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Moudrakovski, Igor L.; Ripmeester, John A

National Research Council Canada
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Canada

Comment on "Exploring Dynamics and Cage–Guest Interactions in Clathrate Hydrates Using Solid-State NMR"

Igor L. Moudrakovski[†] and John A Ripmeester*[,‡]

[†]Max Planck Institute for Solid State Research, Stuttgart 70569, Germany
[‡]National Research Council Canada, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada

Ⓢ *Supporting Information*

Structure II tetrahydrofuran (THF) hydrate is one of the most frequently studied clathrate hydrates as it is easily made by freezing a solution of composition THF·17H_2O. The resulting hydrate is stable at atmospheric pressure up to a congruent melting point of 277.5 K (4.4 °C).[1,2] This hydrate is often used as a proxy for studies of materials that are more difficult to prepare, such as natural gas hydrates.[3−8] As a system for learning about guest−host interactions, the dynamics of both guest (THF/THF-d_8) and host (H_2O/D_2O) have been of wide interest as shown by the large number of solid-state NMR and dielectric measurements performed over a temperature range from ∼4 K up to near the melting point at 277.5 K.[9−23] Both guest and water molecular reorientation and water diffusion have been observed, and various mechanistic models, including the effects of various defects, have been proposed to account for the experimental results. Transient guest−host hydrogen bond formation in THF and other ether and ketone hydrates was first proposed by Davidson[11] and confirmed from spectroscopic measurements,[15,24] molecular dynamics simulation,[25,26] and single crystal X-ray diffraction.[27] The paper featured in the title of this Comment[23] recently reported yet another set of measurements, six longitudinal ^{1}H relaxation times (T_1) on THF·17D_2O, this time under magic angle spinning (MAS) conditions, purportedly to obtain high resolution information as there are two sets of resolvable protons on the inequivalent methylene carbons. Since the results of these measurements were very different from T_1 measurements taken on static samples, an explanation was proposed that involved changes in the THF reorientational activation energy from ∼4 kJ/m at T < 200 K to nearly 20 kJ/m at T > 200 K. This radical change was attributed to increased hydrogen bonding between THF and D_2O. We think this is rather unlikely for ether−water interactions. If we take the difference in activation energies for guest reorientation for cyclopentane hydrate and THF hydrate, ∼16 kJ/mol, attribute this to hydrogen bond formation in THF hydrate, and compare this to the estimated hydrogen bond energy in ice at 16−32 kJ/mol,[28] it would predict that THF should be a good hydrate inhibitor rather than a weakly interacting hydrate guest as it will compete with the hydrogen bond formation between water molecules. We have taken literature T_1 data obtained for static samples of sII deuteriohydrates of THF (ethylene oxide (EO)-d_4), cyclopentane, and dioxolane (Figure 1) published by Jacobs, Zeidler, and Kanert,[18] (Figure S1) and compared these with the MAS T_1 measurements (gray rectangle marked a,
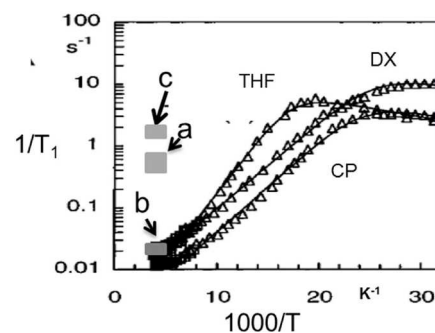

Figure 1. Relaxation rates $1/T_1$ as a function of inverse temperature for the sII doubledeuteriohydrate of tetrahydrofuran and ethylene oxide (1THF·0.5EO-d_4) and the deuteriohydrates of cyclopentane (CP) and 1,3-dioxolane (DX) from ref 18. The original figure is reproduced in the Supporting Information with permission from ref 18. Copyright 1997 American Chemical Society. The a marks the area in which the six MAS $1/T_1$ measurements from ref 25 occur, and b marks the area in which the 11 new MAS $1/T_1$ measurements are found. The c marks the area in which the static sample $1/T_1$ measurements for CP hydrate from ref 25 are located.

