

*Ab Initio* Dynamics Simulation of the Molecular Gyroscope  
(分子ジャイロスコープの第一原理動力学シミュレーション)

(<sup>1</sup> Department of Chemistry, Graduate School of Science, Tohoku University.

<sup>2</sup> Department of Chemistry, Tokushima Bunri University.)

○Anant B. Marahatta<sup>1</sup>, Kunihito Hoki<sup>1</sup>, Wataru Setaka<sup>2</sup> and Hirohiko Kono<sup>1</sup>

I. **Introduction:** The synthesized molecular rotors, which are expected to have unique functions of framed molecular tops, have been receiving attention as a fundamental element of nanotechnology. Molecular gyroscopes with bridged  $\pi$ -electronic systems as a rotator, crystalline solids with internal rotors have many interesting physicochemical properties. For example, a dipolar unit in the crystal can be reoriented by conserving its volume under the influence of external stimuli [1]. Recently, an X-ray crystallography of the first silicon-based molecular gyroscope which has a phenylene rotator encased in three long siloxaalkane spokes has been presented (Fig. 1) [2]. In this case, the rotator is supposed to rotate facily and repeatedly. To probe its rotational dynamics, molecular dynamics simulation has been performed for the first time. The notable results explored currently are reported herein.

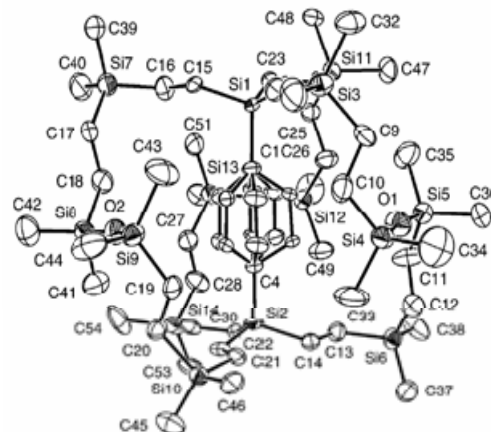


Fig.1. X-ray crystallography of a molecular gyroscope at 223 K [2]. Three positions around the 1,4-axis of the central phenylene are indicated.

II. **Method:** For the determination of the molecular packing structure and the dynamics of this molecular gyroscope, the Density Functional based Tight Binding (DFTB) method [3] implemented in DFTB+ program package is employed [4]. In accordance with the experimental condition of this crystalline molecular solid, a periodic boundary condition (PBC) is imposed. By using the force constants obtained from the DFTB method, the motions of all nuclei are evaluated based on the classical mechanics with a constraint on the volume and shape of the unit cell.

III. **Results and Discussions:** The X-ray geometry of the unit cell is almost reproduced by the DFTB except the flexible Si-O-Si angles of the siloxaalkane spokes. The way the energy of a molecular system varies upon the phenylene rotation is specified by its potential energy surface. At first, the validity of the DFTB method which could produce the similar features of the potential energy surface as that of DFT (B3LYP) calculation is confirmed in reference to the isolated siloxaalkane gyroscope. The potential energy surface derived by the DFTB under PBC is found to be asymmetric, which exhibits directional as well as Ratchet motion. Furthermore, the rotational

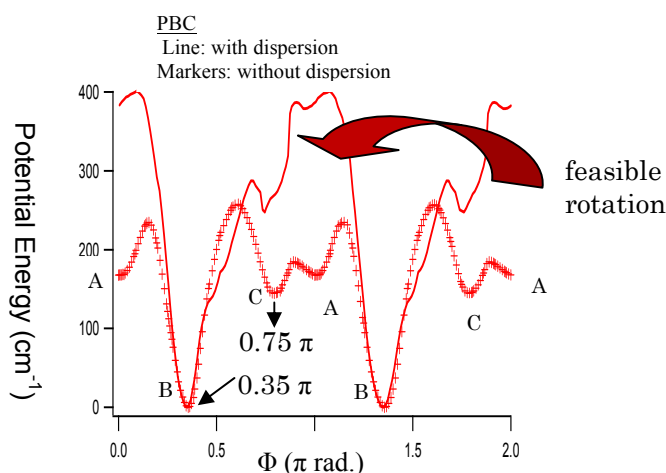


Fig.2. Potential energy as a function of the dihedral angle ( $\Phi$ )

heights of  $\sim 400\text{ cm}^{-1}$  and  $\sim 250\text{ cm}^{-1}$  are observed with and without van der Waals interaction respectively (Fig. 2). Similarly, the appearance of the three stable positions as in X-ray crystallography (Table 1) and the relation of the two degenerate positions by  $180^\circ$  flip are other notable features. DFTB/MD simulations without dispersion at high (1200K, 800K) and at low temperatures (300K, 600K) are performed to understand the flipping dynamics. At all temperatures, the initial angle of rotation is one of the local minima at around  $\Phi = 0$ . At 1200K, the phenylene rotator at first goes to a more stable position at around  $1.75\pi$  in  $\sim 500\text{ fs}$  and is followed by  $1.4\pi$  flipping and reaches the most stable position ( $\sim 0.35\pi$ ) in  $\sim 35\text{ ps}$ . At 800K, the time required for the  $1\pi$  flipping is  $\sim 55\text{ ps}$ .

