

The High Pressure Response of Uranyl Nano-cages

Insights on the roles of chemistry and cluster topology

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Research Questions:

- How do uranyl nano-cages change at elevated pressures?
- Do their crystal structures undergo phase transitions and amorphization?
- Do their cluster topologies change?
- At what pressures do uranyl nano-cages cease to remain intact?
- Does their fundamental uranyl-peroxide-hydroxide chemistry change?
- Do they evolve reversibly?
- Do they behave similarly to their carbon analogues?

Research Methods

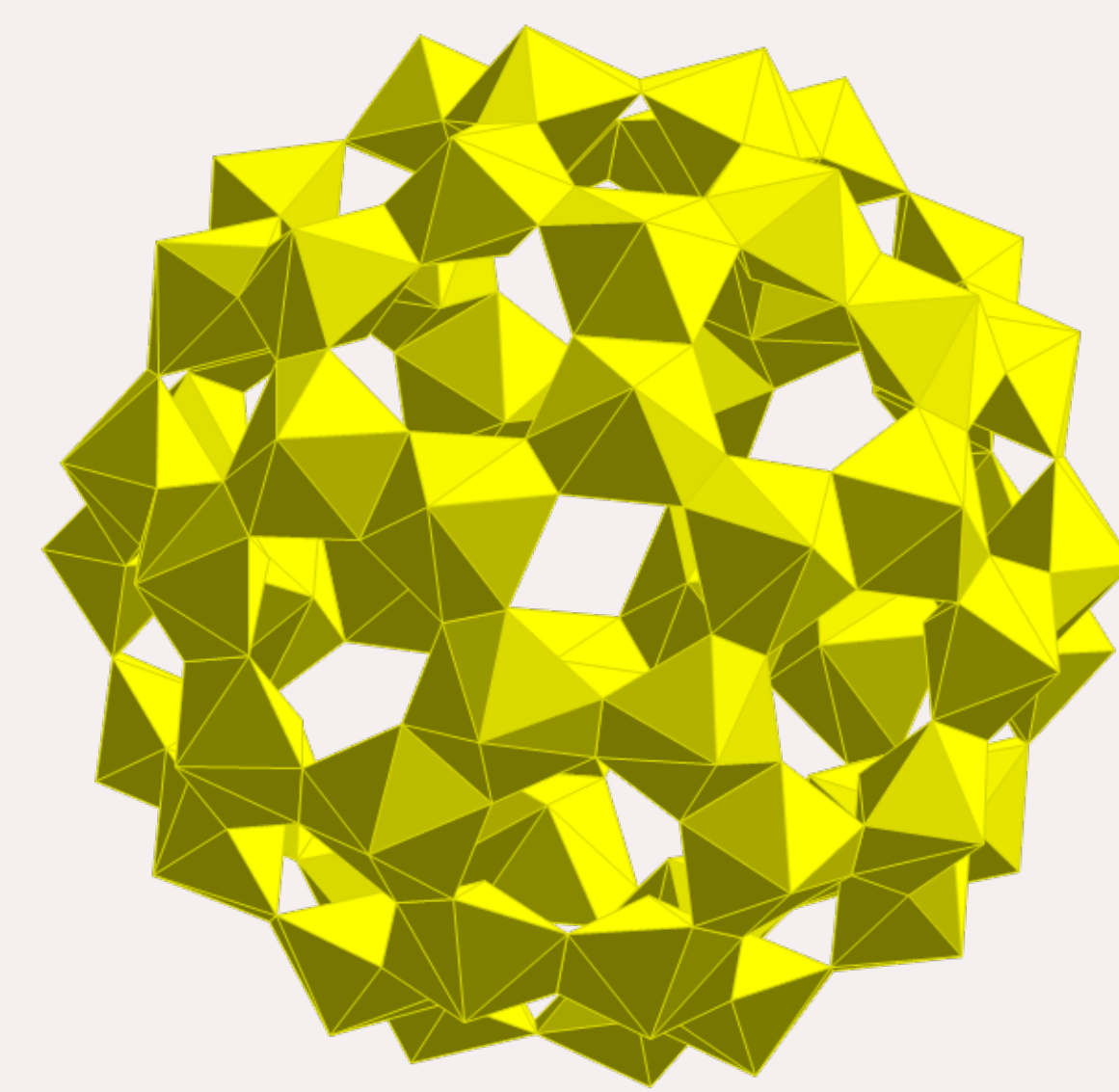


Nano-cages are created using optimized syntheses at the University of Notre Dame. Single crystals of desired clusters are isolated based on size (<100 microns) and quality.

