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Intermolecular double-quantum coherence NMR spectroscopy in moderate inhomogeneous fields

Wen Zhang, Congbo Cai, Shuhui Cai*, Xi Chen, Zhong Chen

Department of Physics, State Key Laboratory of Physical Chemistry of Solid Surfaces, Fujian Key Laboratory of Plasma and Magnetic Resonance, Xiamen University, Xiamen, Fujian 361005, China

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ABSTRACT

Intermolecular multiple-quantum coherences (iMQCs) can be utilized to retrieve high-resolution NMR spectra in inhomogeneous magnetic fields. The application of selective pulses in pulse sequences can greatly simplify 2D iMQC spectra. However, so far high-resolution iMQC methods are mainly used in relatively small field inhomogeneities. In this paper, we took the IDEAL-II sequence as an example to study their applicability in moderate inhomogeneous magnetic fields. The experimental and simulation results show that high-resolution NMR spectra can be obtained in moderate inhomogeneous fields if the excitation range of selective pulse is properly set. Once the field inhomogeneity reaches a certain degree, the appearance of undesirable intermolecular cross-peaks due to the distant dipolar field produced by solute spins is inevitable. The spectral quality may vary with sample even in the same moderate inhomogeneous fields, depending on the chemical shift distributions and the *J* coupling networks of the components under study. The conclusions drawn in this paper are generally applicable to all high-resolution iMQC methods utilizing selective RF pulses.

1. Introduction

High-resolution NMR spectroscopy is a powerful tool for analyzing molecular structures and dynamics through the measurements of physical parameters such as chemical shifts, scalar coupling constants, multiplet patterns and relative peak areas. Although a magnetic field used for NMR spectra is generally designed to maintain high homogeneity, there are many circumstances where the spatial homogeneity of the magnetic field is degraded. For example, heterogeneous samples such as tissues in biomedicine for *in vivo* NMR spectroscopy, rock samples for oil exploration and porous resin beads in combinatorial chemistry are subject to variation in magnetic susceptibility over the sample volume. Distributions of magnetic field inhomogeneity and susceptibility produce spurious field gradients that broaden spectral peaks. Inhomogeneous line broadening may lead to severe signal overlap and loss of fine spectral features. Besides magic-angle spinning (MAS) method [1], a variety of techniques have been proposed to regain the lost spectral information in the presence of magnetic field inhomogeneity. One class is based on the use of scalar coupling interactions within a molecule, such as intramolecular zero-quantum coherences [2,3], total coherence transfer echoes [4] and nutation echoes [5,6] methods. Another approach utilizes spatial encoding and phase correction to obtain high-resolution NMR spectra under inhomogeneous fields [7,8]. Recently, intermolecular multiple-quantum coherences (iMQCs) caused by long-range dipolar interactions have generated tremendous interests [9–17].

Taking advantage of intermolecular long-range dipolar interactions, iMQC methods have been applied to retrieve high-resolution NMR spectra in inhomogeneous fields [9,12,18,19]. In 1996, HOMOGENIZED pulse sequence based on intermolecular zero-quantum coherences (iZQCs) was first proposed by Vathyam et al. to extract high-resolution NMR information from 2D iZQC spectra in inhomogeneous field [9]. Theoretically, this method can be applied in any inhomogeneous field. However, the HOMOGENIZED spectra suffer from strong t_1 ridge noise at solvent position. Furthermore, the existence of conventional solute signals and solute–solute iZQC signals may decrease the resolution and affect the regeneration of high-resolution 1D NMR spectra. To select solvent–solute iZQC cross-peaks and to greatly suppress the t_1 ridge noise, the HOMOGENIZED sequence was improved to Sel-HOMOGENIZED sequence by replacing the second RF pulse with a selective pulse [18]. Since intermolecular double-quantum coherences (iDQCs) possess features similar to those of iZQCs and the intensities of iDQC signals are approximately 30% stronger than those of iZQC signals with no additional phase cycling to get "pure" iDQC signals, iDQC-based IDEAL sequence was proposed later [12]. However, all above sequences require long acquisition time for a 2D spectrum since the whole chemical shift range needs to be cov-

* Corresponding author. Tel.: +86 0592 2180839; fax: +86 0592 2189426.
E-mail address: shcai@xmu.edu.cn (S. Cai).

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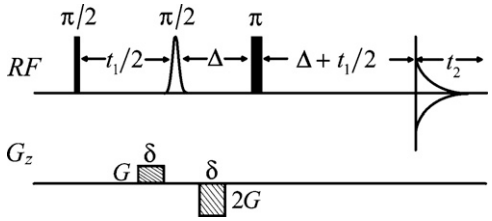

Fig. 1. IDEAL-II pulse sequence.

ered in the indirect dimension F1. Therefore, IDEAL-II sequence was further designed to efficiently achieve high-resolution NMR spectra in inhomogeneous fields [20]. So far, all the improved iMQC methods utilize selective RF pulses and are mainly used in magnetic fields with relatively small inhomogeneity [12,16–18,20]. Their feasibility in moderate or relatively large inhomogeneous fields has not been studied. Taking into account the advantages of IDEAL-II sequence, in this paper we will study the capacity of IDEAL-II sequence in retrieving high-resolution NMR spectra under moderate inhomogeneous fields. The effect of RF pulse selectivity on spectral quality is explored by varying the excitation range of selective pulse. Experiments and simulations are performed upon a same sample in different inhomogeneous fields and different samples in a same inhomogeneous field.

