Modelling of amorphous poly-CO structure with N and He

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Abstract. Density functional theory (DFT) simulations of amorphous poly-CO were performed to understand the stability of the polymerized structure at low pressures (down to 100 bar) and to elucidate the weakest links of the structure. IR and Raman spectra of amorphous p-CO, calculated at 5.02 GPa from the dielectric tensor, are presented and show significant contributions of intact CO molecules, CO fragments decorating chains, and lactones of amorphous p-CO structures. DFT simulations of formation of amorphous polymeric structures were also done with the addition (as a result of replacement of CO molecules) of N or He atoms to the crystalline delta phase of CO. For the CO-N mixtures, the concentration of N was varied in the range from 6.25 % to 50% with different distribution patterns of N atoms in the unit cell. For all studied CO-N concentrations, isotropic compression led to CO polymerization beginning at a pressure of 11 GPa; the N was not incorporated in significant numbers (up to pressures of 20 GPa) in the random p-CO which starts to polymerize. This transition pressure is higher than that for pure p-CO to start to polymerize at 8 GPa. For the CO-He mixtures, the concentration of He atoms in the delta phase of CO was 12.5% of the number of atoms. Formation of random networks begins at 9 GPa and at 11 GPa all CO molecules have formed a combination of closed rings and chain type structures without any isolated CO molecules with a density of 2.40 g/cm³. He atoms appear to facilitate complete formation of the random structure at a lower pressure than that for pure poly-CO, which is almost completely polymerized at a pressure of 18 GPa. He atoms also help stabilize the structure while lowering the pressure down to 100 Bar with only few CO molecules detaching in the process. Without He atoms at the same pressure there are approximately ten times the number CO molecules occupying voids in the random network.

1. Introduction
The high pressure phase of polymeric CO has been of interest since the first publication of experimental evidence that it is a high energy material [1]. Theoretical searches for possible crystalline [2] and amorphous structures [3,4] of polymeric CO are a subject of intense ongoing research. Most likely, polymeric CO is a mainly crystalline (or polycrystalline) material with a certain concentration of amorphous phase, according to X-ray diffraction experiments [5]. Previously we found that transition of the polymeric phase starts at 7-8 GPa, with almost full connectivity of CO molecules to a random network at 18 GPa [4]. In this work, the CO first partially polymerised into CO chains as shown figure 3c from reference [4]. The transition has a hysteresis in density and the polymeric structure is stable down to low pressures [4]. The significant energy content of p-CO was demonstrated for a 432 atom model: the total energy of the polymeric structure at 7 GPa is ~2.3 eV per molecule lower than that of the molecular δ phase at the same pressure [4]. Here we present results on density functional theory (DFT) modelling of amorphous poly-CO structure obtained by
isotropic compression of molecular crystal phase with certain fractions of He and N atoms replacing CO molecules.

2. Methods of calculations
Molecular crystal and amorphous poly-CO structures were obtained through 128 and 432 atom cell optimization (conjugate gradient method) and atomic positions relaxation (LBFGS method) at zero temperature using Quickstep/CP2k package (versions 2.3 and 2.4) [6] with Goedecker-Teter-Hutter (GTH) pseudopotentials within the PBE approximation. IR and Raman were calculated by the plane wave code CASTEP [7] using norm-conserving pseudo potentials. The phonon frequencies are determined from the dynamical matrix, dielectric constant, andBorn effective charges. The Born effective charge tensor of an ion is found from partial derivatives of the macroscopic polarization with respect to a periodic displacement of all the periodic images of that ion at zero macroscopic electric field.

3. Vibration spectra of amorphous p-CO
The structure of amorphous polymeric CO obtained by isotropic compression was previously studied [3,4]. The larger simulation cell size resulted in a wider variety of network motifs: four, five and six member lactones and CO chains decorated by carbonyl groups [4]. Previously we demonstrated that all of the fragments and network motifs contribute to the IR intensity of amorphous p-CO according to calculations using mixed Gaussians plane waves basis set and the Gamma point [4]. Here, using plane waves [7], k-points sampling, and norm-conserving pseudo potentials in GGA/PBE approximation, we have calculated the amorphous polymeric structure with 128 atoms at 5.02 GPa. The optimized structure was calculated by isotropic lowering of the pressure of the polymerised structure obtained previously at 15 GPa. The resulting structure has a mass density of 2.26 g/cm³ (slightly lower than 2.32 g/cm³ found previously) and bulk modulus of 90.6 GPa found from fitting to an equation of state. The norm-conserving pseudo potentials were used for calculating the IR (figure 1a) and Raman (figure 1b) intensities using linear response, and the dielectric tensor with a wavelength smearing of 10 cm⁻¹, temperature smearing of 10 K and typical incident light (argon) of 514.5 nm.

