Supporting Information

Ludwig et al. 10.1073/pnas.0908421107

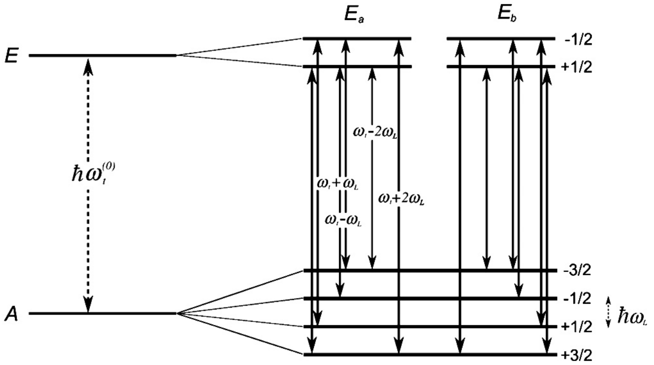

Fig. S1. Energy levels of the ground rotational state of methyl groups in an applied external magnetic field, showing Zeemann splittings. Solid arrows indicate possible transitions. (1).

1 Horsewill A (1999) Quantum tunnelling aspects of methyl group rotation studied by NMR. *Prog Nucl Mag Res Sp* 35:359–389.

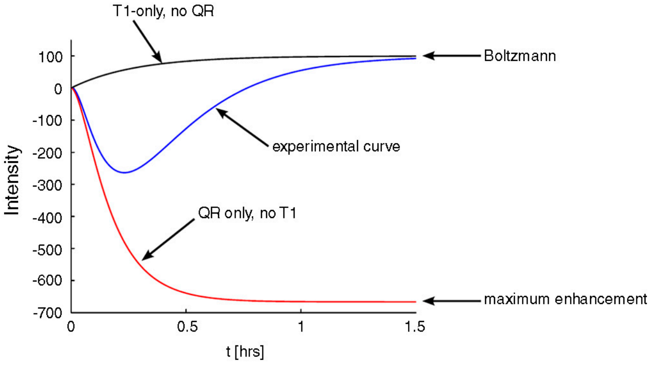

Fig. S2. After the rates in Eq. 6 have been determined by fitting experimental data, the buildup of the quantum rotor and the Boltzmann polarizations are simulated separately by either ignoring longitudinal relaxation or ignoring quantum rotor contributions to the time evolution of magnetization development (red and black lines). The theoretical maximum enhancement can then be defined as the ratio of the value of the quantum rotor curve (red line) and the Boltzmann buildup curve (black line) at infinite time. Although the NMR experiment and the polarization are performed at different magnetic field strengths and temperatures, this definition does not require correction factors for temperature and field ratios because it depends only on the time course determined by the sample in the polarizer. The transfer to the high-field NMR instrument and the conditions in the high-field magnet are constant throughout the time series and do not affect the outcome except for a change in absolute intensity, which is scaled to the fitted Boltzmann polarization level. Loss of polarization during the transfer and the settling delay are accounted for by fitting separate Boltzmann polarization levels for each nucleus.

