A COMPUTATIONAL STUDY OF THE VIBRATIONAL O–H STRETCHING AND H–O–H BENDING SPECTRUM OF THE WATER TRIMER

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We have studied the vibrational O–H stretching and H–O–H angle bending spectrum of the water trimer computationally around the cyclic minimum energy structure. We obtain the energies and intensities of the fundamental and overtone transitions. Earlier we have modeled the water trimer as three individually vibrating monomer units. In this work we have improved our previous model by including the potential energy coupling between the three hydrogen bonded O–H stretching modes. An internal coordinate Hamiltonian is constructed for each water unit using a kinetic energy operator, which is exact within the Born-Oppenheimer approximation for a triatomic molecule. The potential energy coupling terms between the hydrogen bonded O–H stretching modes are added in the model. The O–H distances and the H–O–H bending angles are used as the vibrational coordinates. The potential energy grid is calculated using the coupled cluster method with single, double and perturbative triple excitations (CCSD(T)) with correlation consistent aug-cc-pVTZ basis set around the optimized geometry. The potential energy surface (PES) is obtained by fitting an analytical function to the potential energy grid. The dipole moment surface is calculated using the finite differences method. The vibrational problem has been solved with the variational method with a harmonic oscillator basis for all the vibrational coordinates. We calculate the transition intensities using the wavefunctions obtained from the variational calculation.