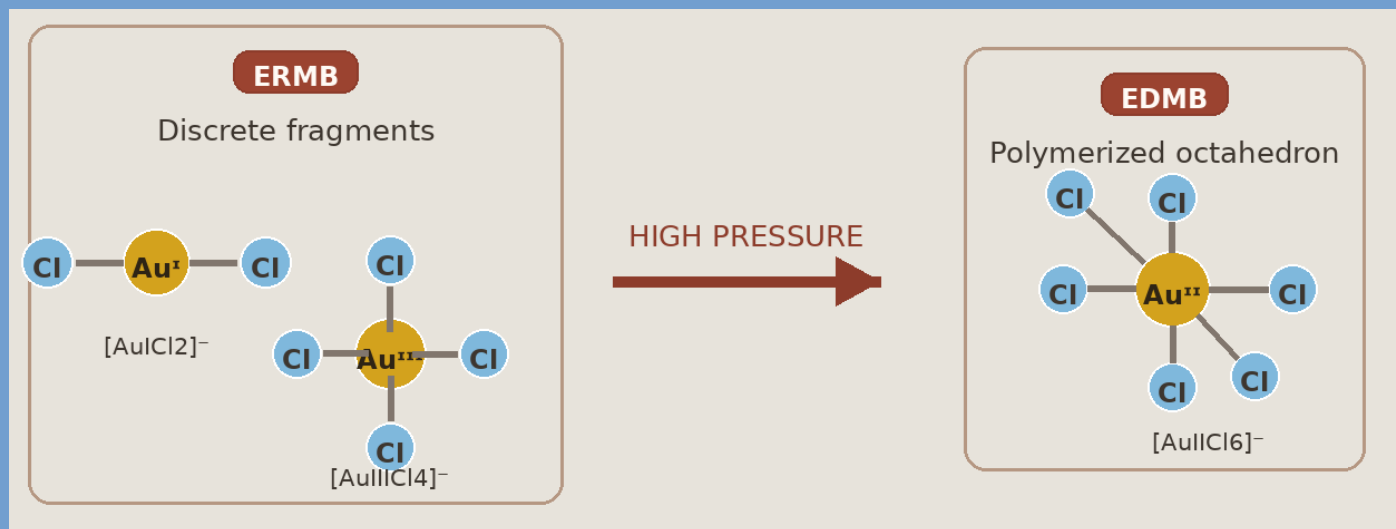




Pressure-driven evolution of Au-Cl bonding in $\text{Cs}_2\text{Au}_2\text{Cl}_6$

From localized multicenter motifs to extended Au-Cl networks under pressure

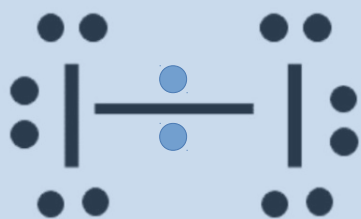
Carlos Echeverría-Arrondo et al.

U. Politècnica de València, Univ. Oviedo, Royal College, U. La Laguna, Presidency Univ., U. Hyderabad

Bonding motifs relevant to gold halide perovskites

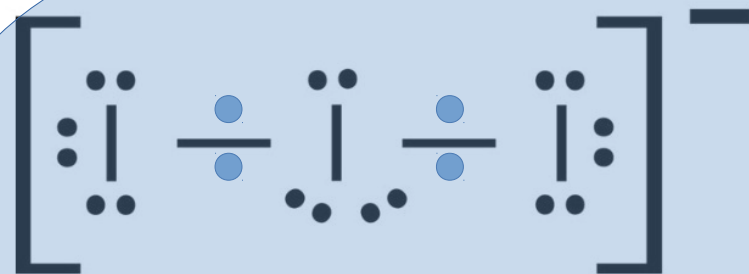
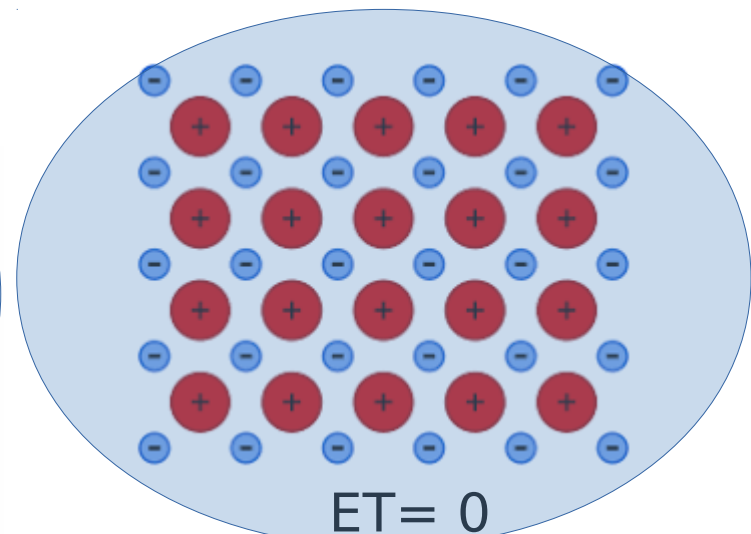
Within the UTMB framework, we ask whether pressure drives Au-Cl bonding from an ERMB-like to an EDMB-like regime.

