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The Electronic, Structural, and Magnetic Properties of  
the Chromium Dihalides - from the Gas-phase to the  
Solid-state

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# Abstract

Unrestricted Kohn-Sham (broken symmetry) density functional calculations have been used to determine the low-energy geometries of the chromium dihalide molecules ( $\text{CrX}_2$ ) and their clusters,  $\text{Cr}_2\text{X}_4$ ,  $\text{Cr}_3\text{X}_6$ , and  $\text{Cr}_4\text{X}_8$ . The monomers are also investigated at a higher level, including coupled-cluster and state-average CASSCF computations. Our calculations show that the monomers have a  ${}^5B_2$  ground state arising from the Renner-Teller distorted  ${}^5\Pi_g$  transition state, leading to a bent geometry. The global minima of the gas-phase clusters of  $\text{CrF}_2$  and  $\text{CrCl}_2$  consist of two-dimensional, anti-ferromagnetically coupled chains of  $\text{CrX}_2$  units forming four-membered, doubly bridged  $\text{Cr}_2\text{X}_2$  rings, closely resembling their solid-state structures. The global minima of the  $\text{CrBr}_2$  and  $\text{CrI}_2$  clusters consist of the same two-dimensional chain-like structures for their dimers, but their trimers and tetramers consist of three-dimensional 'triangular' structures which contain two capping ligands bound to three chromium atoms along with a Cr-Cr bond. Each Cr atom within these clusters has spin quantum number  $S=2$ . There is approximately a constant change in energy, between 45-55 kcal/mol, with every new  $\text{CrX}_2$  unit during cluster formation.

Information about the structure of the  $\text{CrCl}_2$  clusters is used in the reanalysis of high-temperature electron diffraction data. The vapor at 1170 K contains about 77% monomeric molecules, 19% dimers, and a small amount of trimers. Monomeric  $\text{CrCl}_2$  is found to be bent with a bond angle of  $149(10)^\circ$ , in good agreement with our computations.

Solid-state DFT calculations are performed on  $\alpha$ - $\text{CrCl}_2$  to determine the lattice structure and spin-coupling constants for the Cr atoms within the crystals. The GGA (PW91) method produces a structure in good agreement with the literature. In the lowest energy structure, the spins of the Cr atoms within the chains along the crystallographic  $c$ -axis are anti-ferromagnetically coupled with four parallel spins situated almost exclusively in the  $d$ -bands of Cr along these chains. This anti-ferromagnetic coupling is also seen in the  $\text{CrX}_2$  clusters.

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