

# Influence of the Cage Size on the Dynamic Behavior of Fullerenes: A Study of $^{13}\text{C}$ NMR Spin–Lattice Relaxation

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**ABSTRACT** A detailed study on the relaxation mechanisms of higher cage fullerene sizes is done as a prerequisite for studies of the influence of the endohedral structures on fullerene cage carbon relaxation. Recent studies of the dynamic behavior of  $\text{C}_{60}$  and  $\text{C}_{70}$  in aromatic solvents and  $\text{CS}_2$  solution show the influence of the shape and the symmetry of the cage to be highly important as well as the influence of the solvent to be negligible. As higher fullerene cages have more than one stable isomer, the isolation of isomeric pure structures is of high importance for a detailed study of the dynamic behavior of such fullerenes. Here we investigated the three higher fullerene cage isomers  $D_2\text{-C}_{76}$ ,  $C_{2v}(3)\text{-C}_{78}$ , and  $D_2\text{-C}_{80}$  with respect to the relaxation rate of the carbons measured in their temperature dependence. Thus, we study the influence on the relaxation of the carbons and the dynamic behavior of these fullerenes in solution. Besides the diffusion dependence on the shape of the carbon cage, the relaxation behavior at lower temperatures is found to be dependent on the difference in chemical shift anisotropy within the carbon cage. This difference is originated from the changes of symmetry and results in polarization of electron density. Furthermore, the mobility of the carbons is influenced by their pyramidalization.

**KEYWORDS:** fullerenes ·  $^{13}\text{C}$  NMR spectroscopy · carbon relaxation · symmetry ·  $\text{C}_{76}$  ·  $\text{C}_{78}$  ·  $\text{C}_{80}$

Nuclear magnetic resonance relaxation measurements as a powerful tool to investigate molecular motion in solution were used in different NMR studies.<sup>1–5</sup> It has been shown that  $^{13}\text{C}$  relaxation in fullerenes is very slow due to the absence of protons at the carbon atoms of the fullerene cage. Chemical shift anisotropy ( $R_1^{\text{CSA}}$ ) and spin rotation ( $R_1^{\text{SR}}$ ) solely participate in the  $^{13}\text{C}$  relaxation of fullerenes. A separation of these two contributions is realized by the field strength dependence of the  $R_1^{\text{CSA}}$  mechanism and the  $R_1^{\text{SR}}$  mechanism *via* its temperature dependence.<sup>6,7</sup> If a measurement of the relaxation behavior for different field strengths is impossible, the separation of the relaxation mechanism contributions *via* the Hubbard relation gives reliable results.<sup>8</sup> Therefore, the temperature region with small step diffusion has to be localized in the temperature dependence of the relaxation rate. Here, the chemical shift anisotropy

part of the relaxation is dominant, and an easy separation of the two relaxation mechanisms is possible *via* the Hubbard relation.

The thus-separated contributions to the experimental relaxation rate are used to study the molecular motion in solution. The reorientational rotation is studied *via* the chemical shift anisotropy contribution in the temperature range of small step diffusion. The analysis of the spin rotation contribution leads to conclusions on the diffusion behavior of the molecule.<sup>4</sup>

To understand the role of the cluster in endohedral nitride cluster fullerenes,<sup>9</sup> several larger fullerene cages were to be studied. Among the endohedral cluster fullerenes, the highest stability is found for the  $I_h\text{-C}_{80}$  and  $D_{5h}\text{-C}_{80}$  cage isomers, but other cage sizes of cluster fullerenes are stabilized, as well.<sup>10,11</sup> In the arc burning process for fullerene formation,  $\text{C}_{60}$  and  $\text{C}_{70}$  are the most stable cages and are available in larger amounts. Furthermore, these fullerenes exist in only one stable cage isomer. Relaxation measurements of these molecules in  $\text{CS}_2$  solution lead to the conclusion that the shape of the fullerene cage is essential for the relaxation and, therefore, for the rotation as well as diffusion of these fullerene molecules. The two different rotation axes in  $\text{C}_{70}$  were shown to have different rotation energies. The role of the solvent is due to different solvation shells and to the hindrance of motion in solution.<sup>5</sup>

The aim of this work is a detailed study of the relaxation mechanisms of fullerenes with higher cage sizes as a prerequisite for studies on the role of the endohedral nitride clusters in fullerene cage relaxation. As the fullerene cages consist of pentagons and hexagons, the carbon atoms can be divided