ES= 2, ET= 0

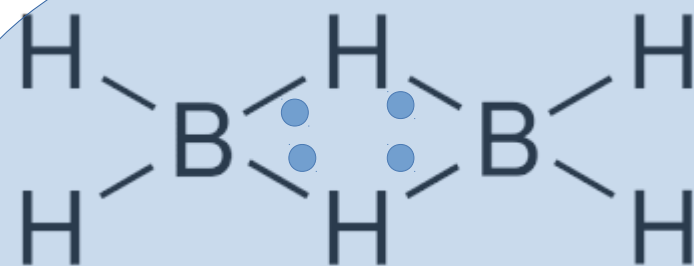


2 centers
2 electrons

ES= 0, ET= 1



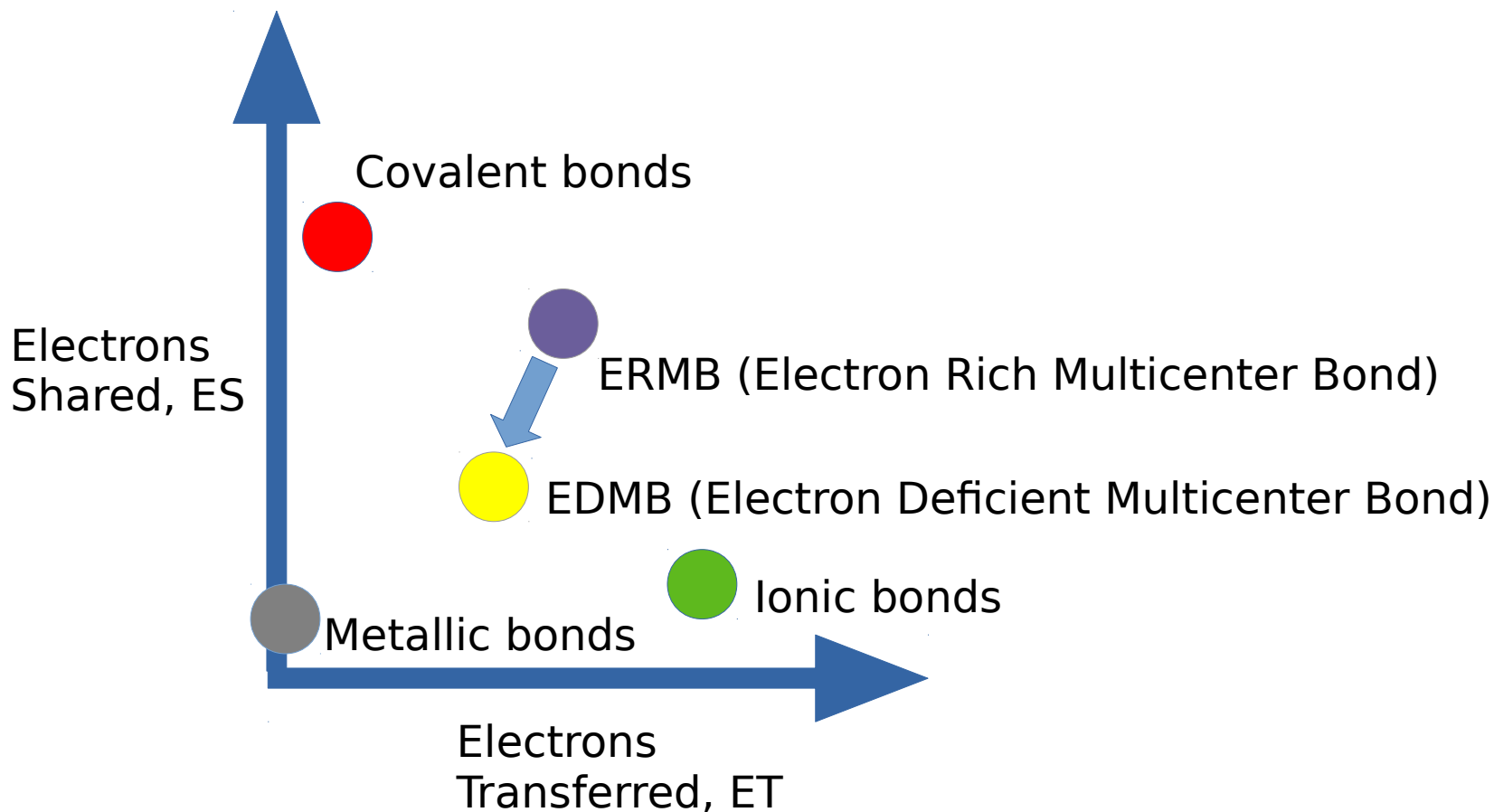
3 centers
4 electrons, ERMB



3 centers
2 electrons, EDMB

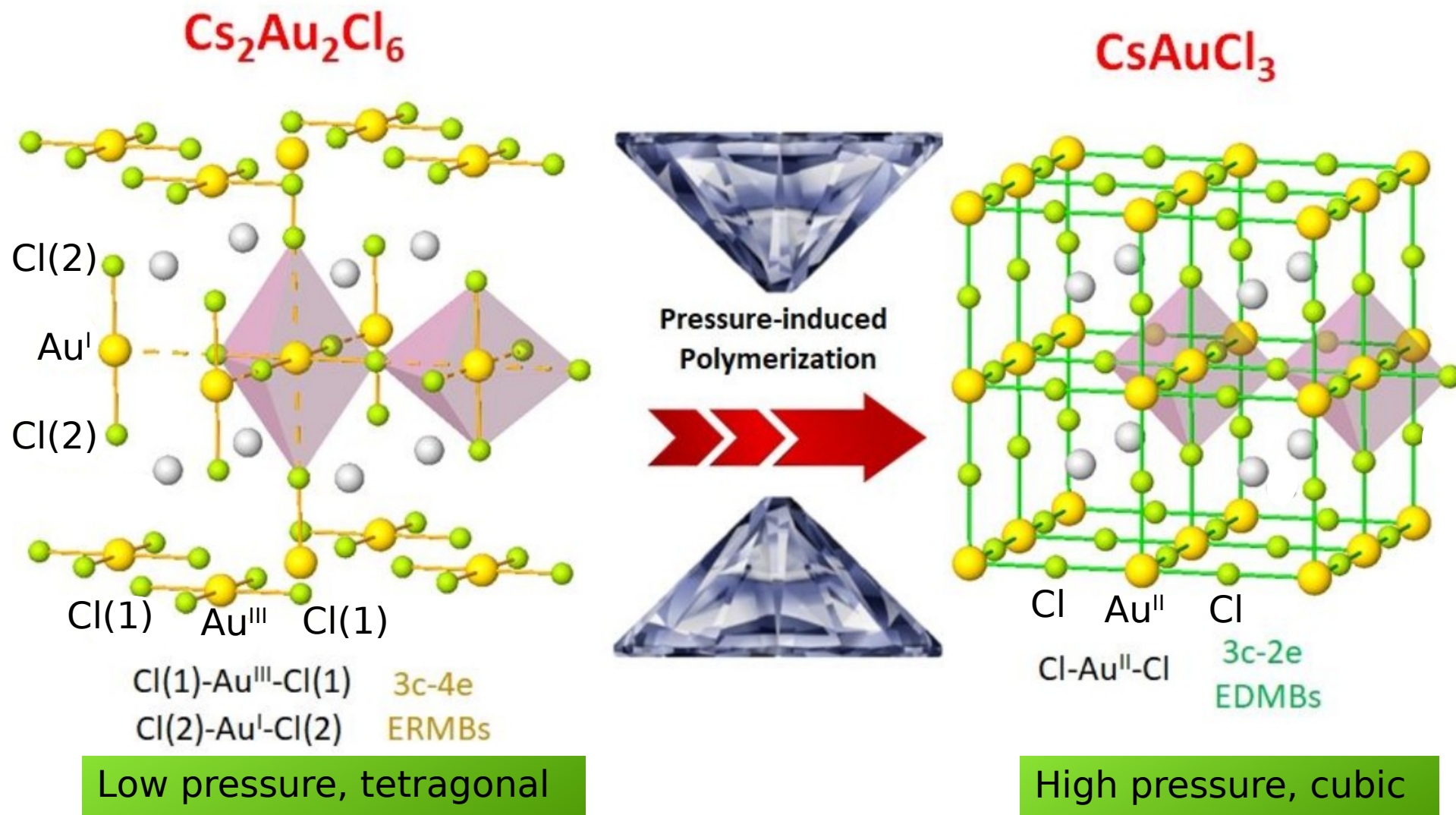
Tracking Au-Cl bonding with the ES-ET map

