

Communication

An inexpensive apparatus for up to 97% continuous-flow parahydrogen enrichment using liquid helium

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ABSTRACT

Nuclear spin hyperpolarization derived from parahydrogen can enable nuclear magnetic resonance spectroscopy and imaging with sensitivity enhancements exceeding four orders of magnitude. The NMR signal enhancement is proportional to $4x_p - 1$, where x_p is the parahydrogen mole fraction. For convenience, many labs elect to carry out the ortho–para conversion at 77 K where 50% enrichment is obtained. In theory, enrichment to 100% yields an automatic three-fold increase in the NMR signal enhancement. Herein, construction and testing of a simple and inexpensive continuous-flow converter for high para-enrichment is described. During operation, the converter is immersed in liquid helium contained in a transport dewar of the type commonly found in NMR labs for filling superconducting magnets. A maximum enrichment of $97.3 \pm 1.9\%$ at 30 K was observed at 4.5 bar and 300 mL/min flow rate. The theoretically predicted 2.9-fold increase in the signal enhancement factor was confirmed in the heterogeneous hydrogenation of propene to propane over a PdIn/SBA-15 catalyst. The relatively low-cost to construct and operate this system could make high parahydrogen enrichment, and the associated increase in the parahydrogen-derived NMR signals, more widely accessible.

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1. Introduction

Hyperpolarization derived from parahydrogen (p-H₂) can enhance the NMR sensitivity by over four orders of magnitude relative to conventional high-field NMR at ambient temperature, enabling a plethora of new applications [1]. When symmetry breaking interactions are introduced, the proton singlet spin order of p-H₂ is transformed into a large, non-equilibrium NMR-observable nuclear spin hyperpolarization. This method is rapidly gaining traction as an inexpensive and robust alternative to dissolution DNP for real-time imaging and spectroscopy [2,3]. In recent years, the universe of molecules that can be hyperpolarized from p-H₂ has exploded with the advent of new variants of the original PASADENA method [4–6]. Common to all parahydrogen-based signal enhancement schemes, the obtained hyperpolarization is proportional to $(4x_p - 1)$ where x_p is the p-H₂ mole fraction [7,8].

Parahydrogen enrichment can be performed by simply flowing normal hydrogen gas (n-H₂, $x_p = 0.25$) through a packed bed of a solid paramagnetic material that catalyzes thermal equilibration between the singlet and triplet manifolds at reduced temperature [9,10]. Commonly used conversion catalysts are iron oxide (Fe(OH)) [11], activated charcoal [12], CrO₃ [13] and NiO [8,10,14]. While enrichment to $x_p = 50\%$ is conveniently obtained by equilibrating H₂ at 77 K (liquid nitrogen temperature), achieving $x_p > 99\%$ is more difficult and requires cooling to below 25 K. With an automatic three-fold increase in the NMR signal enhancement in every experiment, the extra effort of cooling to lower temperature is amply rewarded.

Commercially available cryo-cooler systems utilizing a closed-cycle helium refrigerator provide an efficient means for maintaining conversion temperatures in the 20–40 K range. Using an ARS (Advanced Research Systems, Inc., Macungie, PA) closed-cycle cryo-cooler system, 98% para-enrichment was reported at flow rates of up to 4 L/min and pressures up to 50 bar [11]. However, such cryo-cooler systems are relatively expensive to purchase and maintain and can require >4 h to reach the set temperature.

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The relatively simple and inexpensive apparatus demonstrated here utilizes liquid helium in a 100 L storage dewar like the ones commonly used in NMR laboratories for filling superconducting magnets. This apparatus was developed and tested at the National High Magnetic Field Laboratory at the University of Florida, where 100 L dewars fitted with 79 mm flanges and networked digital level meters are available for storage and transport of locally liquified helium. The helium evaporated during p-H₂ enrichment in an experiment lasting several hours is typically less than a few liquid liters, and the boil-off gas is almost completely recovered and recycled. Here, the cost of helium for p-H₂ enrichment under these conditions is practically negligible compared to the other materials, supplies, and personnel costs of the experiment. Since not all labs have access to low-cost liquid helium, this approach might not always be within reach. On the other hand, liquid helium is usually on-site at regular intervals in most NMR facilities, depending on the age and number of superconducting magnets. Once prepared, p-H₂ can be stored at room temperature in aluminum canisters where the back-conversion relaxation time is roughly 64 days. [15]. The p-H₂ enrichment apparatus described here may be a cost-effective alternative to the closed cycle cryo-cooler based system while affording the highest attainable hyperpolarization levels.

