Ab Initio Vibrational Splittings for Hydrogen Atom Transfer in HO_2^-/O_2H^- Isomerization

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A potential energy surface covering the interconversion between the two symmetry-equivalent geometries of the hydroperoxyl anion, HO_2^- via a symmetric T-shaped saddle point was computed at the QCISD(T)/6-311++G(2df,pd) level of theory. An analytical molecular potential function was fit to the *ab initio* data. The classical barrier to the interconversion was estimated to be 6057 cm^{-1} Using the parameterized function the vibrational states were calculated by the discrete variable representation-distributed Gaussian basis method. Computations predict the onset of tunnelling from about 4 quanta in the bending mode-A splitting of 6 cm^{-1} is observed between the odd and even 040 state. Presence of at least one quanta in the O–O stretching mode enhances splitting significantly.