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C. S. Yoo

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High-Pressure Chemistry of Molecular Solids: Evidences for Novel Extended Phases of Carbon Dioxide

Choong-Shik Yoo*
L-45, H-Division, Physics Directorate
Lawrence Livermore National Laboratory, Livermore, CA 94551, USA
(yool@llnl.gov; (925) 422-2851)

At high pressures and temperatures, many molecular solids become unstable and transform into denser extended phases. Recently, we have discovered evidences for two novel extended phases of carbon dioxide at high pressures and temperatures: (1) an ionic form of dimeric CO\(_2\), CO\(_2^+\)CO\(_2^-\) at 8-13 GPa and above 2000 K [1] and (2) a polymeric phase CO\(_2\)-V above 35 GPa and 1800 K [2,3]. These extended phases can be quenched at room temperature at low pressures, from which their molecular and crystal structures have been determined. These transitions occur to soften highly repulsive intermolecular potentials via delocalization of electrons at high pressures and temperatures. Based on these and other previous results, we conjecture that three fundamental mechanisms of high-pressure chemistry are ionization, polymerization, and metallization, occurring in high-density molecular solids and fluids.

[carbon dioxide, polymeric CO\(_2\), ionic CO\(_2\) dimer, high-pressure chemistry, electron delocalization]

1. Introduction

Application of high-pressure strongly perturbs the nature of chemical bonding, electronic and crystal structures, thermal, mechanical, and optical properties, and chemical reactivities of solids. These perturbations, which often occur systematically, provide opportunities for synthesizing new novel materials. Discoveries of a wide variety of materials unique to high P,T-conditions support this thesis; these include novel-gas compounds [4], metallic hydrogen [5], symmetric ice [6], superhard materials [7], high energy density polymers [8], and alkali-transition metal alloys [9]. Commonly used guidance suggestive to these discoveries has often been inferred from the electronic configuration, intermolecular interaction, crystal structure, effective close-packing and density, solubility and miscibility, group periodicity, and pressure-induced changes of these properties.

Molecular solids are described in terms of strong covalent bonds within molecules and weak van der Waals interactions between molecules. The strong intramolecular bonds make these molecules extremely stable at ambient conditions; whereas, the weak intermolecular interactions make such crystals very soft, at least initially at relatively low pressures. Because of this reason, many simple molecular solids particularly made of the first and second row elements such as CO\(_2\), N\(_2\), C, H\(_2\)O, CH\(_4\), other C-N-O-H compounds are often considered as "inert" at relatively low pressures below 10 GPa. In fact, high stabilities of these molecules are often assumed even at very high pressures (10-40 GPa) and temperatures (1000-5000 K), as CO\(_2\), N\(_2\), H\(_2\)O, C are considered to be four major detonation products of energetic molecules.

At high pressures, however, the nature of these intermolecular interactions rapidly alters and becomes highly repulsive. Electron kinetic energy dominates, and electrons localized within intramolecular bonds become unstable. It is due to the higher power dependence of kinetic energy on density, \(\rho^{2/3}\), than that of potential energy, \(-\rho^{1/3}\) (see Fig. 1). Under these circumstances, molecular solids should undergo physical and chemical changes in order to modify their chemical bonding and to soften their stiff repulsive intermolecular potentials.

Three mechanisms may occur at high pressures to delocalize electrons and soften repulsive potentials: (i) ionization creating attractive electrostatic energy, (ii)
polymerization delocalizing intramolecular electrons between neighboring molecules, and (iii) metallization completely delocalizing electrons through conduction bands. Very recently, we have discovered the experimental evidences for the ionization [1] and polymerization [2,3] of carbon dioxide, both of which occur prior to its metallization at high pressures and temperatures. We defer the detailed experimental results and discussions to those reports [1-3]; whereas, in this paper we will summarize the results in the context of presenting a fundamental rule for chemistry of molecular solids at high pressures and temperatures. That is, the transitions in molecular systems occur as isolated covalent solids → ionic forms → polymeric phases → metallic phases, with increasing pressures.

II. Experiments

The transformations of molecular solids to the extended phases often require relatively large positive volume changes (5-20 cm³/mol) and, thus, are associated with large kinetic barriers (30-150 KJ/mol) [10]. As a result, these transitions are greatly hindered kinetically despite large thermodynamic stabilities of final products. Nitrogen may be a good example, in which system the polymerization has been suggested theoretically at about 60 GPa [8] but recent experiments indicate nitrogen being molecular even at 120 GPa [11].