These crystals are loaded into diamond anvil cells at the University of Michigan and Stanford University, and analyzed *in situ* using Raman spectroscopy, synchrotron XRD, and ESI-MS.

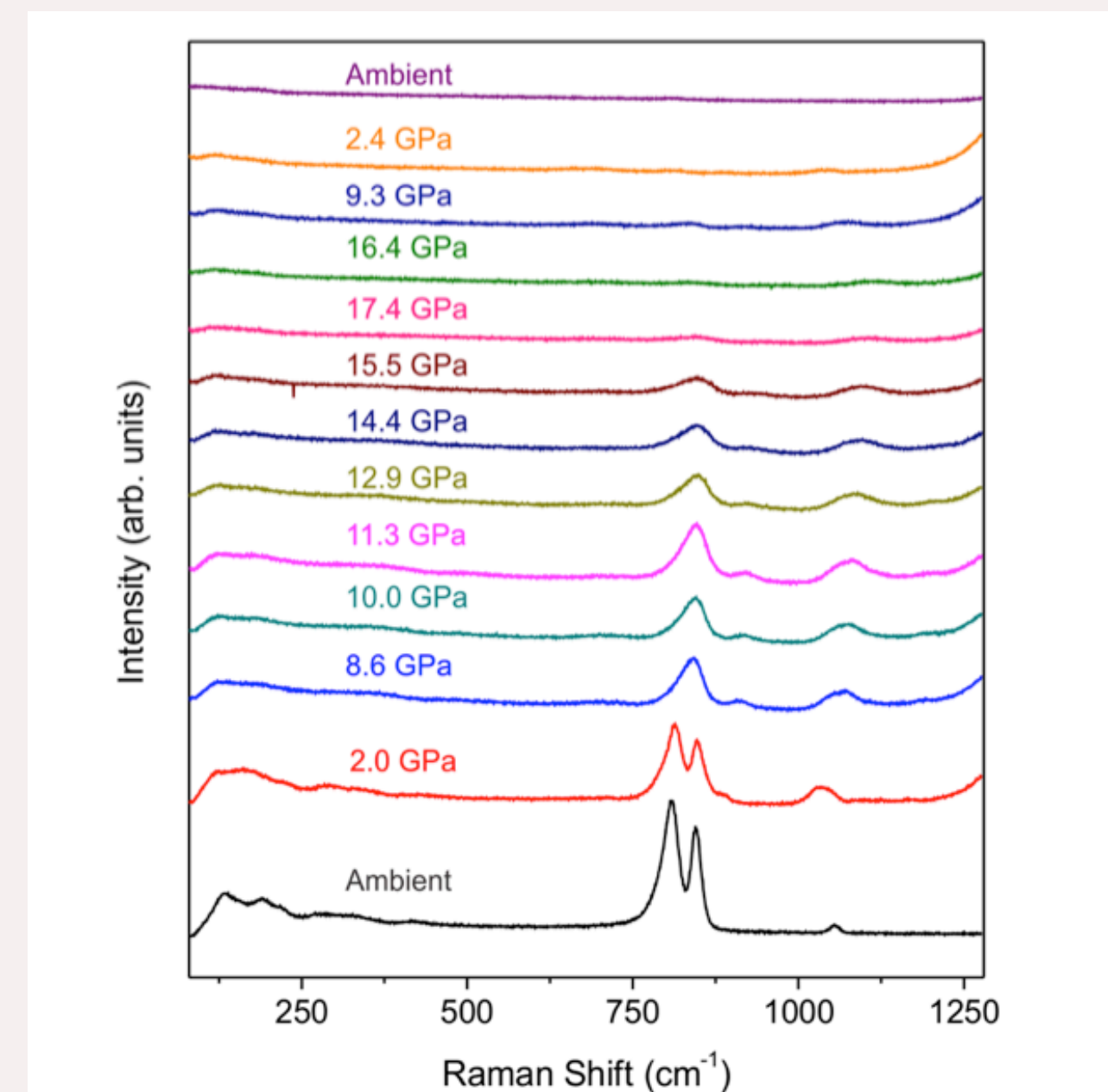
Summary of Results:

U_{60} and $U_{24}Py_{12}$ undergo pressure-induced phase transitions and amorphization. U_{60} clusters amorphize at 17 GPa, and crystals' phase transitions are irreversible. $U_{24}Py_{12}$ crystals begin to amorphize at 10 GPa; their transitions are reversible. In experiments up to 17 GPa, their fundamental chemistry remains intact. Despite identical topology to carbon fullerenes, their differing reactions to high pressure suggests that cluster chemistry plays a large role in influencing extreme environment behavior.

