

Communication

Adiabatic cross-polarization via intermediate dipolar-ordered state

Jae-Seung Lee, A.K. Khitrin *

Department of Chemistry, Kent State University, Kent, OH 44242-0001, USA

Received 4 February 2005; revised 6 July 2005

Available online 3 August 2005

Abstract

It is experimentally demonstrated that an adiabatic demagnetization–remagnetization in the laboratory frame, where the Zeeman order of abundant nuclei is first adiabatically converted into the dipolar order, and then, into the Zeeman order of rare nuclei, can significantly increase polarization of rare nuclei compared to the conventional cross-polarization technique.

© 2005 Elsevier Inc. All rights reserved.

Keywords: Rare nuclei; ADLF/ARLF; Dipolar order; Liquid crystal; Static solid

Cross-polarization (CP) [1] is a standard technique in solid-state NMR for increasing polarization and, therefore, signals of nuclei with low gyromagnetic ratios. It is based on equalizing polarizations of nuclei of different types. When the number of rare nuclei N_S in a sample is much smaller than the number of abundant nuclei N_I , polarization of the rare nuclei can be increased by a factor of γ_I/γ_S , where γ_I and γ_S are gyromagnetic ratios of the abundant and rare nuclei, respectively. Equalizing polarizations is not the most efficient way to transfer the Zeeman order from abundant to rare spins. It has been known a long time ago that adiabatic transfer of order (polarization) would be more efficient. A thermodynamic consideration, based on conservation of entropy, is straightforward and not presented here. It shows that, compared to the conventional CP scheme, adiabatic transfer of polarization from abundant to rare nuclei can additionally increase polarization of rare nuclei by a factor of $(N_I/N_S)^{1/2}$. Several adiabatic CP schemes have been proposed in [1], and the mechanisms of adiabatic transfer have been further studied theoretically in [2,3]. The “total cross-polarization” [1,4–6] uses

adiabatic demagnetization–remagnetization in the rotating frame (ADRF/ARRF). With this scheme, up to 15-fold increase of ^{13}C polarization, compared to a single-pulse acquisition, has been reported for solid powdered adamantane [4], although no spectra or experimental details have been presented. In adiabatic modification of the conventional Hartmann–Hahn cross-polarization (HHCP), the Zeeman order is transferred directly from abundant to rare nuclei. The adiabatic passage through the Hartmann–Hahn condition [7] gives only a moderate increase of polarization, but the advantage of this technique is that it can be used under magic-angle spinning of the sample. The review of such methods can be found in [8].

Here, we present a simple adiabatic CP scheme (ACP), which creates significantly larger polarization of rare nuclei than the conventional HHCP. Similar to the “total cross-polarization” [1,4–6], the Zeeman order of the abundant spin system is first converted into the dipolar order and then, into the Zeeman order of rare nuclei. The difference is that these processes are now performed in the laboratory frame. There are two major advantages in using adiabatic demagnetization–remagnetization in the laboratory frame (ADLF/ARLF). It does not require long irradiation with high-RF power

* Corresponding author. Fax: +1 330 672 3816.

E-mail address: akhitrin@kent.edu (A.K. Khitrin).

(RF amplitudes, $\gamma B_1/2\pi$, of few kilohertz are sufficient), and the relaxation times in the laboratory frame are longer.

The first pulse of the sequence (Fig. 1), with adiabatic frequency sweep and low RF amplitude, starts irradiation on the abundant nuclei far off-resonance and then, its frequency gradually approaches the center of the spectrum. This pulse converts the Zeeman order of the abundant spins into the dipolar order. Secular dipole–dipole interactions between spins with different gyromagnetic ratios consist of ZZ terms only. However, all the spins have a common reservoir of dipole–dipole interactions [9]. Common spin temperature is established by flip-flops of the abundant spins, which adjust orientations of the abundant spins in the vicinity of rare nuclei according to the existing Z-fields produced by the rare nuclei. This equilibration process does not require flips of the rare spins. The second adiabatic frequency-sweeping pulse is applied to the rare spins. Irradiation starts at the center of the spectrum of rare nuclei and then the offset gradually increases. This pulse converts the dipole–dipole order into the Zeeman order of rare spins.

