Practical Aspects of RASER with the Parahydrogen-Induced Polarization Technique

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Radiofrequency amplification by stimulated emission of radiation (RASER) was recently discovered in a low-field NMR spectrometer incorporating a highly specialized radiofrequency resonator, where a high degree of proton-spin polarization was achieved by reversible parahydrogen exchange.[1,2] RASER activity, which results from the coherent coupling between the nuclear spins and the inductive detector, can overcome the limits of frequency resolution in NMR. Here we show that this phenomenon is not limited to low magnetic fields or the use of resonators with high-quality factors. We use a commercial benchtop 1.4 T NMR spectrometer in conjunction with the Parahydrogen-Induced Polarization (PHIP) technique performed in the Earth's magnetic field (ALTADENA condition) or in a high magnetic field (PASADENA condition) to induce RASER without any radiofrequency excitation pulses.[3,4] The results demonstrate that RASER activity can be observed on virtually any NMR spectrometer and measures most of the important NMR parameters with high precision.

Characterizing PHIP Hyperpolarized Products (or the Art of Avoiding RASER)

Our PHIP projects aim at characterizing the kinetics, polarization levels and lifetimes of hyperpolarized products for bioimaging applications. Experiments are based on a p-H_2 generator (>99%), a simple manifold to bubble p-H_2 through the prepared solutions, and a commercial, benchtop NMR spectrometer. Recently, we have realized the occurrence of some "strange FID" signals while detecting hyperpolarized protons, due to RASER activity.

⇒ **We show here results on hyperpolarized diethyl ether (HP DE), for which a delay of 15 s in the Earth's magnetic field is necessary to let the polarization relax (and thus avoid RASER) before inserting the samples in the spectrometer.[4]**