2. Parahydrogen converter design

Since the boiling point of p-H₂ at 1 bar is about 20 K, the goal is to maintain the lowest temperature without condensation. In the current design, the cryostat tube (50.6 mm O.D.) depicted in Fig. 1 is inserted into a wide-neck (50.8 mm neck I.D.) 100 L liquid helium storage dewar fitted with a Ladish style 79 mm gasketed flange. The cryostat tube is clamped to the dewar by a flange adapter with an o-ring compression fitting that provides a sliding seal between the dewar and the cryostat to facilitate slow insertion into the liquid helium. Drawings and photos are provided in Figs. S1 and S2 of the Supporting Information (SI). A 4-port gas manifold was brazed onto the top of the cryostat tube to provide connections to a pressure gauge, vacuum pump, helium gas, and safety valve. The cap of the removable insert assembly that fits inside the cryostat tube incorporates a 10-pin electrical feed-through connector (Amphenol, JMS3116F12-10S) and two 1/8 in. Swagelok compression fitting feed-throughs for the hydrogen inlet and outlet tubing (SS304, 1/8 in. O.D., 0.028 in. wall thickness, McMaster-Carr, 89895K712). Three copper disk baffles with a diameter slightly smaller than the inner diameter of the cryostat tube are brazed onto the shaft of the insert to reduce radiative heat transfer and convection. A bobbin machined from a copper block, similar to the one described by Tam and Fajardo [16,17], is mounted to the bottom of the insert. The upper section of the bobbin is wrapped with 20 turns of 3/16 in. O.D. copper tubing (0.03 in. wall thickness) packed with ~ 10 g of 30–50 mesh iron oxide hydroxide ortho-para conversion catalyst (Sigma Aldrich, 371254), held in place with glass wool. The lower section of the copper bobbin is wrapped with 2.36 Ω/ft resistivity heating wire (California Fine Wire Company, NICO-H-Poly 100147) for a total resistance of 20 Ω. A CERNOX temperature sensor (Lakeshore, CX-1050-SD) is mounted in a groove in the top surface of the copper bobbin and secured with GE varnish. The heating and temperature sensor wires are wound on a helical path around the center tube of the insert and soldered to the 10-pin feed-thru connector. The temperature sensor was calibrated at 4.2 K and 77.3 K for the low and high points using the built-in calibration function on an Oxford ITC 503 PID temperature controller. The conversion coil temperature was sensed and stabilized to the set point on the ITC 503 which supplies a variable heating current. The set temperature is maintained

