

# Molecule Matters

## Carbon Dioxide: Molecular States and Beyond

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Carbon dioxide is a fascinating molecule; its gaseous, liquid, solid and even supercritical fluid states have unique properties and applications. The linear triatomic structure of carbon dioxide molecule with two carbon-oxygen double bonds is all too familiar. However a whole new world has been opened up by high pressure–high temperature experiments that effected the polymerization of this small molecule into a covalent network structure with carbon-oxygen single bonds. The crystalline and amorphous forms of carbonia are built up of linked tetrahedral  $\text{CO}_4$  units.

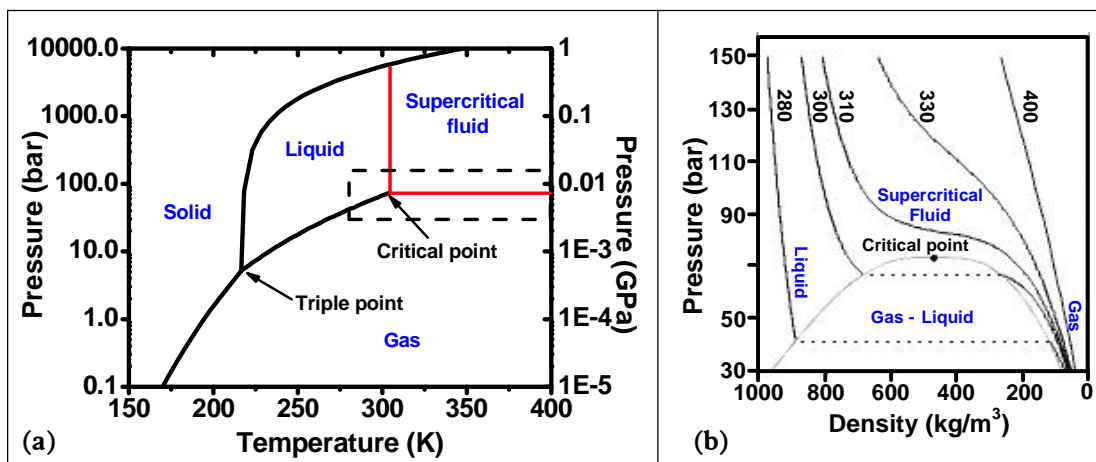
From the drinking of soda to the greenhouse effect and global warming, carbon dioxide touches our lives in myriad ways. It is one of the products of the chemical reaction involved in respiration and an important ingredient for photosynthesis in plants, both processes that sustain life on earth. In the fluid state under supercritical conditions, carbon dioxide is an excellent solvent for many chemical reactions and therefore of increasing significance in green chemistry and environmental safety issues. The solid form, familiar as ‘dry ice’, is an ideal refrigerant, subliming away into thin air after it has served its purpose. The list of unique characteristics and applications of the simple, linear triatomic molecule,  $\text{CO}_2$  can go on.

Under ambient conditions of temperature and pressure,  $\text{CO}_2$  exists in the familiar colourless, odourless, non-toxic and non-inflammable gaseous state. The phase diagram (*Figure 1a*) shows that the ‘triple point’ of  $\text{CO}_2$  occurs at 216.6 K and 5.1 bar; this is the temperature-pressure point at which the three phases – solid, liquid and gas – coexist and are in equilibrium. Gaseous  $\text{CO}_2$  is known to produce the greenhouse effect, by retaining heat in the atmosphere through the absorption of infrared waves re-radiated