2. Theory and method

The IDEAL-II pulse sequence is shown in Fig. 1 [20]. The $\pi/2$ Gaussian pulse is frequency selective on the solvent peak, so that only the spatially modulated longitudinal magnetization of solvent spins gives rise to distant dipolar field. An echo time 2Δ was added for optimal signal intensity. Without losing generality, a homogeneous liquid mixture was considered. It consists of two isolated spin-1/2 systems I and S. It is assumed that I component is solvent and S component is solute. Radiation damping effects are effectively suppressed by probe detuning and field inhomogeneity, so they are ignored in the following discussion. For simplicity, relaxation and diffusion are also neglected. In a homogeneous magnetic field, the detected signals from the IDEAL-II sequence can be expressed as

$$S_{sel} = i\left(\frac{0.5t_1 + t_2 + \Delta}{8}\right)\gamma\mu_0(M_0^I)^2 t_2 e^{-i\omega_I\Delta}e^{-i\omega_I t_1/2}e^{i\omega_I t_2} + i\left(\frac{0.5t_1 + t_2 + \Delta}{6}\right)\gamma\mu_0 M_0^I M_0^S e^{-i\omega_I\Delta}e^{-i\omega_I t_1/2}e^{i\omega_S t_2} \quad (1)$$

where γ is the gyromagenatic ratio, $M_0^{(m)}$ is the equilibrium magnetization per unit volume of spin m ($m = I, S$), μ_0 is the magnetic permeability constant, and ω_m is the frequency offset of spin m ($m = I, S$) in the rotating frame in the absence of field inhomogeneity. Eq. (1) shows that the detected signals are composed of two parts: solvent–solvent iDQC (the first term) and solvent–solute iDQC (the second term). They are located at ($\omega_I/2$, ω_I) and ($\omega_I/2$, ω_S) in the 2D spectrum. It means that different cross-peaks align along the horizontal axis. In inhomogeneous field, since the spins on two molecules coupled by long-range dipolar interactions are physically close to each other, they should experience almost the same magnetic field over the distance between the two spins. So the resonance frequencies for the intermolecular cross-peaks are ($\omega_I/2 + \gamma\Delta B(\boldsymbol{r})/2$, $\omega_I + \gamma\Delta B(\boldsymbol{r})$) and ($\omega_I/2 + \gamma\Delta B(\boldsymbol{r})/2$, $\omega_S + \gamma\Delta B(\boldsymbol{r})$), where $\Delta B(\boldsymbol{r})$ represents the field inhomogeneity in position $\boldsymbol{r}$. The inhomogeneous field makes the peaks extend like streaks along the direction of $\phi = \mathrm{arctg}(\Delta B(\boldsymbol{r})/(\Delta B(\boldsymbol{r})/2)) = \mathrm{arctg}(2) = 63.4^\circ$ with respect to the F1 axis, which is different from the direction of chemical shift alignment. Consequently, peak overlap will not occur even if the field inhomogeneity becomes large. However, when the field inhomogeneity increases to some extent, it would be difficult for a RF pulse to only selectively excite the solvent spins and the result would not be as ideal as expected. In an extreme case, the result would be similar to using non-selective RF pulses in the IDEAL-II sequence. Replacing the selective pulse with a non-selective one, the detected signals in homogeneous magnetic field can be derived

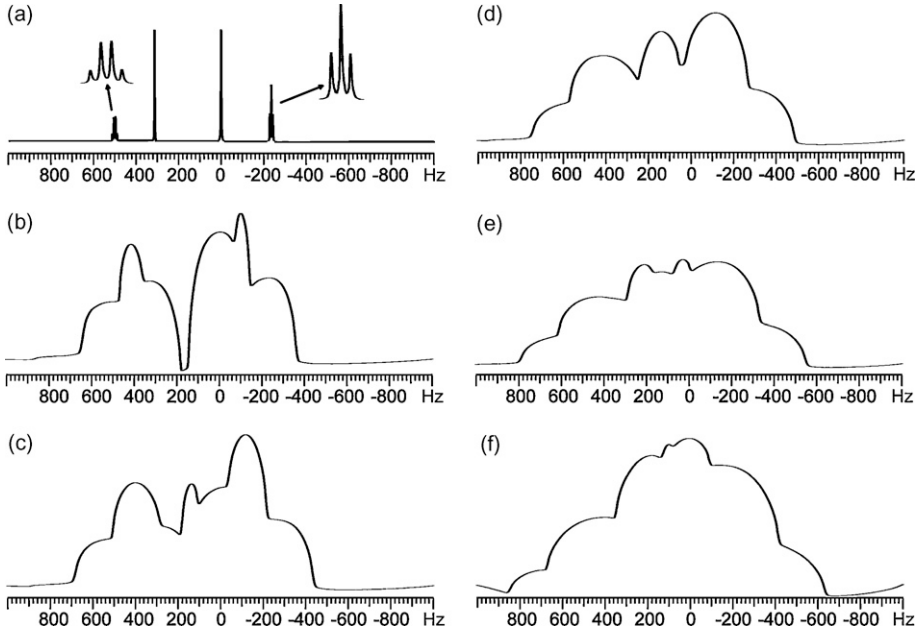

Fig. 2. ^{1}H NMR spectra of MEK in cyclohexane solution. (a) Conventional 1D single-quantum coherence (SQC) spectrum in a well-shimmed field, (b)–(f) conventional 1D SQC spectra in an inhomogeneous field of about 250, 350, 450, 550 and 650 Hz line-width, respectively.

