THEORETICAL STUDY OF THE POTENTIAL ENERGY SURFACE FOR THE REACTIONS $H_3^+ + CO \rightarrow H_2 + HCO^+$ and $H_3^+ + CO \rightarrow H_2 + HOC^+$

HUI LI, TAKAYOSHI AMANO and ROBERT J. LE ROY, *Guelph-Waterloo Centre for Graduate Work in Chemistry and Biochemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*; TSUNEO HIRANO, *Department of Chemistry, Faculty of Science, Ochanomizu University, Tokyo 112-8610, Japan*.

To provide insight regarding the stability of the interstellar ions HCO^+ and HOC^+, the geometries and frequencies of the stationary points (transition state, reactants, intermediates, and products) on the ground potential energy surface of the CO+H_3^+ system have been calculated using coupled-cluster theory with both single and double substitutions (CCSD). The energetics were then refined at the CCSD(T) level of coupled-cluster theory, including core-electron correlation at the complete basis set (CBS) limits. To elucidate the formation reaction and internal relaxation processes, the minimum-energy reaction paths (MEPs) for $H_3^+ + CO \rightarrow H_2 + HCO^+$ and $H_3^+ + CO \rightarrow H_2 + HOC^+$ are studied by performing intrinsic reaction coordinate (IRC) calculations at the second-order Møller-Plesset (MP2) level with single-point energy corrections at higher CCSD(T)/aug-cc-pVTZ levels. This provides important information regarding the dynamics and leads to our construction of a reduced-dimension potential energy surface (PES). Although the most favorable paths to form HCO^+ or HOC^+ via a proton hop from H_3^+ to CO are believed to be the collinear approach of H_3^+ to CO, no high-level *ab initio* calculation of the full potential surface for the H_3^+ plus CO system capable of elucidating the reaction dynamics had been reported. Our objective is to provide theoretical insight regarding the stability and formation dynamics of HCO^+ and HOC^+ and their molecular complexes with H_2. The reactions $H_3^+ + CO \rightarrow H_2 + HCO^+$ and $H_3^+ + CO \rightarrow H_2 + HOC^+$ are found to proceed via both bending and collinear approach of H_3^+ to CO. Approximating the full 9-dimensional PES by an effective 5-dimensional surface constructed from 128 440 *ab initio* points calculated at the CCSD(T)/aug-cc-pVTZ level, should allow a proper description of all of these process.