COMPARISON OF Rg-ClF_3 COMPLEXES WITH Rg-ClF COMPLEXES

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Excellent agreement between experiment and *ab initio* theory is found for the HeClF complex[1]. Similar calculations are carried out on $HeClF_3$ and $ArClF_3$ to produce accurate potential energy surfaces in order to compare the properties of these complexes with those of Rg-ClF complexes. An *ab initio* 3-dimensional potential surface for $HeClF_3$ has been computed at the MP2 level with a large basis set including bond functions. The surface is characterized by four minima, the deepest of which is -46.7 cm^{-1} and is located above the ClF_3 plane slightly offset to one side. This well is steep when moving from front to back, but wide and flat when moving side to side, varying less than 1 cm^{-1} over a 40° span. This minima corresponds to the T-shaped minima found in HeClF at a depth of -29.4 cm^{-1}.[2] The next deepest minima is found at the Cl end in a linear He-Cl-F arrangement with a He-Cl distance of 3.22 Å. The depth here is -43.0 cm^{-1} as compared to -51.8 cm^{-1} with a He-Cl distance of 3.00 Å for the corresponding minima in HeClF. Two much shallower minima, -27.3 cm^{-1} and -20.6 cm^{-1}, occur at the lone F end and near the outside F's, respectively. Calculations on $ArClF_3$ are carried out at the same level but focused on finding the depth and position of the two deepest potential wells. In this case the well at the Cl end is found to be deeper, -281.6 cm^{-1}, than the out-of-plane well, -232.1 cm^{-1}. The Ar-Cl distance for the linear well is 3.39 Å as compared to 3.26 Å for ArClF. Well depths for ArClF are -291.9 cm^{-1} linear, and -160.6 cm^{-1} T-shaped. For both ClF_3 complexes, several points are calculated using the MP4 method. These points are used to confirm the overall shape of the MP2 potential surface. Previous studies of helium and argon complexes of ClF[1,3,4] have shown a triple-minima potential as a general feature of the Rg-ClF interaction. These studies will be reviewed along with an updated ArClF MP4 potential in making the comparison with Rg-ClF_3 complexes. Differences in the positions and depths of the minima will be discussed in light of the various models of bonding for the two molecules.

[1] K. J. Higgins, F.-M. Tao, and W. Klemperer, in preparation.

[2] Note: Rg-ClF energies and distances are given for MP2 surfaces for comparison. MP4-level surfaces have also been calculated.

[3] S. J. Harris, S. E. Novick, W. Klemperer, and W. E. Falconer, *J. Chem. Phys.* **61**, 193 (1974).

[4] F.-M. Tao and W. Klemperer, *J. Chem. Phys.* **97**, 440 (1992).