as follows:

$$S_{non\text{-}sel} = \sum_{m=I,S} i\left(\frac{0.5t_1 + t_2 + \Delta}{8}\right)\gamma\mu_0(M_0^{(m)})^2 t_2 e^{-i\omega_m\Delta}e^{-i\omega_m t_1/2}e^{i\omega_m t_2} + \sum_{m,n=I,S}^{m\neq n} i\left(\frac{0.5t_1 + t_2 + \Delta}{6}\right)\gamma\mu_0 M_0^{(m)}M_0^{(n)} t_2 e^{-i\omega_m\Delta}e^{-i\omega_m t_1/2}e^{i\omega_n t_2} \quad (2)$$

Eq. (2) demonstrates that the detected signals are composed of following parts: the first term corresponds to solvent–solvent and homologous solute–solute iDQCs; the second term corresponds to solvent–solute, solute–solvent and inhomologous solute–solute iDQCs. The signals of solute–solute and solute–solvent cross-peaks are undesirable, for they will disrupt the iDQC spectrum and reduce the signal to noise ratio. The appearance of undesirable cross-peaks and the extension of the frequency range along the F1 and F2 dimensions of the cross-peaks may lead to serious peak overlap. On the other hand, the line-width of the streak-like peaks become wider and the J coupling information may be concealed with the increase of field inhomogeneity. Thus no high-resolution NMR spectra can be retrieved.

3. Experiments and simulations

All experiments were performed at 298 K using a 500 MHz Varian NMR System with a 5 mm indirect detection probe. The IDEAL-II pulse sequence was applied (Fig. 1). The magnetic field was intentionally deshimmed by altering the currents in the X1 and Y1 coils to produce different inhomogeneous fields. The field inhomogeneity was described by the half-height width of solvent peak and briefly denoted as the spectral line-width in the following discussion. Since the inhomogeneous line broadening caused so serious peak overlap that the line-width recognized by the spectrometer for the mixture was not reliable, a pure solvent sample instead of

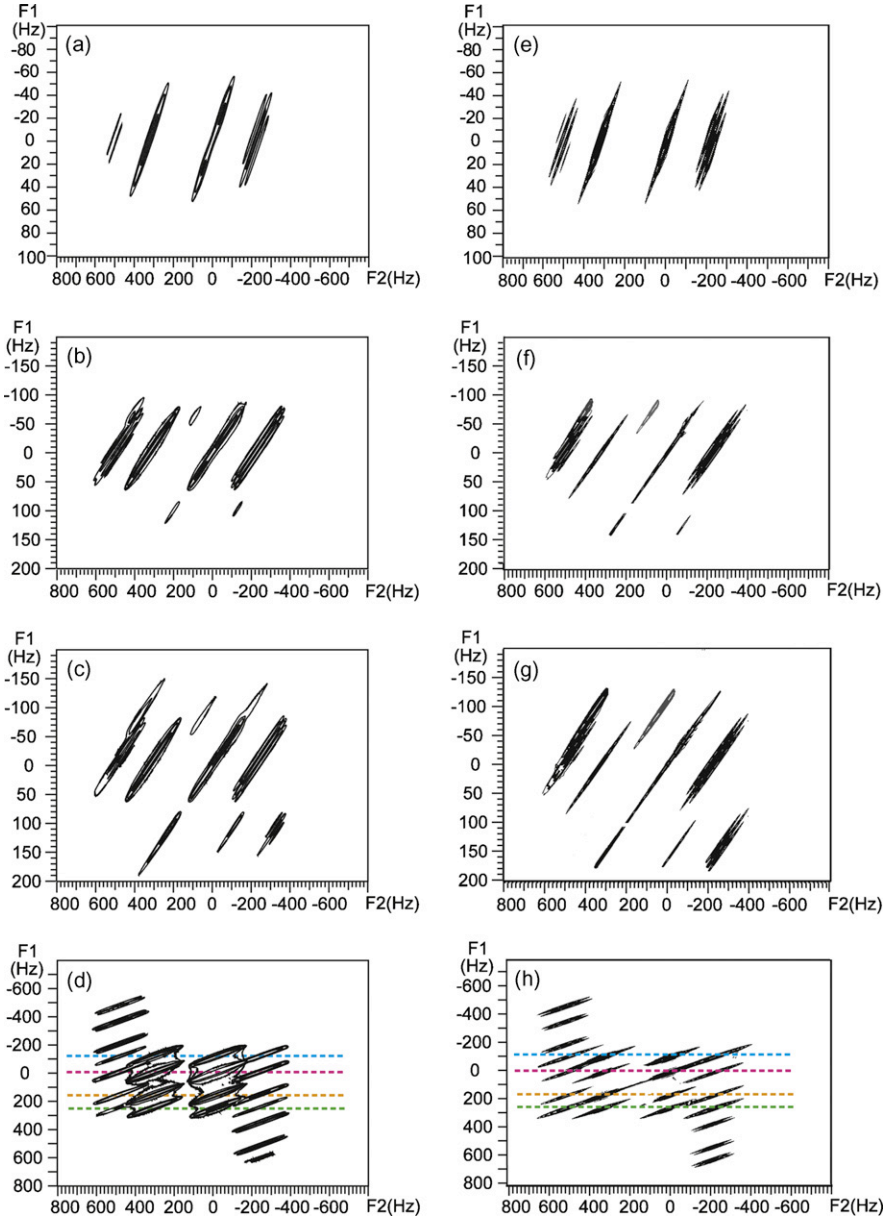

Fig. 3. Experimental and simulated 2D ^{1}H iDQC spectra of MEK in cyclohexane solution in an inhomogeneous field of 250 Hz line-width. (a)–(c) Experimental spectra with the length of the selective $\pi/2$ pulse in the IDEAL-II sequence set to 17.6, 9.1 and 5.7 ms, respectively; (d) experimental spectrum with the selective pulse replaced by a non-selective one; (e)–(h) simulated spectra corresponding to (a)–(d), respectively.

the mixture was used for deshimming the magnetic field and measuring the line-width. The field inhomogeneity was keep unchange during an acquisition. Besides field inhomogeneity, the radiation damping effect was further reduced by detuning the probe.

