

NMR study of solid $C_{60}(\gamma\text{-cyclodextrin})_2$

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Abstract

A solid complex of C_{60} with γ -cyclodextrin (γ -CyD) was examined with NMR spectroscopic methods in order to understand the dynamics of C_{60} , and the interaction between C_{60} and γ -CyD. A ^{13}C solid-state cross-polarization magic angle spinning (CP/MAS) NMR spectra shows C_{60} resonance at 142.6 ppm. This provides the evidence of interaction between ^{13}C spins in C_{60} and ^1H spins in the γ -CyD host. Ambient temperature experiments on the ^{13}C CP/MAS NMR, with varying contact time, shows that the water associated with γ -CyDs plays an important role in the nuclear relaxation processes. The dynamics of C_{60} in γ -CyD was investigated using temperature and field-dependent ^{13}C spin-lattice relaxation time measurements. The influence of water on the dynamics of C_{60} was less significant below 250 K. © 1997 Elsevier Science B.V.

Keywords: C_{60} ; γ -cyclodextrin (γ -CyD); Solid state NMR; Cross-polarization (CP); Spin-lattice relaxation

1. Introduction

The guest–host chemistry of the fullerenes has attracted exceptional attention recently, since these bulky molecules are considered as potential hosts for small metal ions and inert gas molecules [1,2]. In addition, fullerenes can themselves be guests accommodated in other large host matrices [3–9], and interesting physical, chemical and biological properties may be expected in such complexes. After the exciting report of the inhibition of HIV-1 protease by

C_{60} derivatives [10], many investigators have devoted their efforts to increase the solubility of fullerenes in water, particularly through fullerene inclusion chemistry [11–18]. It has been suggested that cyclodextrins (CyDs) with a cavity size of the same order as C_{60} are among the most suitable molecules for such a purpose. This has renewed the interest in cyclodextrin inclusion compounds which have been studied thoroughly since the 1940s [19]. Stable, water-soluble complexes of C_{60} – γ -CyD [11–16], C_{60} –DM β -CyD [17] and C_{70} – γ -CyD [18] have recently been reported. Molecular modeling [11] was used to predict the structure of C_{60} – γ -CyD complex (for γ -CyD structure, see Fig. 1) as being $C_{60}(\gamma\text{-CyD})_2$. FAB/SIMS [15,16], elemental analysis [13], ^{13}C and ^1H NMR [14,15], and photophysical [11–13] studies all confirmed this prediction.

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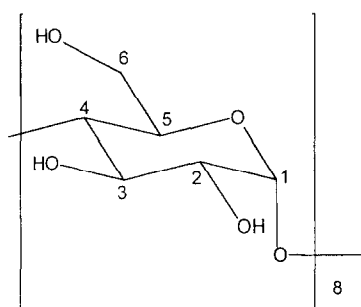


Fig. 1. Structure of the glucosidic unit of the γ -CyD molecule. Carbons are numbered.

Kim and Jeon [20] have reported the theoretical calculations of the inclusion–complexion kinetics for C_{60} and γ -CyD. They showed that in order to accommodate C_{60} , the internal strain energy is required to make the conformation of γ -CyD more symmetrical. This more symmetrical conformation of γ -CyD is not the most stable structure in itself. Along with this internal energy contribution, the hydrophobic van der Waals' interaction is believed to play the role of stabilizing the complex, while the electrostatic interaction between C_{60} and γ -CyD has been estimated to be much smaller in comparison with these former factors [20]. Water molecules associated with the complex were not included into the energy calculation, because they are considered to have a negligible effect on the lowering of the total energies calculated for the $C_{60}(\gamma\text{-CyD})_2$ molecule. However, it has been reported that hydration water do indeed transform the conformation of γ -CyD in aqueous solution [21]. Circular dichroism spectra, which are sensitive to intramolecular interactions, also demonstrated an increase in band intensity with the extent of dehydration of the $C_{60}(\gamma\text{-CyD})_2$ powders [14]. Therefore, water molecules may have a different effect on the complex with varying temperature.

In order to verify the role of water, a solid-state investigation of $C_{60}(\gamma\text{-CyD})_2$ depending on the water content was carried out in the present study with the help of NMR spectroscopic techniques. A solid-state study may provide crucial information on the mechanisms of interaction between C_{60} and γ -CyD, which is not easily carried out for the 1:2 complex in aqueous solution. The complex's very low solubility about 10^{-5} M in aqueous solution [11,13], and its

poor stability due to the equilibrium between the 1:1 and 1:2 complexes [13,16] make its study in solution problematic.

In this study, the cross-polarization time, T_{CH} , and relaxation times, $T_{1\rho}^H$, $T_{1\rho}^C$ and T_1^C , of the complex which employed the CP/MAS technique were used to show the effects of water molecules in the complex. Field and temperature dependent T_1^C of C_{60} in the complex. The experimental data obtained for the lyophilized samples were compared with those of the hydrated samples in order to reveal the differences in water effect.

2. Theoretical approach in NMR relaxation experiments

2.1. Dynamics of cross-polarization

In ^{13}C CP/MAS experiments, magnetization, $M(t)$, is a function of a set of the following parameters: the ^{13}C - ^1H CP time constant (T_{CH}); the proton spin-lattice relaxation time in the rotating frame ($T_{1\rho}^H$); the carbon spin-lattice relaxation time in the rotating frame ($T_{1\rho}^C$); and the ^{13}C - ^1H CP contact time (τ). The equation relating $M(t)$ with T_{CH} , $T_{1\rho}^H$, $T_{1\rho}^C$ and τ is as follows [22]:

$$M(t) = \frac{M_0}{\lambda} \left[1 - \exp\left(-\frac{\lambda\tau}{T_{CH}}\right) \right] \exp\left(-\frac{\tau}{T_{1\rho}^H}\right) \quad (1)$$

where

$$\lambda = 1 + \frac{T_{CH}}{T_{1\rho}^C} - \frac{T_{CH}}{T_{1\rho}^H} \quad (2)$$

and M_0 is a proportionality constant. In this case, to avoid ambiguous fitting, $T_{1\rho}^H$ and $T_{1\rho}^C$ for each sample were obtained in independent experiments and inserted into Eqs. (1) and (2) for further fittings to get T_{CH} values for each ^{13}C signal of the complex.

