AB INITIO POTENTIAL ENERGY SURFACES FOR PROTON TUNNELING DYNAMICS STUDY OF HO_2^-/O_2H^- AND HF_2^+/F_2H^+ ISOMERIZATIONS

WAI-TO CHAN AND I. P. HAMILTON, *Department of Chemistry, Wilfrid Laurier University, Waterloo, N2L 3C5, Canada*.

Ab Initio potential energy surfaces for the two titled reactions were computed using the QCISD(T) method with the 6-311++G(2df,pd) and 6-311++G(2df,2pd) basis sets. The fitting procedure for triatomic molecules proposed by Aguado and Paniagua (*J. Chem. Phys.* **96**, *1265-1275 (1992)*) was employed to fit these two surfaces. The purpose is to provide reliable analytical molecular potential energy functions for future theoretical studies of multi-dimensional nuclear tunneling dynamcs. The intrinsic reaction path from the equilibrium structure to the T-shaped saddle point is shorter for HF_2^+/F_2H^+ than for HO_2^-/O_2H^-. The barrier of 8340 cm^{-1} to the former proton transfer process is however substantially higher than the barrier of 4752 cm^{-1} for the latter process. Splitting of vibrational energy levels is calculated from the two PESs and compared in light of their different features. Finally in order to determine the extent to which the hydrogen atoms in both the cation and the anion are truely protons partitioning of charges along the tunneling pathways will be presented.