NMR lineshapes and scalar relaxation of the water-endofullerene $H_2{}^{17}O@C_{60}$

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Abstract: *The ^{17}O isotopomer of the water-endofullerene $H_2O@C_{60}$ displays a remarkable proton NMR spectrum, with six well resolved peaks. These peaks are due to the J-coupling between the water protons and the ^{17}O nucleus, which has spin-5/2. The resolution of these peaks is enabled by the suppression of water proton exchange by the fullerene cage. The six peaks display an unusual pattern of linewidths, which we model by a Liouville-space treatment of scalar relaxation due to quadrupolar relaxation of the ^{17}O nuclei. The data are consistent with rotational diffusion of the water molecules on the sub-picosecond timescale.*

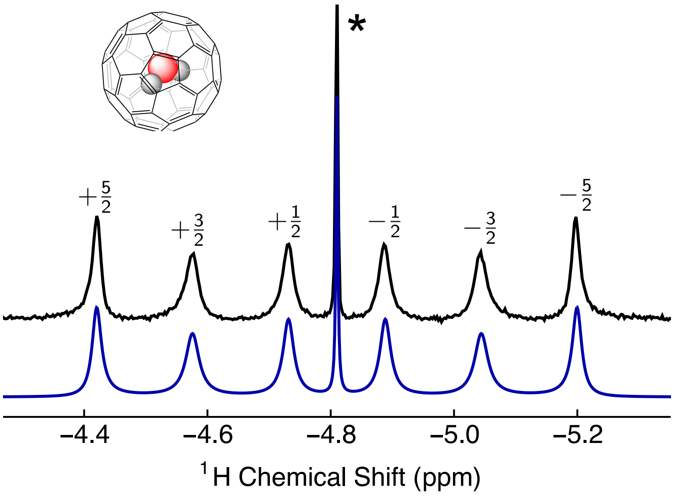

Figure 1: Relevant portion of the experimental proton spectrum for 36.2 mM $H_2{}^{17}O@C_{60}$ in degassed ODCB-d_4 solvent acquired at 11.7 T (^{1}H Larmor frequency = 500 MHz) and 25°C with 1024 transients. See the Supporting Information (SI) for the full ^{1}H spectrum. Black line: experimental spectrum; blue line: simulated spectrum. The simulation assumes extreme-narrowing ^{17}O relaxation, with the following parameters: J_{OH} = -77.9 Hz, $T_1(^{17}O)$ = $T_2(^{17}O)$ = 81 ms. The peak of the $H_2{}^{16}O@C_{60}$ impurity is denoted by an asterisk. The labels $M_S \in \{\pm 5/2, \pm 3/2, \pm 1/2\}$ refer to the magnetic quantum number of the ^{17}O nucleus assuming a negative ^1H-^{17}O J-coupling. Inset: schematic representation of $H_2{}^{17}O@C_{60}$. Red sphere denotes ^{17}O atom, grey spheres denote ^1H atoms.

The synthetic procedure known as “molecular surgery” consists of opening fullerene cages by chemical reactions, impregnating the cages with guest molecules, and resealing the fullerene cages by further chemical reactions. This method has led to a variety of caged molecular systems, including $H_2@C_{60}$, $H_2O@C_{60}$ and $HF@C_{60}$ [1–3]. The confined molecules behave as free rotors with a well defined energy level structure [4] and have been probed by numerous spectroscopic methods including infrared spectroscopy, inelastic neutron scattering, and nuclear magnetic resonance (NMR) [3, 5–9]. Nuclear spin isomer interconversion has been studied [5, 8, 10], and the dielectric constant of $H_2O@C_{60}$ was found to depend on the ortho/para ratio of the confined molecules [11].

Endofullerenes provide a sheltered environment for the inserted small molecules, with the confining arena limiting interactions with other molecules. In the case of $H_2O@C_{60}$, proton exchange between water molecules is completely suppressed by the fullerene encapsulation. Molecular dynamics (MD) simulations of quantum rotors inside C_{60} suggest that the guest molecules reorient on a sub-picosecond timescale [12].