### Keywords

Carbon dioxide, phase diagram, supercritical fluid, polymeric  $\text{CO}_2$



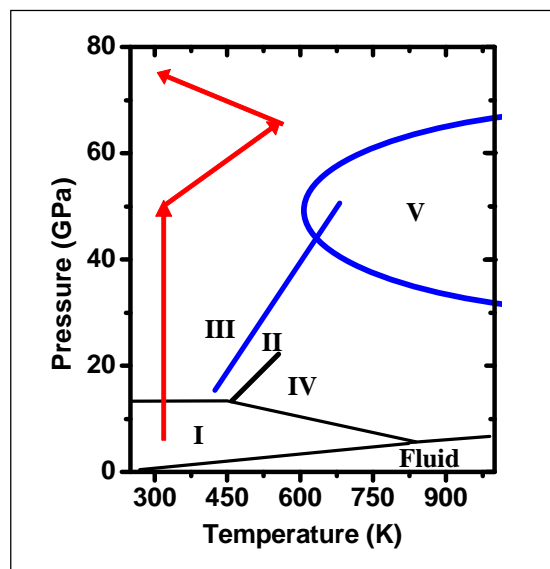


from the earth surface subjected to solar irradiation. Cooling  $\text{CO}_2$  gas at 1 bar pressure will take it directly into the solid phase without going through the liquid state (Figure 1a), solid  $\text{CO}_2$  thus earning the name 'dry ice'. Dry ice is a crystalline material (belonging to the crystallographic space group [1] with cubic symmetry,  $Pa3$ ) [2] held together by weak interactions of the nonpolar molecules of  $\text{CO}_2$ . Its easy sublimation under ambient conditions makes it a convenient refrigerant for chemicals, pharmaceutical items and food products. Cooling  $\text{CO}_2$  to about 258 K and pressurizing to 15.5 bar produces liquid  $\text{CO}_2$  that is also used as a cooling agent. Supercritical  $\text{CO}_2$  is obtained in the region above 304.1 K and 73.8 bar, the critical temperature and pressure of  $\text{CO}_2$  respectively. At the critical point and above, the gaseous and liquid states attain identical density (Figure 1b) and cannot be distinguished from each other resulting in a single fluid phase [3]. Thanks to its low viscosity, fast diffusion into solids and ease of processing after reactions, supercritical  $\text{CO}_2$  is becoming the preferred solvent for several polymerization reactions, extraction of natural products and pharmaceuticals and even semiconductor processing, dry cleaning and paint industry; it is being used in established industrial processes for decaffeination of coffee and tea!

It is interesting to see what would happen if  $\text{CO}_2$  was subjected to high pressures and temperatures, well beyond the region shown

**Figure 1. (a) Phase diagram of  $\text{CO}_2$ . The red lines demarcate the region corresponding to the super-critical fluid. The broken line box represents the pressure – temperature region described in Figure 1b. (b) Pressure-density plot for  $\text{CO}_2$  at different temperatures (values in K are indicated on the curves). The dashed horizontal lines indicate gas-liquid equilibrium in the 2-phase region below the critical point. This figure is adapted from [4].**

**Figure 2. High temperature–high pressure phase diagram of  $\text{CO}_2$ ; note the change in the scale of the axes with respect to that in Fig. 1. I – IV are the solid phases of molecular  $\text{CO}_2$ . The blue lines indicate kinetic barriers between phases. V is the crystalline solid phase of polymeric  $\text{CO}_2$ ; its real thermodynamic phase probably starts at a lower temperature. The red arrows indicate a route to the amorphous form, *a*-carbonia. This figure is adapted from [5] (see also [6]).**



in the phase diagram in Figure 1a. A complex scenario emerges with several phases in the solid state; a schematic representation of the current understanding of this region is shown in Figure 2. ‘Dry ice’ is designated as  $\text{CO}_2$ -I. Increasing the pressure to about 12 GPa at 300 K transforms  $\text{CO}_2$ -I to a new crystalline phase  $\text{CO}_2$ -III, which has a different crystalline arrangement of the  $\text{CO}_2$  molecules and belongs to the orthorhombic space group *Cmca* [2]. The transition is mechanically driven by shear, and involves mainly reorientation of the  $\text{CO}_2$  molecules with no significant change in the crystal density (i.e., no volume discontinuity). Two phases designated  $\text{CO}_2$ -II and  $\text{CO}_2$ -IV have been proposed to occur between the stable regions of  $\text{CO}_2$ -I and  $\text{CO}_2$ -III; in spite of extensive work that has been carried out, there is still no complete consensus on the actual structure of these phases. It should be stressed further that there is still considerable debate on several aspects of the high pressure-high temperature phases of  $\text{CO}_2$  [6].