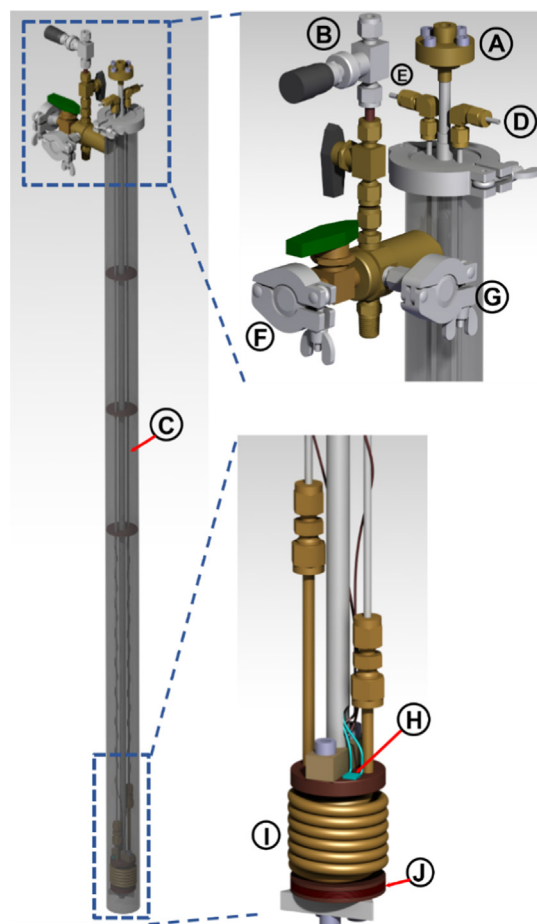


Fig. 1. Home-built cryostat. (A). 10-pin connector wired to Oxford ITC 503, heating wires, and temperature sensor. (B). Inlet of helium exchange gas. (C). ~ 250 mtorr of He exchange gas is admitted to cryostat to slow the heat exchange process. (D). H₂ inlet. (E). p-H₂ outlet. (F). connection to vacuum pump. (G). connection to pressure gauge. (H). Lakeshore CERNOX temperature sensor. (I). 3/16 in. O.D. copper tubing packed with ~ 10 g iron oxide (i.e. Fe(O)(OH)) ortho-para conversion catalyst. (J). 2.36 Ω/ft resistivity heating wires, where the heat output is controlled by PID program in Oxford ITC 503. Note: The 1/16 in. PEEK tubing insert described in the text is not shown in this drawing of the prototype.

by balancing the cooling power from the helium gas exchange between the walls of the cryostat can and the coil against the resistive heating of the coil. In the prototype of our converter, the para-enriched H₂ exited from the cryostat through the stainless steel tubing. As will be shown below, significant back-conversion can occur in this segment of stainless tubing at lower flow rates. This was remedied by inserting a section of 1/16 in. O.D./0.03-in. I.D. PEEK tubing (McMaster-Carr, 51085 K48) into the outlet of the 1/8-in. O.D. stainless tubing until it reached the top of the conversion coil. The gap between the 1/16 in. PEEK tubing and the 1/8 in. SS304 tubing was sealed using a Swagelok reducing union compression fitting. Thus, only H₂ molecules at the outlet of the conversion coil can exit the cryostat through the PEEK insert. Additional details about the construction and a parts list can be found in the SI. The total cost of the parts and materials, listed by supplier in Table S1 of the SI, was about US\$1200. In our lab, a spare Oxford ITC 503 temperature controller and a Varian WV100-2 vacuum gauge were available for use with our converter. These items would have added considerably to the total cost if they had to be purchased. However, cheaper alternatives are certainly available. For example, Vacuum Research Corp. (Pittsburgh, PA, www.vacuumresearch.com) offers a suitable Pirani gauge for around US\$800.

3. Methods

3.1. Para-enrichment

Fig. 2 is a block diagram of the setup employed to measure x_p by NMR on a 300 MHz Varian Mercury spectrometer fitted with a 5 mm liquids probe. The manual valves labelled a,b,c,d allow the converter to be bypassed in order to acquire the reference spectrum of n-H₂ which is used in the calculation of x_p . Pressure gauges P1 and P2 are installed at the inlet and outlet of the converter. The hydrogen gas flow rate is controlled by a mass flow controller (MFC, Alicat Scientific, MC-1SLPM-D/5M). Prior to operating the converter, a high vacuum is drawn on the cryostat and then about 250 mTorr of helium heat exchange gas is admitted. The flow path of the system is purged with helium gas for about 15 min prior to cool down. The cool-down time to attain stable para-enrichment was found to be less than 90 min.

