

Nuclear Relaxation of H₂ and H₂@C₆₀ in Organic Solvents

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We report an investigation of the nuclear spin–lattice relaxation of H₂ and H₂@C₆₀¹ as a function of solvent and temperature. These studies explore and compare the nature of the interactions of a guest H₂ molecule confined transiently within the walls of a solvent cavity and a guest H₂ molecule encapsulated within the walls of the C₆₀ cavity.

The relaxation time (*T*₁) of H₂ has been extensively studied in the gas phase and in liquid hydrogen at low temperatures.^{2,3} However, there are few reports of the magnetic resonance of H₂ in solution^{4,5} and none in ordinary organic solvents. To generate data for comparison with H₂@C₆₀ we measured the *T*₁ values of H₂ in a range of organic solvents.

The chemical shifts of H₂ and H₂@C₆₀ appear at ~4.5 ppm and ~−1.3 ppm, respectively. The value of *T*₁ of H₂ at 300 K varies significantly with solvent (Table 1): from 1.44 s (benzene) to 0.84 s (CCl₄). A somewhat larger variation of *T*₁ with the same set of solvents was found for H₂@C₆₀ (Table 1): from 0.118 s (benzene) to 0.046 s (CCl₄).⁶ The values of *T*₁ are 10–20 times smaller for H₂@C₆₀ than for H₂ even though the ratios of *T*₁ for H₂ and H₂@C₆₀ are similar in all the solvents.

The temperature dependences of *T*₁ for H₂ and H₂@C₆₀ were investigated in detail for toluene-*d*₈ (Figure 1) and for benzene-*d*₆, 1,1,2,2-tetrachloroethane-*d*₂, 1,2-dichlorobenzene-*d*₄, and chloroform-*d*₁. Striking features of the data are the occurrence of a maximum for *T*₁ at ~240 K for both the H₂ and H₂@C₆₀ in toluene-*d*₈ and a ratio of *T*₁ values which is nearly independent of temperature. A maximum of the value of *T*₁ with temperature is also found in 1,1,2,2-tetrachloroethane-*d*₂ and chloroform-*d*₁. For benzene-*d*₆ and 1,2-dichlorobenzene-*d*₄ in the available range of temperatures, only a decrease of *T*₁ with increasing temperature was observed.

This kind of dependence of *T*₁ on temperature is uncommon, although a maximum of *T*₁ has previously been observed for small molecules such as H₂O,⁷ HCl, and HBr in solution,^{8,9} and it is consistent with two relaxation mechanisms with different temperature dependences dominating in turn below and above 240 K for both H₂ and H₂@C₆₀. Since the value of *T*₁ for both H₂ and H₂@C₆₀ does not significantly change in going from benzene-*d*₆ to benzene-*d*₄ (Table 1), the dominating interactions determining H₂ and H₂@C₆₀ nuclear relaxation must be *intramolecular*. Furthermore, the intramolecular dipole–dipole interaction and spin-rotation interaction are known² to be responsible for the relaxation of gaseous H₂ and their magnitude has been measured for H₂ in molecular beams.¹⁰ Therefore it is likely that the relaxation of H₂

Table 1. *T*₁ of H₂ and H₂@C₆₀ at 300 K in Various Solvents, at a Field of 11.7 T (500 MHz); Ratio *T*₁(H₂)/*T*₁(H₂@C₆₀) and Viscosity of the Solvents, at 25 °C

solvent	<i>T</i> ₁ (s) ^a		<i>T</i> ₁ ratio	<i>η</i> (cP)
	H ₂	H ₂ @C ₆₀		
CCl ₄	0.84	0.046	18	0.884 ^b
chloroform- <i>d</i> ₁	1.21	0.082	15	0.539 ^c
1,2-dichlorobenzene- <i>d</i> ₄	1.27	0.101	13	1.322 ^c
toluene- <i>d</i> ₈	1.28	0.104	12	0.548 ^d
1,1,2,2-tetrachloroethane- <i>d</i> ₂	1.37	0.108	13	1.629 ^e
benzene- <i>d</i> ₆	1.42	0.118	12	0.636 ^e
benzene	1.44	0.118	12	0.599 ^e

^a ± 5%. ^b Reference 22. ^c *η* of protonated solvents, ref 22. ^d Reference 18. ^e Reference 23.

in solution also depends on the competition between intramolecular dipole–dipole interaction and spin-rotation interaction.

The contribution to 1/*T*₁ (in extreme narrowing conditions) from intramolecular dipolar and spin-rotation interaction may be estimated by eq 1² and eq 2,^{11,12} respectively:

$$\frac{1}{T_{1\text{dip}}} = \frac{3\gamma_{\text{H}}^4\hbar^2}{2r^6} \tau_{\text{dip}} \quad (1)$$

$$\frac{1}{T_{1\text{sr}}} = \frac{4Ik_{\text{B}}TC^2}{3\hbar^2} \tau_{\text{sr}} \quad (2)$$

where γ_{H} is the magnetogyric ratio for the proton, *r* is the equilibrium internuclear distance of H₂ (0.74 Å), *C* is the spin-rotation coupling constant (7.16 × 10⁵ rad s^{−1}),¹⁰ *I* is the moment of inertia of H₂ (4.6 × 10^{−48} kg m²), and *k*_B is the Boltzmann constant. The correlation times τ_{dip} and τ_{sr} are measures of the time-dependent fluctuations in the orientation and angular velocity of H₂, respectively. Both correlation times are expected to be functions of viscosity and temperature which depend on the details of the motion of H₂ molecules and the surrounding medium.¹¹