The CP process occurs through the ^{13}C - ^1H dipole–dipole interaction, and its effect is inversely proportional to the sixth power of the ^{13}C - ^1H distance (r_{CH}) in a rigid molecular system. Another factor that will affect the CP process is the internal motion of molecules. The faster the internal motion of the molecule, the less effective the CP process and the longer the T_{CH} value [23,24].

2.2. ^{13}C relaxation of $\gamma\text{-CyD}$

The major relaxation process for the carbons of $\gamma\text{-CyD}$ is the $^{13}\text{C}\text{-}^1\text{H}$ dipole–dipole interaction, since each of them is bonded to at least one proton. In order to elucidate the character of the motion of $\gamma\text{-CyD}$ carbons in the $\text{C}_{60}(\gamma\text{-CyD})_2$ complex, the effective reorientational correlation time (τ_c) from the dipolar relaxation was calculated using the carbon spin-lattice relaxation time in the laboratory frame (T_1^C). The effective reorientational correlation time was evaluated on the assumption that molecules are subject to Brownian motion. Though one may suspect jump motion, there is no direct way to distinguish between Brownian and jump motion on the basis of NMR relaxation studies. The following equations for a pure dipole–dipole interaction can be used for the calculation of τ_c [25].

$$\left(\frac{1}{T_1^C}\right)_{\gamma\text{-CyD}} = \frac{2}{15} \frac{\gamma_C^2 \gamma_H^2 \hbar^2 S(S+1)}{r_{\text{CH}}^6} \times [J(\omega_C - \omega_H) + 3J(\omega_C) + 6J(\omega_C + \omega_H)] \quad (3)$$

where the spectral density function, $J(\omega)$, is expressed by

$$J(\omega) = \frac{\tau_c}{1 + \omega^2 \tau_c^2} \quad (4)$$

γ_C and γ_H are carbon and proton gyromagnetic ratios, respectively; \hbar is the reduced Planck's constant; ω_C and ω_H are the Larmor frequencies of carbon and proton, respectively, under static magnetic field, B_0 ; S is the proton nuclear spin which is equal to $1/2$. The required $r_{\text{CH}} = 1.08 \text{ \AA}$ [26] was used in the present work for the evaluation of τ_c for $\gamma\text{-CyD}$.

2.3. ^{13}C relaxation of C_{60}

The dynamics of C_{60} capped by two $\gamma\text{-CyD}$ molecules was examined in this work by also measuring T_1^C for the C_{60} ^{13}C NMR signal at different static magnetic field strengths and various temperatures. In general, the carbon spin-lattice relaxation rate $1/T_1^C$ may include two terms: the contribution from the chemical shift anisotropy (CSA) interaction,

$1/T_1^{\text{CSA}}$, and the contribution from interactions other than chemical shift anisotropy (non-CSA, NCSA), $1/T_1^{\text{NCSA}}$, hence the total spin-lattice relaxation rate can be expressed as [25]:

$$\left(\frac{1}{T_1^C}\right)_{\text{C}_{60}} = \frac{1}{T_1^{\text{CSA}}} + \frac{1}{T_1^{\text{NCSA}}} \quad (5)$$

The $1/T_1^{\text{CSA}}$ term is given by

$$\frac{1}{T_1^{\text{CSA}}} = \frac{2}{15} \gamma_C^2 B_0^2 (\sigma_{\parallel} - \sigma_{\perp})^2 J(\omega) \quad (6)$$

where σ_{\parallel} and σ_{\perp} are principal components of the CSA tensor and refer to the shielding along and transverse to the symmetry axis in the axial symmetry system respectively. $J(\omega)$ is defined analogously in Eq. (4) with τ_c given as the effective reorientational correlation time due to the relaxation of anisotropic chemical shift interaction on ^{13}C of C_{60} in the complex. The effective reorientational correlation time was evaluated on the same assumption as for $\gamma\text{-CyD}$ in Section 2.2. The temperature dependence of τ_c is represented in a regular form

$$\tau_c = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad (7)$$

where E_a is the activation energy for the reorientation of the C_{60} molecule, R is the gas constant and T is the temperature in Kelvin. In Eq. (5), the main contribution to the second term $1/T_1^{\text{NCSA}}$ for this system is associated mainly with dipolar interaction between carbons of C_{60} and protons of $\gamma\text{-CyD}$ [13].

3. Experimental section

3.1. Synthesis of lyophilized $\text{C}_{60}(\gamma\text{-CyD})_2$

C_{60} (of 99.9% purity; natural abundance of ^{13}C isotopes) and $\gamma\text{-cyclodextrin}$ were purchased from Material and Electrochemical Research Corp. (AZ, USA) and from Merck respectively. The violet solid complex was synthesized in accordance with the following procedures. The analogous procedures was also used and published elsewhere [14]. We mixed two liquid phases consisting of a solution of 335 mg $\gamma\text{-CyD}$ in 50 ml water and a solution of 100 mg C_{60}

in 50 ml toluene. After the mixture was refluxed at 110°C for 2 to 3 days with vigorous magnetic stirring, a violet suspension solution was observed. Then the mixture was centrifuged to remove the supernatant and the violet solid complex was obtained. After that we added about 30 ml water to the violet solid with supersonics and repeated the previous procedure four times in order to remove the excess C_{60} and γ -CyD as much as possible. Immediately after the final removal of the supernatant, the violet powder was frozen in liquid nitrogen to be ready for the next freeze-dry step. The violet precipitate was finally freeze-dried with a commercial setup Virtis 10-324 at -57°C for 15 h under a vacuum about 50 mTorr. Elemental analysis was performed on a Perkin-Elmer 2400-CHN elemental analyzer. The typical C:H atomic ratio was revealed to be 51.66:5.96 for the lyophilized sample, which is best suited to a $C_{60}(\gamma\text{-CyD})_2$ formula.

