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Synthesis and characterization of crystalline polymeric carbonic acid (H_2CO_3) with sp^3 -hybridized carbon at elevated pressures

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The existence of polymeric carbonic acid (H_2CO_3) at elevated pressures has been predicted, but has not been investigated experimentally. Here, polymeric carbonic acid containing sp^3 -hybridized carbon was synthesized and characterized at ≈ 40 GPa. H_2CO_3 single crystals were obtained by laser-heating a $\text{H}_2\text{O} + \text{CO}_2$ mixture in a diamond anvil cell. The orthorhombic crystal structure ($Cmc2_1$ with $Z = 4$) was refined from synchrotron single crystal X-ray diffraction data and is in agreement with a structural model predicted earlier. The crystal structure of $\text{H}_2\text{CO}_3\text{-}Cmc2_1$ is characterized by $[\text{CO}_4]^{4-}$ building blocks which are connected via corner sharing, forming chains along the c -axis. The combination of single crystal X-ray data with experimental Raman spectroscopy and DFT-calculations confirms that the structural model of $\text{H}_2\text{CO}_3\text{-}Cmc2_1$ is appropriate. The synthesis condition of polymeric carbonic acid points towards its potential existence in ice giants including the ones present in our solar system.

Carbonic acid (H_2CO_3) is an extensively studied, but still enigmatic, compound. It is well established that H_2CO_3 forms in small quantities by the reaction between H_2O and CO_2 in aqueous solutions, but either decomposes back or rapidly dissociates^{1,2}. This poses significant experimental challenges for the crystallization of H_2CO_3 , which is a prerequisite for single-crystal structure determinations. Numerous approaches have been employed to overcome this hurdle, including particle or light irradiation of H_2O -ice: CO_2 mixtures and synthesis at high-pressures^{3–9}.

Due to the experimental challenges, a number of problematic results were obtained. For example, the conclusions regarding the existence of α - H_2CO_3 , based on spectroscopic evidence, needed to be revised, as it was later shown that in fact the monomethyl ester of H_2CO_3 , ($\text{CH}_3\text{OCO}_2\text{H}$) had been obtained^{10–13}. This led to the conclusion that β - H_2CO_3 was the only ambient pressure phase, but its exact crystal structure remained unknown¹³. More recently, there were attempts to combine density functional theory (DFT)-based calculations and high-pressure studies to obtain and confirm structural models for crystalline H_2CO_3 . However, a recent neutron powder diffraction study on a deuterated sample, which yielded a low pressure (≈ 2 GPa) monoclinic structure, $\text{H}_2\text{CO}_3\text{-}P2_1/c$ (Fig. 1b), is problematic, as it is evident from the published data that the amount of H_2CO_3 in the sample

was minute in comparison with the co-existing CO_2 -I phase (dry ice), and the refinements relied on constraints and restraints⁵.

Earlier, a crystal structure prediction study had been published in which several polymorphs of H_2CO_3 were proposed⁶. Specifically, for the pressure range of 1–44 GPa, a phase with space group $Pnma$ was predicted (Fig. 1c). For the pressure range from 44 to 314 GPa, it was predicted that carbon would be sp^3 -hybridized, and that the $[\text{CO}_4]^{4-}$ -tetrahedra would polymerize to form chains in two orthorhombic structures both having space group $Cmc2_1$ (Fig. 1d, e)⁶. A phase transition between two $\text{H}_2\text{CO}_3\text{-}Cmc2_1$ polymorphs was predicted to occur at 240 GPa. The high pressure phase of $\text{H}_2\text{CO}_3\text{-}Cmc2_1$ was predicted to remain stable up to its reaction with H_2O to orthocarbonic acid (H_4CO_4) above 314 GPa⁶. It was proposed that the computed vibrational spectra for the low pressure phase $\text{H}_2\text{CO}_3\text{-}Pnma$ were in agreement with the experimentally obtained IR and Raman spectra measured at ≈ 4 GPa in a study reported earlier^{6,7}.

Recently, we provided the first X-ray single crystal structure solution of water-free H_2CO_3 at low pressures (≈ 8 GPa) with $P2_1/n$ space group symmetry (Fig. 1a)⁸. The geometry of the H_2CO_3 molecules in *cis-cis* configuration is in reasonable agreement with their geometry in the chemically closely related carbonic acid monohydrate ($\text{H}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), which has also