In this communication, we report the observed NMR lineshapes of single ^{17}O-labelled water molecules encapsulated in C_{60}, see figure 1. The suppression of water proton exchange by the fullerene cage allows the observation of well-resolved ^1H-^{17}O scalar couplings. The ^1H peak splits into a well-resolved sextet through coupling to the spin-5/2 ^{17}O nucleus. The sextet components display an unusual linewidth pattern, which is explained by scalar relaxation of the second kind, associated with ^{17}O quadrupolar relaxation. An estimate of the rotational correlation time for $H_2{}^{17}O$ encapsulated in C_{60} is obtained from ^{17}O quadrupole relaxation.

$H_2{}^{17}O@C_{60}$ was synthesised as in references [11, 13] with 90% ^{17}O labelled H_2O starting material. See the Supporting Information (SI) for details regarding preservation of the ^{17}O labelling level. 26.77 mg of $H_2{}^{17}O@C_{60}$ was dissolved in 1 mL of orthodichlorobenzene-d_4 (ODCB-d_4) leading to a concentration of 36.2 mM. All samples were subjected to thorough degassing using 4 standard freeze-pump-cycles in a Wilmad low pressure/vacuum NMR tube (5 mm outer diameter) to remove the majority of dissolved molecular oxygen.

The relevant portion of the proton NMR spectrum of $H_2{}^{17}O@C_{60}$ is shown in figure 1 (for the full spectrum, see the Supporting Information). A similar spectrum was previously obtained in the laboratory of the late Prof. Nick Turro (Columbia University, New York) but was not published. The spectrum shows a sextet splitting due to the ^1H-^{17}O scalar coupling, with $|J_{OH}| = 77.9 \pm 0.9$ Hz, in agreement with data on very dilute solutions of $H_2{}^{17}O$ in organic solvents [14]. The ^1H signal resonance of $H_2{}^{16}O@C_{60}$ is at -4.81 ppm referenced with respect to

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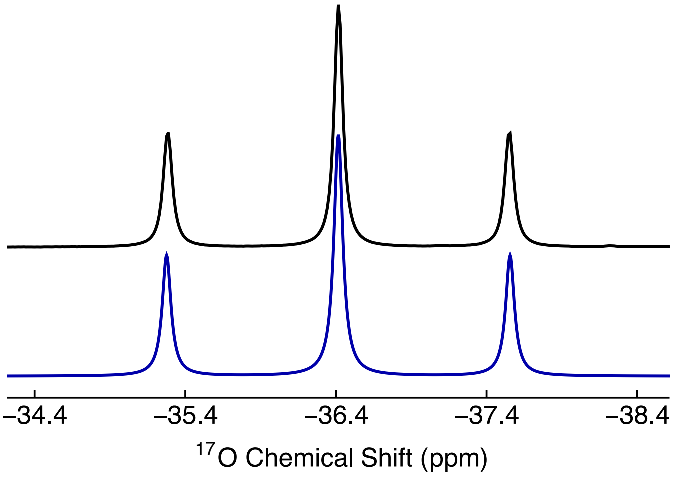

Figure 2: Relevant portion of the experimental oxygen-17 NMR spectrum for 36.2 mM $H_2{}^{17}O@C_{60}$ in degassed ODCB-d_4 solvent acquired at 11.7 T (^{17}O Larmor frequency = 67.8 MHz) and 25°C with 32768 transients. Black line: experimental spectrum; blue line: simulated spectrum. The simulation assumes extreme-narrowing ^{17}O relaxation, with the following parameters: J_{OH} = -77.9 Hz, $T_1(^{17}O) = T_2(^{17}O)$ = 81 ms.