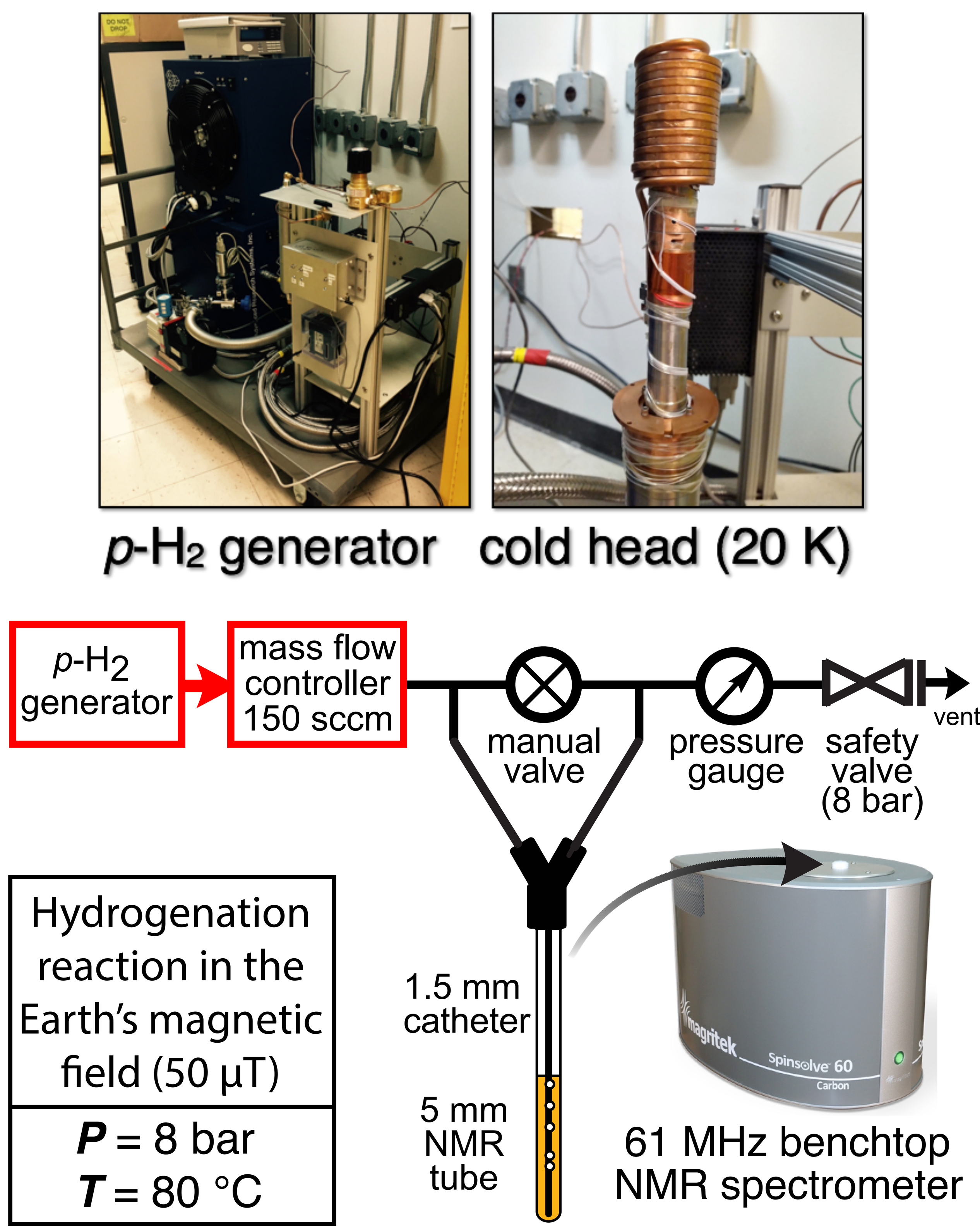


Figure 1: Experimental setup. The samples are pressurized at 8 bar with p-H_2 and heated at 80 °C for 30 s. The pairwise addition reaction is achieved by bubbling p-H_2 though the solution at a flow rate of 150 sccm in the Earth's magnetic field (50 µT), corresponding to ALTADENA conditions. Polarization levels are measured with a benchtop NMR spectrometer (Magritek, SpinSolve Carbon, 61 MHz / 1.4 T).