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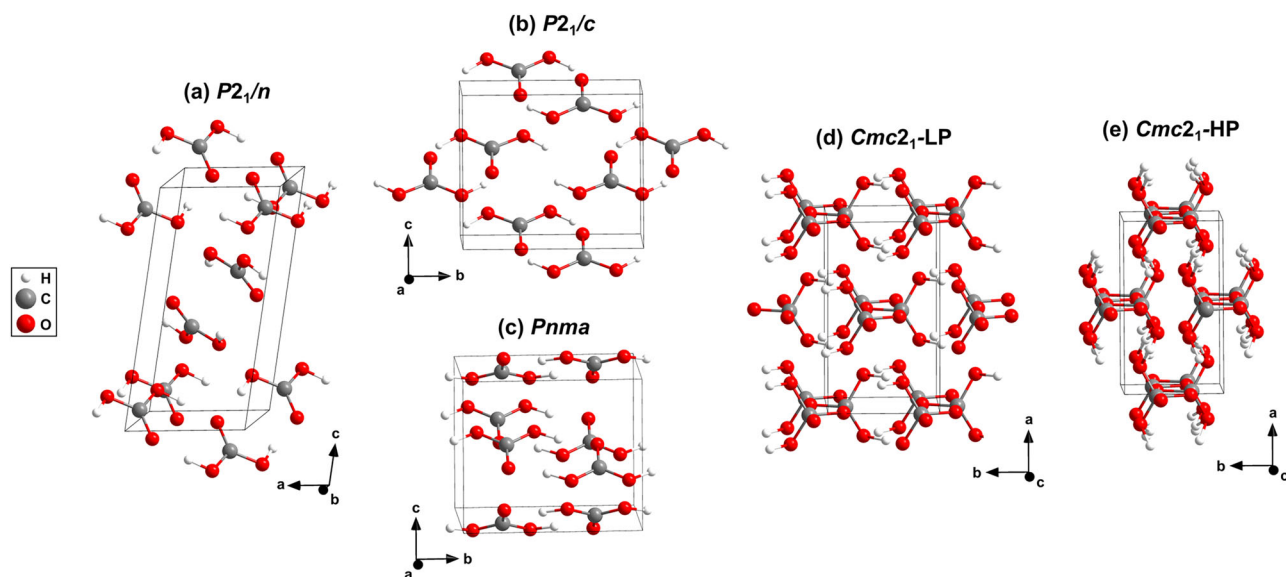


Fig. 1 | Experimental and calculated crystal structures of the H_2CO_3 phases.

a Experimental crystal structure of H_2CO_3 - $P2_1/n$ (≈ 8 GPa) from single crystal X-ray diffraction⁸. **b** Experimental crystal structure of deuterated H_2CO_3 - $P2_1/c$ (≈ 2 GPa)⁵.

Predicted crystal structures of: **c** H_2CO_3 - $Pnma$ (1 GPa)⁶, **d** the low-pressure phase of H_2CO_3 - $Cmc2_1$ (100 GPa)⁶ and **e** the high-pressure phase of H_2CO_3 - $Cmc2_1$ (400 GPa)⁶.

been studied by single crystal X-ray diffraction (at 6.5 GPa) in earlier experiments⁹. We complemented our diffraction study by a combination of experimental Raman spectroscopy and DFT calculations.

A single crystal structure determination, with a high reflection-to-parameter ratio (>8) and low R -values (a few %), is the gold standard for establishing new structures, even if reciprocal space has not been fully explored, as is typical in DAC-based studies. This is especially the case if the structure is then reproduced in full geometry optimizations in DFT calculations and the latter reproduce the Raman spectrum. This implies that not only the structure correspond to a local energy minimum, but also that the second and third derivatives of the energy hypersurface have been obtained correctly. There is no example of a moderately complex structure where the experimental Raman spectrum has been reproduced by DFT calculations for a wrong structure, and hence the crystal structure of H_2CO_3 - $P2_1/n$ at pressures of 5–13 GPa is now established⁸. Its crystal structure is distinct from H_2CO_3 - $Pnma$ or H_2CO_3 - $P2_1/c$ ^{5,6}. In H_2CO_3 - $P2_1/n$ carbon is sp^2 -hybridized, i.e., this is a “conventional” carbonate, characterized by nearly trigonal $[\text{CO}_3]^{4-}$ -groups. Two H_2CO_3 molecules in *cis-cis* geometry are connected by two hydrogen bonds forming layers. This crystal structure had not been predicted in the study by Saleh and Oganov⁶.

