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Supplementary Information for

Pressure-induced amorphization and existence of molecular and polymeric amorphous forms in dense SO_2

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This PDF file includes:

Supplementary text
Figs. S1 to S11

Supporting Information Text

Cif file of molecular Pc structure at 8 GPa

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data_SO2
_symmetry_space_group_name_H-M   Pc
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_cell_length_b   4.57591917
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_cell_angle_gamma   90.00000000
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  S  S1  2  0.554690  0.319303  0.022006  1
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  O  O3  2  0.486078  0.129163  0.201626  1
  O  O4  2  0.714298  0.439791  0.592999  1
  O  O5  2  0.979235  0.065598  0.948884  1
```

Cif file of molecular *Cc* structure at 8 GPa

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loop_
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Cif file of polymeric $Pmc2_1$ structure at 20 GPa

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  4  'x, -y, z+1/2'
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  O  O3  2  0.000000  0.396266  0.444518  1
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Cif file of polymeric *Ama2* structure at 20 GPa

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  4  'x+1/2, -y, z'
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  8  'x+1/2, -y+1/2, z+1/2'
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 _atom_site_symmetry_multiplicity
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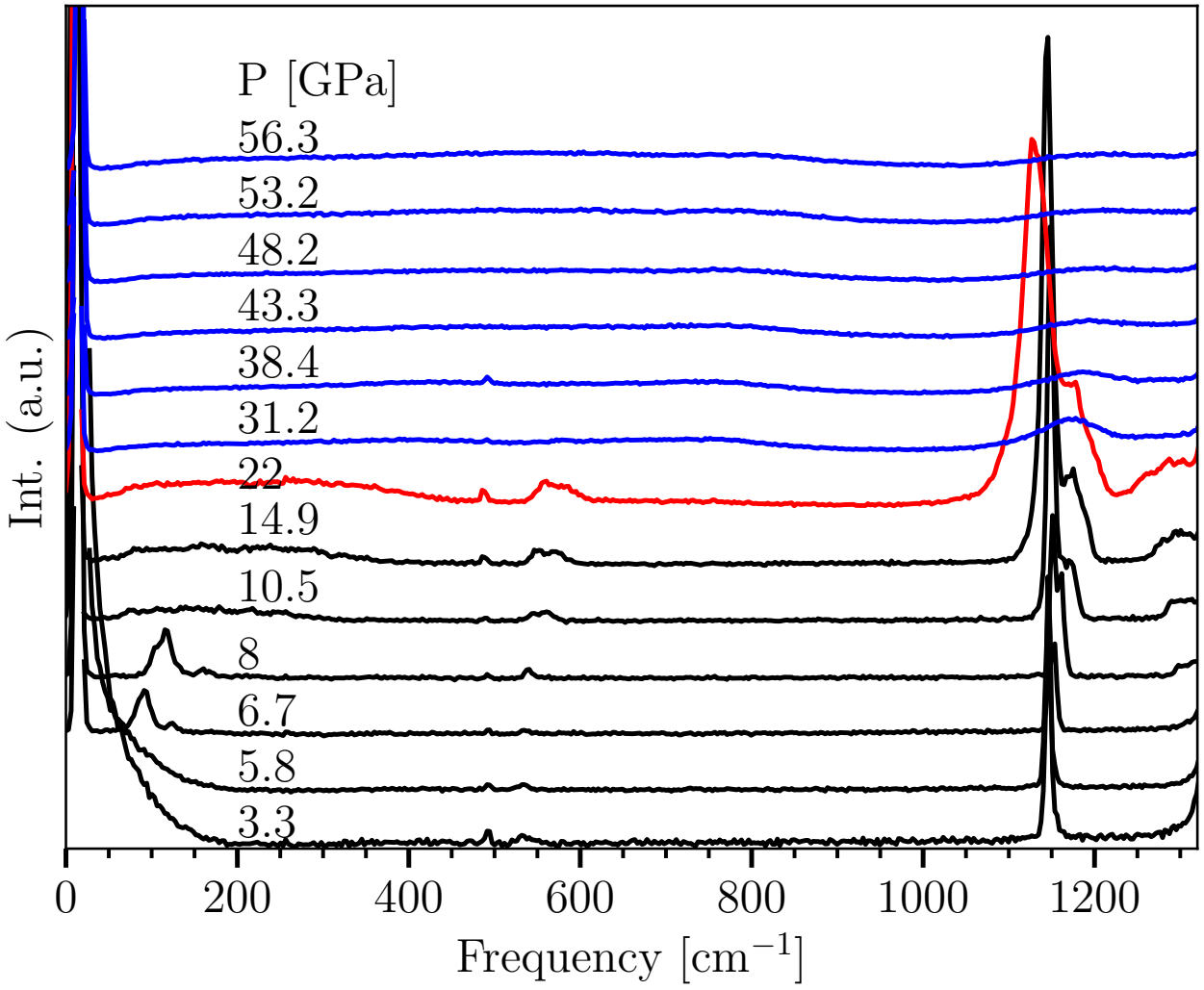

Fig. S1. Raman spectra of solid SO_2. Selected Raman spectra of an SO_2 sample upon increasing pressure at 210 K.

