Preparing High Purity Initial States for Nuclear Magnetic Resonance Quantum Computing

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Here we demonstrate how parahydrogen can be used to prepare a two-spin system in an almost pure state which is suitable for implementing nuclear magnetic resonance quantum computation. A 12 ns laser pulse is used to initiate a chemical reaction involving pure parahydrogen (the nuclear spin singlet of H_2). The product, formed on the μs time scale, contains a hydrogen-derived two-spin system with an effective spin-state purity of 0.916. To achieve a comparable result by direct cooling would require an unmanageable (in the liquid state) temperature of 6.4 mK or an impractical magnetic field of 0.45 MT at room temperature. The resulting spin state has an entanglement of formation of 0.822 and cannot be described by local hidden variable models.

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Introduction.—While quantum computing [1] offers the potential of using new quantum algorithms to tackle problems that are intractable for classical processors, its implementation requires the development of quantum devices, which are as yet unavailable. The most complex implementations of quantum algorithms to date have used techniques adapted from nuclear magnetic resonance (NMR) spectroscopy [2–5], but current liquid state NMR approaches cannot be extended to systems with many quantum bits, as it is not possible to prepare pure initial states by directly cooling the spin system into its ground state [6]. Furthermore, it has been shown that current NMR experiments involve only separable states [7], and thus could in principle be described by local hidden variable models.

The conventional approach in NMR quantum computing [4] is to use an ensemble of spins and to prepare a pseudopure ground state [2,4] of the form

$$\rho = (1-\varepsilon)\frac{\mathbb{1}}{2^n} + \varepsilon|0\rangle\langle 0|, \tag{1}$$

where $\mathbb{1}/2^n$ is the maximally mixed state of an n-spin system, and ε is the polarization of the state. In the high temperature regime this approach is exponentially inefficient [6]. Furthermore if the polarization lies at or below a critical bound then any apparently entangled states prepared from the pseudopure state are in fact separable [7]; for two qubits [8–10] this bound is $\varepsilon = 1/3$, corresponding to a fractional population of $1/2$ in the ground state and $1/6$ in each of the three other eigenstates. A radically different approach is to prepare initial states using nonthermal means [11], e.g., by using the pure singlet nuclear spin state isomer of H_2 (called "parahydrogen") [12–15] as a cold spin-state reservoir.

Parahydrogen induced polarization.—A pure singlet nuclear spin state can be described using product operator notation [16] as

$$\tfrac{1}{2}(\tfrac{1}{2}E - 2I_xS_x - 2I_yS_y - 2I_zS_z), \tag{2}$$

where $E = \mathbb{1}\otimes\mathbb{1}$, $I_x = \frac{1}{2}(\sigma_x \otimes \mathbb{1})$, $S_x = \frac{1}{2}(\mathbb{1}\otimes\sigma_x)$, and so on. The existence of parahydrogen is a consequence of the Pauli principle [17], which requires the overall wave function of the molecule to be antisymmetric with respect to particle interchange. Dihydrogen molecules in even rotational states ($J = 0, 2, \ldots$) possess an antisymmetric nuclear wave function and correspond to nuclear spin singlets [$S_0 = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2} = \Psi^-$, termed *para*]. Molecules in odd rotational states ($J = 1, 3, \ldots$) have symmetric nuclear wave functions and consist of the three nuclear spin triplets [$T_0 = (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2} = \Psi^+$, $T_{-1} = |\uparrow\uparrow\rangle$, and $T_{+1} = |\downarrow\downarrow\rangle$, termed *ortho*]. Note that the $T_{\pm 1}$ states are *not* the same as $\Phi^\pm = (|\uparrow\uparrow\rangle \pm |\downarrow\downarrow\rangle)/\sqrt{2}$ (the other two Bell states), but that an equal mixture of T_{+1} and T_{-1} is also an equal mixture of Φ^+ and Φ^-.

Isolation of the parahydrogen spin isomer is possible because spin-isomer interconversion is forbidden by angular momentum selection rules. Adsorption onto a suitable surface breaks the symmetry of the H_2 molecules, allowing spin-isomer interchange. The new ortho/para ratio therefore *remembers* the temperature of the last conversion surface encountered. Upon moving away from this surface interconversion is again suppressed. A temperature of 20 K is sufficiently low to form the $J = 0$ state and hence produce pure parahydrogen. The resulting para-H_2 molecule cannot be used directly, as it is NMR silent due to its high symmetry. By means of a chemical reaction, producing a new molecule, the two hydrogen atoms can be made distinct (I and S) and *can* be separately addressed. This phenomenon is well known from mechanistic NMR studies of catalytic hydrogenation and hydroformylation, where it is usually referred to as parahydrogen induced polarization, or PHIP [12–15].