Due to the disagreement between the crystal structure prediction approach for the low-pressure phase of H_2CO_3 and the experimental data in this pressure range and the absence of any experimental high pressure structural studies, the high pressure polymorphism of H_2CO_3 is unresolved. Determining the high pressure polymorphism of H_2CO_3 is a relevant effort for several reasons. From a crystallographic and crystal chemical point of view, the crystal structure prediction of Saleh and Oganov⁶ is exciting, as the polymorph predicted to be stable at pressures between 44 and 314 GPa was thought to contain polymerized $[\text{CO}_4]^{4-}$ -groups forming chains. The polymerization of $[\text{CO}_4]^{4-}$ -groups in carbonates has been well established for more than a decade now. However, pressure-induced polymorphic transitions from sp^2 - to sp^3 -carbonates occur only at much higher pressures (e.g., at ≈ 85 GPa for MgCO_3 , at ≈ 105 GPa for CaCO_3 , and at ≈ 115 GPa for $\text{Ca}_{1.5}\text{Fe}_{0.9}\text{Mg}_{0.6}\text{C}_3\text{O}_9$)^{14–16}. In contrast, sp^3 -carbonates can be obtained at much lower pressures if instead of pressure induced polymorphic transitions reactions with a corresponding oxide (e.g., at ≈ 20 GPa for Sr_2CO_4) or with CO_2 (e.g., at ≈ 34 GPa for $\text{Ca}_2\text{C}_4\text{O}_{10}$) are induced^{17,18}. In carbonates, the polymerization of $[\text{CO}_4]^{4-}$ -groups into infinite chains is very rare and has been observed only in CaCO_3 - $P2_1/c$ at ≈ 105 GPa¹⁵.

Solid H_2CO_3 is also relevant for astrophysical studies. H_2O and CO_2 are components of interstellar dust, and very large stellar objects exist which contain enormous amounts of H_2O and CO_2 ¹⁹. Furthermore, H_2O and CO_2 are present in the frozen nuclei of comets and on/in icy bodies in our solar system^{20–25}. High pressures up to ≈ 1000 GPa and temperatures up to several thousand Kelvin in combination with the presence of large H_2O -ice containing shells have been found in ice giants such as Uranus and Neptune^{26,27}. As CO_2 is present in their atmosphere²⁸, it is possible that high pressure polymorphs of H_2CO_3 form inside of ice giants. Hence, an understanding of the system H_2O - CO_2 as a function of pressure and temperature is required to establish spectral libraries for their remote identification. The relevance of H_2CO_3 in our solar system is also evident from the recent spectroscopic evidence of its presence on the surface of Ganymede reported by the Jovian Infrared Auroral Mapper (JIRAM) or by the detection of CO_2 together with H_2O_2 on the stratified surface of Charon using the James Webb Space Telescope (JWST)^{29,30}. Furthermore, the JWST detected H_2O together with CO_2 in the atmosphere of the hot Super-Neptune WASP-166b³¹.

Results and discussion

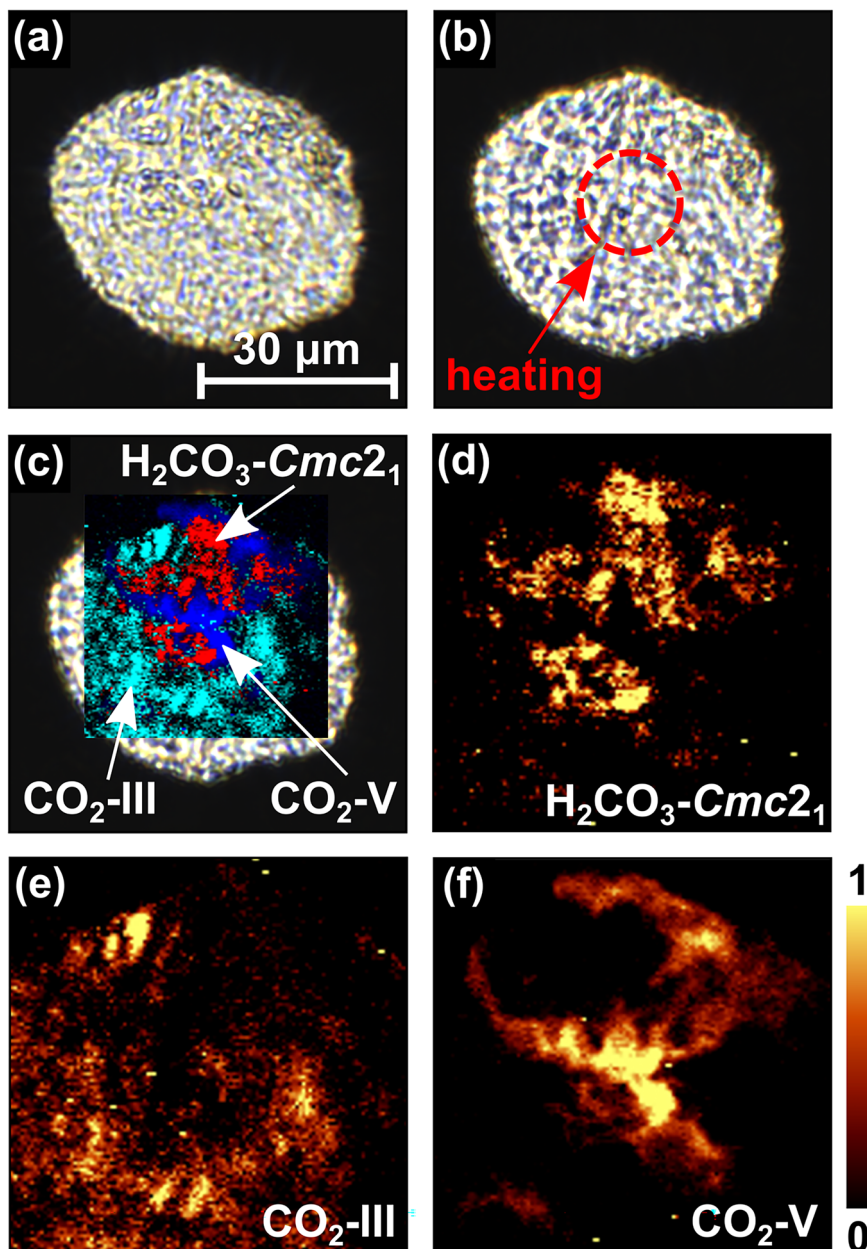
The high-pressure experiments on the H_2O - CO_2 system were carried out in laser-heated diamond anvil cells (LH-DACs). In a first step, a drop of H_2O was added into the sample chamber of a DAC. A significant amount of water was then allowed to evaporate before closing the DAC tightly. In the next step, the DAC was cooled down. After reaching ≈ 273 K the DAC was reopened before being cooled further to ≈ 100 K. At this temperature dry ice was directly condensed into the sample chamber from a CO_2 gas jet. The DAC was tightly closed after the sample chamber was completely covered with dry ice and then compressed to the target pressure of the experiment without intermediate heating. The sample pressure during compression was derived from the position of the high frequency edge of the diamond Raman band³². After tightly closing the DAC the pressure in the sample chamber was ≈ 10 GPa. At this pressure, CO_2 -I ($Pa\bar{3}$) is the stable phase up to its melting temperature^{33,34}. In a Raman experimental spectrum, obtained after the cryogenic loading, we could identify the characteristic Raman modes of CO_2 -I (Fig. S2a) at low wavenumbers ($<300\text{ cm}^{-1}$)³⁵. In addition, we observed the characteristic Raman signal of H_2O -VII at high wavenumbers (≈ 3000 – 3400 cm^{-1}) (Fig. S2b), confirming that H_2O is present in the sample chamber^{36,37}.