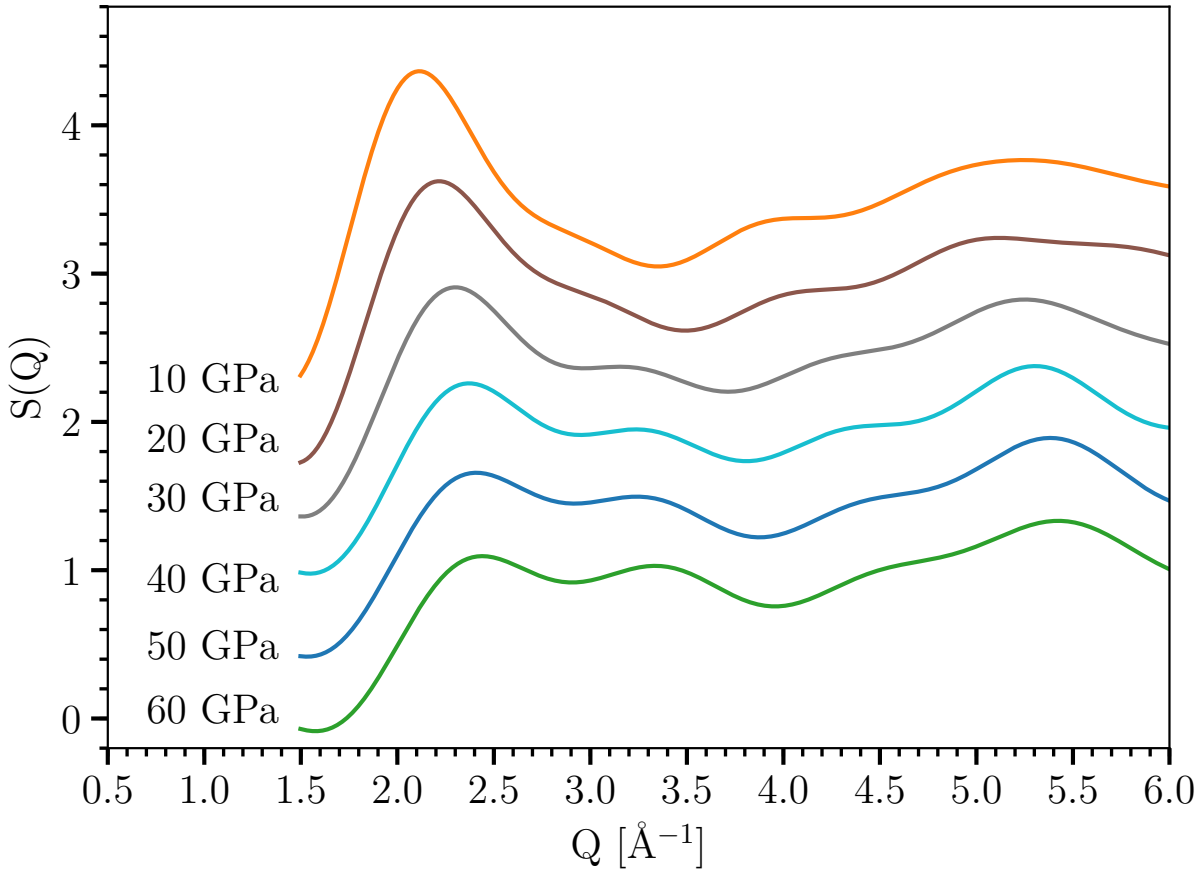

Fig. S2. Static structure factor of solid SO_2 during compression (see also the decompression structure factor in Fig. 2 B (main paper)).

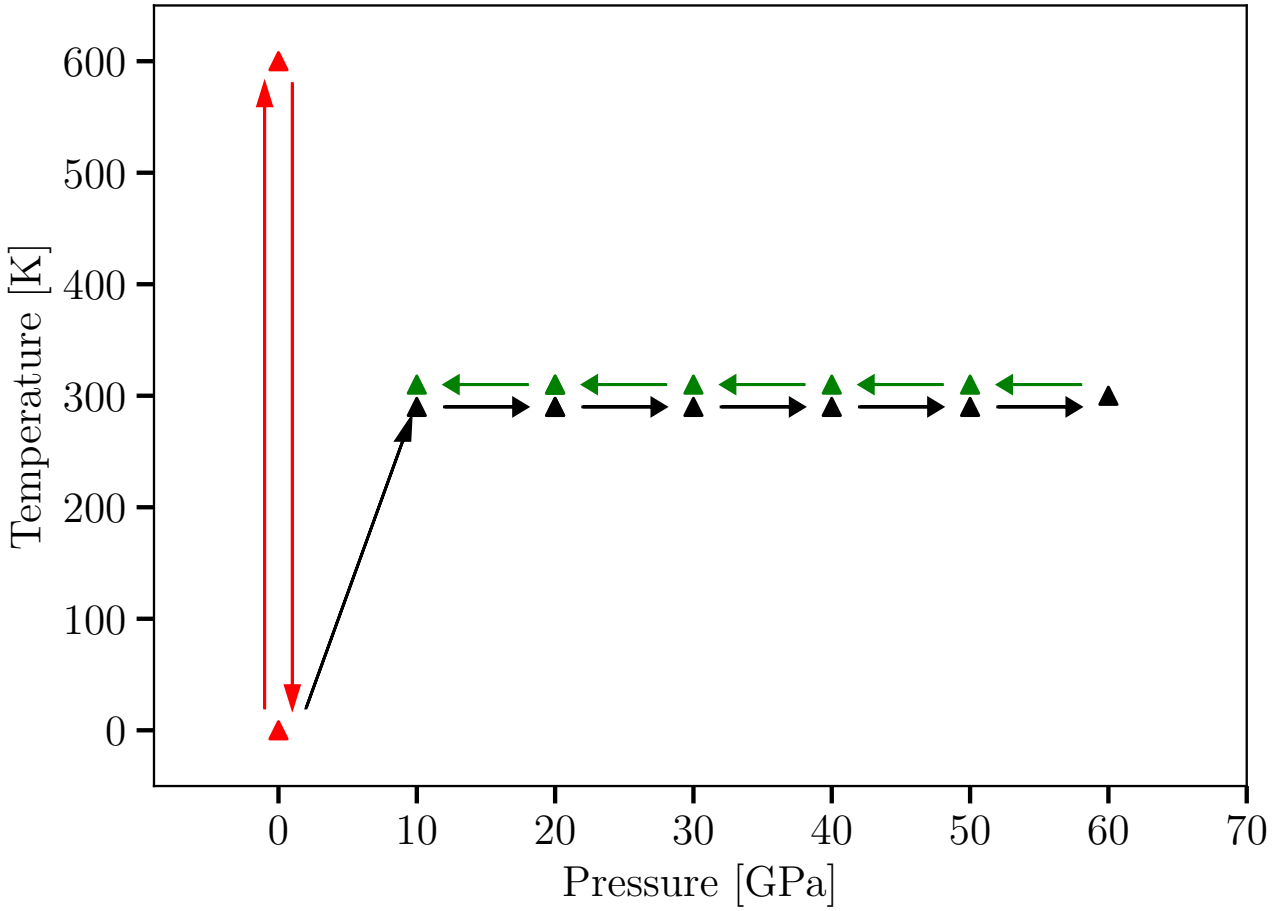

Fig. S3. Simulation protocol: red is preparation of amorphous SO_2 sample by heating perfect *Aea2* molecular crystal to 600 K and