

## A theoretical investigation on the structure and dynamics of crystalline molecular gyroscopes

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The structure, synthesis and function of molecular rotors have attracted much attention in recent years. They are a class of compounds that are essential parts of molecular machinery in general. Rotation on the molecular scale occurs naturally in bacterial and archaeal flagella and ATP synthase. Synthetic molecular rotors find applications in fluorescent probes for biological studies, real-time monitoring of aggregation and polymerization processes, protein conformational changes, measurement of bulk viscosity and many others. The initiation and control of molecular rotation through pulsed lasers, thermal, and electrical means is also an interesting subject.

Setaka et al.<sup>1</sup> succeeded in synthesizing a molecular gyroscope (a device that invariably includes a rotor) whose fluorine-substituted *p*-phenylene rotor is protected by three polysiloxaalkane macrocages (Figure 1). A bulky stator enlarges the free space around the rotor thus ensuring a facile rotation. Fluorination of the rotor gives it a finite dipole moment which opens up the possibility of optically controlling the dynamics of the gyroscope. <sup>1</sup>H NMR spectroscopy revealed rapid internal rotation in solution between 175 K and 298 K. We aim to investigate the rotational dynamics of Setaka's molecular gyroscope with a fluorinated rotor.

We used the Density Functional based Tight Binding (DFTB) approximation to determine the structure and dynamics of the fluorinated molecular gyroscope. There are two levels of theory for DFTB: a self-consistent-charge determination that includes a second-order correction to the Kohn-Sham total energy in DFT with respect to charge fluctuations (SCC-DFTB) and a non-self-consistent one (non-SCC-DFTB). Either of the two methods is used depending on computational viability. All numerical simulations are carried out using the DFTB+<sup>2</sup> suite of programs. In a previous study,<sup>3</sup> a similar molecular gyroscope having a nonpolar rotor has been the subject of our theoretical investigation wherein we found excellent agreement among the results derived from experiment, the DFTB method and the more computationally-demanding DFT method.

The geometry of a unit cell (containing four molecules) of Setaka's molecular gyroscope is optimized using SCC-DFT with the pbc parameter set under periodic boundary conditions. There are two stable structures obtained though the SCC-DFTB method, in agreement with x-ray crystal structure data. We call these structures "A" and "B", respectively. Table 1 summarizes the rotor dihedral angles obtained. The simulation results differ by as much as 23° from the experimental data in this structural parameter. The non-SCC potential energy surface in Figure 2 shows that the two structures are separated by a 5 kcal/mol rotational barrier in both directions. We used non-SCC DFTB to examine the thermally-induced rotational dynamics of the

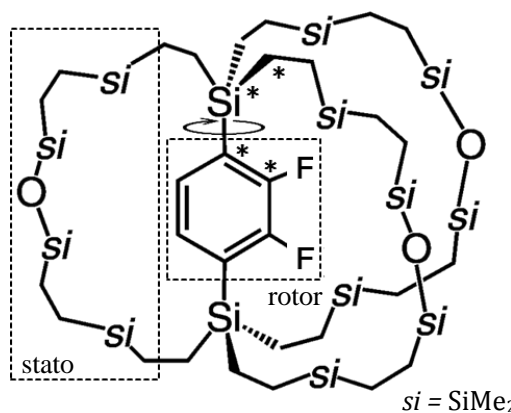


Figure 1. A single molecule of Setaka's molecular gyroscope. The dihedral angle indicative of the phenylene ring (the rotor) rotation is highlighted with asterisks. There are four of these molecules in a single orthorhombic unit cell.

Table 1. Dihedral angle of the *p*-phenylene ring with respect to the polysiloxaalkane macrocages in degrees.

	Structure A	Structure B
X-ray structure	-76.9°	101.0°
DFTB, unit cell	- 68.8°	78.5°
DFTB, single molecule	- 64.2°	78.8°

gyroscope at several temperatures between 300 K and 600 K. Figure 2 clearly shows the rotation of the fluorinated *p*-phenylene rotor from the initial structure “B” to structure “A” after around 40 ps and rotating further to structure “B” after another 170 ps to complete a 360° rotation at 400 K. Using an Arrhenius plot of  $\ln k$  vs.  $1/T$  at several temperatures, the rotational rate constant  $k$  at 298 K is estimated. Detailed kinetic analysis of the rotational dynamics reveals that  $k$  is about  $4 \times 10^8 \text{ s}^{-1}$  at 298 K, equivalent to one flip between two stable structures every 3 ns at room temperature.