Figure 2 a shows the sample chamber of the DAC after cold-compression of the $\text{CO}_2 + \text{H}_2\text{O}$ mixture to 40(2) GPa before laser heating.

Fig. 2 | Sample chamber of the DAC and Raman maps of H_2CO_3 and CO_2 after the synthesis.

a Sample chamber of the DAC with the $\text{H}_2\text{O} + \text{CO}_2$ mixture before the laser heating at 40(2) GPa.

b Sample chamber after heating the mixture up to a maximum temperature of ≈ 1000 K. **c** 2D-Raman map showing the distribution of $\text{H}_2\text{CO}_3\text{-Cmc}2_1$, $\text{CO}_2\text{-III}$, and $\text{CO}_2\text{-V}$ overlaid on a picture of the sample chamber. Raman map of: **d** $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ ($\approx 910\text{ cm}^{-1}$), **e** $\text{CO}_2\text{-III}$ ($\approx 380\text{ cm}^{-1}$) $\text{CO}_2\text{-V}$ ($\approx 810\text{ cm}^{-1}$), and **f** $\text{CO}_2\text{-V}$ ($\approx 810\text{ cm}^{-1}$) after laser heating at 40(2) GPa.



During compression a phase transition from $\text{CO}_2\text{-I}$ ($P\bar{a}3$) to $\text{CO}_2\text{-III}$ (Cmca) occurs in a broad (≈ 5 GPa) pressure interval around ≈ 12 GPa^{33,35}. The experimental Raman data of unheated $\text{CO}_2\text{-III}$ at 40(2) GPa are in good agreement with the Raman spectrum derived from our DFT-based calculations (Table S3) in space group Cmca (Fig. 3a). At 40 GPa the stable phase of water is $\text{H}_2\text{O-VII}$ ($Pn\bar{3}m$)^{38,39}, but due to the overtone of the diamond the characteristic Raman modes of $\text{H}_2\text{O-VII}$ at high wavenumbers cannot be observed at this pressure³⁶.

