SOLID-STATE ^{25}Mg NMR OF CHLOROPHYLL A AT NATURAL ABUNDANCE

A. Wong (Queen's University); Z. Gan (NHMFL); X. Mo, J. Poh, G. Wu (Queen's University)

Introduction

In recent years, solid-state NMR has emerged as a viable technique to study metal binding sites involving low-γ quadrupolar nuclei in organic and biological compounds. In the context of solid-state ^{25}Mg (spin-5/2) NMR, several research groups have extended solid-state ^{25}Mg NMR to organic systems [1-4]. These initial studies have demonstrated the great potential of solid-state ^{25}Mg NMR in probing Mg(II) binding environment in organic and biomolecular systems. Here we report observation of natural abundance solid-state ^{25}Mg NMR spectra for chlorophyll a, the most important Mg-containing compound in nature; see Fig.1.

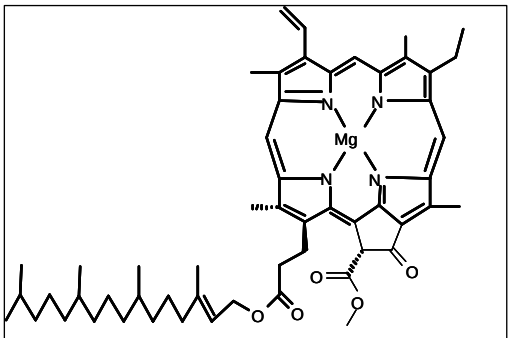

Figure 1. Molecular structure of chlorophyll *a*.

Experimental

Chlorophyll *a* was extracted from fresh spinach leaves. All solid-state ^{25}Mg NMR experiments were performed at the NHMFL in the 19.6-T magnet. A Bruker Avance console and a NHMFL wide-line probe were used. At 19.6 T, the Larmor frequency for ^{25}Mg is 50.77 MHz.

Results and Discussion

Fig.2 shows the observed and calculated static ^{25}Mg NMR spectra for chlorophyll *a*. The ^{25}Mg quadrupole coupling constant (C_Q) and the asymmetry parameter (η_Q) were determined to be 12.92 MHz and 1.0, respectively. In chlorophyll a, the Mg(II) ion is coordinating to four nitrogen atoms and a water molecule in a square-pyramidal geometry. The observed large value of C_Q is consistent with this very asymmetrical geometry. This is the first time that a Mg(II) ion in square-pyramidal coordination geometry has been characterized. These ^{25}Mg NMR parameters are in agreement with the quantum mechanical calculations using density functional theory [5].

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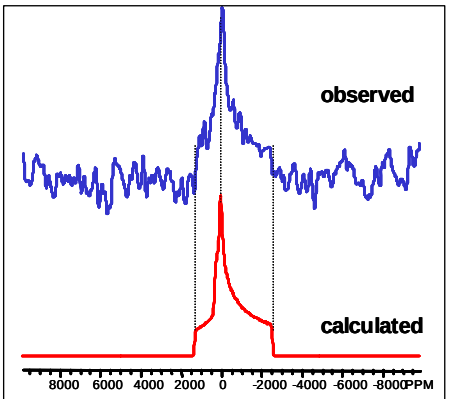

Figure 2. Static ^{25}Mg NMR spectra of chlorophyll a at 19.6 T. A total of 512,00 transients were collected with a recycle time of 0.5 s.

Conclusions

We have obtained solid-state ^{25}Mg NMR spectra for chlorophyll a at natural abundance. The observed ^{25}Mg quadrupole coupling is among the largest ones reported to date for Mg-containing organic compounds. The molecular weight for this complex, ca. 950 Da, is also the largest among the Mg-containing complexes studied so far. The demonstrated NMR sensitivity at 19.6 T suggests that it is possible to study larger systems close to 10 kDa if the ^{25}Mg isotope can be enriched to 99%.

Acknowledgements

This research was supported by NSERC of Canada.

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