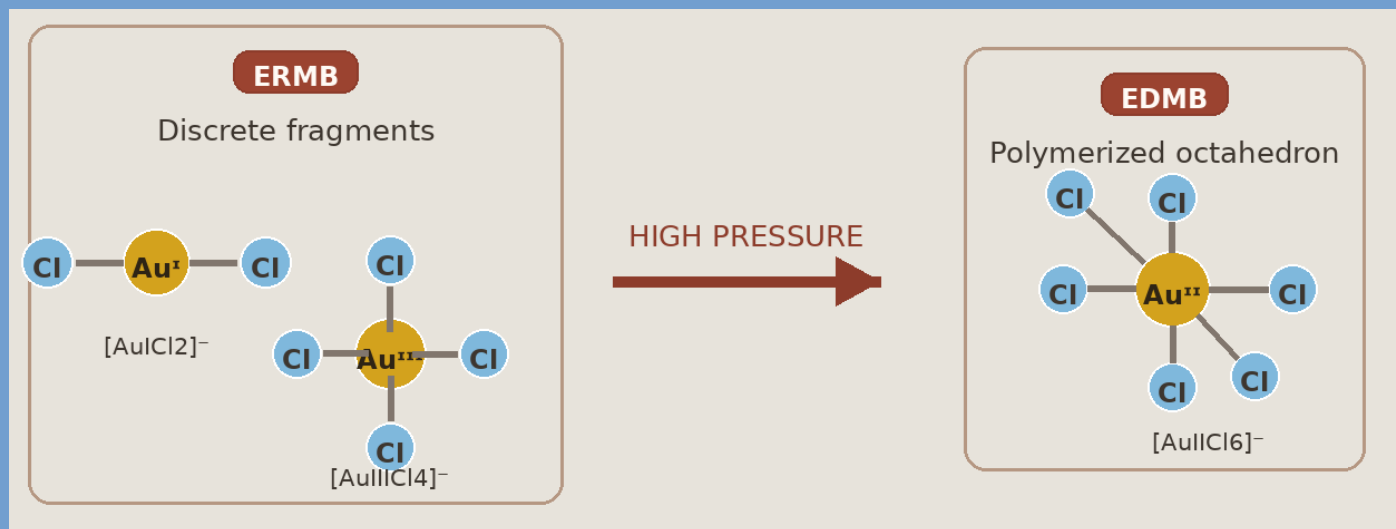




Pressure-driven evolution of Au-Cl bonding in $Cs_2Au_2Cl_6$

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

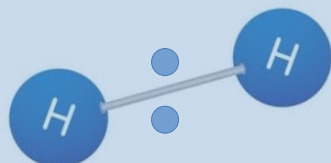
Carlos Echeverría-Arrondo et al.

Instituto de Diseño y Fabricación, U. Politécnica de València

Bonding motifs relevant to gold halide perovskites

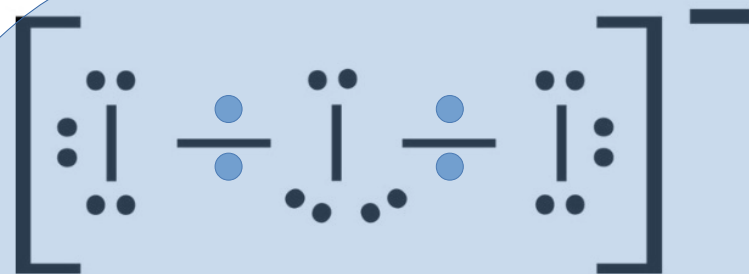
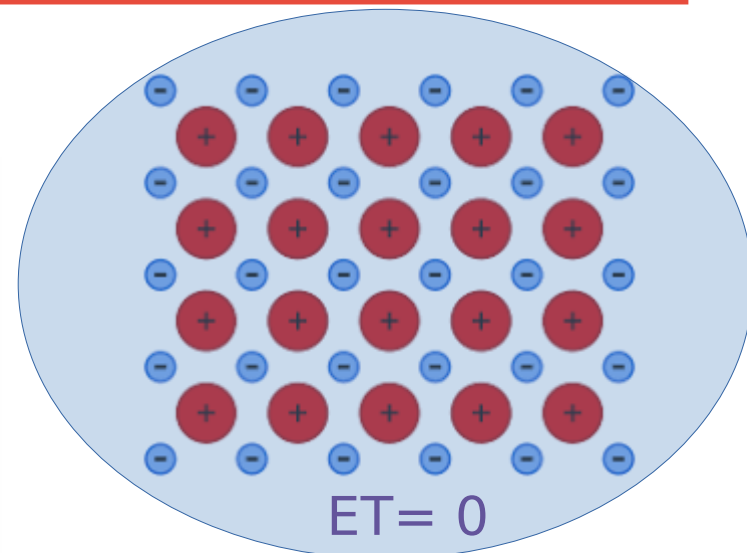
Within the UTMB framework, we ask whether pressure drives Au-Cl bonding from an ERMB-like to an EDMB-like regime.

