Haupt magnetic double resonance

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(Received 18 February 2003; accepted 19 March 2003)

The coupling of the tunneling- and proton dipolar reservoirs of a weakly hindered methyl group is used to dynamically polarize the rare-spin nuclei by combination with suitable radio-frequency irradiation schemes. $^1H \rightarrow ^{13}C$ and $^1H \rightarrow ^{15}N$ double-resonance experiments below 60 K in a pure γ-picoline matrix and with 1.5 % ^{15}N-acetonitrile as a guest are reported at a field of 5.17 Tesla. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1573635]

A striking effect resulting from the strict correlation between the methyl rotational and nuclear spin states was discovered by Haupt[1] who demonstrated that a large dynamic polarization, or ordering, of the proton spins with respect to the local dipolar field can be obtained after a sudden change in temperature of the solid. The effect is largest for a compound with a low potential barrier to the C_3 rotation of its methyl group and can be explained by the slow interconversion of the tunnel-split A ($I=3/2$) and E ($I=1/2$) methyl-spin isomers.[2] The interconversion process is coupled to rotational relaxation as a consequence of Pauli's exclusion principle restrictions on the CH_3-rotor state function.[2,3] As such, Haupt's observation is somewhat related to the *PASADENA* effect[4] since in both cases the enhanced nuclear alignment is ultimately caused by the spin statistics of indistinguishable proton particles.

In order to introduce the Haupt effect and also to estimate the proton polarization enhancement in our 220 MHz NMR apparatus, a direct comparison of the tunneling-induced dipolar and thermal Zeeman NMR signal in γ-picoline [Fig. 1(a)] was made. The experiments were carried out with a home-built cryogenic probe assembly fitted into a continuous-flow helium cryostat CF1200 (Oxford Ltd.). Typical $\pi/2$ pulse lengths of 5-6 μs were used. The γ-picoline sample (Aldrich, 99 %) was purified by distillation with lithium aluminum hydride, degassed by four freeze-pump-thaw cycles, and sealed in a glass tube at 10 mPa.

In Fig. 1 we show the dynamic ^{1}H magnetization in γ-picoline following a temperature jump from 4 K to 55 K after 40 min of thermal equilibration at 4 K. It is clearly seen that a transient dipolar signal (90° phase shifted with respect to the Zeeman signal) is induced. About 3 min after the temperature step it reaches a maximum and decays to zero thereafter. The detailed shape of the Haupt curve depends on the amplitude and duration of the temperature step, the A-E interconversion time T_c, and the dipolar relaxation time T_{1d}.[1,2] Under the present experimental conditions (see caption of Fig. 1) we obtain a maximum enhancement factor of ~ 70 compared to the equilibrium Zeeman signal at 55 K and an enhancement of ~ 9 with respect to the equilibrium Zeeman signal at 4 K. Obviously, the coupling of the CH_3 spin- and rotational degrees of freedom results in a dramatic cooling of the proton dipolar reservoir with spin temperatures as low as 80 μK when taking into account the experimental linewidth of $\delta_{\mathrm{fwhm}} \simeq 40$ kHz in γ-picoline. Due to the comparatively large splitting of the lowest rotational A- and E levels ($\nu_t \simeq 130$ GHz)[2] the tunnel system has a much larger heat capacity than the dipole system explaining the polarization enhancement after the temperature jump.

