Solid-State Inertial Rotation of a Guest Ball in a Tight Tubular Host

The dynamics of molecules in the solid state are greatly influenced by molecular contact and are usually restricted. We found that rotational motions of C_{60}, a spherical carbonaceous ball, were liberated in a tight tubular host in the solid state. The rotational motions reached an inertial regime, and variable-temperature crystallographic analyses and solid-state ^{13}C NMR spectroscopy revealed the detailed dynamics of C_{60}. The rotational frequency at 335 K was determined to be 213 GHz.

The dynamics of molecules in the solid state are an interesting subject, which can connect molecular-scale events with properties of bulk materials. However, molecular motions are severely restricted in solids. Thus, although a fullerene molecule, C_{60}, is known to rotate in solids, its dynamics are not free from restrictions: a restricted ratchet phase emerges by intermolecular face-to-face contacts, and motions below 260 K are severely restricted [1, 2]. As a tight host to trap C_{60}, a finite segment of helical carbon nanotubes, [4]cyclo-2,8-chrysenylene ([4]CC), has previously been synthesized [Fig. 1(a)] [3]. Although the enthalpy gain of the complex formation is as large as 14 kcal/mol, the ball guest in the tube host was found to be rotating in solution and, interestingly, in the solid state [4, 5]. In this work, we reveal a unique, complete picture of the solid-state dynamics of the guest in [4]CC⊃C_{60} [6].

The solid-state motions of C_{60} in [4]CC⊃C_{60} were first indicated by variable-temperature crystallographic analyses. Six single crystals of [4]CC⊃C_{60} were in-

dependently subjected to X-ray diffraction analysis at AR-NE3A, which were respectively performed at 95, 140, 180, 220, 260, and 295 K. A molecular structure at 95 K is shown in **Fig. 1(b)**. Throughout the temperature range, one C_{60} molecule was commonly observed at several disordered orientations with the center of gravity being unchanged in the tube. Electron densities visualized for different temperature conditions (95, 180, 220 and 260 K) are shown in **Fig. 1(c)**. The electron density mapping ($2F_o$–F_c) showed that biased locations of electrons of C_{60} (95 and 180 K) became blurred upon elevating the temperature (220 and 260 K), which could be ascribed to the dynamic motions of the guest at the higher temperatures.

The solid-state dynamics of C_{60} in [4]CC⊃C_{60} were next investigated by solid-state ^{13}C NMR analysis in a quantitative manner. The spectra were recorded without using magic angle spinning (MAS) which is normally required to obtain sharp resonance peaks. In the absence of MAS conditions, however, a sharp peak of
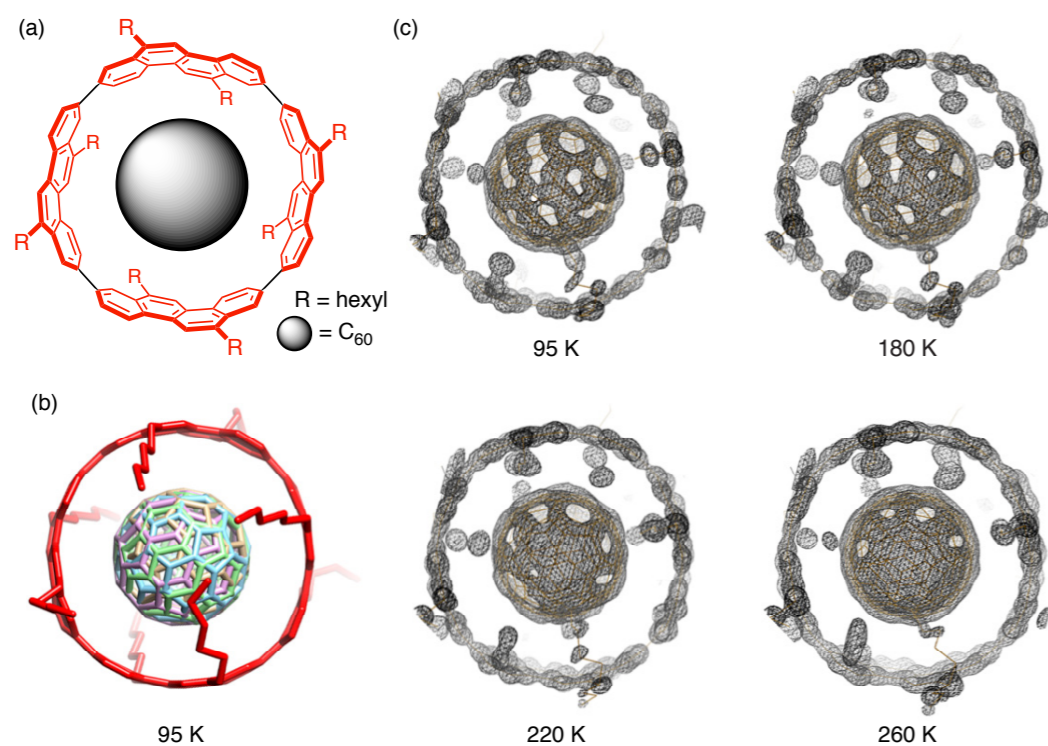