ES = 2, ET = 0

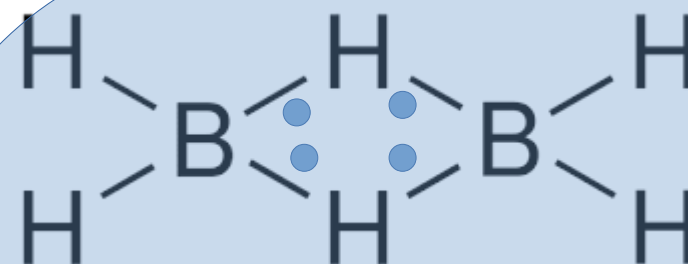


2 centers
2 electrons

ES = 0, ET = 1



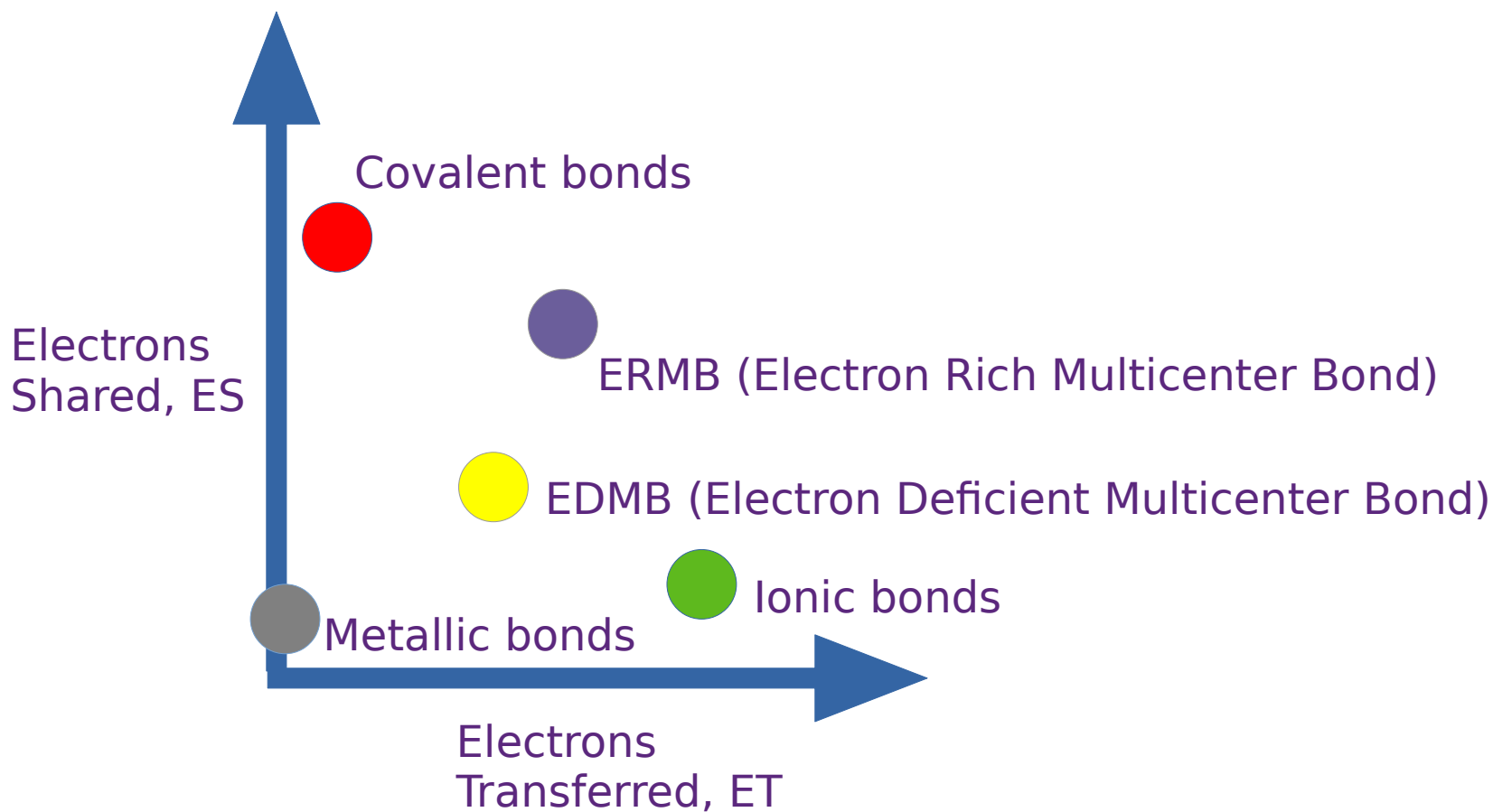
3 centers
4 electrons, ERMB



3 centers
2 electrons, EDMB

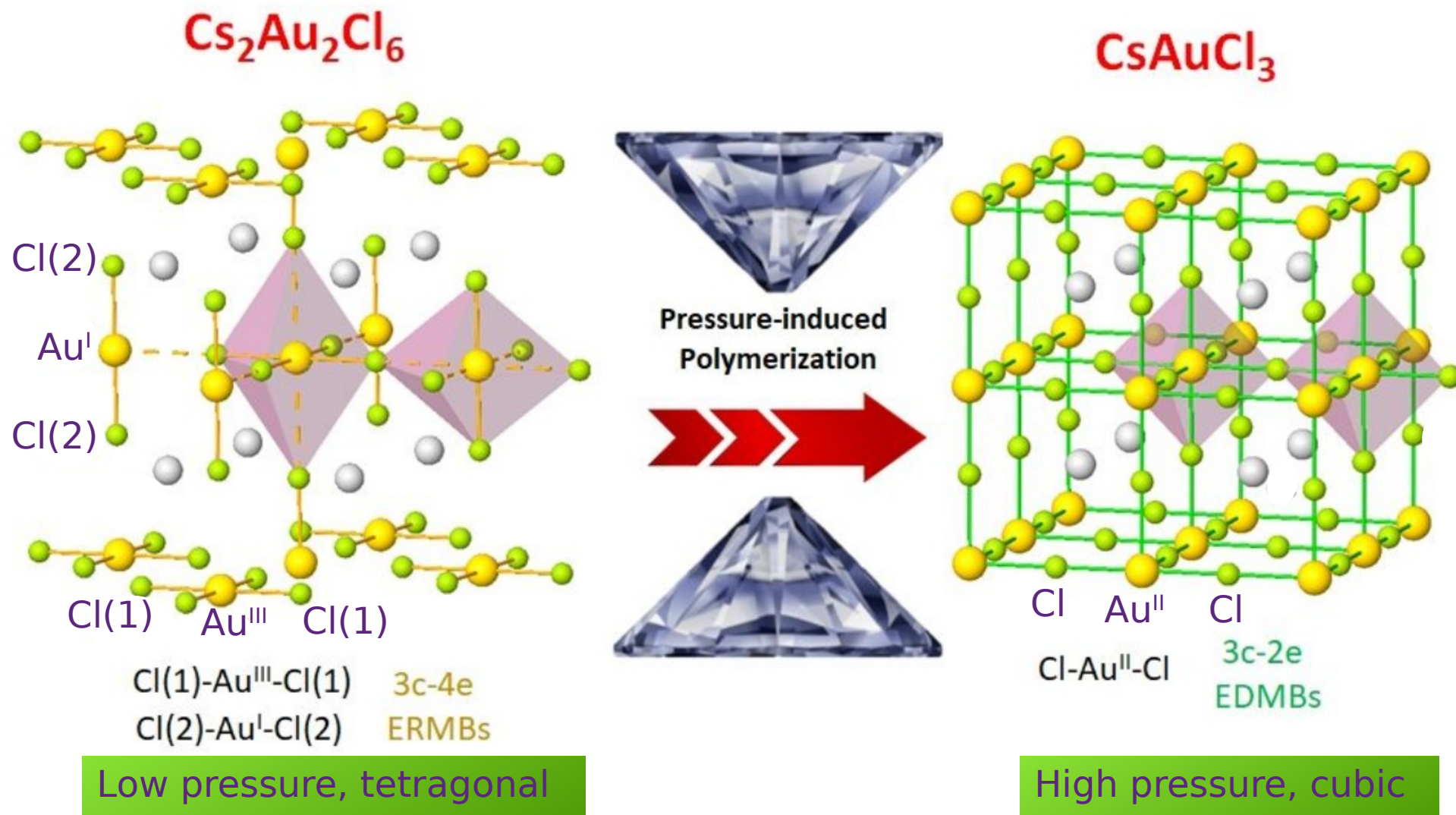
Tracking Au-Cl bonding with the ES-ET map