3.2. Preparation of hydrated $C_{60}(\gamma\text{-CyD})_2$

To prepare samples of enhanced residual water content, the lyophilized $C_{60}(\gamma\text{-CyD})_2$ was soaked in water and then dried at 60°C for 2 h under a poor vacuum of about 10 Torr. The color of powder changed from violet to deep violet and showed no brown color of free C_{60} . The hydrated samples are denoted by $C_{60}(\gamma\text{-CyD})_2/\text{H}_2\text{O}$.

3.3. Preparation of physical mixtures of C_{60} and $\gamma\text{-CyD}$

120 mg C_{60} and 432.4 mg $\gamma\text{-CyD}$ (mole ratio 1:2) were physically mixed by grinding them together with a mortar and pestle till a homogenous brownish color appeared.

3.4. Characterization techniques

The powder X-ray diffraction (XRD) patterns of samples were recorded with a Scintag X1 diffractometer, using Ni-filtered Cu K_α radiation.

NMR measurements were performed on Bruker DMX-300 (7.05 T), AMX-400 (9.04 T) and MSL-500 (11.75 T) spectrometers at ^{13}C frequencies of 75.5 MHz, 100.6 MHz and 125.8 MHz, respectively. Tetramethylsilane (TMS) was used as the reference

for the chemical shift of ^{13}C . Room-temperature ^{13}C CP/MAS experiments with varying τ were performed in a magnetic field of 7.05 T with a typical $\pi/2$ pulse of 5 μs which corresponds to a 50 kHz B_1 field for both ^{13}C and ^1H and with a spinning rate of 3 kHz. $T_{1\rho}^{\text{C}}$ and $T_{1\rho}^{\text{H}}$ were measured with the CP $T_{1\rho}$ pulse sequence. T_1^{C} was measured with the CP T_1 pulse sequence, while the temperature- and field-dependent T_1^{C} of C_{60} was measured with the inversion-recovery technique using pulse sequence $\pi-\tau-\pi/2$. Samples were sealed under a vacuum of 10^{-2} to 10^{-3} Torr for all NMR relaxation measurements except for CP/MAS. A commercial software package, Microcal Origin, was used to calculate the relaxation time constants ascribed in Section 2.

4. Results and discussion

4.1. Powder X-ray diffraction

Fig. 2a–d shows the XRD patterns of the pristine C_{60} , $\gamma\text{-CyD}$, lyophilized $C_{60}(\gamma\text{-CyD})_2$ and physical mixtures of C_{60} and $\gamma\text{-CyD}$, respectively. The XRD pattern of the physical mixtures shows mainly the diffraction peaks of C_{60} , because the X-ray diffraction intensity is much stronger for C_{60} than for that of $\gamma\text{-CyD}$. While the XRD pattern of $C_{60}(\gamma\text{-CyD})_2$ is totally different from C_{60} and $\gamma\text{-CyD}$ and shows no diffraction peaks from C_{60} , indicating that no evidence of crystalline C_{60} observed in the sample.

4.2. ^{13}C CP/MAS nuclear magnetic resonance spectra

In the ^{13}C CP/MAS NMR (75.5 MHz, spinning at 3 kHz) spectra (Fig. 3a), the lyophilized sample produced a sharp line at 142.6 ppm, which was a slight upfield shift from the 143.0 ppm line of pristine C_{60} (Table 1). This minor difference 0.4 ppm reflected that $\gamma\text{-CyD}$ host only slightly disturbed the local magnetic field seen by C_{60} . This is further evidence that the main interaction between C_{60} and the $\gamma\text{-CyD}$ cages is the hydrophobic van der Waals' interaction ([13,20], rather than the charge transfer process proposed by Yoshida et al. [14]).

As with the NMR result for the aqueous solution [13], there were some minor differences between the

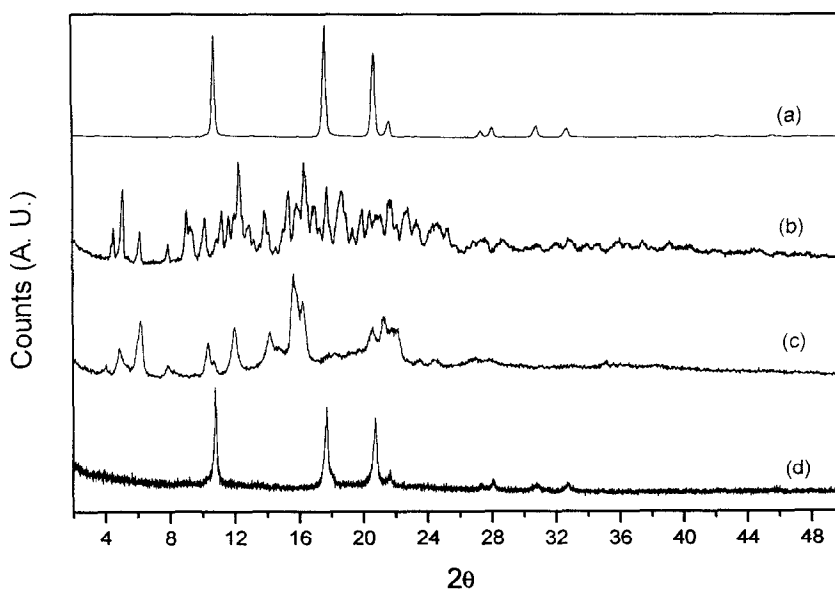


Fig. 2. Powder X-ray patterns of (a) the pristine C₆₀, (b) the pristine γ-CyD, (c) the lyophilized C₆₀(γ-CyD)₂ and (d) the physical mixtures of C₆₀ and γ-CyD.