Qualitatively, the dipole–dipole interaction (eq 1) might account for the observed increase of *T*₁ with temperature because faster molecular reorientations correspond to shorter τ_{dip} . On the other hand, the spin-rotation interaction might account for the observed decrease of *T*₁ with temperature both through the explicit temperature dependence (eq 2) and through τ_{sr} temperature dependence.¹³ Assuming that the relaxation at the lowest temperature is dominated by the dipolar interaction, from the value of *T*₁ at 200 K and eq 1 it is possible to estimate the correlation time τ_{dip} of the process that modulates this interaction: $\tau_{\text{dip}}(\text{H}_2) = 0.20$ ps and $\tau_{\text{dip}}(\text{H}_2@\text{C}_{60}) = 2.1$ ps. In a similar way, assuming that at the highest temperature the relaxation is dominated by the spin-rotation interaction, from

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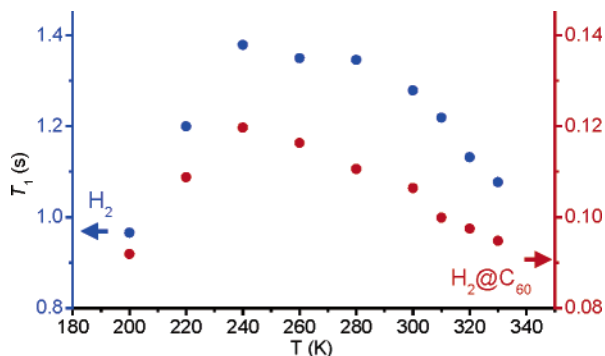


Figure 1. T_1 (s) of H_2 (blue dots) saturated at room temperature in deoxygenated toluene- d_8 and $H_2@C_{60}$ (red dots) dissolved in toluene- d_8 , at temperatures ranging from 200 to 330 K, at a field of 11.7 T.

the values of T_1 at 330 K and eq 2, the correlation time τ_{sr} of the process which modulates this interaction is obtained: $\tau_{sr}(H_2) = 0.72$ ps and $\tau_{sr}(H_2@C_{60}) = 8.2$ ps.¹⁴

It is instructive to compare these values to the characteristic free rotation times,¹⁵ $\tau_{FR} = (2\pi/9)(I/k_B T)^{1/2}$, of 0.02 and 3 ps calculated for H_2 and C_{60} , respectively, at 330 K, and the values for the reorientation time measured for C_{60} in toluene at room temperature: $\tau_{dip}(C_{60}) = 7$ –10 ps and extrapolated at 200 K: ~ 30 ps.^{16,17} An estimate of τ_{dip} can be made for H_2 in toluene- d_8 at 200 K using the Stokes–Einstein–Debye relationship ($\tau = 4\pi r^3 \eta / 3k_B T$), the viscosity at 200 K (4.5 cP),¹⁸ and the van der Waals radius (1.38 Å¹⁹): $\tau_{SED} \approx 18$ ps.

Comparisons of the various estimates of correlation times for H_2 and $H_2@C_{60}$ in toluene- d_8 lead to the following qualitative conclusions.

Modulation of the angular velocity of H_2 in both environments occurs somewhat more slowly than the frequency of reorientation ($\tau_{sr} > \tau_{dip}$), since at 330 K τ_{dip} may be safely assumed even shorter than those calculated at 200 K and in the case of $\tau_{dip}(H_2)$ close to τ_{FR} of H_2 . This implies that the H_2 rotates through large angles between collisions with the solvent or walls of the C_{60} cavity.²⁰

The value of τ_{dip} for H_2 in solution is much smaller than expected from simple Stokes–Einstein–Debye behavior ($\tau_{dip}(H_2) \ll \tau_{SED}$). This is consistent with the reduced influence of viscous forces on reorientation expected for a nearly spherical molecule rotating under “slip” conditions.²¹

$\tau_{dip}(H_2@C_{60})$ is larger than $\tau_{dip}(H_2)$. This suggests sufficient interaction between H_2 and the walls of the C_{60} cavity to entice the smaller molecule to follow the rotation of the larger, although $\tau_{dip}(C_{60})$ is still one order of magnitude larger than $\tau_{dip}(H_2@C_{60})$. The absence of correlation between solvent viscosity and the value of T_1 in the different solvents (Table 1) is expected for H_2 in solvents under slip conditions and does not conflict with the latter hypothesis on $H_2@C_{60}$ because $\tau_{dip}(C_{60})$ is much smaller than its τ_{SED} , being close to its τ_{FR} at room temperature¹⁶ and showing no dependence on viscosity when measured in different solvents.¹⁷

The value of T_1 of H_2 and $H_2@C_{60}$ varies with solvent (Table 1), although a correlation between the values of T_1 and viscosity or dielectric constant of the solvent could not be found.²⁴ These observations and the above considerations on the correlation times support an approximate model in which it is the motions of the H_2 and $H_2@C_{60}$ in the solvent cages that are significant, along with the collisions or interactions of H_2 with the concave walls of C_{60} . The similarity of the ratio of the values of T_1 for all of the solvents investigated suggests that the motions of H_2 and $H_2@C_{60}$ generate fluctuating fields with corresponding correlation times. Further theoretical studies are required to determine the validity of these speculations.

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