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

A thesis submitted in partial fulfillment of the requirements of the degree

of

Doctor of Philosophy

in

Theoretical Chemistry

at

Massey University, Albany

New Zealand

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June 10, 2008

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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 (CrX_2) and their clusters, Cr_2X_4, Cr_3X_6, and Cr_4X_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 CrF_2 and $CrCl_2$ consist of two-dimensional, anti-ferromagnetically coupled chains of CrX_2 units forming four-membered, doubly bridged Cr_2X_2 rings, closely resembling their solid-state structures. The global minima of the $CrBr_2$ and 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 CrX_2 unit during cluster formation.

Information about the structure of the $CrCl_2$ 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 $CrCl_2$ is found to be bent with a bond angle of 149(10)°, in good agreement with our computations.

Solid-state DFT calculations are performed on α-$CrCl_2$ 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 CrX_2 clusters.

Acknowledgements

First and foremost, I would like to give many thanks to my advisor Prof. Peter Schwerdtfeger. He has helped me more times than I can count with getting this thesis written and encouraged me to see the entire forest and not just the trees. I also want to thank him for his guidance, encouragement, and wonderful sense of humour. I would also like to thank Behnam Assadollahzadeh for his help with Gaussian and LaTeX templates and commands. He has also provided me with invaluable knowledge of various fishing spots around New Zealand and has taught me how to speak "proper" German. I want to also thank Andreas Hermann for his help with the solid-state of $CrCl_2$ and creating nice EPS files. Christian Thierfelder also deserves my thanks for helping me with various physics, mathematics, and Xmgrace problems. Lastly, I would like to thank Dr. Magdolna Hargittai for her help in understanding gas-phase electron diffraction.