This map provides one descriptor of bonding evolution within the UTMB framework, later supported by ICOBI, QTAIM, and phonons.



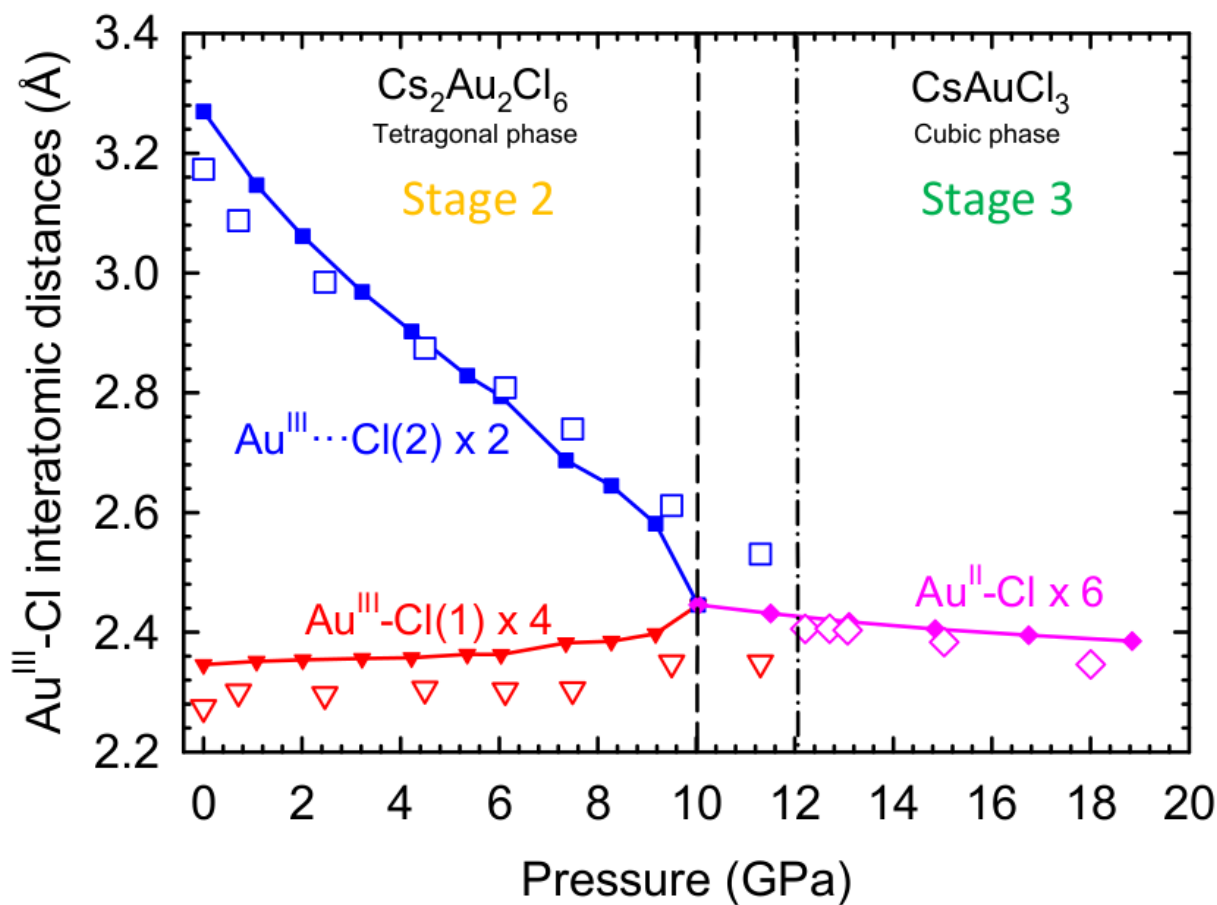
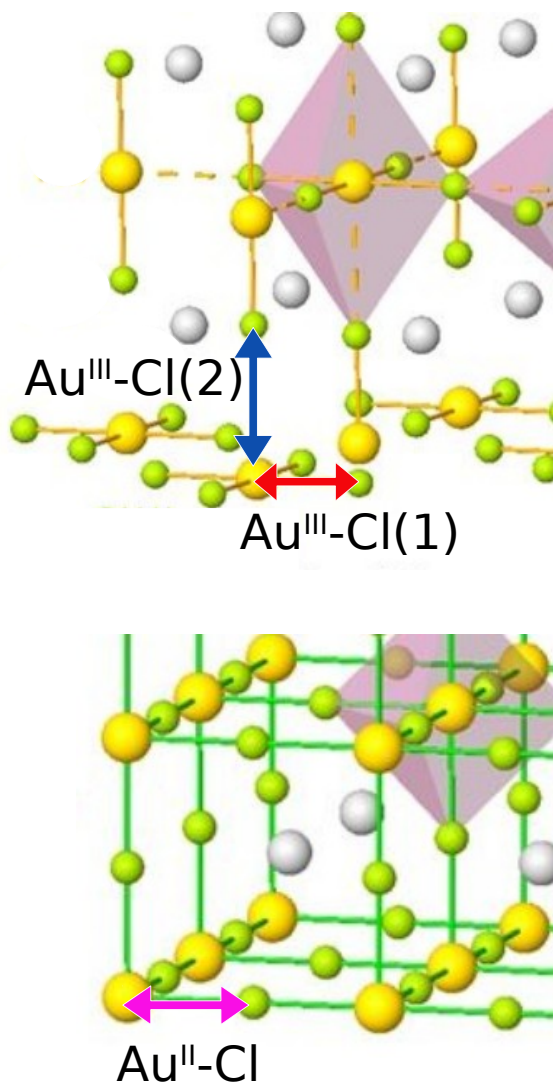
Polymerization of $[\text{Au}^{\text{I}}\text{Cl}_2]^-$ and $[\text{Au}^{\text{III}}\text{Cl}_4]^-$ units into a 3D network

