Chemical Physics 351 (2008) 33–36

Contents lists available at ScienceDirect

Chemical Physics

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

Double quantum CRAZED NMR signal in inhomogeneous fields

Bin Jiang [a,b], Huili Liu [a,b], Maili Liu [a,*], Chaohui Ye [a], Xian Mao [a,c,*]

[a] Wuhan Center for Magnetic Resonance, State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China
[b] Graduate School of Chinese Academy of Sciences, Beijing 100049, China
[c] Department of Physiology and Biophysics, Case Western Reserve University School of Medicine, Cleveland, OH 44106, USA

ARTICLE INFO

Article history:
Received 19 June 2007
Accepted 28 March 2008
Available online 3 April 2008

Keywords:
NMR
CRAZED experiment
Double quantum
Echo
Inhomogeneous fields

ABSTRACT

It has been well accepted that the double quantum (DQ) correlated-spectroscopy revamped by asymmetric z-gradient echo detection (CRAZED) signal is enveloped in the profile function $t_2\exp[-(t_2+2t_1)/T_2]$, but this function is too simple to describe the spin echo characteristics of the CRAZED free induction decay signal. In this paper the DQ CRAZED experiment is analyzed by including the homogeneous and inhomogeneous broadening effects, and a formula for the time domain DQ CRAZED signal is obtained. This formula includes the chemical shift echo and the inhomogeneous echo, both appearing at $t_2 = 2t_1$. Experiments have confirmed the theory.

1. Introduction

In recent years the correlated-spectroscopy revamped by asymmetric z-gradient echo detection (CRAZED) experiment [1,2] has attracted much attention. CRAZED is the modification of the pulsed field gradient enhanced correlation spectroscopy (PFG-COSY) experiment whose symmetric 1:1 gradient pulse pair has been replaced by the asymmetric 1:n ($n = 0,2$) gradient pulse pair. With the CRAZED experiment, correlation peaks between chemically uncorrelated species (like chemicals in separate glass tubes) and high-resolution spectra from inhomogeneous fields can be detected [1–4]. Applications of CRAZED are being expanded in various fields of nuclear magnetic resonance (NMR). Because the CRAZED signal intensity has a unique M_0 (the magnetization at thermal equilibrium) square dependence, CRAZED magnetic resonance imaging (MRI) has shown a different contrast from normal MRI [5–7] and would be very important in MRI studies. In the meantime, relaxation and diffusion measurements based on the CRAZED experiment have also been proposed [8–11].

The double quantum (DQ) CRAZED signal is known to have the simple form in Eq. (1), when the longitudinal relaxation and the molecular diffusion are neglected and when the condition of a weak demagnetization field ($\gamma\mu_0 M_0 t_2 \ll 1$) is satisfied [9,12]

$$s(t_1,t_2) = K\exp(-i2\omega_0 t_1 - 2t_1/T_2)[t_2\exp(i\omega_0 t_2 - t_2/T_2)] \tag{1}$$

where K is a constant when the pulse flip angles are fixed. The recorded free induction decay (FID) of the DQ CRAZED signal is enveloped in the profile function $t_2\exp(-t_2/T_2)$, which is known to behave like an echo [1]: when t_2 is short, the FID grows up because the function is proportional to t_2. When t_2 is long, the FID decays due to the transverse relaxation. However, this description is too simple to depict the spin echo characteristics of the DQ CRAZED signal in fairly inhomogeneous fields, which was documented as early as 1996 [13], but so far no equation has been available for the echo. As most CRAZED experiments are performed in inhomogeneous fields, to quantitatively describe the echo is of great importance. In this study, we have found that the DQ CRAZED signal is best described by

$$s(t_2,t_1) = Kt_2\exp[i\omega_0(t_2-2t_1)]\exp[-(t_2+2t_1)/T_2] \times \frac{1}{\pi}\int_{-\infty}^{\infty}\exp[i\omega'(t_2-2t_1)]g(\omega')\,d\omega' \tag{2}$$

where $g(\omega')$ is the inhomogeneous distribution function. Eq. (2) contains not only the chemical shift echo $\exp[i\omega_0(t_2-2t_1)]$ and the homogeneous relaxation $\exp[-(t_2+2t_1)/T_2]$, which are seen in Eq. (1), but also the inhomogeneity echo which is expressed as the integration in the frequency space. The inhomogeneous echo can be easily observed in experiments.

