High-pressure boundary of hydrate formation in the tetrahydrofuran–water system

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Using Raman spectroscopy, we found that at a pressure of 28.5 kbar tetrahydrofuran pentahydrate decomposes to solid tetrahydrofuran and ice; solid tetrahydrofuran retains its structure in the pressure range 1 bar–105 kbar.

The aim of this work was to study the hydrate formation in the tetrahydrofuran (THF)–water system at high pressures. Clathrate hydrates with cubic structure II $THF\cdot 17H_2O$ (CS-II, stable in the pressure range 1 bar–2.3 kbar)[1] and cubic structure I $THF\cdot 7H_2O$ (CS-I, stable in the pressure range 2.3 –5.3 kbar)[1,2] are known to form in this system. The pentahydrate $THF\cdot 5H_2O$ is stable at higher pressures (5.3–15 kbar).[1,4] Data concerning the temperature dependence of the heat conductivity of the pentahydrate show that this hydrate is not of the clathrate type. The phase diagram of the THF–water system at pressures up to 15 kbar was reported in refs. 1 and 4.

In this work we present the Raman spectra of the hydrate $THF\cdot 5H_2O$ (in the pressure range 7–30 kbar) and pure THF (in the pressure range 7–105 kbar). All of the spectra were recorded at room temperature (20±1 °C). A high-pressure apparatus with a diamond-anvil cell (DAC) was used.[5] A DILOR OMARS 89 spectrometer equipped with a CCD Princeton Instr. LN/CCD-1100Pb detector was used for recording the Raman spectra. The Raman spectra were excited by a 514.5 nm line of an argon ion laser. The detector was calibrated using the characteristic lines of a neon plasma. The pressure was measured by the frequency shifts of the R_1 ruby luminescence line ($\Delta\nu = \pm 0.3$ cm^{-1}).[6] Small pieces of ruby were placed in the high-pressure cell together with the samples. Tetrahydrofuran used in our experiments was purified to remove peroxides, dried with $LiAlH_4$ and then twice distilled. A 75% THF solution in water was loaded into the DAC for examining the Raman spectra of the pentahydrate. Spectral data were collected from single crystals of the hydrate which were grown in the DAC at a pressure of about 7 kbar. In the case of pure THF, spectral data were collected from liquid or polycrystalline solid THF samples.

Data concerning the spectra are summarised in Table 1, and typical spectra are shown in Figure 1. Crystals of the $THF\cdot 5H_2O$ hydrate are in equilibrium with the liquid phase in the pressure range 7–28 kbar. No qualitative changes were observed in the system in this region. The visually observed shape of $THF\cdot 5H_2O$ crystals can be characterised as more or less distorted hexagonal prisms. At a pressure of 28.5 kbar, solidification of the equilibrium liquid phase takes place (crystallization of a tetrahydrofuran-rich eutectic mixture and crystallization of pure THF take place at the same pressure). At a pressure of 30.5 kbar, a transformation accompanied by significant changes in the THF spectra takes place in the $THF\cdot 5H_2O$ hydrate (Figure 1). A careful analysis of the spectra of pure solid THF and the $THF\cdot 5H_2O$ hydrate after the transformation demonstrated that these spectra are identical to within the experimental error. This fact allowed us to conclude that the transformation observed is decomposition of the $THF\cdot 5H_2O$ hydrate to pure solid THF and ice VII. The density (or, equivalently, the packing density) of the hydrate phases is the main factor responsible for the stability of these phases at high pressures: the phase (or a mixture of phases) with the lowest volume is most stable, all other factors being the same. We may conclude that the formation of a new close-packed phase in the system (solid THF) causes decomposition of the $THF\cdot 5H_2O$ hydrate. Thus, the high-pressure boundary of the hydrate formation was experimentally found for the systems in which CS-II clathrate hydrates are formed at ambient pressure. All steps of the transformations occurring in such systems with increasing pressure[1] were experimentally illustrated for the first time:

CS-II clathrate hydrates → CS-I clathrate hydrates → non-clathrate hydrates → absence of the hydrate formation