the H_2O impurity peak in ODCB-d$_4$ at 1.39 ppm [2]. The proton spectrum of $H_2{}^{17}O@C_{60}$ was acquired with an acquisition time of 1.638 s and was processed without additional line broadening. The proton peak linewidths (full width at half maximum) are as follows: 9.1 ± 0.3 Hz ($M_S = \pm5/2$), 13.2 ± 0.3 Hz ($M_S = \pm3/2$), and 10.7 ± 0.1 Hz ($M_S = \pm1/2$). All peaks have the same integral value within experimental error (2 %). The intense narrow line at -4.81 ppm is attributed to $H_2{}^{16}O@C_{60}$, which has a linewidth (full width at half maximum) of ∼2.5 Hz. From spectral integration the fraction of the $H_2{}^{17}O$ isotopomer in the encapsulated water is ∼88.1% with the remaining ∼11.9% being the ^{16}O isotopomer. This is in good agreement with the ^{17}O labelling levels of the ^{17}O enriched H_2O starting material (90%), indicating that the synthetic procedure only changed the ^{17}O enrichment by ∼1.9%, in agreement with the experimental error for the peak integrals.

The relevant portion of the oxygen-17 NMR spectrum of $H_2{}^{17}O@C_{60}$ is shown in figure 2. A similar spectrum was reported previously by Chen et al. [7]. A triplet with $|J_{OH}|$ = 77.9 Hz is observed. The ^{17}O peak is at -36.4 ppm referenced with respect to a sample of $H_2{}^{17}O$ water (signal resonance placed at 0 ppm), in agreement with the literature [7]. The oxygen-17 spectrum of $H_2{}^{17}O@C_{60}$ was acquired with an acquisition time of 0.603 s and was processed without line broadening.

The proton and oxygen-17 T_1 times for $H_2{}^{17}O@C_{60}$ are shown in table 1 for two different temperatures. The ^{1}H T_1 decreases with increasing temperature, while the ^{17}O T_1 remains approximately constant over this temperature range. The proton T_1 values of $H_2{}^{17}O@C_{60}$ and $H_2{}^{16}O@C_{60}$ were found to be the same within experimental error. T_1 was estimated by using the inversion-recovery pulse sequence, in all cases. As shown in the Supporting Information (SI), each component of the ^{1}H NMR spectrum of $H_2{}^{17}O@C_{60}$ recovers with the same longitudinal relaxation time, within experimental error, which is indicative of the extreme-narrowing motional regime.

Table 1: Proton and oxygen-17 longitudinal relaxation times of 0.36 mM $H_2{}^{17}O@C_{60}$ in degassed ODCB-d_4 solution acquired at 11.7 T (500 MHz for ^{1}H and 67.8 MHz for ^{17}O), for two different temperatures.

	$H_2{}^{17}O@C_{60}$		$H_2^{16}O@C_{60}$
Temperature/°C	$T_1(^1H)$/ms	$T_1(^{17}O)$/ms	$T_1(^1H)$/ms
25	755 ± 55	81 ± 7	704 ± 52
57	547 ± 56	90 ± 11	578 ± 80

Details of ^{13}C NMR are found in the Supporting Information (SI). The ^{13}C spectrum shows a 110 ppb splitting between empty and filled fullerene cages, in agreement with the literature [9, 13].

A large variety of relaxation mechanisms may contribute to the observed spectral lineshapes and longitudinal relaxation times of $H_2{}^{17}O@C_{60}$. As well as the dipole-dipole interactions between all three magnetic nuclei [15, 16], there is also the quadrupolar relaxation mechanism of the ^{17}O nucleus [17–20], scalar relaxation of the second kind (SR2K) [21, 22], induced by the ^{17}O relaxation, and spin rotation [23, 24]. In this section, we examine the mechanisms responsible for the reported NMR spectra and T_1 times of $H_2{}^{17}O@C_{60}$.

The high degree of rotational freedom within the fullerene cage allows $H_2{}^{17}O@C_{60}$ to be modelled as a spherical top undergoing rapid isotropic rotational diffusion, described by a rotational correlation time τ_C. We assume that τ_C is short enough relative to the nuclear Larmor period to invoke the extreme narrowing approximation [18].

