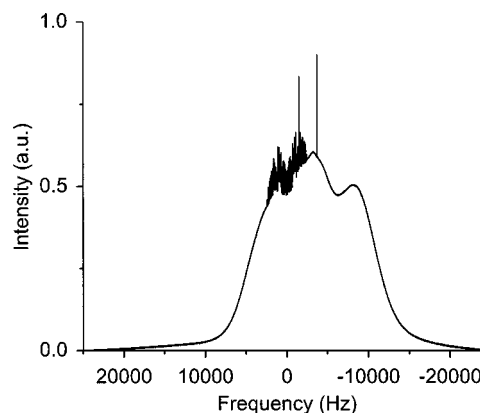


FIG. 1.  $^1\text{H}$  NMR spectrum of  $^{13}\text{C}_6$ -benzene in liquid crystal MLC-6815 at 25 °C.

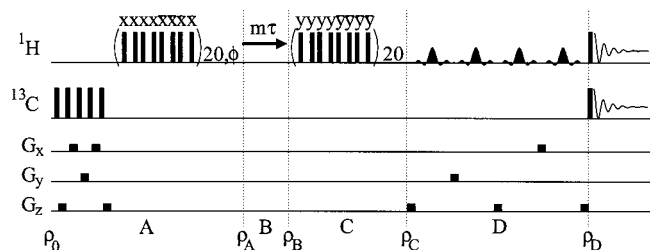


FIG. 2. Pulse sequence. Step A: presaturation of the  $^{13}\text{C}$  spins' magnetization and filtering the 6Q protons coherence with phase cycling;  $\rho_A = I_C \otimes i(|u\rangle\langle d| - |d\rangle\langle u|)_H$ . Step B: evolution of the 6Q coherence under heteronuclear dipole-dipole interactions. Arrayed evolution times  $m\tau$  with  $m = 0, 1, 2, \dots$  are used for the second filtering;  $\rho_B = (|u\rangle\langle u| + |d\rangle\langle d|)_C \otimes i(|u\rangle\langle d| - |d\rangle\langle u|)_H$ . Step C: conversion of the 6Q coherence back to the diagonal state;  $\rho_C = (|u\rangle\langle u| + |d\rangle\langle d|)_C \otimes (|u\rangle\langle u| - |d\rangle\langle d|)_H$ . Step D: Partial saturation;  $\rho_D = (|d\rangle\langle d|)_C \otimes (|d\rangle\langle d|)_H$ .

perature (zero magnetization). As a result, saturation at two frequencies outside the spectrum of  $^{13}\text{C}_6$ -benzene completely eliminates the signal of a liquid-crystalline matrix. The “purified”  $^1\text{H}$  spectrum of  $^{13}\text{C}_6$ -benzene presented in Fig. 3(a) is symmetric and has a flat baseline. The impurity peak is marked with an asterisk.  $T_1$  and  $T_2$  relaxation times have been found to be 1.7 and 0.25 s for  $^1\text{H}$  and 2.5 and 0.26 s for  $^{13}\text{C}$ , respectively.

For further discussion it will be convenient to use compact notations for spin states. The symbols  $|u\rangle_H = |\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\rangle_H$  and  $|d\rangle_H = |\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\rangle_H$  denote the states of the proton spins with all six spins up and down, respectively. Similarly, the notations  $|u\rangle_C$  and  $|d\rangle_C$  will be used for the  $^{13}\text{C}$  spin states with all six carbon spins up or down.