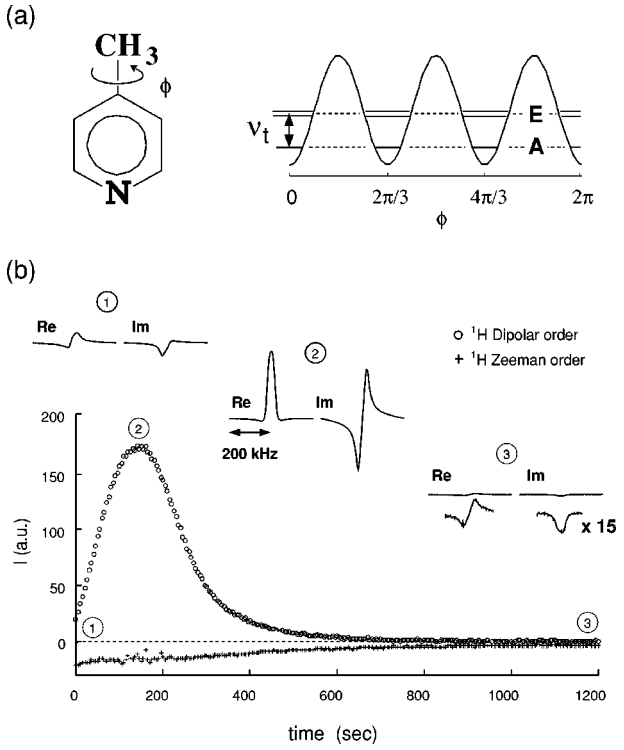

FIG. 1. (a) γ-picoline including a simplified, schematic diagram of the CH_3 potential. (b) ^{1}H magnetization intensity traces in γ-picoline at 55 K following a temperature jump (4→55 K within 20 sec) after 40 min of thermal equilibration at 4 K. The transient signal was sampled every 5 sec with ~0.05° tip-angle pulses. The Zeeman order is proportional to the negative intensity of the imaginary component (crosses) and the tunneling-induced dipolar order to the intensity of the real component (circles) of the complex signal. The Zeeman polarization, initially at its 4 K thermal equilibrium value, relaxes independently to the new 55 K thermal equilibrium value. A T_1 relaxation time of 250 sec is extracted. ^{1}H spectra at three different times (1), (2) and (3) are shown in the corresponding insets.

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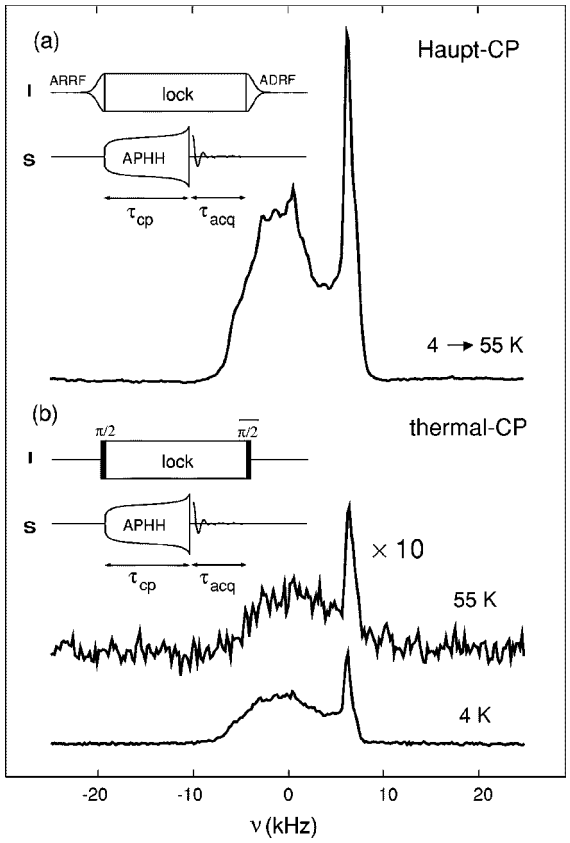

FIG. 2. (a) Single-shot $^1H \rightarrow ^{13}C$ Haupt-CP spectrum of γ-picoline for a 4 $\rightarrow$55 K temperature jump (40 min thermal equilibration at 4 K). Half-Gaussian ^1H ARRF and ADRF ramps (1 ms length with $\sigma_{arrf}=\sigma_{adrf}=0.3$ ms) were used to toggle between dipolar and Zeeman order. A tangential APHH step (tangent depth $\Delta=30$ kHz and angular velocity $\alpha=34°$ ms^{-1} assuming a coupling constant of $d_{IS}\simeq 20$ kHz) was used for polarization transfer ($\tau_{cp}=4$ ms). The ^1H locking field for CP and decoupling had an amplitude of 50 kHz. (b) Thermal $^1H \rightarrow ^{13}C$ CP spectra at 55 K and 4 K obtained with a single shot using pulse-timing diagram shown in the figure. Identical ^1H locking and APHH parameters were used as in (a).