Figure 1).[23] The literature T_1 data for the three hydrates show that the relaxation rates decrease with increasing temperature, with some flattening out of the curves at the highest temperature of measurements. In agreement with other measurements, this trend in T_1 is associated with ^{1}H dipolar relaxation due to the reorientational motion of guest molecules in the hydrate cavities in the fast motion limit. The flattening out of the T_1 curves leads to a T_1 maximum,[10,12] and then to a decrease in T_1 with increasing temperature as slow water motion starts to contribute to the relaxation. This gives a frequency-dependent T_1 decrease, evident from measurements at lower frequencies (10 and 30 MHz[10,12]) to a new T_1 minimum, not observed as it would occur above the sample melting point. This new motion is a reorientation of the water molecules, which is also observable by $T_{1\rho}$ measurements and usually assigned to be a process driven by the diffusion of Bjerrum defects.[29,30] The guest T_1 relaxation responds to this motion by (a) cross relaxation of ^{1}H to ^{2}H in water, (b) spin diffusion to residual ^{1}H in the D_2O, and (c) changes in guest

motion as the symmetry of the hydrate cages changes when the disorder in the water proton positions becomes dynamic. This picture is generally consistent with all static line width, T_1, and $T_{1\rho}$ experimental results.

Upon examination of the MAS T_1 data that were recently reported (Figure 1, gray area marked as a), the question that arises is why the results for the spinning sample are so different (by a factor of ~25) from the static sample results obtained from the literature. The authors also measured T_1's for a static sample of THF deuteriohydrate which were somewhat different from the spinning sample results, but again this T_1 data set is well over an order of magnitude different from the other static sample measurements reported in the literature. As explanation, the authors offer the following, "This further illustrates the importance of using MAS rather than static NMR for proper characterization of the dynamics of the guest at these temperatures" but offer no reason as to why one set of data is "better" than the other, or why both sets of their measurements are over an order of magnitude different from previously measured values. We note further that the cyclopentane deuteriohydrate T_1 measurements reported in the paper[23] suffer from the same problem as those for THF deuteriohydrate; in this case, the new measurements[23] differ from previously published data by nearly 2 orders of magnitude (see Figure 1). Considering NMR fundamentals, in going from nonspinning to spinning samples, one might expect the T_1 values to increase as some of the contributing relaxation pathways may become less efficient. Thus, this cannot explain the data from ref 23, and it leaves us to consider experimental problems as a possible cause of the differences in relaxation time measurements. The most straightforward approach to check the validity of the data set that does not appear to match previous work is just to repeat the measurements. Following proper procedures for eliminating air from the samples during preparation, loading, and running the experiments, a new set of data was obtained. Figure S2 shows ^1H MAS spectra, and Table S1 lists MAS $1/T_1$ values obtained for a sample of THF deuteriohydrate, and these are shown in outline in the gray box marked b in Figure 1 and in detail in Figure 2. We note that the T_1's obtained on our MAS sample agree with the previously reported data obtained for the static sample from ref 18. The detailed plot shown in Figure 2 indicates that the data follow the expected behavior as does the data set from the literature
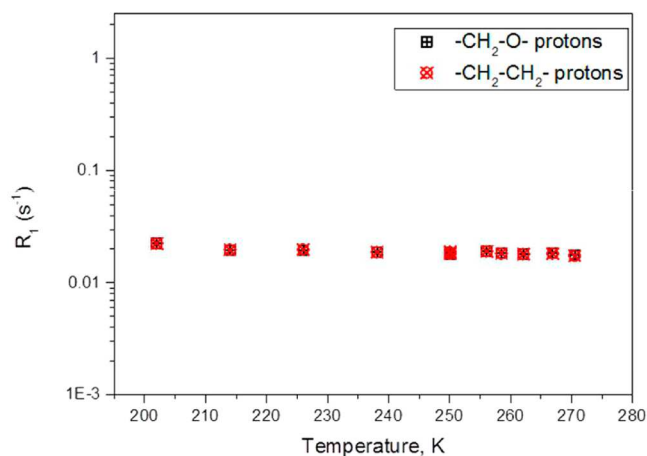
shown in Figure 1. The main point of our Comment is to point out that the T_1 measurements reported in ref 23 are not correct, as can be seen by comparison of the data in ref 23 with both our measurements and previously published measurements.[18] We also conclude that T_1 measurements taken for static and MAS samples of THF·17D$_2$O are very similar, so that there are no particular advantages in using MAS methods in this case. A further conclusion is that the mechanism based on the data in ref 23 should not be considered as meaningful in coming to an understanding of guest–host interactions in clathrate hydrates. It is beyond the scope of this Comment to explore the reasons for the discrepancies between the data in ref 23 and the other data presented. Most likely, the cause of the differences lies in oxygen contamination of the sample and/or poor sample quality.