This map provides one descriptor of bonding evolution within the UTMB framework, later supported by ICOBI(3), $|V|/G$, and phonons.



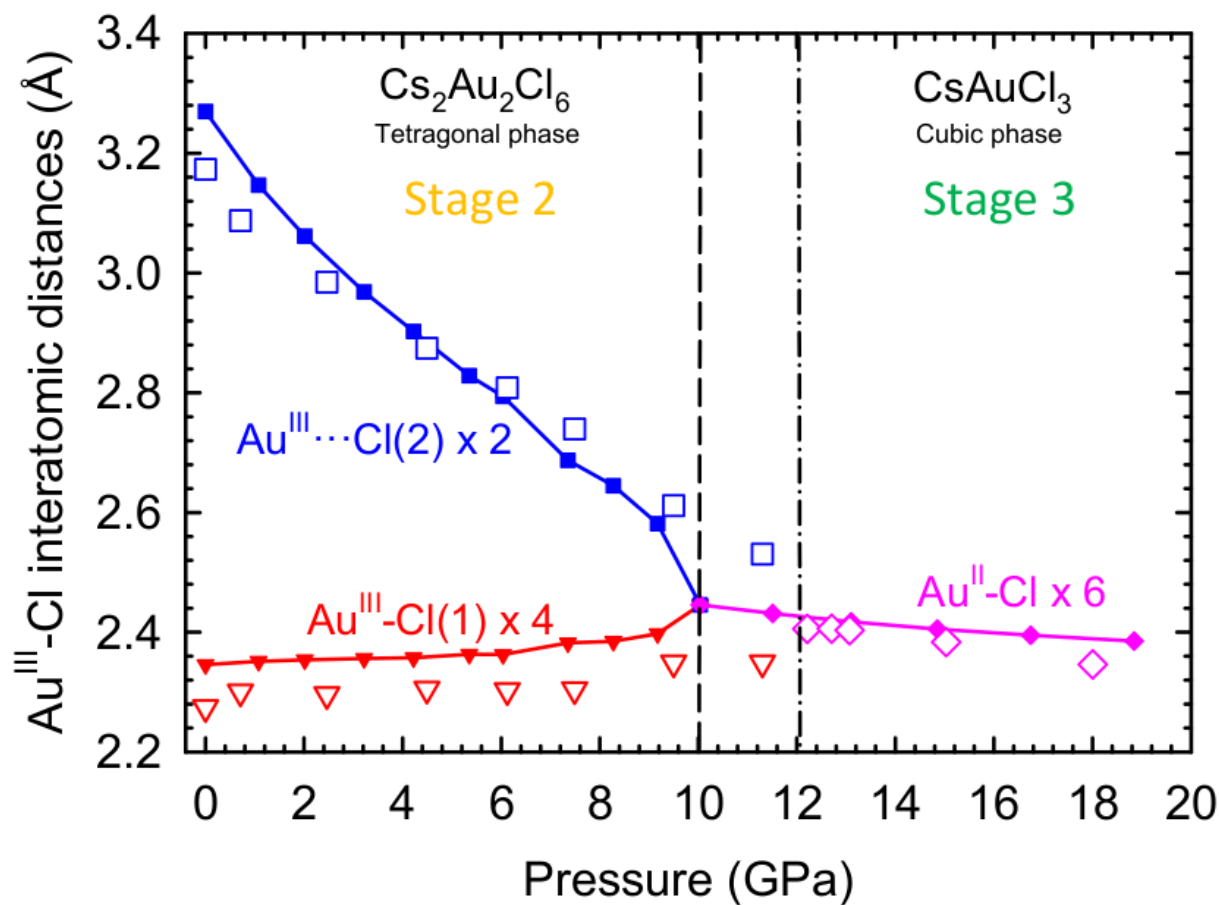
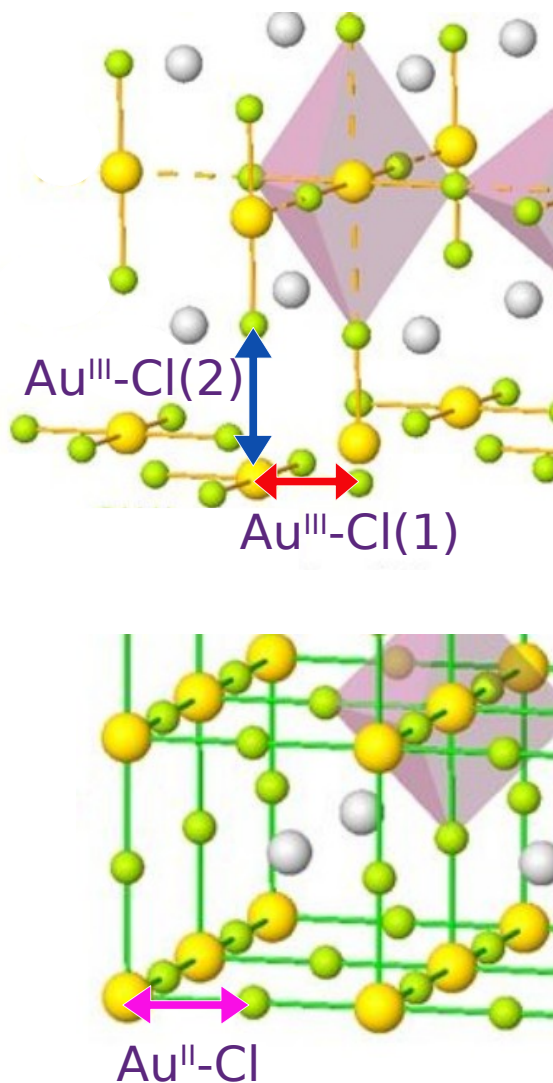
Polymerization of $[\text{Au}^{\text{I}}\text{Cl}_2]^-$ and $[\text{Au}^{\text{III}}\text{Cl}_4]^-$ units into a 3D network

