

Basis Set and Correlation Effects on H₂S–Ar Potential Energy Surfaces

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Substitution of deuterium for hydrogen in the weakly bound cluster Ar–H₂S is known to produce an anomalous effect in the ground vibrational state's average rotational constant $(B + C)/2$ in contrast to deuteration of Ar – H₂O, or most complexes. The anomalous effect develops from the vibrational dynamics, and the characteristics of the potential energy surface (PES) for the complex. The nuances of the PES and the fact that higher order dispersion terms play a significant role make this a challenging system to represent accurately. The intrinsic challenges of this system represent an opportunity to test the limits of computational methodologies intended to evaluate dispersion interactions.

In the past, we were successful in explaining the unusual isotope substitution effect in Ar–H₂S by generating high-level *ab initio* potential energy surfaces and conducting quantum dynamics calculations (rigid-body diffusion quantum Monte Carlo). Nevertheless, small empirical corrections to the surface had to be included, and it was not clear whether the main deficiencies were due to limitations in the methods used (insufficiently accurate evaluations of electron correlation) or limitations in the basis set. In this work we explore higher order correlation effects, basis set effects, and the effectiveness of a few functionals in order to represent the main features of the PES.