New Transformations of CO_2 at High Pressures and Temperatures

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CO_2 laser heating of solid CO_2 at pressures between 30 and 80 GPa shows that this compound breaks down to oxygen and diamond along a boundary having a negative P-T slope. This decomposition occurs at temperatures much lower than predicted in theory or inferred from previous experiment. Raman spectroscopy and x-ray diffraction were used as structural probes. At pressures higher than 40 GPa the decomposition is preceded by the formation of a new CO_2 phase (CO_2-VI). These findings limit the stability of nonmolecular CO_2 phases to moderate temperatures and provide a new topology of the CO_2 phase diagram.

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Condensed molecular systems under pressure can undergo transitions to dense phases by way of major changes in bonding character to form metallic or one- to three-dimensional covalent structures. Examples of the latter include pressure-induced polymerizations in CO [1], N_2 [2], and CS_2 [3,4]. Recently there has been important evidence for transformations of CO_2 to network structures [5–7]. At ambient pressure CO_2 solidifies in a cubic structure with oriented CO_2 molecules located on fcc lattice sites. With increasing pressure CO_2 undergoes transitions to lower symmetric molecular phases based on distortions of the structure [8,9]. Recent experimental studies, however, reported the transformation of molecular, solid CO_2 (CO_2-III [8]) to a covalently bonded network structure [5,7] at pressures higher than 35 GPa after laser heating above 1800 K. This new structure was identified as an analog of tridymite, one of the ambient-pressure, high-temperature phases of SiO_2 [7]. Along with this experimental study, *ab initio* calculations [6] indicated that at 1000 to 2000 K crystalline covalent phases of CO_2 are more stable than any molecular CO_2 phase as well as a mixture of diamond and oxygen. Other calculational work supported the suggestion that covalent bonded CO_2 assumes structures analogous to SiO_2 [10,11]. Here we show that solid CO_2 decomposes to carbon and oxygen along a reaction boundary that substantially limits the range of stable covalent C-O structures. In addition to CO_2-V, we find evidence for another high pressure CO_2 phase stable at moderate temperatures, which we designate CO_2-VI. Thermodynamic analysis shows that the breakdown occurs as a result of the combined effects of density and entropy.

CO_2 was condensed in a cooling trap. Transparent pieces of solid CO_2 of about $50 \times 50 \times 30$ μm^3 size were retrieved from the cooling trap and loaded in diamond cells. Typically the load was increased to 20–70 GPa and the sample was heated with a CO_2 laser at 60 W power by focusing the beam to a spot of less than 30 μm diameter. Above 40 GPa the absorbance of CO_2 at 10 μm wavelength was too low to heat above 1800 K under these conditions. Therefore in order to reach temperatures between 2500 and 3000 K at pressures above 40 GPa we used ruby or quartz that was ground to ~1 μm diameter grains and then pressed into pellets of $30 \times 30 \times 3$ μm^3 as absorbers. The main contribution to the incandescent light from the sample chamber was from the ruby and silica grains. The relative errors in temperature measurement were estimated to be ±100 K. The indirect heating implied temperature gradients and limited the accuracy of the temperature measurement. Below 40 GPa, however, CO_2 could be heated directly to the required temperatures. We heated the samples for 100 to 200 s. Above 30 GPa, no phenomena related to melting were observed. After temperature quench, some of the samples appeared to be darkened in the area of the hot spot. In addition, we performed an experiment on CO_2 using a pellet pressed from quartz powder as absorber. This pellet was isolated from the lower diamond anvil by a ~3 μm thick layer of NaCl. This assemblage allowed us, for the heating of an area of ~60 μm diameter, to reach even higher temperatures than in the other experiments at a pressure of 63 GPa. The sample was kept for 150 s at 3000 K. Afterwards the surrounding and the outer ranges of the heated area substantially darkened. X-ray diffraction patterns were collected at beam line X17C at the NSLS using polychromatic radiation and a Ge detector. Details of the setup are described elsewhere [12].

