"Off-axis" Mn-Mn bond in $Mn_2(CO)_{10}$ at high pressure

Piero Macchi, Nicola Casati, Fabia Gozzo, Petra Simoncic, Shaun R. Evans and Davide Tiana

Supporting Information

Synchrotron X-ray powder diffraction from Diamond anvil cell

In the following we report the XRPD diffractograms of $Mn_2(CO)_{10}$ taken at the XRPD-MS beamline at PSI, using 20 KeV, Methanol:Ethanol (1:4) mixture as pressure transmission medium and Quartz as calibrant. The calculated diffractogram based on the Rietveld refined model is superimposed (red curves). The difference curve is plot in gray. At $2\theta \sim 17°$, diffraction from the diamond and the stainless steel gasket occurs which obscures diffraction of the sample in a range of about 1°. This region was excluded from the refinements. Above 17°, diffraction is very weak (not shown here), but data were anyway included in the refinements up to 35°, where the DAC shadow becomes dominant. The pressure in the gas membrane and the calibrated pressure in the DAC are reported in the captions. Note that the intensities are particularly affected by severe preferred orientation, due to the fact that only few grains are actually hit by the beam. Moreover the preferred orientation changes upon application of the pressure because of inhomogeneous damage of the particles and rotation/movement occurring during the compression. A model with two preferred orientation was used at each pressure point. Of course the quality of the diffraction and the corresponding fit degrades on increasing the pressure.

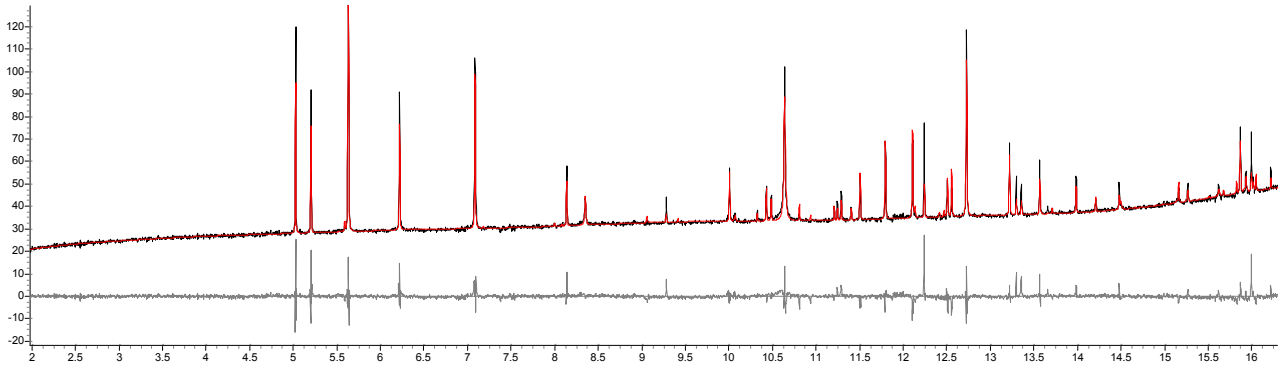

Figure S1: Diffractogram taken at gas membrane pressure of 20.0 bar. Pressure in the DAC 0.0001GPa (gasket indentation obtained at 50 bar)