subsequent cooling to 0 K. Then, amorphous sample was compressed with 10 GPa steps (black) and after reaching 60 GPa decompressed (green) with the reversed procedure.

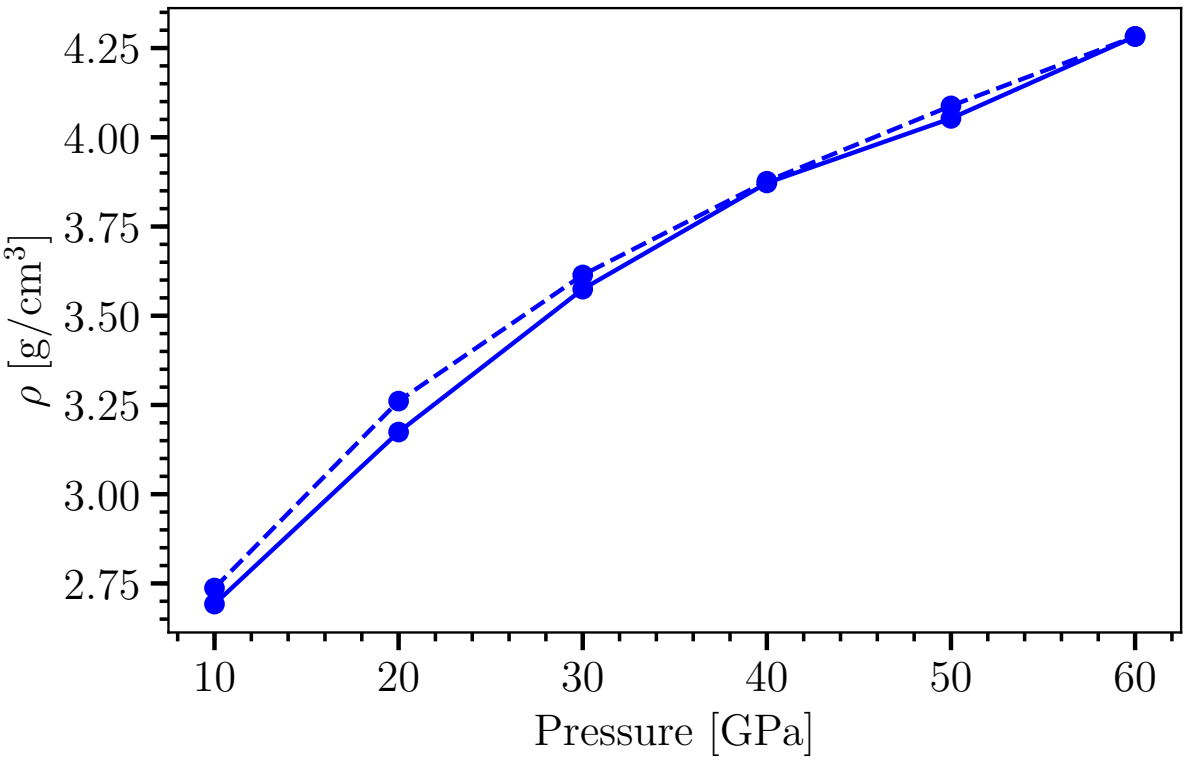

Fig. S4. Density of equilibrated SO_2 samples from simulations. Solid line represents density during compression and dashed line during decompression.

