

Comment on “A deuteron NMR study of the tetrahydrofuran clathrate hydrate. Part II: Coupling of rotational and translational dynamics of water” by T. M. Kirschgen, M. D. Zeidler, B. Geil and F. Fujara, *Phys. Chem. Chem. Phys.*, 2003, 5, 5247

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Received 11th July 2003, Accepted 27th October 2003

First published as an Advance Article on the web 2nd February 2004

A recent paper by Kirschgen *et al.*¹ reports a ²H NMR study of the dynamic properties of the water molecules in the tetrahydrofuran (THF) clathrate hydrate. Their paper leads to some differences in the interpretation on the water dynamics from that reported in our earlier ²H NMR study² of the same material (in which we investigated the dynamics of both the water and THF molecules). Given that Kirschgen *et al.*¹ have chosen to make specific comments (see Appendix in ref. 1) relating to the work described in our paper, we take the opportunity in the present paper to respond to their comments.

There have been several previous studies, using a variety of techniques, of the dynamic properties of the water molecules in the THF clathrate hydrate. This earlier work has been cited in ref. 2. The different experimental approaches used in these previous studies concur on the fact that the dynamic model involves reorientation of the water molecules, and reorientation of the water molecules in the form of a four-site tetrahedral jump motion is indeed a feature of both our model² and the model of Kirschgen *et al.*¹ It is relevant first to elaborate the essential features of the two models.

Analysis of our ²H NMR results for THF-D₂O led² to a dynamic model comprising two dynamically distinguishable types of water molecule, each undergoing the four-site tetrahedral jump motion but at different rates. It was suggested in ref. 2 that the existence of two dynamically distinct types of water molecule might be related to the fact that there are crystallographically different types of water molecule in the crystal structure (the structure contains three different water sites in the ratio 1:4:12, although the contribution of the first type of water molecule to the ²H NMR spectrum might justifiably be neglected due its low relative population). Above 193 K, the dynamics of both components are in the intermediate motion regime (correlation time between 10⁻⁷ s and 10⁻³ s). From fitting the ²H NMR lineshapes to determine the rates of the two components of motion as a function of temperature, the activation energies were determined (for Model B2 in ref. 2) to be 31 kJ mol⁻¹ for the component of higher population and 28 kJ mol⁻¹ for the component of lower population. For comparison, values of the activation energy determined previously have been 30.1 kJ mol⁻¹ from solid state ¹H NMR³ and 30.9 kJ mol⁻¹ from dielectric studies.⁴ The activation energy (56.5 kJ mol⁻¹) obtained from ²H NMR lineshape studies of hexagonal ice⁵ is significantly higher than any of the values reported for THF-D₂O.

The basic dynamic model proposed by Kirschgen *et al.*¹ includes the four-site tetrahedral jump motion discussed

above, but these authors also invoke an additional slower aspect of dynamics, comprising proton jumps between neighbouring water molecules. It is important to recognize the differences in the ²H NMR techniques employed in our work (analysis of quadrupole echo ²H NMR lineshapes and measurement of ²H NMR spin-lattice relaxation times) and in the work of Kirschgen *et al.* (stimulated echo ²H NMR), and to recognize the fact that the slow rate of the proton jump motion, at the temperatures studied, is outside the range of timescales that can be probed using the techniques employed in our work. Indeed, the fact that quadrupole echo (solid echo) ²H NMR lineshapes of the type reported in our paper are unaffected by the proton jump motion is indeed stated explicitly by Kirschgen *et al.* in Section IV.E of their paper. Thus, analysis of our data did not require inclusion of proton jumps between neighbouring water molecules within the dynamic model.

The discrepancy between our dynamic model and that of Kirschgen *et al.*¹ is that the four-site tetrahedral jump motion is based on a single type of behaviour in their model, whereas our model² involves two different types of water molecule undergoing this motion at different rates. As elaborated fully in ref. 2, a model comprising the four-site tetrahedral jump motion at a single rate does not give a satisfactory fit to our experimental ²H NMR lineshapes (see Fig. 4 of ref. 2), whereas a satisfactory fit is obtained for a model comprising the four-site tetrahedral jump motion with two different rates (see Fig. 6 of ref. 2). This fact is indisputable, and on this basis we favoured the model comprising two different dynamic components. Our conclusion that there are at least two dynamically distinguishable types of water molecule in the THF clathrate hydrate is in agreement with conclusions from previous dielectric studies.^{4,6} The physical basis for the existence of dynamically distinguishable water molecules (or, in the terminology used by Kirschgen *et al.*¹ the occurrence of two or more rates of diffusion of orientational Bjerrum defects) within the THF clathrate hydrate structure may originate from differences in the rate of Bjerrum defect diffusion along different pathways within the structure, recognizing that different pathways are not crystallographically equivalent. From the comments in the Appendix of their paper, it is apparent that Kirschgen *et al.* do not appreciate this possibility. In addition to this point, it is also relevant to note that one plausible means of introducing Bjerrum defects into the water framework could be *via* the occasional formation of hydrogen bonding from a water molecule in the host framework to the THF guest molecule (which may act as a hydrogen bond acceptor), and clearly

the propensity for this to occur may be different for the crystallographically different water sites, with corresponding consequences in regard to differences in dynamic properties.

According to the paper of Kirschgen *et al.*,¹ it is claimed that our observation of two types of water molecule undergoing four-site tetrahedral jumps at different rates is *not* due to having two dynamically different types of water molecule within the THF clathrate hydrate, but rather that the sample used in our studies was not a single phase, and instead comprised hexagonal ice together with the THF clathrate hydrate. We refute this claim based on the following points.