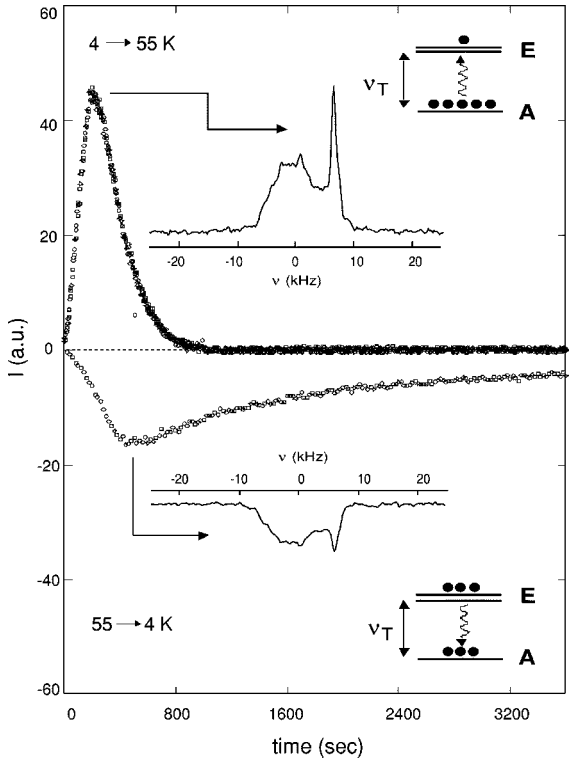

FIG. 3. Transient $^1H \rightarrow ^{13}C$ Haupt-CP curves in γ-picoline for upward (4 $\rightarrow$55 K) and downward (55$\rightarrow$4 K) temperature jumps sampled every 3 sec and 20 sec, respectively. The multiple-contact CP experiments were performed with the pulse sequence of Fig. 2(a) using identical parameters as described in the caption of Fig. 2.

The subject of this Communication is the transfer of the Haupt-induced ^1H dipolar order to the Zeeman order of rare spin species, such as ^{13}C and ^{15}N of matrix-isolated guest molecules, constituting a potential approach of sensitivity enhancement for solid-state NMR. Thermal contact among the different spins is thereby accomplished by making use of an adiabatic variation of the cross-polarization (CP) schemes introduced by Pines, Gibby, and Waugh.[5] In Fig. 2 single-shot $^1H \rightarrow ^{13}C$ cross-polarization spectra of γ-picoline are compared. The tunneling-enhanced ^{13}C spectrum [Fig. 2(a)] was obtained after a temperature jump from 4 K to 55 K and sampled at the maximum of the Haupt-curve. Cross polarization is induced by an adiabatic proton magnetization period (ARRF)[6] followed by an adiabatic passage Hartmann-Hahn (APHH) step.[7] After ^{13}C signal acquisition the proton spins are demagnetized again to dipolar order (ADRF)[6] allowing also for multiple-contact type experiments [see pulse-timing diagram as an inset in Fig. 2(a)]. Evidently, alternative CP schemes applying a ^{13}C ARRF ramp during τ_{cp}[5,8] are equally feasible. The Haupt-CP spectrum can be compared to the single-shot ^{13}C spectra at 55 K and 4 K obtained with cross polarization from ^1H Zeeman order at thermal equilibrium [see Fig. 2(b)]. We extract a signal-to-noise (S/N) enhancement factor of $\sim$40 and $\sim$5 *per shot* with respect to the thermal CP experiments at 55 K and 4 K, respectively.

