

High-resolution ^{17}O - ^1H correlation solid-state NMR spectroscopy

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Solid-state ^{17}O NMR has in recent years developed into a powerful tool to study hydrogen bonding in nucleic acids, amino acids, peptides, and proteins [1,2], as it gives direct access to one of the hydrogen-bonding partners in X-H...O (X=O, N, C) hydrogen bonds. High-resolution ^{17}O - ^1H correlation spectroscopy is the ideal method to identify (^{17}O , ^1H) spin pairs covalently bound or in close proximity to each other. Here we present ^{17}O - ^1H heteronuclear single-quantum correlation (HSQC) spectra [3] based on either the heteronuclear J -coupling (J -HSQC) or the dipolar coupling (D-HSQC) between the ^{17}O and ^1H nuclei. The experiments were performed on a sample of [$^{17}\text{O}_3$]-L-tyrosine-HCl (structure shown in Fig. 1) at an external field of 21.1 T and magic-angle-spinning (MAS) frequency of 25 kHz using a 2.5 mm Bruker probehead. In case of the D-HSQC experiment, the ^{17}O - ^1H dipolar coupling was recoupled using the symmetry-based SR4₁² sequence [4]. Figure 2 shows the experimental J -HSQC and D-HSQC spectra, where in both cases strong (Oⁿ, Hⁿ), (Oⁿ, Hⁿ) and (Oⁿ, Hⁿ) correlations can be observed. The projection onto the ^1H axis in the D-HSQC spectrum reveals a weak signal stemming from the NH₃ group, however a longer dipolar recoupling interval is required to definitely observe correlations involving the O' site.

References

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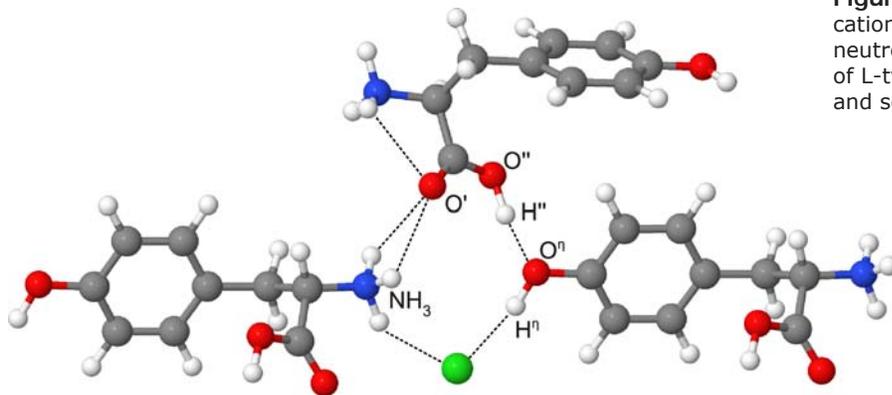


Figure 1: Three adjacent L-tyrosine cations and one chlorine anion in the neutron-diffraction-determined structure of L-tyrosine-HCl. The ^{17}O labeled sites and selected proton sites are indicated.

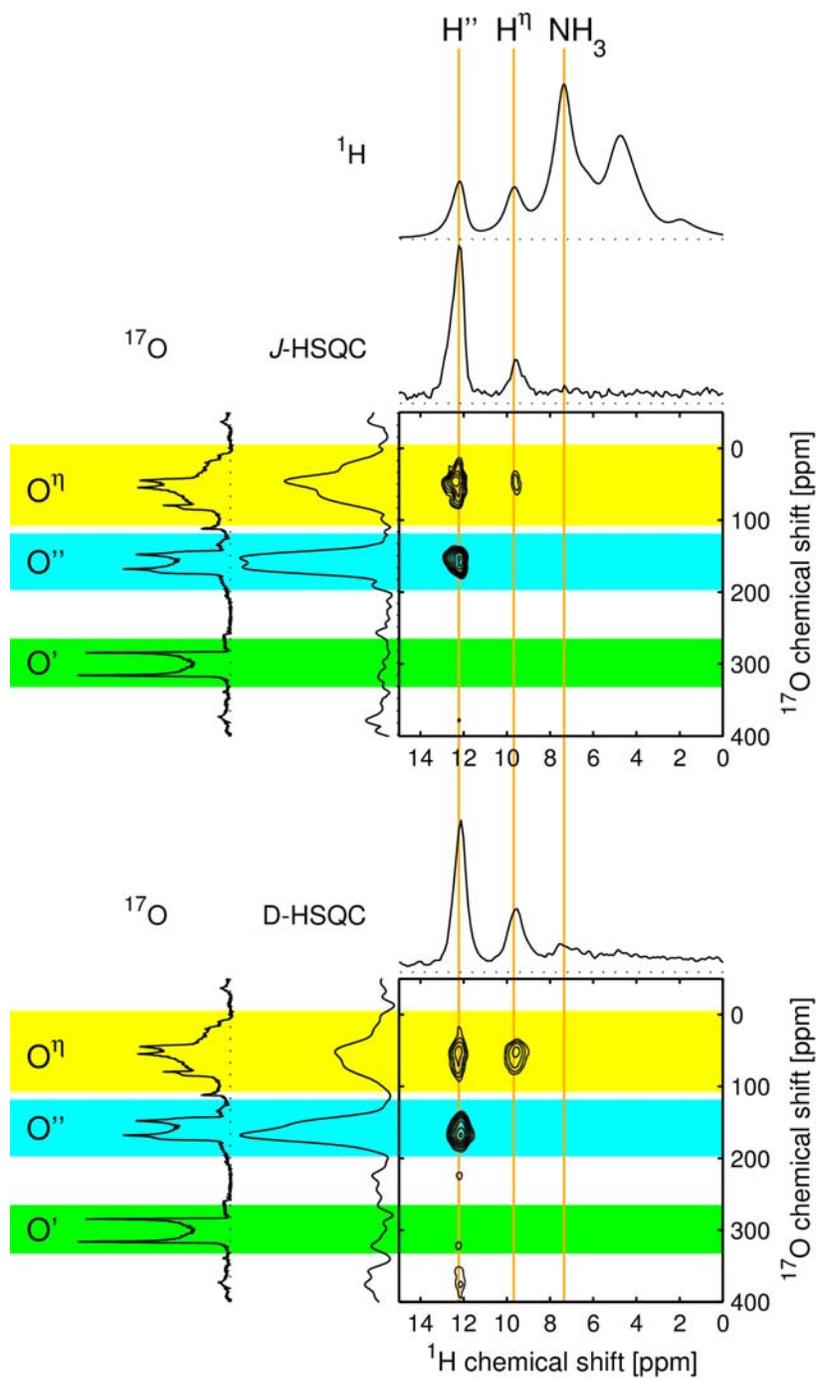


Figure 2: Experimental ^{17}O - ^1H HSQC correlation spectra obtained at an external field of 21.1 T and 25 kHz MAS frequency. The heteronuclear single-quantum coherences are excited by: (top) evolution under the J -coupling for a period of 240 μs , (bottom) evolution under the dipolar coupling recoupled by a SR4_1^2 sequence of duration 96 μs .