AB INITIO AND EXPERIMENTAL STUDIES OF ISOMERISM IN INERT GAS MOLECULE COMPLEXES

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The potential energy surface of many inert gas molecule complexes contain multiple local minima which support localized rovibrational states. This leads to different "structural" isomers of the same complex as demonstrated with the HeClF complex.[a] Helium complexes are particularly well suited to the study of isomerism in inert gas molecule complexes because the weak binding and low mass of the helium atom lead to easily observable transitions between low lying states of differing geometry. In addition, helium complexes exhibit qualitatively similar behavior to other inert gas molecule complexes while their potential energy surfaces are easier to calculate with *ab initio* techniques. In the present studies, *ab initio* potential energy surfaces are calculated at the MP4 level with a large basis set including bond functions for the complexes HeOCS and HeClCN. Close-coupling and collocation calculations performed with the MP4 surfaces are used to determine rovibrational energies and wavefunctions, which in turn are used to guide the experimental search for and assignment of transitions in the microwave and millimeter-wave region. The potential surfaces of both complexes exhibit two minima, the deepest of which is in a T-shaped position, with a secondary minimum in the linear position at the S or Cl end of the molecule. The ground state of each complex is T-shaped. A linear excited state is predicted to lie 4.3 cm^{-1} above the ground state for HeClCN and 8.8 cm^{-1} above the ground state for HeOCS. As of this writing, ten rotational transitions of the T-shaped ground state of HeOCS have been observed in a Fraser-type molecular beam spectrometer, and spectroscopic searches for transitions between the T-shaped and linear configurations of both complexes are underway.

[a] K. Higgins, F-.M. Tao, and W. Klemperer, J. Chem. Phys., submitted, and 51st International Symposium on Molecular Spectroscopy, Paper TD02 (1996).