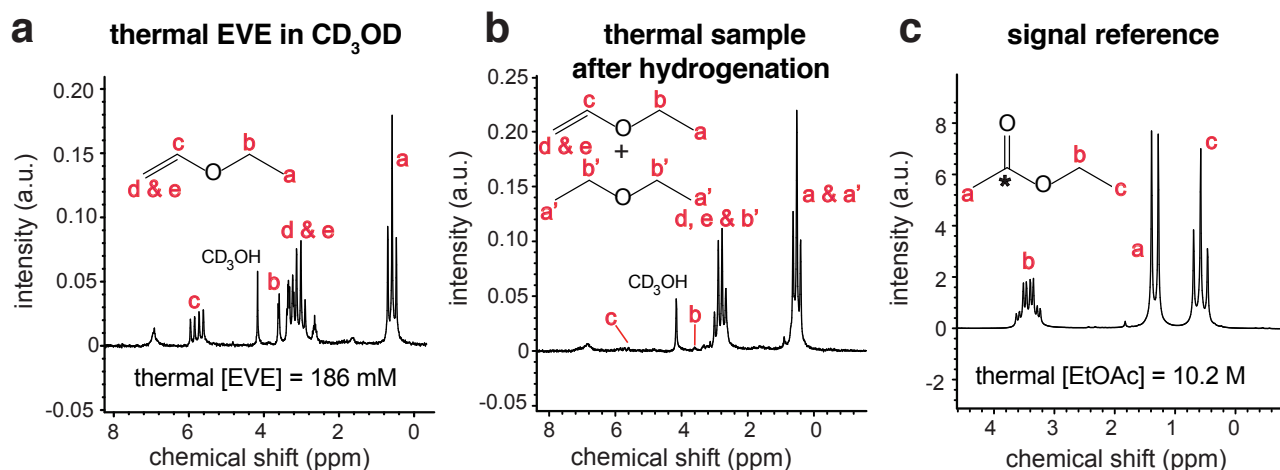
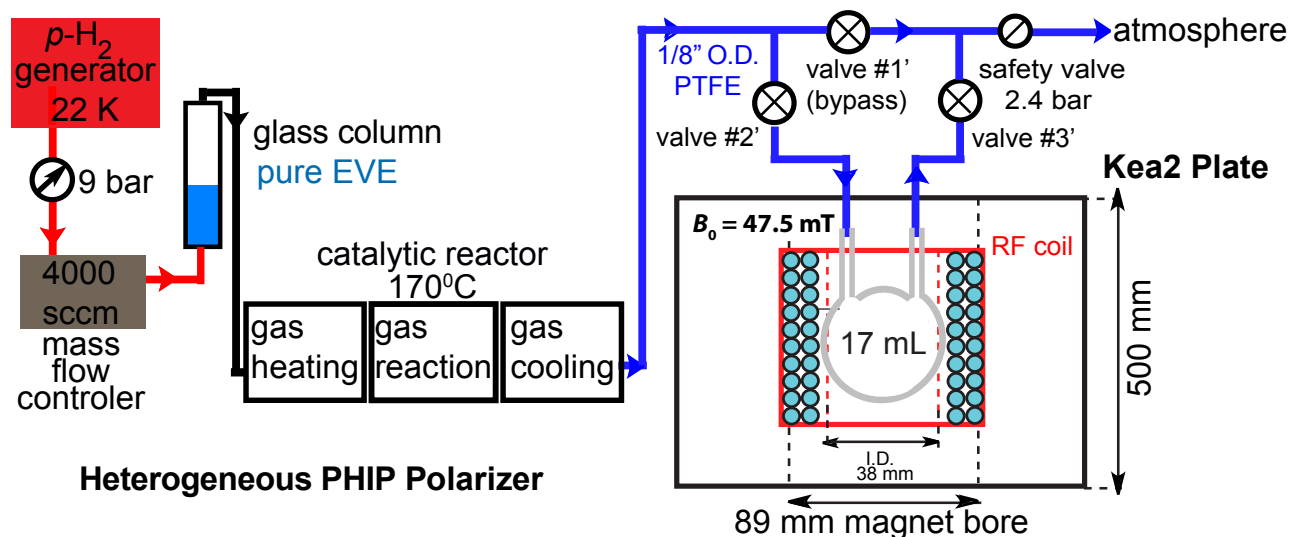