Each NMR spectrum was acquired by accumulating 16 free induction decays (FIDs). Solenoid valves (Parker Hannifin, 20CC02GV4C4F) f and g in Fig. 2 are opened to circulate H₂ gas through the NMR tube. The spectra of n-H₂ and para-enriched H₂ at a specified pressure and flow rate were collected under identical conditions. The H₂ pressure in the NMR tube (P2 in Fig. 2) was kept the same in the experiments with and without the p-H₂ converter in the flow path by fine adjustment of the pressure regulator (P1 in Fig. 2). The FID was apodized with a 10 Hz exponential line-broadening factor prior to Fast Fourier Transformation. Minor distortions in the baseline of the resulting spectra were removed by subtracting away a third order Bernstein polynomial fit to the baseline. The H₂ peaks were integrated over a fixed frequency range, and the p-H₂ mole fractions were calculated using Eq. (1):

$$x_p = 100\% - \frac{S_p}{S_n} \times 75\% \quad (1)$$

where S_p and S_n are the NMR peak integrals of para-enriched H₂ and n-H₂, respectively.

3.2. Parahydrogen enhanced NMR

Since the signal enhancement is proportional to $(4x_p - 1)$, a 97% para-enrichment is predicted to give a factor of 2.90 greater signal enhancement than 50% enrichment. This was tested experimentally by comparing the spectra of propane gas formed by hydrogenation of propene in interrupted-flow ALTADENA experiments performed using a 400 MHz Varian VNMRs spectrometer equipped with a Varian 400 MHz triple resonance H(C/N) LC flow probe. A 3 mg sample of PdIn/SBA-15 (2.8 wt% Pd and 2.8 wt% In measured by ICP-MS) catalyst was loaded into a 0.25 in. O.D. quartz U-tube reactor and held in place with quartz wool. Details of the catalyst synthesis, characterization, and activation are provided in the SI. A K-type thermocouple probe was inserted into the exit side of the U-tube to enable real-time monitoring and control of the reaction temperature. The reactor was placed inside of a ceramic heating element mounted outside of the 5-gauss line of the 89 mm bore 9.4 T Bruker Ultrashield magnet. The field at the reactor location was 0.7 gauss. A reactant stream containing 100/220/80 mL/min of H₂/N₂/propene was prepared by mixing the outputs of three mass flow controllers. The gas mixture was fed into the U-tube reactor which was maintained at a temperature of 200 °C. Mixtures containing either 50% or 97% p-H₂ were used (as confirmed by NMR) when acquiring p-H₂ enhanced NMR spectra. To collect parahydrogen-enhanced spectra under static (non-flowing) conditions, the gas flow through the probe was interrupted (by TTL-controlled solenoid valves gated from the pulse program) and spectra acquired after an 0.2 s settling delay. During the interruption of flow through the probe, the gas was diverted around the probe so as not to perturb the steady-state reaction conditions.