The experimental scheme is shown in Fig. 2. (Step A) It

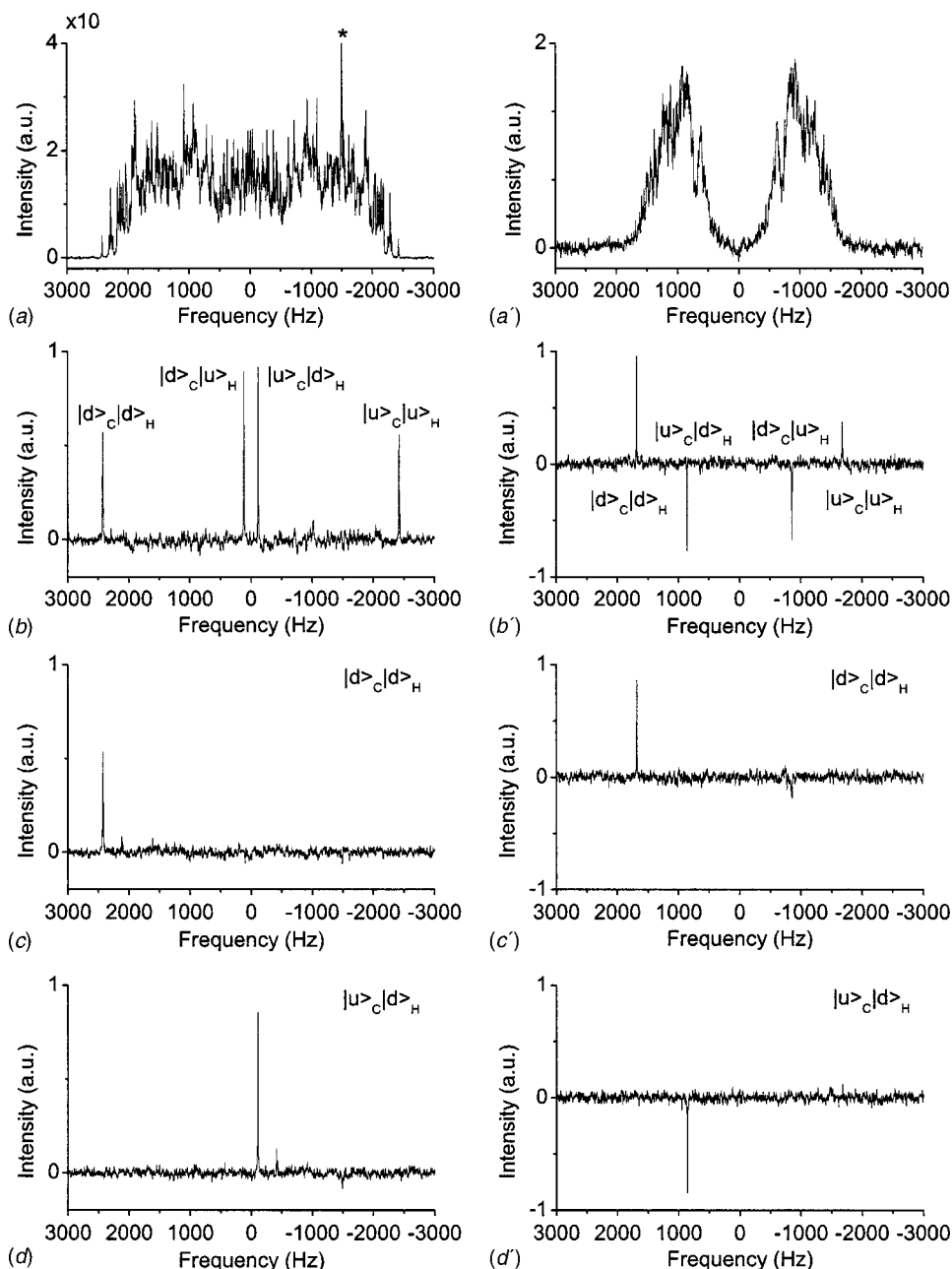


FIG. 3.  $^1\text{H}$  (a) and  $^{13}\text{C}$  (a') spectra of the thermal equilibrium state;  $^1\text{H}$  (b) and  $^{13}\text{C}$  (b') spectra of the mixture of four states:  $\rho_C = (|u\rangle\langle u| + |d\rangle\langle d|)_C \otimes (|u\rangle\langle u| - |d\rangle\langle d|)_H$ ;  $^1\text{H}$  (c) and  $^{13}\text{C}$  (c') spectra of the pseudopure state  $|d\rangle_C|d\rangle_H$ ;  $^1\text{H}$  (d) and  $^{13}\text{C}$  (d') spectra of the pseudopure state  $|u\rangle_C|d\rangle_H$ .