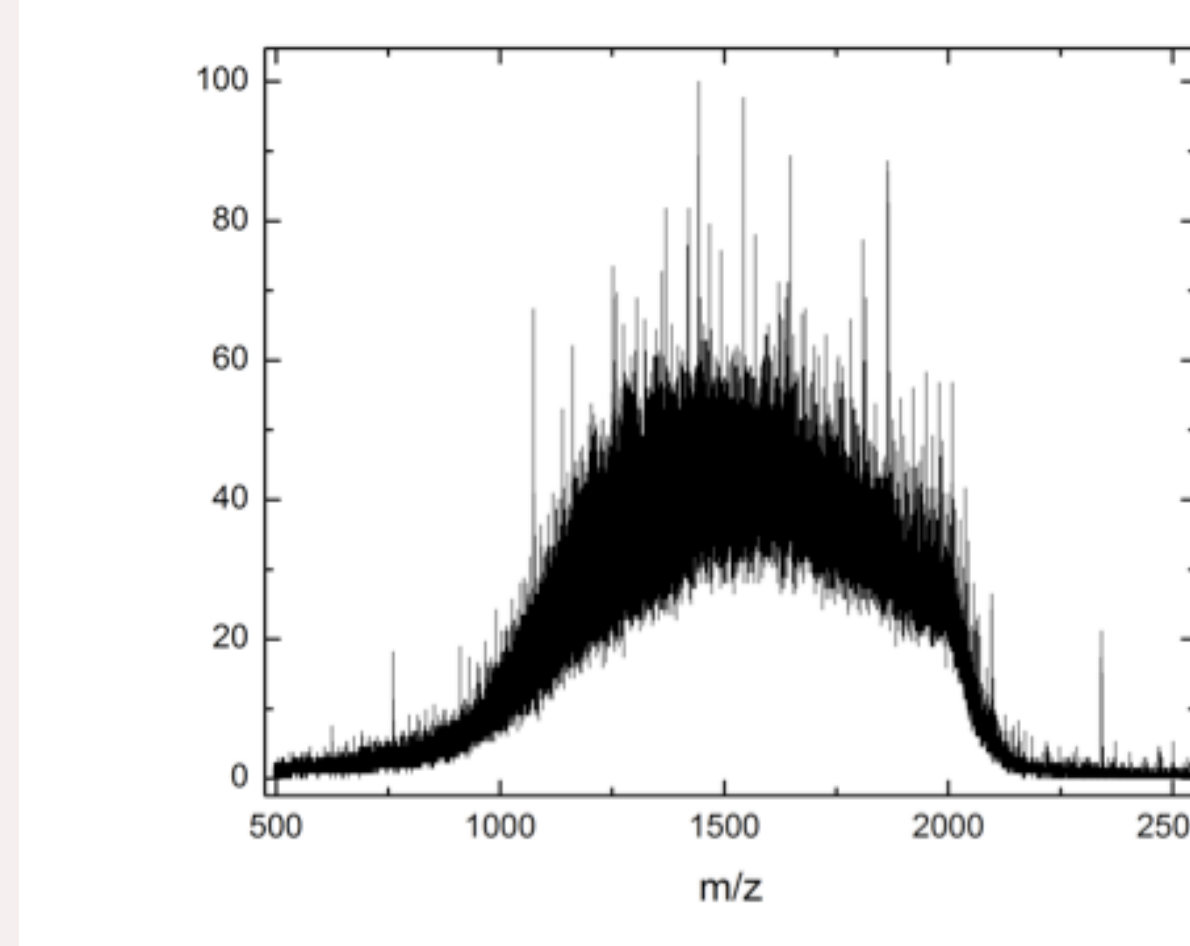


U60 Polyhedral Representation (Burns 2009)

Cluster Formula $[UO_2(O_2)(OH)]_{60}^{60-}$
 Crystal Formula $Li_{68}K_{12}(OH)_{20}[UO_2(O_2)(OH)]_{60}(H_2O)_{310}$
 Symmetry* Fm-3
 Lattice Parameter* $a=37.884(2) \text{ \AA}$



Raman spectra of U_{60} as pressure is applied (max 17.4 GPa), and quenched (ambient 0.1 GPa). Modes are a symmetric stretch of uranyl U-O bond and a stretch of the coordinating peroxide in uranyl peroxide nano-cages (McGrail 2014). Transition at 8.6 GPa indicates disorder in the crystal.