In many previously described PHIP experiments the addition process is slow in comparison with the frequency difference between the I and S spins of the reaction product. This causes the off-diagonal terms in the density matrix to dephase, resulting in an equal mixture of singlet and T_0 triplet states in the spin ensemble [18], which is separable [8–10]. One possible method that has been suggested to overcome this problem is to perform the slow addition while applying an isotropic mixing sequence [19] to remove the dephasing effect [20]. In principle (and neglecting relaxation effects) this should completely conserve the hydrogen spin state, and this method has been used [20] to achieve states with $\epsilon \approx 0.1$.

A much simpler approach is to ensure that the addition is rapid in comparison with the dephasing and relaxation time scales. This requires an addition to a highly reactive species, but a fast reaction would go to completion and the spin system would decohere before the sample could be studied. In this paper we solve this problem by using photochemistry to prepare a reagent which will react instantaneously with parahydrogen to produce the molecule for examination. This means we can start and stop the formation of the reactive species in a controlled manner. We then show that the resulting two-spin system forms in an almost pure state.

Experimental methods.—In this study the precursor molecule was $Ru(CO)_3$(dppe), where dppe indicates 1,2-bis(diphenylphosphino)ethane. This was prepared from $Ru_3(CO)_{12}$ by warming a benzene solution to 373 K under 30 atmospheres of CO in the presence of three equivalents of dppe [21]. The $Ru(CO)_3$(dppe) was dissolved in d_6-benzene in a 5 mm NMR tube fitted with a Young's valve to permit attachment to a vacuum line. Dissolved gases were removed by freeze-pump-thaw cycles and the tube was covered in foil to exclude light. Parahydrogen was prepared at a temperature of 20 K using a charcoal-based ortho-para interconversion catalyst; at this temperature the thermal state is essentially pure para. The parahydrogen was then introduced to the sample; as the catalyst is no longer present ortho-para interconversion is suppressed. After warming, shaking ensures that the H_2 gas (with a pressure of about three atmospheres) dissolves.

The NMR tube was placed in a 400 MHz NMR spectrometer fitted with a $^1H/^{31}P$ tuned NMR probe equipped for *in situ* photolysis [22]. (The transfer was performed in a darkened room to prevent premature photolysis by ambient light.) The reaction was initiated by a 12 ns pulse of 308 nm UV light (pulse energy 32 mJ) from an MPB Technologies MSX-250 pulsed XeCl excimer laser triggered by the NMR spectrometer. This generates the reactive intermediate $Ru(CO)_2$(dppe), *in situ* from its stable precursor $Ru(CO)_3$(dppe) by laser flash photolysis (see Fig. 1). Subsequent reaction of $Ru(CO)_2$(dppe) with H_2 occurs on the submicrosecond time scale [23] and leads to the product of interest, $Ru(H)_2(CO)_2$(dppe).

The two hydride resonances of the product appear at $\delta = -7.55$ ppm (spin I) and $\delta = -6.32$ ppm (spin S). For the analysis a spin I selective pulse was implemented using two hard 90° pulses separated by a delay of $1/(4\delta\nu)$, where $\delta\nu = 492$ Hz is the difference between the resonance frequencies, with relative phases of 135° and with the rf frequency centered on the midpoint of the two resonances. Such pulses, based on jump and return sequences, have been described previously [24]. Broadband decoupling [25] was applied throughout signal acquisition to remove couplings to ^{31}P nuclei. To avoid the necessity for complete quantum state tomography [26] a filtration sequence was developed which has no effect on the desired singlet state, but dephases most other states.

