Abstract:
We have studied the geometrical and electronic structures of the series of group 12 (Zn, Cd, Hg) dihalides, as monomers, dimers, and extended solids. The solids are particularly interesting, ranging from pretty ionic extended networks to molecular crystals. We explored the “memory” the solids have of the monomer structures, and how the solid begins to be built up.

In another study, various SnH₄ structures were examined as pressure was increased. Especially interesting is the elemental layering that was found at lower pressures, and the presence of intermediate pressure phases in which H₂ molecules coexist with Sn-H networks.

Summary of Research:

1. Group 12 Dihalides: Structural Preferences from Gases to Solids. Connections between the structures of group 12 dihalides in their vapor and crystal phases are sought and discussed. The molecular structures of all monomers and dimers (MX₂: 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 ZnX₂ and CdX₂ structures are similar. The shorter Hg-X distances are traced back to relativistic effects. For the dimers, many possible geometrical arrangements were considered (Figure 1).

The zinc and cadmium dihalide dimers have the usual D₂h-symmetry geometry, while the mercury dihalide dimers are loosely-bound units with C₂h symmetry. The origins of this C₂h structure are discussed from different points of view, including frontier orbital interactions.

Figure 1: Minimum-energy structural isomers of the group 12 (shown in (a) and (b)) and group 2 (shown in (a) and (c)) dihalides.

Figure 2: Structure types of the group 12 metal dihalide crystals.
The crystals of group 12 dihalides span a wide range of structure types, from three-dimensional extended solids to molecular crystals (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 (1) are analyzed. This work has just appeared in print [1].

2. **SnH₄ Under Pressure: New Structural Suggestions.** Hydrogen-rich molecules may provide a way to realize the metallization of hydrogen, by creating “chemically precompressed” structures [2-4]. In our search for stable structures for tin tetrahydride (SnH₄), stannane, at high pressure, we encountered a pressure regime (relatively low pressure) in which slabs of tin atoms and molecular hydrogen are most stable. Recently, the same trend toward layered structures has been seen theoretically in similar systems such as silane and germane [5]. The positive formation energy of these compounds renders them thermodynamically unstable, yet kinetically persistent to decomposition. Under pressure, the layered structures might then arise as a compromise between the stability of a new structural type, new bonding, and decomposition in its elements.

We started probing some possible structures by setting up layered structures with both molecular and atomic hydrogen geometries, so as to allow the structure to seek out molecule formation if it wanted. Figure 3 shows one of the resulting structures at 50 GPa. At around 150 GPa, the layered structures cease to be stable, and more complicated arrangements of Sn and H atoms evolve.

References: