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A Chiral Gas–Hydrate Structure Common to the Carbon Dioxide–Water and Hydrogen–Water Systems

Daniel M. Amos,[†] Mary-Ellen Donnelly,[†] Pattanasak Teeratchanan,[†] Craig L. Bull,[‡] Andrzej Falenty,[§] Werner F. Kuhs,[§] Andreas Hermann,^{*,†} and John S. Loveday^{*,†}

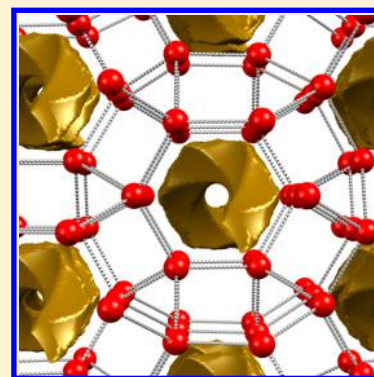
[†]SUPA, School of Physics and Astronomy and Centre for Science at Extreme Conditions, The University of Edinburgh, Edinburgh EH9 3JZ, United Kingdom

[‡]ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton, Oxon, OX11 0QX, United Kingdom

[§]GZG Abteilung Kristallographie, Universität Göttingen, Goldschmidtstrasse 1, 37077 Göttingen, Germany

Supporting Information

ABSTRACT: We present full in situ structural solutions of carbon dioxide hydrate-II and hydrogen hydrate C_0 at elevated pressures using neutron and X-ray diffraction. We find both hydrates adopt a common water network structure. The structure exhibits several features not previously found in hydrates; most notably it is chiral and has large open spiral channels along which the guest molecules are free to move. It has a network that is unrelated to any experimentally known ice, silica, or zeolite network but is instead related to two Zintl compounds. Both hydrates are found to be stable in electronic structure calculations, with hydration ratios in very good agreement with experiment.



Gas hydrates—guest–host compounds formed from water and simple gases—are an important group of materials. They are stabilized by the interplay of hydrogen bond formation between host water molecules and hydrophobic–hydration interactions between the host and the guest gas species.¹ These forces play a crucial role in biochemical processes like protein folding and the molecular architecture of cell structures.² Gas hydrates provide relatively simple model systems against which to test models of intermolecular potentials³ and they also occur commonly in nature: methane clathrate hydrate on the ocean floor accounts for one-third of Earth's methane⁴ and methane hydrate is believed to have been the dominant methane-containing phase in the nebula from which the outer planets (Saturn, Neptune, Uranus and Pluto) and their satellites formed.⁵ Finally, gas hydrates have potential technological applications, for example, in the transport and storage of gases.⁶

Seven gas hydrate structures are commonly found. Three are based on distortions of the H-bonded networks of known phases of ice and four on agglomerates of cages formed by H-bonded water molecules.⁷ While this variety seems quite rich, it is small compared to the versatility exhibited by other network-forming materials like zeolites and Zintl phases. For example, there are 229 different zeolite (alumina-silicate) networks⁸ with predictions of many more. The versatility of zeolites may be attributed to the fact that Si–O-based tetrahedral networks form four-membered rings more readily than water networks, but water networks show an increased tendency to adopt four-

membered rings at modest pressures,⁷ suggesting that many more gas hydrate networks remain to be discovered at high-pressure.⁹ Two examples of unknown or poorly characterized hydrate structures are found in the apparently unrelated carbon dioxide–water and hydrogen–water systems.

At low pressures, CO_2 hydrate adopts the cubic clathrate-I structure (CS-I) which has two types of cages: one large and one small.⁷ Hirai et al. found using XRD and Raman spectroscopy that CS-I transforms at ~ 0.5 GPa to ice VI and a new hydrate-II phase.¹⁰ This decomposes on further compression above ~ 1 GPa into CO_2 and ice VII or VIII. Most of the other simple gas hydrates follow one of two variants of a common structural sequence on compression. Systems that start as CS-I (methane, krypton) transform with loss of water to the hexagonal clathrate structure (SH) at ~ 1 GPa and then to the methane hydrate-III (MH-III) structure at around 2 GPa with further loss of water such that the high pressure phase is a dihydrate. Systems which adopt the CS-II structure (argon and nitrogen) at low pressure follow the same sequence but interpolate the tetragonal clathrate structure (ST^{11,12}) in between the SH and the MH-III structures.⁷ Hirai et al. concluded that CO_2 hydrate-II did not adopt any of these known hydrate structures.¹⁰ This conclusion was contradicted by Tulk et al., who performed *in situ* neutron diffraction and

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concluded that the hydrate had a ‘filled ice’ MH-III structure.¹³ However, the MH-III structure cannot account for the diffraction peaks reported by Hirai et al. and we were unable to obtain a fit to our data (presented below) with this structure.

