

Characterization of the potential energy surfaces of the P_2 dimer and the PCCP dimer

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This work fully characterizes seven stationary points of the P_2 dimer and five stationary points of the PCCP dimer with the MP2 electronic structure method. Full geometry optimizations and corresponding harmonic vibrational frequencies were computed using the following basis sets: aug-cc-pVXZ, aug-cc-pV(X+d)Z and aug-cc-pCVXZ ($X=T,Q$). In addition, single point energies on the MP2/aug-cc-pCVQZ optimized geometries using the canonical MP2 and CCSD(T) methods as well as the explicitly correlated MP2-F12 and CCSD(T)-F12 methods are computed using the aug-cc-pVXZ ($X=D,T,Q,5$) and VXZ-F12 ($X=D,T,Q$) basis sets. Extrapolation to the complete basis set limit for the MP2 and CCSD(T) interaction energies is done using up to a pentuple- ζ basis set. The following stationary points have been identified on both potential energy surfaces: parallel-slipped structure with C_{2h} symmetry, T-shaped structure with C_{2v} symmetry, cross structure with D_{2d} symmetry, the rectangle structure with D_{2h} symmetry and the linear structure with $D_{\infty h}$ symmetry. A V-shaped structure with C_{2v} symmetry and an L-shaped structure with C_2 symmetry have also been identified on the P_2 dimer MP2 potential energy surface. Only the L-shaped P_2 dimer and parallel-slipped PCCP dimer configurations correspond to a minimum at the MP2 level of theory. MP2 significantly overbinds the P_2 and PCCP dimers with respect to CCSD(T) by as much as $1.5 \text{ kcal mol}^{-1}$ and $4.0 \text{ kcal mol}^{-1}$, respectively. The explicitly correlated MP2-F12 and CCSD(T)-F12 methods exhibited similar higher-order correlation effects.