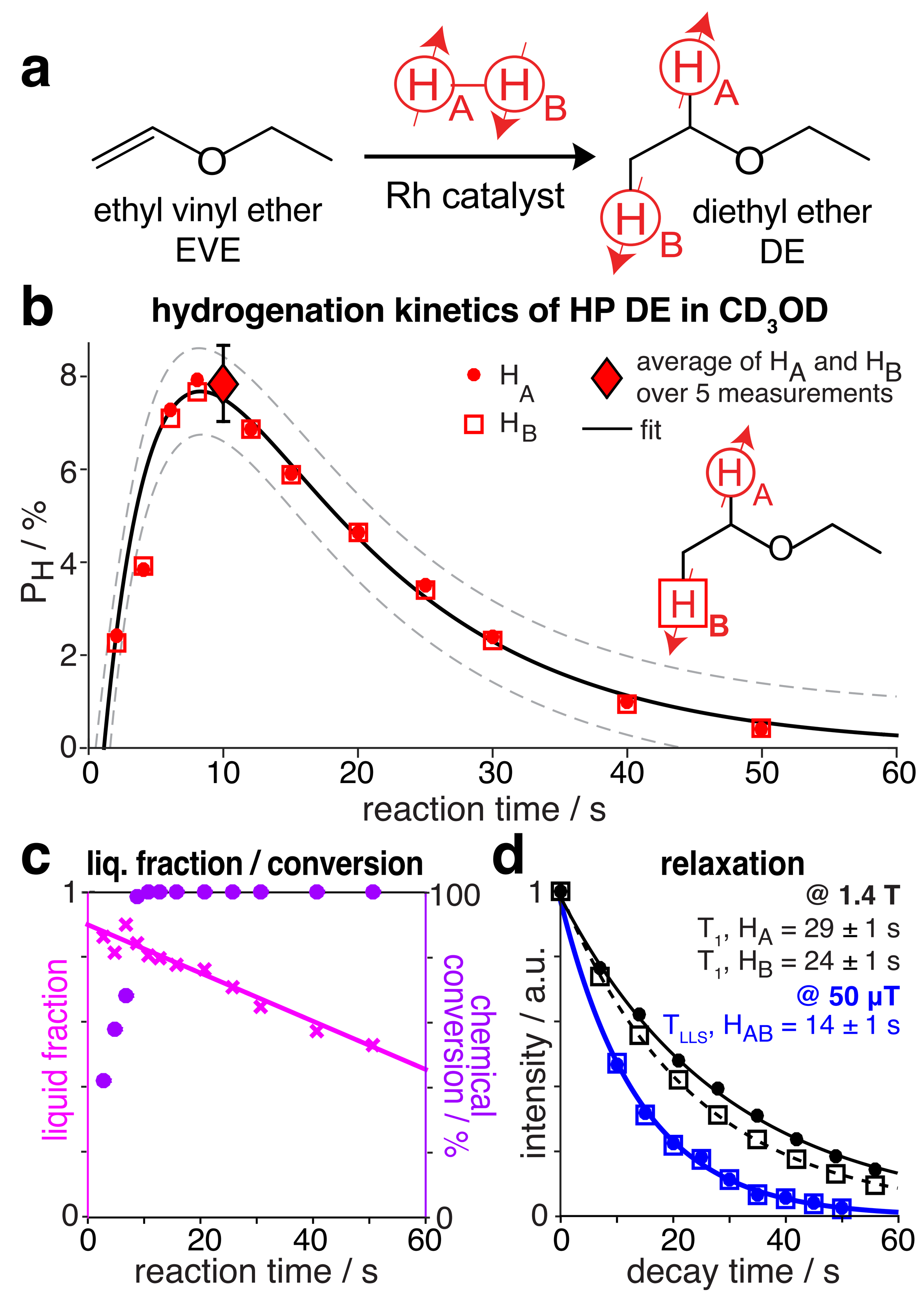
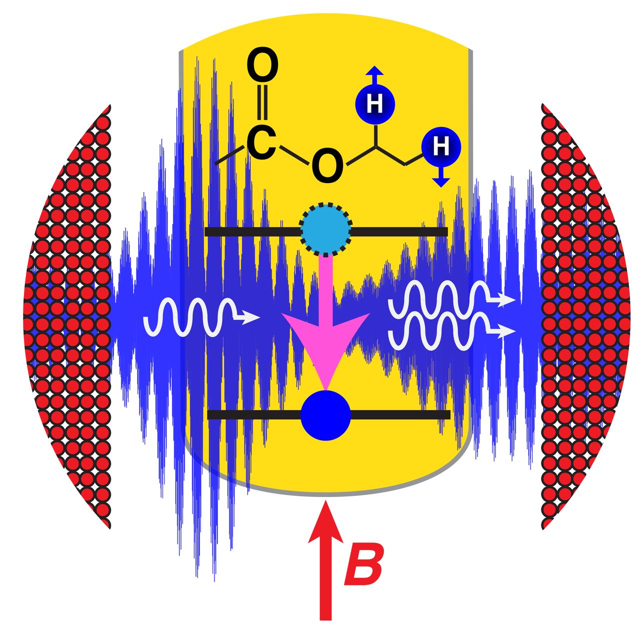


Figure 2. Hyperpolarized (HP) diethyl ether (DE). a) Reaction scheme. b) Back-calculated ^1H polarization levels of HP DE in CD_3OD as a function of reaction time in the Earth's magnetic field (50 µT). Dashed lines indicate 95% confidence boundaries of the fit c) DE liquid fraction and chemical conversion of EVE to DE. d) Exponential decays of HP DE NMR signals at 1.4 T and 50 µT.

RASER in the Eye



The radiation damping rate $1/\tau_{RD}$ can be expressed as:

$$1/\tau_{\mathrm{RD}} = -(\mu_0/4)\eta\, Q\, \gamma^2\, \hbar\, n_S\, P$$

RASER activity is initiated when $1/\tau_{RD}$ satisfies the following condition:

$$1/\tau_{\mathrm{RD}} > 1/T_2^*$$

$1/\tau_{RD}$	radiation damping rate
$1/T_2^*$	modified spin-spin relaxation rate
μ_0	vacuum permeability
η	filling factor of the resonator
Q	Quality factor of the resonator
γ	gyromagnetic ratio
$\hbar$	Planck constant
n_S	spin density
P	spin polarization

⇒ If $P > 0$, , $1/\tau_{RD} < 0$ and the associated line is additionally broadened by radiation damping with a total damping rate $k_{tot} = (1/T_2^* - 1/\tau_{RD}) > 1/T_2^*$

⇒ If $P < 0$, which corresponds to a population inversion, $1/\tau_{RD} > 0$ and the line is narrowed due to the decreased total damping rate $k_{tot} < 1/T_2^*$ ⇒ **RASER**

