Approaching the Intrinsic Resolution Limit of ^{39}K NMR for Organic Solids

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Introduction

Direct spectroscopic detection of K^+ ions bound to biological macromolecules is a challenging task. If high-quality single crystals are available, crystallography is certainly the best technique for directly localizing K^+ ions in biological structures such as ion channel proteins [1] and DNA oligomers [2]. In 2003, we demonstrated that magic-angle spinning (MAS) ^{39}K NMR at high magnetic fields can provide useful information about K^+ coordination in organic and biological solids [3]. However, one major obstacle is that the spectral resolution in ^{39}K MAS spectra is rather limited because of the incomplete averaging of second-order quadrupole interactions by MAS, making it difficult to apply the technique to molecular systems containing multiple K^+ sites. Here we report the first set of ^{39}K multiple-quantum MAS (MQMAS) [4] NMR spectra for organic solids in which remarkably high spectral resolution is obtained.

Experimental

All solid-state ^{39}K NMR experiments were performed at the NHMFL with the 19.6-T magnet. A Bruker Avance console and an NHMFL-built 4-mm MAS probe was used. At 19.6 T, the Larmor frequency for ^{39}K is 38.7 MHz.

Results and Discussion

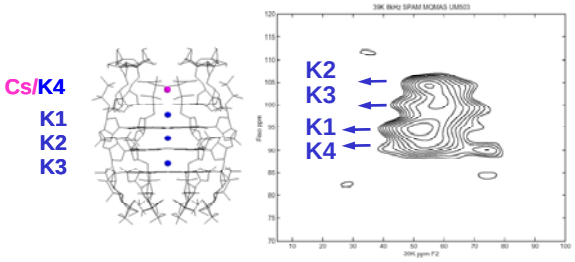

Fig. 1: (left) Crystal structure and (right) ^{39}K MQMAS spectrum of **G1**.

Fig. 1 shows the two-dimensional (2D) ^{39}K MQMAS NMR spectrum of a G-quadruplex structure formed by self-assembly of 5′-*tert*-butyl-dimethylsilyl-2′, 3′-*O*-isopropylidene guanosine (**G1**). This 2D ^{39}K MQMAS spectrum clearly shows the presence of four distinct K^+ signals. Because the crystal structure of this compound is known, spectral assignment can be made. K1, K2, and K3 are due to K^+ ions residing inside the quadruplex channel while K4 is the capping K^+ ion which shares the occupancy with Cs^+. The molecular weight of the entire structure is ca. 9 kDa. The strategy employed in the present study for overcoming practical difficulties in obtaining ^{39}K MQMAS signals is to utilize an ultrahigh magnetic field, 19.6 T, and a probehead that can deliver very high RF power at the very low Larmor frequency for ^{39}K nuclei. We have also found that the resolution along the isotropic dimension of the MQMAS spectrum is primarily limited by the ^{39}K transverse relaxation time, which is the intrinsic spectral limit of ^{39}K NMR.

Conclusions

We have obtained ^{39}K MQMAS NMR spectra for organic solids. The observed spectral resolution along the isotropic dimension approaches the intrinsic limit of ^{39}K NMR. We have demonstrated detection of a single K^+ ion out of a 9 kDa molecular system. The demonstrated NMR sensitivity at 19.6 T suggests that it is possible to apply this approach to other organic and biological systems.

Acknowledgements

This research was supported by NSERC of Canada.

References

[1] Doyle, D. A., et al., Science, **280**, 69-77 (1998).
[2] Parkinson, G. N., et al., Nature, **417**, 876-880 (2002).
[3] Wu, G., et al., J. Am. Chem. Soc., **125**, 7182-7183 (2003).
[4] Frydman, L., et al., J. Am. Chem. Soc., **117**, 5367-5368 (1995).