A solution sample of methyl ethyl ketone (MEK, $CH_3COC_2H_5$) in cyclohexane (C_6H_{12}) (molar ratio 2.4:1) was used. The length of the $\pi/2$ hard RF pulse was 68.2 μs. The coherence selection gradients (CSGs) with strength $G \approx 0.2$ T/m and duration $\delta = 1.2$ ms were applied. The pulse repetition delay was 3.0 s, the optimized echo time (2Δ) was 80 ms, and the acquisition time t_2 was 0.5 s. To remove the residual unwanted signals, a four-step phase cycling was used: the phases for the first RF pulse and the receiver were (x, y, $-x$, $-y$) and (x, $-x$, x, $-x$), respectively. The spectral width was 1600 Hz in the F2 dimension and 600 Hz in the F1 dimension with 128 increments. To study the effect of RF pulse selectivity on spectral quality, the length of the selective $\pi/2$ pulse was set to a series of values to excite different frequency range at a specific inhomogeneous field. To test the effect of field inhomogeneity itself on spectral quality, experiments on the same sample in different inhomogeneous fields were done with the same experimental parameters.

Besides the above sample, a solution sample of tyrosine in water (molar ratio 1:5) was used to demonstrate the effect of sample difference on spectral quality in the same inhomogeneous field. The spectral width was 3000 Hz in the F2 dimension and 600 Hz in the F1 dimension with 128 increments. The pulse repetition delay was 5.0 s and the optimized echo time (2Δ) was 130 ms. The duration of the selective $\pi/2$ pulse was 3.9 ms. The CSGs with strength $G \approx 0.24$ T/m and duration $\delta = 1.2$ ms were applied. The phase cycling scheme was the same as the one mentioned above.

In order to verify the theoretical predictions and experimental observations, the modified Bloch equations were used to simulate the 2D iDQC experiments. All simulations were carried out using the software package SPROM developed by our group [21,22]. The parameter sets for the simulations were chosen to be as close to the experimental ones as possible.

4. Results and discussion

4.1. RF pulse selectivity

The conventional 1D high-resolution spectrum of MEK in cyclohexane solution in a well-shimmed magnetic field was first acquired (Fig. 2a). The differences of chemical shifts between cyclohexane (solvent) and MEK (solute) are about 510 Hz (–C**H**$_2$), 330 Hz (–COC**H**$_3$) and 220 Hz (–CH$_2$C**H**$_3$), respectively. The static mag-

