Lineshape analysis of signals originated from intermolecular multiple-quantum coherences

B. Zheng[1], Z. Chen[1,2], J. Zhong[3]

[1]Physics, Xiamen University, Xiamen, Fujian, China, People's Republic of, [2]Radiology, University of Rochester, Rochester, NY, United States, [3]Radiology, BME, Physics, University of Rochester, Rochester, NY, United States

Introduction

Although the theory and applications of intermolecular multiple-quantum coherences (iMQCs) have been developed for over a decade, the discussions are mainly confined in the time domain [1-5]. Based on our previous works [4,5], we have extended the discussion to the frequency domain and developed a full expression to describe the signals originated from iMQCs for the first time. The peak height, linewidth, and phase of the signal were investigated in detail under linear approximation [2]. For the iMQC signals at different coherence orders, Fourier transformation of FID no longer results in Lorentizian or Gaussian lineshapes, but particular lineshapes distorted by an oscillating cosine term. The resonance line profiles presented here show a good coincidence with numerically simulated data.

Methods

For a general discussion of iMQCs, we consider the basic CRAZED sequence consisting of two RF pulses in combination with suitably matched field gradient pulses [1]. In order to derive an explicit expression, we use the Taylor expansion of the Bessel function [2]. The real part of the complex Fourier transformation for the different coherence orders ($n \neq 0$) is given by,

$$S(\omega,n)=i^{n-1}M_0\times\sum_{j=0}^{\infty}\frac{(-1)^{j+n}\Gamma(2j+n)\chi^{2j+n-1}[n-(2j+n)\cos\beta]}{\Gamma(j+1)\Gamma(n+j+1)2^{2j+n}}\times\cos[(2j+n)\arctan((\omega_0-\omega)/\lambda)]\times\left[\frac{1}{\lambda}+(\omega_0-\omega)^2\right]^{-j-n/2} \qquad (1)$$

where β is the flip angle of the second RF pulse, $\chi=e^{-\tau/T_2}\sin\beta/\tau_d$, and $1/\lambda=1/T_2+(2j+n-1)[k^2D+1/T_1]$. Eq. (1) represents a superposition of a series of weighted particular lineshapes given by Gamma functions and distorted by an oscillating cosine term. The terms proportional to χ^{2j+n-1} arise solely from the $\Im^{2j+n}$ term in the equilibrium density matrix [3]. It should be emphasized that, for the linear approximation $\gamma\mu_0 M_0 t e^{-\tau/T_2} e^{-(k^2D+1/T_1)t_2} << 1$ to be valid in most situations [3], the attenuation terms of relaxation and diffusion need to be introduced. To further verify the validity of the Eq. (1), inverse Fourier transforms of Eq (1) were calculated and the results are equated to the first point (*t*=0) of the relevant FID.

Results and Discussion

The theoretical and simulated lineshapes are plotted in Fig. 1, respectively. For simplification, we confine the discussions of the intensity and linewidth to the first order approximation (*j*= 0) of Bessel Taylor expansion with $\beta=90^0$. It is essential to include the effects of diffusion, longitudinal, and transverse relaxation over a long time scale. The expression of peak height (for $n \neq 0$) is,

$$S(\omega=\omega_0,n)=\lambda^n\chi^{n-1}M_0/2^n=\frac{(\gamma\mu_0e^{-\tau/T_2})^{n-1}{M_0}^n}{2^n\{1/T_2+(n-1)[k^2D+1/T_1]\}^n} \qquad (2)$$

Eq. (2) shows that the peak height is proportional to M_0^n and directly related to the concentration of the samples. The linewidths, which are inversely proportional to the coherence order *n,* are calculated with software MATHEMATICA 4.2. The basic relation is $\Delta\nu=1/\mathrm{n}\pi\lambda$ for phase-sensitive mode, and $\Delta\nu=(4^{1/n}-1)^{1/2}/\pi\lambda$ for average-value mode. The linewidth is independent of the flip angle, a property that is completely different from that of radiation damping [6]. With the increase of coherence orders, the linewidths become narrower and the phases are more distorted by the oscillating term. Although the lineshapes originating from iMQCs are very similar to those from radiation damping, their expressions in the frequency domain are indeed different (?) [6]. The results thus demonstrated that iMQCs and radiation damping are of different physical mechanisms in highly polarized liquid state NMR experiments despite their similar lineshapes. A better understanding of the physical mechanisms of iMQCs will be useful to quantitatively interpret the iMQC spectra and design experiments in the field of MRS and MRI.

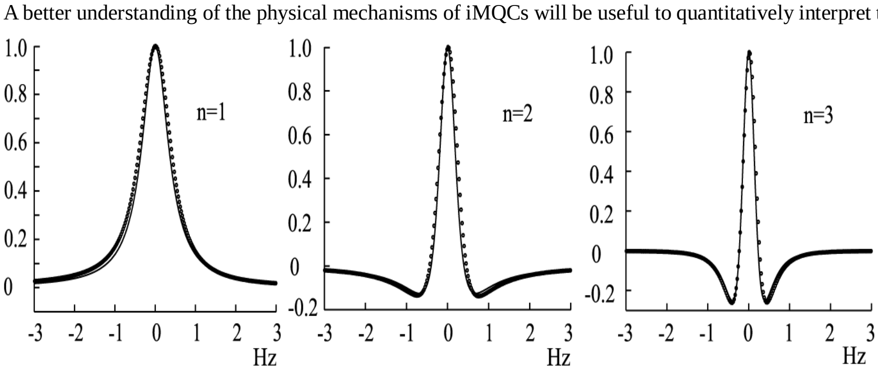

Fig.1 Theoretical (solid lines) and simulated (dot lines) lineshapes for iMQC signals of different orders. The calculated results based on Eq. (1) agree well with the simulated data based on the revised Bloch equations.

Acknowledgment

This work was partially supported by the NIH under Grants NS32024 and NS41048, and NNSF of China under Grants 10005006 and 10234070.

References

1. Warren, W.S., et al., Science, 262, 2005, 1993.
2. Ramanathan, C., et al., J. Chem. Phys., 114, 10854, 2001.
3. Lee, S., et al., J. Chem. Phys., 105, 874, 1996.
4. Chen, Z., et al., J. Chem. Phys., 115, 10769, 2001.
5. Zhong J., et al., Magn. Reson. Med., 43, 335, 2000.
6. Mao, X.A., et al., Phys. Rev. B., 49, 15702, 1994.