Finally, a comment can be made regarding the magnitude of the THF–hydrogen bonding interaction with the hydrate lattice. The activation energy for guest reorientation in THF· 17D$_2$O is 4.0 ± 0.2 kJ/m, and that in CP·17D$_2$O is 2.6 ± 0.2 kJ/m. Because of the similar shape and size of these two guests, the difference between the two activation energies could be associated with H-bond formation of THF with cage water which amounts to ~1.4 kJ/m. Thus, this indicates that there are differing degrees of "stickiness" between the guest molecules THF and CP and the cage walls because of multidirectional, transient hydrogen bonding of the THF guest.

■ EXPERIMENTAL DETAILS

The THF clathrate hydrate sample was prepared from anhydrous, inhibitor-free tetrahydrofuran (Sigma-Aldrich) and deuterium oxide (99.9 at. % D, Sigma-Aldrich), mixed in 1:17 molar ratio. The THF–D$_2$O mixture was placed in a glass tube equipped with a vacuum stopcock, connected to a vacuum line, and thoroughly outgassed by 5 consecutive freeze–pump–thaw cycles. The freezing was done in liquid nitrogen, and the frozen mixture was evacuated each time down to 10^{-2} mbar. For avoidance of contamination with oxygen, the outgassed solution was transferred into a Bruker 4 mm o.d. ZrO$_2$ MAS spinner in a glovebag flushed multiple times with dry nitrogen gas (99.999%, Westfalen AG, Muenster). After being filled with the mixture, the spinner was closed with a cap equipped with a Viton ring to prevent any leaks. Solid clathrate hydrate was formed directly in a rotating MAS spinner by cooling it from the room temperature down to 240 K and keeping it at that temperature overnight. All NMR measurements were performed on a Bruker Avance-III 400 MHz instrument using a standard Bruker 4 mm double resonance MAS probe. Dry nitrogen is used as spinning, bearing, and cooling gas. The spinning rate was kept between 9.1 and 7.5 kHz, with the higher spinning rates used for the higher temperatures. The temperature during experiments was regulated with a Bruker BVT3000 temperature controller. Actual temperature inside the spinner was calibrated with Pb(NO$_3$).[31] Most relaxation time measurements were performed using standard saturation recovery (SR) pulse sequence.[32] Several experiments were performed also using the inversion recovery (IR) sequence with virtually identical results. The RF field on the proton channel was set to 62.5 kHz (π/2 pulse of 4 μs), and 16 appropriately spaced time delays were used in each experiment.

Figure S2 shows the ^1H NMR spectra for the complete range of temperatures studied. Above 270 K there is a small contribution of liquid THF which is resolved from the spectrum of the solid. Similarly, a tiny signal from ^1H in

Figure 2. Relaxation rate of THF·17D$_2$O obtained under MAS conditions (this work).

HDO is observable above 270 K at 4.8 ppm. Below the eutectic at around 270 K, the liquid contributions to the THF spectrum are no longer observed. This attests to the absence of excess liquid THF.