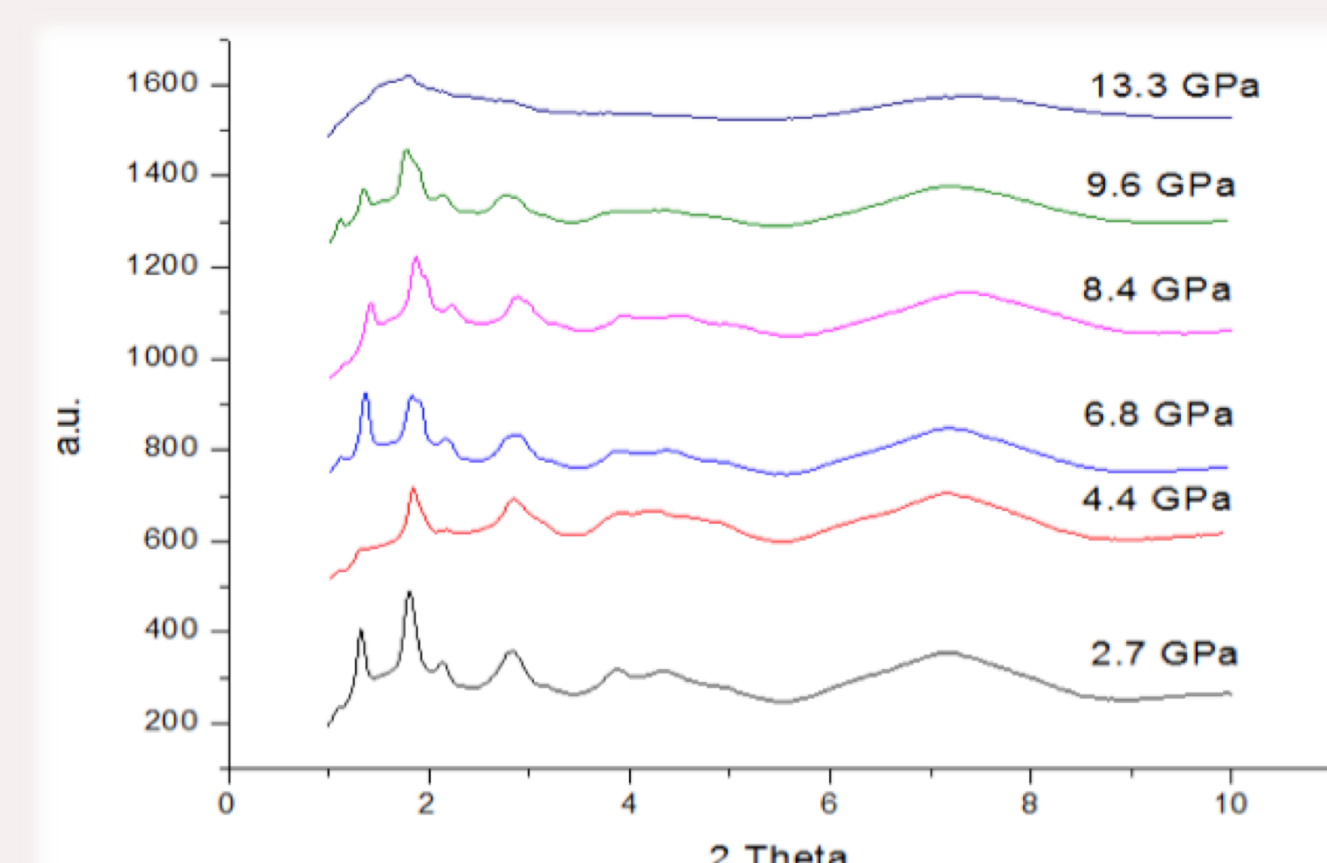


ESI-MS pattern of quenched phase of U_{60} . Pattern showing a broad-shouldered peak with m/z smaller than that of U_{60} clusters; indicating cluster has ultimately fragmented into smaller units as a result of pressure application.

