Group 12 Dihalides:
Structural Preferences from Gases to Solids

We have been working on the connections between the structures of group 12 dihalides in their vapor and crystal phases. The molecular structures of all monomers and dimers (MX$_2$: M = Zn, Cd, Hg and X = F, Cl, Br, I) were calculated. All the monomers are linear, with the mercury dihalide molecules having shorter bonds than their cadmium analogues; the ZnX$_2$ and CdX$_2$ structures are similar. The shorter Hg-X distances are traced back to relativistic effects.

For the dimers, many possible geometrical arrangements were considered (see Figure 1 for the ones that are preferred; the C3v structure is seen only for the Group 2 dihalides). The zinc and cadmium dihalide dimers have the usual D$_{2h}$-symmetry geometry, while the mercury dihalide dimers are loosely-bound units with C$_{2h}$ symmetry. The origins of this C$_{2h}$ structure are discussed from different points of view, including frontier orbital interactions.

The crystals of group 12 dihalides span a wide range of structure types, from three-dimensional extended solids to molecular crystals (see Figure 2). There is an obvious connection between the structures and characteristics of monomers, their dimers, and the crystals they form. The similarities as well as startling differences from the group 2 dihalides are analyzed in our work.

A paper on this work has been submitted to Chemistry, a European Journal.