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



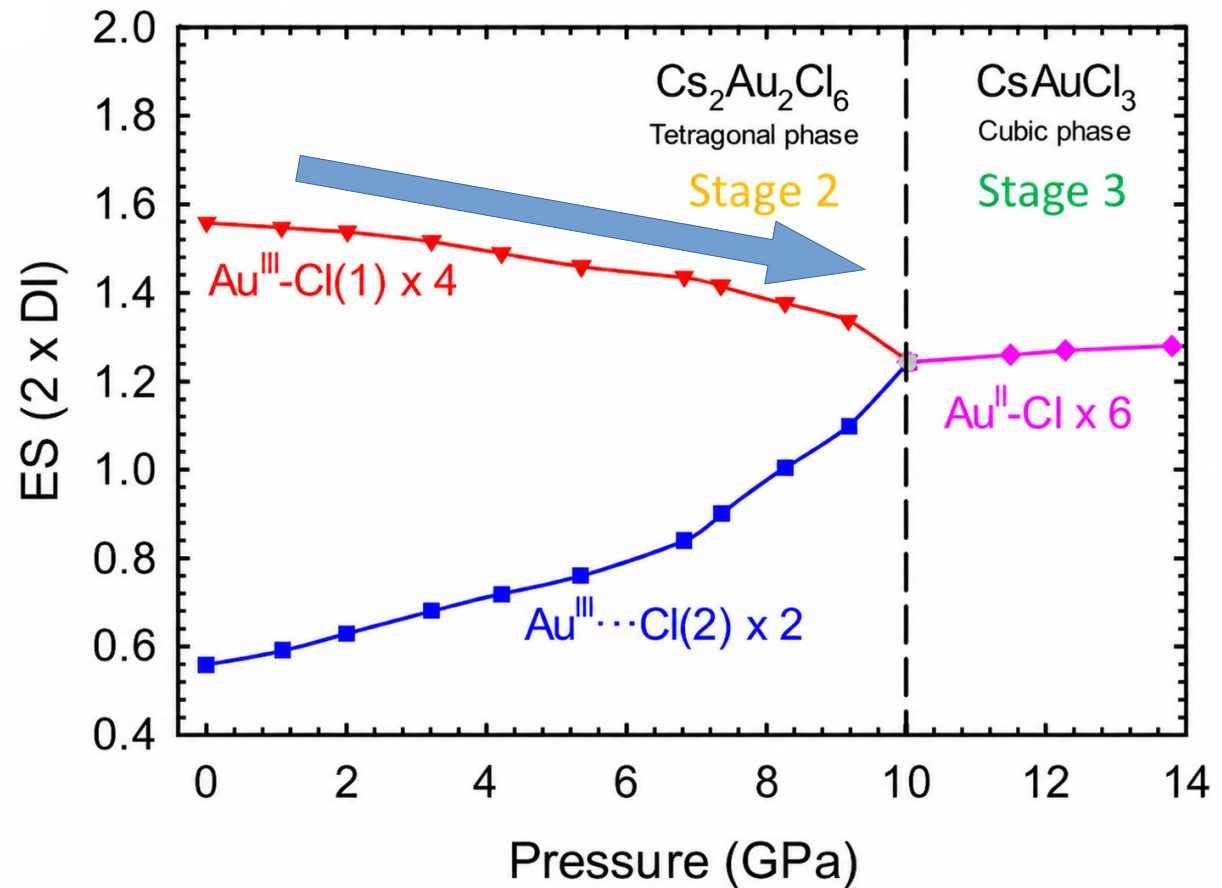
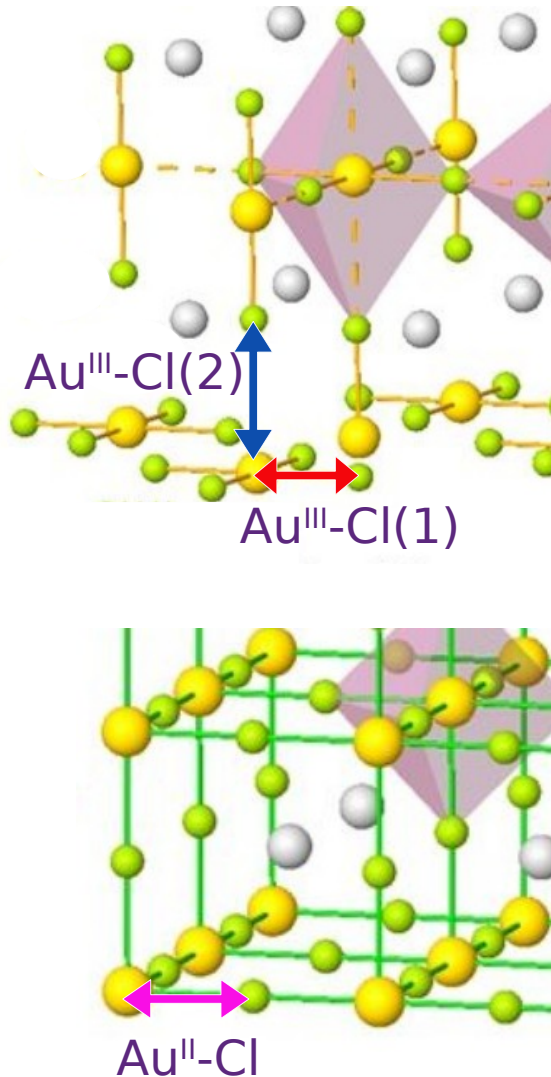
Pressure-driven symmetrization of Au-Cl bond lengths