Point 1: In our sample preparation and handling procedure, precautions were taken to minimize the risks of ice being present in the sample used for our solid state NMR studies. First, the molar THF:D₂O ratio (1:16.9, see ref. 2) used in our preparation procedure represents an excess of THF over the stoichiometric ratio (1:17) in THF clathrate hydrate; independent studies (see also Point 2 below) have shown that the use of a deficit of D₂O (*i.e.* excess of THF) in this manner inhibits the co-formation of ice during formation of the THF clathrate hydrate. Second, as stated in ref. 2, all handling of our material after crystallization was carried out in a cold room at a temperature below the melting temperature of the THF clathrate hydrate but above the melting temperature of ice. After removing the flasks containing the solid material from the cold bath used for crystallization, the flasks were allowed to stand in the cold room for an appreciable time before collecting the crystals and transferring them to the sample tubes to be used in the solid state NMR studies. Any ice present in the initially-formed solid sample would have melted at the temperature of the cold room; no actual melting was observed during this handling procedure, suggesting that the amount of ice present, if any, was negligible.

Point 2: Independent studies,⁷ involving *in situ* preparation of the material within a differential scanning calorimetry (DSC) apparatus using the same procedure for preparation of THF clathrate hydrate employed in our work, indicate that no appreciable amounts of ice are formed. These studies involved preparation of the solid material by cooling the liquid water/THF mixture within the DSC apparatus; the relative amounts of ice and THF clathrate hydrate present within the solid material were assessed by subsequent heating of the solid material and by measuring the magnitudes of endotherms at the temperatures associated with melting of ice and melting of the THF clathrate hydrate.

Point 3: As stated above, independent ²H NMR studies of the dynamic properties of the water molecules in hexagonal ice have been reported previously.⁵ Although the same four-site tetrahedral jump motion occurs, the evolution of the ²H NMR lineshape as a function of temperature (and hence the rate of motion as a function of temperature) differs between our sample of THF clathrate hydrate (see Fig. 6 of ref. 2) and the sample of ice studied by Wittebort *et al.* (see Fig. 1 of ref. 5). The different rates as a function of temperature correspond to different activation energies. As already stated in ref. 2 and quoted above, the activation energies obtained in our work are significantly lower than that reported for ice.

Point 4: Other aspects of comparison between our results and the independent ²H NMR study of hexagonal ice⁵ support the view that our sample of THF clathrate hydrate does not contain ice. In Fig. 2 of ref. 2, we show our experimental ²H NMR lineshapes from 193 K to 263 K. At 243 K, the lineshape comprises a narrow central line and a broad component. The broad component (and part of the central line) arises from the slow component in our dynamic model. At 263 K, *only* the narrow central line is observed, and there is no evidence (even on close inspection following baseline expansion) that the lineshape contains any broad component at this temperature. In contrast for ice, as reported in ref. 5, the ²H NMR lineshape contains a broad component at all temperatures in the

range covered by our work (for example, the lineshape at 262 K for ice in ref. 5 clearly contains a broad component, whereas the lineshape at 263 K for our sample in Fig. 2 of ref. 2 does not contain a broad component). Thus, if (as implied by Kirschgen *et al.*)¹ our slow component is due to the presence of ice, *i.e.* if the broad component in our ²H NMR lineshape at 243 K is due to ice, then (notwithstanding the attenuation factor on passing through the intermediate motion regime, which has been taken into consideration in our analysis) a broad component should *also* be observed in our ²H NMR lineshape at 263 K. As discussed above, there is no evidence for a broad component in our ²H NMR lineshape at 263 K, from which it is concluded that the slow component in our material gives a contribution to the ²H NMR lineshape that has a *different* temperature evolution to that of ice. We may thus discount the suggestion that the broad component in our ²H NMR lineshape is due to ice.

In conclusion, we refute the claim of Kirschgen *et al.*¹ that the sample used in our work reported in ref. 2 was a mixture of ice and THF clathrate hydrate. Our solid state ²H NMR results fully support the assignment that there are two dynamically distinguishable types of water molecule in the THF clathrate hydrate, which undergo four-site tetrahedral jump motions at different rates, in agreement with previous reports in the literature⁴ using a different experimental approach. We emphasize that our work and that of Kirschgen *et al.* employed different ²H NMR techniques and that proton jumps between neighbouring water molecules, as invoked in the dynamic model of Kirschgen *et al.*, occur on a longer timescale (*i.e.* slower process) than that probed by the quadrupole echo ²H NMR lineshape analysis and ²H NMR spin-lattice relaxation time measurements reported in our paper. The activation energy (12.3 kJ mol⁻¹) reported by Kirschgen *et al.* for the proton jumps between neighbouring water molecules in their work on THF clathrate hydrate is interesting, as it appears to be substantially lower than would be expected for a process involving breakage of a covalent bond.

Finally, while the majority of the work described in the paper of Kirschgen *et al.*¹ is focused on the use of different solid state NMR techniques from those employed in our own work,² they nevertheless also report (see Fig. 8 of ref. 1) ²H NMR lineshapes recorded using the solid echo (quadrupole echo) technique analogous to those reported in our paper (see Fig. 6 of ref. 2). It is noteworthy that the quality of fit between experimental and simulated ²H NMR lineshapes in Fig. 8 of the paper by Kirschgen *et al.* is substantially poorer than that in Fig. 6 of our paper. The fact that there are some differences between the actual experimental ²H NMR lineshapes reported in refs. 1 and 2 might suggest that the samples of THF hydrate used in the work of Kirschgen *et al.* and in our work are not identical, although the possibility that these differences may arise due to other factors, such as the history of the sample or details of the NMR measurements, cannot be discounted.

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