$\text{CO}_2$ -III was found to be stable at ambient temperature, even when subjected to pressures as high as 80 GPa. However, it was observed that the strength of this solid increased substantially at high pressures; this feature is uncommon in molecular solids



held together by weak van der Waals interactions and could be considered a sign of the emergence of strong intermolecular interactions. This is particularly significant when one recalls that elements such as silicon, germanium and tin which occur in the same group (IV, also designated as 14) of the periodic table as carbon, form solid dioxides with extended network of covalent bonds, for example, silica ( $\text{SiO}_2$ ) in the familiar forms of crystalline quartz and amorphous glass. An analogous state for  $\text{CO}_2$  (carbonia) was unknown until experiments in 1999 showed that,  $\text{CO}_2$ -III confined inside a diamond anvil cell under 40 GPa pressure and subjected to laser heating was transformed into a new solid phase,  $\text{CO}_2$ -V; the temperature at which it formed was estimated to be  $\sim 1800$  K [7]. Vibrational spectroscopy including study of the pressure-dependence of different vibrations revealed that  $\text{CO}_2$ -V resembled silica. Interestingly this solid was shown to double the frequency of laser light incident on it, just like quartz does; this is a nonlinear optical effect that can be realized in materials with a lattice structure lacking centre of inversion symmetry [8]. Detailed X-ray investigations [2] indicated that the conversion of  $\text{CO}_2$ -III to  $\text{CO}_2$ -V is accompanied by a volume decrease of  $\sim 15\%$  implying that the molecules have come closer together.  $\text{CO}_2$ -V is a 'super-hard' polymeric form of  $\text{CO}_2$ , a covalent solid constituted of vertex-sharing  $\text{CO}_4$  polyhedra with extended network of carbon-oxygen single bonds (Figure 3). It belongs to the orthorhombic space group  $P2_12_12_1$  and is structurally similar to tridymite, a high temperature form of silica.

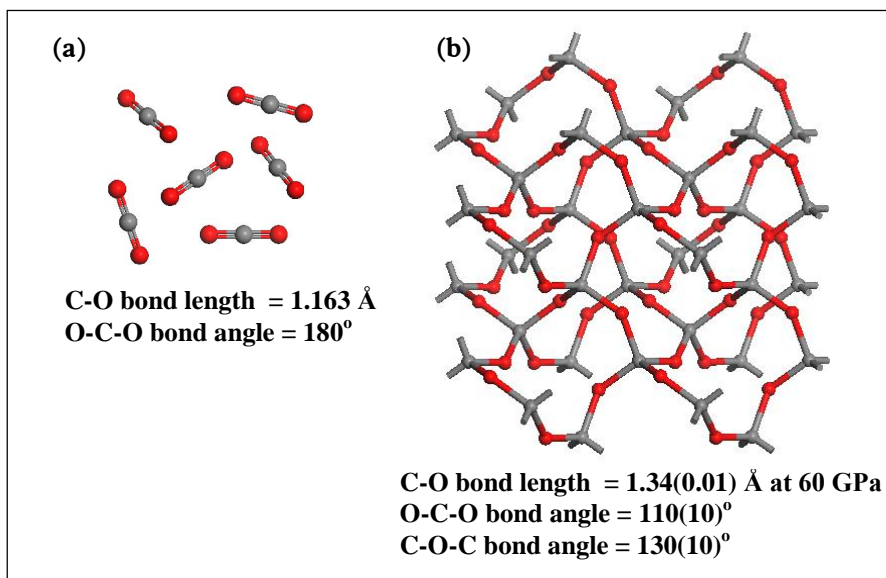
A natural question that arises at this point is whether the polymeric  $\text{CO}_2$  can exist in an amorphous form, the state that we are very familiar with in the case of silica-based glasses. It turns out that the glassy form of polymeric  $\text{CO}_2$  can be prepared by compressing  $\text{CO}_2$ -III to above 40 GPa and heating to moderate temperatures (Figure 2) [5].