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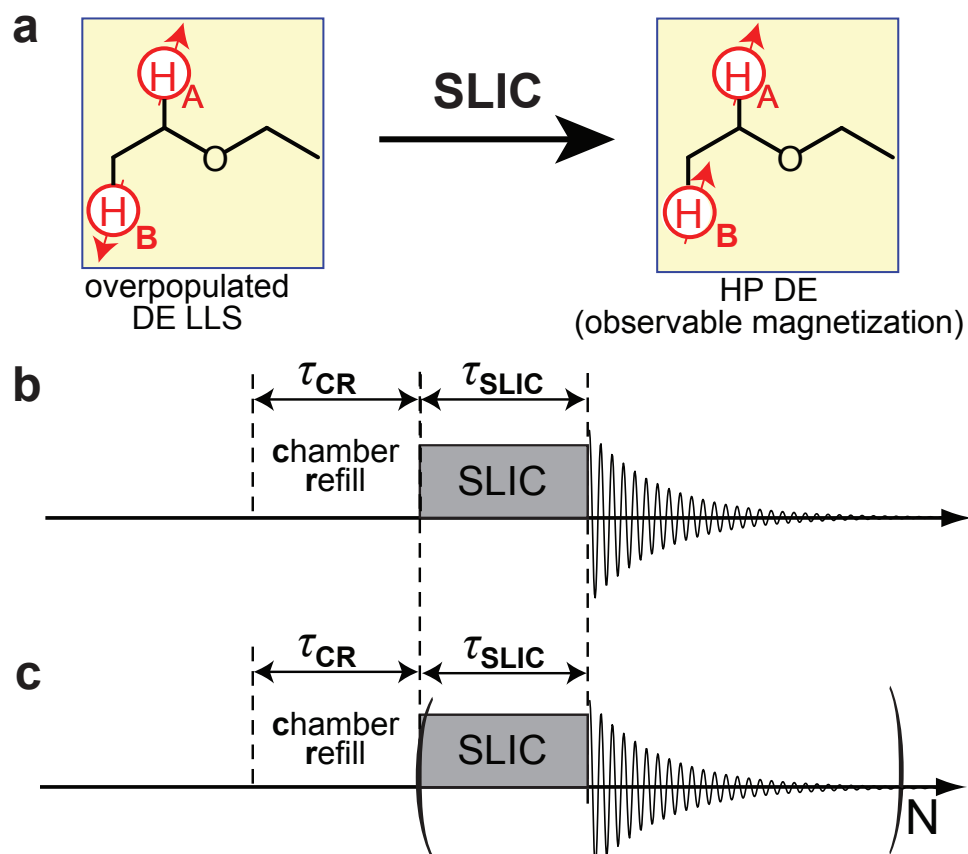
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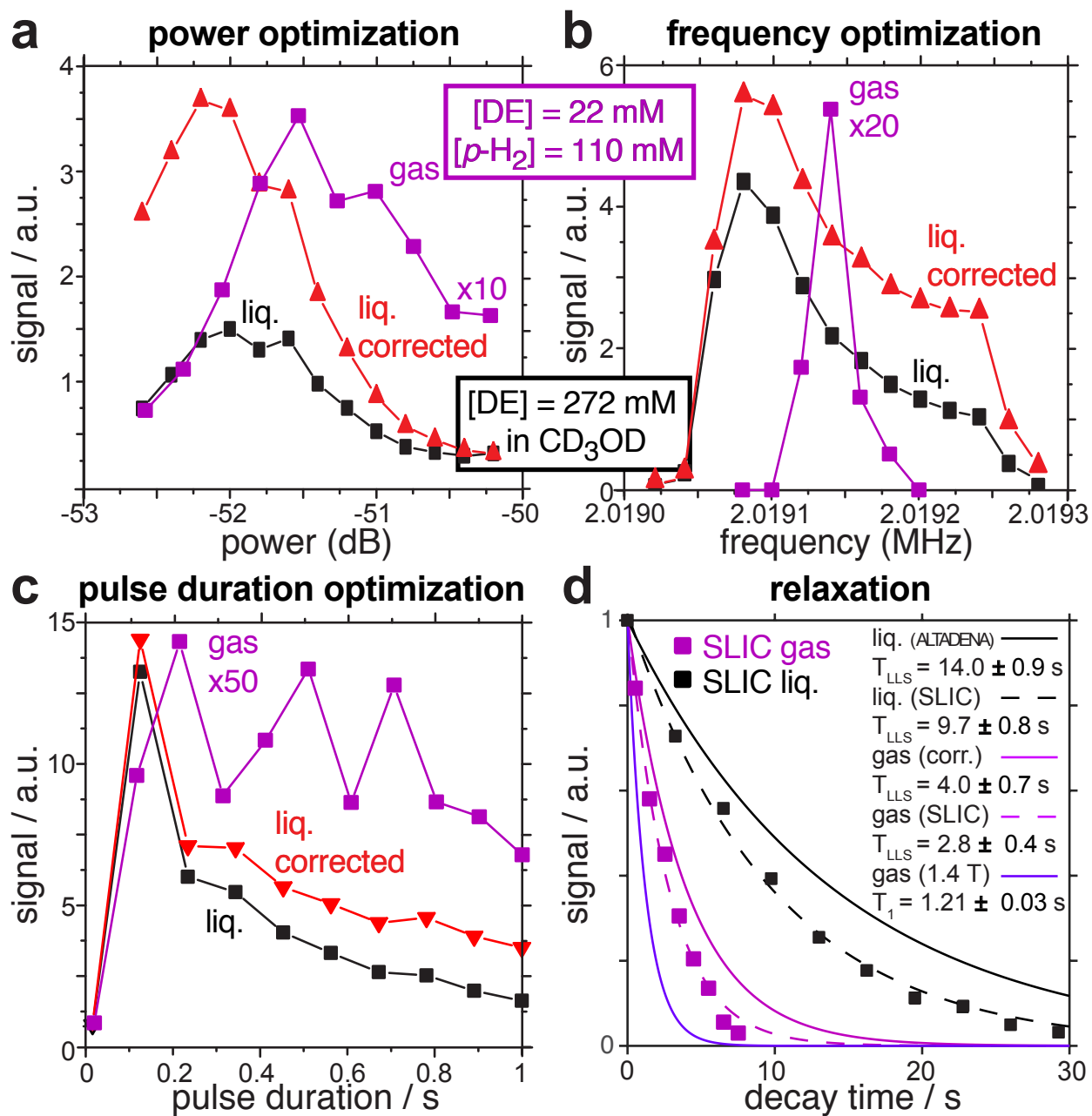
**Figure S1. NMR spectra of thermally polarized samples.** (a) Thermal  $^1\text{H}$  NMR spectrum of EVE in the liquid phase. (b) Thermal  $^1\text{H}$  NMR spectrum after hydrogenation. (c) Thermal  $^1\text{H}$  NMR spectrum of the signal reference ethyl acetate- $1\text{-}^{13}\text{C}$  recorded using the same acquisition protocol. All spectra were recorded with  $90^\circ$  pulse single scan. Note the NMR spectra were not calibrated: e.g.  $\text{CD}_3\text{OH}$  resonance should occur at  $\sim 4.78$  ppm.



