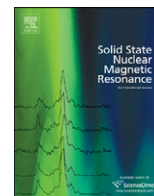




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Solid State Nuclear Magnetic Resonance

journal homepage: www.elsevier.com/locate/ssnmr

Investigation on the artificial exchange signals induced by the RIDER effect in CODEX experiments

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ARTICLE INFO

Article history:

Received 6 May 2012

Received in revised form

17 July 2012

Available online 20 August 2012

Keywords:

Slow motion

Organic solids

NMR

CODEX

RIDER

ABSTRACT

The CODEX (center-band only detection of exchange) NMR experiment is widely used for the detection of slow motions in organic solids, especially polymers. However, the RIDER (relaxation-induced dipolar exchange with recoupling) effect may result in artificial exchange signals in the CODEX pure exchange spectrum, which greatly limits the application of CODEX method. Herein, we investigate the distance range that the RIDER effect can reach by performing CODEX experiments on two typical organic solids, hexadecyltrimethylammonium bromide (CTAB) and semi-crystalline polyamide-6 (PA6) where there are no slow molecular motions at room temperature. Our experimental results demonstrate that generally two-bond distance is far enough to ignore the RIDER effect resulted from the dipolar interactions between ^{13}C and the fast relaxing heteronucleus ^{14}N . From the built-up curve of RIDER signals as a function of recoupling time and mixing time, it is clearly revealed that the RIDER effect can greatly affect the signal from ^{13}C directly bonded with ^{14}N . However, this RIDER effect accounts less than 3% of the reference intensity for signals from ^{13}C not directly bonded with ^{14}N if typical recoupling (~ 0.5 ms) and mixing times (~ 0.5 s) are used for the investigation of slow motions. When longer recoupling and mixing time are used, there are small RIDER signals even for the ^{13}C far away from the ^{14}N . These signals, to a large degree, result from the spin diffusion effect and/or the special microscopic molecule arrangement. However, they are so small compared to the reference signal ($\sim 5\%$) that they can be ignored. Finally, according to the simulation results, it is worth noting that the RIDER signal is still generally negligible compared to the signals due to slow motions if the chemical shift anisotropy reorientation during the mixing time is not too small (larger than 20°) under the condition of $4t_r$, recoupling time at the magic-angle-spinning speed of 6.5 kHz.

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1. Introduction

The properties of materials are closely related with the molecular motions in organic solids [1–3]. In general, the flexibility of a bulk polymer has directly resulted from the mobility of the constituent molecules. And a material's ability to withstand a stress depends on whether the energy of the stress could be absorbed by the molecules through the motions of chemical groups, including side chains and the backbone chains [4]. The behavior of polymers near the glass transition temperature is closely related with molecular motions, especially the slow motion, which can further be used to reveal the connection between macroscopic properties and microscopic mechanism in polymers [5–7].

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As a powerful technique for elucidating details of microstructures and segmental dynamics in solid material [1], two-dimensional (2D) exchange NMR methods have been successfully applied to detect molecular motions in organic solids [8–10], but the necessarily long experimental time often prohibits a detailed study of the dynamic processes. On the other hand, 1D exchange method exhibits unique superiority in saving experimental time [2,11–14]. Especially, the center-band only detection of exchange (CODEX) experiment is a rather important NMR method for detecting the slow motions of molecules in the range of 1–100 Hz on the basis of chemical shift anisotropy (CSA) reorientation during the mixing period [15,16]. Utilizing this method, the slow molecular motions can be quantified based on the intensities of the center-band in a high resolution MAS spectrum without the necessity of observing sidebands. Furthermore, detailed information about the characteristic time scale of the dynamic processes, the geometry and the amplitude of the slow motions can also be extracted [17]. Moreover, through the application of Arrhenius or WLF model for analysis of the

temperature-dependent CODEX exchange intensities, one is also able to determine the activation energy for chain reorientation, the correlation constants and quantitative correlation time distributions, which is extremely important in understanding the nature of glass transition behavior and the macroscopic properties of polymers [6,18].

However, in many natural or synthetic polymers, in particular biomacromolecules, there usually exists another kind of fast relaxing atoms, such as ^{14}N (about 99.63% in abundance), in the chains. It was found that these fast relaxing atoms can result in the relaxation-induced dipolar exchange with recoupling (RIDER) signals in the final pure exchange spectra of ^{13}C CODEX experiments [19]. Tycko et al. also theoretically calculated the ^{14}N effect on 2D ^{13}C MAS exchange spectra [20]. As a result, even when there do not exist any molecular slow motions in a chain, there may still exist signals in the CODEX pure exchange spectrum which is due to the RIDER effect instead of intrinsic slow motions of molecules. The RIDER effect can be well used to determine the distance between unlike spins without irradiating one of the two spins [19,21], or as a guide for investigating the factors affecting the performance of a CODEX experiment [22]. However, there is no efficient way to distinguish the signals resulting from the RIDER effect and intrinsic slow motions of molecules, which is a big obstacle for obtaining true and quantitative dynamic information from a CODEX experiment for a polymeric system. On the other hand, ^{15}N labeling is an important method for the assignment of individual residues in proteins, and it can be used to study the molecular motions. Hong and coworkers [23,24] used ^{13}C detected ^{15}N CODEX experiment to detect molecular motions by utilizing ^{15}N CSA, and Krushelnitsky et al. [25] tactfully utilized dipolar-CODEX to probe protein molecular motions by taking advantage of ^{15}N - ^1H uniaxial dipolar interactions. Still, appropriate isotope labeling is a good approach of eliminating the RIDER effect in a CODEX experiment. However, this approach is rather inconvenient and difficult for most polymers.