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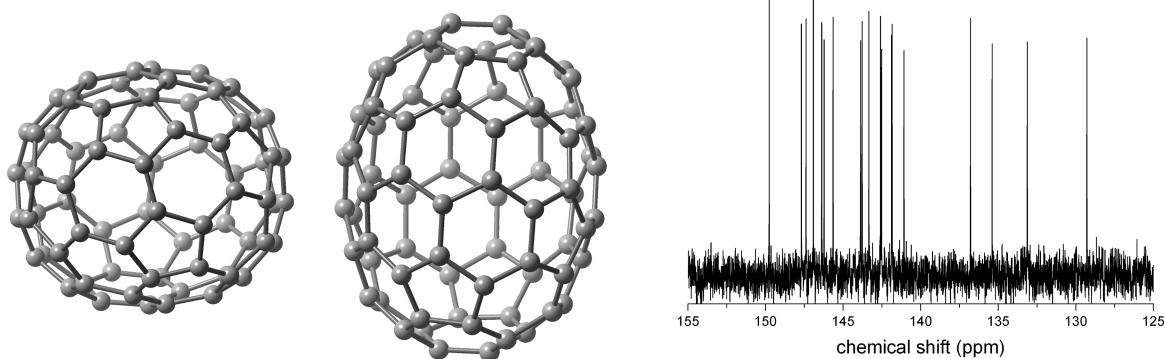
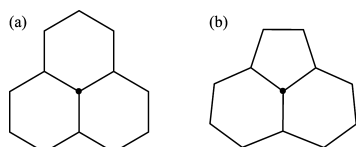


Figure 1.  $D_2$ - $C_{76}$  molecule symmetry and its  $^{13}\text{C}$  NMR spectrum.



Scheme 1. Pyrene carbons (a) and corannulene carbons (b) in fullerenes.

into two different types. Pyrene-like carbons are situated at linked hexagons, whereas corannulene-like carbons are those in the center of two hexagons and one pentagon (see Scheme 1). To extend the family of fullerenes, the possible cage sizes  $C_{72}$ ,  $C_{74}$ ,  $C_{76}$ ,  $C_{78}$ , and  $C_{80}$  have to be considered with regard to additional parameters in  $^{13}\text{C}$  relaxation. While  $C_{72}$  and  $C_{74}$  are not stable to be isolated as an empty fullerene structure,<sup>12</sup> other cages offer at least one stable isomer which can be isolated in an isomeric pure form in reasonable amounts. One isomer of every of these fullerenes was isolated by a multistep HPLC separation of a fullerene soot produced by arc synthesis.<sup>13</sup> These isomers were used to study the relaxation rate of the different carbons in their temperature dependence to extend our knowledge on the influence of the cage size, symmetry, and shape on the dynamic behavior of these fullerenes in solution.

## RESULTS AND DISCUSSION

Here we study  $C_{76}$  as the  $D_2$  isomer and  $C_{78}$  as the  $C_{2v}(3)$  isomer, while the main  $C_{80}$  cage isomer has a  $D_2$  symmetry. To start with the lowest cage size in the row, the  $D_2$  isomer of  $C_{76}$  is investigated. The  $^{13}\text{C}$  NMR spectrum (Figure 1) has 19 different carbon signals, as expected for the symmetry of the molecule. The shape of the molecule (Figure 1) is rather similar to the  $D_{5h}$ - $C_{70}$  cage. The relaxation rates were measured in dependence on the chemical shift of the 19 independent carbon signals for two different temperatures (Figure 2). At 268 K, a correlation of the relaxation rate and the chemical shift is observed. At higher chemical shifts, the relaxation rate increases. At 298 K, the relaxation rate values are more scattered and the correlation to the chemical shift is lower. The temperature depen-

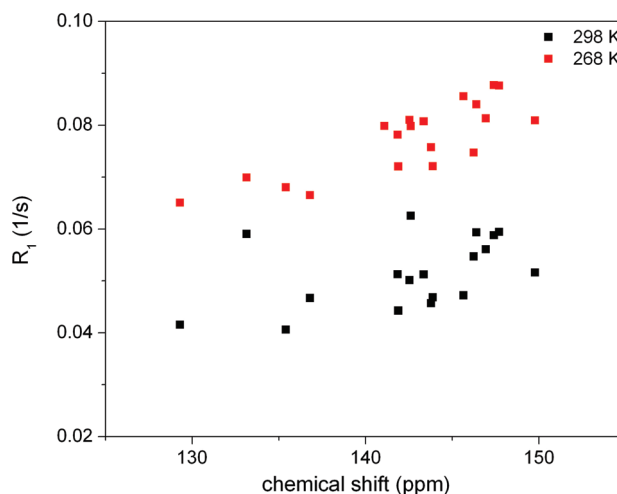


Figure 2. Correlation of the relaxation rate  $R_1$  and the chemical shift of the 19 different carbon signals of  $D_2$ - $C_{76}$  at 268 and 298 K.