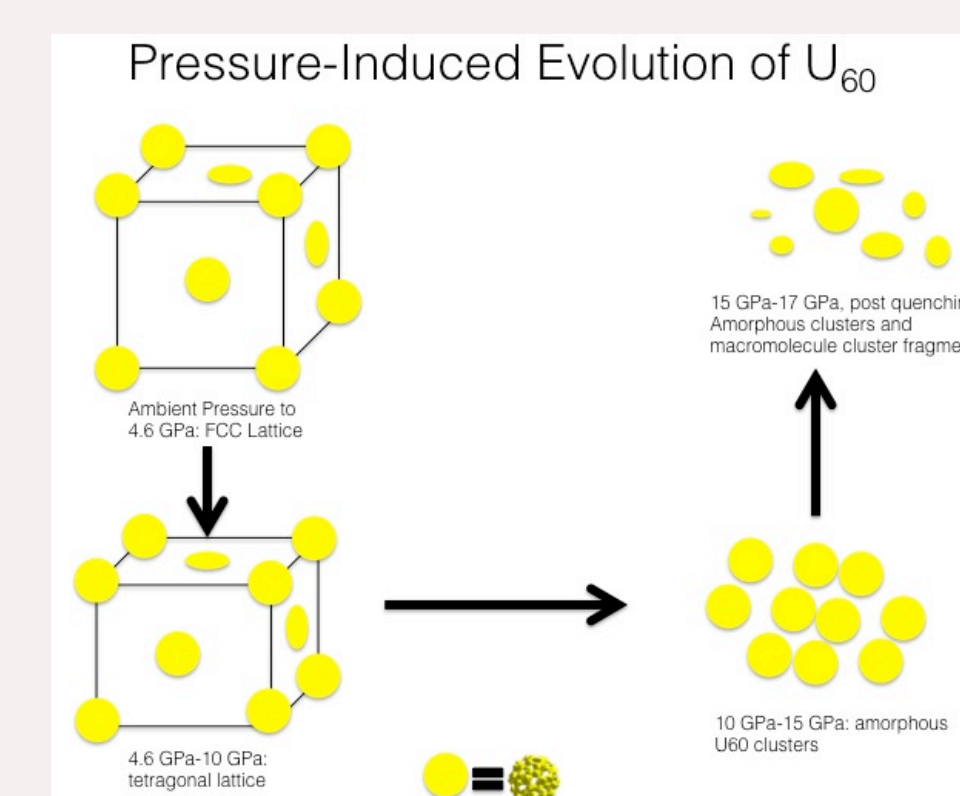
U_{60} : Irreversible Transitions

When taken from ambient pressures to 4.6 GPa, U_{60} undergoes a phase transition from its isometric structure to a tetragonal lattice, as indicated in Raman spectroscopy and synchrotron XRD. At 10 GPa, this tetragonal structure amorphizes. These transitions are irreversible. The amorphous phase created from U_{60} has been shown by ESI-MS to include macromolecules with as many as 20 uranyl-peroxide units.

Relative to C_{60} , which loses its short range order before its hcp lattice (Wang 2012), U_{60} follows a different path. Their identical topologies suggests that the uranyl peroxide chemistry of U_{60} strongly influences high-pressure behavior.