At the target pressure of the experiment (40(2) GPa) we used double-sided CO_2 laser-heating to induce the reaction. The sample was heated to a maximum temperature of ≈ 1000 (300) K in one spot of the sample chamber (Fig. 2b). At this pressure, the direct and indirect heating of $\text{CO}_2\text{-III}$ causes the appearance of the high-pressure polymorph $\text{CO}_2\text{-V}$ in several parts of the sample chamber (Fig. 2f), which is the stable polymorph of CO_2 to pressures above 100 GPa.^{34,40} $\text{CO}_2\text{-III}$ is still present in some unheated regions of the sample chamber (Fig. 2e). The experimental Raman spectra of $\text{CO}_2\text{-V}$ show a strong characteristic Raman mode at $\approx 810\text{ cm}^{-1}$ and are in very good agreement with our calculated Raman spectra (Table S4) in space group $I\bar{4}2d$ (Fig. 3b). In addition, we found that laser heating at 40(2) GPa

causes the formation of a phase with a strong new Raman mode at $\approx 910\text{ cm}^{-1}$ (Fig. 3c). Strong Raman modes of carbonates occurring at such low wavenumbers are typically present in sp^3 -carbonates such as Sr_2CO_4 or Ca_2CO_4 and characteristic for the C–O stretching mode in a $[\text{CO}_4]^{4-}$ -group^{17,18}. From spatially resolved Raman spectroscopy we found that the distribution of the unknown phase in the sample chamber is not identical with the one of $\text{CO}_2\text{-V}$ (Fig. 2d, f).

We obtained synchrotron X-ray diffraction patterns on regularly spaced grid points across the sample chamber in order to locate promising positions for the subsequent collection of single crystal diffraction data. We collected diffraction data suitable for single crystal X-ray diffraction analysis using a $\approx 2 \times 2\text{ }\mu\text{m}^2$ -sized X-ray beam at selected locations (see SI). From these data we solved the crystal structure of the new phase and found that it is orthorhombic $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ with $Z = 4$ (Fig. 4a).

This structure had been predicted by evolutionary algorithm in the C–H–O ternary system (Fig. 1c), where a stability field of 44–240 GPa was proposed⁶. The lattice parameters from single crystal structure data analysis at 40(2) GPa (Fig. 4a) are $a = 7.286(3)\text{ }\text{\AA}$, $b = 4.275(1)\text{ }\text{\AA}$ and $c = 3.809(4)\text{ }\text{\AA}$ ($V = 118.6(1)\text{ }\text{\AA}^3$). The relatively low R_1 -value of 4.6% for a DAC experiment

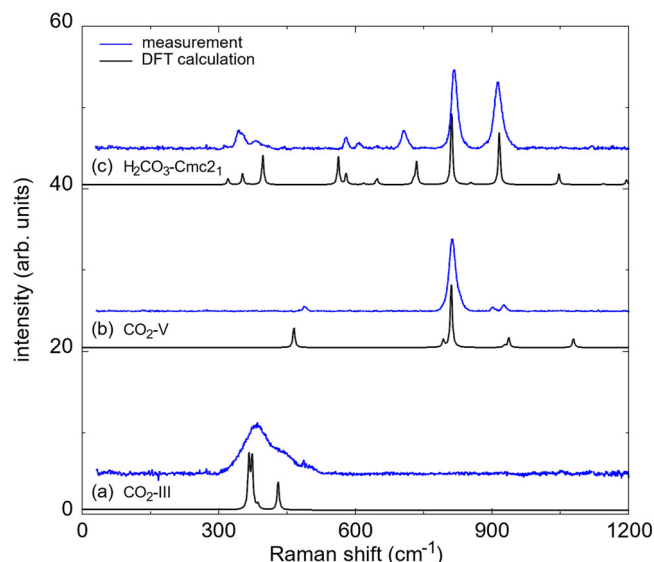


Fig. 3 | Experimental and calculated Raman spectra before and after the synthesis of $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ at 40(2) GPa. a Raman spectra for the untransformed low-pressure phase $\text{CO}_2\text{-III}$. **b** Raman spectra for the high-pressure polymorph $\text{CO}_2\text{-V}$. **c** Raman spectra of $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ after the synthesis. Experimental Raman spectra (blue lines) were collected in the same DAC corresponding to the 2D-Raman maps in Fig. 2c–f. DFT-based calculations (black lines) were rescaled by 1–3%.

is indicative of a reliable structure refinement (see SI). Our DFT-based full geometry optimizations accurately reproduce the experimentally determined structure and earlier predictions (Table S1)⁶. Furthermore, our experimental Raman spectrum is in good agreement with the theoretical one derived from our DFPT-based calculations (Fig. 3c, Table S5), providing further confirmation that the structural model of $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ is appropriate at elevated pressures.

The crystal structure is characterized by polymerized $[\text{CO}_4]^{4-}$ -tetrahedra forming infinite chains along the *c*-axes (Fig. 4b). The single crystal structure determination of $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ is the first experimental proof for the polymerization of sp^3 -hybridized $[\text{CO}_4]^{2-}$ -groups in carbonic acid. Each of the $[\text{CO}_4]^{4-}$ -tetrahedra is protonated by two hydrogen atoms. The location of hydrogen positions is often assumed to be experimentally challenging in high-pressure diffraction experiments. However, we demonstrated earlier that in favorable circumstances, i.e., the absence of strongly scattering heavy elements, the hydrogen positions can be reliably located with our experimental approach^{8,41}. Nevertheless, as in all X-ray diffraction experiments, an accurate determination of the O–H distance is often not possible, and so, in order to reduce the error associated with the bond distance, we introduced a restraint for the O–H bond distance in our experimental model (≈ 0.9 Å).