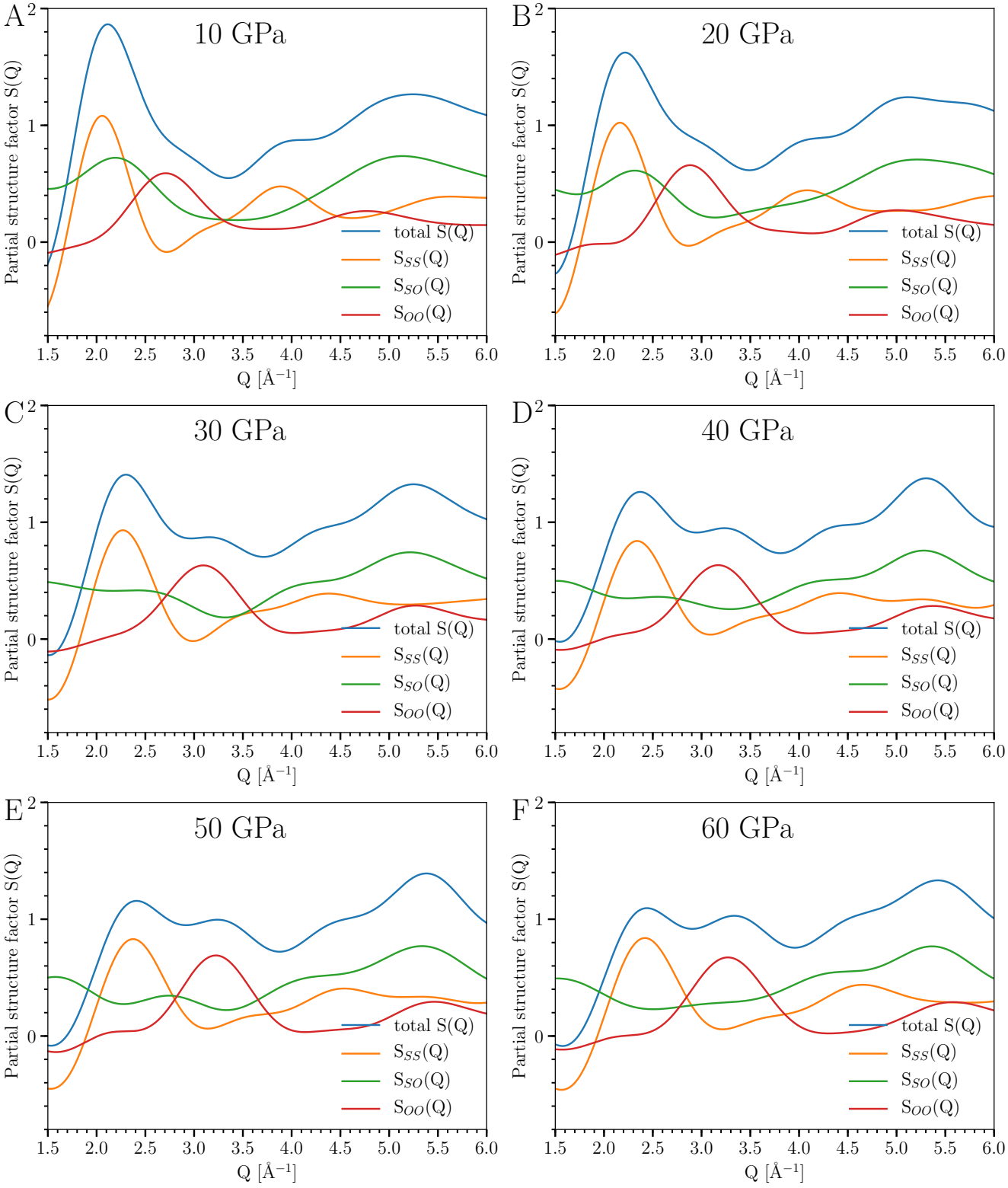

Fig. S5. Partial structure factors $S_{\alpha\beta}(Q)$ from compression at pressures from 10 to 60 GPa with 10 GPa steps through A to F.