The H₂–water system has been studied extensively and is known to form an ice-II related hydrate (C₁), an ice-I_c based structure (C₂), as well as the cubic clathrate-II structure (CS-II).^{14,15} More recently, Efimchenko et al. discovered another form, C₀, at pressures around 0.5 GPa, and proposed, based on powder X-ray diffraction (XRD) on a recovered sample, a trigonal structure with a spiral H-bond network with channels that contain partially occupied water sites.¹⁶ This arrangement violates the ice rules and seems improbable. Strobel et al. collected *in situ* XRD data and concluded that the diffraction pattern of C₀ was consistent with an α - or β -quartz arrangement, and the tetragonal structure, ST.¹⁷ A classical molecular dynamics study by Smirnov et al. suggested that C₀ had a spiral structure with H₂ in the channels and that the partially occupied sites were in fact N₂ molecules incorporated during recovery.¹⁸ Recent *in situ* XRD results concluded that the oxygen sublattice was close to that proposed by Smirnov et al. but with hexagonal symmetry.¹⁹ Finally, a neutron diffraction study of the *empty* C₀ water network recovered to ambient pressure found that the structure (named ice XVII) has hexagonal symmetry with spacegroup P6₁22.²⁰ Thus, while there is a significant amount of structural data on the C₀ hydrate, there is currently no full determination of its structure including proton-ordering and guest occupancies.

In this Letter we report neutron and synchrotron X-ray diffraction studies performed *in situ* and on recovered samples, which show that both CO₂ and H₂ hydrates adopt the *same* water network,^{21,22} based on neither a known hydrate nor ice structure but instead related to two Zintl phases. This chiral network topology (called S _{χ} from here on) differs qualitatively from both the cage-clathrates (as it features open channels) and the filled-ice hydrate structures (as it is not related to any stable ice structure).

Our CO₂ hydrate studies used a combination of neutron diffraction carried out on the PEARL instrument²³ of the ISIS pulsed neutron facility using the Paris–Edinburgh press²⁴ and X-ray diffraction (XRD) on recovered samples, carried out on beamline ID15-B at the ESRF. For the D₂–water experiments, an aluminum gas cell in an ILL-pattern “orange” cryostat and PEARL were used. Total-energy calculations based on density functional theory (DFT) were performed on sets of candidate structures, varying both the water host networks with their hydrogen bond topology and the guest molecule content. Details on sample growth, experiments, and calculations are given in the Supporting Information (SI).

Figure 1 shows neutron diffraction patterns collected from CO₂ hydrate-II and H₂ hydrate C₀ at elevated pressures. The two hydrates have very similar diffraction patterns. Ab-initio structure solution was first achieved for CO₂ hydrate-II. The unit cell was determined to be hexagonal/trigonal with $a \sim 6.25$ Å and $c \sim 6.27$ Å. Based on the systematic absences, the symmetry was no higher than P6₁22/P6₃22 if hexagonal or P3₁21/P3₂21 if trigonal. Charge flipping using the XRD data gave a satisfactory partial solution for the heavy atoms—O atoms at $6b(0.76, 0.76, \frac{11}{12})$ and CO₂ molecules centered at $6b(0.1, 0.1, \frac{11}{12})$ —with a weighted profile R factor R_{wp} of 3.783%.²⁵ This model was used along with the neutron data to