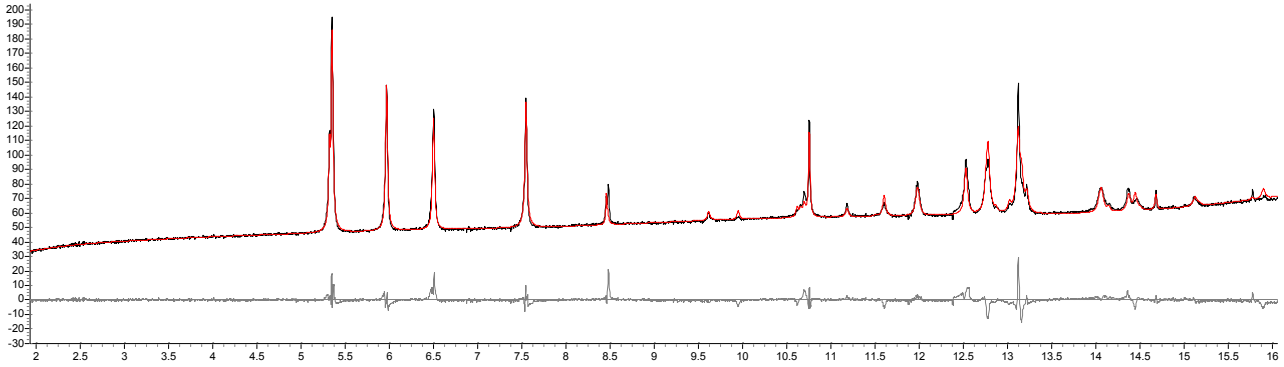

Figure S2: Diffractogram at gas membrane pressure of 62.7 bar. Pressure in the DAC 1.5 GPa

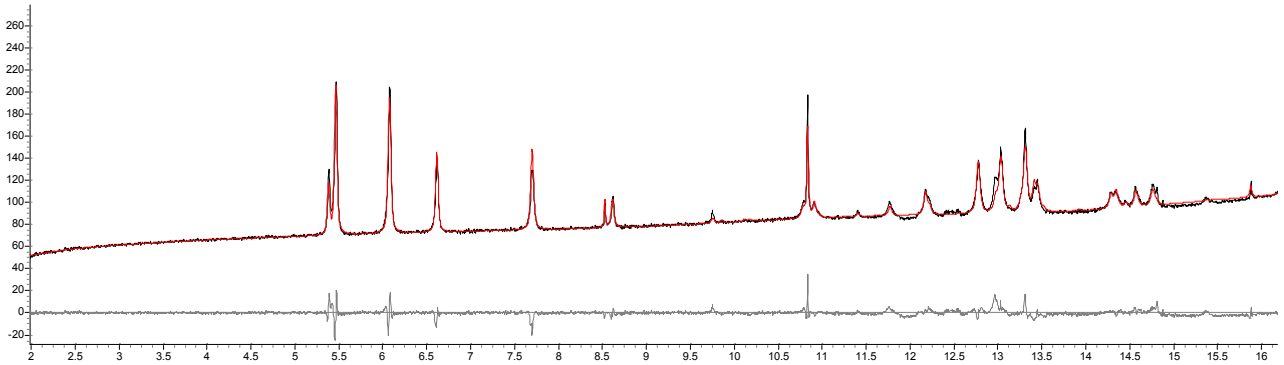

Figure S3: Diffractogram at gas membrane pressure of 70.0 bar. Pressure in the DAC 2.5 GPa

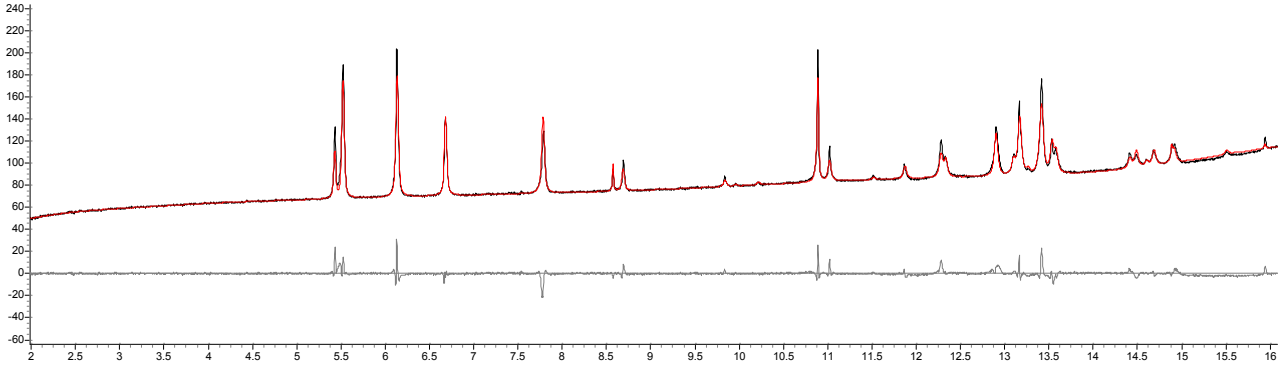

Figure S4: Diffractogram at gas membrane pressure of 75 bar. Pressure in the DAC 3.25 GPa

