# Direct Measurement of the Symmetric Hydrogen Bond Distance in Potassium Hydrogen Maleate by Solid-State $^{17}$O NMR

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## Introduction

Potassium hydrogen maleate (KHM, KH[OOCH=CHOO]) is a classic case where the O···H···O hydrogen bond (HB) is perfectly symmetric in the solid state with the hydrogen atom located at the center of the two oxygen atoms [1]. Plane-wave DFT calculations also confirmed that the potential function for the proton motion between the two oxygen atoms exhibits a single well [2]. The single-crystal neutron diffraction data collected for KHM at 5 K show that the O···O and O···H distances are 2.427, and 1.215 Å, respectively, with the O···H···O angle being 176° [1]. While solid-state $^{17}$O NMR has been previously used to study KHM [3], the O···H distance in KHM has not been measured directly by NMR. In this work, we used KHM as a benchmark to test the reliability of NMR distance determination methodology which is based on the measurement of the $^{1}$H-$^{17}$O dipolar coupling constant.

## Experimental

[1,2-$^{17}O_2$]KHM was synthesized at the $^{17}$O enrichment level of 20%. Solid-state $^{17}$O MAS NMR spectra were obtained at 19.6 and 21.1 T (NHMFL) with Bruker consoles and 3.2 mm Low-E $^{1}$H-X MAS probes built and designed at the NHMFL.

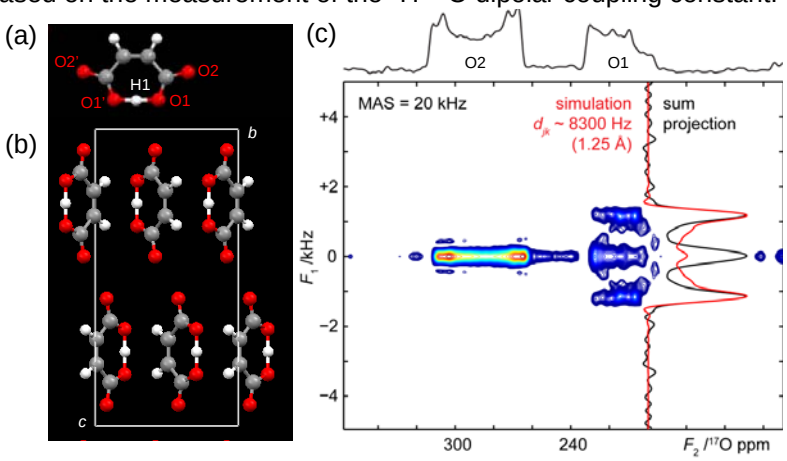


Fig.1 (a) Molecular structure and (b) molecular packing in the crystal lattice of KHM [1]. All potassium ions are omitted for clarity. (c) 2D $^{17}$O{$^{1}$H} DIPSHIFT spectrum of [1,2-$^{17}O_2$]KHM obtained at 19.6 T at 298 K, together with spectral simulation (red trace). The R18$^{5}_{2}$ symmetry-based pulse sequence was used.

## Results and Discussion

Fig. 1 shows that $HM^-$ monoanion is planar. In the 1D $^{17}$O MAS spectrum of [1,2-$^{17}O_2$]KHM, the O1 signals exhibits an isotropic $^{17}$O chemical shift of 233 ppm, consistent with the fact that this oxygen is involved in strong hydrogen bonding. To measure the $^{1}$H-$^{17}$O distance, we performed the 2D $^{17}$O{$^{1}$H} DIPSHFIT experiment. As seen from Fig.1, the measured $^{1}$H-$^{17}$O dipolar splitting can be modeled with a $^{1}$H-$^{17}$O distance of 1.25 Å. We also performed the DIPSHIFT experiment at 203 K and obtained essentially the same $^{1}$H-$^{17}$O distance. This distance is slightly longer (by 0.04 Å or 3%) than that obtained from neutron diffraction, 1.215 Å. While this observation is consistent with the well-known trend that NMR internuclear distances are typically longer than the corresponding values determined from diffraction methods, it is still worth examining the exact sources for this discrepancy. In KHM, it is likely that the out-of-the-plane librational motion of the hydrogen atom is largely responsible for the averaging of the $^{1}$H-$^{17}$O dipolar coupling. Further investigation is underway to model this type of librational motion.

## Conclusions

We have used solid-state $^{17}$O NMR to measure the H···O distance in the symmetric HB in KHM. The NMR distance is slightly longer than that obtained from the neutron diffraction experiments. KHM is a system where it is possible to pin-down the exact mode of librational motion that is responsible for this discrepancy.

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## References

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