Comparison of Nuclear Spin Relaxation of H_2O@C_{60} and H_2@C_{60} and Their Nitroxide Derivatives

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ABSTRACT: The successful synthesis of H_2O@C_{60} makes possible the study of magnetic interactions of an isolated water molecule in a geometrically well-defined hydrophobic environment. Comparisons are made between the T_1 values of H_2O@C_{60} and the previously studied H_2@C_{60} and their nitroxide derivatives. The value of T_1 is approximately six times longer for H_2O@C_{60} than for H_2@C_{60} at room temperature, is independent of solvent viscosity or polarity, and increases monotonically with decreasing temperature, implying that T_1 is dominated by the spin-rotation interaction. Paramagnetic nitroxides, either attached covalently to the C_{60} cage or added to the medium, produce strikingly similar T_1 enhancements for H_2O@C_{60} and H_2@C_{60} that are consistent with through-space interaction between the internal nuclear spins and the external electron spin. This indicates that it should be possible to apply to the *endo*-H_2O molecule the same methodologies for manipulating the ortho and para spin isomers that have proven successful for H_2@C_{60}.

SECTION: Spectroscopy, Photochemistry, and Excited States
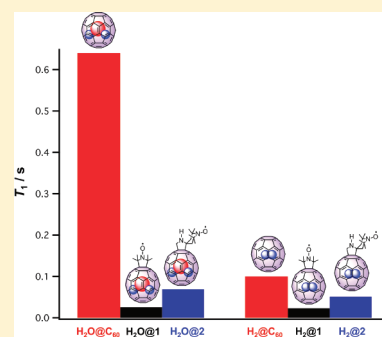
The successful preparation[1] of H_2O@C_{60} marks the appearance on the scene, after H_2@C_{60}, of the second small molecule to be incorporated into the C_{60} cage using the molecular surgery methodology and the first encapsulation of a polar species. In previous studies, we investigated nuclear spin relaxation (T_1) of H_2 in H_2@C_{60} in organic solvents with[2] and without[3] the addition of relaxation reagents. Relaxation of the endohedral H_2 by nitroxide spins covalently attached to the C_{60} cage was also measured.[4] We report here similar measurements for H_2O@C_{60} and two paramagnetic derivatives, H_2O@1 and H_2O@2 (Chart 1), and compare the results with those for H_2@C_{60}. The goal is to compare the motions of the two molecules inside the C_{60} cage and also the degree to which their magnetic properties are influenced by the region outside the cage. The latter has proved to be essential in developing methods to manipulate the ratio of ortho and para nuclear spin isomers of H_2 within the cage and study the mechanism of the conversion.[5] Similar studies for the conversion of ortho and para H_2O@C_{60} are in progress.

Table 1 summarizes the results of the following types of measurements of T_1, reported as the inverse rate, $1/T_1$, for H_2O and H_2: (1) The intrinsic T_1 for the small molecules in three organic solvents with different viscosities and polarities; (2) the T_1 values for the molecules in the covalently bonded nitroxides, **1** and **2**, and the corresponding diamagnetic hydroxylamines, **1D** and **2D** (Chart 1); and (3) the bimolecular relaxivity, R_1,

obtained from measurements of T_1 as a function of the added nitroxide TEMPO.

The most striking feature of Table 1 is the similarity of the data for the two molecules under the same conditions, the largest difference being the T_1 values in a diamagnetic environment. The implications of the data from each type of measurement are considered below.

(1) Spin−lattice relaxation in H_2 occurs by both dipole−dipole (dip) and spin-rotation (sr) mechanisms.[3] Relaxation of H_2O protons in solution has traditionally been explained by a combination of intra- and intermolecular dipole−dipole interactions.[6] At high temperatures in supercritical water, however, it has been shown that an appreciable contribution from spin-rotation occurs.[7] We therefore consider both mechanisms here. As previously discussed,[3] for a classical rotational diffusion model, these two contributions to the relaxation rate may be written as

$$1/T_{1dip} = \omega_{dip}^2 \tau_{dip}; \qquad \omega_{dip} = 3\gamma_H^4 \hbar^2/2r^6 \qquad (1)$$

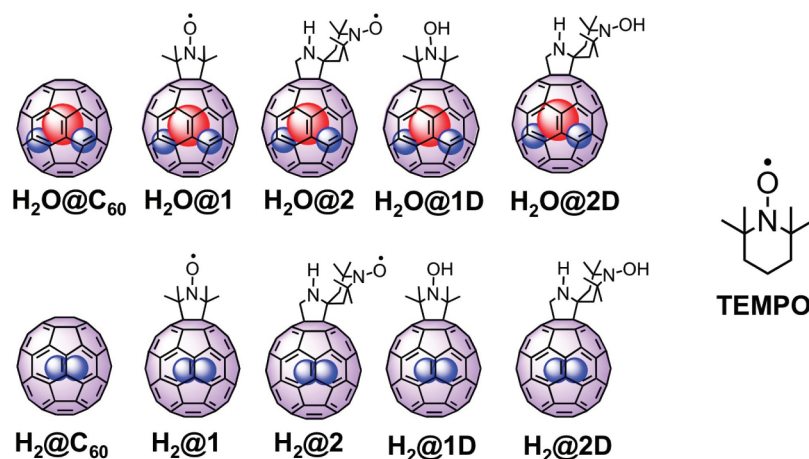$$1/T_{1sr} = \omega_{sr}^2 \tau_{sr}; \qquad \omega_{sr} = 16\pi^2 I k_B T C^2/3\hbar^2 \qquad (2)$$

where, aside from physical constants, r is the interproton distance, I is the moment of inertia of the molecule, C is the