**Figure S2. Heterogeneous hydrogenation and low field experimental setup.** The PHIP polarizer incorporates a catalytic reactor of  $\text{Rh}/\text{TiO}_2$  and an NMR spectrometer (Kea2, Magritek). The  $p\text{-H}_2$  flow is regulated by a mass flow controller and passed through a high-pressure glass column (prepared from modified HPLC column) filled with neat EVE substrate. The saturated gas mixture is sent through the catalytic reactor for hydrogenation at  $170^\circ\text{C}$ . The outgoing gas mixture ( $[\text{EVE}] = 22$  mM,  $[p\text{-H}_2] = 110$  mM) is collected in a 17 mL phantom sphere and  $^1\text{H}$  NMR spectroscopy performed at 2.0 MHz (47.5 mT) with Spin-Lock Induced Crossing (SLIC) radio frequency pulse sequences.



**Figure S3. SLIC pulse sequences for low field detection.** (a) Scheme of the transformation of the long-lived singlet state of diethyl ether into triplet state with observable magnetization by a SLIC pulse sequence. (b) Pulse sequence for optimizing SLIC transformation by varying RF amplitude, power, and frequency, (c) Pulse sequence used for the measurement of HP DE  $T_{LLS}$ .



**Figure S4. SLIC detection of hyperpolarized diethyl ether.** (a) Power optimization curve with liquid-phase values corrected for the relaxation losses assuming  $T_{LLS} = 9.7$  s (in red). (b) Frequency optimization curve. (c) Pulse duration variation. (d) Relaxation decays of DE. SLIC data obtained with 200 ms pulse duration. The mono-exponential decay fits lead to  $T_{LLS} = 9.7 \pm 0.8$  s and  $T_{LLS} = 2.8 \pm 0.4$  s for HP DE in the liquid and gas phase, respectively (dashed lines). Note the effect of SLIC pulses is not taken into account for calculation of  $T_{LLS}$ . Given that  $T_{LLS} = 14.0 \pm 0.9$  s in CD<sub>3</sub>OD under ALTADENA condition (black, continuous line), *i.e.*,  $\sim 1.4$  time longer than the partial SLIC value, the LLS lifetime in the gas phase is assumed to be equally underestimated by the SLIC approach, leading to  $T_{LLS} = 4.0 \pm 0.7$  s for HP DE in the gas phase (purple, continuous line). The spin-lattice relaxation at high field ( $T_1$ ) is shown in violet for comparison.

## Description of parahydrogen-induced RASER experiment

*p*-H<sub>2</sub> was bubbled for 10 s into a solution of ~200 mM EVE substrate and 4 mM Rh catalyst in CD<sub>3</sub>OD at Earth's magnetic field, corresponding to the maximum of polarization (8%) measured under ALTADENA condition. The pulse-acquisition sequence was initiated 2-3 seconds before inserting the NMR tube in the 61 MHz benchtop NMR spectrometer, with a pulse angle < 0.1° and the <sup>1</sup>H detector channel opened for 32 s. In these conditions, no radiofrequency pulse was applied to the HP pool so that the occurrence of RASER activity was spontaneous. The relaxation dynamics of RASER shows a variety of non-linear phenomena at play, such as a two-mode RASER regime with both H<sub>A</sub> and H<sub>B</sub> emitting allowing J<sub>H<sub>A</sub>H<sub>B</sub></sub> to be measured directly.

## Description of low field experiments with SLIC detection

### 1. Liquid phase

*p*-H<sub>2</sub> was bubbled into a solution of 272 mM EVE substrate and 4 mM Rh catalyst in CD<sub>3</sub>OD placed in an NMR tube. The NMR tube was inserted in the 47.5 mT magnet before hydrogenation. The hydrogenation reaction was carried out for ~10 seconds before running the pulse sequence and acquisition. NMR spectra were acquired using automated Prospa software (Magritek, New Zealand) with a custom-made program for running Spin-Lock Induced Crossing (SLIC) rf pulse sequences, which transform overpopulated LLS into observable magnetization. SLIC was applied immediately after hydrogenation reaction and signal optimization was performed for RF amplitude, power and frequency (Figure S4a-c). *T*<sub>LLS</sub> of hyperpolarized DE in CD<sub>3</sub>OD (Figure S4d) was measured with 200 ms SLIC pulses ("partial" SLIC) applied every 3.2 seconds.