chemical shifts of C₆₀(γ-CyD)₂ and γ-CyD (Table 1). The line widths for the lyophilized γ-CyD were broader than for the lyophilized C₆₀(γ-CyD)₂ (Fig. 3a, b). This reveals that the conformation of the

former is more disordered than the latter. The effect of C₆₀ molecule bicapped by the two γ-CyDs may account for the more ordered conformation of the γ-CyD of the complex. Splitting in a number of

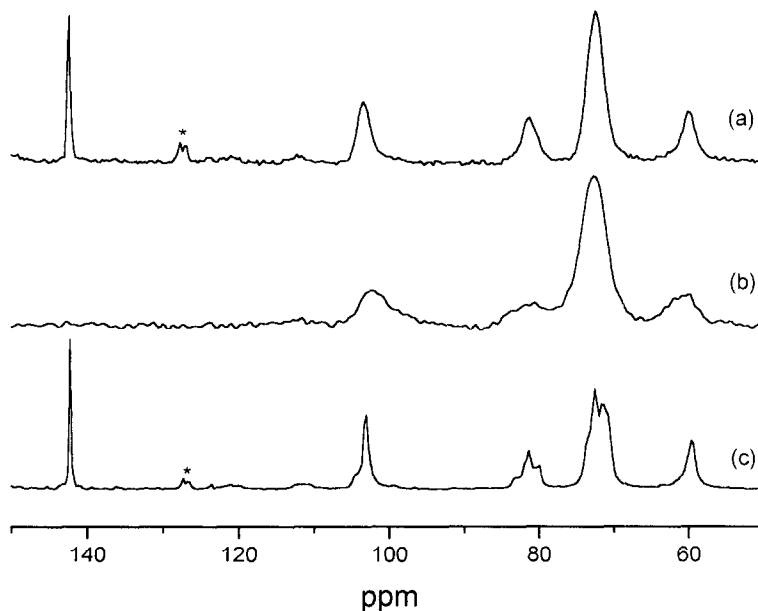


Fig. 3. ¹³C CP/MAS NMR spectra of (a) the lyophilized C₆₀(γ-CyD)₂, (b) the lyophilized γ-CyD, (c) the hydrated C₆₀(γ-CyD)₂/H₂O at 7.05 T field and MAS rate of 3 kHz. Asterisk marks a resonance from the residual toluene.

Table 1
 ^{13}C CP/MAS NMR chemical shifts of the lyophilized $\text{C}_{60}(\gamma\text{-CyD})_2$ and $\gamma\text{-CyD}$ taken at a 7.05-T field and MAS rate 3 kHz

Carbon	Chemical shift (ppm)			Difference
	C_{60}	$\gamma\text{-CyD}$	$\text{C}_{60}(\gamma\text{-CyD})_2$	
C_{60}	143.0		142.6	-0.4
C-1		101.8	103.5	+1.7
C-2,3,5		72.3	72.0	-0.3
C-4		80.2	81.1	+0.9
C-6		59.6	59.9	+0.3

peaks was observed for the hydrated sample (Fig. 3c) which is likely to be associated with the conformational variations of $\gamma\text{-CyD}$. This is similar to the case of amylose, where it is due to alternation in the type of the intra- and intermolecular hydrogen bonding during the hydration process [27].

In general, the full line width at half maximum (fwhm) for C_{60} signal was reduced after the hydration process (Fig. 3a, c). For polycrystalline C_{60} , lyophilized $\text{C}_{60}(\gamma\text{-CyD})_2$ and hydrated $\text{C}_{60}(\gamma\text{-CyD})_2/\text{H}_2\text{O}$, the fwhm's measured at 7.05 T are 3.7, 31.8 and 24.1 Hz, respectively. Two facts are worth noting here. First, the C_{60} signal in $\text{C}_{60}(\gamma\text{-CyD})_2$ was essentially broader (31.8 Hz) compared to that for polycrystalline C_{60} (3.7 Hz). This could be caused by the ^{13}C - ^1H interaction [13,20], and/or by the slowing down of the reorientation of the guest fullerene molecule. Second, the fwhm of the C_{60} line in the hydrated sample was typically narrower than in lyophilized ones: 24.1 Hz vs. 31.8 Hz. This fact might indicate faster C_{60} motion and therefore a weaker dipole-dipole interaction for the hydrated sample. Because the secondary hydroxyl groups form the intramolecular hydrogen bonding with the adjacent glucose units, the variation of the fwhm shows that water near the complex may modify some features of the system through interacting with the primary hydroxyl groups of $\gamma\text{-CyD}$.

4.3. ^{13}C CP/MAS nuclear magnetic resonance: relaxation and the role of water

In order to elucidate the influence of water in the solid complex, NMR relaxation time constants in the lyophilized and hydrated samples were examined in CP/MAS experiments with varying contact time, τ .

Fig. 4 presents typical curves for $M(\tau)$ versus τ for the C_{60} resonance in lyophilized $\text{C}_{60}(\gamma\text{-CyD})_2$ and hydrated $\text{C}_{60}(\gamma\text{-CyD})_2$. Analogous curves for the carbon resonances of $\gamma\text{-CyD}$ in the same samples are presented in Fig. 5. The corresponding relaxation data are presented in Table 2 and will be discussed in Sections 4.3.1 and 4.3.2.

