

A Clathrate Hydrate of Formaldehyde[†]

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Clathrate hydrates, crystalline ices with voids suitable for guest molecules, occur naturally on earth with hydrocarbons, CO₂, O₂, N₂, and H₂S as guests and have been proposed to occur in extraterrestrial environments as well. Here we report a clathrate hydrate of formaldehyde prepared by vapor deposition of water vapor and formaldehyde generated by thermolysis of a polymeric poly(oxymethylene) precursor. Since formaldehyde is one of the more abundant interstellar gases and poly(oxymethylene) was the first extraterrestrial polymer identified, it is likely that formaldehyde hydrate exists in icy extraterrestrial environments. This hydrate cannot be expected to occur under ambient conditions on earth, as aqueous formaldehyde tends to hydrolyze to form a geminal diol.

Davy prepared the first clathrate hydrate nearly 200 years ago,¹¹ and even today clathrate hydrates continue to draw a great deal of interest as a research topic. One reason for this is that in the 1930s hydrates were implicated in the formation of solid plugs in natural gas pipelines,¹² and much effort continues to be directed at finding satisfactory methods of hydrate control.^{13,14} The microscopic nature of clathrate hydrates remained a mystery until in the 1950s their structures were shown to be of the guest–host type by X-ray diffraction,¹⁵ and an appropriate thermodynamic model was proposed.¹⁶ Today three families of clathrate hydrate structures are known for each of which a large number of guests have been identified.^{1,17,18} The cubic structure I hydrate has the ideal stoichiometry 2M_s•6M•46H₂O (M_s and M represent guests in small and large cages, respectively) and its structure belongs to space group *Pm3n*, with a cell constant $a \cong 1.2$ nm. Structure II hydrate, of ideal stoichiometry 16M_s•8M•136H₂O, belongs to space group *Fd3m*, with $a \cong 1.7$ nm.^{15,17} These hydrates also are known to form naturally, with guests which range in size from methane to *n*-butane, and they have been found both offshore and associated with permafrost.^{2,3} Also, “air” hydrates, belonging to the structure II family, have been identified inside glacier cores.⁵ The third family, hexagonal structure H hydrate of ideal stoichiometry 2M_s•3M_s•M•34H₂O, suggested to be isostructural with the clathrasil Dodecasil-1H,²⁰ was first identified as a unique structure from NMR and X-ray powder diffraction measurements in 1987¹⁹ (space group *P6/mmm*, $a \cong 1.22$ nm, $c \cong 1.00$ nm), although its detailed structure is still unknown. This hydrate can hold guests such as methylated butanes and pentanes, cycloalkanes such as cycloheptane, cyclooctane, methylcyclopentane and methylcyclohexane and other guests with van der Waals radii up to ~ 0.86 nm, and requires a small “helpgas” guest in the small cages for stability.¹⁹ Its natural existence was suggested in the original papers,^{18,19} and confirmatory evidence was published only very recently.⁴

Clathrate hydrates with guests such as CO₂, CO, CH₄, O₂, and N₂ also have been suggested to occur in association with the icy environments of the outer planets and comets.^{6,7} Since extraterrestrial conditions are entirely different from those on earth, there is considerable scope for the existence of hydrates

with unusual guest species. It has already been recognized that clathrate hydrates form quite readily from intimate mixtures of guest and water co-deposited at low temperatures,²¹ by annealing such mixtures, or by annealing highly porous amorphous solid water first exposed to low pressures of gases such as O₂, N₂, Kr, and CO^{22,23} and, recently also NO.²⁴ Formaldehyde is a molecule that has been associated with the extraterrestrial environment for a long time,⁸ and its linear polymer poly(oxymethylene) was the first polymer to be identified in space.⁹ Wickramasinghe went so far as to discuss the formation of anhydrous as well as hydrated polymers from the polymerization of formaldehyde on dust grains but did not consider hydrate formation.⁸ Normally, in a terrestrial environment, gas hydrates are formed by direct contact between liquid water or water vapor and guest material at suitable temperatures and pressures.^{1,14} Under such conditions formaldehyde hydrate cannot be expected to form, as formaldehyde in aqueous solution is hydrolyzed rapidly to give a geminal diol,¹⁰ and hence it is deemed to be unsuitable as a guest for the clathrate hydrates. However, we considered it entirely possible that deposition of formaldehyde gas along with water vapor at low temperatures may well allow a clathrate hydrate to form without interference from hydrolysis or polymerization. From the largest van der Waals diameter of formaldehyde, 0.47 nm, the molecule should be suitable as a guest for the structure I hydrate large cage, although there could be some occupancy of the small cage as well.¹