In pursuit of a faster rate of flipping or rotation of the rotor, we explored this possibility by optical control of the dynamics. The SCC-DFTB MD simulation of large periodic clusters is too computationally expensive at this time. Thus, a single molecular gyroscope having a fluorine-substituted *p*-phenylene rotor enclosed by three polysiloxaalkane macrocages is extracted from the crystal structure. The geometry of the molecule is optimized under the SCC-DFTB approximation. Using the optimized geometry as the starting geometry, a 10-ps MD simulation at 0 K initial temperature was performed under the influence of a simulated 5.0 GV/m continuous-wave (CW) laser having a THz frequency of  $29.6 \text{ cm}^{-1}$ , the intramolecular rotational frequency of the rotor. The polarization direction of the field is perpendicular to the plane of the *p*-phenylene ring.

Shown in Figure 3 is the temporal profile of the dihedral angle described in Figure 1. In the case of the restricted rotor (where six silicon atoms of the polysiloxaalkane macrocages near the shaft are fixed in their optimized geometry positions in order to mimic solid-state conditions), the rotor appears to be trapped in the same structure with small oscillation amplitude in response to the THz electric field. On the other hand, the fully-free rotor overcomes the rotational barrier between structures A and B after around 4 ps and gets trapped around structure B with the dihedral angle reaching as far as  $210^\circ$ , about a 130-degree flip from the optimized structure. The flipping is completed within picoseconds under the influence of the THz field.

The restricted rotor failed to rotate even when the dynamics is initiated by an electric field. It should be noted, however, that the temperature of the system in the laser-induced simulation was 0 K and that it is anticipated that successful picosecond rotation should be attained at higher temperatures. This hypothesis is being verified at present.

We have studied the rotational dynamics of a novel molecular gyroscope. Initiation of the dynamics by thermal means leads to a slow flipping motion in the nanosecond time scale. The above simulation also reveals the possibility of optically controlling the intramolecular rotation of the rotor for a much faster dynamics. We have shown that the DFTB approximation is suitable enough for a semiquantitatively accurate simulation of the phenomenon.

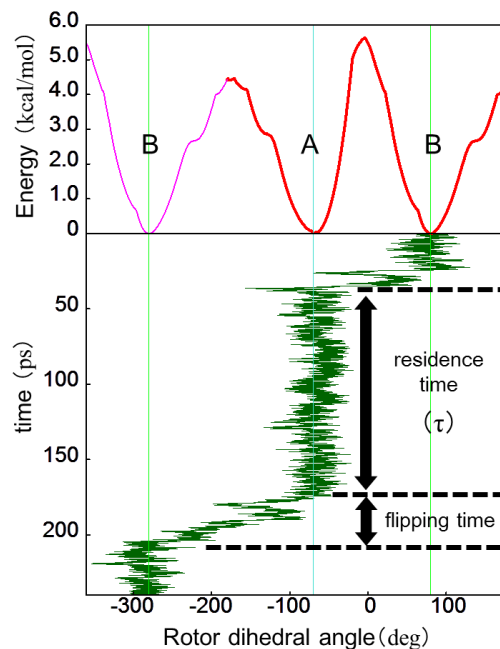


Figure 2. (Top) Non-SCC DFTB potential energy surface of the molecular gyroscope with respect to the rotor dihedral angle. The leftmost PES around structure B is a reflection of the one on the right. (Bottom) Temporal profile of the rotor dihedral angle in a typical trajectory under thermally-induced conditions at 400 K.

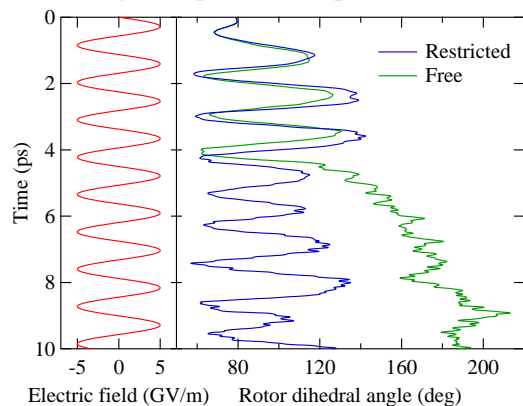


Figure 3. Temporal profile of the rotor dihedral angle under laser-induced conditions at 0 K.

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