XII Escuela de Altas Presiones

Revisiting the Chemical Bonding in Compressed Hydrogen Halides

Within the framework of the Unified Theory of Multicenter Bonding (UTMB)

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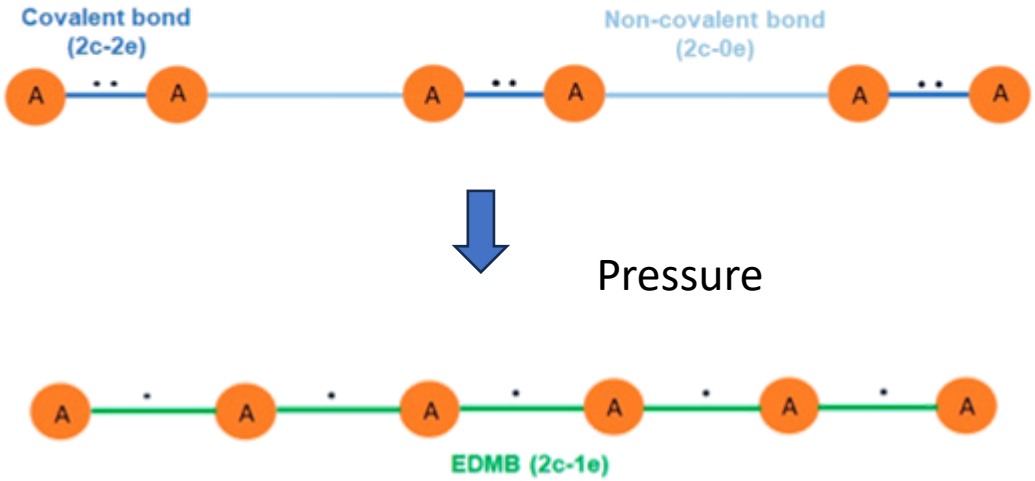
Unified Theory of Multicenter Bonding (UTMB)

Stability and interaction do not always arise from simple pairwise connections



Stability/Instability arises from the whole bonding network

Conventional framework

Pairwise descriptions become insufficient

Three-center or multicenter bond

The Hydrogen Bond

IUPAC Definition

X–H···Y interaction where H carries a partial positive charge (Hδ+), traditionally viewed as a closed-shell, non-covalent bond.

Strong H-Bonds (FHF^-)

Donor-acceptor interactions with covalent-like character. Gilli's ECHBM model classifies the strongest as **3c-4e electron-rich multicenter bonds (ERMBs)**.

The Open Question

Whether this sort of bonding can be described as two distinctive bonds or if a collective picture is more appropriate

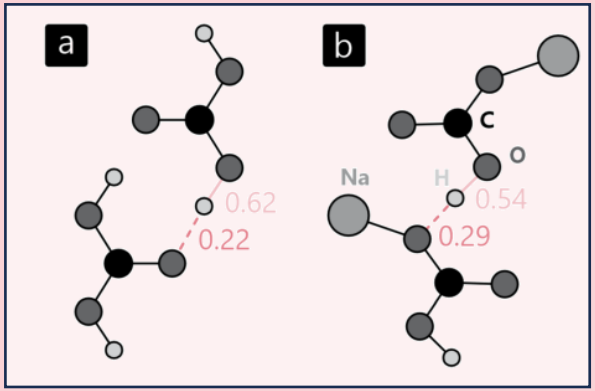


Fig. 1 - Sketches of intermolecular interactions (and corresponding bond orders) in the crystal structures of (a) H_2CO_3 and (b) $NaHCO_3$. ICOBI values are indicated.

The inter- and intramolecular bond orders sum to approximately 0.83 in both cases suggests that the bonding capacity is conserved and redistributed through a cooperative mechanism.

Pressure-Induced Phase Transition in HX Halides

High-pressure studies enable the stepwise investigation of how chemical bonds evolve in materials

Methodology

First Principles Calculations
Periodic DFT Framework

VASP

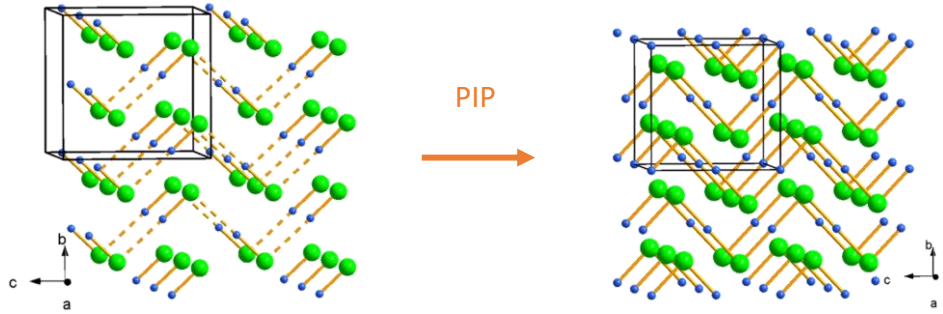
PBE0 Functional

K-point meshes with an reciprocal-space resolution of 0.03 Å–1

Deviation of the stress tensor was less than 0.15 GPa with a convergence of the total energy within 10–8 eV

From $Cmc2_1$ to Cmcm

HF and HBr crystallize at room pressure in the **$Cmc2_1$ phase** — zigzag chains with asymmetric X–H···X bonds. Under compression, a transition occurs above ~20 GPa to the **Cmcm phase**, where H atoms sit symmetrically between two X atoms, forming linear X–H–X trimers.



