Hydrogen bond disappearance and electron-deficient multicenter bond formation in compressed hydrogen halides

Samantha CUSTODIO LEMOS (Universitat Politècnica de València, Spain)
Carlos ECHEVERRÍA (Universitat Politècnica de València, Spain)
Hussien Helmy Hassan OSMAN (Universidad de Oviedo, Spain),
Alfonso MUÑOZ (Universidad de La Laguna, Spain)
Oscar GOMIS (Universitat Politècnica de València, Spain)
Francisco Javier MANJÓN (Universitat Politècnica de València, Spain)

Abstract

Pressure-induced hydrogen bond symmetrisation (PIHBS) has been thoroughly studied in hydrogen halides HX (X= F, Cl, Br), mostly in relation to the search for metallic hydrogen and the high-temperature superconductivity in hydrogen-related systems [1-3]. In these molecular systems, the PIHBS occurs due to the pressure-induced polymerization of the HX molecules. Using ab initio calculations, we demonstrate that the resulting symmetric X–H–X bonds in dense HX halides form through a gradual redistribution of electron density, evolving from localized two-center bonds into delocalized multicenter interactions. A systematic bonding analysis reveals that this process does not result in the formation of electron-rich multicenter bonds (ERMBs), or three-center four-electron (3c-4e) bonds, as might be expected for a hydrogen bond according to the IUPAC definition, and as occurs in the biflouride anion, HF_2^- (Fig. 1a). Instead, electron-deficient multicenter bonds (EDMBs), more specifically three-center two-electron (3c-2e) bonds concatenated in a zigzag arrangement, are formed in dense HX halides (Fig. 1b). The formation of EDMBs proceeds in several stages as already verified in other compounds, e.g. pnictogens and chalcogens [4], alkaline AX_3 halides [5], and AIO_3 perovskites [6], as proposed in the Unified Theory of Multicenter Bonding (UTMB) [7,8], which enables the characterization of bonding regimes that challenge classical definitions and expand our understanding of molecular and solid properties.

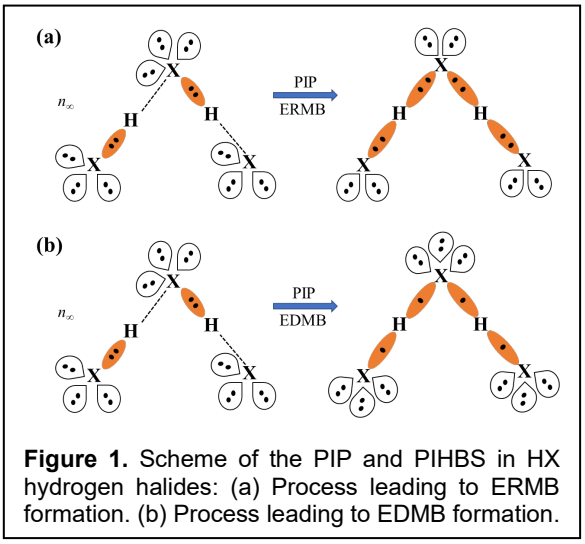

Figure 1. Scheme of the PIP and PIHBS in HX hydrogen halides: (a) Process leading to ERMB formation. (b) Process leading to EDMB formation.

[1] C. Chen et al., Novel superconducting phases of HCl and HBr under high pressure: an ab initio study, J. Phys. Chem. C 119, 17039 (2015).

[2] S. Lu et al., Prediction of novel crystal structures and superconductivity of compressed HBr, RSC Adv. 5, 45812 (2015).

[3] Q. Gu et al., High-temperature superconducting phase of HBr under pressure predicted by first-principles calculations, Phys. Rev. B 96, 064517 (2017).

[4] H. H. Osman et al., Electron-deficient multicenter bonding in pnictogens and chalcogens: Mechanism of formation. J. Mater. Chem. C 12, 10447 (2024).

[5] E. Bandiello et al., From Polyanions to Infinite Chains: Chemical Bonding Evolution in AX3 Polyhalides under Pressure, J. Mater. Chem. C 13, 21936 (2025).

[6] H. H. Osman et al., Unconventional Electron-Deficient Multicenter Bonds in AIO3 Perovskites. Chem. Mat. 37, 4187 (2025).

[7] H. H. Osman et al., A Unified Theory of Electron-Rich and Electron-Deficient Multicenter Bonds in Molecules and Solids: A Change of Paradigms, J. Mater. Chem. C 13, 3774 (2025).

[8] F.J. Manjón et al., Introduction and Extension of the Unified Theory of Multicenter Bonding: The Role of the Charge-Shift Bonding, Molecules 31, 82 (2026).