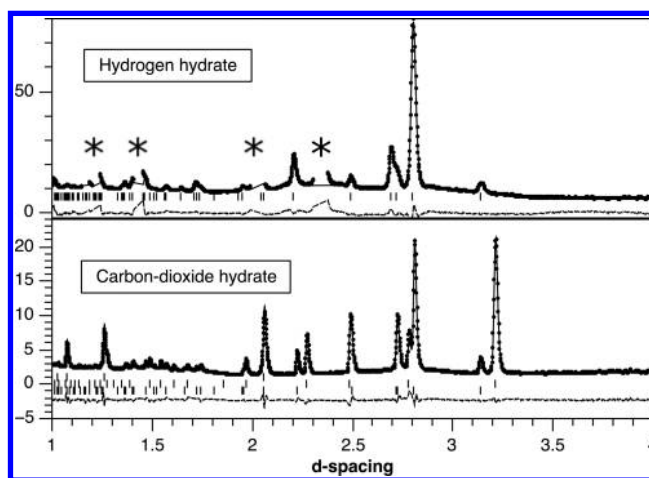


Figure 1. Rietveld profile refinements of neutron diffraction data for both hydrates. The data are shown as dots, calculated fits as solid lines, and their differences as dashed lines. Upper panel: H₂ hydrate C₀ at 0.30 GPa and 175 K. Tickmarks denote reflections from the sample. Scattering from the Al pressure cell (marked by asterisks) has been excluded. Lower panel: CO₂ hydrate-II at ~ 0.4 GPa and 260 K. Tickmarks denote reflections from CO₂ hydrate (bottom), CO₂ (middle) and the sintered-diamond pressure-cell anvils (top).

locate the deuterium atoms. The symmetry of P6₁22 implies that the H-bonds must be disordered with two half-occupied deuterium sites along each H-bond. As with the XRD data, this model produced an acceptable fit.

For the pattern shown in Figure 1, the refined structure has $a = 6.2753(5)$ Å and $c = 6.2988(6)$ Å, and water oxygens on $6b(0.7623(5), 0.5246(10), 0.25)$, half-occupied water deuteriums on $12c(0.3741(10), 0.0726(9), 0.5208(13))$ and $12c(0.5782(8), 0.3309(15), 0.4605(14))$, and carbon and oxygen of CO₂ on $6b(0.08618, 0.1724, 0.25)$, $12c(0.189(3), 0.061(4), 0.044(3))$, and $12c(0.233(3), 0.017(3), 0.044(3))$. The CO₂ occupancy was 1.69(4) per unit cell or 3.55(3) water molecules per CO₂ and, based on this composition, the density is 1.502 g/cm³ for the deuterated form.

For the H₂ hydrate C₀ we tested all proposed structures^{16–19,26} and rejected those that are not variants of the spiral structure first proposed by Smirnov et al.¹⁸ Our *in situ* solution results in the same oxygen network identified with XRD and in the empty network.^{19,20} As with CO₂ hydrate, no ordered or partially ordered network gave a significant improvement in fit, so the most plausible arrangement has proton-disordered H-bonds and spacegroup P6₁22 (or P6₃22). For final refinements, the structure used had $a = 6.2763(5)$ Å and $c = 6.1875(10)$ Å, water oxygens on $6b(0.7637(6), 0.527(11), 0.25)$, half-occupied water deuteriums on $12c(0.3771(12), 0.0707(17), 0.5317(17))$, and $12c(0.5626(17), 0.3345(16), 0.4578(17))$, and a guest D₂ molecule on $6b(0.1067(15), 0.213(3), 0.25)$. For a fully deuterated sample with dihydrate composition, this structure has a density of 0.991 g/cm³.

Figure 2 shows the hydrogen-bond network of S _{χ} . The figure also shows the Si–Si network of β -quartz. Strobel et al. argued that the S _{χ} network is related to that of β - and α -quartz¹⁹ (β -quartz has a topologically identical network to α -quartz and, because it has higher symmetry, is more regular). While clearly different, both β -quartz and S _{χ} have close-packed arrays of hexagonal channels when viewed along the c -axis. These channels are formed of double helices. In the β -quartz network,