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



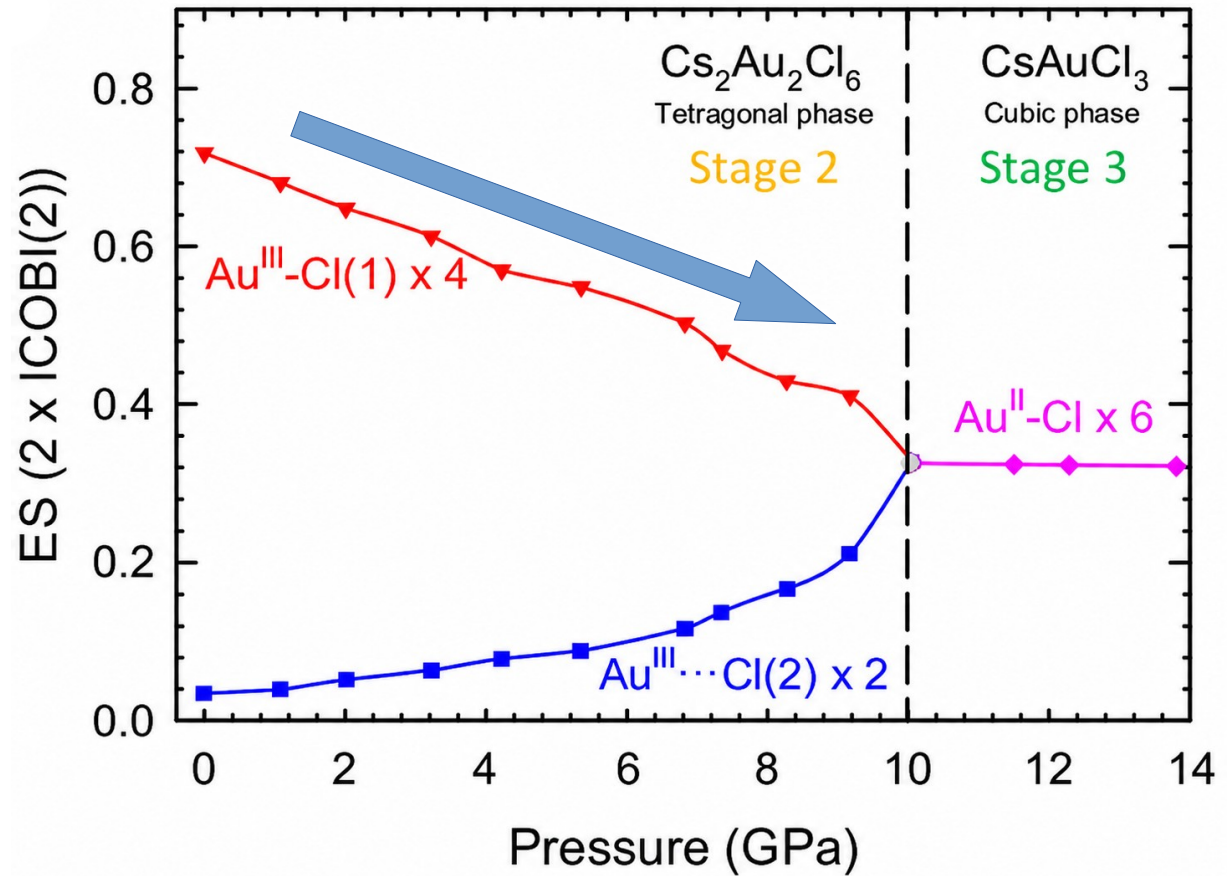
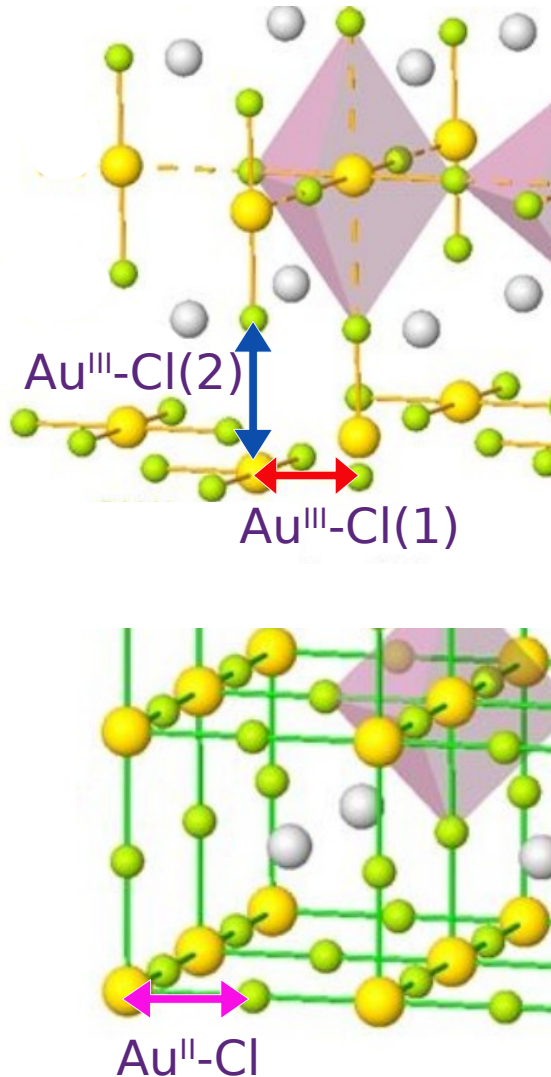
Pressure-driven signatures of ERMB-to-EDMB evolution