For the first test of this scheme, we have chosen a liquid-crystalline sample with natural isotope abundances, where a high-resolution ^{13}C spectrum can be acquired without magic-angle spinning of the sample. The experiment has been performed using a Varian Unity/Inova 500 MHz NMR spectrometer. Liquid crystal 5CB has been used as purchased from Aldrich, without further purification. Both ^1H and ^{13}C adiabatic frequency-sweeping pulses are shaped pulses with constant RF amplitude and time-dependent phase. The number of constant-phase steps in each of the pulses is 50 K. Each of the two pulses has 100 ms duration and 40 kHz frequency-sweeping range. The RF fields' amplitudes ($\gamma B_1/2\pi$) for ^1H and ^{13}C pulses are 1.6 and 4.2 kHz, respectively. The spin–lattice relaxation time of the dipole–dipole reservoir T_{1D} was measured to be 0.54 s. The hetero-nuclear decoupling sequence used in all experiments is SPINAL-64 [10].

The results are shown in Fig. 2. The spectrum (A) is acquired with a single ^{13}C pulse, starting with a thermal equilibrium state. The spectrum (B) is recorded after 2.65 ms CP with the matched Hartmann–Hahn RF fields of 19 kHz amplitudes. The result of the ACP with

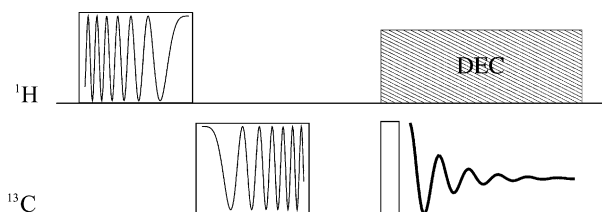


Fig. 1. Pulse sequence.

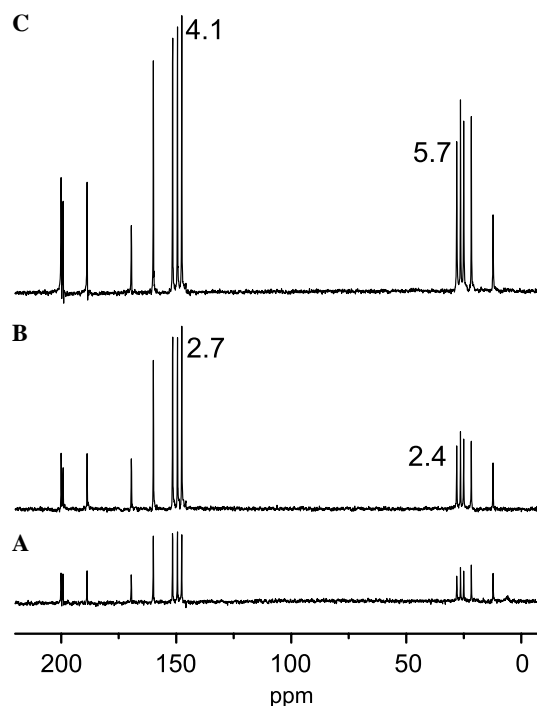


Fig. 2. ^{13}C spectra of 5CB at 298 K: (A) single-pulse acquisition; (B) cross-polarization; (C) adiabatic cross-polarization.

the pulse sequence in Fig. 1 is shown in Fig. 2C. The numbers near the peaks in Figs. 2B and C show the relative intensities of those peaks compared to the single-pulse acquisition.

One can see that the ^{13}C magnetization created by our ACP sequence is significantly higher than the magnetization resulting from the conventional HHCP. In fact, it is even higher than the theoretical limit of the HHCP in this system. We have found that the sequence also works well for static organic solids. One of the examples, static powder spectrum of adamantane, is shown in Fig. 3. Compared to a single-pulse acquisition (Fig. 3A), the ACP scheme produced a 6-fold increase in ^{13}C polarization (Fig. 3B). In this experiment, the proton and carbon shaped pulses had, respectively, 100 and 300 ms durations, 40 and 13 kHz sweeping ranges, and 1.0 and 4.8 kHz RF fields' amplitudes ($\gamma B_1/2\pi$). At the same time, this ACP scheme failed to work under magic-angle spinning of the samples.

The mechanisms of cross-polarization are extensively described in the literature. The details can be found in the monographs [9,11,12]. As an example, the ADRF/ARRF CP is discussed in [12, p. 191]. Here, we will only briefly mention some features of the ADLF/ARLF CP used in the present work. In practice, T_{1D} relaxation sets the time frame. The slow limiting process is the transfer of order from the dipolar to the Zeeman reservoir of rare spins, performed by the second frequency-sweep pulse. Its kinetics can be described by the Provotorov's thermodynamic theory [13,9] and viewed as