In extreme narrowing, the quadrupolar contribution to the relaxation rate constant of a nuclear spin with quantum number I is given by [20]:

$$T_1^{-1} = \frac{1}{5}\,(2I-1)\,(2I+3)\,\|A_Q\|^2\,\tau_C, \tag{1}$$

where τ_C is the rotational correlation time, and the norm of the quadrupolar interaction tensor is given by:

$$\|A_Q\| = \omega_Q\left[\frac{1}{2}\left(3+\eta^2\right)\right]^{\frac{1}{2}}, \tag{2}$$

with the quadrupole coupling frequency:

$$\omega_Q = \frac{2\pi C_Q}{2I(2I-1)} = \frac{e^2qQ}{2I(2I-1)\hbar}. \tag{3}$$

Here C_Q is the quadrupolar coupling constant, eQ is the electric quadrupolar moment, eq is the largest principal value of the electrical field gradient at the nucleus, and η

is the biaxality (asymmetry) of the electrical field gradient tensor [19]. In the case of ^{17}O ($I = 5/2$), equation 1 corresponds to:

$$T_1^{-1} = \frac{32}{5}\,\|\mathrm{A_Q}\|^2\,\tau_\mathrm{C}. \tag{4}$$

Other T_1 mechanisms, such as dipole-dipole coupling and spin-rotation, are far weaker than the quadrupolar mechanism and may be neglected.

The ^{17}O quadrupole coupling tensor for ^{17}O-water has been estimated quantum chemistry [25], and verified by microwave spectroscopy [26], and is given by: $\mathrm{C_Q} = 10.11\,\mathrm{MHz}$ and $\eta = 0.76$. This corresponds to the following norm of the quadrupole coupling tensor: $\|\mathrm{A_Q}\|/2\pi = 0.675\,\mathrm{MHz}$. From the ^{17}O relaxation time $T_1(^{17}\mathrm{O}) = 81 \pm 7\,\mathrm{ms}$ and equation 4 we obtain the following estimate for the rotational correlation time of water inside the fullerene: $\tau_\mathrm{C} = 107 \pm 9\,\mathrm{fs}$. This is similar to that for $\mathrm{H_2O}$ dissolved in weakly interacting solvents as estimated by microwave spectroscopy [27]. The estimate is 1 to 2 orders of magnitude smaller than previously reported for bulk water [17].

The rotational motion of water trapped inside $\mathrm{C_{60}}$ has also been studied by computational molecular dynamics [12], leading to the following prediction of the rotational diffusion constant: $D_R = 32.56\,\mathrm{rad^2ps^{-1}}$. The rotational correlation time may be deduced from this by invoking the relationship [20]: $\tau_\mathrm{C} = (6D_R)^{-1}$. This leads to a predicted rotational correlation time of 5.1 fs, which is a factor of $\sim$21 shorter than the experimental observation from ^{17}O NMR. The reasons for this discrepancy are not known at present.

The rotational correlation time for the $\mathrm{C_{60}}$ cages may be estimated from T_1 measurements for the cage ^{13}C nuclei. The dominant mechanism in this case is chemical shift anisotropy (CSA) [28]. Analysis of ^{13}C T_1 relaxation times over a range of magnetic fields provides the following estimate for the rotational correlation time τ_cage of the $\mathrm{C_{60}}$ cage: $10.6 \pm 0.6\,\mathrm{ps}$ [29] (see Supporting Information). Since τ_cage is two orders of magnitude larger than the rotational correlation time τ_c of the endohedral water molecules, we conclude that the endohedral and cage rotations are uncorrelated.

The ^{1}H splitting (figure 1) is due to the J-coupling of the two equivalent protons to the spin-5/2 ^{17}O nucleus, with $|J_\mathrm{OH}| = 77.9\,\mathrm{Hz}$. The opposite signs of the gyromagnetic ratios for ^{1}H and ^{17}O suggests that the J-coupling is likely to be negative, J_OH = -77.9Hz, although the sign cannot be determined directly from the spectrum. The differential broadening of the 6 proton peaks is due to ^{17}O relaxation. This is an example of scalar relaxation of the second kind (SR2K) [18].