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



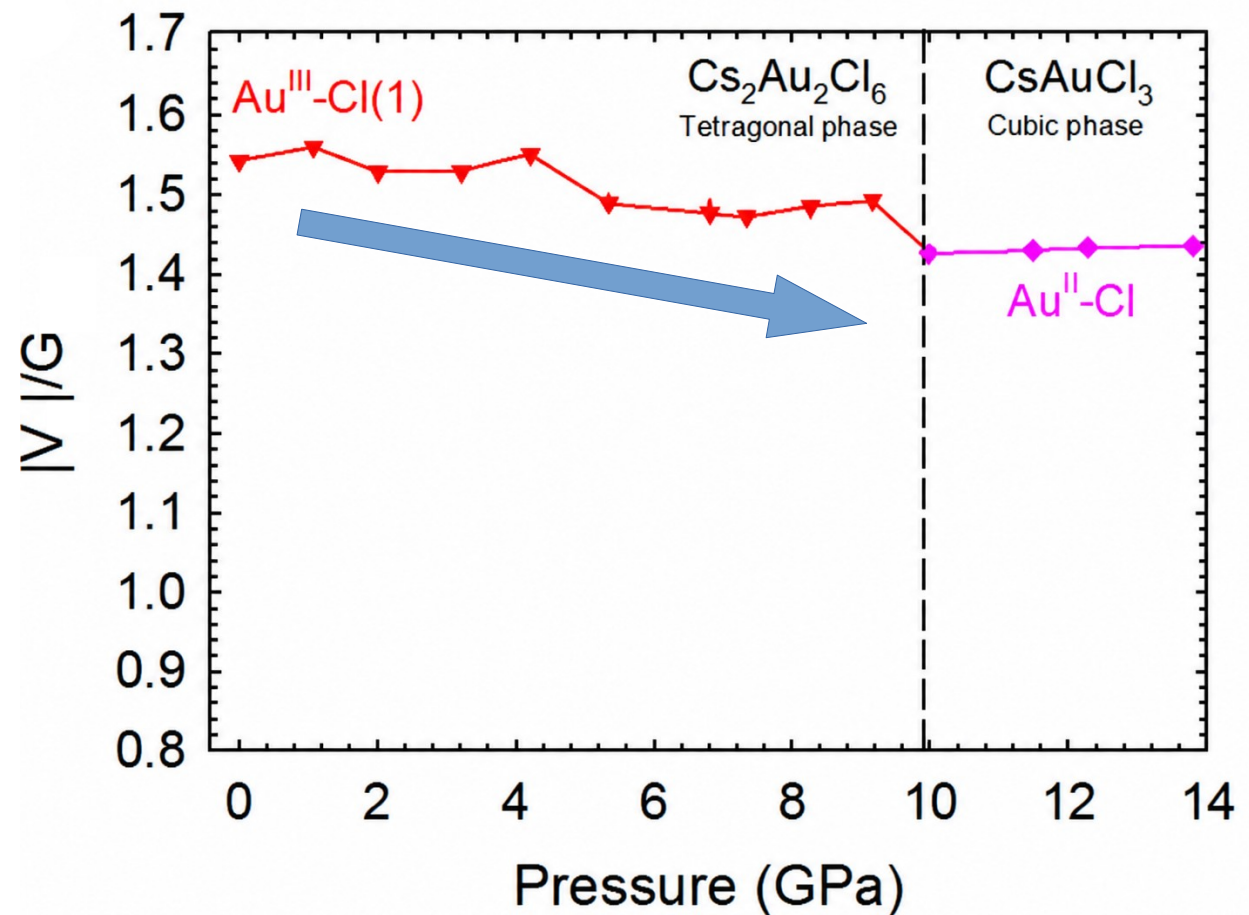
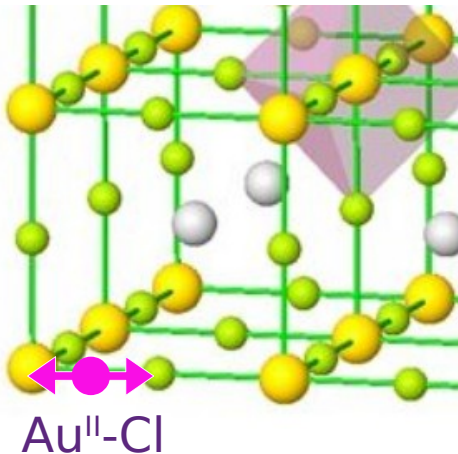
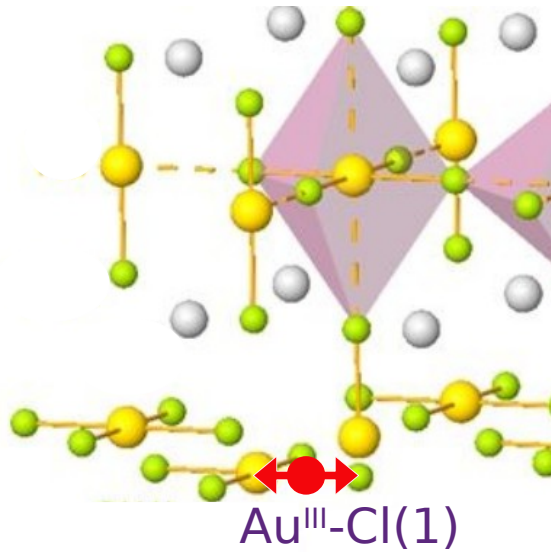
Pressure-driven signatures of ERMB-to-EDMB evolution