At 40 GPa two of the four C–O bond distances within one $[\text{CO}_4]^{4-}$ -tetrahedron (Fig. 5a) are identical (1.342(3) Å) due to symmetry constraints, while the other two are slightly longer (1.375(5) Å/1.370(9) Å). The DFT model predicts C–O bond lengths between 1.352 and 1.399 Å. The Mulliken population of the C–O bonds decrease from 0.66 to 0.55 $e^-/\text{Å}^3$ with the C–O distance. These values are indicative of predominantly covalent bonds. Due to the polymerization of the $[\text{CO}_3]^{2-}$ -groups in $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ to $[\text{CO}_4]^{4-}$ tetrahedra, the sp^3 -hybridized C–O bond distances are significantly longer in $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ than in the sp^2 -hybridized $[\text{CO}_3]^{2-}$ -groups of hypothetical $\text{H}_2\text{CO}_3\text{-P}2_1/n$ at 40 GPa (1.25–1.28 Å)⁸. The increase of the C–O bond length ($\approx 7\%$) is in good agreement with other sp^2 – sp^3 phase transitions. For example, $\text{Ca}[\text{CO}_3]\text{-P}2_1/c$ undergoes a sp^2 – sp^3 transition at 105 GPa, which is accompanied by an increase of the C–O bond distances from 1.228 to 1.315 Å ($\approx 7\%$)¹⁵. In the DFT model the covalent O–H bond is 1.016 Å long and has a Mulliken bond population of 0.53 $e^-/\text{Å}^3$, in contrast to the $\text{O}\cdots\text{H}$ bond which is 1.455 Å long and has a population

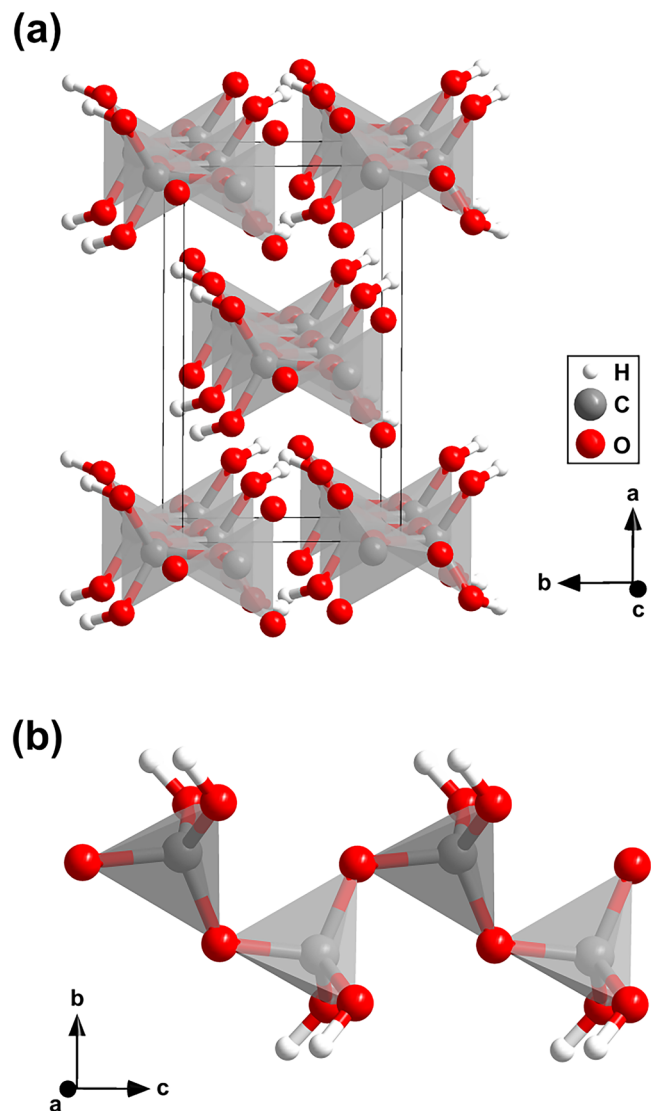


Fig. 4 | Crystal structure of $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ and polymerized protonated $[\text{CO}_4]^{4-}$ -tetrahedra. a Orthorhombic crystal structure ($\text{Cmc}2_1$, $Z = 4$) of polymeric carbonic acid (H_2CO_3) at 40(2) GPa from single crystal structure refinement. **b** Polymerized protonated $[\text{CO}_4]^{4-}$ -tetrahedra in the crystal structure of $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ forming chains along the *c*-axes.

of 0.17 $e^-/\text{Å}^3$. At 40 GPa, the hydrogen bonds are slightly kinked ($\angle \text{O–H}\cdots\text{O} = 163^\circ$) and the O–H $\cdots$ O distance is 2.444 Å indicating the presence of very strong hydrogen bonds¹².