Chart 1. Structures of Compounds Used in This Study

Table 1. Proton Relaxation Rates in H$_2$O@C$_{60}$ and H$_2$@C$_{60}$ and Their Nitroxide Derivatives

		$1/T_1$ (s^{-1})^a	
X	solvent	H$_2$O@X	H$_2$@X
	toluene-d_8 (2.4^b, 0.548^c)	1.56 (1.98^d)	9.5 (11.5^d)
fullerene C$_{60}$	CDCl$_3$ (4.8, 0.539)	1.64	12.2
	TCE-d_2 (8.2, 1.629)	1.54	9.3
1D		0.88	6.3
2D		0.90	6.6
1 (r = 7.5 Å^e)	toluene-d_8 (2.4, 0.548)	52.6 (51.7^f)	76.9 (70.6^f)
2 (r = 8.9 Å^e)		16.9 (16.0^f)	19.6 (13.0^f)
fullerene C$_{60}$	toluene-d_8 (2.4, 0.548)	R_1 (M^{-1} s^{-1}, TEMPO)^g	
		42.9 ± 2.5	70 ± 10

^{a}Unless indicated otherwise, measured at 300 K. ^{b}Dielectric constant. ^{c}Viscosity, cP. ^{d}T = 340 K. ^{e}Distance between centers of the endo molecule and the nitroxide radical. ^{f}Paramagnetic contribution, $1/T_{1p}$, by subtracting $1/T_1$ for the hydroxylamine from that of the nitroxide. ^{g}TEMPO used as an external relaxant.

spin-rotation constant, in hertz, and τ_{dip} and τ_{sr} are the correlation times for molecular reorientation and rotational angular momentum change, respectively. The parameters for H$_2$O and H$_2$ are summarized in Table 2. The values of I and C for H$_2$O are the averages used in the analysis of data for supercritical water.[7]

The two correlation times in eqs 1 and 2 are treated as adjustable parameters to be determined by experiment. Unfortunately, in the present case, they cannot be determined

Table 2. Properties of H$_2$O and H$_2$ and Relaxation Parameters

parameters	H$_2$O	H$_2$
I (kg·m^2)	19.6 × 10^{-48}	4.50 × 10^{-48}
C (kHz)	32	113
r_{HH} (Å)	1.58	0.74
r_{vdw} (Å)^a	1.44	1.38
$1/T_1$ (s^{-1}, 340 K)	1.98	11.5
ω_{dip} (rad s^{-1})	2.3 × 10^5	22.1 × 10^5
ω_{sr} (rad s^{-1}, 340 K)	6.7 × 10^5	11.4 × 10^5
τ_{dip} (max, ps, 340 K)	37	2.2
τ_{sr} (max, ps, 340 K)	4.4	8.8

^{a}Data from ref 8.

independently because T_1 is the only observable.[9] On the basis of the values of the ω_{dip} and ω_{sr} factors, however, it would be expected that for similar correlation times the dipole−dipole mechanism should be much weaker for H$_2$O than for H$_2$, and the spin-rotation mechanism should therefore be dominant for H$_2$O@C$_{60}$. The temperature dependence of T_1 in the two cases (Figure 1) bears this out: the monotonic decrease in relaxation
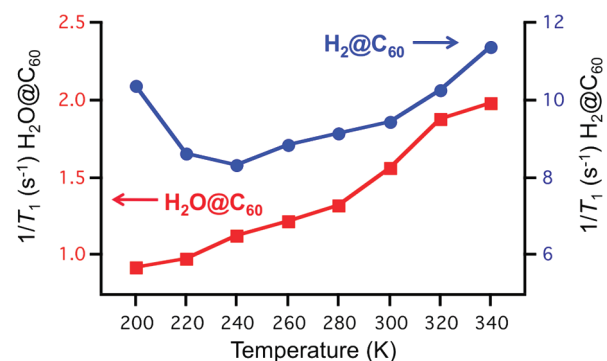
Figure 1. Temperature dependence of relaxation rate, $1/T_1$, for H$_2$O@C$_{60}$ and H$_2$@C$_{60}$ in toluene-d_8.

rate for H$_2$O with decreasing temperature is consistent with weakening of the spin-rotation mechanism without the presence at low temperature of a compensating contribution from the dipole−dipole mechanism, as occurs[3,10] with H$_2$@C$_{60}$.