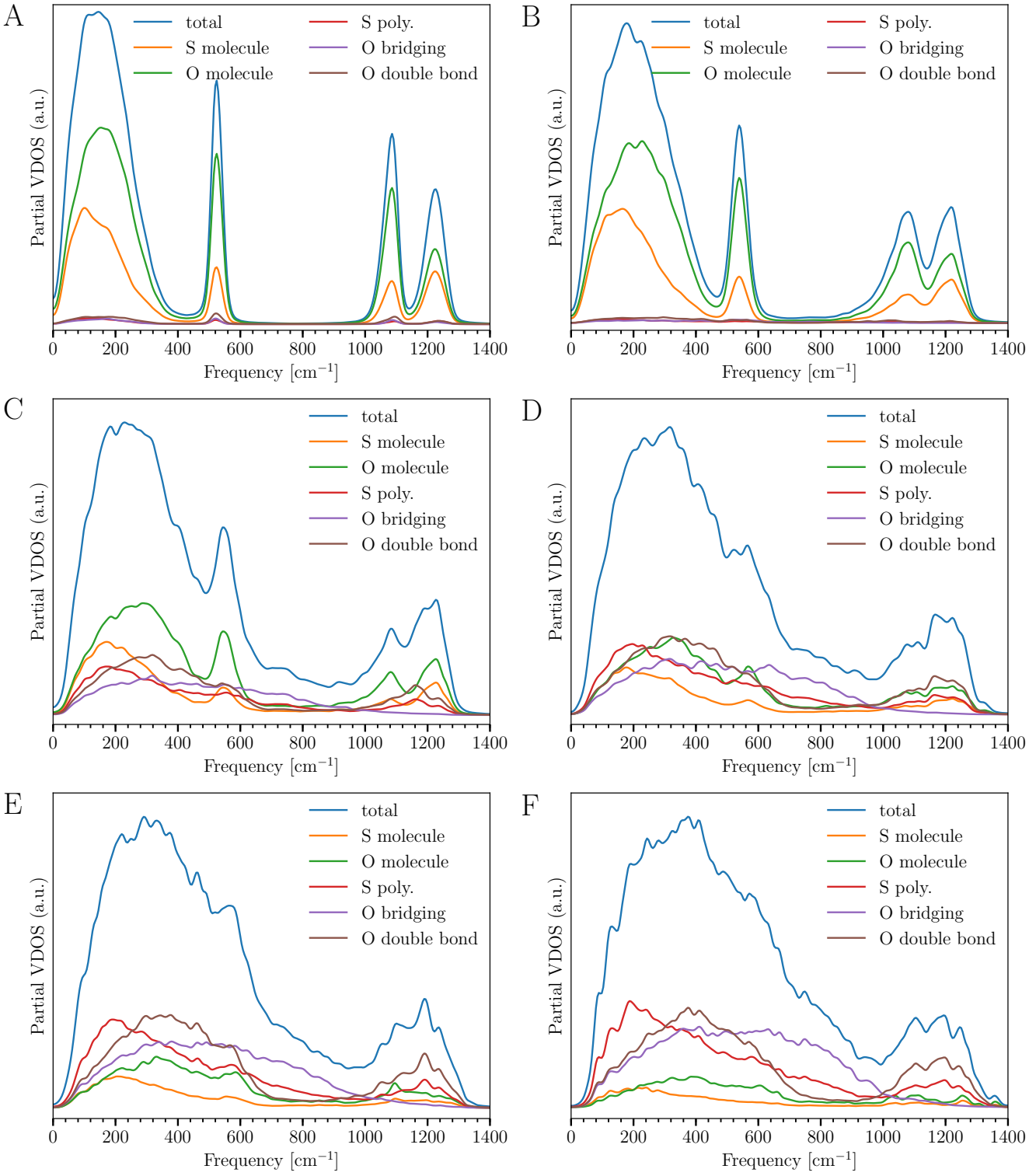

Fig. S6. Partial VDOS from compression for pressures form 10 to 60 GPa with 10 GPa steps (from A to F).

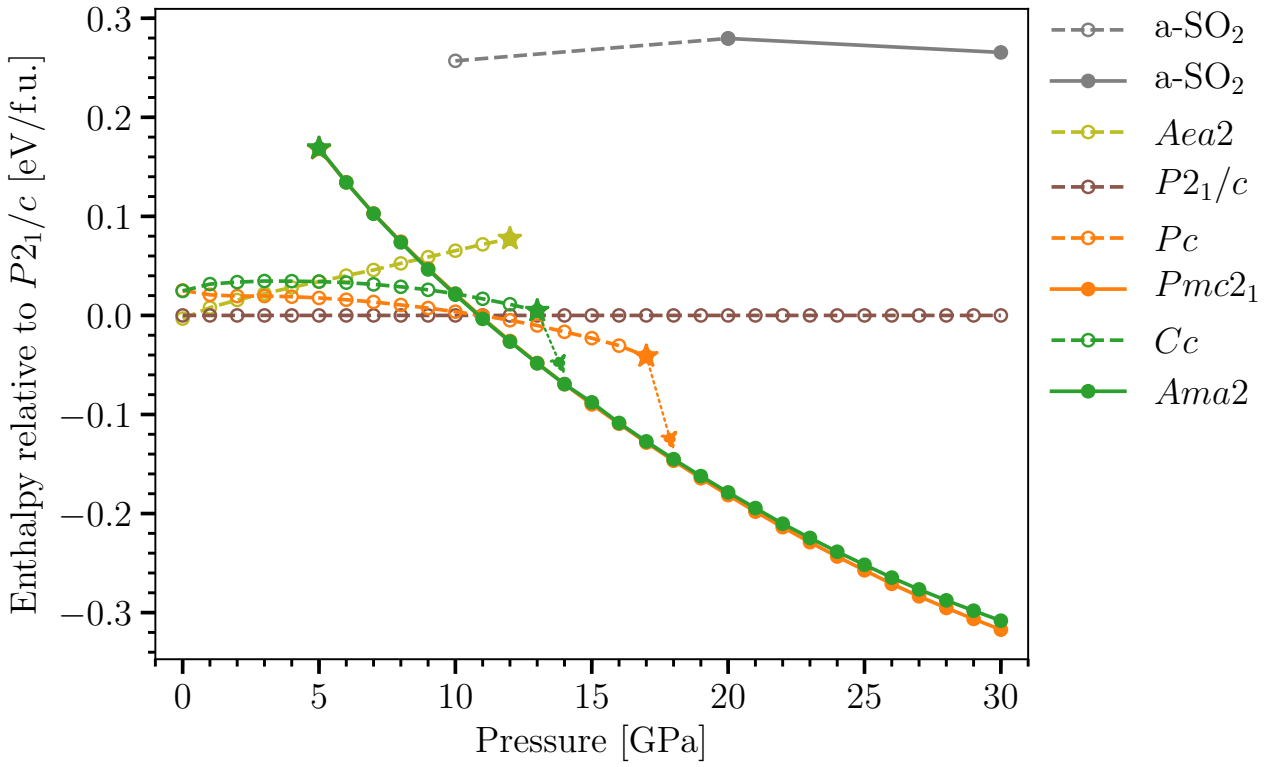

Fig. S7. Evolution of relative enthalpy (per formula unit with respect to the reference $P2_1/c$ structure) with pressure calculated for selected crystal structures found by evolutionary search. Below 1 GPa the stable structure is the experimentally observed *Aea2* molecular crystal and between 1 and 11 GPa a $P2_1/c$ molecular crystal is stable. Two metastable molecular crystal structures, *Cc* and *Pc* transform above 13 and 17 GPa, respectively, into polymeric structures with space groups *Ama2* and $Pmc2_1$. The latter structures become thermodynamically stable with respect to the molecular ones