Theoretical treatments of SR2K often introduce a fluctuating process to describe the relaxation of the coupled spin (^{17}O in this case) [18]. Here we propose a more general direct analysis of SR2K using the Liouville-von Neumann equation of the spin density operator $\rho(t)$:

$$\frac{d}{dt}\rho(t) = \hat{L}\rho(t), \tag{5}$$

where:

$$\hat{L} = -i\hat{H} + \hat{\Gamma}. \tag{6}$$

Here $\hat{H}$ is the commutation superoperator of the coherent Hamiltonian (given in the current case by the Hamiltonian for the ^{1}H-^{17}O J-couplings) and $\hat{\Gamma}$ is the relaxation superoperator, which is dominated in the current case by the ^{17}O quadrupolar relaxation. For an ensemble of $^1\mathrm{H_2}^{17}\mathrm{O}$ molecules, this superoperator may be represented as a 576 × 576 square matrix in a basis of orthogonal spin operators. Fortunately, only a 6 × 6 sub-block of this large matrix is relevant for the analysis of the ^{1}H spectrum. This matrix is spanned by 6 basis operators of the form $I^- \otimes |S, M_S\rangle\langle S, M_S|$ where I^- is the shift operator for the protons and $|S, M_S\rangle\langle S, M_S|$ is the population operator for the $S = 5/2$ ^{17}O nucleus with quantum number $M_S \in \{-5/2, -3/2, ... + 5/2\}$. As shown in the Supporting Information (SI), this block of the Liouvillian matrix may be derived by the *Mathematica*-based software package *SpinDynamica* [30] and has the form:

$$\begin{bmatrix}
-i5\pi J_\mathrm{OH} - \frac{60}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & 8\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & 4\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & 0 & 0 & 0 \\
8\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & -i3\pi J_\mathrm{OH} - \frac{92}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & \frac{16}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & \frac{36}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & 0 & 0 \\
4\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & \frac{16}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & -i\pi J_\mathrm{OH} - \frac{72}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & 0 & \frac{36}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & 0 \\
0 & \frac{36}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & 0 & i\pi J_\mathrm{OH} - \frac{72}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & \frac{16}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & 4\|\mathrm{A_Q}\|^2\tau_\mathrm{C} \\
0 & 0 & \frac{36}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & \frac{16}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & i3\pi J_\mathrm{OH} - \frac{92}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & 8\|\mathrm{A_Q}\|^2\tau_\mathrm{C} \\
0 & 0 & 0 & 4\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & 8\|\mathrm{A_Q}\|^2\tau_\mathrm{C} & i5\pi J_\mathrm{OH} - \frac{60}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C}
\end{bmatrix} \tag{7}$$

The frequencies of the spectral components correspond to the imaginary parts of the matrix eigenvalues, while the linewidths (as half-widths at half-height in radians per second) correspond to minus the real parts of the eigenvalues. In the current case, the quadrupole relaxation is sufficiently slow that the regime $T_1^{-1}(^{17}\mathrm{O}) \ll |2\pi J_\mathrm{OH}|$ applies. In this limit, the frequencies correspond to the ordinary J-coupled multiplet frequencies, and the halfwidths (in $\mathrm{rads^{-1}}$) are given by minus the diagonal elements of $\hat{\Gamma}$. The following general equation for these diagonal elements