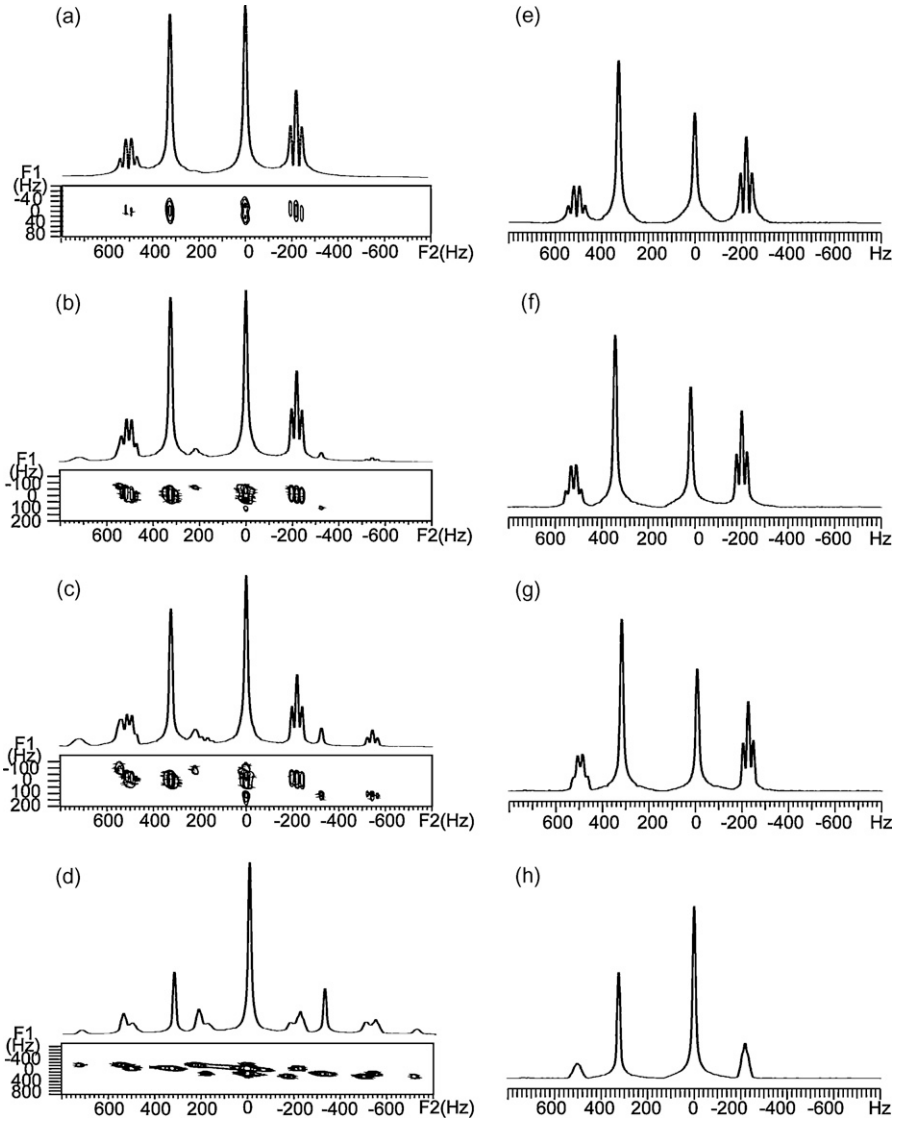

Fig. 4. 1D ^{1}H spectra extracted from the 2D iDQC spectra in Fig. 3(a)–(d). (a)–(d) Accumulated sheared projection and (e)–(h) cross-sections along F1 = 0 without shearing.

netic field was then intentionally deshimmed to produce a spectral line-width of 250 Hz. The conventional 1D spectrum of the mixture acquired in this inhomogeneous field is shown in Fig. 2b. For 2D iDQC spectra, the $\pi/2$ Gaussian pulse is frequency selective on cyclohexane (I spin). Its length was set to 17.6, 9.1 and 5.7 ms, which corresponds to the excitation range of about 150, 300 and 470 Hz, respectively. Note that in homogenous magnetic field, the selective pulse works well as long as its excitation frequency range is smaller than half of the smallest frequency difference between solvent and solute. However, in inhomogeneous field, the smallest frequency difference between solvent and adjacent solute peaks is reduced due to the inhomogeneous line broadening. When the solvent peak overlaps with the solute one, the selective pulse may also excite some solute spins. The results are shown in Fig. 3a–c. The spectrometer reference frequency is set to coincide with the resonance frequency of the I spin, i.e. $\omega_I = 0$, so the inter-

