Ab initio and DFT study of ^{31}P-NMR chemical shifts of sphingomyelin and dihydrosphingomyelin lipid molecule

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One of the phospholipids, sphingomyelin (SM, *N*-acyl-sphingosine-1-phosphorylcholine) is the most abundant component of mammalian membranes in brain and nervous tissues. It plays an important role for apoptosis, aging, signal transduction with cations. Recently, Yappert and co-workers have shown that human lens sphingomyelin and its hydrogenated derivative, dihydrosphingomyelin (DHSM) are interacted with Ca^{2+} ions to develop human cataracts [1, 2].

Previously we have investigated conformational differences between an isolated SM / DHSM molecule and Ca^{2+}-coordinated form by using density functional theory (DFT) which B3LYP functional and 6-31G(*d*,*p*) double-ζ split-valence basis set is applied for geometry optimization and normal mode analysis. As a result, one of conformers of SMs has hydrogen bonding between hydroxyl group and phosphate group, whereas another conformer has hydrogen bonding between hydroxyl and phosphate amide group [3].

In this study, ^{31}P- Nuclear Magnetic Resonance (NMR) shielding constants of the obtained conformers are investigated by using *ab initio* and DFT NMR- gauge invariant atomic orbitals (NMR-GIAO) calculations. The experimental ^{31}P-NMR chemical shifts of SMs and DHSMs have significant small value around 0.1 ppm [4]. We consider the relative conformational changes between SMs and DHSMs affect the slight deviations of ^{31}P-NMR chemical shifts, and discuss intermolecular hydrogen-Ca^{2+} interaction of the phospholipids with ration to NMR experimental results.

[1] M. Rujoi, D. Borchman, D. B. Dupré, and M. C. Yappert, Biophys. J. **82**, 3096–3104 (2002).
[2] M. C. Yappert and D. Borchman, Chem. Phys. Lipids **129**, 1–20 (2004).
[3] K. Sugimori, H. Kawabe, H. Nagao and K. Nishikawa, Int. J. Quantum Chem. **108**, 2935–2942 (2008).
[4] L. Huang, V. Grami, Y. Marrero, D. Tang, M. C. Yappert, V. Rasi and D. Borchman, Invest. Ophthalmol. Vis. Sci. **46**, 1682–1689 (2005).