Figure 1: Crystallographic analyses of (*P*)-(12,8)-[4]CC⊃C_{60}. (a) Chemical structure of molecular bearing. (b) A crystal structure at 95 K. Disordered alkyl chains and hydrogen atoms are omitted for clarity. (c) Temperature-dependent electron density mappings with $2F_o$–F_c (RMSD: 1.5σ).
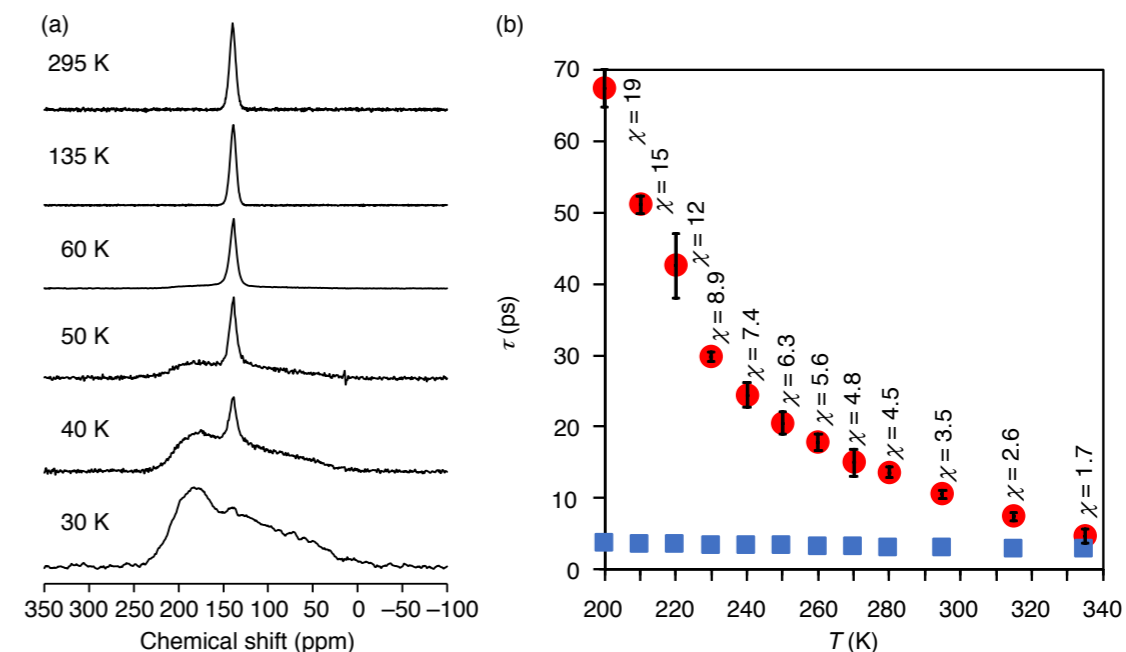

Figure 2: NMR analyses of solid-state dynamics. (a) Variable-temperature solid-state ^{13}C NMR of [4]CC⊃C_{60} under static conditions without MAS. (b) Temperature-dependence of rotational correlation time τ obtained from field-dependent spin-lattice relaxation. Red dots and blue squares indicate τ and τ_{FR}, respectively.

C_{60} was observed at 295 K [**Fig. 2(a)**], which remained unchanged at a lower temperature down to 60 K. When we further cooled the specimen, a broad shoulder peak started to appear from 50 K, and at 30 K a powder pattern was observed from non-averaged chemical shift anisotropy (CSA). The peak at 50 K for [4]CC⊃C_{60} was similar to that of intact C_{60} at 143 K [1], which indicated the liberation of C_{60} from motional restrictions in the presence of the tubular host. Rotational kinetics such as rotational correlation time (τ) and rotational frequency (k_{rot}) were determined by measurements of spin-lattice relaxation time (T_1). A series of T_1 values was obtained under three different magnetic fields to exclude field-independent non-CSA contributions contained in the T_1 values, which allowed us to determine the τ values. For instance, the temperature-dependent τ values were 4.7 ps at 335 K, which was converted to an extremely high k_{rot} value of 213 GHz. The τ values as well as the theoretical limit, τ_{FR}, of the inertial motions are plotted in **Fig. 2(b)**.

An interesting test, the so-called χ-test, clarified the presence of unique dynamics. The χ value is defined as τ/τ_{FR}, which gives a good measure of motional regimes. Thus, it is suggested that when the χ value is less than 2, the rotational motion can be regarded as non-Brownian in the inertial regime [7]. As shown in **Fig. 2(b)**, the χ value of our system started from 19 at 200 K, and gradually decreased upon elevating the temperature. The smallest χ value was recorded at 335 K and was 1.7, which was indeed smaller than 2. The χ-test thus demonstrated the presence of inertial motions of C_{60} that was trapped in the tubular [4]CC host. The solid-state dynamics of C_{60} were liberated from

restricting intermolecular contact by encapsulation in a tubular host. Interestingly, the association enthalpy was as large as 14 kcal/mol, which did not hamper the rotational motions. On the contrary, the tight host allowed the guest to rotate freely in the inertial regime in the solid state. Furthermore, we recently found a method of manipulating the direction of rotation via CH-π hydrogen bonds without changing the rotational enthalpy barrier [8]. An additional unique feature of the host is the presence of chirality: the rotational dynamics took place in a (*P*)-helical environment of the segmental nanotube. Exploration of the chirality-related phenomena should be of great interest in future.

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