4.3.1. The cross polarization time of the complex

Since, as discussed in the Section 2.1, the CP process occurs through the ^{13}C - ^1H dipolar interaction, the magnitudes of T_{CH} for the carbons of the same sample should be in the order of CH_2 (C-6 of $\gamma\text{-CyD}$) < CH (C-1 ~ C-5 of $\gamma\text{-CyD}$) < C (C_{60}). From Table 2, it can be seen that the T_{CH} values for the carbons of $\gamma\text{-CyD}$ were indeed about two orders shorter than that for the carbons of C_{60} . C_{60} has a much larger proton to carbon distance than $\gamma\text{-CyD}$, and the molecular motion of the bicapped C_{60} is much faster than that for $\gamma\text{-CyD}$. These two factors may reduce the CP efficiency considerably.

Although the C-6 has two direct bonding hydrogens, for the same sample, the T_{CH} values of the $\gamma\text{-CyD}$ carbons were almost in the same order. This is due to the internal motion of the primary hydroxyl groups which reduces the effectiveness of the dipolar interaction and therefore the CP rate. Thus, the T_{CH} value for C-6 was found to be close to those of all the other carbons of $\gamma\text{-CyD}$ in the complex.

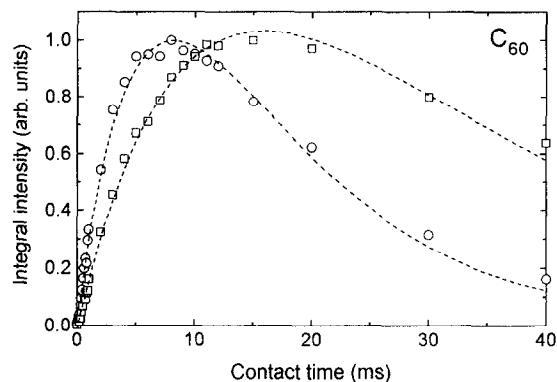


Fig. 4. Normalized integral intensity of the ^{13}C CP/MAS NMR signal vs. contact time for C_{60} in the lyophilized $\text{C}_{60}(\gamma\text{-CyD})_2$ (circle) and in the hydrated $\text{C}_{60}(\gamma\text{-CyD})_2/\text{H}_2\text{O}$ (square) at 7.05 T, MAS rate of 3 kHz, 4.67 mT B_1^{C} field and 1.17 mT B_1^{H} field. Dashed line is a fitting result using Eqs. (1) and (2).

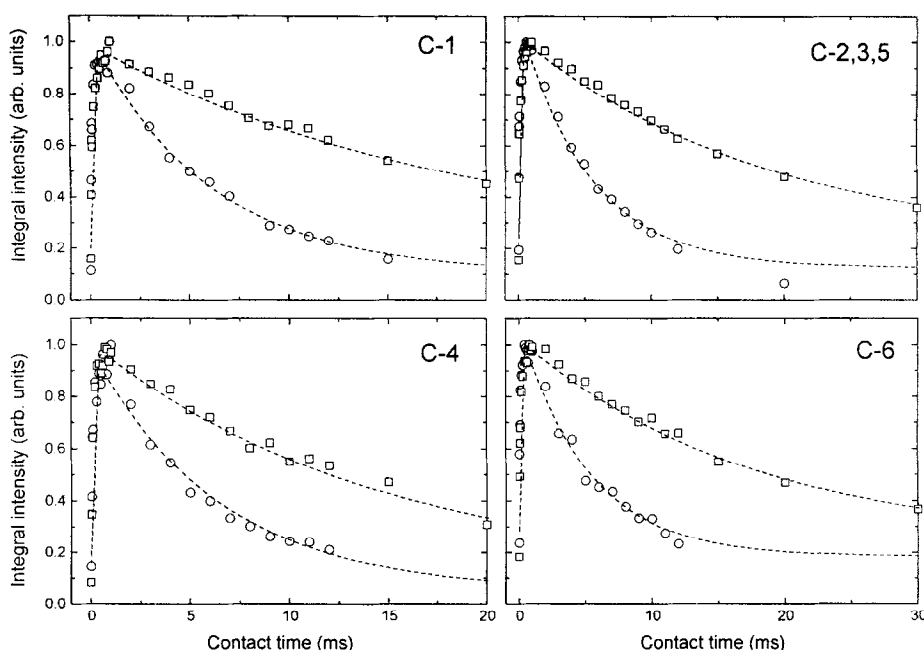


Fig. 5. Normalized integral intensity of ^{13}C CP/MAS NMR signals vs. contact time for γ -CyD carbons in the lyophilized $\text{C}_{60}(\gamma\text{-CyD})_2$ (circle) and in the hydrated $\text{C}_{60}(\gamma\text{-CyD})_2/\text{H}_2\text{O}$ (square) at 7.05 T, MAS rate of 3 kHz, 4.67 mT B_1^{C} field and 1.17 mT B_1^{H} field. Corresponding carbons are indicated in the plots. Dashed line is a fitting result using Eqs. (1) and (2).

If we compare the T_{CH} values of the lyophilized and hydrated samples, the T_{CH} values were longer for the hydrated complex than for the lyophilized one. This may indicate that the flexibility of the complex increases after the hydration process, since the effective ^{13}C - ^1H distance may not vary signifi-

cantly for γ -CyD in the hydrated sample. The effect can also be clearly seen in Fig. 4.

4.3.2. $T_{1\rho}^{\text{H}}$ and $T_{1\rho}^{\text{C}}$ of the complex

For isotopically abundant nonisolated nuclei in solids, the relaxation times of different chemical types are often averaged by the spin diffusion [22,28]. Therefore, no big difference among the values of $T_{1\rho}^{\text{H}}$ was found for any of the signals for each sample due to this effect for the ^1H spins in γ -CyD (Table 2). Contrarily, because of the 1% natural abundance of ^{13}C , the $T_{1\rho}^{\text{C}}$ does not show the same effect as the $T_{1\rho}^{\text{H}}$. The magnitude of the $T_{1\rho}^{\text{C}}$ on different carbons may reflect the differing mobility of the different functional groups in γ -CyD.