Table S1. Refined unit cell parameters, from 20 KeV, Methanol:Ethanol (1:4) data collections

P (GPa)	a (Å)	b (Å)	c (Å)	β(°)	V (Å^3)
0.0001	14.1219	7.1007	14.6192	105.184	1414.
1.55	13.8165	6.6471	13.7355	105.001	1218.
2.55	13.6340	6.5147	13.4319	104.916	1153.
2.80	13.5826	6.4830	13.3624	104.867	1137.
3.25	13.5280	6.4516	13.2931	104.841	1121.
4.10	13.4234	6.3954	13.1690	104.752	1093.
4.70	13.3533	6.3601	13.0903	104.719	1075.
6.60	13.1397	6.2694	12.8891	104.503	1028.

Table S2. Simulated unit cell parameters, from B3PW calculations

P (GPa)	a (Å)	b (Å)	c (Å)	β(°)	V (Å3)
0.00	14.0631	6.65411	13.9084	108.78	1232.
1.00	13.8644	6.62295	13.3436	109.04	1158.
1.50	13.789	6.57275	13.1710	108.59	1131.
2.00	13.7143	6.53236	13.0013	108.08	1107.
3.00	13.3382	6.49331	13.0161	106.97	1078.
5.00	13.0368	6.37467	12.8022	105.98	1023.
7.00	12.7274	6.30400	12.6546	104.79	982.
10.0	12.3825	6.21902	12.4961	103.54	935.
15.0	12.0127	6.11735	12.2747	102.56	880.

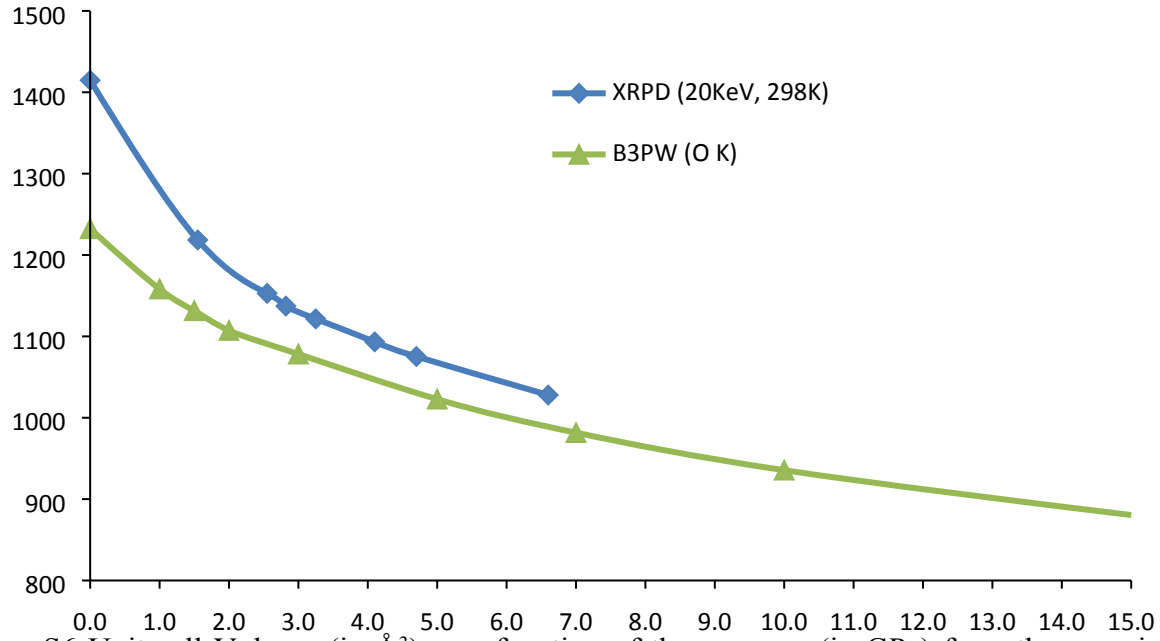

Figure S6 Unit cell Volume (in Å^3) as a function of the pressure (in GPa) from the experimental refinements (XRPD) and the theoretical calculations (B3PW), that are carried out at 0K.

