HIGH-ACCURATE INTERMOLECULAR POTENTIAL ENERGY SURFACE OF HCN – H₂ COMPLEX WITH INTRAMOLECULAR VIBRATIONAL MODE OF HCN INCLUDED

YU ZHAI, HUI LI, Institute of Theoretical Chemistry, Jilin University, Changchun, China.

Hydrogen is one of the most abundant interstellar species. Observation of rotational and vibrational spectra of H₂ containing complexes is of great importance because they are possible candidates for radio-astronomical detection. CO, HCN, HCCH are as isoelectronic molecules of N₂, each with a strong triple bond. It had been a big challenge to predict reliable theoretical rovibrational spectra of complexes including such species because the higher order electron correlation energy plays a non-negligible role in improving the accuracy. However, recent works on CO – H₂ have shown that it is possible to reproduce the experimental spectra quantitatively. In this work, we calculate a five-dimension potential energy surface (PES) of HCN – H₂ complex which explicitly include the intramolecular asymmetric stretching vibrational mode (C – H, Q₃) coordinate at CCSD(T)/aug-cc-pVQZ+3s3p2d1f1g level, corrected with electron correlation energy from the triple and quadruple excitation. Vibrational average over intramolecular vibration mode is made with HCN monomer at ground and the first excited vibrational states respectively, and the averaged data are fitted to two four-dimension Morse/Long-Range (MLR) potential energy functions. Based on the MLR PESs, for the first time, we calculated the spectra of HCN – paraH₂ and HCN – orthoH₂. The results for HCN – orthoH₂ are in good agreement with the published experimental data with root-mean-square-difference (RMSD) only 0.01cm⁻¹, which validates the accuracy of the PESs.

---