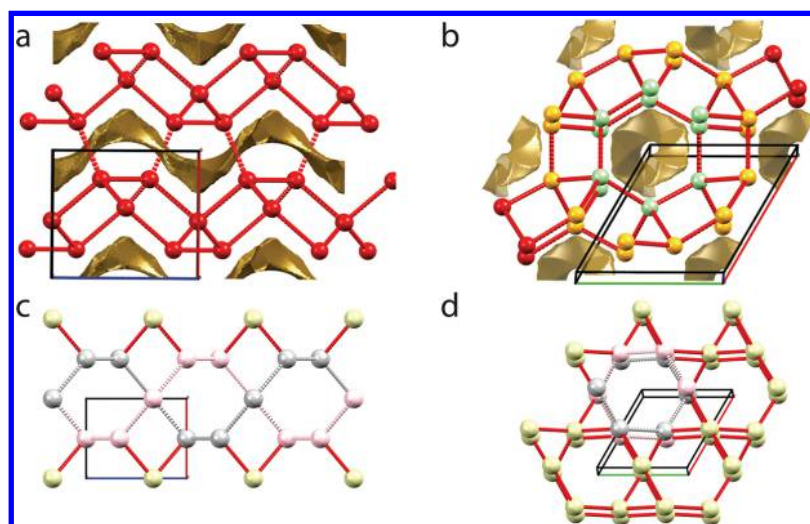


Figure 2. Upper: The H-bonded network of S_χ viewed (a) along the b - and (b) along the c -axis. The green and yellow atoms denote the small and large spirals as described in the text. The gold isosurfaces show the voids in the structure, which are contiguous spirals inside the channels. For clarity, hydrogen atoms have been omitted. Lower: The Si–Si network of β -quartz viewed (c) along the b - and (d) along the c -axis. The gray and pink atoms show one of the double helices that form the straight channels. For clarity, oxygen atoms have been omitted.

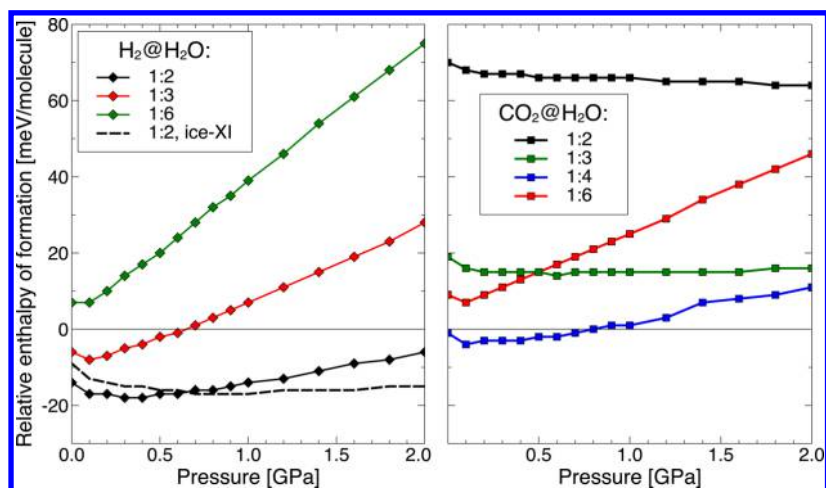


Figure 3. Relative enthalpies of formation of S_χ hydrates with varying guest content (left: H_2 ; right: CO_2). Left panel also considers H_2 in a ice-XI host network (see text).

both helices have the same radius, whereas in the S_χ network there is a “small” helix (shown in green in Figure 2b) and a “large” helix (shown in yellow) so that the wall of the channel has the ridge and furrow form of a screw thread. This means that the channels in S_χ are spirals with a roughly constant diameter and an eccentricity of ~ 1 Å. The voids in S_χ shown in Figure 2 confirm this view, which differs from the cavity topology of any other known hydrate structure (see the SI). It also contrasts with β -quartz, whose channels are straight cylinders. In S_χ , each small spiral atom is also part of the large spiral of an adjacent channel so that the ridge of a given channel is the furrow of its neighbor. As a result, adjacent channels share edges; in the β -quartz structure, adjacent channels share corners (see Figure 2). Therefore, in S_χ , the entire volume of the unit cell is inside a channel and the structure thus has 100% packing efficiency, a feature that the corner-sharing β -quartz structure does not possess.

The S_χ structure is not related to that of any previously made ice—with the obvious exception of ice XVII (see above)—or zeolite phase,⁸ but its network topology is found in the Zintl

compounds $NaGaSn_5$ ²⁷ and Na_2ZnSn_5 ²⁸ and it has been proposed as a hypothetical structure in zeolites²⁹ and as a metastable “chiral framework structure” in the group-IV elements.³⁰ In the two Zintl compounds, a stochastic distribution of the Ga/Sn and Zn/Sn atoms forms the respective host lattices, while Na cations occupy the guest sites in the channels. Following electron transfer from Na to Ga or Zn, the latter are effectively tetravalent and pursue formation of a tetrahedrally connected network together with the Sn atoms. Blase and Cordier speculate that the large size of the Na cations leads to the unusual covalent network structure, in contrast to Li-based mixed-main group Zintl compounds.²⁷ Note that the “guest:host ratio” in the two compounds spans the range from 1:3 to 1:6.