While the signal produced by the parahydrogen is easily seen in one scan, the thermal signal is extremely weak and so difficult to measure directly. It was therefore necessary to increase its intensity by increasing the amount of $Ru(H)_2(CO)_2$(dppe) in the sample. This was achieved by applying a further 999 laser pulses to produce more $Ru(H)_2(CO)_2$(dppe). Even then we needed 3072 scans for the calibration spectrum; these were separated by an interval of 20 s, which is much greater than 5 times the measured T_1 of 1.7 s and so saturation effects can be ignored. The spectra were processed by homewritten software and analyzed by integration. The

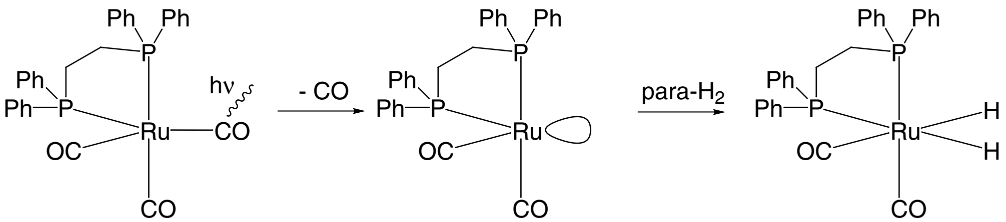

FIG. 1. The reaction scheme used to generate $Ru(H)_2(CO)_2$(dppe) with an almost pure initial spin state. A UV photon knocks one carbonyl group off the $Ru(CO)_3$(dppe) precursor to generate an unstable intermediate, which immediately adds hydrogen to give the desired product. Since para-H_2 has a pure singlet initial state, and addition occurs with retention of spin state, the product should also have a pure singlet spin state.

parahydrogen spectrum comprises a pair of antiphase doublets, which partially cancel [27], and so direct integration will result in an underestimate of the signal intensity; to reduce such effects the spectrum was J doubled [28] 4 times before integration. Even after J doubling and integration slight imbalances were visible between the two multiplets, and these imbalances can be analyzed to determine the imbalance between T_0 and $T_{\pm1}$ triplet states.

Results.—Laser photolysis of the $\mathrm{Ru(CO)_3(dppe)}$ leads to the product $\mathrm{Ru(H)_2(CO)_2(dppe)}$. If the two hydrogen nuclei have inherited the nuclear singlet from the parahydrogen, then a selective 90° I_y pulse will yield the observable NMR terms

$$\tfrac{1}{2}(-2I_xS_z + 2I_zS_x). \tag{3}$$

This corresponds to a pair of antiphase doublets, with intensities $\pm 1/2$. This pattern is indeed seen (Fig. 2), but to show that we have an essentially pure singlet state it is necessary to determine the *intensity* of the signal as well as its form. We calibrated our signal against a standard provided by the thermal state of the same spin system, obtained by allowing the spin system to relax. At high temperatures the thermal state is

$$\tfrac{1}{2}(\tfrac{1}{2}E + \tfrac{1}{2}B[I_z + S_z]), \tag{4}$$

where $B = h\nu/kT$ and ν is the Larmor frequency of the spins. After a 90° pulse the NMR observable terms are

$$\tfrac{1}{4}B(I_x + S_x), \tag{5}$$

that is a pair of in-phase doublets with intensity $B/4$, so that a pure state will give a signal $2/B$ times larger than a thermal state. For our system $\nu = 400$ MHz and $T = 295$ K, and so the parahydrogen signals could be up to 31 028 times more intense than the thermal signals.

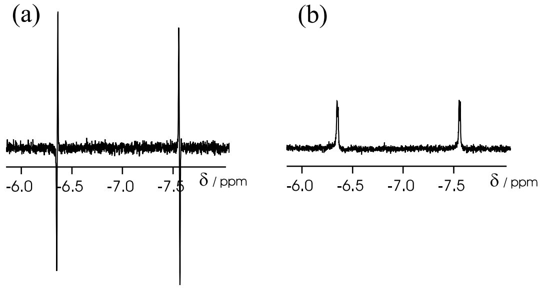

FIG. 2. The parahydrogen enhanced and calibration spectra of $\mathrm{Ru(H)_2(CO)_2(dppe)}$. The parahydrogen spectrum (a) is a single scan after a single laser flash, while the calibration spectrum (b) is the sum of 3072 scans after 1000 laser flashes. The calibration spectrum has been divided by 3072×1000 and then multiplied by the theoretical maximum enhancement (31 028, see main text) before plotting, so that the two spectra should show the same intensity. In fact the parahydrogen spectrum (a) is even more intense than naively predicted.

