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Carbonic acid monohydrate

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Abstract

In the water-carbon dioxide system, above a pressure of 4.4 GPa, a crystalline phase consisting of an adduct of the two substances can be observed to exist in equilibrium with the aqueous fluid. The phase had been found to be triclinic, and its unit-cell parameters determined, but the full crystalline and even molecular structure remained undetermined. Here, we report new diamond-anvil cell, X-ray diffraction data of a quality sufficient to allow us to propose a full structure. The crystal exists in the $P\overline{1}$ space group. Unit-cell parameters (at 6.5 GPa and 140 °C) are a = 5.8508(14), b = 6.557(5), c = 6.9513(6) Å, α = 88.59(2)°, β = 79.597(13)°, and γ = 67.69(4)°. Direct solution for the heavy atoms (carbon and oxygen) revealed CO_3 units, with co-planar, but isolated, O units. Construction of a hydrogen network, in accordance with the requirements of hydrogen bonding and with minimum allowed distances between non-bonded atoms, indicates that the phase consists of a monohydrate of carbonic acid ($H_2CO_3 \cdot H_2O$) with the carbonic acid molecule in the *cis-trans* configuration. This is the first experimental determination of the crystalline structure of a H_2CO_3 compound. The structure serves as a guide for ab initio calculations that have until now explored only anhydrous H_2CO_3 solids, while validating calculations that indicated that high pressures should stabilize H_2CO_3 in the solid state. If 4.4 GPa is the lowest pressure at which the phase is thermodynamically stable, this probably precludes its existence in our solar system, although it may exist on larger, volatile-rich exoplanets. If, however, its range of stability extends to lower pressures at lower temperatures (which possibility has not yet been adequately explored), then it might have been be a stable form of CO_2 within the water-rich moons and dwarf planets prior to differentiation and might still exist on an undifferentiated Callisto.

Keywords: Carbonic acid, CO_2, hydrate, high pressure, single-crystal X-ray diffraction, exoplanets