Pressure-induced polymerization (PIP) accompanies the ERMB-to-EDMB bonding evolution.



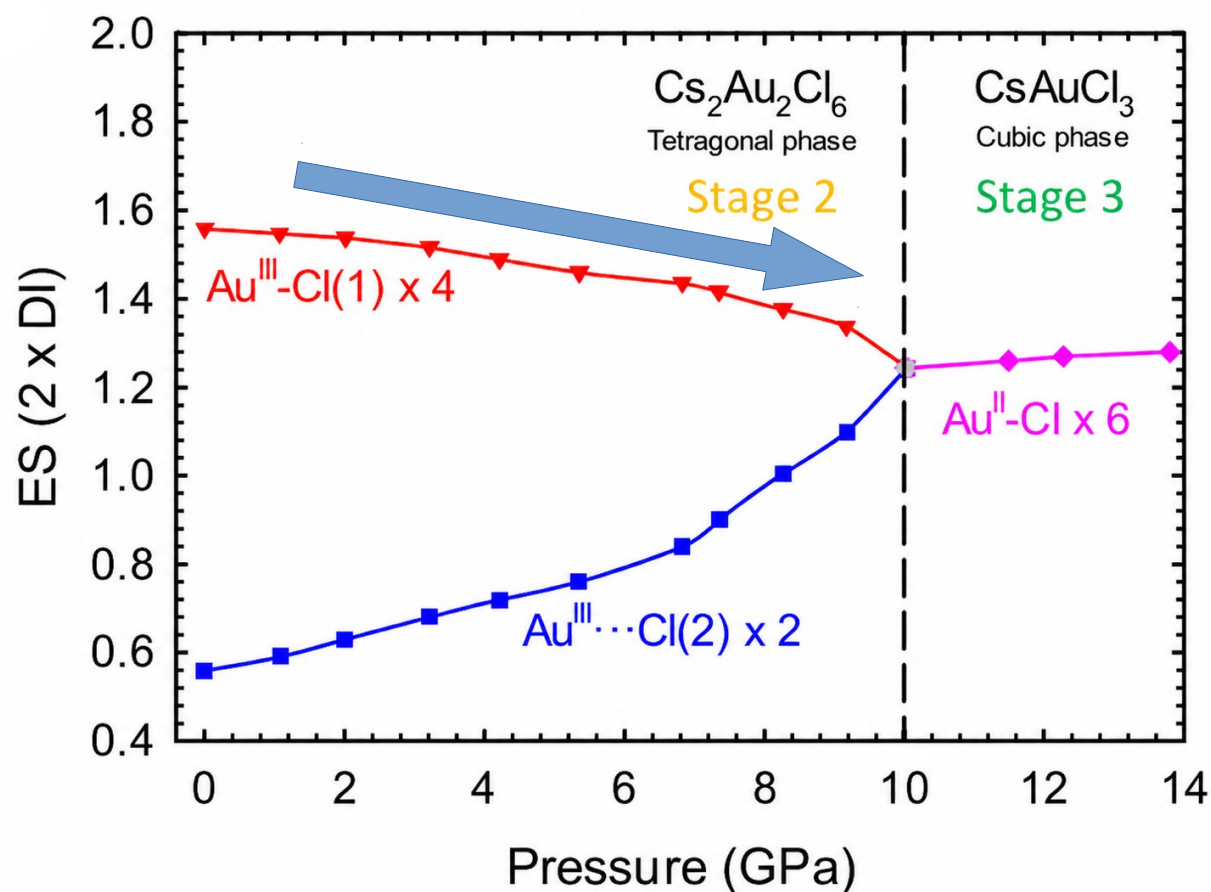
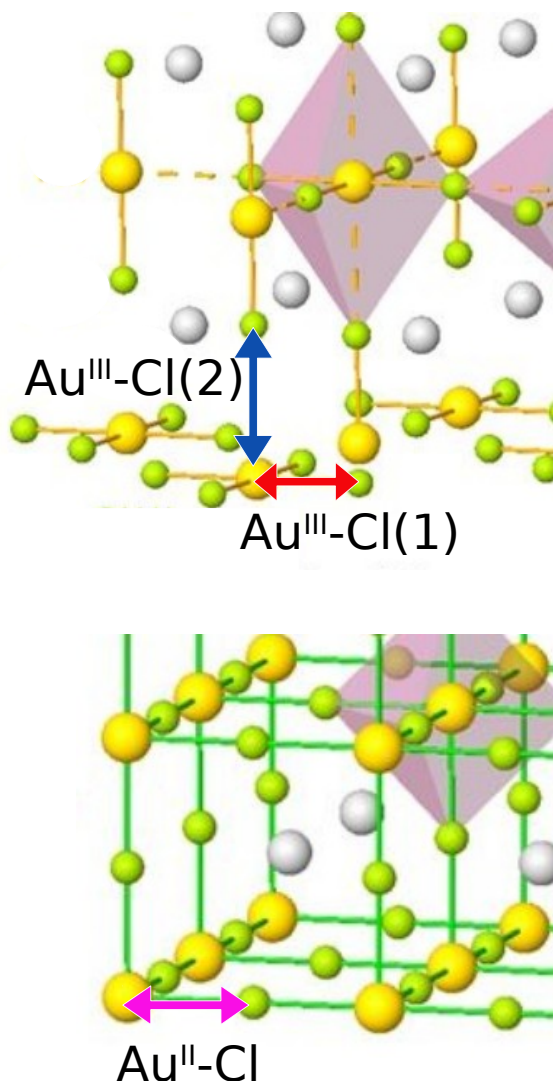
Pressure-driven symmetrization of Au-Cl bond lengths

Long Au $\cdots$ Cl contacts shorten, while short Au-Cl bonds expand anomalously before equalization.