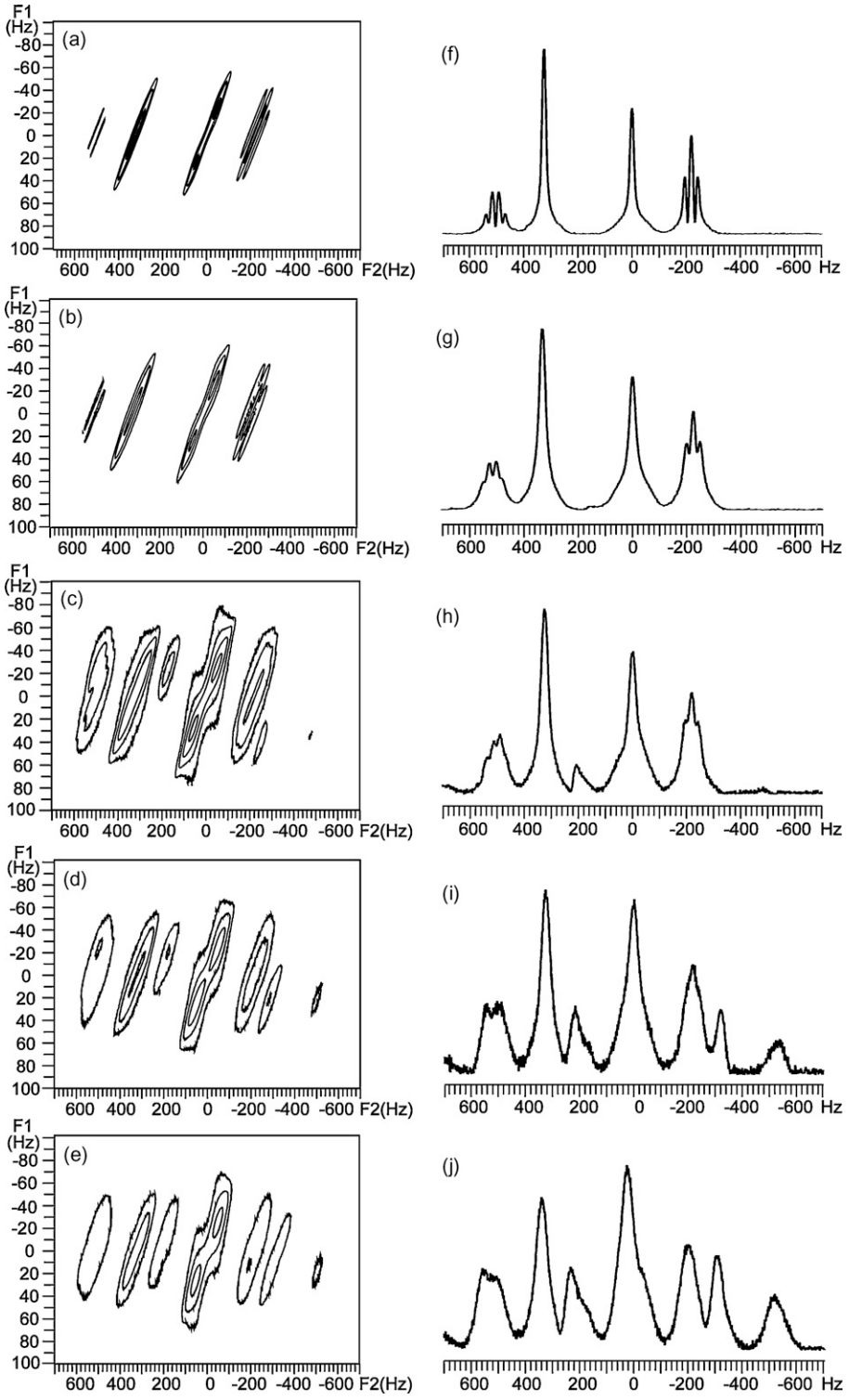

Fig. 5. 2D ^{1}H iDQC spectra of MEK in cyclohexane solution acquired in different inhomogeneous fields. The length of the selective $\pi/2$ pulse was 17.6 ms. (a)–(e) Spectra acquired in the inhomogeneous field of about 250, 350, 450, 550 and 650 Hz line-width, respectively and (f)–(j) cross-sections along F1 = 0 of (a)–(e) without shearing.

molecular cross-peaks between I and S spins center at $(0, \omega_S)$. The peaks appear as separate streaks along a specific direction of arctan 2 with respect to the F1 axis due to the field inhomogeneity. The 1D accumulated projection spectra to the F2 dimension after the streaks are rotated by 63.4° counter-clockwise are shown in Fig. 4.

In the inhomogeneous field with 250 Hz line-width, the cyclohexane peak partially overlaps with the adjacent MEK peak, as shown in Fig. 2b. When the excitation range of the selective pulse is 150 Hz, a "clear" 2D spectrum with only desired solvent–solute iDQC signals is obtained (Fig. 3a). In such a case the selective pulse excites the solvent spins only. Its accumulated projection gives a 1D high-resolution spectrum with chemical shift and scalar coupling information (Fig. 4a). When the excitation range of the selective pulse is set to 300 Hz, unwanted cross-peaks appear due to the partial excitation of the $-C\mathbf{H}_3$ protons in $-CH_2CH_3$ group of solute by the selective pulse (Fig. 3b). These undesired signals disturb the accumulated projection spectrum (Fig. 4b). When the length of the selective pulse is 5.7 ms, more unwanted cross-peaks appear in the 2D spectrum and their intensities increase compared to Fig. 3b (Fig. 3c). In such a case, not only the solvent protons and partial $-CH_2C\mathbf{H}_3$ protons but also partial $-COC\mathbf{H}_3$ protons are excited by the selective pulse. For Fig. 3b and c, solute spins excited by the second RF pulse give rise to distant dipolar fields, as the solvent spins do, thus produces the undesired solute–solute and solute–solvent intermolecular cross-peaks. For comparison, the selective RF pulse in the IDEAL-II sequence was replaced by a non-selective one and a 2D spectrum was acquired. The result is shown in Fig. 3d. The signals aligned along the pink line are solvent–solute and solvent–solvent cross-peaks due to the effect of distant dipolar field produced by the solvent spins; the signals aligned along the blue, orange and green lines are solute–solute and solute–solvent cross-peaks due to the effect of distant dipolar field produced by the $-CH_2C\mathbf{H}_3$, $-COC\mathbf{H}_3$ and $-C\mathbf{H}_2$ protons of MEK, respectively. The other signals are attributed to higher-order intermolecular cross-peaks and COSY-type cross-peaks due to J coupling that are not described in Eq. (2). Compared to Fig. 3d, the spectrum in Fig. 3c is much simple due to the use of selective RF pulse although it also excites some solute spins. These results show that the selectivity of the second RF pulse is important for obtaining a "clear" high-resolution spectrum, especially in moderate or relative large inhomogeneous magnetic fields. The simulated results are presented in Fig. 3e–h. They are in good agreement with the experimental ones.

In principle, the excitation range of the selective pulse can be set as small as possible to ensure that only the solvent spins are excited. However, small frequency range means long length of the selective pulse, which will evidently aggravate the effects of relaxation and diffusion, leading to rapid signal attenuation and low signal to noise ratio. So the excitation range of the selective pulse cannot be infinitely small in practice. It is worth mentioning that although undesirable cross-peaks would appear in 2D iDQC spectra when the selective pulse is imperfect, a "clear" 1D high-resolution NMR spectrum can still be obtained if the cross-section along F1 = 0 is extracted, as shown in Fig. 4f–h. However, this technique is not always applicable and its feasibility also depends on the magnetic field homogeneity. The effect of field inhomogeneity on spectral quality will be discussed below.