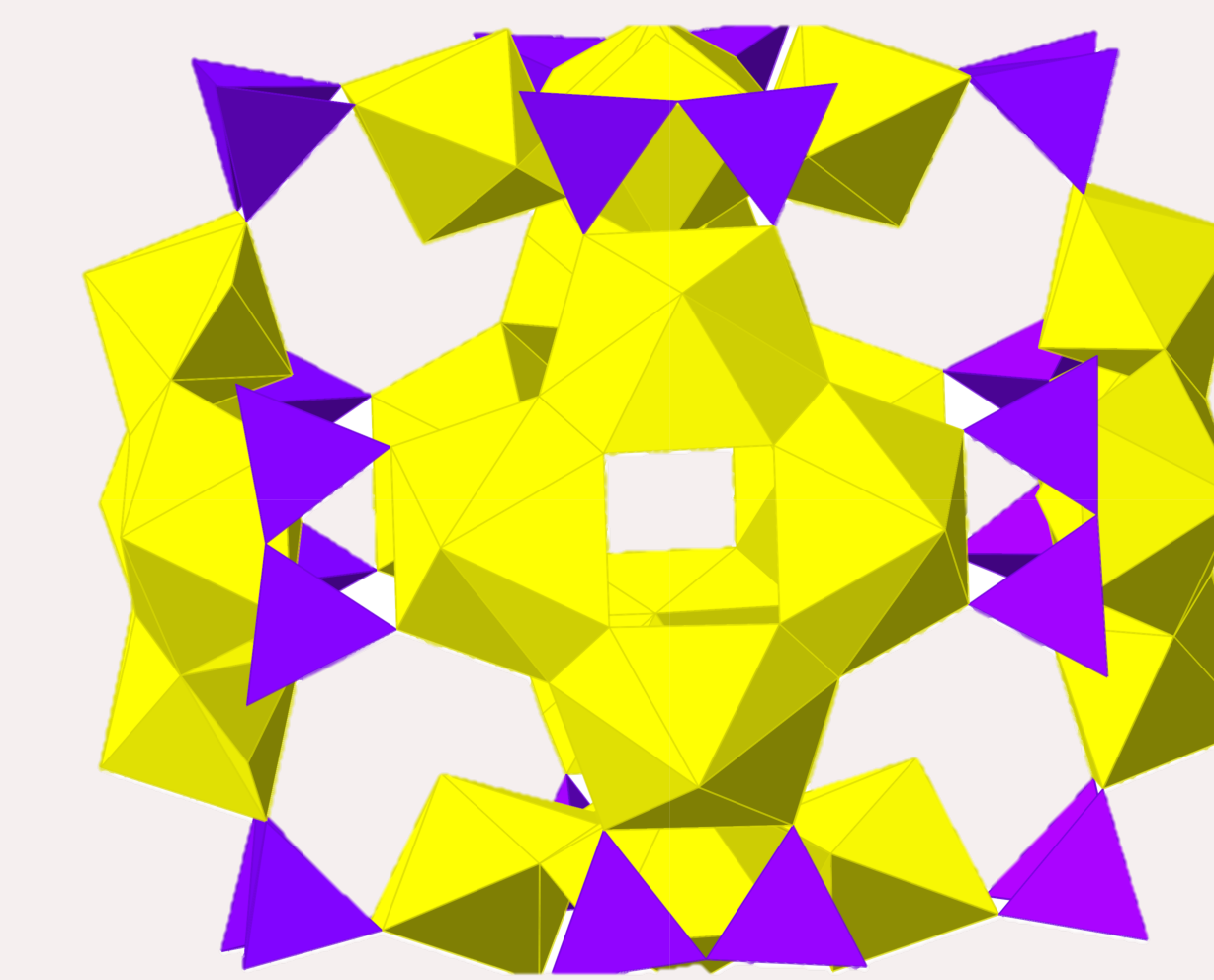


Synchrotron X-Ray Diffraction (XRD) of U_{60} as pressure is applied up to 13.3 GPa. Phase transition to a tetragonal structure at 4.4 GPa, as evidenced by the intruding (022) peak, indicating a change in the c-parameter. Tetragonal structure persists until amorphization at 13.3 GPa. Once amorphized at pressure, quenching XRD patterns indicate amorphous powder, showing the irreversibility of the pressure transition.



Visual schematic model of U_{60} 's evolution and response during pressure application. Isometric crystal structure and U_{60} clusters persist until 4.4 GPa; at this point a tetragonal structure forms and persists until amorphization at 13.3 GPa. Amorphous clusters persist until 17.4 GPa and quenching, after which cluster fragments are present. The entire process is irreversible.