already at 11 GPa. The grey line represents amorphous SO_2, which is at all pressures metastable with respect to the crystalline phases. Molecular phases are represented by dashed lines with empty circles while polymeric phases are shown as solid lines with filled circles. The limit of dynamical stability of molecular phases upon compression and of polymeric phases upon decompression is marked by an asterisk. Transformations from molecular to polymeric phases are shown as dotted lines with arrows.

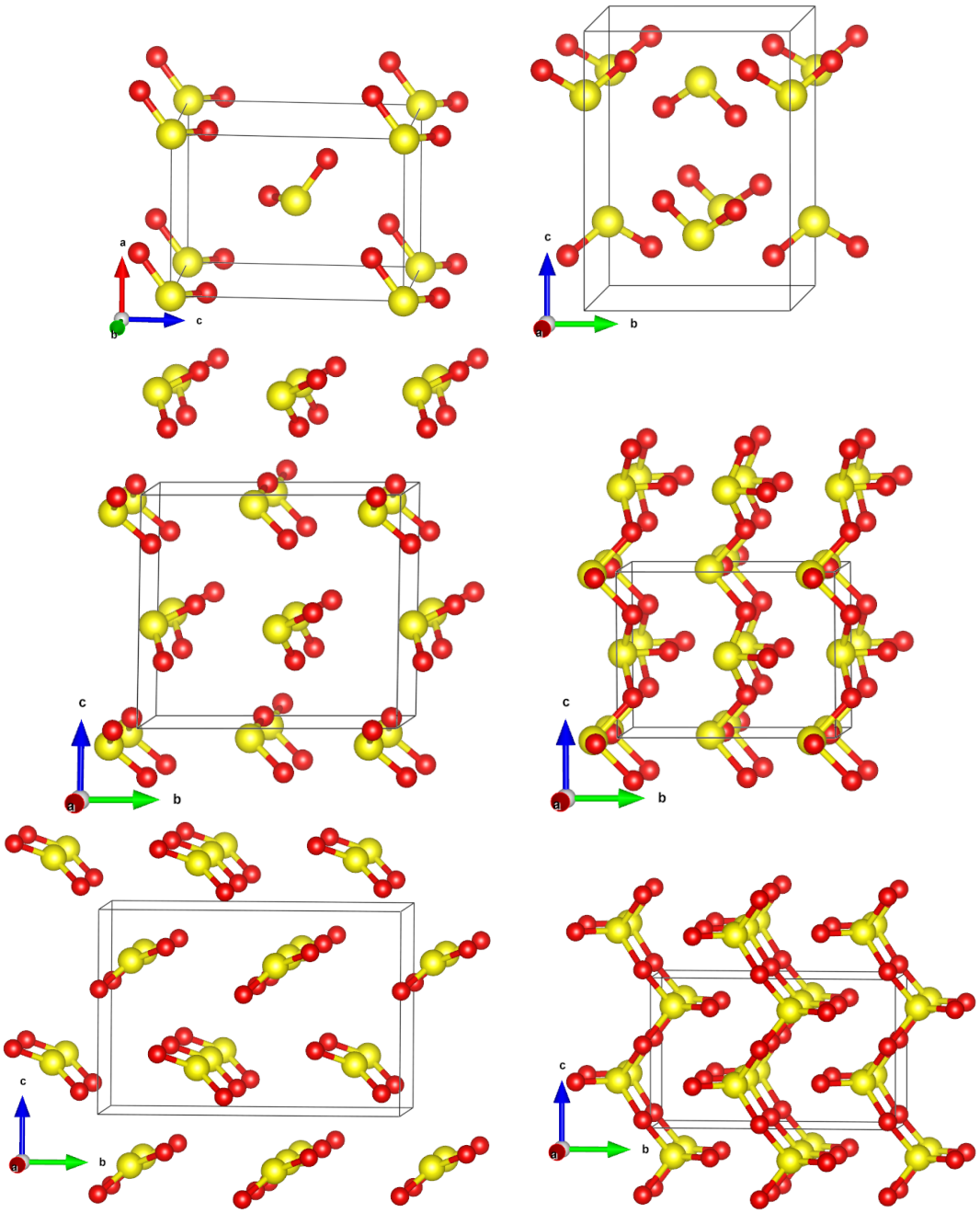

Fig. S8. Selected crystalline structures of SO_2 found by evolutionary search. First row: *Aea2* 0 GPa (left) and $P2_1/c$ 1 GPa (right), second row *Pc* 0 GPa (left) and $Pmc2_1$ 20 GPa (right), bottom row *Cc* 0 GPa (left) and *Ama2* 20 GPa (right).