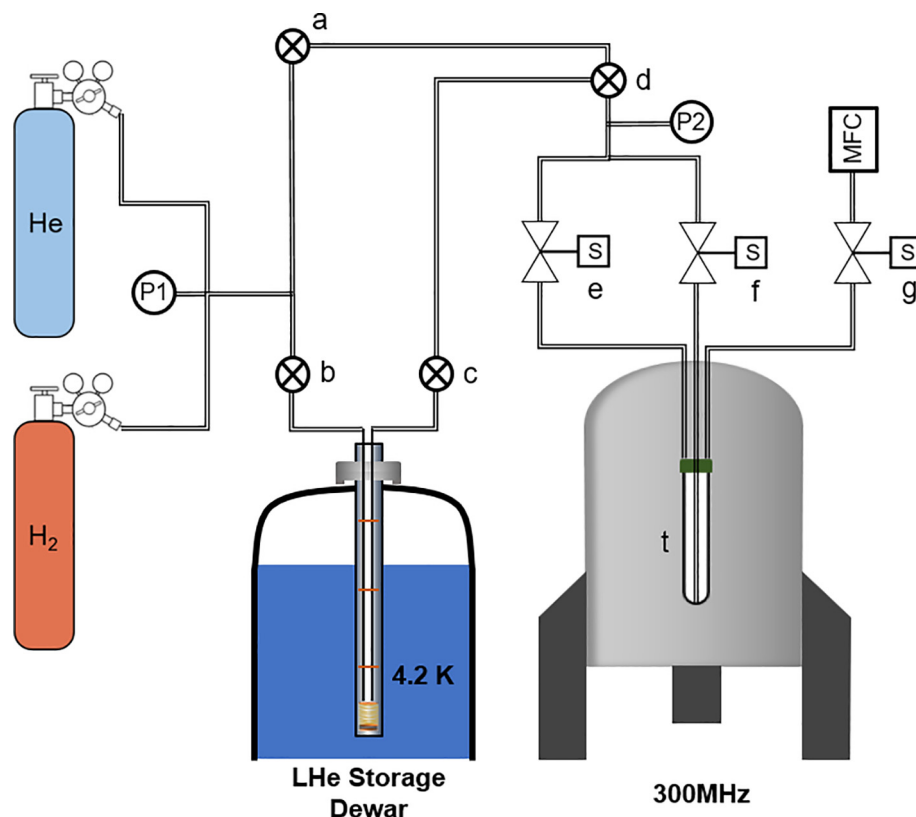


Fig. 2. Experimental setup used for measuring p-H₂ enrichment by proton NMR at 7 T (300 MHz Larmor frequency). MFC: mass flow controller. P1, P2: pressure gauges. a,b,c, d: manual valves. e,f,g: 2-way normally closed solenoid valves. t: 5 mm O.D. medium wall NMR tube with threaded PEEK cap.

After collecting the spectrum, the gas within the detection coil was refreshed by resuming the flow for 3 s before repeating the cycle. The spectrum was accumulated by repeating the refresh-interrupt-acquire cycle a total of 16 times. The thermally polarized spectrum of the propane formed by hydrogenation with n-H₂ (3:1 o-H₂:p-H₂) was acquired by summing 16 transients on a sample of gas sealed in the flow probe using a 5.0 s recycle delay.

4. Results and discussion

Fig. 3 presents an array of 300 MHz spectra of H₂ gas that passed through the converter at a series of different temperatures. These spectra were all acquired with the gas flowing continuously at a rate of 300 mL/min. The residence lifetime of the gas in the NMR tube with a volume 0.5 mL is thus estimated to be 100 ms which has a negligible effect on the proton resonance line width of H₂ gas with $T_1 \approx 1.6$ ms at 7 T. Consistent with para-enrichment, the NMR signal integral decreases with decreasing conversion temperature. A para-enrichment of $97.3 \pm 1.9\%$ was deduced from the spectrum obtained with the converter operating at 30 K at an H₂ pressure of 4.5 bar, in good agreement with the theoretical value of 97.0%. As seen in Fig. 3B, the data agrees well with the theoretical enrichment at all temperatures above 30 K.

The temperature dependence of the enrichment was also measured at a higher pressure of 7.2 bar and those experimental results also agreed with theory (Fig. S3). Lists of the numerical values of the p-H₂ enrichment data are provided in Table S2 in the SI. Unexpectedly, lowering the temperature below 30 K resulted in reduced para-enrichments (Figs. 3B and S4). There are at least two possible explanations, both of which are related to the condensation of hydrogen gas on the surface of the iron oxide catalyst at 4.5 bar. Condensation could either block access of the gas phase H₂ molecules to the surface, or alternatively, adsorption could lead to a decrease in the rotational energy gap due to an orientationally anisotropic confining potential of the adsorbed H₂, as reported for a Pd (210) surface [18]. The plots in Fig. 4 show the effects of flow rate and outlet pressure (P2) on the ortho-para conversion. Fig. 4A demonstrates that at 4.5 bar and 30 K, >95% enrichment is obtained at flow rates between 100 and 500 mL/min. At flow rates higher than 700 mL/min, the enrichment drops below 90%. In the prototype converter that was tested before inserting the 1/16-in. PEEK tube into the outlet of the conversion coil, as described above, the para-enrichment rapidly decreased with decreasing flow rate below 100 mL/min (Fig. 4A). This is attributed to para-ortho back conversion within the warmer stainless-steel tubing sections after the gas exits from the iron oxide catalyst bed. Evidently, the