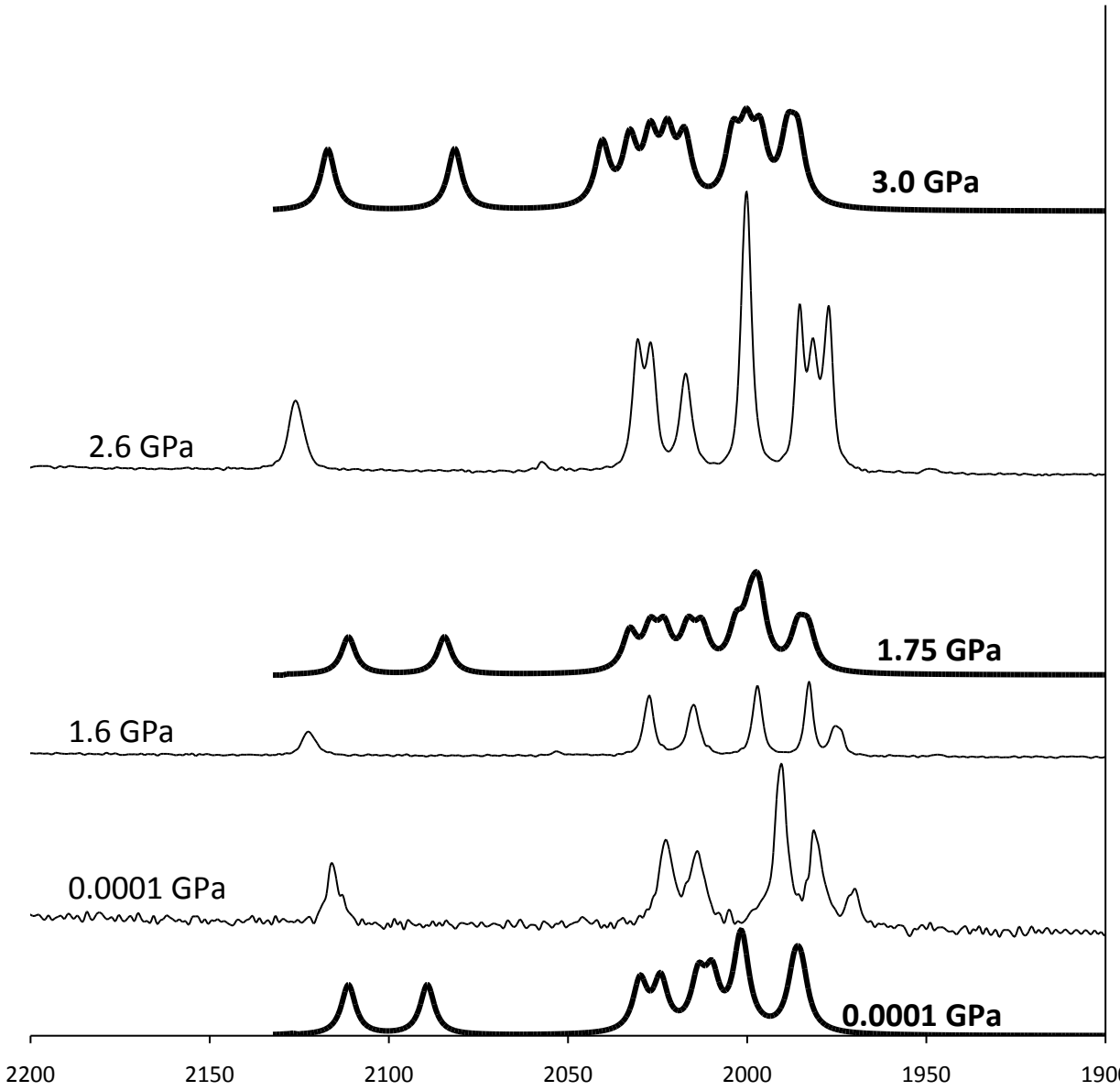

Figure S7: Experimental and calculated Raman Spectra. Note calculations are carried out at B3PW level of theory, the frequencies are re-scaled to account for anharmonic effects. The intensities are not explicitly calculated but are just obtained assigning an equal value to all transitions and a peak broadening of 5 sm^{-1}. The worst agreement on the frequency is for the Bg mode occurring at ca. 2060 cm^{-1} (almost invisible at ambient pressure and very weak at 2.6 GPa), which is predicted at quite higher frequency in the P-DFT calculations.

Results of the Interacting Quantum Atom calculations

The IQA calculations were carried out using the software PROMOLDEN[1] on the molecular geometries as optimized from the P-DFT calculations. The calculations were carried out at the same level of theory as the P-DFT calculations, but without inclusion of dispersive correction. Core electrons were introduced following the procedure described by Tiana *et al.*[2] Here we report the main outcome of the study:

Table S3 Atomic charges, according to Quantum theory of Atoms in Molecules

Pressure (GPa)	0.001	1	3	7
Mn	0.86	0.86	0.84	0.83
C_{ax}	0.88	0.88	0.88	0.88
C_{eq} (average)	0.85	0.85	0.85	0.85
O_{ax}	-1.06	-1.05	-1.05	-1.05
O_{eq}(average)	-1.03	-1.03	-1.04	-1.04