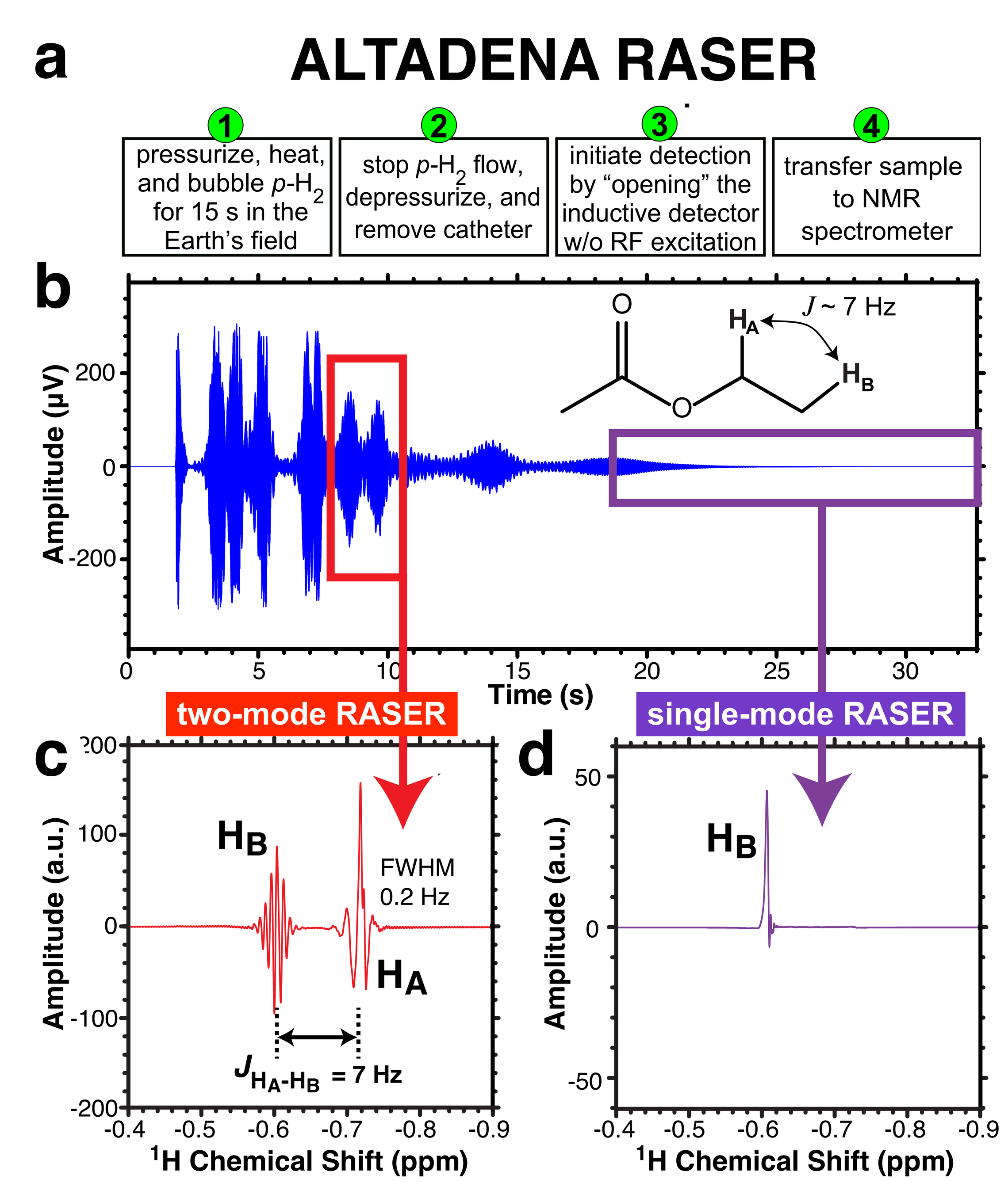


Figure 3. ^1H ALTADENA RASER within hyperpolarized ethyl acetate (400 mM). a) Reaction scheme. b) ALTADENA RASER signal recorded without a RF pulse after hydrogenation in the Earth's magnetic field. c,d,) Fourier spectra of the outlined time lapses.

