

High-resolution proton NMR for NMR crystallography of cellulose

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The detailed crystalline structures of the various forms of cellulose are challenging to fully characterize due to the fibrous nature of cellulose and the polymorphism that exists in natural cellulose samples (Figure 1). The best structural models have been obtained from fibre neutron diffraction experiments. However, there are a number of remaining questions concerning the hydrogen bonding arrangement in the various forms of crystalline cellulose. The aim of this work is to employ ^1H and ^{13}C solid state NMR spectroscopy to provide further structural information about cellulose that may validate or improve the current structural models.

The link between structural models and experimental NMR data is made possible by quantum chemical calculations of NMR parameters with programs such as *CASTEP* or *Quantum ESPRESSO*. In order to develop experimental and theoretical methods to evaluate the structures of cellulose with confidence, we have first investigated two crystalline forms of glucose, the monomer that cellulose is made up of. The projection of the indirect dimension in Figure 2 presents the ^1H CRAMPS NMR spectra of α -glucose obtained at 900 MHz (21.1 T) with a symmetry-adapted windowed PMLG sequence. The

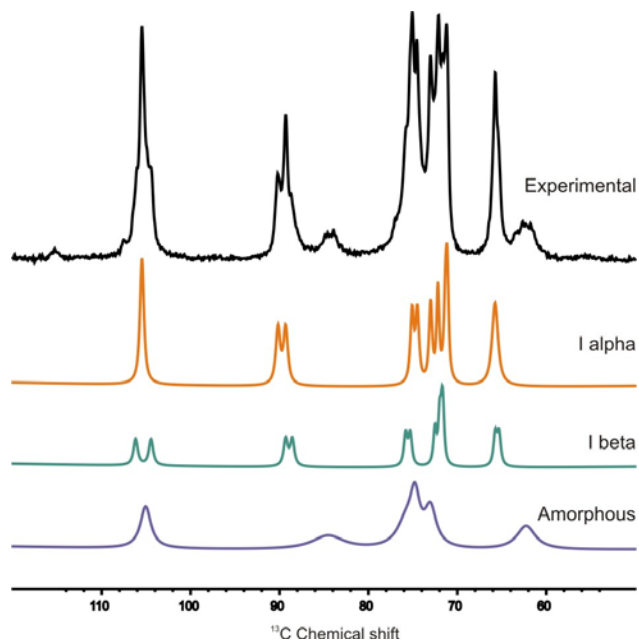


Figure 1: ^{13}C CP MAS NMR spectrum of cellulose bio-synthesized from *Acetobacter xylinum* bacteria. Two crystalline forms and a non-crystalline form are present in the sample.

remainder of Figure 2 presents a $^1\text{H}/^{13}\text{C}$ 2D HETCOR spectrum from which assignments of the ^1H resonances can be made. Although not shown in the figure, the resonances arising from hydroxyl groups can be observed at higher contour levels and assigned to the $-\text{OH}$ groups involved in hydrogen bonding in the crystal structure.

Figure 3 demonstrates that quantum chemical calculations, performed with *Quantum ESPRESSO*, of ^1H chemical shielding tensors are in good agreement with the experimental chemical shifts. This foundational work with glucose model compounds should lead to useful results for cellulose crystal structures in the future.

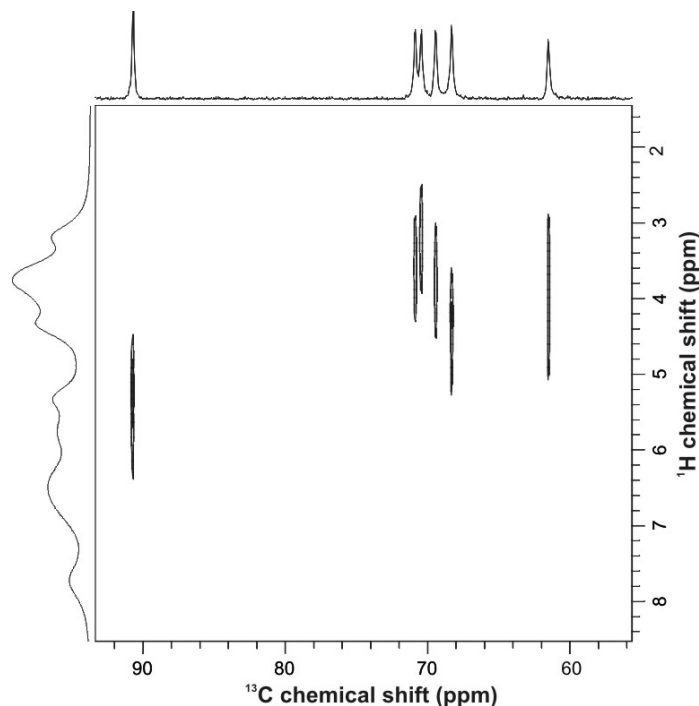


Figure 2: $^1\text{H}/^{13}\text{C}$ CP HETCOR NMR at 21.1 T of α -glucose with a symmetry-adapted version of a windowed PMLG CRAMPS sequence used to obtain the ^1H dimension.

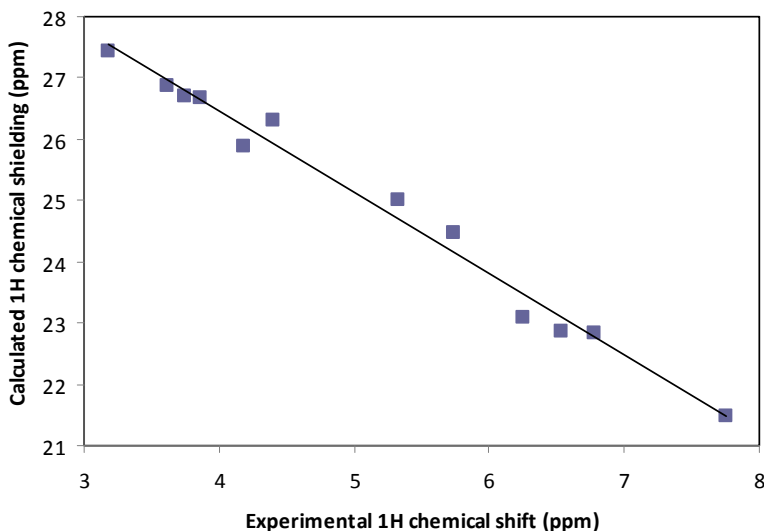


Figure 3: Comparison of quantum chemical calculated isotropic values of ^1H chemical shielding tensors to experimental isotropic ^1H chemical shifts for α -glucose.