In this study, we use a laser-heating technique to overcome the kinetic barrier existing in the molecular-to-extended phase transitions of carbon dioxide. Two types of experiments were performed: (1) polymeric carbon dioxide was synthesized by heating carbon dioxide to high temperatures (>1800 K) at high pressures (>35 GPa). (2) the ionic phase of carbon dioxide was synthesized by catalytic combustion reactions between carbon particles and oxygen at relatively low pressures (8-13 GPa) and high temperatures (> 2000 K). For the latter case, carbon powders (graphite polycrystals of a few- to sub-μm dimensions) were loaded into a diamond-anvil cell with oxygen by an immersion technique. For the former case, liquid CO₂ was loaded in a diamond-anvil cell (DAC) contained in a high-pressure vessel by condensing CO₂ gas at ~40 °C and 10 atmospheres.

Both types of samples were heated by using a Nd:YLF laser. However, because of the low absorption of carbon dioxide at the wavelength of Nd:YLF (1.054 μm), carbon dioxide was indirectly heated through ruby particles. Temperature of the sample was determined by fitting the thermal emission from the heated-area to a gray-body radiation formula. The quenched products were investigated by using Raman spectroscopy and synchrotron x-ray diffraction at both ESRF (ID-30) and SSRL (BL10-2). Angle-resolved x-ray diffraction patterns of several samples were obtained as a function of pressure by using a focused monochromatic x-ray beam and image-plate detectors.

III. Results

**Molecular phases:** Carbon dioxide crystallizes to the cubic Pa3 structure, CO₂-I at 1.5 GPa and ambient temperature [12]. Above 11 GPa, CO₂-I transforms to the orthorhombic Cmca phase, CO₂-III [12], which exists in a wide range of pressures above 70 GPa [3]. The large quadruple moment of linear CO₂ molecule is considered to stabilize both CO₂-I and III at least at relatively low pressures [13]. However, above 30 GPa, CO₂-III develops a very characteristic texture indicative of a highly strained lattice. It also shows an abnormally large pressure gradient exceeding 20% of the maximum pressure of the sample within 100 μm. These observations clearly indicate that CO₂-III has high material strength at these pressures, which is rather unusual for a molecular crystal. In fact, the bulk modulus of CO₂-III has also been found to be unusually high 87 GPa, similar to that of elemental silicon [3]. For comparison, the bulk modulus for CO₂-I is 12 GPa, while those of other molecular solids typically range between 2 and 15 GPa.

**Polymerization:** The highly strained, high strength CO₂-III transforms to a polymeric form of CO₂-V above 35 GPa and 1800K [2]. The vibrational spectrum of CO₂-V suggests that it is an extended-solid with carbon-oxygen single bonds. It is also found that CO₂-V is a non-linear optical material converting the Nd:YLF laser light to its second harmonic with a high conversion efficiency [2].

![Fig. 2. The crystal structure of CO₂-V along the ac-plane made of interconnecting CO₂ tetrahedral units. This structure is analogous to one of tridymite structures in SiO₂.](image)

In our recent x-ray studies [3], we have characterized the crystal structure of CO₂-V to be orthorhombic (P2₁2₁2₁),
analogous to SiO₂ tridymite (a distorted high temperature phase of β quartz) [14,15]. In this structure, all carbon atoms are bonded to four oxygen atoms with the carbon-oxygen distance of 1.36 Å at 40 GPa and an O-C-O angle of 110°. These CO₄ tetrahedral units share their corner oxygen atoms to form a layered structure in the ab-plane; whereas, the apices of the tetrahedra are connected through oxygen atoms along the c-axis (see Fig. 2). This interconnected layer structure of tetrahedra results in a C-O-C angle of 130°, substantially smaller than those of SiO₂ tridymites 174-180° or of quartz 145°. Such rigidity in the C-O-C angles may reflect the fact that oxygen atoms in CO₄-V are more tightly bound than in SiO₂ and result in a higher covalence and bulk modulus for CO₂-V than for any of the SiO₂ polymorphs. In fact, we found that the bulk modulus of CO₂-V is about 362 GPa [3], substantially higher than SiO₂-quartz (37 GPa) and even stishovite (310 GPa). It is nearly the same value with cubic-BN (369 GPa) [16].

