

Solid-state ^{17}O NMR as a new probe to study biological structures

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Oxygen is one of the most important elements in organic and biological molecules. Solid-state ^{17}O (spin-5/2) NMR for organic compounds has, however, remained largely unexplored due to experimental difficulties in detecting ^{17}O NMR signals. Since 2000, we have developed a comprehensive research program in solid-state ^{17}O NMR studies of organic and biological compounds [1]. Using the 900 MHz spectrometer at the National Ultrahigh Field NMR Facility for Solids, we have been able to tackle more challenging problems.

In the past year, we have obtained information about ^{17}O NMR tensors in several new functional groups. In particular, we have used solid-state ^{17}O NMR experiments to measure the ^{17}O quadrupole coupling (QC) and chemical shift (CS) tensors for two α -keto acid compounds: sodium [2- ^{17}O] pyruvate and lithium [2,2'- $^{17}\text{O}_2$]pyruvate. In the solid state, sodium [2- ^{17}O]pyruvate is in the keto form ($-\text{C}(=\text{}^{17}\text{O})-$) whereas lithium [2,2'- $^{17}\text{O}_2$]pyruvate takes the *gem*-diol form ($-\text{C}(\text{}^{17}\text{OH})_2-$); see Figure 1. Because ^{17}O NMR tensors in these different tautomeric forms have been unknown, we carried out a systematic study using multiple magnetic fields. Our results suggest that solid-state ^{17}O NMR can be used as a sensitive probe of the keto and *gem*-diol functional groups in α -keto acid compounds. Because keto \leftrightarrow *gem*-diol transformation is often found during enzymatic reactions, solid-state ^{17}O NMR is potentially useful in probing the reaction intermediates. This study has been published as a cover story in the solid-state NMR themed issue of *PCCP* [2].

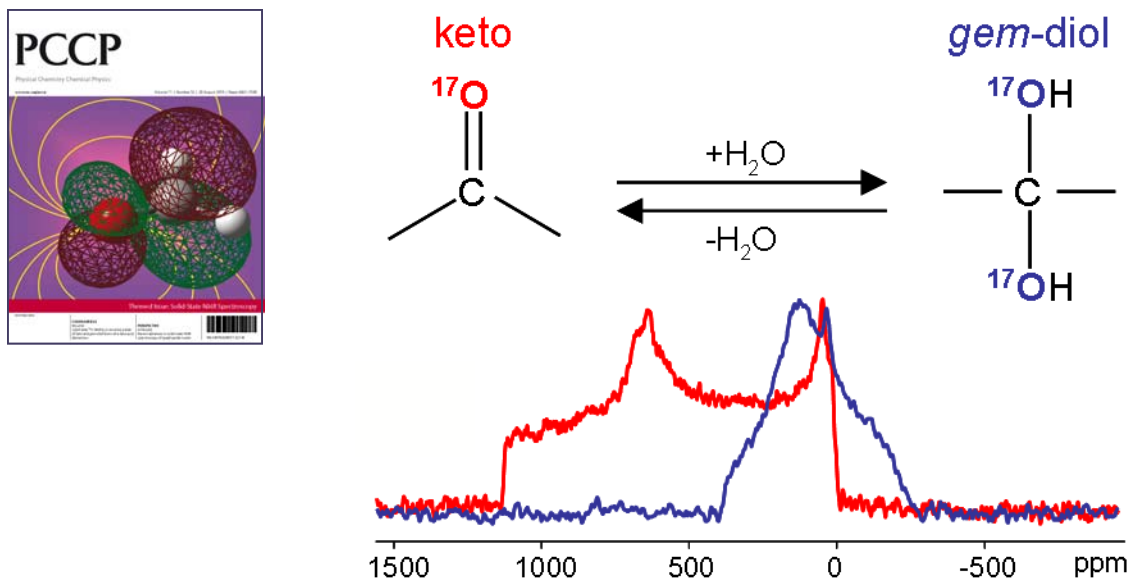


Figure 1: Solid-state 21.1 T ^{17}O NMR spectra of stationary powder samples of (red) sodium [2- ^{17}O]pyruvate and (blue) lithium [2,2'- $^{17}\text{O}_2$]pyruvate monohydrate. This research was featured on the cover of the special solid-state NMR issue of *Physical Chemistry Chemical Physics* [2].