To estimate the S/N amplification *per unit time* multiple-contact CP experiments were performed with the pulse sequences of Fig. 2. The transient Haupt-CP curves, for both upward temperature step (4$\rightarrow$55 K within 20 sec) and downward temperature step (55$\rightarrow$4 K within 2 min), are shown in Fig. 3. The positive and negative intensity traces demonstrate the inversion of the NMR signal occurring when the direction of the temperature jump is changed[1] (emphasized by the absorptive and emissive ^{13}C spectra at the maxima of the Haupt-CP transients as insets in Fig. 3). The population inversion may be interpreted as a reversal in sign of the proton dipolar spin temperature caused by the different initial population imbalance among the CH_3 A- and E levels [see inset in Fig. 3]. The different shape of the multiple-contact CP transients is mainly caused by the temperature dependence of the methyl interconversion time, i.e. $T_c^{55K}\simeq 100$ sec and $T_c^{4K}\simeq 1000$ sec.[1,2] Signal integration leads to the Haupt-enhanced CP spectra shown in Fig. 4(a) which can be compared to the ^{13}C spectra at 55 K and 4 K obtained with multiple-contact cross polarization from thermal ^1H Zeeman order using the same total measurement time [Fig. 4(b)]. The effective S/N enhancement per unit time is $\sim$50 and $\sim$7 over thermal CP experiments at 55 K and 4 K, respectively.[9]

We note here that, although the tunneling-induced dipolar order originates only at the CH_3 sites in γ-picoline, both methyl- and aromatic ^{13}C resonances are equally amplified

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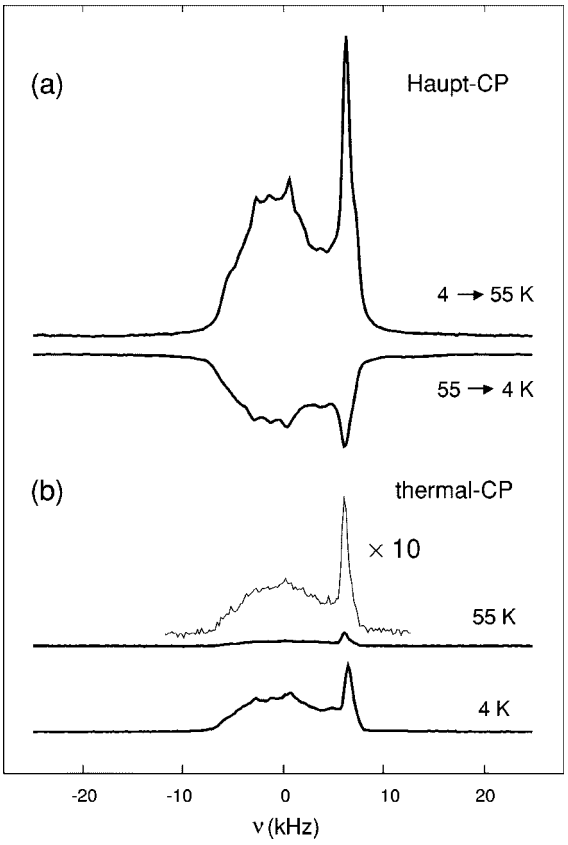

FIG. 4. (a) Integrated Haupt-CP spectra of γ-picoline for the $^1H \rightarrow {}^{13}C$ multiple-contact traces displayed in Fig. 3. (b) Thermal $^1H \rightarrow {}^{13}C$ multiple-contact CP spectra at 55 K and 4 K obtained with the pulse sequence of Fig. 2(b) using identical parameters as described in the caption of Fig. 2. For optimal S/N eight successive CP contacts per experiment were accumulated and signal averaged with a repetition delay of $\tau_r = 1.3 \times T_1$ using the same total measurement time as in (a) [$T_1^{55K} \simeq T_1^{4K} = 5$ min].