4.2. Field inhomogeneity

To see the effect of field inhomogeneity on spectral quality, a series of 2D experiments were performed under the same experimental conditions except for the magnetic field which produced a spectral line-width varied from 250 to 350, 450, 550 and 650 Hz. The results are shown in Fig. 5. In these experiments, the length

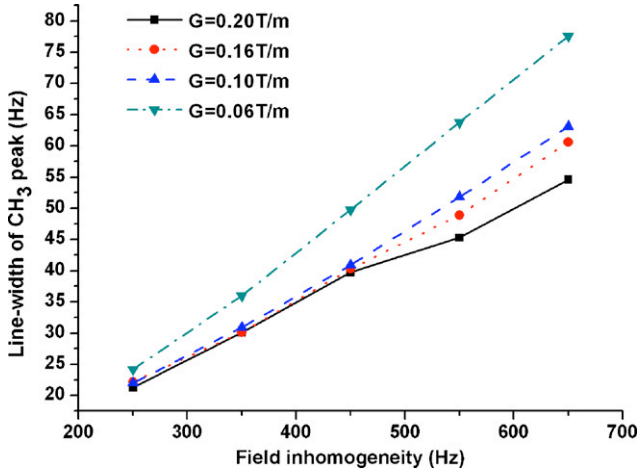

Fig. 6. Variation of the line-width of the singlet ($-CH_3$) of MEK in the accumulated projection of 2D iDQC spectrum with CSG strength.

of the selective pulse is set to 17.6 ms. As shown in Fig. 5b, when the field inhomogeneity reaches 350 Hz, a "clear" high-resolution NMR spectrum can still be obtained. The information of chemical shifts and scalar coupling constants are retained in the 1D accumulated projection. However, when the field inhomogeneity is further increased, the scalar coupling information is concealed and undesired intermolecular solute–solute and solute–solvent cross-peaks appear (Fig. 5c–e). This is because that when the magnetic field inhomogeneity increases, the ranges of the resonance frequencies of the spins become large. The selective pulse excites not only the solvent spins, but also some solute spins. The cross-section along F1 = 0 cannot give correct spectral information any longer (see Fig. 5h–j).

The experimental results (Fig. 5) also show that the greater the field inhomogeneity, the wider the line-width of the streaks. To investigate this phenomenon in more detail, experiments were performed with different CSG strength in different inhomogeneous field. For iMQC methods, it is assumed that the magnetic field within the coherence distance $d_c = \pi/(\gamma G\delta)$ can be taken as uniform. This is of course valid for relatively small inhomogeneous fields. For moderate or even large inhomogeneous fields, the situation may not be entirely the case. Since the field gradient is large, the magnetic field within the coherence distance may not be taken as uniform. Here the CSG strength was set to 0.06, 0.1, 0.16 and 0.2 T/m, respectively. The line-width of the singlet ($-CH_3$) of MEK in the accumulated projection of 2D spectrum was measured. The result is shown in Fig. 6. It can be seen that the line-width of the $-CH_3$ peak obtained with $G = 0.06$ T/m is larger than those obtained with other G values, and it increases more rapidly with field inhomogeneity. When the field inhomogeneity is smaller than 450 Hz, the line-widths of the $-CH_3$ peak obtained with $G = 0.1$, 0.16 and 0.2 T/m are close to each other. However, as the field inhomogeneity becomes large, the difference becomes obvious. So the CSG strength should be properly set for obtaining high-resolution NMR spectra, especially in moderate or relatively large inhomogeneous field.

4.3. Difference of resonance frequencies

The selectivity of the selective RF pulse and the line broadening effect of inhomogeneous field are the main factors influencing the resolution of NMR spectra obtained in moderate or relatively large inhomogeneous fields. If the difference of resonance frequencies between solute and solvent spins is relatively large, will the impact of field inhomogeneity on spectral quality be reduced? A tyrosine in water solution was studied for comparison. The smallest chemical

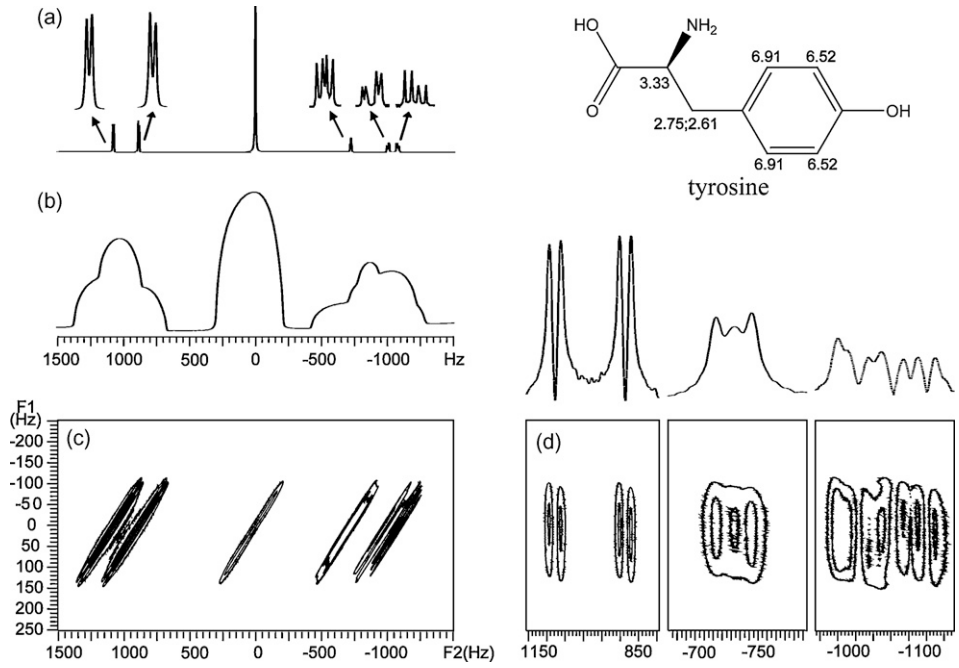

Fig. 7. ^{1}H NMR spectra of tyrosine in water. (a) Conventional 1D SQC spectrum in a well-shimmed field, (b) conventional 1D SQC spectra in an inhomogeneous field of about 450 Hz line-width, (c) 2D iDQC spectrum acquired in the same inhomogeneous field as (b), and (d) expanded regions of iDQC spectrum in (c) after shearing.

shift difference between water and adjacent tyrosine peaks is about 710 Hz, which is much larger than that between cyclohexane and adjacent MEK peaks. The iDQC experiment was carried out in the inhomogeneous field with 450 Hz line-width. The results are shown in Fig. 7.

