High resolution NMR spectra in inhomogeneous fields via intermolecular multiple quantum coherences without coherence selection gradients

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Introduction

Intermolecular multiple quantum coherence (iMQC) method has been shown to be able to recover high resolution NMR spectra from inhomogeneous field [1,2,3]. Unlike a conventional spectrum, the linewidth of which is determined by the absolute homogeneity of magnetic field across the sample, linewidth of a high resolution 1D spectrum based on iMQC methods is generally thought to depend only on the relative homogeneity of magnetic field over the dipolar correlation distance $r_d = \pi/\gamma G\delta$, where G and δ are the amplitude and duration of the coherence selection gradient, respectively [4,5]. Therefore, to get an iMQC high resolution spectrum, the pulse sequence must include coherence selection gradient. The coherence selection gradient is used to produce a distant dipolar field and select signals with expected iMQC order. However, our recent work shown below demonstrate that the coherence selection gradient is not necessary for an iMQC high resolution spectrum in an inhomogeneous field, if an appropriate phase cycle scheme is used.

Experiments

A solution of methyl ethyl ketone in cyclohexane was used as a sample. The pulse sequence shown in Fig.1 was used for intermolecular double quantum coherences (iDQC) [6]. The conventional 1D spectrum under a homogeneous field is shown in Fig.2. Fig.3 shows the 1D and 2D spectra obtained under an inhomogeneous field with line-width about 200 Hz. The inhomogeneous field for Fig. 3(a~c) is linear along the XY plane with the X1 and Y1 coils deshimed, and the inhomogeneous field for Fig. 3(d~f) is non-linear along the XY plane with the XY, X2Y2, X1 and Y1 coils deshimed. The conventional 1D NMR spectra acquired inside these inhomogeneous fields provide little information about chemical shifts and J couplings (Fig. 3(a) and (d)). For the IDEAL-II pulse sequence, a four-step phase cycling with the phases of the first RF pulse (x, $-x$, y, $-y$) and the receiver (x, x, $-x$, $-x$) was employed. The 2D spectra have been sheared by counterclockwise rotating the streaks by 63.4°. High resolution 1D spectra shown were obtained by projecting the sheared 2D spectra along the F2 axis.

Results

Fig.3(c) and (f) show that the IDEAL-II pulse sequence without any coherence selection gradient can produce high resolution 1D spectra in the inhomogeneous field. In fact, the gradient-free iDQC spectra show better resolution for the solute peaks. Compared to the spectra obtained with G=0.09 T/m, the line-width of the singlet from CH_3 group of methyl ethyl ketone was decreased from 16 Hz to 11 Hz for the linear inhomogeneous field (see Fig. 3(b) and (c)), and from 23 Hz to 14 Hz for the non-linear inhomogeneous field (see Fig. 3(e) and (f)). This may be because that coherence selection gradient introduces additional diffusion decay.

Discussion

The above results mean that the ability of iDQC method in reconstructing high resolution NMR spectra from inhomogeneous fields does not depend on coherence selection gradient, i.e. coherence selection gradient is not necessary for iMQC high resolution spectra. However, by analysing the coherence selection path, it can be found that the observing signal is coming from iDQCs. So the method is still iDQC-related. Therefore, the line-width of the reconstructed 1D high resolution spectrum is almost independent of the inhomogeneity within the dipolar correlation distance defined by the coherence selection gradient. The explanation about the source of iMQC high resolution spectra must be corrected to some extent. In fact, either inhomogeneous background field or coherence selection gradient can produce a modulation on magnetization, and the modulation of magnetization yields dipolar field. Without coherence selection gradients, the dipolar correlation distance must be defined in another way. For simplicity, assume that the background inhomogeneous field is linear along the Z direction, the dipolar correlation distance from it is defined as

$$r = \pi / \gamma g T , \qquad (1)$$

where T is the maximal t_1 in the indirect dimension, and g is the amplitude of the background field gradient. The inhomogeneous line-width Δf within the dipolar correlation distance generated by the background inhomogeneous field is then given by

$$\Delta f = 2\pi\gamma g r = 1/2T . \qquad (2)$$

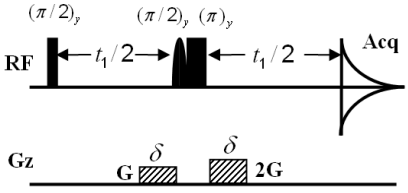

Fig.1. IDEAL-II pulse sequence. The second RF pulse is selective for solvent.

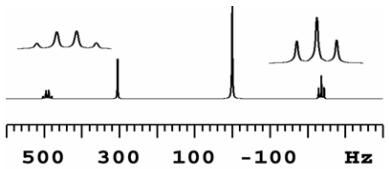

Fig.2. Conventional high resolution 1D spectrum.

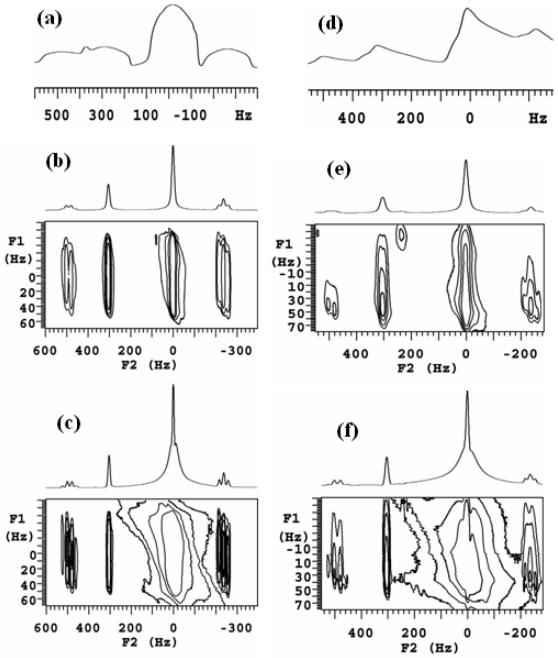

Fig.3. High resolution 2D spectra obtained from inhomogeneous field with about 200 Hz line-width linear (a~c) or non-linear (d~f) along XY plane. (a) and (d) are conventional 1D spectra; (b) and (e) are from IDEAL-II pulse sequence with G=0.09 T/m; (c) and (f) are from IDEAL-II pulse sequence with G=0 T/m.

If the effects of diffusion attenuation and T_2 relaxation are ignored, the line-width of high resolution spectra will only be restricted by Eq. (2). According to discrete Fourier transform theory, the maximal spectral resolution in the indirect dimension is $1/T$ in this situation, so the ability of iMQC method in achieving high resolution spectra from inhomogeneous field may not be restricted by the background field inhomogeneity, but only by T and signal attenuation factors caused by relaxation and diffusion effects. Though Eq. (2) was deduced from linear inhomogeneous field, it may be valid for any general inhomogeneous field. Much work on gradient-free iMQC high resolution method is still needed.

Acknowledgments

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