Investigations on temperature-quenched samples using Raman spectroscopy, synchrotron X-ray diffraction and molecular dynamics simulations suggest that the material obtained is indeed

## Suggested Reading

- [1] See : <http://202.41.85.161/~ch521/x-ray.ppt> for a brief introduction to basics of symmetry and x-ray diffraction.
- [2] C S Yoo, H Cynn, F Gygi, G Galli, V Iota, M Nicol, S. Carlson, D. Häusermann, C Mailhot, Crystal Structure of Carbon Dioxide at High Pressure: 'Superhard' Polymeric Carbon Dioxide, *Physical Review Letters*, Vol. 83, No. 26, pp. 5527 – 5530, 1999.
- [3] See images at <http://www.chem.leeds.ac.uk/People/CMR/criticalpics.html>
- [4] [http://en.wikipedia.org/wiki/Image:Carbon\\_dioxide\\_density\\_pressure\\_phase\\_diagram.jpg](http://en.wikipedia.org/wiki/Image:Carbon_dioxide_density_pressure_phase_diagram.jpg)
- [5] M Santoro, F A Gorelli, R Bini, G Ruocco, S Scandolo, W A Crichton, Amorphous Silica-like Carbon Dioxide, *Nature*, Vol. 441, pp. 857 – 860, 2006.
- [6] M Santoro, F A Gorelli, High Pressure Solid State Chemistry of Carbon Dioxide, *Chem. Soc. Rev.*, Vol. 35, pp. 918–931, 2006.
- [7] V Iota, C S Yoo, H Cynn, Quartzlike Carbon Dioxide: An Optically Nonlinear Extended Solid at High Pressures and Temperatures, *Science*, Vol. 283, pp. 1510–1513, 1999.
- [8] T P Radhakrishnan, Molecules to Materials: Part 4. Molecular Nonlinear Optical Materials, *Resonance*, Vol. 3, No. 8, pp. 14–24, 1998.
- [9] P F McMillan, A Glass of Carbon Dioxide, *Nature*, Vol. 441, p. 823, 2006.





**Figure 3. (a) Molecular and (b) polymeric CO<sub>2</sub>; carbon (gray) and oxygen (red). The polymeric structure is generated assuming a silica-like lattice and the continuation of the network is indicated by the half bonds on carbon atoms at the edge; the geometry parameters are from [2].**

amorphous. The network-forming disordered system is homologous to other group IV (group 14) dioxide glasses; it has been christened a-CO<sub>2</sub> (a-carbonia) in analogy to the amorphous forms of SiO<sub>2</sub>, a-silica and GeO<sub>2</sub>, a-germania. Both CO<sub>2</sub>-V and a-CO<sub>2</sub> revert back to the molecular state when brought back to ambient temperature-pressure conditions. Decompression of a-CO<sub>2</sub> appears to produce a glassy state of molecular CO<sub>2</sub>; this is a dramatic case of polyamorphism – materials existing in different amorphous states with phase transitions driven by density or entropy variation.[9].

The crystalline and amorphous forms of polymeric CO<sub>2</sub> provide significant insight into the transformations of light element based molecules under high pressure and temperature and unravel new avenues in solid state chemistry under extreme conditions. If these materials can be recovered to ambient conditions, potential technological applications can be considered. A possible route to this could be the polymerization carried out within chemically inert and stable molecular matrices. Will this lead to new tricks to trap the greenhouse gas and reduce its concentration in the atmosphere?

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