As shown in Fig. 7c, the accumulated projection of the 2D iDQC spectrum after counter-clockwise rotating the spectrum by 63.4° gives a satisfying 1D high-resolution spectrum, while it is impossible for the MEK solution (Fig. 5c). In the inhomogeneous field, the MEK peaks seriously overlap with the cyclohexane peak (Fig. 2d), whereas the water peak is still apart from the neighboring tyrosine peaks (Fig. 7b). Therefore, it is possible for the selective RF pulse to excite only water, resulting in a satisfying high-resolution 2D spectrum. This confirms that the spectral quality of different sample in a same moderate inhomogeneous field can be different, depending on the chemical shift difference between the solute and solvent spins.

5. Conclusion

Selective RF pulse is widely used in iMQC pulse sequences to retrieve high-resolution NMR spectra in inhomogeneous fields. It avoids the generation of undesirable solute–solute and solute–solvent cross-peaks. The prerequisite for the proper application of selective pulse is that the solvent peak can be distinguished from the solute peaks. In relatively small inhomogeneous fields, this is often satisfied, so selective pulse is easy to implement. However, in moderate or relatively large inhomogeneous fields, solvent peak may overlap with solute peaks. The excitation range of selective pulse should then be carefully set to excite the solvent spins only. Otherwise, unwanted intermolecular cross-peaks will arise from the distant dipolar fields of solute spins. Moreover, as the field inhomogeneity increases, inhomogeneous line broadening of the intermolecular cross-peaks in the F1 and F2 dimensions becomes larger. These factors make it impossible to obtain high-resolution spectra by 1D projection or even extract chemical shift information by cross-section. Once the field inhomogeneity reaches to some degree, the selective pulse will be completely incapable of avoiding exciting the solute spins. In essence, the failure of the application of selective pulse is due to the indistinguishable solvent peak from the solute ones. So samples with different space between solvent and adjacent solute peaks may have different spectral quality in the same inhomogeneous field.

Acknowledgements

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References

[1] R. Fu, O. Gunaydin-Sen, N.S. Dalal, J. Am. Chem. Soc. 129 (2007) 470–471.
[2] R.R. Ernst, G. Bodenhausen, A. Wokaum, Principles of Nuclear Magnetic Resonance in One and Two Dimensions, Clarendon Press, Oxford, 1987.
[3] R.A. de Graaf, D.L. Rothman, K.L. Behar, J. Magn. Reson. 187 (2007) 320–326.
[4] D.P. Weitekamp, J.R. Garbow, J.B. Murdoch, A. Pines, J. Am. Chem. Soc. 103 (1981) 3578–3579.
[5] C.A. Meriles, D. Sakellariou, H. Heise, A.J. Moule, A. Pines, Science 293 (2001) 82–85.
[6] J. Perlo, V. Demas, F. Casanova, C.A. Meriles, J. Reimer, A. Pines, B. Blümich, Science 308 (2005) 1279–11279.
[7] B. Shapira, L. Frydman, J. Am. Chem. Soc. 126 (2004) 7184–7185.
[8] B. Shapira, L. Frydman, J. Magn. Reson. 182 (2006) 12–21.
[9] S. Vathyam, S. Lee, W.S. Warren, Science 272 (1996) 92–96.
[10] P.L. de Sousa, D. Gounot, D. Grucker, J. Magn. Reson. 162 (2003) 356–363.
[11] W. Barros, P.L. de Sousa, M. Engelsberg, J. Magn. Reson. 165 (2003) 175–179.
[12] Z. Chen, Z.W. Chen, J.H. Zhong, J. Am. Chem. Soc. 126 (2004) 446–447.
[13] S.D. Kennedy, J.H. Zhong, Magn. Reson. Med. 52 (2004) 1–6.
[14] P.L. de Sousa, D. Gounot, D. Grucker, C. R. Chimie 7 (2004) 311–319.
[15] C.K. Wong, S.D. Kennedy, E. Kwok, J.H. Zhong, J. Magn. Reson. 185 (2007) 247–258.
[16] X. Chen, M.J. Lin, Z. Chen, S.H. Cai, J.H. Zhong, Phys. Chem. Chem. Phys. 9 (2007) 6231–6240.
[17] D.Z. Balla, C. Faber, J. Chem. Phys. 128 (2008) 154522.
[18] Z. Chen, T. Hou, Z.W. Chen, D.W. Hwang, L.P. Hwang, Chem. Phys. Lett. 386 (2004) 200–205.
[19] D. Balla, C. Faber, Chem. Phys. Lett. 393 (2004) 464–469.
[20] Z. Chen, S. Cai, Z. Chen, J. Zhong, J. Chem. Phys. 130 (2009) 084504.
[21] C.B. Cai, Z. Chen, S.H. Cai, J.H. Zhong, J. Magn. Reson. 172 (2005) 242–253.
[22] C.B. Cai, M.J. Lin, Z. Chen, X. Chen, S.H. Cai, J.H. Zhong, C. R. Phys. 9 (2008) 119–126.