It should also be noted that it is surprising that carbon-dioxide hydrate should adopt this structure. As described above, like many simple gas hydrates, it adopts one of the ‘standard’ cubic clathrate structures at low pressures,⁷ and as such it might be expected to transform to SH and then to the ‘filled-ice’ MH-III structure under increased pressure. That it does not, and

instead adopts a structure also found in the hydrogen–water system—which in turn only forms structure-II clathrate with difficulty—is unexpected.

In both hydrates, refinements of the neutron data showed evidence of anisotropy in the guest thermal motion. There is evidence of chain ordering at ~ 115 K in recovered CO₂ hydrate²¹ and H₂ hydrate evolves gas at 77 K.¹⁶ These results all suggest that the guest molecules in S_χ are very mobile in the channels.³¹ It is then difficult to determine occupancies reliably from diffraction data alone. To constrain them, we performed DFT calculations on empty and filled S_χ. We exhaustively constructed all proton-ordered crystal structures of S_χ that fulfill the ice rules within the P6₃22 unit cell and oxygen network. There are 38 such proton distributions, of which 12 are found to be distinct.³² Over the pressure range 0–2 GPa their enthalpies are close, within 4 meV/H₂O, and the lowest enthalpy structure had P3₂ symmetry. We used this water network to describe all hydrate phases, replicated along the *c* axis if necessary. For the CO₂ hydrate, we considered the guest:host ratios 1:2 (occupying every guest site), 1:3, 1:4, and 1:6, and fully relaxed all structures across a range of pressures. For the H₂ hydrate, we studied the 1:(2/3/6) hydrates. Figure 3 shows the resulting enthalpies of formation, relative to the constituents ice and solid CO₂/H₂. CO₂ hydrate is only found stable in the 1:4 composition and up to 0.8 GPa. Hydrates with higher guest content are unstable, presumably due to repulsion between CO₂ molecules, while a 1:6 hydrate is probably unstable due to the metastability of the S_χ network itself. For H₂ hydrate, on the other hand, full occupancy of the guest sites is preferable at all pressures. The S_χ hydrate is stable against decomposition until ~ 2.3 GPa, but superseded by a filled ice-XI hydrate above 0.65 GPa. The occupancies for both hydrates are in good agreement with our experimental findings; quantitative analysis of *in situ* powder patterns from time-dependent studies of the growth of hydrate-II from ice VI and solid CO₂ suggest a hydration ratio of 3.0(6):1,²¹ and together with the difficulty in fitting the highly mobile guest sites, we conclude that experiments and calculations agree and point to a hydration ratio of 2:1 for C₀ and ~ 3.5 :1 for CO₂ hydrate-II.

In summary, we show here that a chiral water network, S_χ, serves as host in two very different hydrate systems. It can be understood as an arrangement of interlocked channels in a close-packed ridge-and-furrow layout. Our structural solution of the hydrates provides the structure of CO₂ hydrate-II, confirms recent work on the empty network,²⁰ and provides the first determination of the hydrogen occupancies in C₀. Stable in calculations, the water network can host CO₂ in a 1:3.5 molecular ratio (41 wt %) and H₂ in a 1:2 molecular ratio (5.2 wt %). A versatile wide-channel structure, the network can be emptied,²⁰ serves as host for two very different small molecules, and appears also to form mixed H₂–CO₂ hydrate, a syngas-like mixture.²¹ With suggestions that N₂ inadvertently entered the hydrate in early experiments,^{16,18} empty S_χ can be considered as a universal microporous material for small gas species. As it is chiral, S_χ could conceivably, either as ice XVII or in a covalent analogue, be used for enantiomeric selectivity. Very few known microporous materials are chiral, but the use of chiral networks for selection of enantiomorphs from racemic mixtures is a field of active research.³³ The pressures required to produce S_χ (0.3–0.5 GPa) lie within the range where industrial scale production is feasible.³⁴ Ice XVII is thus a cheap, environmentally benign, readily producible and potentially very useful microporous material.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.7b01787.

Details of the experimental and computational procedures and the solution of the structures (PDF)

CIF files of the atomic positions (CIF)
(CIF)

The Rietveld refinements in GSAS format and input files for the computational modeling are available via the Internet at <http://datashare.is.ed.ac.uk>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: a.hermann@ed.ac.uk.

*E-mail: j.loveday@ed.ac.uk.

ORCID

Andrzej Falenty: 0000-0001-5995-9900

John S. Loveday: 0000-0003-3985-9982

Notes

The authors declare no competing financial interest.

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