In our sample, made with 99.9% D_2O, the residual protons in HDO are outnumbered by THF protons by a factor of ~240, so it is reasonable to ignore the contribution of the former to THF proton relaxation. We also expect that a larger number of HDO protons in the sample should be visible in the MAS NMR spectrum, since protons are dilute, ^1H−^1H dipolar couplings are very small, and ^1H−^2H dipolar couplings are averaged by MAS. Besides, at temperatures above 200 K, water molecules are mobile, yet again decreasing the various dipolar interactions. Thus, HDO should give a reasonably sharp resonance, and there would not be any spectral overlap of THF and HDO contributions to the spectrum. For these reasons we deem that the application of a T_2 filter, as employed in ref 23, is unnecessary.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.7b00033.

Original figure used for Figure 1, ^1H MAS NMR spectra of THF·17D$_2$O at different temperatures, and a table of T_1 values for THF·17D$_2$O at different temperatures (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*E-mail john.ripmeester@nrc.ca.

ORCID ⓘ
John A Ripmeester: 0000-0002-4091-5120

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Notes
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■ REFERENCES

(1) Gough, S. R.; Davidson, D. W. Composition of tetrahydrofuran hydrate and the effect of pressure on the decomposition. *Can. J. Chem.* **1971**, *49*, 2691−2699.

(2) Makino, T.; Sugahara, T.; Ohgaki, K. Stability boundaries of tetrahydrofuran+ water system. *J. Chem. Eng. Data* **2005**, *50*, 2058−2060.

(3) Davidson, D. W.; Leaist, D. G.; Hesse, R. Oxygen-18 enrichment in the water of a clathrate hydrate. *Geochim. Cosmochim. Acta* **1983**, *47*, 2293−2295.

(4) Parameswaran, V. R.; Paradis, M.; Handa, Y. P. Strength of frozen sand containing tetrahydrofuran hydrate. *Can. Geotech. J.* **1989**, *26*, 479−483.

(5) Dai, S.; Lee, J.; Santamarina, J. C. Hydrate nucleation in quiescent and dynamic conditions. *Fluid Phase Equilib.* **2014**, *378*, 107−112.

(6) Priest, J. A.; Best, A. I.; Clayton, C. R.I. A laboratory investigation into the seismic velocities of methane gas hydrate-bearing sand. *J. Geophys. Res.: Solid Earth* **2005**, *110* (B4), B04203.

(7) Delli, M. L.; Grozic, J. L. H. Prediction performance of permeability models in gas-hydrate-bearing sands. *SPE Journal* **2013**, *18*, 274−284.

(8) Zhao, J.; Yao, L.; Song, Y.; Xue, K.; Cheng, C.; Liu, Y.; Zhang, Y. In situ observations by magnetic resonance imaging for formation and dissociation of tetrahydrofuran hydrate in porous media. *Magn. Reson. Imaging* **2011**, *29*, 281−288.

(9) Gough, S. R.; Hawkins, R. E.; Morris, B.; Davidson, D. W. Dielectric properties of some clathrate hydrates of structure II. *J. Phys. Chem.* **1973**, *77*, 2969−2976.

(10) Hayward, R. J.; Packer, K. J. Proton magnetic relaxation in ethylene oxide, tetrahydrofuran, and triethylene diamine as clathrate deuterates. *Mol. Phys.* **1973**, *25*, 1443−1450.

(11) Davidson, D. W. Clathrate Hydrates. In *Water. A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York, 1973; Vol. 2, pp 115−234.

(12) Garg, S. K.; Davidson, D. W.; Ripmeester, J. A. NMR behavior of the clathrate hydrate of tetrahydrofuran. I. Proton measurements. *J. Magn. Reson.* **1974**, *15*, 295−309.

(13) Davidson, D. W.; Garg, S. K.; Ripmeester, J. A. NMR behavior of the clathrate hydrate of tetrahydrofuran. II. Deuterium measurements. *J. Magn. Reson.* **1978**, *31*, 399−410.

(14) Ripmeester, J. A.; Garg, S. K.; Davidson, D. W. NMR behavior of the Clathrate Hydrate of Tetrahydrofuran. III. Effect of Oxygen. *J. Magn. Reson.* **1980**, *38*, 537−544.