It will be more useful if there are means to obtain a CODEX signal, resulting from the intrinsic molecular motions, with the mixed RIDER signals being suppressed but without the requirement of isotope labeling. It was found that the dipolar coupling between ^{14}N and ^{13}C is very small, generally no more than 1 kHz even when the two atoms are covalently bonded due to the low gyromagnetic ratio of ^{14}N [19]. As the dipolar coupling is inversely proportional to the cube of the distance [26], the dipolar coupling between ^{14}N and remote non-covalent bonded ^{13}C is much smaller. Furthermore, there are many polymer systems where only one ^{14}N atom are positioned in the repeat unit of the polymer chain, which means that in most cases, most of the ^{13}C atoms are far away from the ^{14}N atoms except the directly bonded one, and thus the dipolar coupling between them are largely reduced, probably only about 10 Hz. Therefore, it is expected that out of a distance range the RIDER effect can be ignored and the CODEX signals from these ^{13}C atoms far away

from the ^{14}N can be well used to extract the dynamic information. However, such a distance range has never been studied systematically so far.

In this work, we focus on investigating the distance range that the RIDER effect can reach. Based on this distance range, one can determine the condition under which a CODEX experiment can be effectively used to detect molecular slow motions even when there exists a fast relaxing atom in a polymer chain. As ^{14}N is one of the most common elements in many polymer systems, we will mainly focus on discussing the RIDER effect induced by the ^{14}N - ^{13}C dipolar interactions. Theoretically, other fast relaxing heteronuclei will have the same effects as ^{14}N in a CODEX experiment. In two typical ^{14}N containing crystalline organic solids including small molecules and polymer, it is demonstrated that generally two-bond distance is long enough to neglect the RIDER effect if a proper chemical shift anisotropy recoupling time is used in a CODEX experiment, about 0.6 ms in our current experiments. On the other hand, it is found that the RIDER signal from remote ^{13}C atoms does increase with increasing the CSA recoupling time. However, this signal remains rather small, generally less than 5%, compared to the reference spectrum in the CODEX experiment even when a longer CSA recoupling time is used. So for this kind of polymer systems, the CODEX experiment can be effectively used to detect molecular slow motions through observing the signals from ^{13}C non-bonded with the ^{14}N under the condition of short CSA recoupling time, generally 4 rotor periods ($4t_r$) under the magic angle spinning (MAS) speed of 6.5 kHz in our experiments. We also simulate the CODEX signals for different CSA variation during the mixing time using the two-site jump motion model [15,16], and the simulation results indicate that the RIDER signal of ^{13}C non-bonded with ^{14}N , of the same order of magnitude in the two typical organic solids, is negligible compared to the slow motion signals even when the reorientation angle is only about 20° . Therefore, in a ^{13}C CODEX experiment, in order to reduce the RIDER effect as much as possible, it is well suggested to observe the chemical groups that are away from ^{14}N as far as possible.

2. Experimental section

Materials of samples: The hexadecyltrimethylammonium bromide (CTAB) was purchased from Aldrich Chemical Co., Inc. The semi-crystalline polyamide-6 (PA6) was commercially available. All the samples were directly used in the experiments without further treatment.

Nuclear magnetic resonance (NMR) experiments: Solid-state NMR experiments were performed on a Varian Infinityplus-400 spectrometer at a frequency of 100.5 MHz for ^{13}C and 399.7 MHz for ^1H at room temperature. A conventional 5 mm double-resonance HX CP/MAS NMR probe was used, and samples were placed in a 5 mm thin wall zirconia PENCIL rotor. The MAS speed was

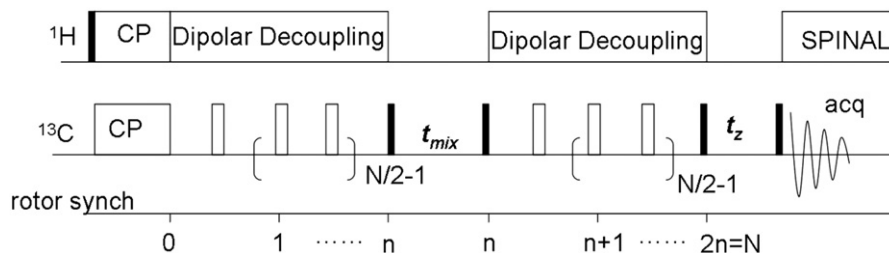


Fig. 1. Pulse sequences for CODEX experiment. The open bars represent the π pulse, and the solid bars correspond to the $\pi/2$ pulses on ^1H and ^{13}C channels. The rotor synchronization is triggered after the cross polarization (CP) period. Continuous wave decoupling is used during recoupling period on ^1H channel, where trains of π pulses on ^{13}C channel are used to refocus chemical shift anisotropy, and SPINAL decoupling is used in the acquisition period.

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