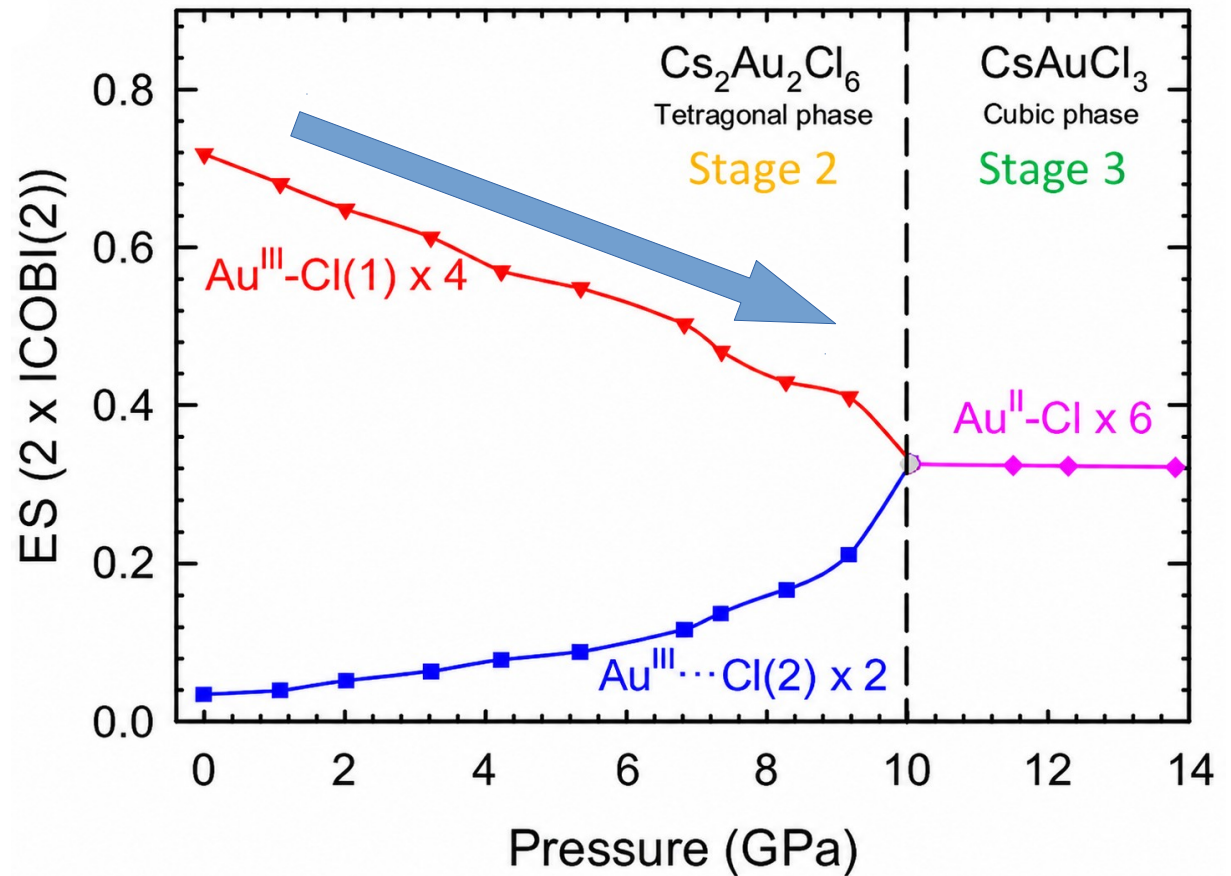
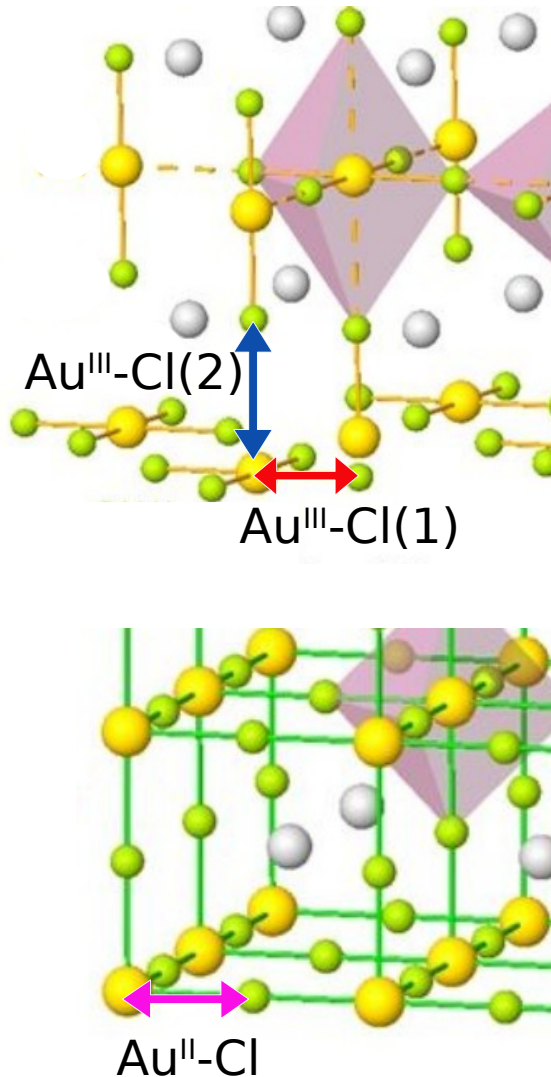
Pressure-driven signatures of ERMB-to-EDMB evolution

Reduced ES from DI is consistent with a shift toward a more electron-deficient bonding regime.