$U_{24}Py_{12}$: Reversible Effects

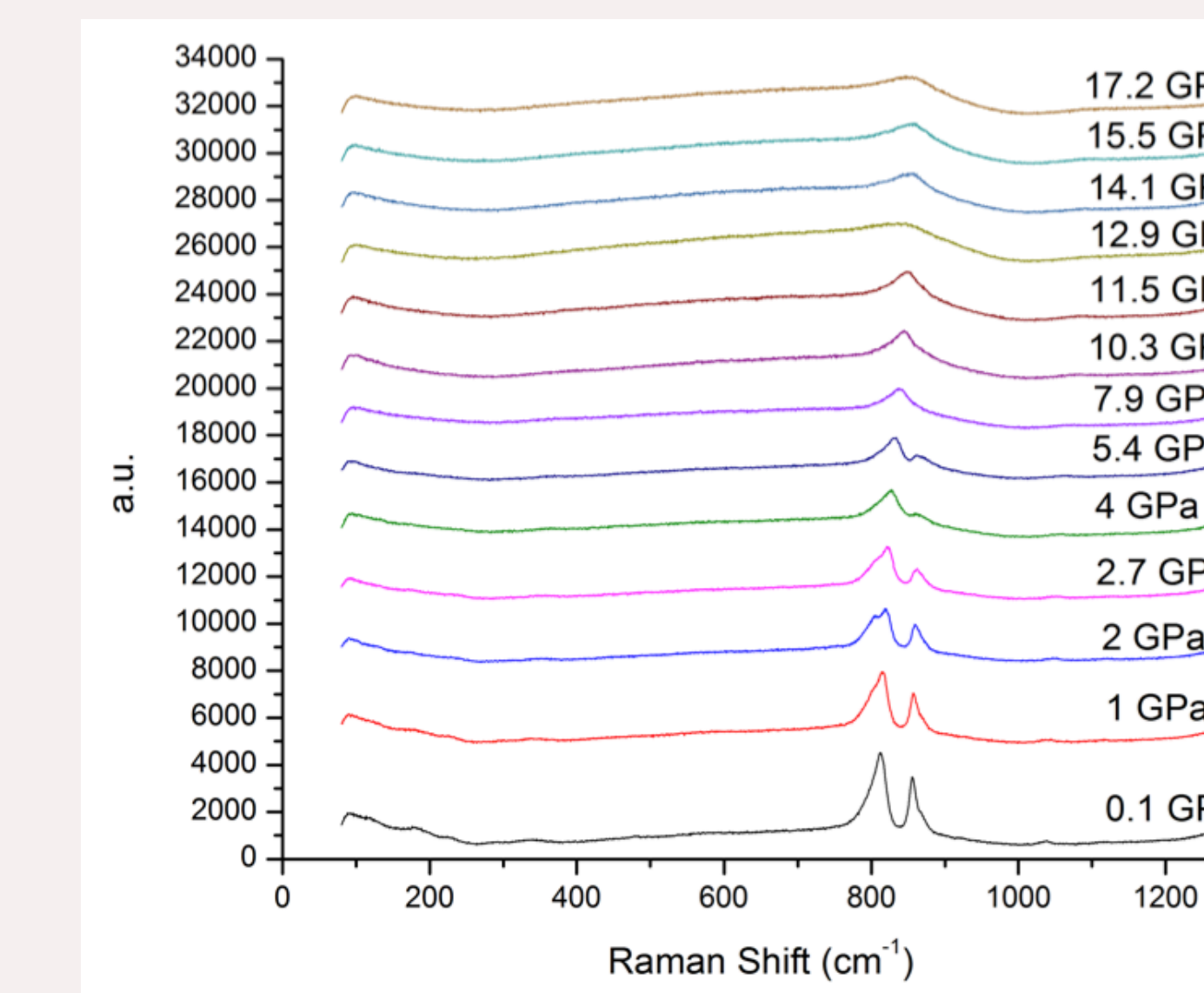


U24Py12 Polyhedral Representation (Burns et al 2011)