Shifts of the Raman bands with pressure were linear for all substances under consideration (liquid THF, solid THF and the $THF\cdot 5H_2O$ hydrate). Relative intensities and band positions approximated to 1 bar in the spectra of liquid and solid THF are in a satisfactory agreement with the published data.[7] The spectra of solid THF being approximated to 1 bar exhibit some qualitative differences from the spectra of solid THF at 1 bar and

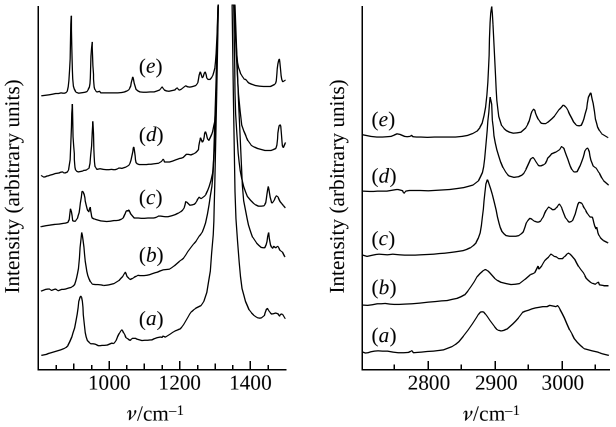

Figure 1 Typical Raman spectra of THF in the regions 800–1500 cm^{-1} (left) and 2700–3100 cm^{-1} (right). A very strong band at 1330 cm^{-1} corresponds to the C–C stretch vibrations in diamond: (*a*) pure liquid THF at 9.2 kbar, (*b*) the hydrate $THF\cdot 5H_2O$ at 13 kbar, (*c*) the hydrate $THF\cdot 5H_2O$ in the course of decomposition at 30.3 kbar, (*d*) the decomposed hydrate $THF\cdot 5H_2O$ at 39.3 kbar (solid THF–ice mixture), (*e*) pure solid THF at 40.8 kbar.

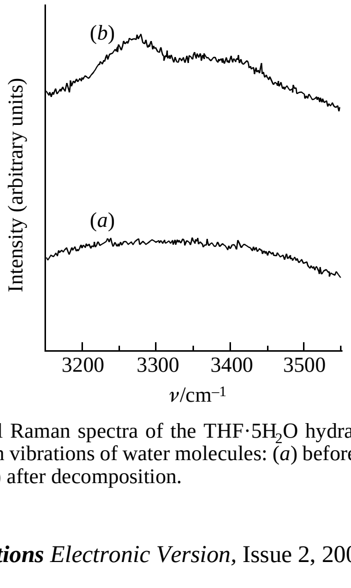

Figure 2 Typical Raman spectra of the $THF\cdot 5H_2O$ hydrate in the region of the O–H stretch vibrations of water molecules: (*a*) before decomposition of the hydrate, (*b*) after decomposition.

Table 1 Raman spectra of liquid THF, solid THF and the THF·$5H_2O$ hydrate at high pressures.[a]