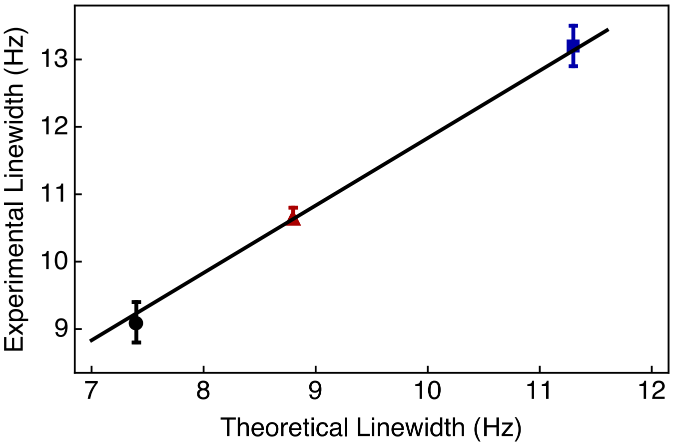

Figure 3: Theoretical vs. experimental linewidths (full width at half maximum) for the ^{1}H NMR spectrum of 36.2 mM $H_2{}^{17}O@C_{60}$ in degassed ODCB-d_4 solvent acquired at 11.7 T (^{1}H Larmor frequency = 500 MHz) and 25°C with 32768 transients. Black line: line of best fit to the data with slope = 1, leading to an intercept = 1.8 ± 0.4 Hz. ●: $M_S = 5/2$; ▲: $M_S = 1/2$; ■: $M_S = 3/2$.

is given in the Supporting Information (SI) [31]:

$$\lambda(M_S) = \frac{1}{5}\|\mathrm{A_Q}\|^2\,\tau_\mathrm{C} \times \Big(S(S+1)(S^2+S-1) + 2S(S+1)M_S^2 - 3M_S^4\Big). \tag{8}$$

For the case $S = 5/2$ this leads to the following spectral linewidths [32]:

$$\lambda(\pm 5/2) = \frac{60}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C}, \tag{9}$$

$$\lambda(\pm 3/2) = \frac{92}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C}, \tag{10}$$

$$\lambda(\pm 1/2) = \frac{72}{5}\|\mathrm{A_Q}\|^2\tau_\mathrm{C}, \tag{11}$$

which predicts the following linewidth ratios for the 6 proton peaks: 15:23:18:18:23:15. The measured ^{1}H linewidths are plotted against the theoretical linewidths, estimated from equations 9-11 with $\|\mathrm{A_Q}\|^2\tau_\mathrm{C}/4\pi^2 = 0.0488\,\mathrm{s}^{-1}$, in figure 3. The fit to a straight line with slope = 1 (and intercept = 1.83 Hz) provides compelling evidence that the proton linewidths are dominated by the scalar relaxation of the second kind mechanism. The intercept is attributed to additional relaxation mechanisms such as dipole-dipole couplings and spin-rotation, which contribute to the intrinsic linewidth of the $H_2{}^{16}O@C_{60}$ peak.

The ^{1}H and ^{17}O spectra of $H_2{}^{17}O@C_{60}$ were simulated using *SpinDynamica* [30]. ^{1}H-^{17}O scalar couplings and ^{17}O relaxation were included. The effect of ^{1}H-^{1}H and ^{1}H-^{17}O dipole-dipole relaxation on the simulated lineshapes was found to be negligible and was neglected. The spectra were simulated by using the following parameters: J_OH = -77.9 Hz, $\|\mathrm{A_Q}\|$ = 0.675 MHz, and τ_C = 107 fs. Good agreement is achieved between experimental and simulated ^{1}H and ^{17}O spectra.

Several mechanisms may contribute to the ^{1}H relaxation in $H_2{}^{17}O@C_{60}$. These include fluctuations of the intramolecular dipole-dipole couplings within each water molecule, fluctuations of the intermolecular dipole-dipole couplings between the endohedral water protons and cage ^{13}C nuclei, and couplings between the ^{1}H spins and the molecular angular momentum of the water (spin-rotation mechanism).

The intramolecular dipole-dipole contributions may be estimated from the ^{1}H-^{1}H and ^{1}H-^{17}O distances of 151.6 pm and 95.8 pm respectively, and the water rotational correlation time of $\tau_\mathrm{C} = 107 \pm 9$ fs from the ^{17}O relaxation. The contributions to T_1^{-1} are given by $3b^2\tau_c/2$ in the homonuclear case and $b^2\tau_c$ in the heteronuclear case, where $b = -(\mu_0/4\pi)\gamma\gamma'\hbar r^{-3}$ is the dipole-dipole coupling constant, assuming isotropic rotational motion in the extreme narrowing limit, and $\{\gamma, \gamma'\}$ are the gyromagnetic ratios. This leads to the following estimates for the contributions to the ^{1}H T_1^{-1} from the ^{1}H-^{1}H and ^{1}H-^{17}O dipole-dipole mechanisms: $(7.5 \pm 0.6) \times 10^{-3}\,\mathrm{s}^{-1}$ and $(1.45 \pm 0.2) \times 10^{-3}\,\mathrm{s}^{-1}$, respectively.