This pressure-induced hydrogen bond symmetrization (PIHBS) is accompanied by polymerization of HX molecules into infinite chains.

The Multicenter Bond Formation Process

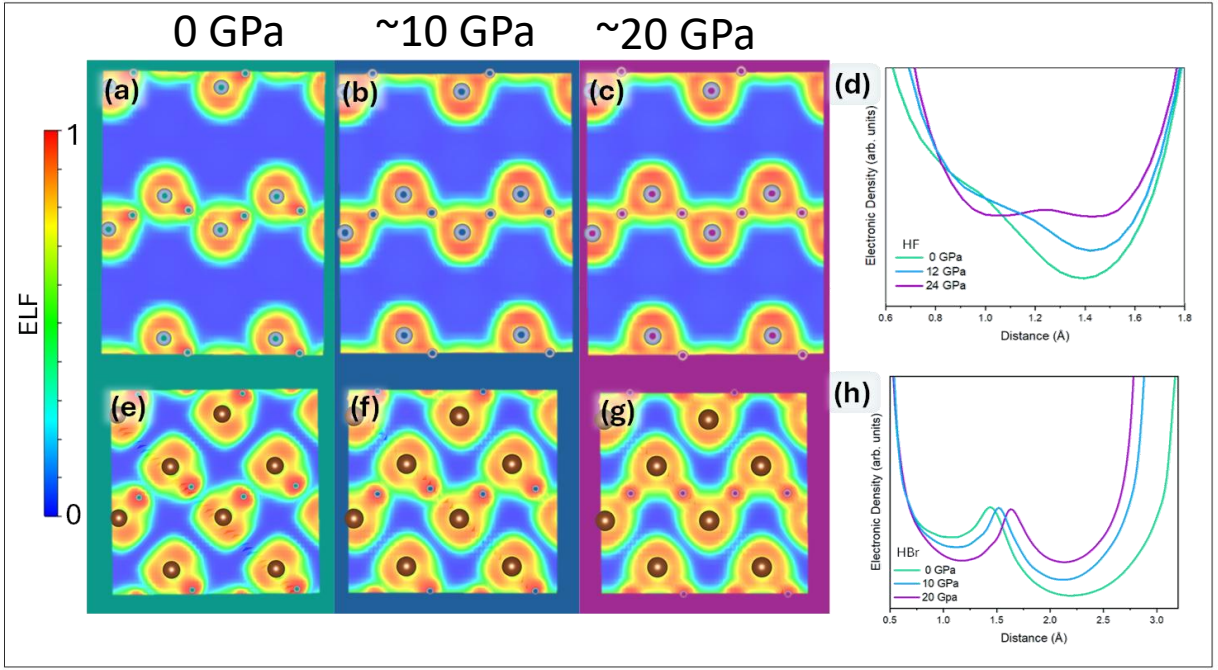
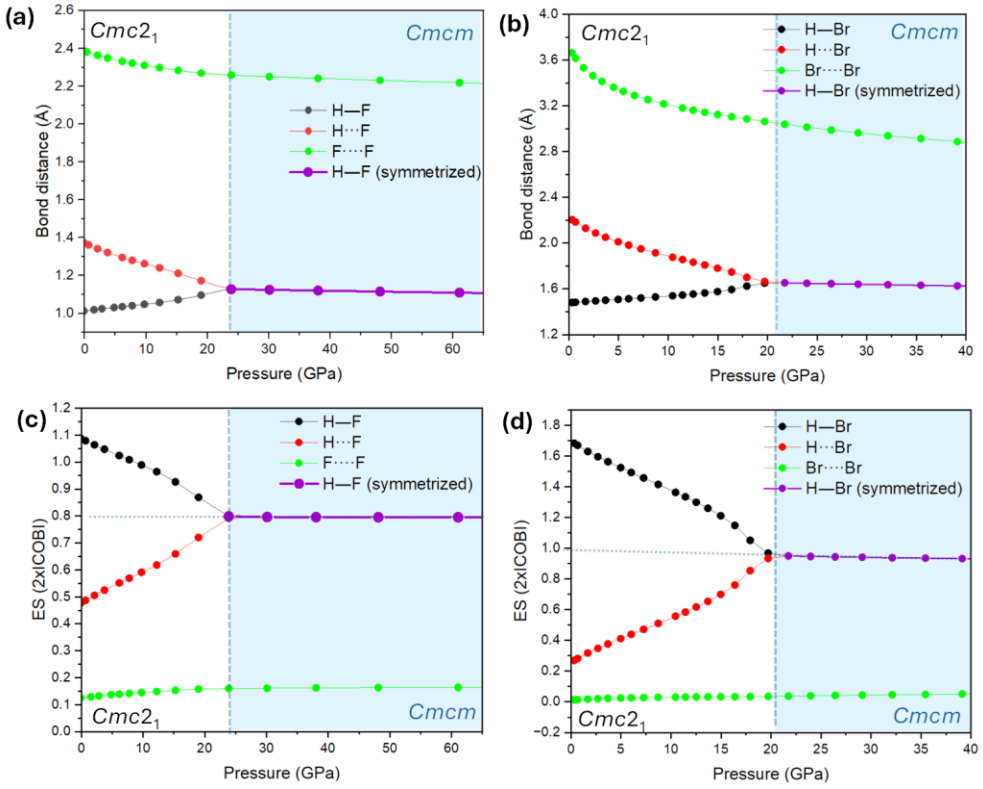