Figure 1a shows Raman spectra collected at various pressures after quenching from high temperatures. Spectra were taken using the 488.0 and 514.5 nm excitation lines of an Ar^+ laser. The generation of oxygen during the high temperature runs is evident from comparing the Raman peaks of the run products to those of ϵ-O_2 [13] as shown in Fig. 2a. We point out that all three prominent Raman peaks of oxygen, the ν_{L1} and ν_{L2} librons as well as the vibron, match our findings (Fig. 2a) in both frequency and relative intensity (Ref. [13]). Oxygen is also generated when SiO_2 is used as absorber instead of Al_2O_3 in the same range of pressures. Between 28 and 40 GPa, we observed ϵ-O_2

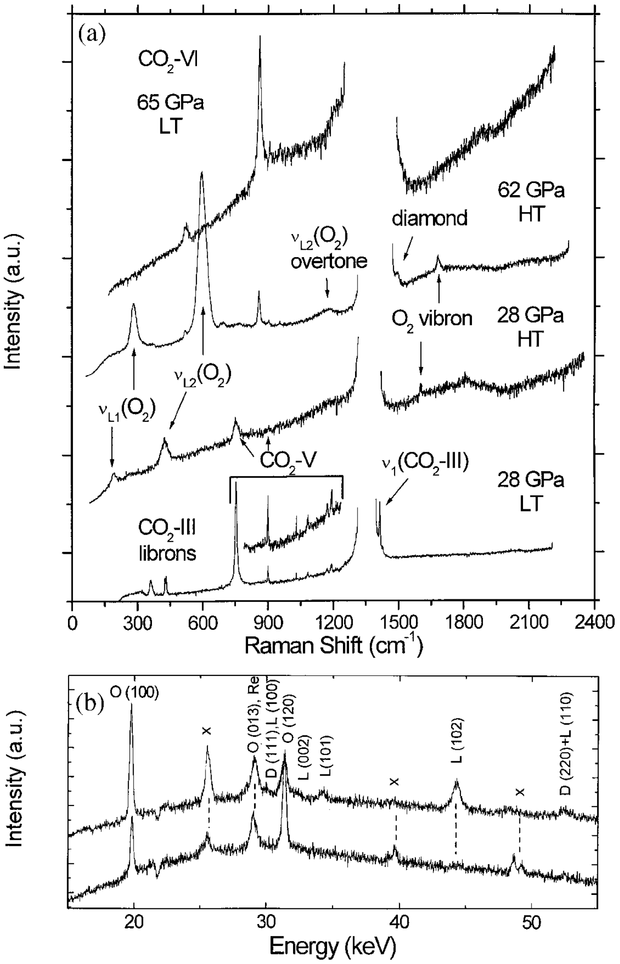

FIG. 1. (a) Raman spectra of CO_2 heated at high pressure. First spectrum: after heating at 65 GPa, 1500 K; second spectrum: the same sample after additional heating to 2500 K; third spectrum: on release and after additional heating up to 3000 K by direct absorbance and melting of most parts of the sample. The lowermost spectrum was collected on a different sample after heating to 1800 K. (b) Diffraction pattern of laser heated (upper spectrum) CO_2 and the surrounding area (lower spectrum). The white x-ray beam was focused to 12×14 μm^2. d-spacings of lonsdaleite (L), diamond (D [19]), ϵ-O_2 (O), and Re are labeled. The (111) peak of diamond is coinciding with the (100) of NaCl. The shoulder on the (120) peak of O_2 is from Re. Crosses: peaks attributed to stishovite or residual C-O phases formed by incomplete decomposition.