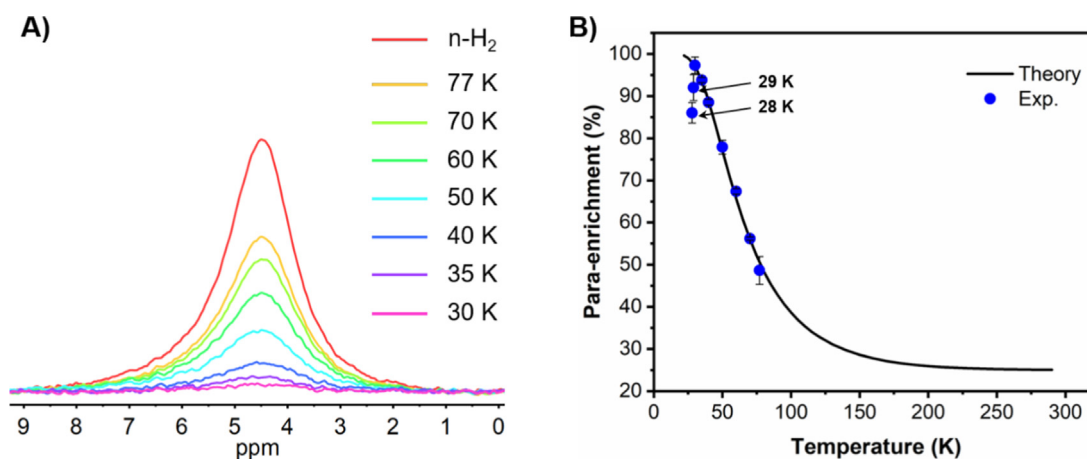


Fig. 3. (A) 300 MHz proton NMR spectra of H₂ gas pressurized at 4.5 bar flowing continuously through the 5 mm O.D. NMR tube at 300 mL/min after conversion at a series of different temperatures. (B) Comparison between the theoretical and measured values of the parahydrogen enrichment at the temperatures indicated in (A).

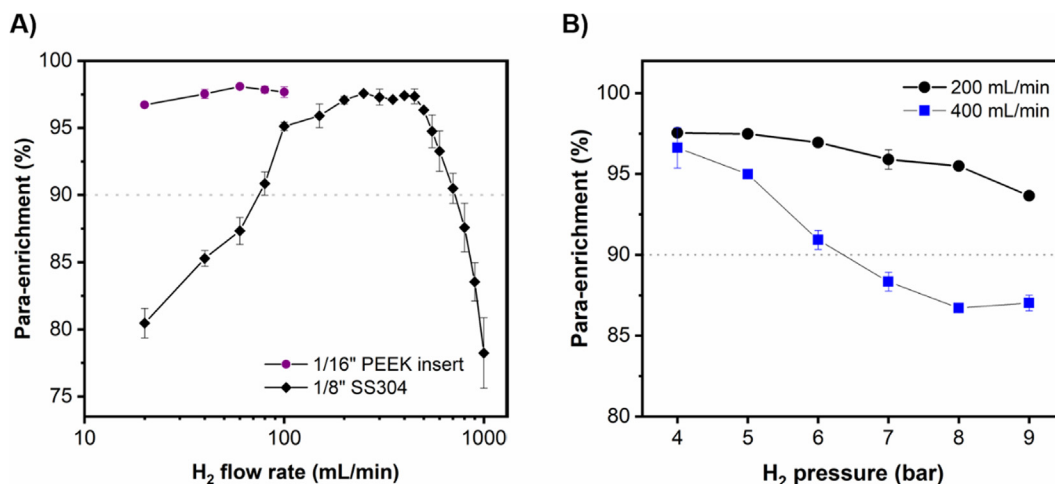


Fig. 4. (A) Parahydrogen enrichment as a function of H₂ gas flow rate at 30 K and 4.5 bar. Black diamonds: bare SS 304 outlet. Purple circles: after installing the 1/16-in. O.D. PEEK insert. (B) Parahydrogen enrichment as a function of system pressure of H₂ gas at 30 K and constant flow rates of 200 mL/min (black circles) or 400 mL/min (blue squares). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