(15) Davidson, D. W.; Ripmeester, J. A. NMR, NQR and Dielectric Properties of Clathrates. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 3, pp 69−123.

(16) Ripmeester, J. A. Pulsed nuclear magnetic resonance study of deuteron lineshapes in clathrate hydrates. *Can. J. Chem.* **1977**, *55*, 78−81.

(17) Albayrak, C. M.; Zeidler, D.; Küchler, R.; Kanert, O. NMR relaxation of tetrahydrofuran in clathrate hydrate. *Ber. Bunsengesellsch. Phys. Chem.* **1989**, *93*, 1119−1122.

(18) Jacobs, D. M.; Zeidler, M. D.; Kanert, O. Proton magnetic relaxation studies of various guest molecules in clathrate hydrates. *J. Phys. Chem. A* **1997**, *101*, 5241−5249.

(19) Bach-Vergés, M.; Kitchin, S. J.; Harris, K. D. M.; Zugic, M.; Koh, C. A. Dynamic properties of the tetrahydrofuran clathrate hydrate, investigated by solid state ^{2}NMR Spectroscopy. *J. Phys. Chem. B* **2001**, *105*, 2699−2706.

(20) Kirschgen, T. M.; Zeidler, M. D.; Geil, B.; Fujara, F. A deuteron NMR study of the tetrahydrofuran clathrate hydrate. *Phys. Chem. Chem. Phys.* **2003**, *5*, 5247−5252.

(21) Ba, Y.; Ripmeester, J. A.; Ratcliffe, C. I. Water molecular reorientation in ice and tetrahydrofuran clathrate hydrate from lineshape analysis of ^{17}O spin-echo NMR spectra. *Can. J. Chem.* **2011**, *89*, 1055−1064.

(22) Nelson, H.; Ihrig, A.; Kahlau, R.; Kibies, P.; Kast, S. M.; Böhmer, R. Deuteron magnetic resonance and dielectric studies of guest reorientation and water dynamics in six clathrate hydrates containing ring-type guests. *J. Non-Cryst. Solids* **2015**, *407*, 431−440.

(23) Sengupta, S.; Guo, J.; Janda, K. C.; Martin, R. W. Exploring dynamics and cage−guest interactions in clathrate hydrates using solid-state NMR. *J. Phys. Chem. B* **2015**, *119*, 15485−15492.

(24) Buch, V.; Devlin, J. P.; Monreal, I. A.; Jagoda-Cwiklik, B.; Uras-Aytemiz, N.; Cwiklik, L. Clathrate hydrates with hydrogen-bonding guests. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10245−10265.

(25) Alavi, S.; Susilo, R.; Ripmeester, J. A; Linking microscopic guest properties to macroscopic observables in clathrate hydrates: Guest-host hydrogen bonding. *J. Chem. Phys.* **2009**, *130*, 174501.

(26) Alavi, S.; Ripmeester, J. A. Effect of small cage guests on hydrogen bonding of tetrahydrofuran in binary structure II clathrate hydrates. *J. Chem. Phys.* **2012**, *137*, 054712.

(27) Alavi, S.; Udachin, K.; Ripmeester, J. A. Effect of guest−host hydrogen bonding on the structures and properties of clathrate hydrates. *Chem. - Eur. J.* **2010**, *16*, 1017−1025.

(28) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W.H. Freeman and Company: San Fransisco, 1960.

(29) Bjerrum, N. Structure and Properties of Ice. *Science* **1952**, *115*, 385−390.

(30) Onsager, L.; Runnels, L. K. Diffusion and relaxation phenomena in ice. *J. Chem. Phys.* **1969**, *50*, 1089−1103.

(31) Bielecki, A.; Burum, D. P. Temperature dependence of [207]Pb MAS spectra of solid lead nitrate. An accurate, sensitive thermometer for variable-temperature MAS. *J. Magn. Reson., Ser. A* **1995**, *116A*, 215−220.

(32) Fukushima, E.; Roeder, S. B. W. *Experimental Pulse NMR*; Addison-Westley Publishing Company, Inc.: Reading, Massachsetts, 1981.