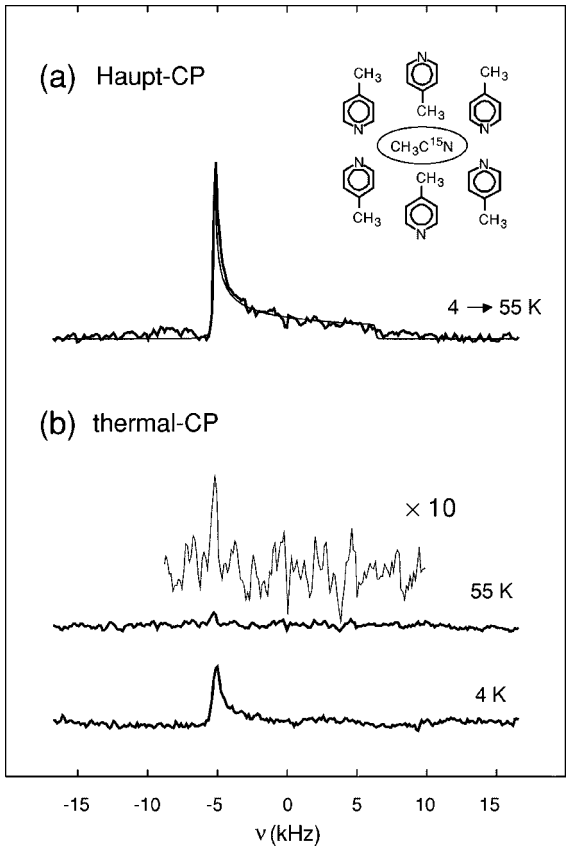

FIG. 5. (a) Single-shot $^1H \rightarrow {}^{15}N$ Haupt-CP spectrum of γ-picoline doped with 1.5 wt.% ^{15}N-acetonitrile (see sketch as inset) for a 4→55 K temperature jump sampled at the maximum of the Haupt curve (40 min thermal equilibration at 4 K). The spectrum was obtained with the pulse-timing diagram displayed in Fig. 2(a) using half-Gaussian ARRF and ADRF ramps (1 ms length with $\sigma_{arrf} = \sigma_{adrf} = 0.3$ ms). The APHH parameters were $\Delta = 15$ kHz, $\alpha = 42°$ ms^{-1} (assumed coupling constant $d_{IS} \simeq 1.5$ kHz), and $\tau_{cp} = 4$ ms. The ^1H locking field had an amplitude of 25 kHz for CP and 50 kHz for decoupling. The solid line represents a fit of the theoretical CSA lineshape to the experimental spectrum [$\delta_{csa} = -345(10)$ ppm, $\eta_{csa} = 0$]. (b) Thermal $^1H \rightarrow {}^{15}N$ CP spectra at 55 K and 4 K obtained with a single shot using the pulse-timing diagram shown in Fig. 2(b). Identical ^1H locking and APHH parameters were used as in (a).

by the polarization transfer. Hence, proton spin diffusion[6] (although symmetry restricted for the CH_3 groups)[3] is efficient in establishing a uniform dipolar spin temperature throughout the lattice. Moreover, the ^1H dipolar polarization at the rare-spin sites is rapidly refreshed after every cross-polarization step in the course of a multiple-contact experiment. Both features suggest the possibility of cross polarization also to a molecular guest species embedded in a 'Haupt matrix,' provided that no proton relaxation sinks (i.e. T_1, $T_{1d} \ll T_c$) are present in the vicinity of the guest molecules.

One example for such a system is described in Fig. 5, where $^1H \rightarrow {}^{15}N$ cross-polarization experiments are shown for γ-picoline doped with 1.5 wt.% ^{15}N-acetonitrile (99 % $CH_3C^{15}N$, Isotec Inc.). The solid mixture for the NMR experiments was prepared by rapid quenching of the liquid γ-picoline (containing 5 mg of ^{15}N-acetonitrile) at 77 K and subsequently transferring the sample to the precooled cryostat at 50 K. No special measures were taken to confirm that a homogeneous matrix was formed. The sensitivity-enhanced ^{15}N spectrum appears in Fig. 5(a), obtained with a single-shot CP experiment 300 sec after a temperature jump from 4 K to 55 K. The ^{15}N chemical-shift anisotropy (CSA) of the acetonitrile guest is clearly visible while the ^{15}N natural abundance contribution of the γ-picoline matrix is too low in intensity to be discernible in a single scan. The measured anisotropy $\delta_{csa} = -345(10)$ ppm for the axially symmetric CSA differs slightly from the value of $\delta_{csa} = -326(6)$ ppm obtained in pure $CH_3C^{15}N$ at 110 K.[10] A S/N enhancement factor of ~25 and ~3 is estimated by comparison with the single-shot ^{15}N spectra obtained by thermal cross polarization at 55 K and 4 K, respectively [see Fig. 5(b)]. The results are in reasonable agreement with the $^1H \rightarrow {}^{13}C$ Haupt CP enhancement obtained for undoped γ-picoline.