dence of the relaxation rates in a range from 268 to 298 K (Figure 3) gives a similar behavior for all 19 different cage carbons. Like for  $D_{5h}$ - $C_{70}$ , the relaxation rate decreases with increasing temperature in the whole temperature range. Generally, the temperature dependence of the relaxation rate shows the very slow diffusion contribution as compared to the rotation of the molecule in the time scale of NMR. The values of the relaxation rate for the whole molecule are larger than

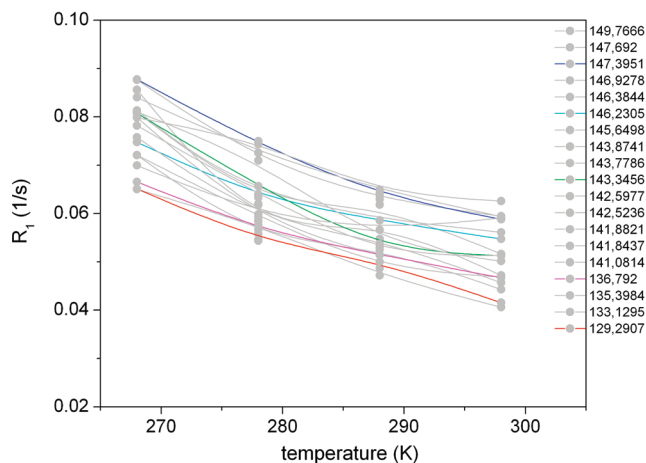


Figure 3. Temperature dependence of the relaxation rate  $R_1$  of  $D_2$ - $C_{76}$ .

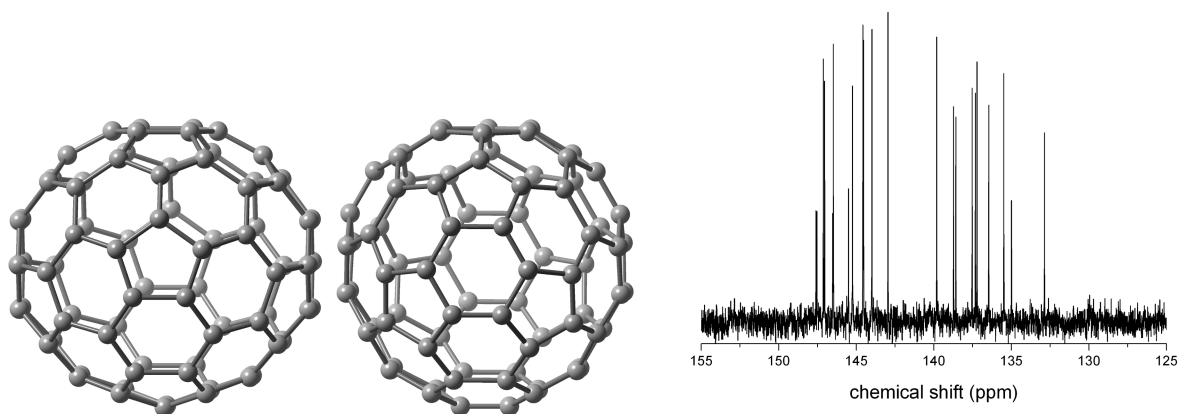


Figure 4.  $C_{2v}(3)$ - $C_{78}$  molecule symmetry and its  $^{13}\text{C}$  NMR spectrum.

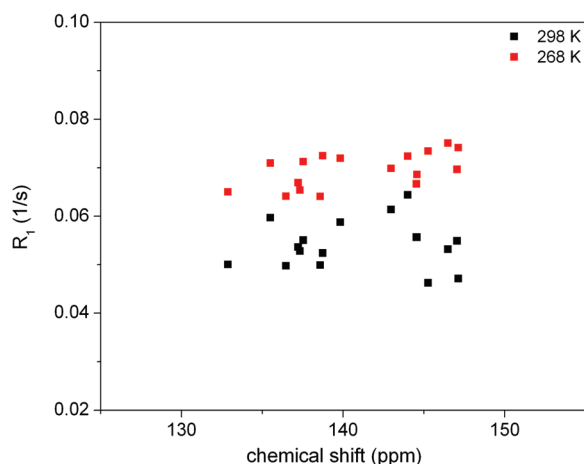


Figure 5. Correlation between relaxation rate  $R_1$  and chemical shift of the 22 different carbon signals of  $C_{2v}(3)$ - $C_{78}$  at 268 and 298 K.

