

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/6692943>

Nuclear Relaxation of H₂ and H₂ @C₆₀ in Organic Solvents

ARTICLE in JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · DECEMBER 2006

Impact Factor: 12.11 · DOI: 10.1021/ja065172w · Source: PubMed

CITATIONS

37

READS

25

9 AUTHORS, INCLUDING:



Elena Sartori

Ministero dell'Istruzione, dell'Università e del...

24 PUBLICATIONS 306 CITATIONS

SEE PROFILE



Marco Ruzzi

University of Padova

38 PUBLICATIONS 710 CITATIONS

SEE PROFILE



Ronald G Lawler

Brown University

118 PUBLICATIONS 2,284 CITATIONS

SEE PROFILE



Koichi Komatsu

Brown University

233 PUBLICATIONS 4,878 CITATIONS

SEE PROFILE

Nuclear Relaxation of H₂ and H₂@C₆₀ in Organic SolventsElena Sartori,[†] Marco Ruzzi,[†] Nicholas J. Turro,^{*,†} John D. Decatur,[†] David C. Doetschman,[‡]
Ronald G. Lawler,^{||} Anatoly L. Buchachenko,[§] Yasujiro Murata,[⊥] and Koichi Komatsu[⊥]*Department of Chemistry, Columbia University, New York, New York 10027, Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13902, Department of Chemistry, Brown University, Providence, Rhode Island 02912, Department of Chemistry, M. V. Lomonosov Moscow State University, Moscow 119992, Russia, and Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan*

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

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	η (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 ^c
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 ($7.16 \times 10^5 \text{ rad s}^{-1}$),¹⁰ *I* is the moment of inertia of H₂ ($4.6 \times 10^{-48} \text{ kg m}^2$), 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 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: $\tau_{\text{dip}}(\text{H}_2) = 0.20 \text{ ps}$ and $\tau_{\text{dip}}(\text{H}_2@\text{C}_{60}) = 2.1 \text{ ps}$. In a similar way, assuming that at the highest temperature the relaxation is dominated by the spin-rotation interaction, from

[†] Columbia University.[‡] State University of New York at Binghamton.^{||} Brown University.[§] M. V. Lomonosov Moscow State University.[⊥] Kyoto University.

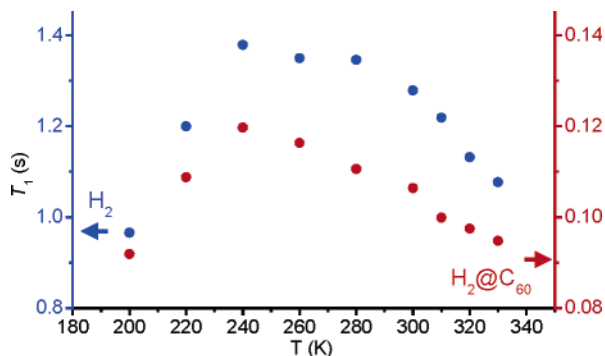


Figure 1. T_1 (s) of H_2 (blue dots) saturated at room temperature in deoxygenated toluene- d_8 and $H_2@C_{60}$ (red dots) dissolved in toluene- d_8 , at temperatures ranging from 200 to 330 K, at a field of 11.7 T.

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.

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.