We carried out DFPT calculations in order to calculate eigenvectors for selected vibration. Figure 5b, c shows the displacements in the H_2CO_3 molecule for the characteristic Raman modes at ≈ 820 cm^{-1} and at ≈ 910 cm^{-1} . Both modes are due to a displacement of the hydrogen atoms only, where in the ≈ 820 cm^{-1} the hydrogen moves perpendicular to the covalent OH-bond, while in the ≈ 910 cm^{-1} there is also a substantial stretching contribution. The strong Raman mode at ≈ 820 cm^{-1} is close to a Raman mode of $\text{CO}_2\text{-V}$, but a closer inspection of the peak positions of the experimental Raman data showed that the Raman mode of $\text{CO}_2\text{-V}$ is at ≈ 810 cm^{-1} while the one of $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ is at ≈ 820 cm^{-1} . This difference in shifts can be resolved experimentally and Raman maps show the strongest intensity of the two phases at different locations in the sample chamber (Fig. 2c–f).

We used our DFT-calculations to obtain the bulk modulus for $\text{H}_2\text{CO}_3\text{-Cmc}2_1$. We fitted an equation of state (EoS) to the p , V relation derived from the calculations (Fig. S4) and obtained a bulk modulus of $K_0 = 50(2)$ GPa

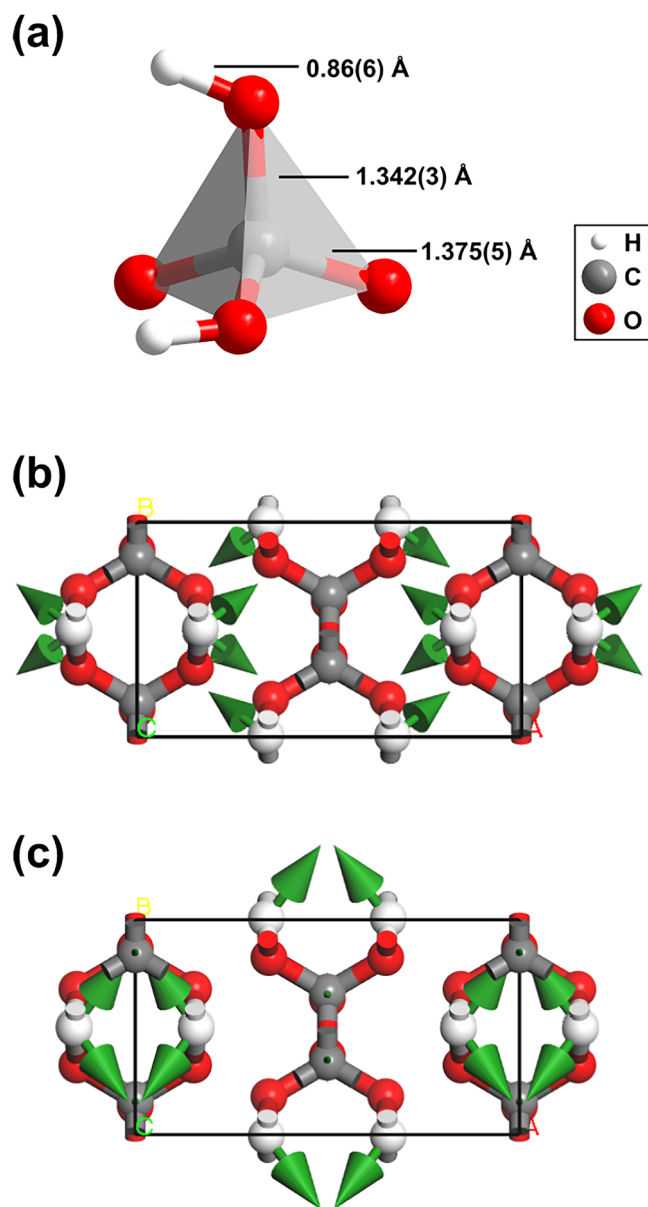


Fig. 5 | Geometry of a protonated $[\text{CO}_4]^{4-}$ -tetrahedron and eigenvectors of the atomic displacements of selected characteristic Raman modes. a Geometry of one protonated $[\text{CO}_4]^{4-}$ -tetrahedron in the crystal structure of $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ from single crystal structure refinement at 40(2) GPa. Eigenvector of the atomic displacements in polymeric carbonic acid for the characteristic Raman mode **b** at $\approx 820\text{ cm}^{-1}$ and **c** at $\approx 910\text{ cm}^{-1}$ from DFPT calculations.