in  $C_{70}$ , which can be attributed to the lower symmetry of the  $C_{76}$  molecule. The pyrene carbons of  $D_2$ - $C_{76}$  have a shift to higher field in the same chemical shift range like the pyrene carbon C-5 of  $C_{70}$ , which might be the consequence of the low pyramidity of the carbons.<sup>14,15</sup> These carbons show a similar relaxation behavior. The corannulene carbons of the  $C_{76}$  molecule

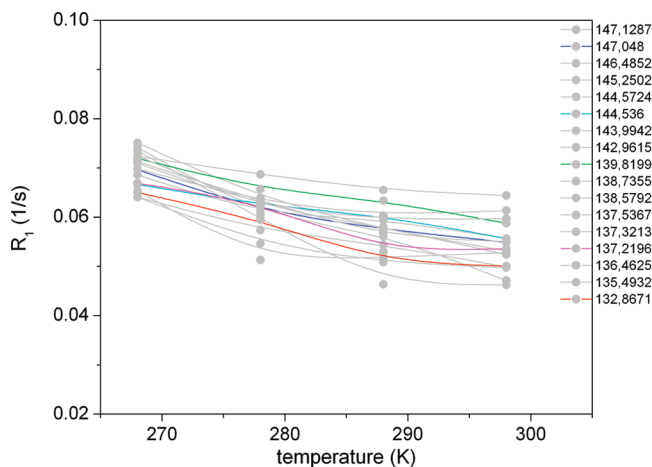


Figure 6. Temperature dependence of the relaxation rate  $R_1$  of  $C_{2v}(3)$ - $C_{78}$ .

can be found at lower fields as a consequence of a higher pyramidity.<sup>15</sup> In comparison to the pyrene carbons, the corannulene carbons show higher relaxation rates like the corannulene carbons C-1 to C-4 in  $C_{70}$ . The similar shape of the molecules leads to a similar distribution of relaxation rates. The lower symmetry of the  $C_{76}$  molecule is the reason for a higher anisotropy in electron density distribution and higher relaxation rates in this molecule.

The isolated  $C_{2v}(3)$  isomer of  $C_{78}$  has a more spherical shape (Figure 4) than the  $D_2$  isomer of  $C_{76}$  and is more comparable to  $I_h$ - $C_{60}$ . The  $^{13}\text{C}$  NMR spectrum (Figure 4) of  $C_{2v}(3)$ - $C_{78}$  consists of 22 lines with 17 lines of double intensity and 5 lines of half intensity as expected from the symmetry of the molecule. The relaxation rates dependent on the chemical shift of the 22 different carbon signals were measured for two different temperatures (Figure 5). With higher chemical shifts of the different carbons, the relaxation rates increase although the slope is more flat as compared to  $D_2$ - $C_{76}$ . The chemical shift range and relaxation rates are smaller compared to  $D_2$ - $C_{76}$ . The pyrene and corannulene carbons do not differ in chemical shift or relaxation rate. The temperature dependence of the relaxation rates (Figure 6) shows the same behavior as the other fullerene cages: the relaxation rates decrease with increasing temperature. Also in this case, the rotation is fast compared to the diffusion of the molecule, but the relaxation rates of the  $C_{2v}(3)$  isomer of  $C_{78}$  at 268 K are lower than that for  $D_2$ - $C_{76}$ , while at 298 K, they are higher than for the  $D_2$  isomer of  $C_{76}$  but smaller than for  $C_{60}$ . Therefore, a stronger influence of the diffusion on the overall relaxation rate but a smaller influence of electron density shifts can be concluded for this molecule with a higher curvature.

