

ISOMERS IN HELIUM COMPLEXES: OBSERVATION OF T-SHAPED AND LINEAR He-CH₃F, AND PREDICTION OF TWO NEARLY ISOENERGETIC FORMS OF He-ClF₃

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The existence of multiple minima on the intermolecular potential energy surface of rare gas-molecule complexes appears quite general. Localization of the rare gas atom in the various potential energy minima results in several "isomeric" forms of a single complex. The combination of *ab initio* calculations and microwave/millimeter wave spectroscopy of helium-molecule complexes has proven quite valuable in the study of this phenomena.

As presented previously,^a the *ab initio* intermolecular potential of He-CH₃F exhibits two main wells: -46.9 cm⁻¹ in the "linear" position at the C end of the C-F axis, and -44.8 cm⁻¹ in the "T-shaped" position on the side of the C-F axis. Bound state calculations place the ground state in the T-shaped position with a state localized in the linear position being 4.0 cm⁻¹ higher in energy. Pure rotational transitions of states localized in each minima, as well as transitions between the states, have now been observed experimentally. The initial observation of the linear state depended upon strong mixing of the $J_{K_a K_c} = 2_{20}$ level of the ground state with the $J_K = 2_0$ level of the linear state. This mixing is accurately predicted by the *ab initio* potential and serves as a sensitive probe of the intermolecular potential. The observed T-shaped to linear gap is 4.4 cm⁻¹.

The intermolecular potential of He-ClF₃ at the MP2 level was previously presented.^b While qualitatively correct, significant quantitative differences existed between the MP2 surface and selected points calculated at the MP4 level. We report a much refined full MP4 surface and bound state calculations. Two primary minima exist: -53.9 cm⁻¹ in the linear position at the Cl end of the C_{2v} axis, and -59.9 cm⁻¹ in the T-shaped position above the molecular plane. Bound state calculations place the ground state in the linear minima, with a T-shaped state less than 1 GHz higher in energy. It is interesting to note that in both He-ClF₃ and He-CH₃F the ground state is localized in the shallower of the two potential minima.

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^b52nd International Symposium on Molecular Spectroscopy (1997)