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



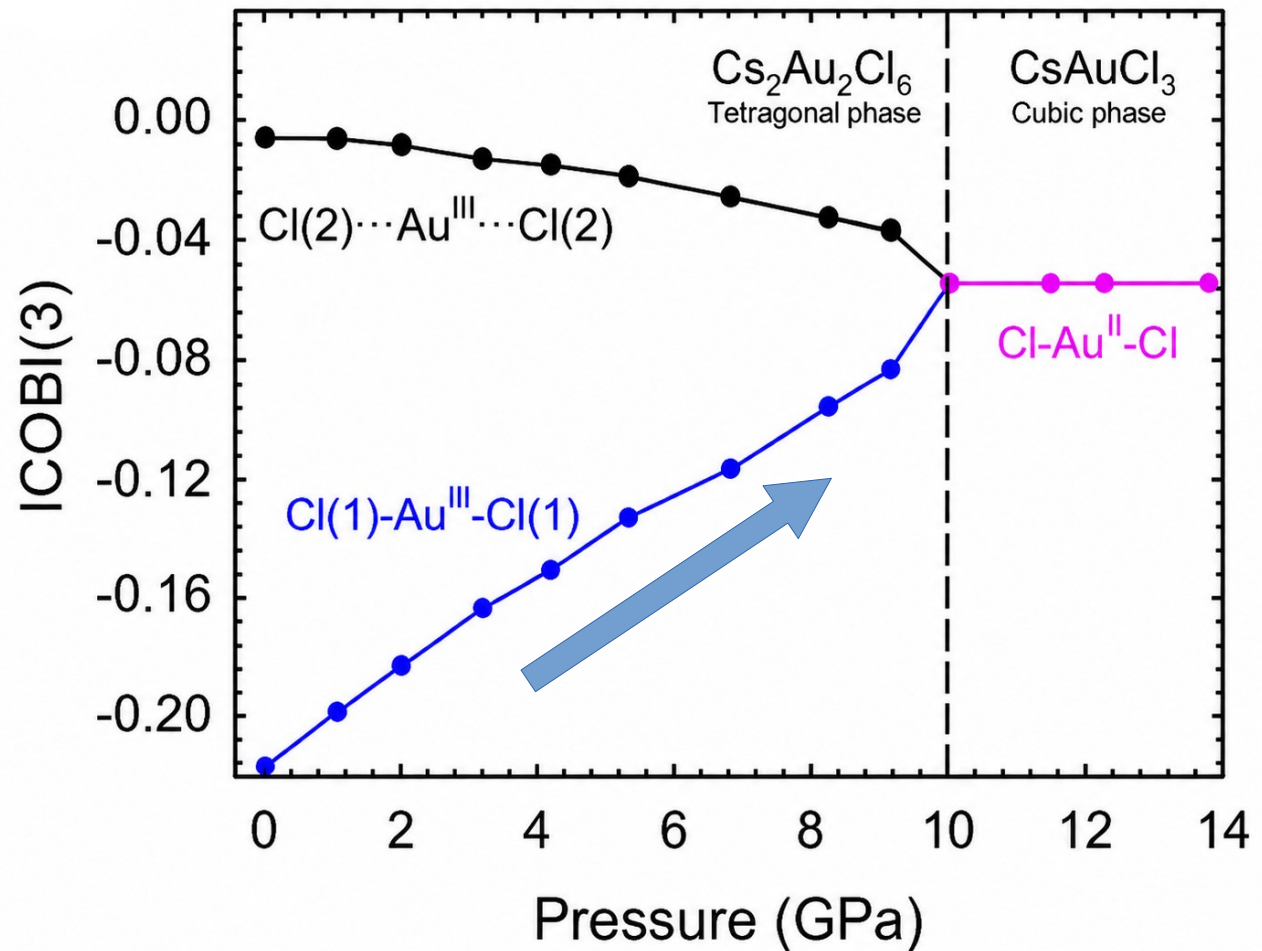
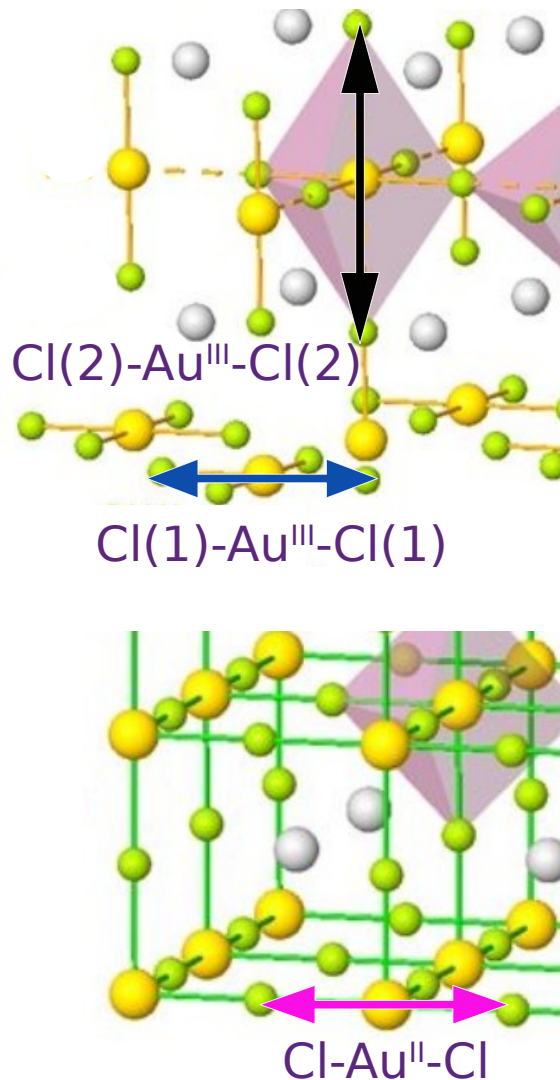
QTAIM evidence for pressure-driven bonding evolution

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



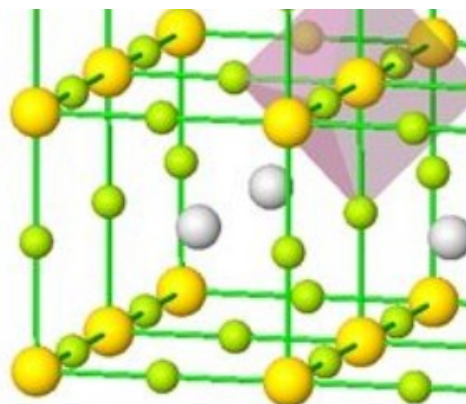
Orbital-based evidence for multicenter bonding evolution