⇒ J-coupling constants

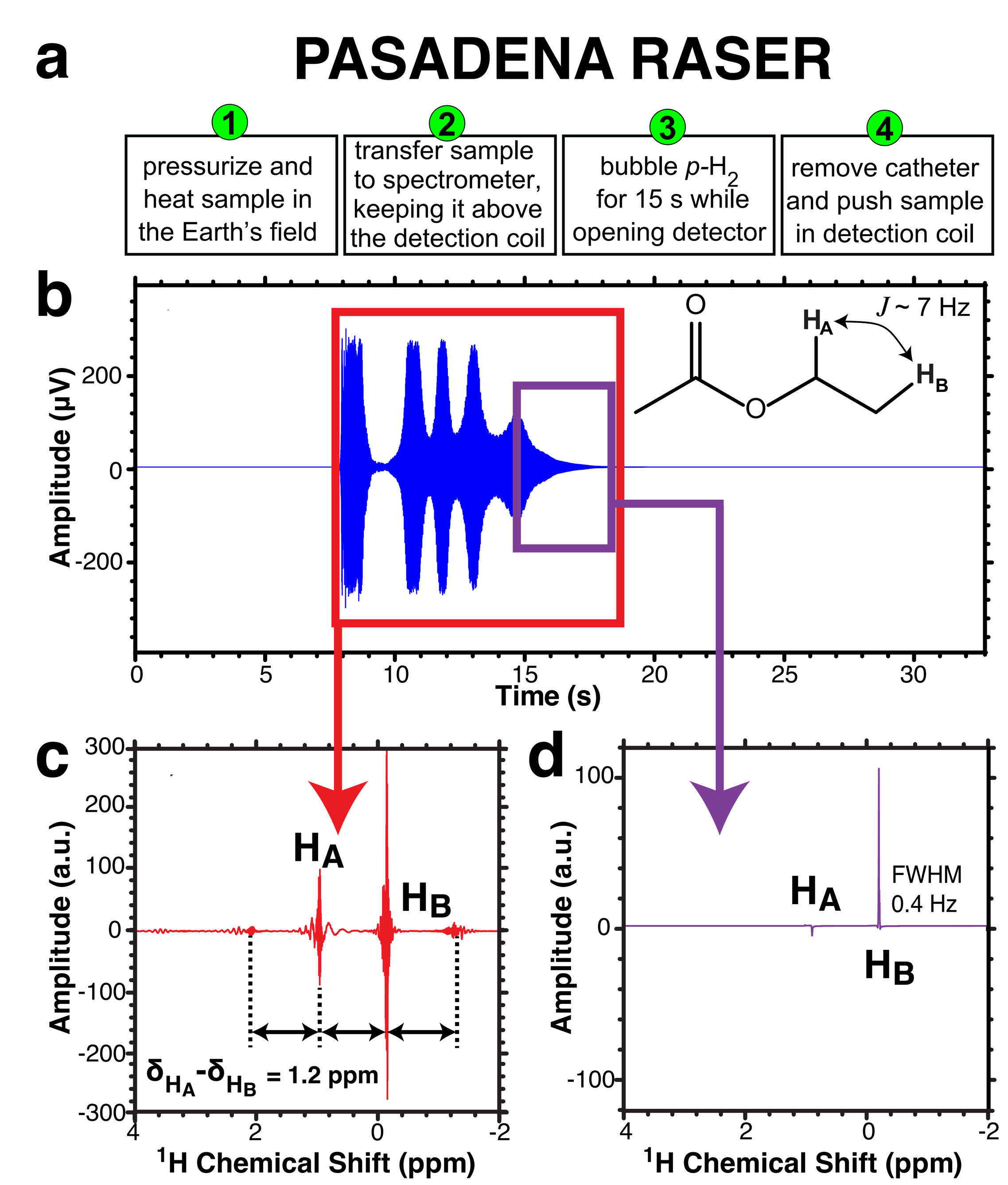


Figure 4. ^1H PASADENA RASER within hyperpolarized ethyl acetate (400 mM). a) Reaction scheme. b) ALTADENA RASER signal recorded without a RF pulse after hydrogenation in the Earth's magnetic field. c,d,) Fourier spectra of the outlined time lapses.

⇒ chemical-shift differences

References

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