In order to examine the form of the signal, we used a filtration sequence (comprising two periods of length $1/\delta\nu$, under a field gradient separated by a hard 90° pulse) which is closely related to "twirl" operations [29,30]. After this, the density matrix is Bell diagonal, comprising a mixture of singlet and triplet states, with equal amounts of the parallel-spin triplet states T_{+1} and T_{-1}. Since this sequence had little effect on the spectrum, the initial density matrix had a similar form.

Our results (Fig. 2) show an apparent enhancement of about 77 000, significantly higher than expected. This discrepancy arises because the NMR probe is not sensitive to the entire sample, but only to that within the rf coil. The hydride forms within the coil region because of the position of the mirror that introduces the UV light, as confirmed by one-dimensional NMR imaging, but is then distributed throughout the sample by convection and diffusion, so that in the calibration spectrum only a fraction of the hydride is detectable. As expected the directly measured enhancement (that is, before correction) shows a linear dependence on the total sample volume (data not shown). The active volume fraction can be estimated using geometrical arguments based on the relative length of the NMR sample and the rf coil. The actual value depends on the length of the NMR sample, but was 0.368 in the experiment described. After correcting for this active volume fraction the observed enhancement is consistent with a polarization of $\varepsilon = 0.916 \pm 0.019$.

Relaxation.—The measured relaxation and decoherence times of the ^{1}H nuclei in the parahydrogen state ($T_1 = 1.7$ s, $T_2 = 0.58$ s) are indistinguishable from those in the thermal state, indicating that the high polarization does not affect the relaxation properties of the molecule. No effects of radiation damping were observed, reflecting the extremely low concentration of the hydride.

Entanglement.—As well as the polarization enhancement, the use of PHIP initializes the system directly into an entangled state. The entanglement threshold of $1/3$ is valid only for mixtures of a Bell state with the maximally mixed state (Werner states). Our density matrix could contain arbitrary states mixed with the singlet and the threshold depends on what is mixed in. The states that most effectively destroy the entanglement of the singlet are T_0 and equal mixtures of T_{+1} and T_{-1}; these are also the only states which survive the filtration sequence.

The positivity of the partial transpose test [8] is a necessary and sufficient condition for separability for two qubit states [9]. It can be shown [10] that for a system comprising a mixture of the singlet and some convex combination of T_0 and an equal mixture of T_{+1} and T_{-1} the state will always be entangled if the total amount of singlet exceeds $1/2$. Detailed analysis of our data shows that the density matrix is not quite a Werner state: instead the state comprises 93.7% S_0, 4.5% T_0, 0.9% T_{+1}, and 0.9% T_{-1}. The excess population of T_0 suggests the presence of some phase decoherence process that we have yet to identify, but this excess has no effect on the entanglement of formation [29,31], which would be 1 for a pure singlet and for our system is 0.822 ± 0.039.

Our results demonstrate that liquid-phase NMR can produce entanglement. The question of whether entanglement really is a necessary resource for universal quantum computers can be answered only by mathematical proofs of their scaling characteristics with and without entanglement. These can only be defined rigorously in the limit as the size of the problem instance (and hence the computer solving it) tends to infinity. Any actual experiment can be performed only on a finite-sized system and can therefore neither prove nor disprove the correctness of the arguments in [7]. We can show only that this particular objection can no longer be leveled at liquid-phase NMR quantum computation.

Conclusions and further work.—We have shown that parahydrogen can greatly benefit NMR quantum computing by the generation of almost pure ($\varepsilon = 0.916 \pm 0.019$) initial states on demand, without the need for lengthy preparation sequences. To achieve a comparable result by direct cooling would require an unmanageable (in the liquid state) temperature of 6.4 mK or an impractical magnetic field of 0.45 MT at room temperature.

Conventional liquid-phase NMR has poor scaling characteristics at low polarization [6], but our effective spin temperature of less than 6.4 mK is much less than the 1 K threshold suggested by Warren for efficient initialization. This approach can in principle be scaled up by adding M molecules of parahydrogen to a single precursor, effectively synthesizing a quantum computer with $2M$ qubits in a pure initial state, and we are currently seeking to implement these ideas. We also expect that the ability to rapidly generate highly spin-polarized hydride species on demand will prove useful in other parahydrogen based studies of reaction mechanisms.

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