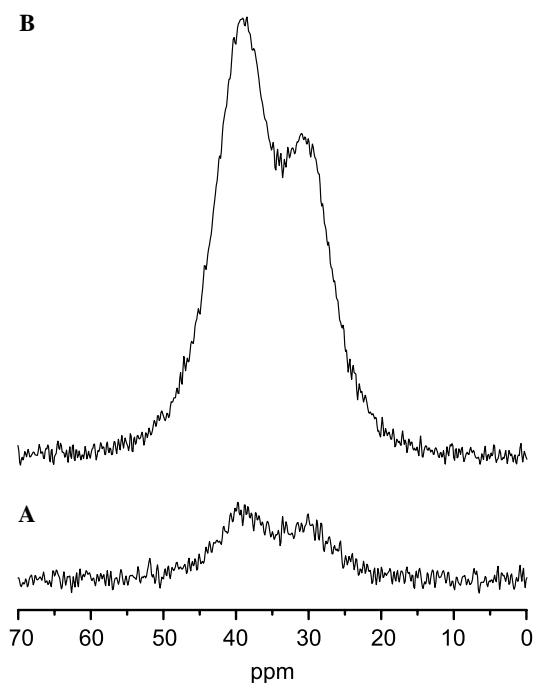


Fig. 3. ^{13}C spectra of adamantane at 298 K: (A) single-pulse acquisition; (B) adiabatic cross-polarization.

Equilibration of the dipolar and Zeeman temperatures in the frame rotating with the RF field ω_1 of the second pulse at the current offset Δ . The rate of this equilibration is $\pi\omega_1^2g(\Delta)$, where $g(\Delta)$ is the lineshape of rare nuclei. Adiabaticity means that Δ changes slowly compared to this equilibration rate. When Δ increases, $g(\Delta)$ decreases and, at some moment, the transfer of order becomes inefficient. The adiabatic enhancement factor gained at this point is $\Delta/\omega_{\text{loc}}$, where ω_{loc} is the dipolar local field [9] for rare nuclei. From the above discussion one can presume that the efficiency of ACP can be further improved by using better-designed pulse shapes with decreasing sweep rate and increasing RF amplitude.

In conclusion, modern NMR spectrometers can conveniently implement CP by adiabatic demagnetization–remagnetization in the laboratory frame. Compared to the conventional HHCP, this may significantly increase

polarization of rare nuclei in liquid crystals and static solids.

Acknowledgment

The work was supported by the Kent State University.

References

- [1] A. Pines, M.G. Gibby, J.S. Waugh, Proton-enhanced NMR of dilute spins in solids, *J. Chem. Phys.* 59 (1973) 569–590.
- [2] P. Hodgkinson, A. Pines, Cross-polarization efficiency in $I_{\text{N}}\text{S}$ systems using adiabatic RF sweeps, *J. Chem. Phys.* 107 (1997) 8742–8751.
- [3] O.W. Sørensen, Polarization transfer experiments in high-resolution NMR spectroscopy, *Prog. Nucl. Magn. Reson. Spectrosc.* 21 (1989) 503–569.
- [4] A. Pines, T.W. Shattuck, Carbon-13 proton NMR cross-polarization times in solid adamantane, *J. Chem. Phys.* 61 (1974) 1255–1256.
- [5] A. Pines, T.W. Shattuck, Enhanced inhomogeneous nuclear spin echoes for dilute spins in solids, *Chem. Phys. Lett.* 23 (1973) 614–616.
- [6] A. Pines, J.J. Chang, R.G. Griffin, Carbon-13 nuclear magnetic resonance in solid ammonium tartrate, *J. Chem. Phys.* 61 (1974) 1021–1030.
- [7] S. Hediger, B.H. Meier, N.D. Kurur, G. Bodenhausen, R.R. Ernst, NMR cross polarization by adiabatic passage through the Hartmann–Hahn condition (APHH), *Chem. Phys. Lett.* 223 (1994) 283–288.
- [8] M. Ernst, B.H. Meier, Adiabatic polarization-transfer methods in MAS spectroscopy, in: D.M. Grant, R.K. Harris (Eds.), *Encyclopedia of NMR*, vol. 9, Wiley, New York, 2002, pp. 23–32.
- [9] M. Goldman, *Spin Temperature and Nuclear Magnetic Resonance in Solids*, Clarendon Press, Oxford, 1970.
- [10] B.M. Fung, A.K. Khitrin, K. Ermolaev, An improved broadband decoupling sequence for liquid crystals and solids, *J. Magn. Reson.* 142 (2000) 97–101.
- [11] C.P. Slichter, *Principles of Magnetic Resonance*, Springer-Verlag, Berlin, 1996.
- [12] R.R. Ernst, G. Bodenhausen, A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Clarendon Press, Oxford, 2003.
- [13] B.N. Provotorov, Magnetic-resonance saturation in crystals, *Zh. Eksp. Teor. Fiz.* 41 (1961) 1582–1590.