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Nuclear Relaxation of H_2 and $H_2@C_{60}$ in Organic Solvents

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Received July 19, 2006; E-mail: njt3@columbia.edu

We report an investigation of the nuclear spin−lattice relaxation of H_2 and $H_2@C_{60}$[1] as a function of solvent and temperature. These studies explore and compare the nature of the interactions of a guest H_2 molecule confined transiently within the walls of a solvent cavity and a guest H_2 molecule encapsulated within the walls of the C_{60} cavity.

The relaxation time (T_1) of H_2 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 H_2 in solution[4,5] and none in ordinary organic solvents. To generate data for comparison with $H_2@C_{60}$ we measured the T_1 values of H_2 in a range of organic solvents.

The chemical shifts of H_2 and $H_2@C_{60}$ appear at ∼4.5 ppm and ∼ −1.3 ppm, respectively. The value of T_1 of H_2 at 300 K varies significantly with solvent (Table 1): from 1.44 s (benzene) to 0.84 s (CCl_4). A somewhat larger variation of T_1 with the same set of solvents was found for $H_2@C_{60}$ (Table 1): from 0.118 s (benzene) to 0.046 s (CCl_4).[6] The values of T_1 are 10−20 times smaller for $H_2@C_{60}$ than for H_2 even though the ratios of T_1 for H_2 and $H_2@C_{60}$ are similar in all the solvents.

The temperature dependences of T_1 for H_2 and $H_2@C_{60}$ 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 H_2 and $H_2@C_{60}$ 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 H_2O,[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 H_2 and $H_2@C_{60}$. Since the value of T_1 for both H_2 and $H_2@C_{60}$ does not significantly change in going from benzene-h_6 to benzene-d_6 (Table 1), the dominating interactions determining H_2 and $H_2@C_{60}$ nuclear relaxation must be *intra*molecular. Furthermore, the intramolecular dipole−dipole interaction and spin-rotation interaction are known[2] to be responsible for the relaxation of gaseous H_2 and their magnitude has been measured for H_2 in molecular beams.[10] Therefore it is likely that the relaxation of H_2 in solution also depends on the competition between intramolecular dipole−dipole interaction and spin-rotation interaction.

Table 1. T_1 of H_2 and $H_2@C_{60}$ at 300 K in Various Solvents, at a Field of 11.7 T (500 MHz); Ratio $T_1(H_2)/T_1(H_2@C_{60})$ and Viscosity of the Solvents, at 25 °C

solvent	T_1 (s)[a] H_2	T_1 (s)[a] $H_2@C_{60}$	T_1 ratio	η (cP)
CCl_4	0.84	0.046	18	0.884[b]
chloroform-d_1	1.21	0.082	15	0.539[c]
1,2-dichlorobenzene-d_4	1.27	0.101	13	1.322[c]
toluene-d_8	1.28	0.104	12	0.548[d]
1,1,2,2-tetrachloroethane-d_2	1.37	0.108	13	1.629[c]
benzene-d_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.

The contribution to $1/T_1$ (in extreme narrowing conditions) from intramolecular dipolar and spin-rotation interaction may be estimated by eq 1[2] and eq 2,[11,12] respectively:

$$\frac{1}{T_{1\mathrm{dip}}} = \frac{3\,\gamma_{\mathrm{H}}^4\hbar^2}{2r^6}\,\tau_{\mathrm{dip}} \tag{1}$$

$$\frac{1}{T_{1\mathrm{sr}}} = \frac{4Ik_{\mathrm{B}}TC^2}{3\hbar^2}\,\tau_{\mathrm{sr}} \tag{2}$$

where γ_{H} is the magnetogyric ratio for the proton, r is the equilibrium internuclear distance of H_2 (0.74 Å), C is the spin-rotation coupling constant (7.16×10^5 rad s^{-1}),[10] I is the moment of inertia of H_2 (4.6×10^{-48} kg m^2), 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 H_2, respectively. Both correlation times are expected to be functions of viscosity and temperature which depend on the details of the motion of H_2 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: $\tau_{\mathrm{dip}}(H_2) = 0.20$ ps and $\tau_{\mathrm{dip}}(H_2@C_{60}) = 2.1$ 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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10.1021/ja065172w CCC: $33.50

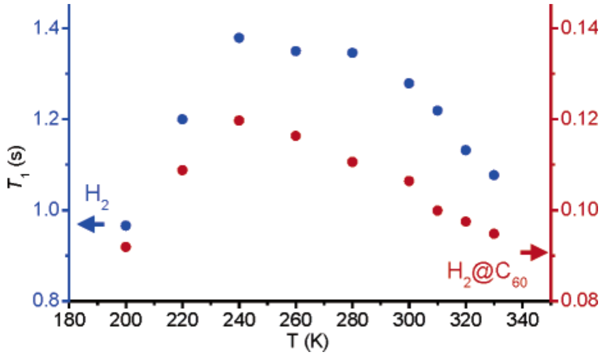

Figure 1. T_1 (s) of H_2 (blue dots) saturated at room temperature in deoxygenated toluene-d_8 and $H_2@C_{60}$ (red dots) dissolved in toluene-d_8, at temperatures ranging from 200 to 330 K, at a field of 11.7 T.

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] $\tau_{FR} = (2\pi/9)(I/k_BT)^{1/2}$, 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 ($\tau = 4\pi r^3\eta/3k_BT$), the viscosity at 200 K (4.5 cP),[18] and the van der Waals radius (1.38 Å[19]): $\tau_{SED} \approx 18$ 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 τ_{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 temperature[16] 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.

Acknowledgment. We thank the National Science Foundation for financial support of this research (Grant NSF 04-15516). We are grateful to Prof. Bruce J. Berne (Columbia University), Prof. M. Francesca Ottaviani (University of Urbino), Prof. Malcolm H. Levitt (Southampton University), and a sharp-eyed reviewer for helpful discussions and insights.

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JA065172W