Hydrate THF·$5H_2O$ in the pressure range 7–30 kbar		Pure solid THF in the pressure range 28.5–105 kbar		Pure liquid THF in the pressure range 7–28.5 kbar	
ν/cm^{-1} at 1 bar	$\frac{\partial\nu}{\partial P}$/ cm^{-1} kbar^{-1}	ν/cm^{-1} at 1 bar	$\frac{\partial\nu}{\partial P}$/ cm^{-1} kbar^{-1}	ν/cm^{-1} at 1 bar	$\frac{\partial\nu}{\partial P}$/ cm^{-1} kbar^{-1}
888(5)	0.8(5)	839(1)	0.21(2)	898(2)	0.2(1)
917.9(7)	0.25(4)	863(3)	0.03(7)	914(2)	0.6(1)
919(6)	0.5(2)	879(3)	0.15(4)	945(1)	0.79(7)
1033.7(6)	0.58(3)	884.8(4)	0.20(1)	1028(1)	0.71(6)
1072(2)	0.3(1)	924(2)	0.15(4)	1064(1)	0.31(5)
1222(2)	0.1(1)	933.4(8)	0.42(1)	1139(2)	0.2(1)
1251(1)	0.10(7)	960(1)	0.27(3)	1179(2)	0.2(1)
1446.9(4)	0.11(3)	1046.9(8)	0.48(1)	1224(3)	0.5(1)
1472(3)	0.0(2)	1145.4(2)	0.09(1)	1244(2)	0.3(1)
1488(2)	0.0(1)	1181.2(7)	0.21(1)	1445(1)	0.19(4)
2723(2)	0.1(1)	1199.2(8)	0.39(1)	1482(2)	0.7(1)
2878(2)	0.4(1)	1244.7(8)	0.30(1)	2719(1)	0.63(5)
2916(2)	0.2(1)	1259.6(3)	0.23(1)	2867(1)	1.15(3)
2944(1)	0.36(4)	1376(1)	0.22(2)	2944(3)	0.2(2)
2964(1)	0.52(3)	1465(1)	0.32(4)	2961(1)	0.52(5)
2961(2)	1.2(1)	1474.5(5)	0.19(1)	2976(1)	1.47(7)
2987(2)	1.4(1)	1483.3(7)	0.31(1)		
		1500.3(8)	0.33(1)		
		2737.1(9)	0.39(2)		
		2870.3(9)	0.57(2)		
		2935(1)	0.52(2)		
		2953(3)	0.82(5)		
		2962(2)	1.01(3)		
		3008(2)	0.77(3)		

[a]Positions of the bands with $\partial\nu/\partial P$ values are given in the 800–1500 and 2700–3100 cm^{-1} ranges. Relative intensities of the bands are shown in Figure 1.

low temperature, which were reported in ref. 7 (for example, a shift of the C–H stretching vibration bands). To our opinion, these differences are caused by the fact that a linear approximation is not valid in this case. According to ref. 8, the compressibility of molecular crystals (and, consequently, the most significant changes in intermolecular interactions) decreases most rapidly at pressures lower than 10 kbar. In the pressure range of interest (above 28.5 kbar), we deal with a strongly compressed crystal of THF. Intermolecular interactions in this crystal differ significantly from interactions in the same crystal at 1 bar; this fact will be responsible for changes in the spectrum of the crystal. It may be assumed that the packing motif of the high-pressure phase of solid THF has minor differences with the structure of solid THF determined at 1 bar.[9] We have not found any phase transitions in solid THF in the pressure range 28.5–105 kbar (20±1 °C). The changes in the THF spectra taking place during THF solidification at 28.5 kbar (20±1 °C) and 1 bar (–108 °C)[7] are identical and may be interpreted by the same way.

The spectra of the THF·$5H_2O$ hydrate are similar to the spectra of liquid THF. According to known data,[3] this hydrate is not a clathrate, and the properties of this hydrate are similar to those of the normal crystal (significant disordering is absent). As it was found by Cadioli *et al.*,[7] the Raman bands related to the ring-stretching C–O and C_α–C_β vibrations are near-degenerated in the spectra of liquid THF at room temperature. In the spectra obtained by us, these bands merged into a strong band at 914 cm^{-1}. Since the degeneracy of these bands is rather occasional any variation of the internal conditions should lead to splitting of them. It really takes place when the pressure increases (second band appears as a shoulder of this band), at low temperatures[7] and during crystallization of THF (Figure 1).[7] In the THF·$5H_2O$ hydrate this band does not split in the whole region of the hydrate stability. Further work is necessary to interpret this observation.

In the spectra of the THF·$5H_2O$ hydrate, the O–H stretching bands of water molecules were not observed in the spectral region which is characteristic of these bands, whereas corresponding bands in the spectra of ice VII (which appears after decomposition of the pentahydrate) were clearly visible (Figure 2). This can be explained by the arrangement of water molecules in the pentahydrate in several significantly different positions, which leads to the broadening of these bands.

In summary, we can say that at a pressure of 28.5 kbar tetrahydrofuran pentahydrate decomposes to solid tetrahydrofuran and ice (this is the first example of systems in which the formation of clathrate hydrates takes place). Solid tetrahydrofuran keeps its structure in the pressure range 1 bar–105 kbar.

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