The CRAZED experiment in inhomogeneous fields has become the subject of a number of papers [3,4], but the inhomogeneous effect has not been quantitatively described. Therefore, Eq. (2) is useful in the CRAZED studies, particularly when the inhomogeneous effect is important.

* Corresponding authors. Address: Department of Physiology and Biophysics, Case Western Reserve University School of Medicine, Cleveland, OH 44106, USA. Fax: +1 216 368 3952 (X.A. Mao); fax: +86 27 8719 9101 (M.L. Liu).
E-mail addresses: ml.liu@wipm.ac.cn (M.L. Liu), xian.mao@case.edu (X.A. Mao).

0301-0104/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemphys.2008.03.027

2. Methods and materials

The sample used in this study was the doped H_2O (1% v/v) in D_2O with the presence of 0.1 g/L $GdCl_3$ which serves as relaxation reagent. The double quantum CRAZED experiment shown in Fig. 1 was performed at 25 °C on a Bruker AVANCE 600 spectrometer with the cryoprobe with z-gradient under homogeneous and inhomogeneous conditions. The intrinsic relaxation time of the doped water proton was 0.166 s, as measured by the saturation-recovery method. The gradient pulse duration δ was 1 ms, and the gradient strength G was 6 Gauss/cm.

3. Results and discussion

3.1. Double quantum CRAZED echo in inhomogeneous fields

The DQ CRAZED signal in the time domain is in fact a DQ echo, as has been directly compared to simple spin echoes [14]. The second gradient pulse, whose area is twice of the first one, refocuses the dephasing caused by the first one. This effect has been well known since the CRAZED experiments was proposed [1,2] and even since the demagnetization field effect in NMR was first discovered [15]. However, just like the conventional echoes, the DQ CRAZED echo can also refocus the inhomogeneous effect at the same time the chemical shift effect is refocused. According to the nonlinearity of the echo phenomena [16], all two-pulse experiments are inherently associated with echoes that are capable of refocusing the inhomogeneous effect. The ability of the CRAZED pulse sequence refocusing the chemical shifts has been shown in Eq. (1), where the chemical shift echo occurs at $t_2 = 2t_1$. The refocusing of the inhomogeneous effects, however, is not included in this well known equation.

Before the theoretical analysis of the DQ inhomogeneous echo is given in the following section, here a series of DQ CRAZED echoes with different t_1 recorded on a Bruker Avance 600 spectrometer with a cryoprobe are presented in Fig. 2. The inhomogeneous effect had been deliberately enhanced by deshimming the magnet so that the line width of the doped water signal in the conventional single-pulse experiment was 35 Hz. Compared with the contribution of the natural (homogeneous) relaxation (1.9 Hz as determined in relaxation measurements) to the line width, the inhomogeneous contribution was overwhelming. In this case, the inhomogeneous effect on the DQ CRAZED echoes was particularly obvious. All echoes precisely appeared at $t_2 = 2t_1$, although the echo looked asymmetric when the evolution time was short (see the top echo in the figure).

In order to see how the inhomogeneity affects the shape and the position of the CRAZED echo, the same experiments were performed under improved homogeneous conditions with $T_2^* = 78$ ms and the echoes are shown in Fig. 3. The echo shape is not sharp at all and the exact echo position is hard to determine.

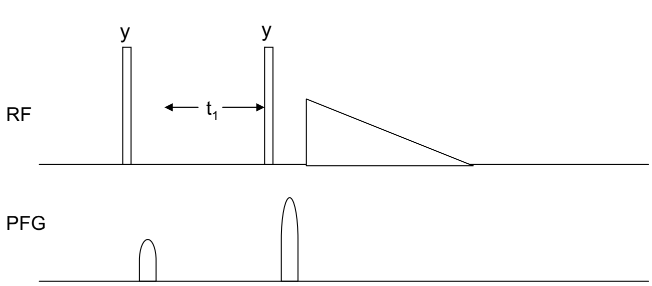

Fig. 1. Double quantum CRAZED pulse sequences used in this study, which consists of two $(90°)_y$ pulses and a pair of gradient pulses with the area ratio = 1:2.

