Simulation of Diffusion Behaviors under Scalar and Dipolar Couplings

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Introduction

Diffusion NMR and MRI is presently the only available noninvasive methods that can provide information about molecular displacements in a spatial scale comparable to cell dimensions of biological systems [1,2]. For the first time, diffusion process of inter-molecular multiple quantum coherences (MQCs) was simulated with a finite difference method, and diffusion under scalar and dipolar couplings was simulated by the combination of non-linear Bloch equations, finite difference method, and product operator matrix. The complex spin system under multiple pulse sequences was investigated. The results were validated experimentally. It shows that the algorithm is simple, efficient and powerful. The unconventional diffusion behaviors of inter-molecular MQCs were validated.

Simulation Methods and Experiments

The effects of relaxation, diffusion, chemical shift, radiation damping, and long-range dipolar field can all be incorporated into spin dynamic calculations by the non-linear Bloch equations. However, Bloch equations fail to describe magnetization vectors when scalar couplings exist in spin systems [3]. Recently, we proposed a product operator matrix, M_{mat}, to depict scalar couplings in the Bloch equations [4]. The diffusion behaviors were simulated by finite difference method which is less time consuming and more effective. The sample used for inter-molecular MQC studies was an AX_2 system corresponding to a concentrated solution of $CH_2BrCHBr_2$ (denoted as AX_2) in acetone (denoted as C) used in measurements at 11.7T. For intra-molecular DQCs, the solvent is $CDCl_3$, and the solution is dilute $CH_2BrCHBr_2$. In the simulation, we assume that the longitudinal and transversal relaxation times are all 1 *s*. The length of the sample is 1 *cm* along the *Z* axis which was divided into 2000 units. The step size is 0.4 *ms*, and the acquisition time is 4.0 *s*. The pulse sequence shown in Fig. 1(a) with α=0 and *G*=0 is used for the simulation of conventional SQC diffusion effects, with α=π/2 and *n*=-2 for the simulation of inter-molecular DQC diffusion effects, and with α=π/2 and *n*=0 for the simulation of inter-molecular ZQC diffusion effects. The pulse sequence shown in Fig. 1(b) is used for the simulation of intra-molecular DQC diffusion effects with *n*=±2.

Table I. Diffusion coefficients of intermolecular MQCs for concentrated solution

Diffusion	SQC(10^{-9}m^2/s)		iDQC(10^{-9}m^2/s)		iZQC(10^{-9}m^2/s)
	solvent	solute	solvent	solute	solute
Theory	/	/	4.64	4.00	4.00
Experiment	2.32±0.10	1.68±0.08	4.76±0.25	3.89±0.19	3.85±0.18
Simulation	2.31±0.01	1.68±0.01	4.63±0.01	3.99±0.01	3.99±0.01

Table II. Diffusion coefficients of intra-molecular MQCs for dilute solution

Diffusion	SQC(10^{-9}m^2/s)	DQC(n=2) (10^{-9}m^2/s)	DQC(n=-2) (10^{-9}m^2/s)
Theory	/	31.40	31.40
Experiment	7.85±0.19	29.82±0.51	31.69±0.53
Simulation	7.91±0.01	31.56±0.02	31.52±0.02

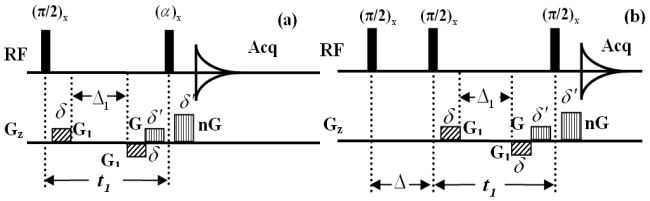

Fig.1 Pulse sequences used in this work: (a) for SQCs and inter-molecular MQCs, (b) for intra-molecular MQCs.

Results and Discussion

The diffusion coefficients of inter- and intra-molecular MQCs during evolution period obtained from theoretical calculations, experiments, and simulations were listed in Tables I and II, respectively. The diffusion attenuation curves were shown in Fig.2. The simulation results are well coincident with theoretical prediction and experiment in Tables I and II. These results suggest that the combination of finite difference method, non-linear Bloch equations, and the product operator matrix method can be used successfully to simulate diffusion behaviors of spin systems under complex pulse sequences and with intra- or inter-molecular MQC effects.

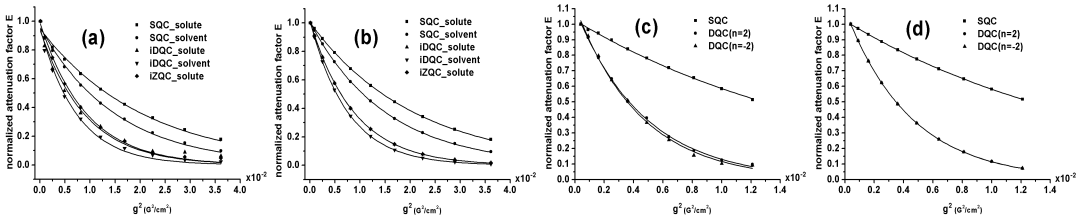

Fig.2 Normalized diffusion attenuation curves. (a) inter-molecular MQCs from experiments, (b) inter-molecular MQCs from simulations, (c) intra-molecular MQCs from experiments, (d) intra-molecular MQCs from simulations.

Conclusions

Finite difference method in combination with the product operator matrix and non-linear Bloch equations was applied to simulate the diffusion behaviors of spin system with intra- and inter-molecular MQCs. Simulation results show that it is efficient and precise for the study of diffusion behaviors of complex spin system under different pulse sequences and with dipolar and scalar couplings. This method can be extended to study the diffusion behaviors in more complicated cases, such as the diffusion in biologic tissue (e.g., lungs) with dipolar and scalar couplings. The diffusion behaviors under the influence of radiation damping can also be studied by this method.

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