Speeding up ^{17}O MQMAS Data Collection for D-glucose by Paramagnetic Doping

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Introduction

Half-integer nuclei such as ^{17}O (I = 5/2) usually have significantly shorter spin-lattice (T_1) relaxation times than spin-1/2 nuclei, such as ^{1}H and ^{13}C because of the large nuclear quadrupole interactions. However, there are also well-documented cases where relaxation times for quadrupolar nuclei in organic solids can also be rather long. For example, the $T_1(^{17}O)$ value in potassium hydrogen [$^{17}O_4$]maleate is about 10 s. It is well known that D-Glucose related compounds have long $T_1(^{1}H)$ values. Recently, we discovered that the $T_1(^{17}O)$ values in ^{17}O-glucose compounds are also long. In [2-^{17}O]-D-glucose, for example, $T_1(^{1}H)$ and $T_1(^{17}O)$ values are ca. 30 and 5 s, respectively. Apart from synthetic difficulties in ^{17}O-labeling, carbohydrate molecules are also the least studied by ^{17}O solid-state NMR [1]. Paramagnetic doping has long been used to shorten the relaxation times for spin-1/2 nuclei such as ^{1}H [2]. Here, we applied the same method to shorten $T_1(^{17}O)$ in D-glucose compounds so that 2D ^{17}O 3QMAS data collection can be significantly accelerated.

Experimental

D-glucose compounds were co-dissolved with $Na_2Cu(II)EDTA$ (10% wt) in aqueous solution. Greenish solids were obtained by drying the solution with a stream of N_2. ^{17}O solid-state NMR spectra were acquired at 19.6 T at the NHMFL, using a Bruker NEO console and a 3.2 mm Low-E MAS probe designed and built at the NHMFL.

Results and Discussion

Figure 1(a) shows that, upon paramagnetic doping, the ^{1}H and ^{17}O relaxation times of [2-^{17}O]-D-glucose were significantly shortened. In fact, both $T_1(^{1}H)$ and $T_1(^{17}O)$ values are now less than 1 s. The ^{13}C CPMAS spectra of the doped glucose compounds do not display any noticeable difference from those of undoped compounds. Now the ^{17}O NMR data can be accumulated at a much faster rate (e.g., with a recycle delay as short as 0.5 s). With this improvement, we were able to acquire 2D ^{17}O 3QMAS spectra for [2-^{17}O]-D-glucose and [3,5,6-$^{17}O_3$]-D-glucose, as shown in Figure 1(b). Interestingly, we note immediately that the hydroxyl groups (O2, O3 and O6) exhibit much shorter T_2 values (thus poorer resolution in the isotropic dimension) than the non-protonated oxygen (O5). However, given that ^{1}H decoupling of >60 kHz was employed during data acquisition, it is surprising to see such a T_2 discrepancy among different sites. It is possible that it is due to the high-order decoupling-induced recoupling effect [3] or unknown dynamics in doped D-glucose. We are currently investigating this phenomenon.

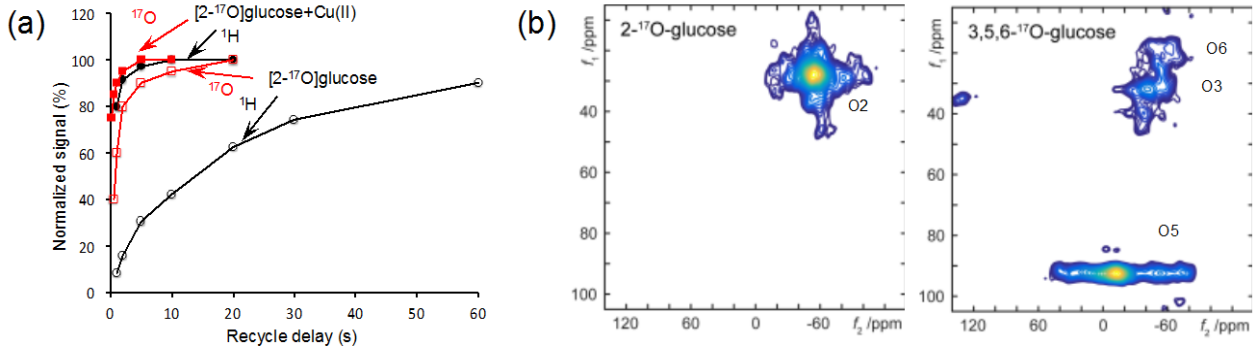

Fig. 1 (a) Effects of paramagnetic doping with $Na_2CuEDTA$ on the relaxation times of [2-^{17}O]-D-glucose. Data were obtained at 14.1 T. (b) ^{17}O shifted-echo 3QMAS spectra of [2-^{17}O]-D-glucose and [3,5,6-$^{17}O_3$]-D-glucose obtained at 19.6 T. The sample spinning frequency was 16 kHz. In each spectrum, a total of 16 complex t_1 points were collected. The numbers of transients were 13632 and 62400 for [2-^{17}O]-D-glucose and [3,5,6-$^{17}O_3$]-D-glucose, respectively.

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References

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