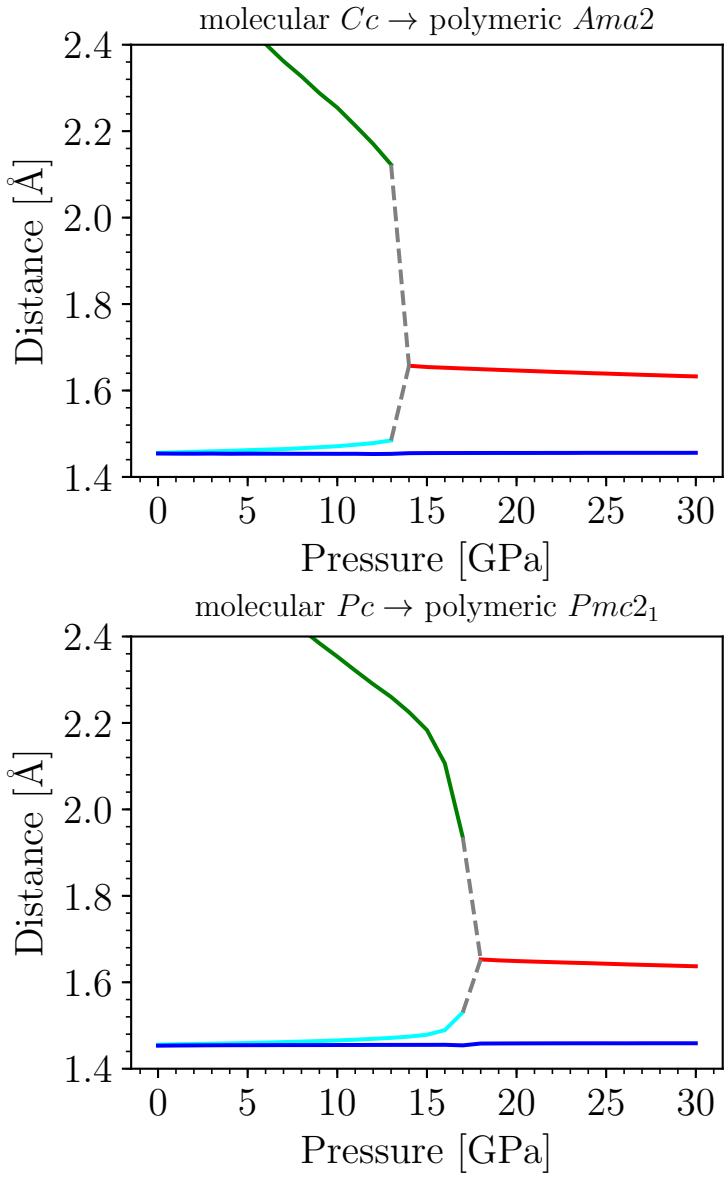

Fig. S9. Mechanism of polymerization of molecular crystal upon compression as illustrated by evolution of short S-O distances with pressure for *Cc* to *Ama2* (upper panel) and *Pc* to *Pmc2₁* (lower panel) transformations. Both transformations start from molecular crystals with SO_2 molecules with equal bond lengths. As pressure increases, SO_2 molecules rotate and one oxygen starts to move towards neighbouring sulfur from another molecule, resulting in unequal SO bond lengths within the molecule (cyan and blue curves). While the shorter one remains practically unchanged and results in S=O bond to terminal oxygen (blue curve), the longer one (cyan curve) grows and eventually becomes an S-O bond to bridging oxygen (red curve). At the same time the intermolecular S-O distance (green curve) (originally longer than 2 Å) dramatically decreases, eventually also resulting in creation of S-O bond to the bridging oxygen (red curve). The process is completed at 14 GPa for *Ama2* and 18 GPa for *Pmc2₁*, where the double bond is replaced by a single one and polymeric chain is formed, with S=O bond length of 1.46 Å and S-O bond length of 1.65 Å. We note that in the amorphous molecular phase the approaching of non-bonded S O atoms upon compression can be seen on the shift of the peak between 2 and 3 Å in the RDF in Fig. 3 A (main paper).