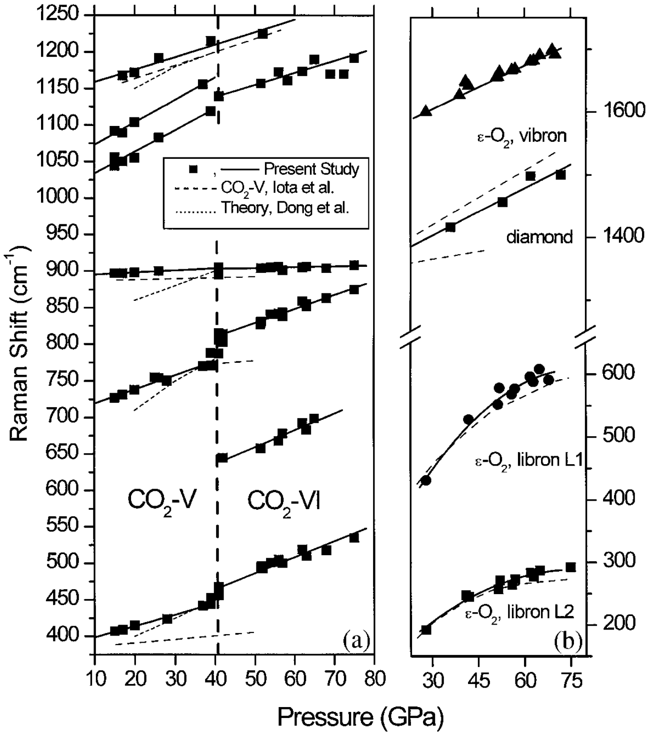

FIG. 2. (a) Raman shifts of heated CO_2 between 15 and 76 GPa. Black lines: fits through present data; dashed lines: CO_2-V according to [5]; dotted lines: CO_2 in the β-cristobalite structure, calculated in Ref. [10]. (b) Frequencies of the Raman shifts of ϵ-O_2 and the diamondlike phase versus pressure. Solid lines: ϵ-O_2 [14]; dashed lines: diamond [15].

after heating the CO_2 directly to 2500 to 3000 K (Fig. 1a). From these findings we conclude that free oxygen was generated by heating CO_2 between 28 and 75 GPa.

In some runs we also observed Raman peaks at frequencies near that of the diamond anvil between 36 and 72 GPa. The comparison to the Raman spectrum of diamond at high pressure [14] indicates that these peaks belong to a carbon phase closely related to diamond (see Fig. 2a). The fact that this Raman shift is at higher wave number than the signal of the anvil and occurs only after heating (shown in the upper spectrum of Fig. 1a) indicates that it belongs to material created inside the sample chamber rather than being related to the anvil. Figure 1b shows the diffraction data of the additional run described above. The upper pattern was collected on the heated area, the lower one is from the surrounding. The approximate positions of diamond, lonsdaleite, and O_2 at 63 GPa are indicated. The heated area exhibits several patterns which match the d spacings of these phases indicating the generation of a diamond polytype similar to lonsdaleite. Outside the heated area these peaks disappear while patterns belonging to CO phases formed by incomplete decomposition are much more pronounced. Furthermore we observed peaks matching those of ϵ-O_2 as reported by Akahama *et al.* [15].

Several of the observed Raman peaks belong to neither ϵ-O_2 nor diamond; we attribute them to C-O compounds. In runs at P-T conditions below the decomposition boundary (see Fig. 3), as well as in the surrounding regions of the heated area where the temperature during heating did not exceed 1500 K and no Raman peaks of oxygen were found, we observed additional bands that we assign to a CO_2 phase rather than a phase of different stoichiometry. Figure 2b shows the pressure dependence of the Raman peaks of CO_2 found in these experiments. Our data are very similar to previously reported results for CO_2-V [5] at pressures below 40 GPa. The only marked exception is for the mode around 400 to 450 cm^{-1}. In this case our data are closer to the theoretical predictions for CO_2 in the β-cristobalite structure [10]. We note that these spectra were collected on directly heated CO_2 and thus show that