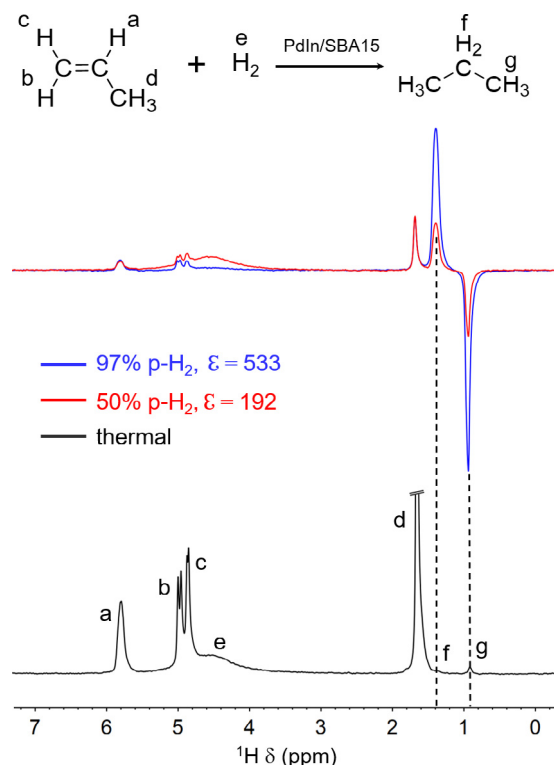


Fig. 5. Parahydrogen enhanced (top) and thermally polarized (bottom) 400 MHz ^1H NMR spectra obtained by flowing a 100/220/80 mL/min mixture of $\text{H}_2/\text{N}_2/\text{propene}$ over 3 mg PdIn/SBA-15 catalyst at 200 °C. The hyperpolarized spectra in blue and red were collected with 97% and 50% $p\text{-H}_2$, respectively. A decrease in the H_2 NMR signal (peak e) at the higher enrichment. The difference in the propene (peak a–d) signal intensities in the $p\text{-H}_2$ enhanced and thermally polarized spectra is due to the incomplete longitudinal magnetization build-up when the gas mixture is rapidly transported from the low-field to 9.4 T. Fig. S6 in the SI proves that by extending the settling delay in the flow probe, the propene signals gradually increase and reach the same intensity as those in the thermally polarized spectrum. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

contact time of $p\text{-H}_2$ with ferromagnetic impurities in the stainless tubing is increased. Another possible explanation is that the outlet tube could have become contaminated with fine particles of the iron-oxide ortho–para conversion catalyst. After installing the 1/16-in. O.D. PEEK tube, the para-enrichment significantly improved at flow rates in the 20–100 mL/min range. Fig. 4B shows how x_p depends on the outlet pressure at 30 K at flow rates of 200 and 400 mL/min. The enrichments exceeded 95% for pressures up to 8 bar at a flow rate of 200 mL/min. Measurements were not made at any pressure higher than 9 bar due to the limitation of the medium-wall glass NMR sample tube. For the flow rate of 400 mL/min, the enrichment exceeded 90% for pressures up to 6 bar and decreased to 87% at 9 bar.

The results of the parahydrogen enhanced NMR experiments using para-enrichments of 50% and 97% are presented in Fig. 5. The ratio of the signal enhancement factors was 2.80 ± 0.10 , in good agreement with the theoretical value of 2.90.

5. Conclusion

The relatively inexpensive home-built apparatus demonstrated here provides an economical means for continuous-flow para- H_2 enrichment to > 95% at flow rates up to 500 mL/min at 4.5 bar, which should be sufficient for most parahydrogen enhanced NMR experiments. The commercial cryocooler system filled with the same catalyst material, as reported in Ref. [11], was able to achieve

similar enrichment but at higher flow rates up to 4 L/min due to the much larger volume (33 cm^3) of catalyst. Interestingly, a decrease in the para-enrichment was observed upon reducing the temperature below 30 K, which could arise from the effects of condensation of the H_2 gas onto the surface of the iron oxide conversion catalyst. Highly para-enriched H_2 gas produced when liquid helium is available could be stored for weeks in aluminum canisters [15], which would provide a convenient means for dispensing it in remotely located NMR labs or user facilities.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jmr.2020.106869>.

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