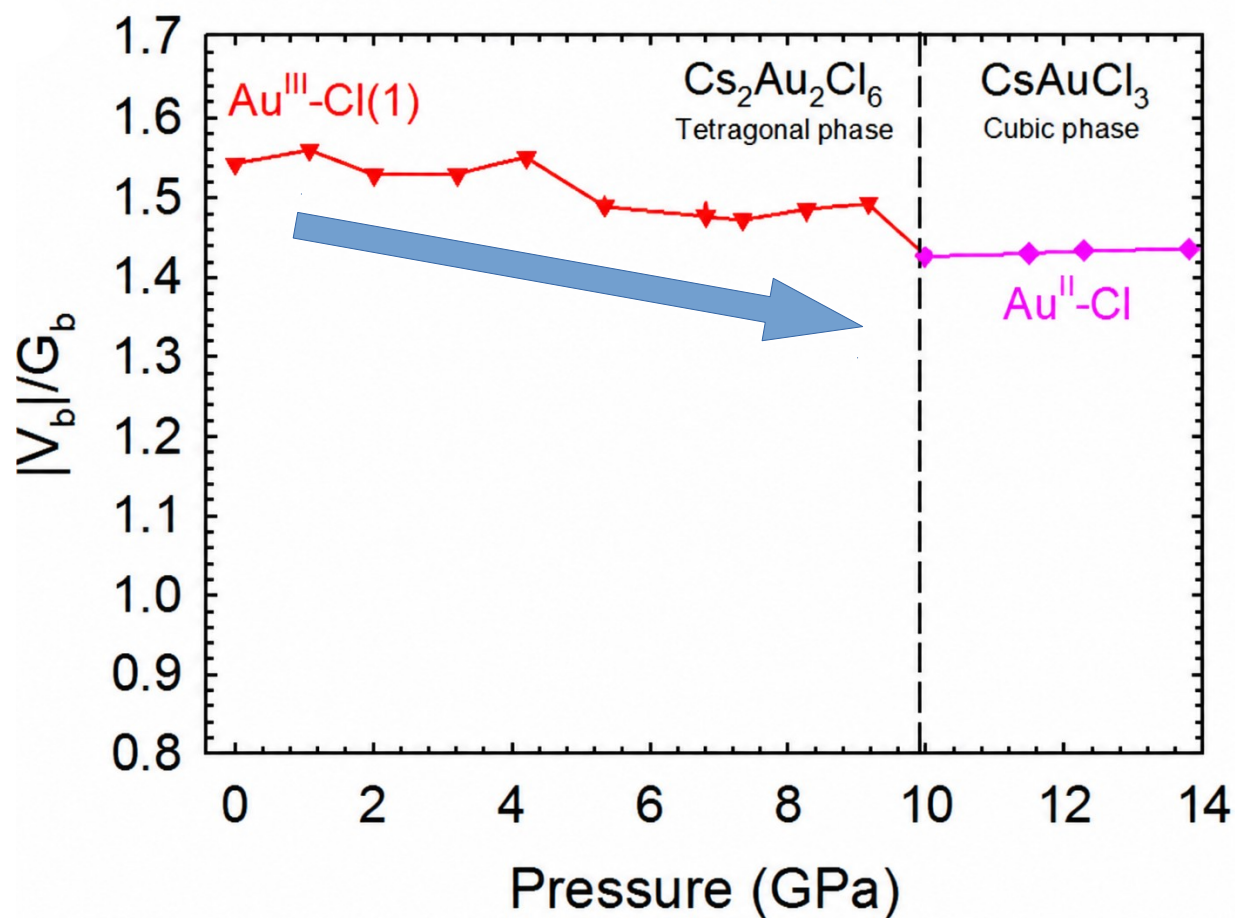
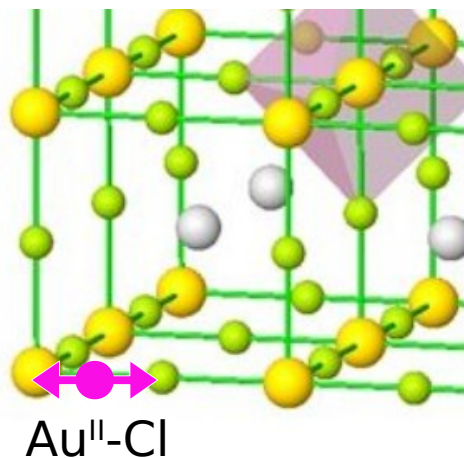
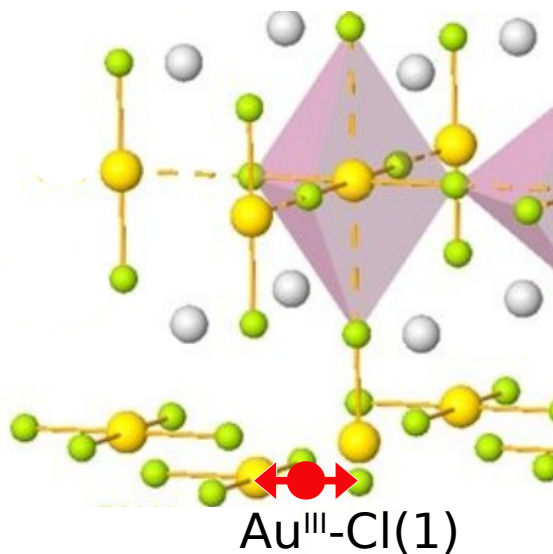
Pressure-driven signatures of ERMB-to-EDMB evolution

Reduced ES from ICOBI is consistent with a shift toward a more electron-deficient bonding regime.