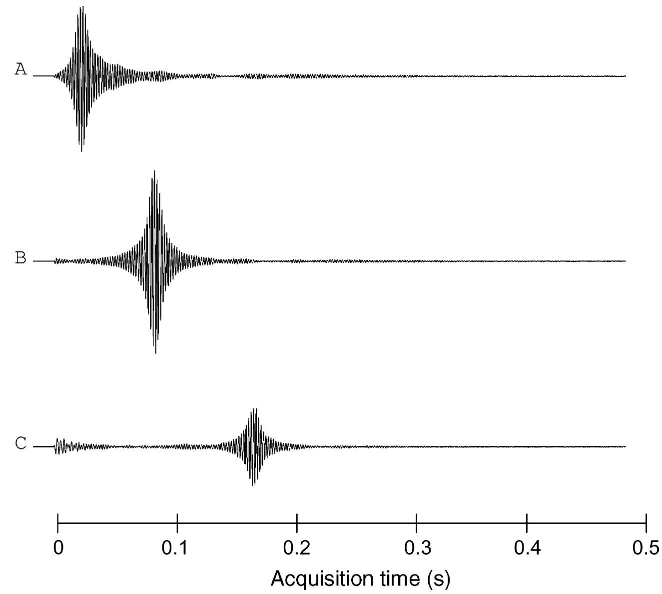

Fig. 2. Double quantum CRAZED echoes from a sample of doped H_2O in D_2O with varied t_1: (A) 10 ms, (B) 40 ms and (C) 80 ms. All echoes appeared precisely at $t_2 = 2t_1$. The experiments were conducted in an inhomogeneous field with an effective $T_2^* = 9$ ms (line with 35 Hz), while the homogeneous T_2 was 166 ms (contributing 1.9 Hz to the total line width). The water resonance was purposely moved to −200 Hz off the carrier so that the echo shape was better seen.

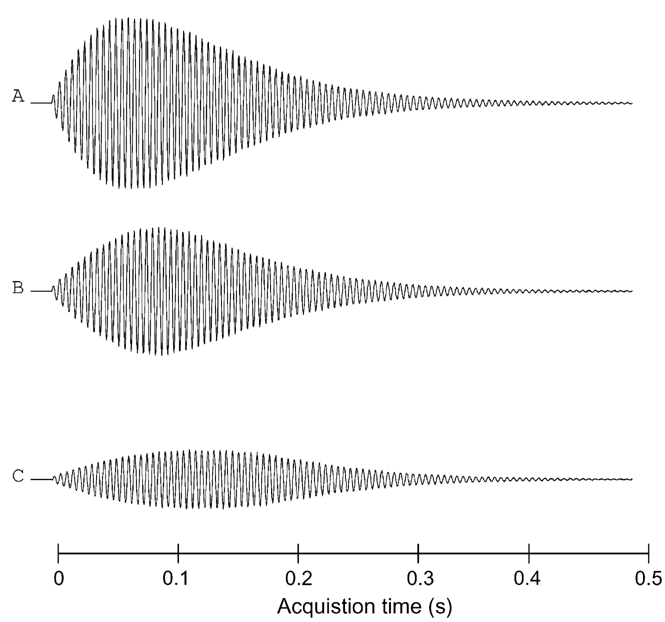

Fig. 3. The same experiments as Fig. 2 (t_1 = 10, 40 and 80 ms for A, B and C, respectively) but with improved homogeneity ($T_2^* = 78$ ms, T_2 = 166 ms).

In this case the function $t_2\exp(-t_2/T_2)$ apparently plays a more important role than the inhomogeneous contribution.

3.2. Formalism of the CRAZED echo by including the inhomogeneous effect

To understand the DQ CRAZED echo in inhomogeneous fields, it is necessary to analyze the DQ CRAZED experiment. It is known that in the CRAZED experiment the demagnetization effect occurs only after the second pulse and that the demagnetization field forces the precessing transverse magnetization to be multiplied by the longitudinal magnetization [1,2,17,18]. Although the