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

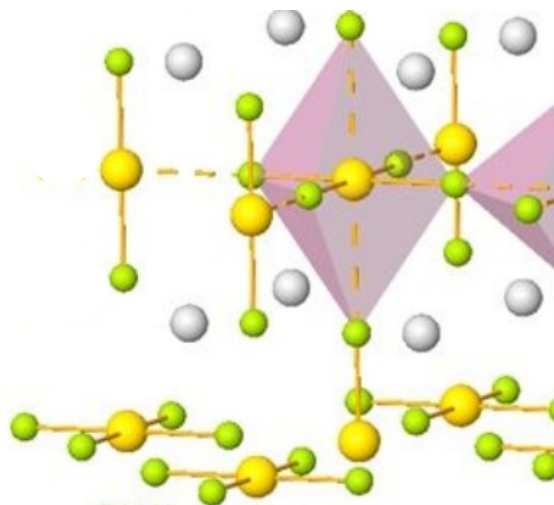


Pressure induces hardening of Au-Cl phonon modes

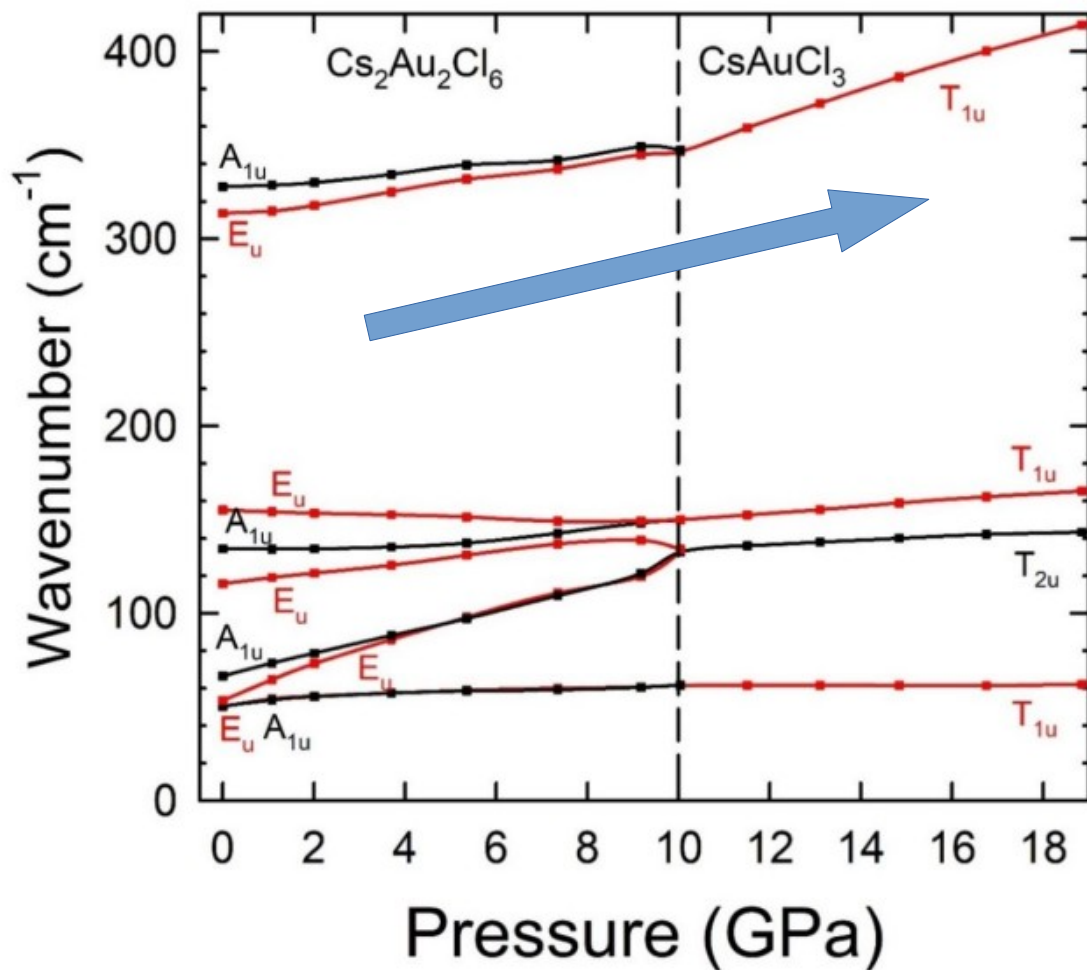
Phonon hardening supports a shift toward a more polarized bonding regime.



High pressure, cubic



Low pressure, tetragonal



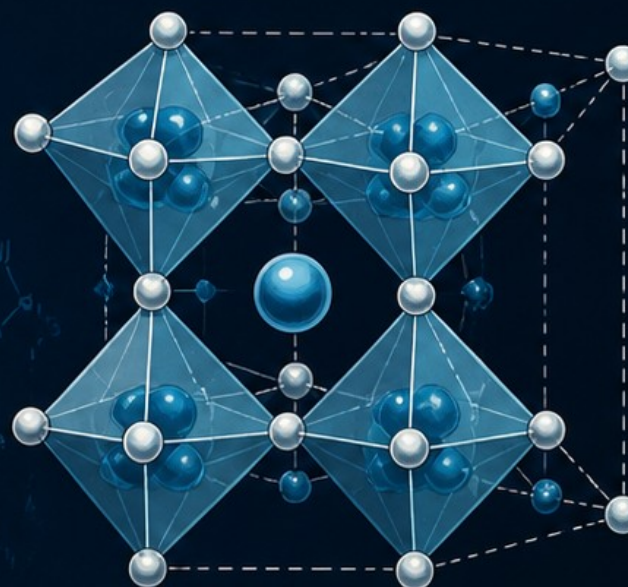
Take-home messages:

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)