We have also fully characterized the ^{17}O NMR tensors for the phenolic oxygen of L-tyrosine in both protonated and deprotonated states. Again, the solid-state ^{17}O NMR parameters exhibit remarkable sensitivity toward the protonation state of the phenolic oxygen. Since the isotropic ^{13}C chemical shift of the C_1 carbon in a phenol group ($-\text{C}_1-\text{OH}$) is known to be insensitive to the protonation state of the phenolic oxygen, ^{17}O NMR provides a new sensitive means of detection; see Figure 2 [3].

In summary, we have continued to make significant progress in this long-term project. In the next year, we plan to focus on solving some biochemical problems using ^{17}O NMR spectroscopy.

References

- [1] G. Wu, *Progress in NMR Spectroscopy*, **52** (2008) 118-169.
 [2] J. Zhu, A.J. Geris and G. Wu, *Phys. Chem. Chem. Phys.* **11** (2009) 6972-6980.
 [3] J. Lau, Honours Thesis, Department of Chemistry, Queen's University, 2009.

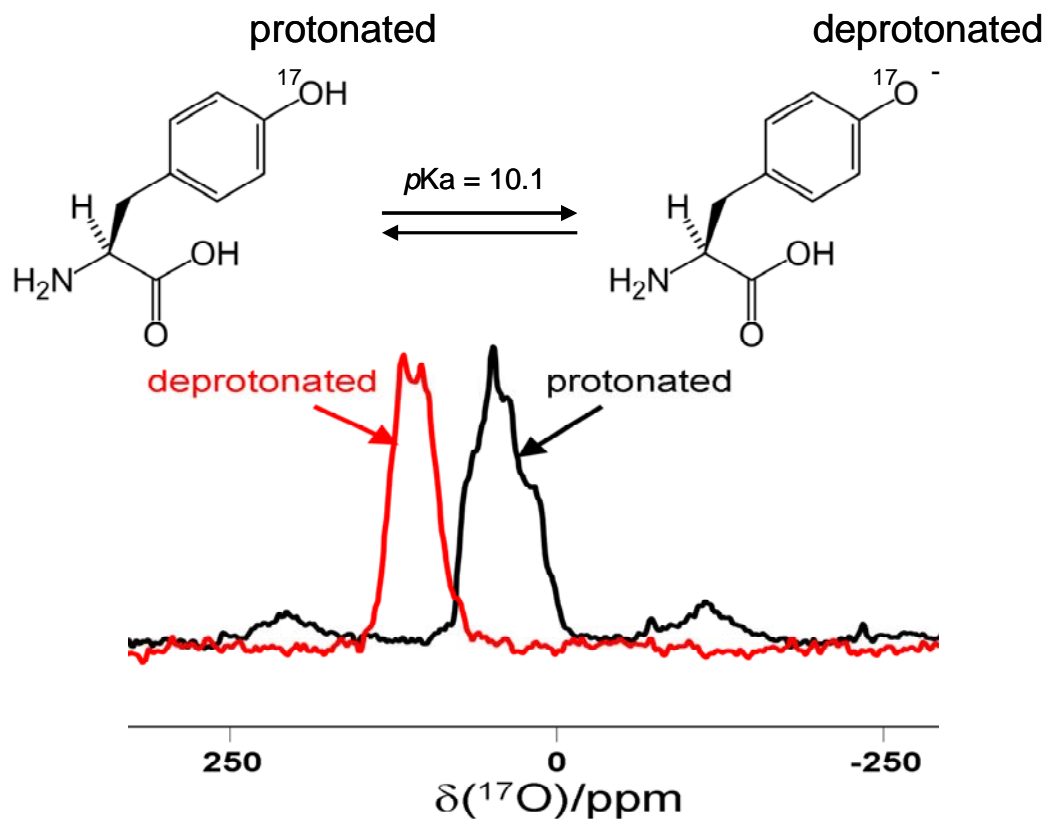


Figure 2: Solid-state 21.1 T ^{17}O MAS spectra of (red) sodium L- ^{17}O tyrosinate and (black) L- ^{17}O tyrosine.