Although the isolated amount of the  $D_2$  isomer of  $C_{80}$  was smaller compared to the other cages, the  $^{13}\text{C}$  NMR spectrum shows a sufficient signal-to-noise ratio (Figure 7). The 19 lines among which one is of higher intensity point to the 20 independent carbons in the cage where 2 lines overlap. The concentration in solution was too low for a detailed temperature-dependent

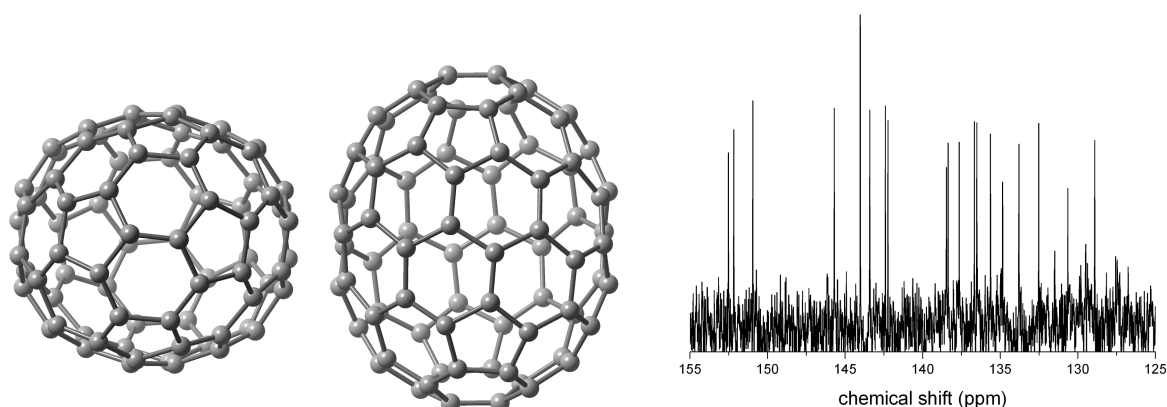


Figure 7.  $D_2$ - $C_{80}$  molecule symmetry and its  $^{13}\text{C}$  NMR spectrum.

analysis of the relaxation behavior. Only the relaxation rate at 298 K could be measured in a reasonable experimental time scale. The relaxation rate of the 19 carbon signals in relation to their chemical shift (Figure 8) gives no clear correlation between chemical shift and relaxation rate, although a trend similar to that in  $D_2$ - $C_{76}$  is observable. The relaxation rates are slightly increased as compared to  $D_2$ - $C_{76}$  at the same temperature. Here a small cage size effect on the relaxation behavior can be seen. In this larger fullerene cage, the electron density distribution of the molecule is more polar and, therefore, the anisotropy in the molecule is stronger.

In summary, the relaxation rate of fullerenes with larger cage sizes is higher than for smaller cage sizes of  $C_{60}$  and  $C_{70}$ . The shape of the molecule has an influence on the diffusion rate of the fullerene. The difference in rotation of the molecules is also determined by the shape for the two different rotation axes in  $C_{70}$ .<sup>5</sup>

The relaxation behavior at lower temperatures shows a difference in anisotropy of the chemical shift within the carbon cage. A polarization of the electron density in the molecule originates from the different symmetry and can result in a different shielding of the carbon nuclei by electrons. Therefore, the chemical shifts as well as the relaxation rates are influenced by a higher shielding effect of the electron density and are correlated with each other. While in molecules with larger curvature such as  $C_{2v(3)}$ - $C_{78}$  the relaxation rates are rather similar, larger deviations in relaxation rates are observed for the different kinds of carbons in egg-shaped molecules like  $D_{5d}$ - $C_{70}$  and  $D_2$ - $C_{76}$ . Investigating chemical shifts and relaxation rates in a positively charged fullerene should result in an increase in relaxation rate and chemical shift by a reduced electron density in the molecule, but the cations of these fullerenes are difficult to produce in solution because of their high oxidation potentials.

The relaxation rate of the carbons is also correlated to their pyramidity. As the relaxation rate is a matter of mobility of atoms in the molecular backbone, the higher pyramidal carbons show higher vibrating mobility. This effect might increase their relaxation rate. The

differences of the relaxation rates of carbons at the top of an egg-shaped molecule compared to that at the side can also result from the different rotation around the two rotation axes, which is not obtained for spherical molecules.<sup>5</sup>

Furthermore, the cage size effect for the same cage symmetry has a similar influence on the anisotropy in the molecule, and therefore, the relaxation is increased. Here, the comparison with larger cages such as  $C_{84}$  for different isomers should give additional insights into the relaxation behavior.

