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Abstract

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Ab initio computational studies of pressure-induced polymerization in crystals made of simple molecules

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Simple molecular systems under the pressure is a field studied in a great detail for almost a century. It has far reaching applications in the industry and sheds a light on origin of planetary surface conditions. We focus on two particular systems, sulfur dioxide SO_2 and carbon disulfide CS_2, for which we observed completely distinct phenomena. SO_2 undergoes pressure-induced amorphization and reversible structural transformation between two amorphous forms at 26 GPa, which was observed in both *ab initio* and machine-learned potential molecular dynamics. The results were corroborated by Raman spectroscopy and diamond anvil cell X-ray diffraction experiments, performed by our colleagues. The structural change is resolved as polymerization of SO_2 molecules with multiple bonds to polymeric chains made of three-coordinated sulfur atoms linked by oxygen atoms, with a few intact residual molecules. CS_2 is a longly studied molecular system, with a tendency to chemically decompose. We showed, contrary to previous believes, that CS_2 under around 10-11 GPa undergoes polymerization to disordered, three- (C3) and four-coordinated (C4) carbon atom polymers. Further compression leads to increase of C4/C3 ratio, which is partially reversible on decompression. Our study shows that double C=C bonds could be achieved without chemical decomposition of CS_2. All theoretical results are consistent with Raman and IR spectroscopy, as well as diamond anvil cell X-ray diffraction experiments provided by our collaborators.