Abstract

In Chapter 1, a study of the topological effects in CO^+_2 has been carried out by calcu- lating non-adiabatic coupling terms (NACTs) between $1\,^2A'$, $2\,^2A'$ and $3\,^2A'$ states. Using the NACTs, the adiabatic-to-diabatic transformation (ADT) angle (γ_{12}) for $1\,^2A'$, $2\,^2A'$ states of CO^+_2 have been calculated. The ADT angle can be used to calcu- late diabatic potential energy surfaces from the adiabatic potential energy surfaces. Required number of states have been used to achieve quantization. NACTs have been calculated using the MOLPRO package at the state-averaged CASSCF level using the cc-pVTZ basis set. In Chapter 2, the effect of hydration on cation-π interaction has been studied using Gaussian 09 suite of programs. The π–system under study is benzene (B) and the cations (M) studied are Na^+ , K^+ , Mg^{+2}, Ca^{+2} and Al^{+3} . Interaction energy values for the complexes $M\,B_mW_n$, $0 \leq n, m \leq 3$, $m + n \leq 3$ have been calculated at the MP2 level of theory using the 6-31G(d,p) basis set. Using these interaction energy values, the qualitative trend of relative affinity of different cations for benzene and water has been determined. The π–cloud thickness values have also been calculated for these system.