The analysis of the role of the cluster in the relaxation of endohedral nitride cluster fullerenes and other endohedral fullerenes can be based on these results. The most stable endohedral nitride cluster fullerenes are the family of  $C_{80}$  cage size, where mainly the  $I_h$  and in lower amount the  $D_{5h}$  isomer are formed. Unfortunately, these cages are among the most unstable  $C_{80}$  cage isomers within the family of empty fullerenes, and the isolation in larger amounts for a detailed  $^{13}\text{C}$  NMR study is not possible.<sup>12</sup> As to the analysis of endohedral nitride cluster fullerenes of the  $I_h$ - $C_{80}$  cage isomers, the higher symmetry as well as the spherical shape of the

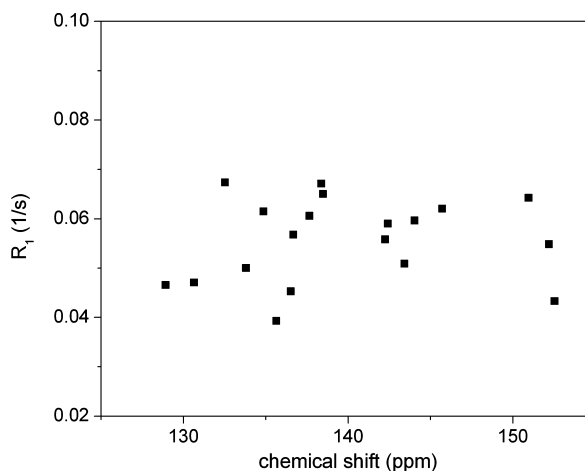


Figure 8. Relaxation rate  $R_1$  versus chemical shift of the 19 different carbon signals of  $D_2$ - $C_{80}$  at 298 K.

molecule leads to a similar electron density distribution and should result in a dynamic behavior of the  $I_h$ -C<sub>80</sub> carbon cage similar to  $I_h$ -C<sub>60</sub>.

## CONCLUSION

To extend the family of empty fullerenes, we investigated the three higher fullerenes  $D_2$ -C<sub>76</sub>, C<sub>2v</sub>(3)-C<sub>78</sub>, and  $D_2$ -C<sub>80</sub>. The isomeric pure fullerene structures were isolated by recycling HPLC from a fullerene soot produced by arc discharge synthesis. The influence of different parameters such as cage size, symmetry, and shape on the <sup>13</sup>C relaxation rate

in these fullerenes was studied. While the shape of the fullerene molecule has an influence on the diffusion rate, the difference in rotation of the molecules is negligible. The relaxation behavior at lower temperatures is dependent on the cage symmetry, causing a difference in anisotropy of the chemical shift at the carbon cage by polarization of the electron distribution. The cage size effect at the same symmetry is caused by a higher polarization of the electron density, resulting in an additional influence on the anisotropy of the molecule and an influence on the relaxation.

## METHODS

Fullerenes under study were obtained from a Krätschmer–Huffmann arc synthesis of graphite rods.<sup>10,11,14</sup> The soot from the arc discharge synthesis was washed with acetone and extracted by Soxhlet extraction with CS<sub>2</sub> for 20 h. The extract was dried and redissolved in toluene for HPLC separation. The fullerenes were isolated by multistage HPLC separation with toluene as solvent.<sup>13</sup> In a final step, the isolated fullerene was dried and washed with acetone and *n*-hexane to remove toluene and PAHs and redissolved in CS<sub>2</sub>.

NMR measurements were performed on a Bruker Avance II 500 (Bruker Biospin) at a magnetic field strength of 11.74 T. Relaxation times were obtained using the standard inversion recovery pulse sequence ( $D_1$ - $\pi$ - $D_2$ - $\pi/2$ ) with waltz-decoupling sequence for proton decoupling and relaxation durations ( $D_1$ ) of 5 times the expected  $T_1$  and with a variation of  $D_2$  from 1 to 50 s. Samples were prepared in a 5 mm tube under nitrogen atmosphere to avoid any oxygen influence on  $T_1$  measurements. As an external lock, acetone- $d_6$  and DMSO- $d_6$  in a coaxial tube were used. The spectra were calibrated using the signal of the lock solvent. Temperature control *via* a heating and cooling unit BC-U 05 (Bruker Biospin) leads to a temperature accuracy of 0.1 K.

The signal intensities in dependence on the  $D_2$  time are observed showing an exponential decay. From the exponential fit of intensities *versus*  $D_2$ , the relaxation rates  $R_1$  were extracted and relaxation times  $T_1$  calculated.

The obtained relaxation rates are given as the sum of the different contributions to the relaxation mechanism. In the case of fullerene molecules, only the chemical shift anisotropy and spin rotation contribute to the relaxation rate (eq 1):<sup>6</sup>

$$R_1 = 1/T_1 = R_1^{\text{CSA}} + R_1^{\text{SR}} \quad (1)$$

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