Table 1: X-ray stable structures

Position of the rotator	Angle $\Phi$ ( $\pi$ )	
	Experiment <sup>2</sup>	theory
First	0	0
Second	0.28	0.35
Third	0.58	0.75

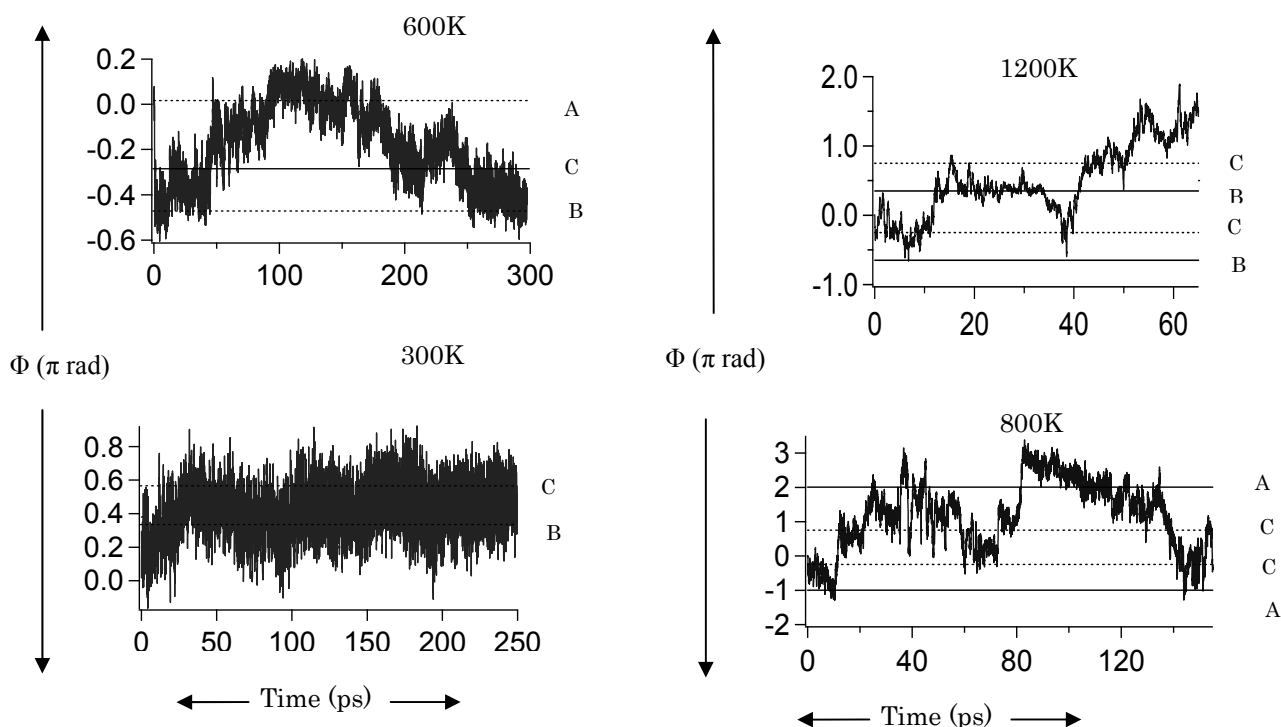


Fig.3 The rotational angle of phenylene as a function of time at different temperatures

At 600K, the trajectory reaches to one of the local minima ( $\sim 1.75\pi$ ) from the global minimum ( $\sim 1.35\pi$ ) via the initial position in  $\sim 180\text{ ps}$ . Similarly, at room temperature the rotator flips to one of the local minima ( $\sim 0.75\pi$ ) from the global minimum in  $\sim 50\text{ ps}$ . The rotational height calculated from the flipping rates is  $300\text{ cm}^{-1}$  which is consistent with the height observed at the potential energy surface.

**IV Conclusion:** The comparatively low rotational barrier, which is highly demandable, signifies one of the promising architectures for the synthesis of the crystalline free rotor. The facile phenylene flipping within the cage of the siloxaalkane spokes at low as well as high temperatures indicates the gyroscopic behavior.

[1] Garcia-Garibay et al. *JACS*, **124** (2002) 7719. [2] W. Setaka et al. *Lett.* **36** (2007) 1076.

[3] D. Porezag et al. *Phys. Rev. B*, **51** (1995) 12947. [4] B. Aradi et al. *J. Phys. Chem. A*, **111** (2007) 5678. [5] C. Köhler et al. *Phys. Rev. B*, **64** (2001) 085333.