Fig. 3 ELF maps projected on the (100) plane for HF and HBr in the *Cmc*2_1 phase at 0 GPa (a,e) and approximately 10 GPa (b,f), and in the *Cmcm* phase at 24 GPa (c) and 20 GPa (g). Electronic density along the X-H···X bond for HF (d) and HBr (h) at three different pressures.

In HX halides, the $Cmc2_1$ phase corresponds to **stage 2** (multicenter interactions) and the Cmcm phase to **stage 3** (fully formed multicenter bonds), confirmed by bond distance.

Bonding Analysis



LOBSTER

Electron sharing
& multicenter index

ICOBI – Orbital-based bond orders

The integrated crystal orbital bond index for two centers, ICOBI(2) determine the number of electrons shared (ES) between two atoms

Electron Sharing (ES)

ES of short H–X bonds decreases while long H···X bonds strengthen upon compression. Total ES is conserved — **charge redistributes** from primary to secondary bond, the hallmark of EDMB formation.

Multicenter bond index

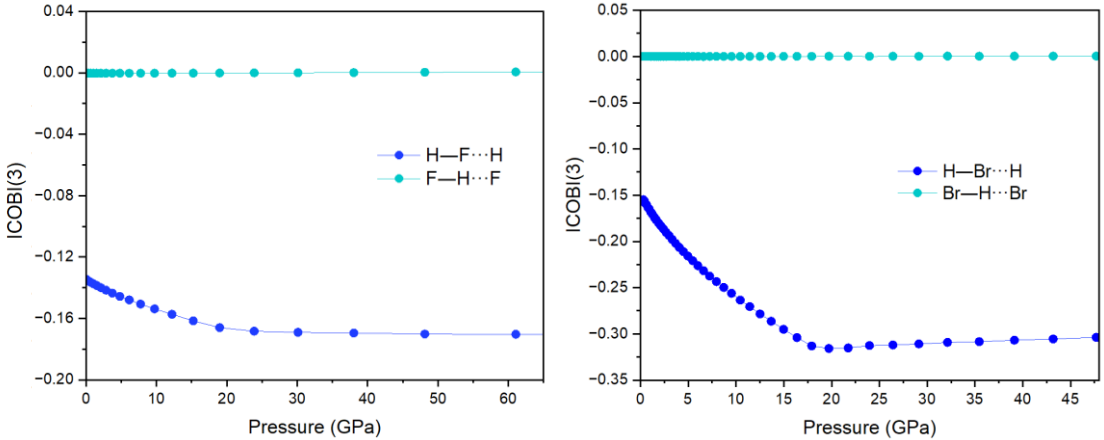


Fig. Pressure dependence of ICOBI(3) for linear F–H···F and angular H–F···H trimers (a) and linear Br–H···Br and angular H–Br···H trimers (b). Linear X–H···X are represented by dark blue circles while angular H–X···H trimers are represented by light blue circles.

ICOBI(3)

ICOBI(3) for linear X–H···X trimers increases with pressure (– 0.13 → – 0.17 in HF, – 0.30 in HBr), confirming **multicenter character** in the Cmcm phase.

The negative values of ICOBI(3) do not allow us to distinguish between ERMBs and EDMBs

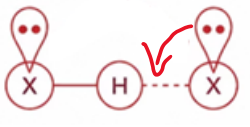
The Paradigm Shift: ERMBs vs. EDMBs

Comparison of two bond formation mechanisms:

ERMB (3c-4e)

Contribution from two non-bonding electrons

~2 electrons shared per H–X contact, LEPs participate



EDMB (3c-2e)

charge transfers from H–X primary bond to H···X secondary bond,

~1 electron shared per H–X contact, LEPs remain non-bonding

UTMB

The charge-transfer mechanism from H–X to H···X matches UTMB predictions for EDMB formation.

Additional analysis

ELF

- Identification of LEPs, regiones de enlace
- Integration of ELF basins

COHP

Crystal Orbital Hamilton Population

- Bonding and antibonding interactions

Acknowlwdments

Universidad de Oviedo

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