After the hydration process, significant elongations of $T_{1\rho}^{\text{H}}$ and $T_{1\rho}^{\text{C}}$ were observed (Table 2). We attribute these elongations to the rise of γ -CyD flexibility due to the increased free volume of the macro-ring segments in the presence of the water. A similar effect has been widely studied in polymers when plasticizers are applied to control polymer flexibility [29,30].

Table 2

Room temperature relaxation times evaluated from ^{13}C CP/MAS NMR experiments performed at a 7.05-T field for the lyophilized $\text{C}_{60}(\gamma\text{-CyD})_2$ and for the hydrated $\text{C}_{60}(\gamma\text{-CyD})_2/\text{H}_2\text{O}$. Accuracy of determination of T_{CH} , $T_{1\rho}^{\text{H}}$ and $T_{1\rho}^{\text{C}}$ was 10%. The spin locking frequency, ω_{H} , for measuring $T_{1\rho}^{\text{H}}$ and $T_{1\rho}^{\text{C}}$ was 50 kHz and the contact time was 2 ms. Labels of the γ -CyD carbons are shown in Fig. 1

Carbon	$\text{C}_{60}(\gamma\text{-CyD})_2$			$\text{C}_{60}(\gamma\text{-CyD})_2/\text{H}_2\text{O}$		
	T_{CH} (ms)	$T_{1\rho}^{\text{H}}$ (ms)	$T_{1\rho}^{\text{C}}$ (ms)	T_{CH} (ms)	$T_{1\rho}^{\text{H}}$ (ms)	$T_{1\rho}^{\text{C}}$ (ms)
C_{60}	10.2	5.5	—	12.7	20.5	—
C-1	0.07	5.1	34.9	0.15	20.1	122.0
C-2,3,5	0.10	5.7	18.2	0.13	19.3	53.8
C-4	0.08	5.4	39.3	0.11	18.6	83.1
C-6	0.08	5.1	2.5	0.13	17.3	12.0

4.3.3. T_1^C of the complex

In order to understand the motion characteristics of the complex, the T_1^C data and the effective reorientational correlation time, τ_c , involved are listed in Table 3. In general, no significant change in T_1^C was observed for C-1, C-2,3,5 and C-4 with the hydration process. Since C-1 and C-4 are the carbons which form the glucosidic bonds between two adjacent glucose units, the reorientational motion should be the same. Thus, they could represent the overall motion of the complex. From Table 3, the τ_c calculated for C-1 and C-4 were almost the same for both the lyophilized and hydrated samples. Because of the size of the complex, it is believed that this motion is on the slow motional side of the T_1^C minimum, the τ_c being in the order of 10^{-7} s. Otherwise, if one supposes that it is on the fast motional side of the T_1^C minimum, then the experimental data leads τ_c to be in the order of 10^{-12} s, which is too fast to be true for the reorientational process of $C_{60}(\gamma\text{-CyD})_2$ in the solid state. Thus one may conclude that the excess water did not cause much change in the dynamics of the entire $C_{60}(\gamma\text{-CyD})_2$ complex.

For the C-6, the T_1^C was measured in both samples and found to be much shorter than those for C-1 and C-4 (Table 3). One of the reasons for this was that there are two protons bonded to the C-6 methylene carbon. The T_1^C of C-6 was reduced from 2.7 s to 1.2 s (Table 3). It has been shown that the crystal structure of $\gamma\text{-CyD}$ accommodates 19 molecules of H_2O per $\gamma\text{-CyD}$ molecule and 12 of them are in the torus of the primary C(6)–OH hydroxyl groups [31].

Table 3

The room temperature T_1^C and the τ_c evaluated from ^{13}C CP/MAS NMR experiments performed at a 7.05-T field for the lyophilized $C_{60}(\gamma\text{-CyD})_2$ and for the hydrated $C_{60}(\gamma\text{-CyD})_2/H_2O$. Accuracy of determination of T_1^C is 12%. Labels of the $\gamma\text{-CyD}$ carbons are shown in Fig. 1

Carbon	$C_{60}(\gamma\text{-CyD})_2$		$C_{60}(\gamma\text{-CyD})_2/H_2O$	
	T_1^C (s)	τ_c (s)	T_1^C (s)	τ_c (s)
C_{60}	10.2	1.1×10^{-10a}	16.3	7.5×10^{-11a}
C-1	17.8	6.1×10^{-7}	21.6	7.3×10^{-7}
C-2,3,5	14.2	—	15.4	—
C-4	19.8	6.7×10^{-7}	19.3	6.5×10^{-7}
C-6	2.7	—	1.2	—

^a The value was evaluated from the field-dependent T_1^C which is discussed in field-dependent T_1^C measurements in Section 4.4.

Therefore, the H_2O molecules introduced into the complex interact mainly with the primary hydroxyl groups and create a hydrogen bonding network with them. Therefore the water molecules in the hydrated sample hindered internal rotation (which was presumably in the motional narrowing region) [32] of the C-6, and further reduction of T_1^C was observed.