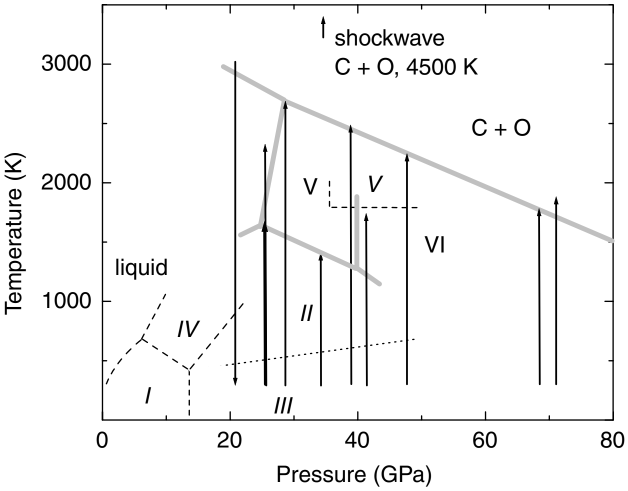

FIG. 3. Reaction diagram of CO_2 at high pressures and temperatures. Dashed lines indicate phase boundaries according to Ref. [16]. Gray lines: Reaction boundaries according to present work. Arrows: P-T paths of selected runs (not including thermal pressure corrections). Italic numerals are the phase fields identified in Ref. [16].

phase V is not a product of reactions with absorbers (Ref. [5]). At higher pressures, the observed Raman peaks and those of CO_2-V and the predicted β-cristobalite phase show marked differences. Without heating, the Raman spectrum of CO_2-V changes continuously between 15 and at least 80 GPa. This and the sudden change in spectral features around 40 GPa after heating indicate a transition to a new phase of CO_2 generated at elevated temperature. This phase is not a product of reactions with absorbers since it was formed in samples heated directly to temperatures below 1800 K as well as in indirectly heated material. Below 40 GPa the spectrum shows two peaks between 1050 and 1150 cm^{-1} which were not previously reported [5]. The overall pressure dependence of the Raman spectrum of CO_2 before and after the 40 GPa transition suggests that these two peaks belong to CO_2-V. Further, we note that CO_2-V and the new high pressure phase of CO_2 are generated within 20 s if the temperature is between 1500 to 1800 K and replace CO_2-III even outside the hot spot completely after heating for longer times (100–200 s). The transition from CO_2-III to these two phases is thus not subject to strong kinetic barriers and apparently takes place at temperatures much below 1000 K.

Figure 3 summarizes our findings in a reaction diagram. As discussed above, the boundary between molecular and nonmolecular CO_2 is likely to be lower than 1000 K at pressures above 50 GPa. The high P-T stabilities of CO_2-V and CO_2-VI, respectively, are constrained by experiments at 38 GPa, 2500 K and 69 GPa, 1700 K both showing decomposition. Above 50 GPa, there was no sign of melting observed up to 2800 K. These findings show that the nonmolecular CO_2-V and CO_2-VI are high-pressure phases stable at moderate temperatures. The low pressure phase boundary of CO_2-V appears to be almost 10 GPa lower than previously reported [5]. CO_2-V transforms back to a molecular phase similar to phase IV [16] when heated at 26 GPa to more than 2000 K. We show a data point based on shock experiments that were interpreted as decomposition at very high temperature [17]. At 21 GPa, diamond and oxygen that were formed at higher pressure recombined when heated to 3000 K. Heating CO_2 at 28 GPa to 2800 K resulted in decomposition. This, as well as the higher pressure runs starting with CO_2, define an upper P-T boundary for the decomposition. We emphasize that the diagram in Fig. 3 does not include any possible carbon suboxide phases which may coexist stably with O_2 at pressures and temperatures where diamond has not been observed as a reaction product [18].

To further understand the origin of the decomposition and other transformations, we examine the thermodynamic stability of the various phases in the CO_2 system based on existing experimental data starting from the equations of state of CO_2 and C + O_2. Figure 4 shows the molar volumes of diamond and ϵ-O_2 [15,19], as well as those of CO_2-III [20] and CO_2-V (as reported in Ref. [7]) at 300 K. The assemblage of diamond plus ϵ-O_2 has a lower molar volume than both CO_2-III over its entire range of stability and that reported for CO_2-V above 22 GPa (reaching a difference of ~6% around 100 GPa). This observation was not noted in previous work [20]. It indicates that in the absence of another transition, CO_2 decomposes at high enough pressure. The volume of liquid CO_2 where decomposition was reported from shock experiments at 4500 K [17] is also indicated. Figure 4 also shows the 0 K volumes of CO_2 in the β-cristobalite structure as calculated by Dong *et al.* [21]. The calculated β-cristobalite has a much smaller volume than those reported for CO_2-V. It might be, however, underestimated by the applied calculational method [21].