References

- (1) Komatsu, K.; Murata, M.; Murata, Y. *Science* **2005**, *307*, 238–240.
- (2) Abragam, A. *Principles of Nuclear Magnetism*; Oxford University Press: Oxford, 1961; pp 316–322; pp 349–352. Bloembergen, N.; Purcell, E. M.; Pound, R. V. *Phys. Rev.* **1948**, *73*, 679–712. Bloom, M. *Physica* **1957**, *23*, 237–247. Waugh, J. S.; Johnson, C. S. *Discuss. Faraday Soc.* **1962**, *34*, 191–198. Lipsicas, M.; Hartland, A. *Phys. Rev.* **1963**, *131*, 1187–1193.
- (3) Bloom, M.; Oppenheim, I. *Can. J. Phys.* **1963**, *41*, 1580–1590.
- (4) Gilboa, H.; Chapman, B. E.; Kuchel, P. W. *J. Magn. Reson. A* **1996**, *119*, 1–5.
- (5) Conradi, M. S.; Luszczynski, K.; Norberg, R. E. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1979**, *19*, 20–31. Burnell, E. E.; de Lange, C. A.; Snijders, J. G. *Phys. Rev. A: At., Mol., Opt. Phys.* **1982**, *25*, 2339–2350.
- (6) These values of T_1 of H_2 in $H_2@C_{60}$ are in agreement with those of H_2 in an open-cage fullerene measured by solid state NMR: 160 ms at 295 K: Carravetta, M.; Murata, Y.; Murata, M.; Heinmaa, I.; Stern, R.; Tontcheva, A.; Samoson, A.; Rubin, Y.; Komatsu K.; Levitt, M. H. *J. Am. Chem. Soc.* **2004**, *126*, 4092–4093.
- (7) Powles, J. G.; Smith, D. W. G. *Phys. Lett.* **1964**, *9*, 239–241.
- (8) Krynicki, K.; Powles, J. G. *Phys. Lett.* **1963**, *4*, 260–262.
- (9) In the only study⁴ of the temperature dependence of the H_2 relaxation in a homogeneous molecular solvent (D_2O), the value of T_1 was found to increase as the temperature increased in the range 283–323 K.
- (10) Kellogg, J. M. B.; Rabi, I. I.; Ramsey, N. F.; Zacharias, J. R. *Phys. Rev.* **1939**, *56*, 728–743.
- (11) Hubbard, P. S. *Phys. Rev.* **1963**, *131*, 1155–1165.
- (12) An equation derived for spin-rotation interaction in small molecules undergoing angular diffusion steps of arbitrary size is perfectly equivalent to eq 2: Gordon, R. G. *J. Chem. Phys.* **1966**, *44*, 1830–1836.
- (13) τ_{sr} is related to collisions changing the speed and/or the orientation of the rotation of the molecule. As the temperature is increased the molecule rotates faster and according to theory the frequency of effective collisions in liquid decreases, τ_{sr} becoming longer and longer. Green, D. K.; Powles, J. G. *Proc. Phys. Soc.* **1965**, *85*, 87–102.
- (14) An extreme alternative to the continuum model expressed by eqs 1 and 2 is the theory of gas phase relaxation of H_2 .² In gas phase both the dipolar and the spin-rotation interaction depend on J through: $1/T_{1sr} = 2/3\gamma_H^2 H'^2 J(J+1)\tau_c$ and $1/T_{1dip} = 6\gamma_H^2 H''^2 J(J+1)/((2J-1)(2J+3))\tau_c$, respectively, where $H' = 27$ G and $H'' = 34$ G¹⁰ and τ_c depends on the frequency of collisions. The increase of T_1 with increasing temperature would arise from the expected decrease of τ_c with increasing collision frequency in gas phase and from the dependence of T_{1dip} on J , while the decrease of T_1 would arise from the dependence of T_{1sr} on J . The contributions to T_1 from different J states may be modeled quantitatively by weighting the T_1 calculated for each J by the Boltzmann population of the J state.³ Thus, it is possible to calculate from the experimental values of T_1 a correlation time τ_c of 0.51 and 0.39 ps for H_2 and 5.2 and 4.4 ps for $H_2@C_{60}$, respectively, at 200 and 330 K. Extension of this model to the temperature dependence of T_1 is presently being explored. (M. H. Levitt, private communication).
- (15) Warnock, J.; Awschalom, D. D. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1987**, *35*, 1962–1964.
- (16) Rubtsov, I. V.; Khudiakov, D. V.; Nadochenko, V. A.; Lobach, A. S.; Moravskii, A. P. *Chem. Phys. Lett.* **1994**, *229*, 517–523. Irwin, A. D.; Assink, R. A.; Henderson, C. C.; Cahill, P. A. *J. Phys. Chem. A* **1994**, *98*, 11832–11834.
- (17) Shang, X.; Issa, M. H.; Rodriguez, A. A. *J. Phys. Chem. A* **1998**, *102*, 7731–7734.
- (18) Santos, F. J. V.; de Castro, C. A. N.; Dymond, J. H.; Dalaouti, N. K.; Assael, M. J.; Nagashima, A. *J. Phys. Chem. Ref. Data* **2006**, *35*, 1–8.
- (19) Loeb, L. B. *The Kinetic Theory of Gases*; Dover Publications, Inc.: New York, 1961; Appendix I.
- (20) Similar conclusions about the motion of H_2 in both the gas and liquid phases are inferred from T_1 measurements.² Further, Raman spectra of H_2 in water indicates that H_2 retains its rotational angular momentum in solution: Taylor, D. G., III; Strauss, H. L. *J. Chem. Phys.* **1989**, *90*, 768–772.
- (21) Hu, C.-M.; Zwanzig, R. *J. Chem. Phys.* **1974**, *60*, 4354–4357. Dote, J. L.; Kivelson, D. *J. Phys. Chem.* **1983**, *87*, 3889–3893.
- (22) Yaws, C. L. *Handbook of Viscosity*; Gulf Publishing Company: Houston, TX, 1995.
- (23) Holz, M.; Mao, X.-A.; Seiferling, D. *J. Chem. Phys.* **1996**, *104*, 669–679.
- (24) As for H_2 in solvents, extending the measurement of T_1 to more solvents, there is a rough correlation of T_1 with molar volume of the solvent and a significantly better correlation with molar free volume (molar volume corrected by the actual molecular volume).