For C_{60} in the motional narrowing region of the T_1^C minimum after the hydration process, the T_1^C of C_{60} is increased from 10.2 s to 16.3 s. It is suggested that this increase is caused by the rise of the reorientational rate of C_{60} . First, in accordance with the molecular mechanics calculation for $\gamma\text{-CyD}$ itself [33,34], the secondary C(2)–OH and C(3)–OH hydroxyl groups attached to the wider rim of $\gamma\text{-CyD}$ are oriented inward, while the primary C(6)–OH hydroxyl groups attached to the narrower rim are directed outward. This has been revealed to be the most stable conformation and has been predicted to be the only one [35]. For $C_{60}(\gamma\text{-CyD})_2$, the conformation of $\gamma\text{-CyD}$ is opposite to that for empty $\gamma\text{-CyD}$. To include C_{60} and avoid contact with the hydrophobic surface of C_{60} , the secondary hydroxyl groups are orientated outward while the primary hydroxyl groups are directed inward [20]. Second, water molecules have the tendency to interact with the primary hydroxyl groups, which directs the C(6)–OH bonds further inward. As a result, hydration increases the opening of the secondary hydroxyl rim and raise the flexibility of the macro-ring of $\gamma\text{-CyD}$. Consequently, the reorientational rate of C_{60} increased. The same effect was also observed by circular dichroism which showed an increase in band intensity with increasing dehydration of the initial $C_{60}(\gamma\text{-CyD})_2$ powders dissolved in water [14].

4.4. Dependence of C_{60} carbon T_1^C upon the NMR field strength

Fig. 6 presents plots of the spin-lattice relaxation rate $1/T_1^C$ vs. B_0^2 taken at 250 K and 300 K for the lyophilized $C_{60}(\gamma\text{-CyD})_2$. For both temperatures, because of the linear dependency of relaxation rate on B_0^2 , the reorientational rate of the C_{60} falls in the $\omega_c \tau_c \ll 1$ region and the data can be analyzed by using Eq. (5) on the assumption that the CSA term for this case is given by Eq. (6). The slopes gave

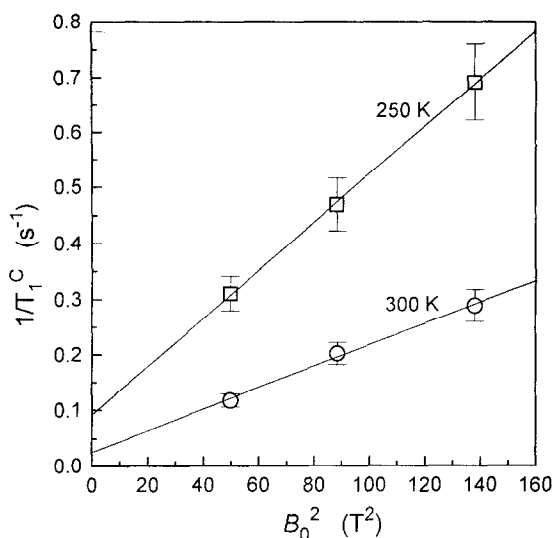


Fig. 6. A reciprocal ^{13}C spin-lattice relaxation time vs. the square of the magnetic-field strength measured at 250 K and 300 K for C_{60} in the lyophilized $\text{C}_{60}(\gamma\text{-CyD})_2$. Experimental points are fitted by a linear regression. Error bar represents 10% error.

products of $\tau_c(\sigma_{\parallel} - \sigma_{\perp})^2$ as 7.2×10^{-18} s and 3.2×10^{-18} s at 250 K and 300 K, respectively. We used the principal components of the CSA tensor of the pristine polycrystalline C_{60} [36], 30 ppm for σ_{\parallel} and 200 ppm for σ_{\perp} , to elucidate the τ_c for C_{60} in the complex. The effective reorientational correlation time was elucidated with these tensor components and found to be 2.5×10^{-10} s and 1.1×10^{-10} s at 250 K and 300 K, respectively. This gave two conclusions. First, because the τ_c of C_{60} at room temperature has been revealed to be within the time scale of $10^{-11} \sim 10^{-12}$ s [37,38,33,34], the elongation of τ_c by about one to two orders for C_{60} bicapped by $\gamma\text{-CyDs}$ indicates that, when compared to pristine C_{60} , its reorientational motion essentially slows down. Second, in accordance with the intercept obtained from Fig. 6, the $1/T_1^{\text{NCSA}}$ term was one order smaller than the $1/T_1^{\text{CSA}}$, hence the main relaxation mechanism is due to the CSA interaction.

The present data showed that the main interaction between the guest C_{60} and the host $\gamma\text{-CyD}$ is the van der Waals' interaction, which, when compared with pristine C_{60} , should not alter the magnitude of CSA components significantly. However, even if that weak interaction is taken into account, it should mostly affect σ_{\parallel} rather than σ_{\perp} . Therefore, a minor chemi-

cal shift of 0.4 ppm observed for C_{60} in the complex as compared to that of pristine C_{60} gives an estimate for the variation of σ_{\parallel} to be only 1.2 ppm. Such a small value does not change $(\sigma_{\parallel} - \sigma_{\perp})$ significantly and enables the use of the principal components of pristine C_{60} in our calculation.

4.5. Dependence of C_{60} carbon T_1^{C} upon the temperature

Fig. 7 shows a plot of temperature vs. T_1^{C} for C_{60} carbons taken in the range 180–320 K in an 11.75-T field for the lyophilized and hydrated samples. Above 250 K, T_1^{C} was systematically shorter for the lyophilized sample than for the hydrated one. The shorter T_1^{C} reflected the longer reorientational correlation time which is consistent with the previous result from fwhm measurements. Therefore, a difference in T_1^{C} showed that the reorientational motion of C_{60} in the lyophilized complex was somewhat slower than that in the hydrated counterpart.