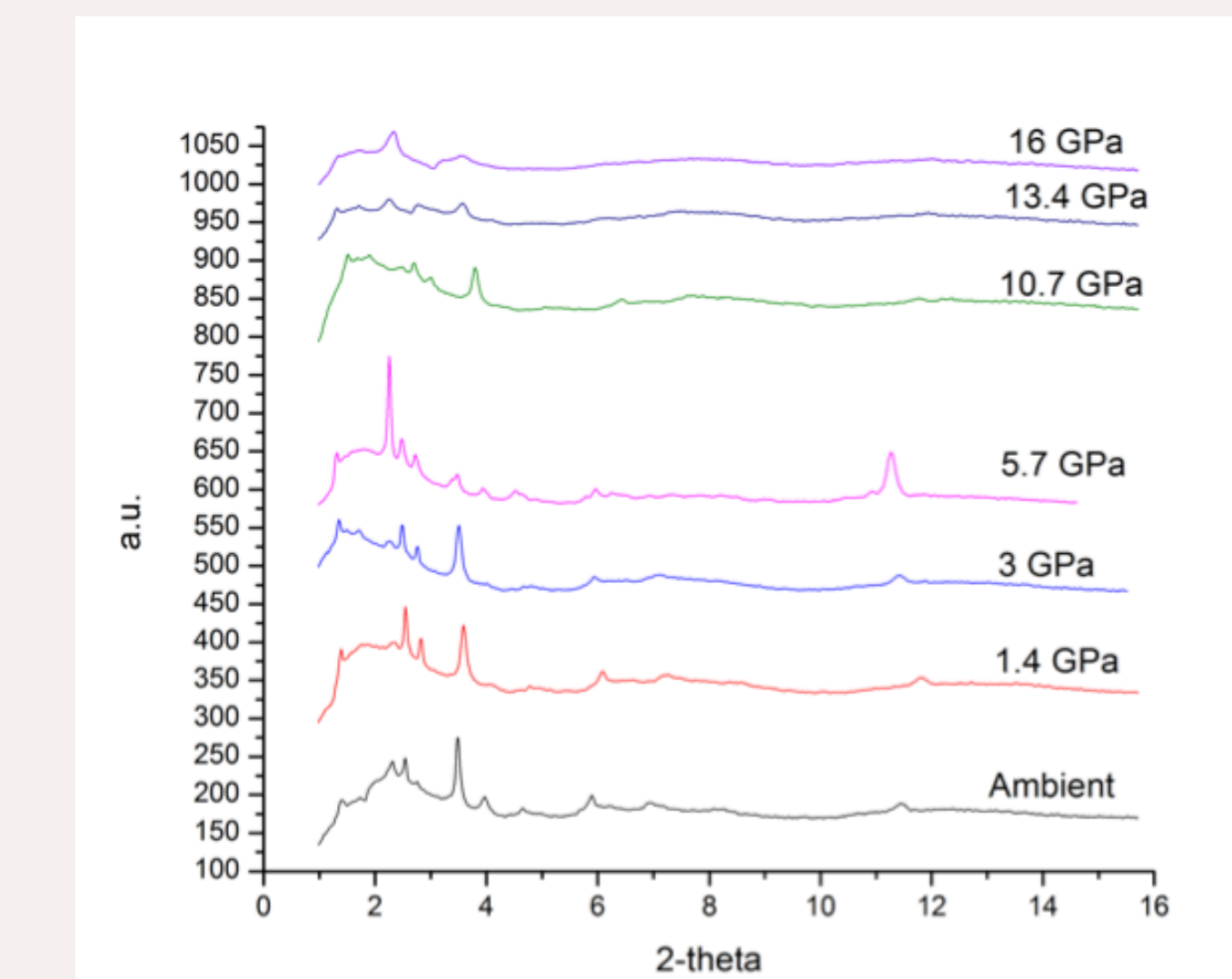
Cluster Formula $[(UO_2)_{24}(O_2)_{24}(HP_2O_7)_6](H_2P_2O_7)_6]^{30-}$
 Crystal Formula $Na_8[(UO_2)_{24}(O_2)_{24}(P_2O_7)_{12}]$
 Symmetry* P42/mnm
 Lattice Parameters* $a=22.746(2) \text{ \AA}$; $c=30.426(4) \text{ \AA}$

$U_{24}Py_{12}$ undergoes reversible pressure-induced amorphization. The crystal structure begins to amorphize at 10 GPa, but XRD data can be indexed to the published $U_{24}Py_{12}$ structure until 16 GPa. Raman intensity is maintained up to pressures of 50 GPa.

$U_{24}Py_{12}$ exhibits relatively different behavior compared with U_{60} . Although they have identical Raman modes, they amorphize at different pressures. Only U_{60} undergoes a phase transition before amorphizing. Only $U_{24}Py_{12}$ displays reversibility in pressure-induced transitions.



$U_{24}Py_{12}$ Raman Spectra up to 17.2 GPa. Raman modes present are a symmetric stretch of the uranyl U-O bond, and a stretch of the coordinating peroxide (McGrail 2014). Raman intensity is maintained as high as 50 GPa, and individual peaks can be resolved up to 50 GPa. Post quenching, the original ambient pressure (0.1 GPa) Raman spectra returns, indicating reversibility in the structural changes undergone during pressure application.



Synchrotron XRD of $U_{24}Py_{12}$ as pressure is applied up to 16 GPa. $U_{24}Py_{12}$'s lattice is maintained until 10.7 GPa, when the structure begins to amorphize. However, individual peaks can be resolved up to 16 GPa. Post-pressure quenching, the structure as determined in 2011 by Burns et al can be indexed, indicating structural reversibility.