One can obtain a further sense of the relative importance of the two mechanisms for H$_2$O and H$_2$ by considering the value of each correlation time that would be required to yield the observed T_1 if that were the *only* mechanism. Table 2 lists the corresponding values, τ_{dip} (max) and τ_{sr} (max), calculated from T_1 values at 340 K, the maximum temperature studied, where the influence of the spin-rotation mechanism should be greatest. This is analogous to the asymptotic method previously employed[3] for H$_2$@C$_{60}$, where it was assumed that only the spin-rotation mechanism operated at high temperature and the dipole−dipole mechanism operated at low temperature. As expected, this approach yielded estimates of ca. 2 and 8 ps, respectively, for τ_{dip} and τ_{sr}, the same values[9] as those shown in Table 1 for H$_2$@C$_{60}$. It can be seen that the required values of τ_{sr} (max) for H$_2$O and H$_2$ are quite similar, which might be explained if collisions with the cage wall were changing the rotational angular momenta of the two molecules at about the

same rate. The insufficiency of the dipole–dipole mechanism to account exclusively for the value of T_1 for $H_2O@C_{60}$ is consistent with the value of 37 ps for τ_{dip} (max), a value significantly longer than the 10 ps upper limit of τ_{dip} for C_{60} in toluene.[3] Whereas it might be expected that the somewhat larger H_2O molecule (see Table 2 for van der Waals radii, r_{vdw}) would be closer to the walls of the cage and therefore more influenced by cage rotation, it seems unlikely that the endo-H_2O molecule could be reorienting more slowly than the cage itself.

Comparison of the T_1 values for H_2O and H_2 in the C_{60} environment with those of the hydroxylamines 1D and 2D (Chart 1), synthesized by reduction of the corresponding nitroxides wth biphenylhydrazine,[11] shows a two-fold decrease in relaxation rate at room temperature for both endo molecules in both cages. A qualitative explanation for this effect is a decreased τ_{sr} and/or τ_{dip} induced by the slightly less symmetrical environment of the C_{60} derviatives.

The absence of sensitivity of T_1 to solvent viscosity is consistent with a degree of uncoupling of the rapid motion of the endo-H_2O molecule from the slower rotation of the cage, as was previously[3] deduced for $H_2@C_{60}$. Similarly, the lack of sensitivity to solvent polarity for relaxation of $H_2O@C_{60}$ would indicate that the endo-H_2O is sufficiently electrically isolated from the surrounding solvent that its motion is not detectably affected by interaction of the electric dipole moment with a polar medium.

(2) In Table 1 are shown the relaxation rates of H_2O and H_2 in the C_{60} nitroxides 1 and 2, corrected for the diamagnetic contribution to relaxation (values in parentheses). As expected, the effect of the paramagnetic center decreases with distance and to about the same extent with both H_2O and H_2. The slightly larger effect for H_2 in 1 and the opposite in 2 may be indicating small changes in the rotational averaging of H_2O and H_2 in the asymmetric environment that would translate into slightly closer approach of H_2 to the nitroxide in 1 and the opposite in 2. The effect of structure on positioning of the endo molecule might, in principle, be explored theoretically by extending to $H_2O@$fullerenes the methods applied to $H_2@C_{60}$ and its asymmetric open forms.[12]

(3) The relaxivity, R_1 ($M^{-1}s^{-1}$), represents the bimolecular contribution to T_1, calculated using the equation: $1/T_1 = 1/T_{1,0} + R_1[S]$, where $1/T_{1,0}$ is the relaxation time in the absence of paramagnetic relaxant, S. The values shown in Table 1 for H_2O and H_2 in the presence of TEMPO are nearly the same, as expected if the magnitude and timing of the interaction between the endo protons and the externally diffusing paramagnet were essentially the same for the two molecules. It is perhaps a bit surprising that the relaxivity of H_2 is slightly larger than that of H_2O. In H_2, the protons lie 0.37 Å from the center of mass whereas in H_2O the distances for rotation about the three principal axes are 0.52, 0.76, and 0.92 Å.[13] It might therefore be expected that if the average position of the center of mass were the center of the cage then the H_2O protons would on the average be closer to the surface of the cage and therefore closer to and more affected by an external paramagnet. One possible explanation for a smaller-than-expected relative relaxivity for H_2O would be that the additional mechanism needed to explain the larger relaxivity[2] for $H_2@C_{60}$ may not be as effective for H_2O.

In summary, we have found that the proton relaxation time of $H_2O@C_{60}$ in the presence and absence of paramagnets is very close to what would be predicted from analogous observations for $H_2@C_{60}$, with similar dynamics in both cases. Small deviations from expectations raise interesting questions about the average position of the protons for H_2O in the C_{60} cage and two nitroxide derivatives. The similarity of magnetic properties also suggests that the methodology developed to manipulate the ortho and para spin isomers of H_2 in fullerenes[5,14,15] might also succeed for the spin isomers of H_2O in the endofullerene environment. Such studies are underway.

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Notes
The authors declare no competing financial interest.

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