Table S4. Results of the IQA analysis for geometries in the pressure range 0-7 GPa. DI is the delocalization index, E_{int} is the total interaction energy, E_{coul} is the coloumb interaction energy and E_{xc} is the exchange energy (all energies in a.u.).

0.0001GPa	DI	E_{int}	E_{Coul}	E_{XC}
Mn-Mn	0.283	0.0686	0.1131	-0.0445
Mn-C_{ax}	1.069	-0.0788	0.1703	-0.2491
Mn---O_{ax}	0.231	-0.2071	-0.1855	-0.0216
Mn-C_{eq}	0.917	-0.0631	0.1508	-0.2139
Mn---O_{eq}	0.181	-0.1893	-0.1725	-0.0168
1.0GPa	DI	E_{int}	E_{Coul}	E_{XC}
Mn-Mn	0.284	0.0695	0.1146	-0.0451
Mn-C_{ax}	1.069	-0.0786	0.1707	-0.2493
Mn---O_{ax}	0.230	-0.2048	-0.1834	-0.0214
Mn-C_{eq}	0.918	-0.0614	0.1531	-0.2145
Mn---O_{eq}	0.181	-0.1887	-0.1718	-0.0169
3.0GPa	DI	E_{int}	E_{Coul}	E_{XC}
Mn-Mn	0.287	0.0657	0.1121	-0.0464
Mn-C_{ax}	1.070	-0.0813	0.1692	-0.2506
Mn---O_{ax}	0.227	-0.2007	-0.1794	-0.0213
Mn-C_{eq}	0.923	-0.0639	0.1531	-0.2169
Mn---O_{eq}	0.182	-0.1862	-0.1692	-0.0170
7.0GPa	DI	E_{int}	E_{Coul}	E_{XC}
Mn-Mn	0.290	0.0638	0.1121	-0.0483
Mn-C_{ax}	1.071	-0.0823	0.1700	-0.2524
Mn---O_{ax}	0.225	-0.1991	-0.1780	-0.0211
Mn-C_{eq}	0.934	-0.0671	0.1551	-0.2221
Mn---O_{eq}	0.183	-0.1848	-0.1676	-0.0172

1 A. M. Pendas, University of Oviedo
2 D. Tiana, E. Francisco, M. A. Blanco, and A. M. Pendas *J. Phys. Chem. A*, 2009, **113**, 7963.