![Figure 1](image)

Figure 1. (a) IR spectrum of amorphous p-CO, (b) Raman spectrum of amorphous p-CO at 5.02 GPa obtained by lowering pressure from 15 GPa.
Maximum peaks in the IR spectrum correspond to modes from the carbonyl groups that decorate chains, lactones and the few intact CO molecules located in the voids of the random network. The broad peak around 1600-1700 cm$^{-1}$ is in general agreement with the experimental peak [8] attributed to amorphous arrangement of sp2 and sp3 bonds of carbon. The multi peak structure of calculated IR and Raman spectra of amorphous p-CO reflects the fact that 60% of CO molecules of the generated amorphous p-CO structure are connected to the random network of 4, 5 and 6 member lactones, and 40% of them form the bent chains decorated by carbonyl groups which are not connected to the closed loops. Under the lowering of the pressure from 15 GPa down to 0.01 GPa the number of molecules unconnected to the network increases (figure 3). Our calculations show that the fragments of the free ends of the chains are the weakest links of the amorphous polymeric structure. They are the first to be disconnected from the network and become CO molecules located in the voids of polymeric structure.

4. Amorphous p-CO with N
Starting from the delta phase of molecular CO, three different concentrations of N atoms were used in the simulations. The concentration for N atoms was 12.5, 18.75, and 50% by number of atoms. Three different types of N$_2$ molecules distribution were studied: 1) located next to each other in certain part of molecular crystal with concentration 50% of N$_2$ (figure 2a), 2) randomly distributed with concentrations 6.25 and 12.5% (figure 2b), 3) at disk disordered [9] positions with concentration 18.75%. In first two studied cases polymerization began in the CO part of the molecular crystals at ~9 GPa and N$_2$ molecules were not involved in formation of a random network (figure 2a,b), in third case of disk disordered positions one molecule of nitrogen was incorporated in polymeric structure (figure 2c).

![Figure 2](image)

Figure 2. Optimized amorphous polymeric structures at 15 GPa with 50% N$_2$+CO (a), 12.5% N$_2$ (b), 18.75% N$_2$-CO (c). Blue – nitrogen, grey – carbon, red – oxygen atoms.

Our calculations show that the N$_2$ molecules slightly increase the pressure for the onset of polymerization of CO but the incorporation of nitrogen molecules into the poly-CO network up to pressures of 20 GPa is quite small (2 atoms out of 24 for disk like case as shown in figure 2c).

5. Amorphous p-CO with He
The properties of the random network are different for the He mixture. The concentration of He atoms in the delta phase of CO was 12.5% by number of atoms. Formation of random networks begins at 9 GPa and at 15 GPa all CO molecules have formed a combination of closed rings and chain type
structures without isolated CO molecules with a density of 2.40 g/cm\(^3\) and the polymeric phase exists down to 0.005 GPa (figure 3).

![Density dependence of p-CO with 12.5 at.% of He (a), concentration of CO intact molecules as function of decreasing pressure for amorphous p-CO obtained at 15 GPa, red line – pure p-CO, blue with He (b).](image)

**Figure 3.** Density dependence of p-CO with 12.5 at.% of He (a), concentration of CO intact molecules as function of decreasing pressure for amorphous p-CO obtained at 15 GPa, red line – pure p-CO, blue with He (b).

Helium appears to facilitate complete formation of the random structure at lower pressure than that for pure p-CO, which isn’t completely polymerized until compressed to a pressure above 18 GPa (figure 3b). It also appears to help stabilize the structure while lowering the pressure down to 100 Bar with only a few CO molecules detaching in the process. Without He atoms there are approximately ten times the number CO molecules occupying voids in the random network at the same pressure (figure 3b). To understand the size effect we did calculation of 432 atom system with the same 12.5 % concentration of He atoms as for 128 atom model. We found similar but less pronounced trend of the He assisting in the formation of a polymeric network. Only eight intact molecules found at 15 GPa (figure 4) whilst without He at the same pressure there are 13 CO molecules not incorporated in random network.
Our analysis indicates that free ends of the chains not connected to rings are the weakest links and CO molecules from the free ends are the first to detach after decreasing the pressure. The increased stability may be due to some combination of factors possibly including the partial pressure from helium in the voids, differences in the structure caused by He facilitated polymerization, and the enhanced mobility of He to respond to changes in pressure (among others).

6. Conclusions

We suggest a possible mechanism of dissociation of the amorphous p-CO network at low pressure, in which the transition occurs by gradual loss of CO molecules from free ends of chains of CO. He atoms facilitate formation of p-CO amorphous structure under isotropic compression and help to preserve the polymeric random network while decreasing the pressure down to 0.005 GPa. N$_2$ molecules are not incorporated in significant numbers in the amorphous poly-CO network up to 20 GPa. The presence of N$_2$ molecules slightly increases the pressure for the onset of polymerization of CO. We identify that the highest IR spectrum intensities of amorphous p-CO at 15 GPa are originated with intact CO molecules, carbonyl groups of chains and lactones of polymeric structure. Calculations of Raman intensities of amorphous p-CO structure are in reasonable agreement with experimental peak position showing formation of sp2 and sp3 coordinated amorphous carbon in the random network.
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