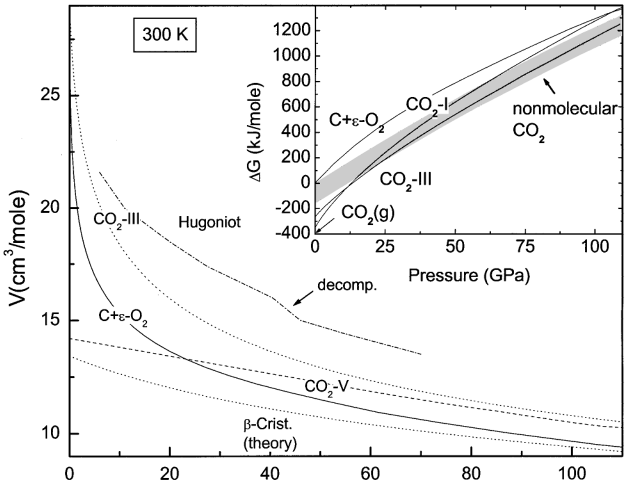

FIG. 4. Molar volumes of diamond plus ϵ-O_2 (solid), CO_2-V (dashed), the molecular phase CO_2-III (dotted), calculated proposed β-cristobalite [21], and the Hugoniot of CO_2 [17]. Inset: Calculated free energies of CO_2 phases, and diamond plus ϵ-O_2. Shaded area: nonmolecular CO_2 phases (see text).

Estimates of the free energies of diamond and ϵ-O_2, the molecular phases CO_2-I and -III, and CO_2-V based on the reported data [7] at 300 K are also shown in Fig. 4. The formation energy of CO_2, the energy of fusion of phase I [22], and the transition of CO_2-I to CO_2-III at 11.8 GPa [8] allow us to constrain the increase in free energies of these phases with pressure. Because thermochemical data are lacking for nonmolecular CO_2, we give an approximate upper limit of the free energies of such phases by using the volumetric data on CO_2-V [7] with bounds on the free energy of formation at zero pressure between 0 kJ/mole and that calculated for CO_2 in α-quartz structure (suggested to become stable at a pressure as low as 15 GPa and 0 K [11]). The free energy diagram shows that, despite the lower volumes of diamond plus oxygen, CO_2 phases are favored at 300 K. The decomposition of solid CO_2 above 30 GPa requires relative changes in the free energies of CO_2 and a diamond-oxygen assemblage of 200 to 500 kJ/mole. Hence the observed breakdown of CO_2 at elevated temperature occurs because of the combined effects of volume and entropy.

In summary, we show that solid CO_2 decomposes to oxygen and diamond above 30 GPa and moderate temperatures. Both CO and carbon suboxide apparently are not stable under these conditions; otherwise they would be an end product of the decomposition of CO_2 and a diamond polytype would not form. CS_2 has been shown to become polymeric under moderate pressure and decomposes at both high pressure and temperature [4]. Thus, the C-O system at high pressure appears to be more similar to that of C-S rather than Si-O at high pressure though expanded to a much larger scale of pressure and temperature. The evolution of chemical properties of carbon-oxygen compounds with pressure seems to be dominated by changes in the electronic structure of O rather than C. Above 40 GPa the Raman spectrum of CO_2-laser heated CO_2 differs from that of CO_2-V, indicating another high *P-T* phase. The lower stability of CO_2 tetrahedral networks in comparison to SiO_2 suggests less variety of such CO_2 phases along with increasing pressure. At very high pressures partial decomposition may occur even at moderate temperatures.

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