The polymerization of CO₂ to a SiO₂-like structure is in a systematic accordance with other phase transitions such as β-C₃N₄ in the β-Si₃N₄ structure [7], carbon in the Si-diamond structure, polymeric N₂ in the black-P structure [8]. That is, compression of the 2nd-row elements transform to their 3rd-row analog structures. These new analogs of the 2nd-row elements then result in higher cohesive energies with extremely lower compressibilities and higher thermal conductivities than those of the 3rd-row materials.

**Ionization:** In contrast to the polymerization at high pressures, CO₂ molecules are very stable at low pressures below 30 GPa even at high temperatures above 3000 K. This clearly indicates that there is even higher kinetic barrier for breaking C=O bonds at low pressures than at high pressures.

Therefore, we have used the catalytic combustion reactions between hot carbon particles and oxygen molecules to investigate other extended forms of CO₂ at low pressures. In these carbon combustion experiments, we found that the carbon and oxygen mixtures transform to CO₂ and CO₂⁺CO₂⁻, an ionic form of (CO₂)₂ as evident from Fig. 3 [1].

Similar ionization reactions have previously been observed in the nitrogen dioxide dimer (N₂O₅) both at high pressure and high temperature [17] and at ambient pressure and low temperature [18]. It transforms to NO⁺NO₂ whose vibrational characteristics are strikingly similar to those of CO₂⁺CO₂⁻ in Fig. 3. The ionization reactions create attractive electrostatic energies and thus soften the repulsive intermolecular potentials at high pressures and temperatures. The densification resulting from the dimerization also favors the formation of these dimer species at high pressures and temperatures.

**IV. Discussion**

Based on these and other previous studies on carbon dioxide at high pressures and temperatures, one can construct the phase diagram as shown in Fig. 4. Four molecular phases have been suggested at high pressures and room temperatures: two well known phases of CO₂-I and III and two less known phases of CO₂-II [19] and IV [20]. The latter two phases (not shown in Fig. 4) were respectively proposed between 0.5 and 2.3 GPa and between 10 and 20 GPa; however, their structures and existences have never been confirmed.

![Fig. 3. Raman spectrum of C+O₂ reaction products quenched from 2000 K at 8.9 GPa, showing the evidence for CO₂⁺CO₂⁻, an ionic form of CO₂ dimer.](image)

![Fig. 4. A proposed phase diagram of carbon dioxide illustrating the transitions of molecular carbon dioxide to novel extended phases at high temperatures and pressures.](image)
These molecular phases of carbon dioxide transform into the extended forms at high pressures and temperatures: to an ionic dimer below 13 GPa with half of the carbon atoms being three-fold coordinated and to a polymorphic form above 35 GPa with all carbon atoms being four-fold coordinated. It is not known if other types of CO₂ multimers, perhaps with all carbon atoms three-fold coordinated, exist at high temperatures between 15 and 35 GPa. However, the laser heating studies of CO₂-III at these pressures have as yet shown no apparent evidence for such a hypothetical multimer.

Unlike most "soft" molecular solids, carbon dioxide at high pressures, CO₂-III in particular, supports a large pressure gradient attributing to a relatively high material strength. This may reflect an enhanced intermolecular interaction or even weak intermolecular bonding amongst neighboring CO₂ molecules. Such an increase in the intermolecular interaction would result in two counteracting consequences: (1) Delocalization of electrons in CO₂ molecules would soften the evidence for such a hypothetical multimer.

The existence of highly interacting ionic species of carbon dioxide at high pressures and temperatures may have critical implications for understanding the detonation chemistry of energetic molecules. For example, the interactions and chemical reactivities of ionic species certainly differ from those of neutral species that most current detonation models assume to be the major detonation products over a wide range of pressures and temperatures. The polymorphic CO₂, on the other hand, may have very important technological implications for developing a high-power second harmonic generator, a high strength glass, and a superhard material, especially if it can be recovered metastably at ambient pressure. Finally, these molecular-to-extended phase transitions also provide a fundamental insight to the high-pressure chemistry of many other simple molecular solids including H₂, N₂, H₂O, CO, O₂.

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