IDEAL-II: Improved IDEAL (Intermolecular Dipolar Interaction Enhanced All Lines) Method for High-Resolution MRS in Inhomogeous Fields

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Introduction

In the long pursuit of high-resolution MR spectroscopy, higher magnetic fields and advanced devices are developed to simplify spectra and increase resolution. Various pulse techniques have also been developed to achieve the goal. Recently, techniques such as HOMOGENIZED [1] and IDEAL [2] utilizing intermolecular dipolar interactions to obtain high-resolution spectra in inhomogeneous magnetic fields were proposed. Although the latter has higher resolution and signal-to-noise ratio than the former, the IDEAL method requires long acquisition time, large data size, and complicated data post-processing. In this study, an improved method labeled IDEAL-II was proposed to overcome the shortcomings of IDEAL.

Theory and Experiments

In our recent work [2], intermolecular double quantum coherence (iDQC) technique was used to obtain high-resolution spectra in inhomogeneous fields. Further improvement to the IDEAL method is made as follows. Similar to J resolved spectra, a π pulse was inserted into the IDEAL pulse sequence as shown in Fig.1, which divides the evolution time into two parts. To test the modified method, the IDEAL-II sequence was applied to a sample of tyrosine (molecular structure as shown in Fig.2) in water in an inhomogenoues field (~100Hz in linewidth), with a Varian Unity $^+$ 500 spectrometer. Figure 3 shows the 2D IDEAL-II spectrum in the inhomogeneous field. To understand how the sequence works, we consider a spin system consisting of different molecules of an *I* (solvent) and *S* (solute) spins with the second RF pulse selective for the *I* spin only. If $\Delta B(x,y,z)$ is the width of the spatially dependent field inhomogeneity, the resonance frequency for the *S* spins in the F2 dimension ranges between $\Delta\omega_{SQC}(x,y,z) = \Delta\omega_S \pm(1/2)\gamma\Delta B(x,y,z)$. After the third π refocus pulse removing the chemical shift of S and inhomogeneity of field in time t_1, the frequency in the F1 dimension ranges between $\Delta\omega_{DQC}(x,y,z) = \Delta\omega_I \pm (1/4)\gamma\Delta B(x,y,z)$. If the frequency offset of I spin was set to zero, i.e, $\Delta\omega_I = 0$, the intermolecular cross peaks between *I* and *S* spins will be centered at $(0, \omega_S)$ with separate streaks along the specific direction ϕ =arctg(1/2), where ϕ is the angle with respect to the F2 axis. Combined with the IDEAL sequence, it is possible to scale the multiplet splittings by different factors. The scaling factor of the multiplet splitting is given by $1+\cot\phi$, where $\cot\phi$=0.5 for IDEAL and $\cot\phi$=2 for IDEAL-II. IDEAL-II possesses the ability to retain multiplicity information in spin system with extensive resonance overlaps. Since the spatial correlation via dipolar field of the solvent affects all the spins of the solutes equally, the relative areas and chemical shifts from iDQCs are the same for all resonances as those in routine 1D MR spectrum. On the other hand, the correlation of spatial distribution of field inhomogeneity is independent of *J* couplings, so the spins of the solute evolve under *J* coupling in both F1 and F2 dimensions.

To obtain a projection spectrum which is similar to a conventional 1D one, an anticlockwise rotation of $(\pi/2\text{-}\phi)$ of spectra was performed first. After this shearing operation, a projection along the F1 direction retains chemical shifts, relative areas, and J multiplet patterns while inhomogeneous broadening is suppressed (Fig. 4c). These operations were performed in the VNMR software equipped with Varian spectrometer. In addition, the projection of the 2D spectra (inset in Fig. 4c) has much higher resolution than the original 1D spectrum shown in Fig. 4b. The linewidth is reduced from 96 to about 3 Hz, remarkably similar to the conventional high-resolution ^{1}H spectrum (Fig. 4a). In contrast to the original IDEAL method, all rows of data streaks are located in the center of F1 dimension and occupies a narrow range of frequency in F1 (~ (1/2) $\Delta B(x,y,z)$). This enables a large decrease in acquisition time and data space. The expansion of J coupling constant brings much higher resolution of weakly coupled system (i.e. see the peak C of tyrosine in Fig. 4c), though it may aggravate the coupling patter of strong coupling system in certain way.

Conclusion

Based on long-range dipolar interactions between spins of solvent and solute molecules, a modified pulse sequence, IDEAL-II, was proposed to greatly save experimental time and reduce data size. Except for a 3-fold magnification in the scale factor for *J* couplings, other parameters from IDEAL-II spectra in an inhomogeneous field such as chemical shifts, patterns of multiplicity, and relative areas are in good agreement with those extracted from one-dimensional spectra obtained in a homogeneous field.

Acknowledgment

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References

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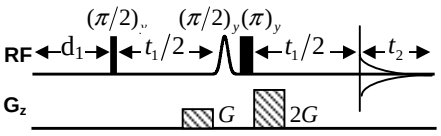

Fig. 1 IDEAL-II pulse sequence

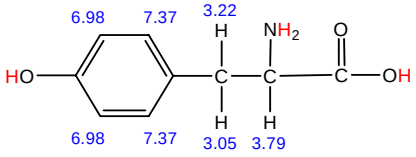

Fig. 2 Molecular structure of tyrosine. Active protons are colored red.

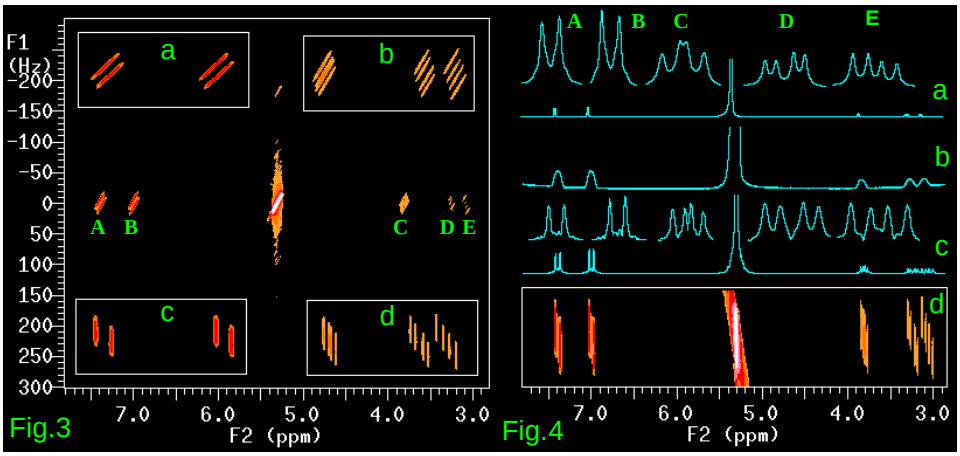

Fig. 3 iDQC 2D spectrum acquired via IDEAL-II sequence in an inhomogeneous field about 100Hz. (a) and (b) in box are the insets of data streaks before rotation, (c) and (d) in box are the insets of data streaks after rotation

Fig. 4 (a) Conventional 1D ^{1}H spectrum in a well-shimmed field (~ a few Hz), (b) Conventional 1D ^{1}H spectrum in the inhomogeneous field used in Fig. 3, and (c) accumulated projection of the sheared spectrum shown in Fig. 3, and (d) is an expanded view of each multiplet in interested regions.