The clathrate precursor was prepared on a pyrex vacuum line by the slow co-condensation of metered amounts (6:1 ratio) of water vapor, and formaldehyde generated by thermolysis from poly(oxymethylene) (paraformaldehyde, Fisher), on a coldfinger cooled by liquid nitrogen. Deuterated, or partially deuterated, versions of the material were prepared by using heavy water and/or deuterated poly(oxymethylene) (paraformaldehyde-*d*₂, MSD Isotopes). Samples of the product were loaded into the variable-temperature sample cell of a Rigaku θ – θ X-ray powder diffractometer, or Pyrex sample tubes suitable for insertion into the solenoid coil of a low-temperature NMR probe, meanwhile handling the sample in liquid nitrogen. X-ray powder diffraction patterns were recorded with Co K α ($\lambda = 0.178\,92$ nm) radiation and temperatures were controlled with a Paar controller. Results showed that at 90 K most of the co-deposit was amorphous, although a few reflections can be attributed to ice Ic (Figure 1a). Annealing at 150 K showed that essentially all of the remaining amorphous material was converted to crystalline

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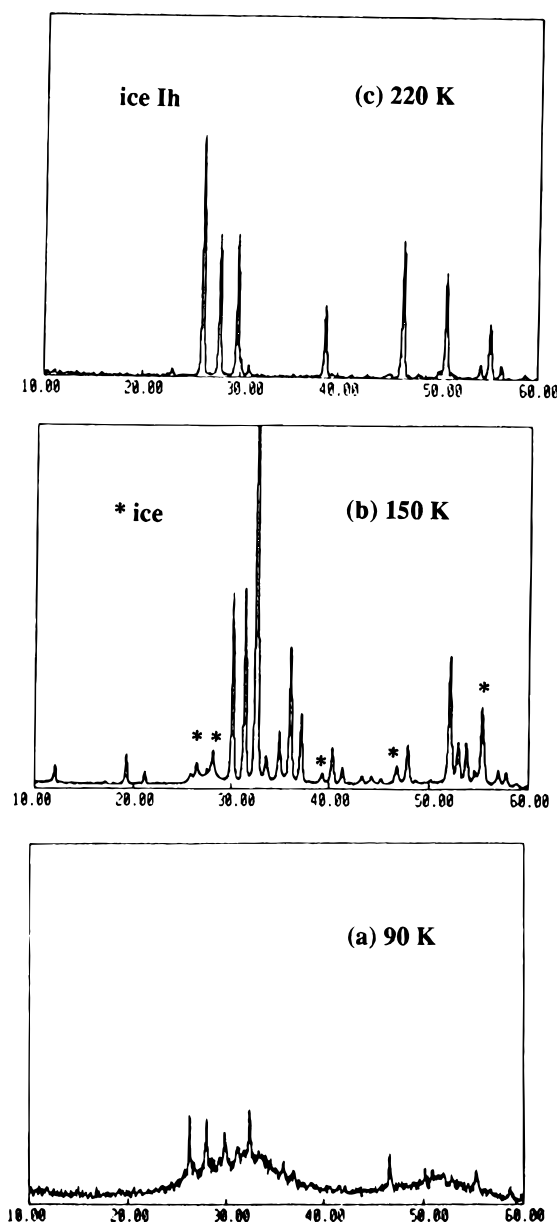


Figure 1. X-ray powder diffraction pattern of (a) a vapor deposit of water vapor and formaldehyde gas prepared from a paraformaldehyde precursor at 90 K; (b) after annealing at 150 K; (c) after annealing at 220 K.

product (Figure 1b). Most (17 of 20) of the reflections can be indexed in terms of a cubic structure **I** clathrate hydrate and a small quantity of ice Ic. Especially the low-angle reflections (110, 210, and 211) are diagnostic of the structure **I** lattice with its relatively large unit cell. A least-squares fit to 14 reflections yielded a lattice constant of 1.1971(3) nm, well within the usual range of values observed for the structure **I** hydrate lattice.^{1,15,17} Annealing in the open X-ray powder cell at temperatures above about 220 K converted much of the clathrate and ice Ic into ice Ih (Figure 1c).

²H NMR line shapes were recorded at 30.7 MHz on a Bruker MSL-200 NMR spectrometer. Figure 2a shows the ²H NMR line shape of formaldehyde-*d*₂ at 77 K. The doublet pattern with a splitting of 116.7 kHz leads to a quadrupole coupling constant $\chi (=e^2qQ/h)$ of 155.6 kHz, and is characteristic of the formaldehyde CD₂ group held rigidly in the formaldehyde/water deposit. For an annealed co-deposit of water and formaldehyde-*d*₂, a broad line (width at half-height 13 kHz) without much discernable structure is observed (Figure 2b). This is charac-