For both samples, in the given temperature range higher than 250 K, the τ_c is fairly approximated by the activation law given by Eq. (7) for the reorienta-

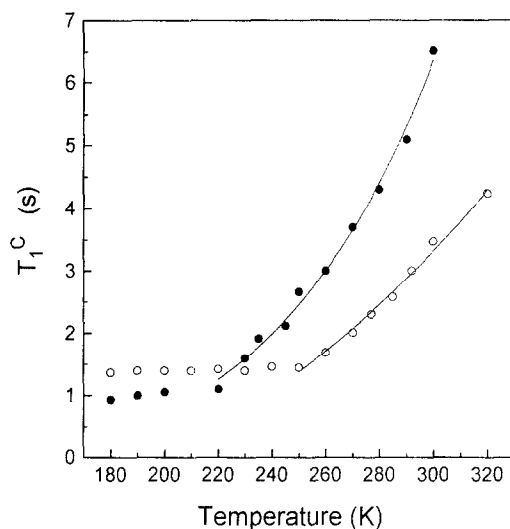


Fig. 7. The ^{13}C nuclear spin-lattice relaxation time T_1^{C} vs. the temperature taken at 11.75 T for the carbons of C_{60} . Open circles are for the lyophilized $\text{C}_{60}(\gamma\text{-CyD})_2$, solid circles are for the hydrated $\text{C}_{60}(\gamma\text{-CyD})_2/\text{H}_2\text{O}$. The solid line in the high-temperature region is a fitting result using the activation law for the reorientational motion.

tional motion. The activation energy was elucidated to be 10.7 ± 0.4 and 10.9 ± 0.4 kJ/mol for the lyophilized and the hydrated samples, respectively. For the former sample, T_1^C was also measured in a 9.04 T field in the same temperature range (data are not shown). The activation energy was 10.0 ± 0.4 kJ/mol. All values of E_a were in good agreement with each other. It is noted that current values of E_a are larger than the 4.04 kJ/mol (42 MeV) in pristine C_{60} reported by Tycko et al. [37]. The higher activation energy in our case supports the assumption that hindered motion of C_{60} in the complex compared to the motion in pristine C_{60} .

When comparing the reorientational motion of both samples, it seems that to reach the same reorientational rate, much lower temperatures were required for C_{60} in the hydrated complex than for the lyophilized one. Indeed, the temperature independent T_1^C process occurred below 220 K for the hydrated sample and below 250 K for its counterpart (Fig. 7). These turning points represented neither a usual minimum for the temperature-dependent spin-lattice relaxation time nor the minimum in the orientation ordering associated with the phase transition in pristine C_{60} [37]. For the lyophilized sample, we estimate the magnitude of $\omega\tau_c$ at 250 K to be only 0.03. This gave the condition $\omega^2\tau_c^2 \ll 1$ and a T_1^C minimum at this temperature was unexpected. Furthermore the respective temperature-dependent T_1^C for the complex and the solid C_{60} are absolutely different. For pure C_{60} , the T_1^C value decreases linearly down to 260 K and drops down abruptly due to the phase transition. With further decrease in temperature, it reaches the minimum center at 240 K and monotonously grows below 240 K. For $C_{60}(\gamma\text{-CyD})_2$, the T_1^C value decreases monotonously between 320 K and 220 K for the hydrated sample or 250 K for the lyophilized sample. Below the temperature specified by the turning point, T_1^C becomes almost temperature-independent. Moreover, if the turning point observed for $C_{60}(\gamma\text{-CyD})_2$ complex should represent the phase transition of solid C_{60} , it will occur at the same temperature for both the lyophilized and the hydrated samples. Actually this was not the case observed in the experiment. Position of the turning point systematically shifted with the decrease or increase of water content. For the hydrated sample, it was observed at about 220 K, which is much lower

than the temperature of the phase transition in solid C_{60} . Probably, at low temperature the change in the conformation of $\gamma\text{-CyDs}$ created a new environment for C_{60} , which led to a situation distinct from a regular shortening of the relaxation time with lowering temperature. This factor compensated the thermal activation of the reorientational motion of C_{60} and gave rise to the flat region in the temperature dependency graph (Fig. 7).

It is worth noting that once it fell to the flat region, T_1^C was almost the same for both the lyophilized and the hydrated samples (Fig. 7). The similarity in the relaxation behavior for both samples meant that the proposed low-temperature conformation of $\gamma\text{-CyDs}$ was no longer significantly affected by the excess water associated with the complex. This fact agrees with the results of the molecular mechanics calculation done by Kim and Jeon [20], who showed that the participation of water molecules did not alter the total energies of the system minimized for the $C_{60}(\gamma\text{-CyD})_2$ system. It should be noted that the most stable structure of the complex was only observable in low-temperature experiments. Our results may arise from the same situation. We conclude that in the low-temperature region, the reorientational rates for C_{60} in the lyophilized and hydrated samples were almost the same.

5. Conclusions

Solid $C_{60}(\gamma\text{-CyD})_2$ complex has been systematically studied in this work by NMR spectroscopic techniques. The data obtained conclusively demonstrates that the van der Waals' interaction between the host C_{60} and the guest $\gamma\text{-CyD}$ is the main interaction. From the field-dependent T_1^C measurements, the effective reorientational correlation time for C_{60} capped between two $\gamma\text{-CyDs}$ was found to be about 10^{-10} s at room temperature which is one to two orders longer than that published for pristine C_{60} . For the entire $C_{60}(\gamma\text{-CyD})_2$ complex itself, the reorientational correlation time was evaluated to be in the order of 10^{-7} s.

Water molecules introduced into the system brought about essential elongation of the NMR relaxation times for both the carbons of C_{60} and $\gamma\text{-CyD}$. Hence, the reorientational motion of C_{60} in

the deliberately hydrated samples was much faster than in the lyophilized ones and the flexibility of γ -CyD is raised by the water due to the increase of free volume in the γ -CyD macro-ring. Experiments on the temperature-dependent ^{13}C relaxation showed that the influence of water associated with γ -CyD on the dynamics of C_{60} was less significant below 250 K. This may suggest that the conformation of the complex occurring at low temperature is close to the most stable conformation.

Acknowledgements

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