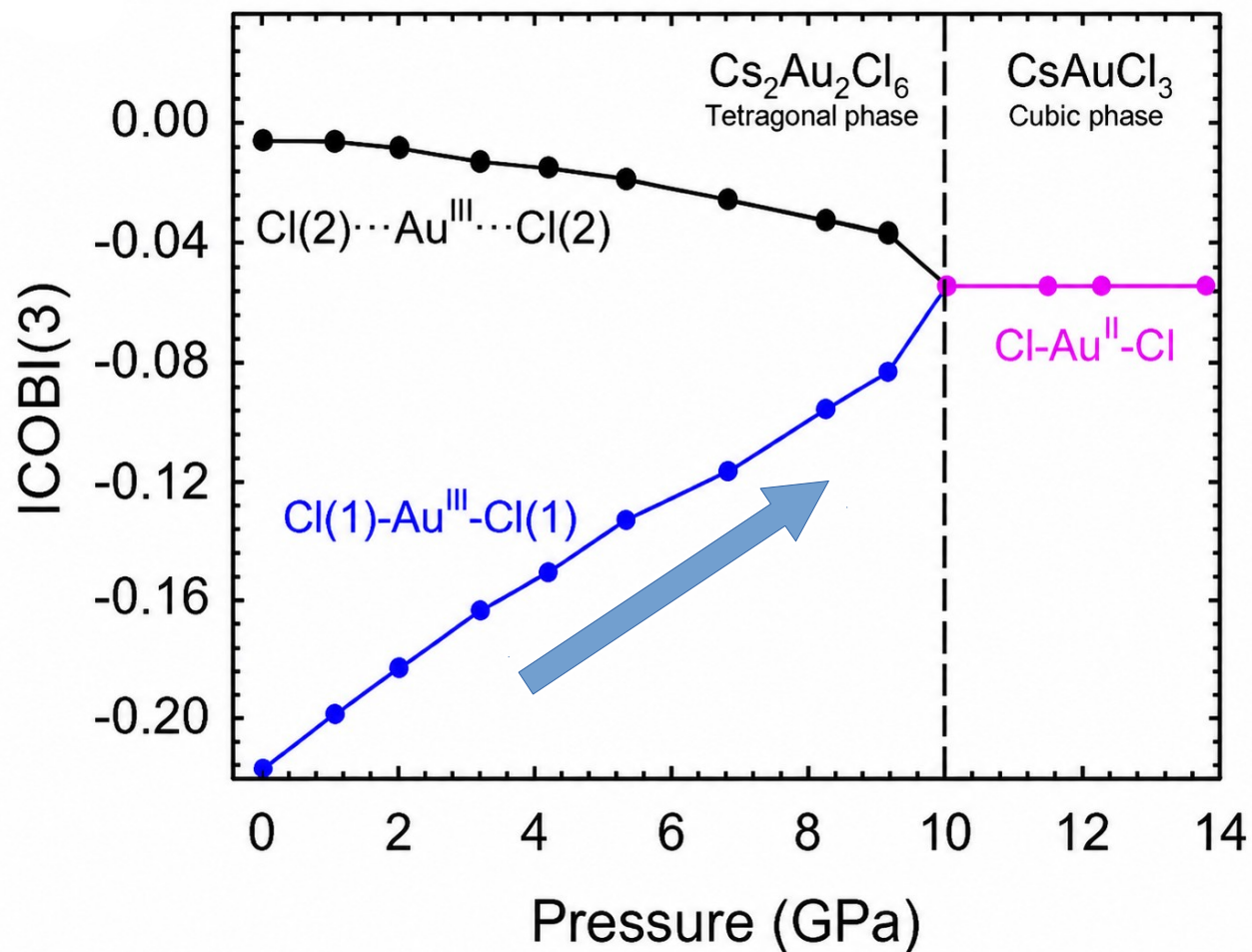
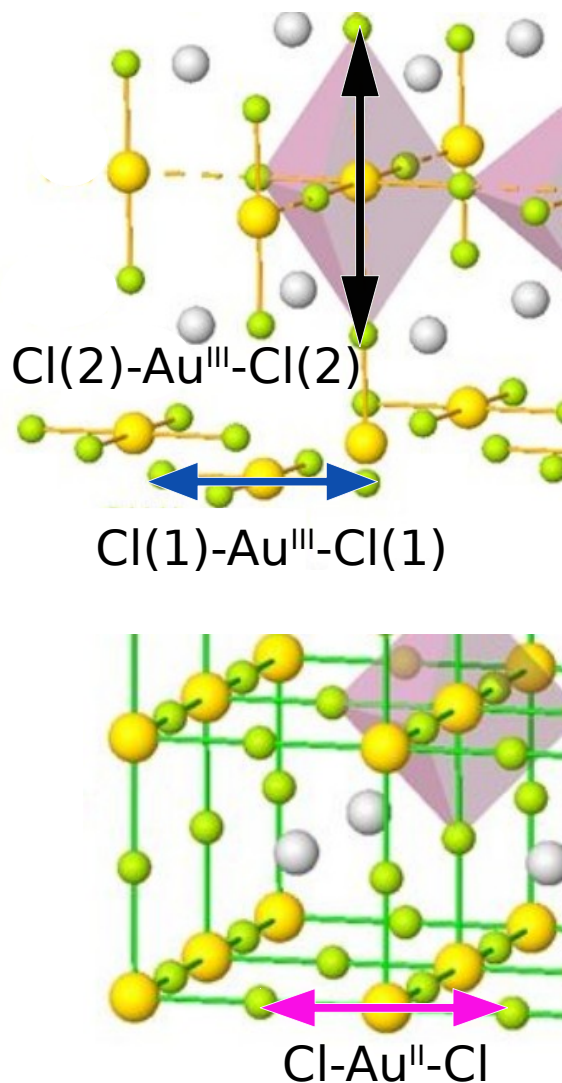
QTAIM evidence for pressure-driven bonding evolution

A decrease in $|V|/G$ at the BCP is consistent with a shift toward a more polarized bonding regime.



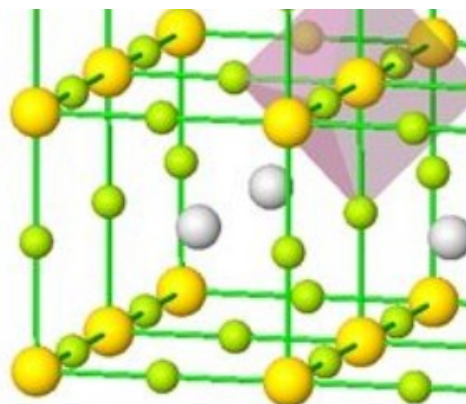
Orbital-based evidence for multicenter bonding evolution

Smaller $|\text{ICOB}(3)|$ values support a shift toward an EDMB regime.