Approximately 60% of the C_{60} cages contain a ^{13}C nucleus, so it is conceivable that dipolar interactions between the cage carbons and the endohedral protons could also contribute to the ^{1}H T_1^{-1}. In order to scope the largest possible magnitude of this contribution we used the minimum ^{1}H-^{13}C distance between the water protons and the cage carbon nuclei, which was estimated to be 276.6 pm by using *Gaussian 09*. This corresponds to a ^{1}H-^{13}C dipole-dipole coupling constant of -1.4 kHz. Taking the rotational correlation time τ_cage =10.6 ps as the appropriate correlation time for the fluctuations of this interaction, we estimate the ^{1}H-^{13}C dipole-dipole contribution to the ^{1}H relaxation rate constant T_1^{-1} to be $(0.85 \pm 0.05) \times 10^{-3}$ s^{-1}. This is a maximum estimate. Rapid rotational motion of the endohedral molecule with respect to the cage is expected to reduce this contribution further. We conclude that the influence of the cage ^{13}C nuclei on the endohedral ^{1}H relaxation is negligible.

The combined dipole-dipole mechanisms are much too weak to explain the observed ^{1}H relaxation rate constant, which is $T_1^{-1}(^1\mathrm{H}) = 1.3 \pm 0.1\,\mathrm{s}^{-1}$ at a temperature of 298 K. We conclude that the spin-rotation mechanism [23, 24] dominates the ^{1}H relaxation in $H_2{}^{17}O@C_{60}$. This conclusion is supported by the temperature dependence of the ^{1}H T_1 which becomes shorter at higher temperature, unlike the ^{17}O T_1, which increases at higher temperature. This hypothesis is further supported by the observation that the proton T_1 of $H_2{}^{16}O@C_{60}$ equals the proton T_1 of $H_2{}^{17}O@C_{60}$ within experimental error.

The NMR lineshapes of an intermediate in the synthesis of $H_2{}^{17}O@C_{60}$ in which the cage orifice is not fully closed are shown in the Supporting Information (SI). In this case the low symmetry of the water environment leads to hindered rotational diffusion of the $H_2{}^{17}O$ molecules, and consequently a longer rotational correlation time ($\tau_\mathrm{C} = 1.4$ ps) and more rapid ^{17}O quadrupolar relaxation, which in turn manifests as a more severe broadening of the ^{1}H spectrum by scalar relaxation and only partial resolution of the sextet structure.

In summary, we have reported the exotic NMR lineshapes of $H_2{}^{17}O@C_{60}$. The ^1H NMR spectrum displays a sextet splitting due to the ^1H-^{17}O scalar coupling. The resolution of this multiplet structure is made possible by the free rotation of the water molecule inside the fullerene cage and the suppression of water proton exchange. We have demonstrated that scalar relaxation of the second kind is responsible for the variation of peak linewidths. A motional model was proposed in which the $H_2{}^{17}O$ molecules undergo rapid isotropic rotational diffusion. The rotational tumbling modulates the nuclear quadrupole interaction driving the scalar relaxation of the second kind mechanism for the proton spins. Good agreement between experimental and simulated spectra was achieved. The T_1 relaxation time of the ^{17}O nucleus allowed an estimate of the rotational correlation time: $\tau_C = 107 \pm 9\,\text{fs}$. This estimate is similar to that found for dilute water molecules in organic solvents, but much shorter than that found for bulk water.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: NMR lineshape · scalar relaxation · endofullerene

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