In summary, we have shown that the tunnel polarization of a weakly hindered methyl group can be transferred to a rare nuclear spin species by making use of the dipolar Haupt effect. ARRF/ADRF ramps combined with cross polarization were used to achieve the transfer, yielding anisotropic ^{13}C and ^{15}N chemical-shift spectra which are significantly enhanced in sensitivity over those obtained by thermal cross-polarization experiments at a field of 5.17 T (220 MHz proton frequency).

Haupt cross polarization is strongly favored in compounds possessing low-barrier methyl groups. The present

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experiments have all been performed on γ-picoline which contains one of the freeest methyl rotors known in the solid state ($\nu_t \simeq 130$ GHz). Although this molecule has an intrinsically low barrier of methyl rotation in the gas phase,[11] the crystal packing in the solid affects the hindering potential substantially: In fact, we have observed experimentally that the presence of guests in the γ-picoline matrix (acetonitrile and other dopant molecules) can destroy the Haupt effect completely and/or introduce proton T_1 and T_{1d} relaxation sinks which inhibit a Haupt-CP transfer. In this case the methyl-group matrix acts more like a non-paramagnetic relaxation agent and sensitivity enhancement at low temperature can still be achieved by signal averaging compared to the undoped case. Nevertheless, an alternative matrix material containing low-barrier methyl groups which are not or much less sensitive to intermolecular packing effects might be beneficial. Hitherto, only about 100 methyl groups have been investigated in detail with respect to their tunneling characteristics in the solid state.[12] It is conceivable that suitable 'Haupt CH_3 rotors' can be found or even designed with the help of systematic molecular dynamics and *ab initio* calculation procedures.

An interesting aspect is whether Haupt cross polarization can be combined with magic-angle spinning for high-resolution applications.[8] Sample rotation with frequencies well below the proton dipolar linewidth (i.e. $\nu_r \ll \delta_{\mathrm{fwhm}}$) has been shown[13] to considerably speed up the decay of dipolar order and as a result, also the tunneling-induced polarization is expected to be continuously saturated in this case. For $\nu_r \gtrsim \delta_{\mathrm{fwhm}}$, however, the relaxation of the average dipolar energy will be equal again to that of the static sample[14] and Haupt cross polarization should be feasible. The latter case requires spinning speeds of ~ 30 kHz or higher which is experimentally challenging at cryogenic temperatures. Alternatively, switched-angle spinning or stop-and-go strategies[15] could also be envisioned in the low-speed regime. No attempts in combining the Haupt effect with sample rotation have been reported so far.

Finally, it should also be pointed out that in contrast to the Zeeman polarization the tunneling-induced[16] polarization does not scale with magnetic-field strength. Hence, only $\sim 1/5$ of the enhancement reported in this study is expected at a field of 23.5 T (1 GHz proton frequency). In this respect, further extensions making use of the Haupt effect might be more attractive at low or even zero field. An exciting possibility is the combination of the tunneling-induced spin alignment with alternative NMR detection schemes (e.g. dc-SQUIDS)[16] or with alternative line-narrowing techniques, such as magic-angle rotation of the external magnetic field,[17] enabling one to perform measurements over a range of very low frequencies.

The authors thank M.H. Levitt for directing their attention towards the Haupt effect.

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