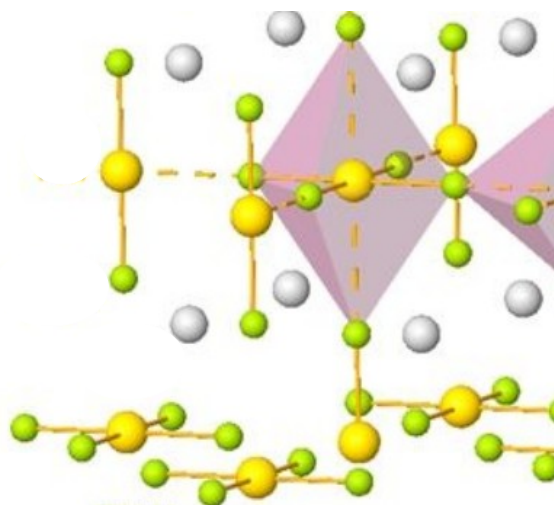


Pressure induces hardening of Au-Cl phonon modes

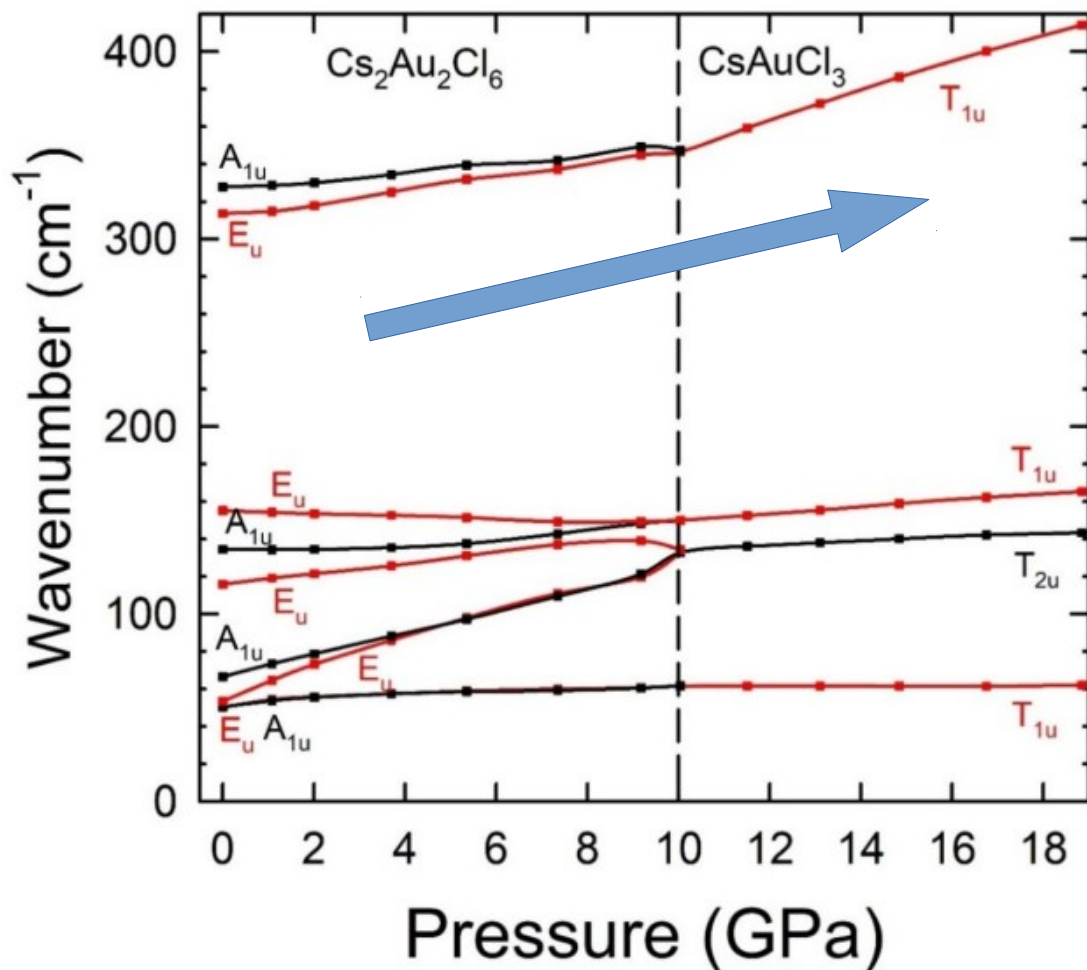
Phonon hardening supports a shift toward a more polarized bonding regime.



High pressure, cubic



Low pressure, tetragonal



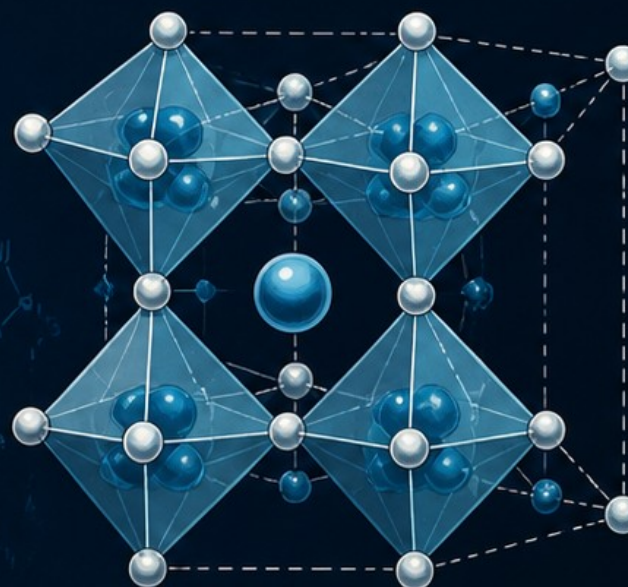
Take-home messages:

Pressure reshapes Au-Cl bonding

- 1) Pressure drives the tetragonal-to-cubic transition in $\text{Cs}_2\text{Au}_2\text{Cl}_6$**
- 2) Units $[\text{Au}^{\text{I}}\text{Cl}_2]^-$ and $[\text{Au}^{\text{III}}\text{Cl}_4]^-$ polymerize under pressure into a 3D network.**
- 3) Au-Cl bonding evolves from finite ERMBs to extended EDMBs.**
- 4) This evolution is supported by orbital- and density-based descriptors.**

THANK YOU FOR YOUR ATTENTION

★
PEROVSKITES WANT *YOU*
FOR MULTICENTER BONDING



-  A
(cations)
-  B
(cations)
-  X
(anions)