### 2. Gas phase

*p*-H<sub>2</sub> gas was bubbled at a flow rate of 4000 sccm in a high-pressure glass column at 20 °C. The column was filled with pure EVE (5-10 mL) and the gas mixture was passed through the Rh/TiO<sub>2</sub> catalytic reactor at 170 °C. The resulting gas mixture was thermalized at 35°C when filling the 17 ml phantom hollow sphere placed in the NMR spectrometer. The filling was ceased by using valves #2 and #3 (Figure S2) immediately before application of the SLIC pulse sequence. Optimization of the SLIC signal was also performed for RF amplitude, power and frequency (Figure S4a-c). *T*<sub>LLS</sub> of hyperpolarized DE gas (Figure S4d) was obtained by monitoring the signal decay every second using 200 ms SLIC duration and a single gas refill.

## Chemical conversion, liquid fraction, and polarization levels

### 3. Chemical conversion of EVE to DE, $\alpha$

If no evaporation were taking place, it would be convenient here to monitor the chemical conversion by measuring the ratio between the integrated signal intensity of the vinyl group ( $S_{CH}$ ), which is unique to EVE, and its value before the reaction ( $S_{CH}^0$ ). However, the evaporation of both EVE and DE is expected to be quite significant during the reaction. For a given reaction time, the chemical conversion must therefore be assessed only within the thermal spectrum acquired after the reaction so that DE and EVE signal intensities are compared to each other but not to the initial concentration of EVE. Assuming that the integrated signal intensity of the overlapping EVE and DE methyl groups is proportional to  $[EVE] + 2 [DE]$  and cumulates 3 protons of EVE and 6 protons of DE, the chemical conversion  $\alpha = [DE] / ([EVE] + [DE])$ , independent of evaporation, can be determined as:

$$\alpha = (S_{CH3} - 3 \cdot S_{CH}) / (3 \cdot S_{CH} + S_{CH3})$$

### 4. Liquid fraction, $x$

The fraction of EVE and DE remaining in the liquid phase, i.e., the liquid fraction  $x$ , corresponds to the ratio  $S_{CH3}/S_{CH3}^0$  of the intensities of the methyl groups, with  $S_{CH3}$  normalized by the numbers of protons changing while EVE (3 methyl protons) is converted into DE (6 methyl protons). Hence, using chemical conversion  $\alpha$ :

$$x = \frac{S_{CH3}}{(1 + \alpha) S_{CH3}^0}$$

### 5. Enhancement, $\epsilon$ and polarization, $P$

Enhancement  $\epsilon$  is calculated as follow:

$$\epsilon = ( \exp^{15/TLLS} \cdot S_{HP}^{DE} \cdot [REF] \cdot 1.167 ) / ( S_{thermal}^{REF} \cdot [EVE]_0 \cdot x )$$

with  $S_{HP}^{DE}$  the signal intensity of HP DE,  $S_{th}^{REF}$  and  $[REF]$  the signal intensity and concentration of the thermal reference sample (neat ethyl acetate), respectively, and  $[EVE]_0$  the concentration of EVE before hydrogenation. 1.167 is a correction due to the difference of effective detection volume in the presence of the catheter for HP samples versus no catheter for thermally polarized samples. The mono-exponential term  $\exp^{15/TLLS}$  accounts for the relaxation losses occurring through the delay of 15 s necessary to avoid RASER activity (HP DE  $T_{LLS} = 14$  s at Earth's field). Polarization  $P$  is computed by multiplying enhancement  $\epsilon$  with the thermal polarization of protons at 1.4 T, which is equal to  $4.8 \cdot 10^{-4} \%$ .