High Pressure Investigations of Liquid and Polymerized CO up to 20 GPa Using Pair Distribution Function Analysis

Nadine Rademacher,[a] Lkhamsuren Bayarjargal,[a] Wolfgang Morgenroth,[a] Jennifer Ciezak-Jenkins,[b] Sasha Batyrev,[b] Björn Winkler[a]
[a]Institute of Geosciences, Goethe University, Frankfurt am Main, Germany, [b]US Army Research Laboratory, Aberdeen Proving Grounds, USA. Email: Rademacher@kristall.uni-frankfurt.de

The analysis of the pair distribution function (PDF) is a powerful method for the determination of accurate structural parameters of crystalline as well as disordered, amorphous and nanocrystalline materials.[1] *In situ* PDF studies at high pressure in diamond ancil cells (DAC) are challenging, because the set-up of DAC experiments in principle does not fulfill the requirements for high-quality PDF data, such as access to large scattering angles and high signal-to-background ratios.[2]

The chemical reaction of carbon monoxide at high pressures has been studied extensively since a first report in 1983 and stability/phase diagrams have been proposed.[3–6] Assumptions were made that polymeric CO (p-CO) consists of anhydride groups connected by linear chains and that the presence of chemical groups like ethers, esters and ketones is probable.[6] However, structural information obtained from total scattering experiments is lacking. The diamond anvil cell (DAC) studies presented here have been performed with mixtures of 10–25 vol% CO in He in order to ensure quasi-hydrostatic conditions. During compression of the gas mixture CO separated from the He at around 3.6(2) GPa with He forming a large bubble within the liquid CO phase (see figure 1). Polymerization was induced photochemically at 4.8–5.8 GPa with a blue laser (473 nm, 80 mW) yielding a yellow to dark red solid (see figure 1). Total scattering experiments of liquid CO and p-CO up to 20 GPa were performed at the Extreme Conditions Beamline P02.2 at PETRA III (DESY, Hamburg) using 43 keV radiation.[7] The PDFs of liquid CO and p-CO do not show structural correlations beyond 10 Å confirming the lack of long-range order in both phases (see figure 1). DFT-based atomistic model calculations revealed that the local atomic arrangement of liquid CO resembles the crystalline high pressure ε-CO phase. For the p-CO data analysis is still in progress, but a preliminary analysis shows the presence of interatomic distances characteristic of C–C and C–O bonds.

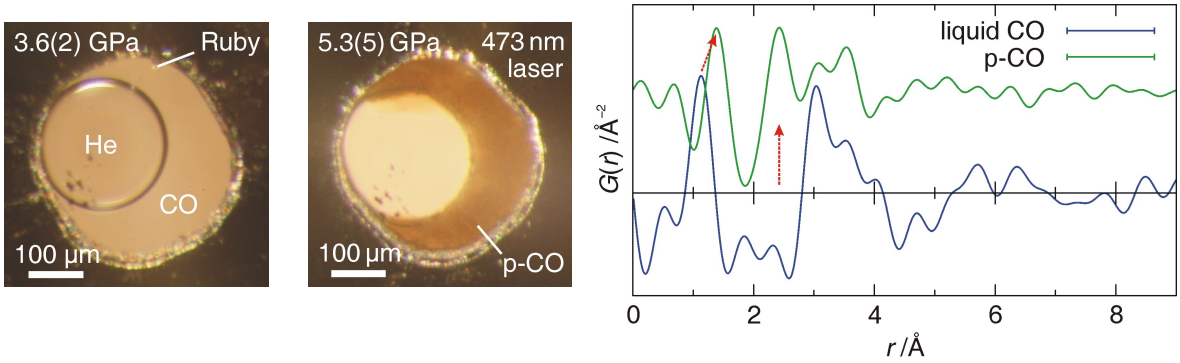

Figure 1: Left: Phase separation of CO and He in the DAC at 3.6(2) GPa. Middle: p-CO in He in the DAC at 5.3(5) GPa. Right: Experimental PDFs of liquid CO (blue) and p-CO at 0 GPa (green). The first-neighbour peak moves from 1.13 Å in liquid CO to around 1.4 Å in p-CO and a new peak appears at around 2.4 Å indicating the formation of the extended molecular solid p-CO.

Financial support from the BMBF (grant 05K10RFA) and the US Army Research Office (contract W911NF-12-2-0063) is gratefully acknowledged.

[1] T. Proffen and H. J. Kim; *J. Mater. Chem.*, 2009, 19, 5078–5088. [2] K. W. Chapman, P. J. Chupas, G. J. Halder, J. A. Hriljac, C. Kurtz, B. K. Greve, C. J. Ruschman and A. P. Wilkinson; *J. Appl. Cryst.*, 2010, 43, 297–307. [3] Cromer, D. T., Schiferl, D., LeSar, R. & Mills, R. L. (1983) *Acta Cryst.* C39, 1146–1150. [4] Katz, A. I., Schiferl, D., Mills, R. L. (1984). *J. Phys. Chem.* 88, 3176–3179. [5] Evans, W. J., Lipp, M. J., Yoo, C.-S., Cynn, H., Herberg, J. L., Maxwell, R. S. (2006) *Chem. Mater.* 18, 2520–2531. [6] Ceppatelli, M., Serdyukov, A., Bini, R., Jodl, H. J. (2009) *J. Phys. Chem.* B113, 6652–6660. [7] Liermann, H.-P., Morgenroth, W., Ehnes, A., Berghäuser, A., Winkler, B., Franz ,H., Weckert, E. (2010) *J. Phys. Conf. Ser.* 215, 012029.