

AN *AB INITIO* STUDY ON THE EXPLICIT  $r_{XF}$  DEPENDENCE OF THE INTERMOLECULAR POTENTIALS OF ArHF AND ArCIF: WHEN DOES Ar-X REPULSION BEGIN TO SHOW?

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The dependence of the ArHF intermolecular potential upon  $v_{HF}$  is now known through experiment for  $v_{HF} = 0 - 4$ . For the ground state hydrogen-bonded structure Ar-HF it can be characterized by an increasing red shift and increasing rotational constant as the HF is stretched from  $v = 0$  to  $v = 4$ . This indicates that the intermolecular bond is getting stronger and the heavy atom distance (Ar-F) is shrinking. Less well known is the explicit  $r_{HF}$  dependence of the potential and at what point will the Ar-H repulsion become evident? In addition, does this same behavior extend to other, non-hydrogen bonded systems? In order to answer these and other questions, CCSD(T) *ab initio* calculations have been performed on ArHF and ArCIF to generate full three-dimensional  $(R, \theta, r)$  potential energy surfaces for a wide range of  $r_{XF}$  values. In addition, three-dimensional quantum calculations of the bound states for the two systems have been performed to provide comparison with experiment and predictions for future experiments. The results for ArHF are in excellent agreement with experiment in terms of red shift and change in rotational constant. They predict that the increase in the red shift will slow at  $v_{HF} = 7$  and turn around at  $v_{HF} = 9$ . While this is well beyond current experimental accessibility, the results also predict that the rotational constant should be smaller for ArHF  $v_{HF} = 5$  than for  $v_{HF} = 4$ , thus showing the first signs of Ar-H repulsion. ArHF  $v_{HF} = 4$  experimental results have recently been obtained by Chuang and Klemperer, and ArHF  $v_{HF} = 5$  should be accessible with their current set-up. The intermolecular potential of ArCIF shows a dramatic increase in depth for wells at both ends of CIF upon stretching of the CIF bond. Accompanying this is a decrease in Ar-Cl and Ar-F distance until  $r_{CIF} = 2.0\text{\AA}$ , at which point the well depths begin to decrease and the atom-atom distances begin to increase. Bound state calculations show a steady increase in red shift and a steady decrease in Ar-Cl distance from  $v_{CIF} = 0$  to at least  $v_{CIF} = 11$  for the ground state Ar-CIF configuration. It appears the increase in binding energy and the decrease in intermolecular distance upon stretching of the HF bond observed in ArHF is a general phenomena in atom-diatomic molecule systems.