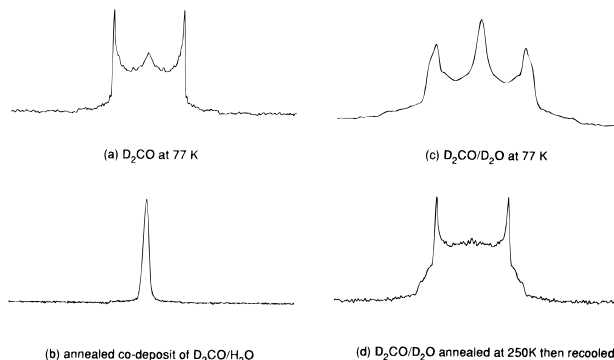


Figure 2. ²H NMR line shapes of (a) solid formaldehyde-*d*₂ at 77 K, (b) formaldehyde-*d*₂ clathrate hydrate made from annealing vapor-deposited water vapor and formaldehyde-*d*₂ annealed at 150 K and recorded at 77 K; (c) formaldehyde-*d*₂ clathrate deuteriohydrate at 150 K made by vapor depositing D₂O and formaldehyde-*d*₂ at 77 K; sample (c) but warmed to 250 K and recooled to 150 K.

TABLE 1: X-ray Diffraction Powder Pattern of Formaldehyde Clathrate Hydrate Listing Experimental *d* Spacings, and Those Calculated from the Least-Squares Fit Which Gives a Lattice Constant of 1.1972(3) nm for the Structure **I Hydrate Cell**

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}
1	1	0	8.4570	8.4653
2	1	0	5.3692	5.3539
2	1	1	4.9038	4.8874
2	2	2	3.4662	3.4559
3	2	0	3.3179	3.3204
3	2	1	3.2052	3.1996
4	0	0	2.9928	2.9929
4	1	0	2.9079	2.9036
3	3	0	2.8190	2.8218
4	2	1	2.6128	2.6124
3	3	2	2.5524	2.5524
5	2	0	2.2227	2.2231
4	4	1	2.0865	2.0840
5	3	0	2.0530	2.0531

teristic of a formaldehyde molecule undergoing rapid anisotropic motions inside the structure **I** hydrate large cage. It is well documented that guest molecules inside clathrate hydrate cages have a great deal of motional freedom and that at low temperatures the motional modes are distributed due to the hydrogen bond disorder in the clathrate ice lattice.²⁵ A second sample, prepared with heavy water and formaldehyde-*d*₂ shows a doublet ($\chi = 217.8$ kHz) with fine structure due to the asymmetry parameter ($\eta = 0.096$) characteristic of the hydrate lattice, plus a central line due to mobile formaldehyde molecules (Figure 2c). When the sample is annealed at temperatures above 250 K and recooled, the spectrum shows that the clathrate has decomposed (Figure 2d). The ²H line shape now consists of a number of overlapping doublets which can be assigned to the CD₂ group (inner doublet, $\chi = 157.6$ kHz) of the geminal diol of formaldehyde rigidly trapped in a solid matrix, and the ice lattice and hydroxyl deuterons (outer doublet, $\chi = 217.1$ kHz, $\eta = 0.086$). These latter observations are consistent with the known hydrolysis behavior of formaldehyde.

Formaldehyde hydrate is an example of a clathrate hydrate of possible astrophysical significance which, because of the chemistry of the guest, would not be stable under terrestrial conditions. Earlier it was reported that a clathrate hydrate of methanol had been identified in vapor deposits of water and methanol,²⁸ and indeed such a clathrate cannot be prepared under equilibrium conditions.²⁹ However, other interpretations of the data that do not require postulation of a methanol clathrate are also possible.²⁷ The experiments presented here suggest that formaldehyde clathrate hydrate may act as a storage reservoir

for formaldehyde monomer. The exchange between the free molecule and the condensed clathrate hydrate phase is energetically much less demanding than the polymerization–depolymerization cycle which connects the monomer and polymer. Clathrate hydrate formation can also be considered as an alternative reaction pathway for formaldehyde which has been shown to undergo a number of reactions in simulated astro-physical ices.³⁰

This work shows that the usual chemical processes such as formaldehyde hydration do not occur at low temperature for kinetic reasons but that clathrate formation itself is not prevented. All that appears to be necessary for clathrate formation is sufficiently fast relaxation of the water molecules. It has been suggested that this depends on the presence of a sufficiently large number of defects of the Bjerrum type,²⁶ which oxygen-containing molecules such as formaldehyde should be able to generate quite well.¹ For the formaldehyde–water vapor co-deposit we have observed that hydrate formation takes place even at 77 K on a time scale of several months. Even for nonpolar guests such as xenon, relatively slow clathrate hydrate formation competes with the amorphous to cubic ice transition in the 140–170 K range in co-deposits of xenon and water.²⁷ Although equilibrium thermodynamics should by no means be neglected, it is now clear that it may be possible to generate other rather unstable guests from precursors by thermolysis or irradiation and that these also may be stabilized inside hydrate lattices at low temperatures without interference from reactions with water molecules. Therefore, one may expect to find other unusual and unexpected hydrates in association with icy extraterrestrial environments.

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