starts with a sequence of  $^{13}\text{C}$  rf-pulses and gradient pulses to saturate the  $^{13}\text{C}$  magnetization. Evolution with twenty cycles of the eight-pulse sequence<sup>16</sup> creates even-order multiple-quantum coherences for the proton spins. The sequence automatically decouples the carbon spins. The highest-order multiple-quantum coherence for protons, six-quantum (6Q), is filtered by phase cycling,<sup>17</sup> which eliminates all other multiple-quantum coherences including the zero-order coherence. The deviation density matrix after this initial filtering becomes  $\rho_A = 1_C \otimes i(|u\rangle\langle d| - |d\rangle\langle u|)_H$ . **(Step B)** The secular dipole-dipole interactions between heteronuclei consist of ZZ-terms only. The ZZ-interaction with the  $^{13}\text{C}$  spins causes a rotation of the proton spins' 6Q coherence, which does not evolve under the homonuclear dipole-dipole interactions between proton spins, as explained elsewhere.<sup>8,9</sup> The phase of this rotation is proportional to the evolution time  $\tau$  and the total Z-component of the  $^{13}\text{C}$  spins. Similar to filtering the 6Q coherence using an array of phases, it is possible to filter out the two states of the  $^{13}\text{C}$  spins with the extreme values of Z-component of the total  $^{13}\text{C}$  spin, which are  $\pm 3$ , using an array of the evolution times  $m\tau$  with  $m=0,1,2,\dots$ . The unit of the evolution time  $\tau=65.6\ \mu\text{s}$  corresponds to a rotation of the protons' 6Q coherence by  $\pi$  when the  $^{13}\text{C}$  spins are in the state  $|u\rangle_C$  or  $|d\rangle_C$ . After this second filtering, the deviation density matrix becomes  $\rho_B = (|u\rangle\langle u| + |d\rangle\langle d|)_C \otimes i(|u\rangle\langle d| - |d\rangle\langle u|)_H$ . The total number of experiments in this phase-time double array is only  $12 \cdot 6 = 72$ .

**(Step C)** The second 20-cycle evolution period converts the protons 6Q coherence into a diagonal state. This creates the density matrix  $\rho_C = (|u\rangle\langle u| + |d\rangle\langle d|)_C \otimes (|u\rangle\langle u| - |d\rangle\langle d|)_H$  which is a mixture of the four pure states:  $|u\rangle_C|u\rangle_H$ ,  $|u\rangle_C|d\rangle_H$ ,  $|d\rangle_C|u\rangle_H$  and  $|d\rangle_C|d\rangle_H$ . Due to the high symmetry of this system, there is only one  $^1\text{H}$  or  $^{13}\text{C}$  allowed single-quantum transition from each of these four states. The linear-response spectra of  $^1\text{H}$  and  $^{13}\text{C}$  for the four-state mixture are shown in Figs. 3(b) and 3(b'), respectively. **(Step D)** A single pseudopure state has been selected by a partial saturation with four  $^1\text{H}$  sinc-shaped pulses. The pulses have an approximately rectangular excitation spectrum with decaying oscillations at the edges. They irradiate the entire spectrum except for the leftmost peak in Fig. 3(a) by setting their frequency so that the position of the leftmost peak coincides with the first zero of the excitation profile. As a result, there are no transitions from the state  $|d\rangle_C|d\rangle_H$  and its population remains "trapped", while the populations of the other states are equalized by numerous stimulated transitions. The linear-response  $^1\text{H}$  and  $^{13}\text{C}$  spectra of the pseudopure state

$|d\rangle_C|d\rangle_H$  are presented in Figs. 3(c) and 3(c'), respectively.

The proton peak intensity of Fig. 3(c) was estimated to be 0.02% of the integrated intensity of the thermal equilibrium spectrum. The theoretical maximum<sup>18</sup>  $N2^{-N}$  is 0.3% for our system. It is interesting that no pulses, except the initial saturation pulses, have been applied to the carbon spins for building the pseudopure state of the entire system. Using the state  $|d\rangle_C|d\rangle_H$  as an initial state, the other three states:  $|u\rangle_C|u\rangle_H$ ,  $|u\rangle_C|d\rangle_H$ , and  $|d\rangle_C|u\rangle_H$  can be obtained by applying nonselective "hard"  $\pi$ -pulses to carbon and proton spins. One of the examples is shown in Figs. 3(d) and 3(d'), where  $^{13}\text{C}$   $\pi$ -pulse has been applied to the state  $|d\rangle_C|d\rangle_H$  to create the state  $|u\rangle_C|d\rangle_H$ . Starting with one of these four states, many other pseudopure states can be created with sequences of transition-selective  $\pi$ -pulses.

In conclusion, we have demonstrated a pseudopure state of a twelve-spin system using an NMR technique. This shows that individual quantum states can be addressed and coherently manipulated in large clusters of coupled spins with unresolved conventional spectra.

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