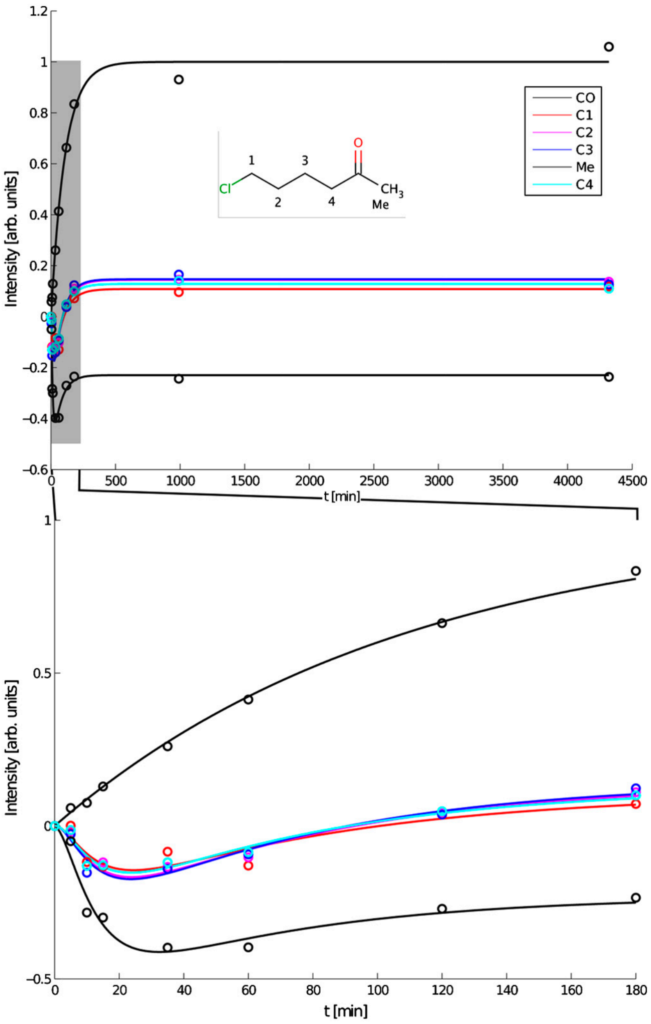

Fig. S3. ^{1}H decoupled ^{13}C spectra for the quantum rotor (QR) buildup of 6-chloro-2-hexanone, different time frames for experimental and fitted curves. (*Lower*) Focus on the first 180 min. (*Upper*) Time course over 75 h. Black, experimental data and simulated curves for CO and CH_3, respectively; C1, C2, C3, and C4 in red, magenta, blue, and cyan, respectively. Remarkably there is a fast buildup and relaxation during the first 3–4 h, after which relaxation becomes negligible and the polarization stays constant over the next >70 h with the methyl group maintaining a negative polarization compared to the rest of the molecule.

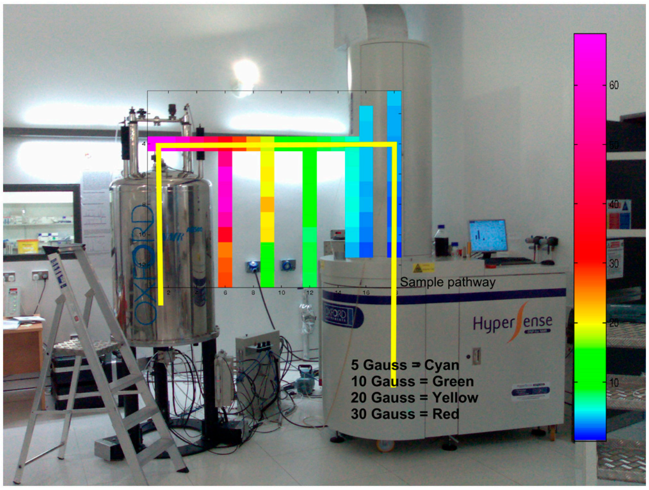

Fig. S4. Magnetic field map of the experimental setup. The magnetic stray fields of the two magnets always keep the sample in a field >5 G. To overcome the relatively low field at the top of the polarizer, a permanent magnet was fitted to the top of the polarizer magnet to ensure sufficient field strength at this location. The presented field map was recorded before this additional permanent magnet was fitted.

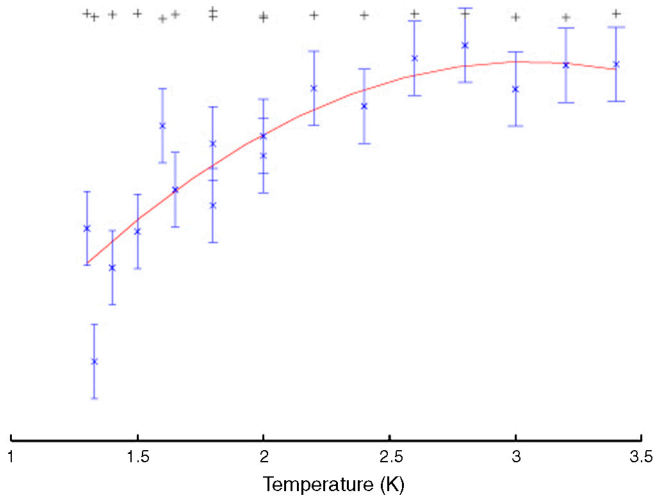

Fig. S5. Temperature dependance of the signal intensity of the acetic acid methyl group. The red line shows a fit of the signal intensity to a quadratic function, experiencing an absolute minimum around 3 K. The error bars show the rmsd to the quadratic fit and the black plus signs show the signal intensity of a baseline region in the NMR spectrum. At lower temperature, the quantum rotor effect is clearly more pronounced. This simulation follows a simple model proposed by Akagi and Nakamura (1), where nuclear T_1s increase as $\frac{1}{T_1} \propto T^2$ at temperatures below 3 K due to the low-frequency excitation intrinsic to amorphous substances. Nuclear T_1s also increase with external magnetic field. At operating temperatures of ≈1.5 K in a magnetic field of 3.35 T, the proton T_1s become sufficiently long to allow the QR polarization to accumulate. There have been more sophisticated approaches to describe the temperature dependence of tunnel splittings (reviewed in ref. 2) although little is known about the effects at temperatures <4 K. Nevertheless, these measurements show that the observed effects increase toward lower temperatures.

1 Akagi Y, Nakamura N (2000) Tunnelling molecular motion in glassy glycerol at very low temperatures as studied by 1H SQUID nuclear magnetic resonance. *J Phys—Condens Mat* 12:5155–5168.
2 Prager M, Heidemann A (1997) Rotational tunneling and neutron spectroscopy: A compilation. *Chem Rev* 97:2933–2966.