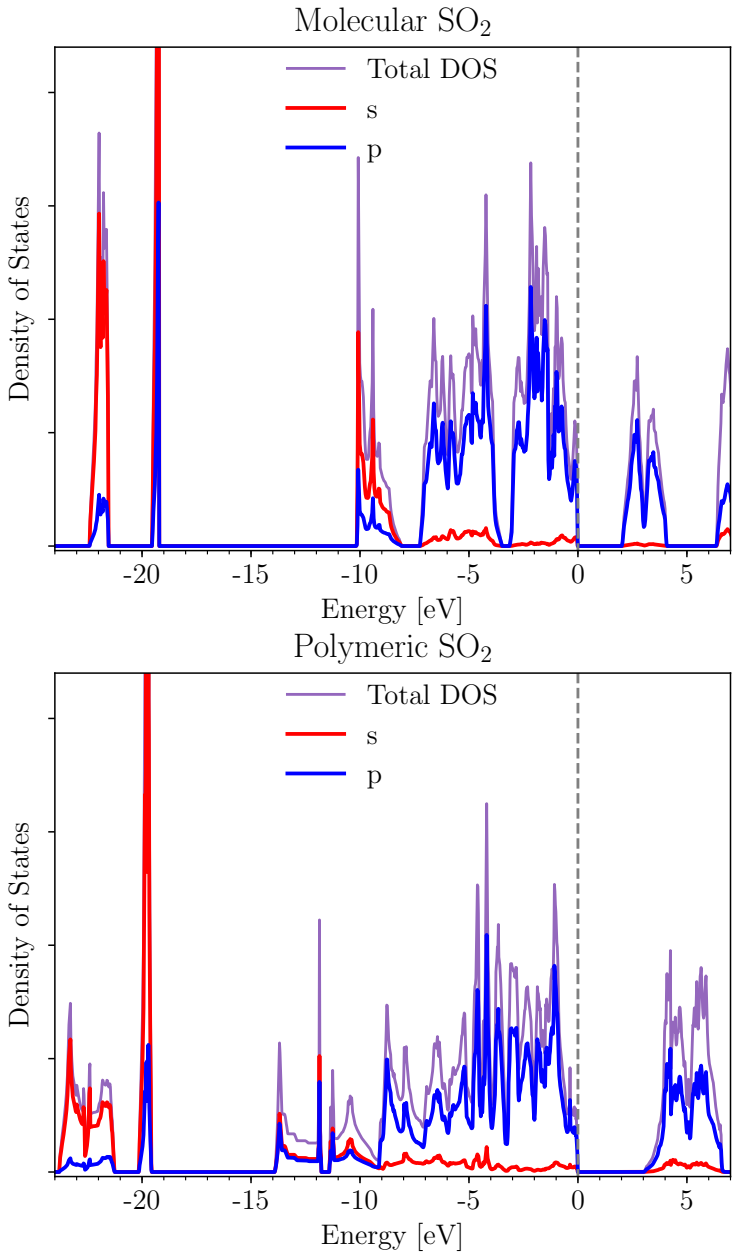

Fig. S10. Total and projected electronic density of states of the *Cc* molecular phase at 9 GPa (upper panel) and *Ama2* polymeric phase at 14 GPa (lower panel). The occupancy of *d*-orbitals is zero. Energy is measured relative to the Fermi level.

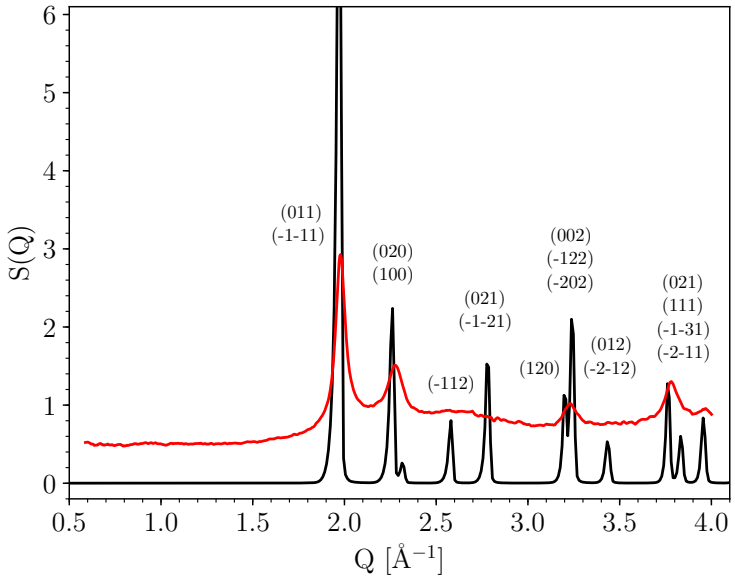

Fig. S11. Comparison of the experimental XRD pattern from decompression to 6.5 GPa (red curve) with the calculated one for the crystalline *Aea2* phase at 6 GPa (black curve). The Bragg peaks can be partially indexed on the basis of a *Aea2* space group with a=5.5430 Å, b=5.4011 Å, c=5.5356 Å as obtained from simulations.

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