with $K_p = 5.2(1)$. As expected, this is significantly higher than the one obtained for the unpolymerized, low-pressure sp^2 -polymorph $\text{H}_2\text{CO}_3\text{-P}2_1/n$ ($K_0 = 14.2(4)$ GPa with $K_p = 6.1(1)$)⁸. The bulk modulus of $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ is between the relatively high bulk modulus of polymeric $\text{CO}_2\text{-V}$ ($K_0 = 136(11)$ GPa with $K_p = 3.7(4)$) and the significantly lower bulk modulus of $\text{H}_2\text{O-VII}$ ($K_0 = 23.9(7)$ GPa with $K_p = 4.2(5)$)^{40,43}. We found that the compression behavior of $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ is significantly anisotropic since strong hydrogen bonds are located at the *b*, *c*-plane (Fig. S5). Between 30 and 90 GPa, the compression along the *a*-axis is $\approx 10\%$, while it is only $\approx 6\%$ along the *b*- and *c*-axes in the same pressure range.

Conclusion

In summary, we have synthesized and characterized single crystals of a high pressure polymorph of carbonic acid $\text{H}_2\text{CO}_3\text{-Cmc}2_1$, obtained by a reaction between H_2O and CO_2 at elevated pressures and temperatures

(≈ 40 GPa and ≈ 1000 K). This polymorph is characterized by polymerized $[\text{CO}_4]^{4-}$ -tetrahedra, which form chains along the *c*-axis by corner-sharing. The experimental crystal structure of $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ confirms the model predicted earlier based on an evolutionary algorithm⁶. In addition to the experimental description of the crystal structure, we calculated the *p*, *V*-relation and derived parameters of the $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ EoS. Moreover, we have provided an experimental and calculated Raman spectrum for this compound, which will facilitate its identification in future experiments.

Our results significantly advance the understanding of the crystal chemistry of carbonates at high pressures, as this is only the second system, after CaCO_3 ¹⁵, which is known to form linear infinite chains by corner sharing of $[\text{CO}_4]^{4-}$ -tetrahedra. $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ is a reference point in high-pressure research to study the influence of the hydrogen bonding on the formation conditions and crystal structures of hydrous sp^3 -carbonates. While the detailed examination of the stability field of $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ was outside the scope of the current study, our experimental data suggest that $\text{H}_2\text{CO}_3\text{-Cmc}2_1$ may occur inside the H_2O -rich ice shells in ice giants such as Uranus or Neptune, making it relevant for astrophysical research. This is supported by the presence of H_2O and CO_2 in the atmosphere of the hot Super-Neptune WASP-166b³¹.

Methods

The high-pressure experiments were carried out in Boehler-Almax type diamond anvil cells (DACs)⁴⁴. For the loading of the DACs, we used bidistilled water obtained from a GFL Glass Bi-Distiller and CO_2 -gas as purchased (Nippon gases, purity $\geq 99.995\%$). CO_2 was loaded as dry ice by cryogenic loading into the DAC using a custom-built cryogenic loading system (see Spahr et al.⁴⁵), derived from an earlier concept developed for similar studies⁴⁶. At the target pressure of the experiment laser-heating was performed from both sides using a custom-built set-up equipped with a Coherent Diamond K-250 pulsed CO_2 laser ($\lambda = 10,600\text{ nm}$)⁴⁷. Raman spectroscopy was performed using an Oxford Instruments WITec alpha 300R Raman imaging microscope equipped with an Olympus SLMPan N 50 $\times$ objective. The measurements were performed using the 532 nm laser and the 1800 grooves mm^{-1} grating of the WITec UHTS 300S (VIS-NIR) spectrograph. Single-crystal synchrotron X-ray diffraction was carried out at the synchrotron PETRA III (DESY) in Hamburg, Germany, at the Extreme Conditions Beamline P02.2⁴⁸. The beam size on the sample was $\approx 2 \times 2\text{ }\mu\text{m}^2$ (FWHM) using a wavelength of $0.2903\text{ }\text{\AA}$ (42.7 keV). The diffraction data were collected using a Perkin Elmer XRD1621 detector. First-principles calculations were carried out within the framework of DFT, employing the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and the plane wave/pseudopotential approach implemented in the CASTEP simulation package^{49–51}. We employed the correction scheme for van der Waals (v.d.W.) interactions developed by Tkatchenko and Scheffler⁵². A detailed description of the experimental and computational methods is available in the supplementary material.

Data availability

The X-ray crystallographic coordinates for the structure reported in this study has been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 2420110 (single crystal) and 2420111 (DFT calculation). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The supplementary material contains additional information to the results of the single crystal structure determination, Raman spectroscopy, and DFT-based calculations.

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Author contributions

D.S., L.Ba., L.Br., V.K., L.M.W., and M.B. performed experiments. V.M. and B.W. performed DFT calculations. N.G. managed the synchrotron beam line. B.W. and E.B. supervised the project.

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