GIAO-DFT CALCULATIONS OF $^{13}$C CHEMICAL SHIFTS OF PROPANE MOLECULES ENCAGED IN THE CAGES OF STRUCTURE II CLATHRATE HYDRATE

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ABSTRACT
GIAO (gauge-including atomic orbital) - DFT (density functional theory) calculations for the $^{13}$C chemical shifts of propane molecules encaged in 16-hedral cages of a structure II clathrate hydrate were performed to investigate the effect of the host-guest interaction of a pure propane clathrate on the $^{13}$C chemical shifts of propane guests. The calculations for the propane molecules encaged in the 16-hedral cages were performed at the B3LYP level with 6-311 + G (2$d$,p). The inversion of the $^{13}$C chemical shifts of the methyl and methylene carbons in the propane guests to gaseous propane was observed, which was consistent with the experiments. We also performed similar calculations for propane molecules encaged in 16-hedral cages whose size or diameter of the 16-hedral cage was changed. The inversion did not occur when the cage size was about one and a half times as large as that of the 16-hedral cage of the propane hydrate. It was also found that the inversion was caused by the charge transfer to the methyl and methylene carbons from the 16-hedral cages.

Keywords: propane hydrate, NMR, shielding constant, GIAO-DFT, 16-hedral cage

INTRODUCTION
Among the clathrate hydrates of natural gases, propane is a major component of the guest gas molecules and forms a structure II clathrate hydrate [1-6]. The distribution of propane in the 16-hedral cage has been studied using X-ray and neutron diffraction techniques [6-9]. To probe the guest molecules encaged in the polyhedral cages of clathrate hydrates, NMR chemical shifts have been specifically used to assess guest-host interactions or electronic environments around the guest molecule [10,11]. The inversion of the $^{13}$C chemical shifts of the methyl and methylene carbons in the propane guests to gaseous propane was observed in the $^{13}$C NMR measurements of the propane hydrate [12]. The NMR chemical shift