

THE EFFECT OF THE SADDLE POINT POSITION AND THE OH-BONDING FORCE CONSTANT ON THE TRANSITION FREQUENCIES OF H-BOND OF NAPHTHAZARIN

FATEMEH AFSHAR GHAHREMANI, MANSOUREH ZAHEDI-TABRIZI^a, *Department of Chemistry, Alzahra University, Tehran, Iran*; SAYYED FARAMARZ TAYYARI, *Department of Chemistry, Ferdowsi University, Mashhad, IRAN*.

The structure of Naphthazarin (NZ) has been considered in spectroscopic for a long time. However, there are some ambiguity in spectroscopic data up to now. In this work, an easy and feasible method has been introduced for studying the proton tunneling in NZ to assess symmetry. For this purpose, a two-dimensional potential energy surface which has been capable to explain the movement of hydrogen atom with high accuracy has been used. This potential energy function, which couples OH stretching with in-plane bending modes has been applied on a fixed skeleton geometry of NZ calculates the tunneling splitting, OH stretching, and in-plane bending frequencies. To study the effect of the saddle point and the bending force constant of OH on transition frequencies of hydrogen bond, a differentiation was applied on two dimensional function towards X and Y, respectively. The tunneling splitting of 15.3 and 0.8 cm⁻¹ and the barrier height of 65.3 and 127.3 kJ/mol for stepwise and concerted proton transfer, respectively, indicate that both proton transfers are probable to happen, but NZ of D-2h symmetry will last for the longer time. In addition, as the saddle point position and the bending force constant increase, the tunneling frequency increases. It seems that the interaction between these two modes (the bending force constant) is responsible for higher OH stretching and lower OH bending frequencies in the bent hydrogen bonded systems compared to those in linear hydrogen bonded systems. This coupling, also, predicts a strong fermi resonance between OH stretching and the second overtone of OH bending modes in NZ and explains the cause of broadening for OH stretching frequency in the bent H-bonded systems such as those in the enol form of β -diketones.

^a*

NOTE: The horizontal line across the page indicates the maximum allowed length of the abstract including footnotes. If your abstract is close to or exceeds the length limit, it may appear on page 2 of this document.

Time required: 15 min

Session Categories (Keywords) by Relevance: (Hyper)fine structure, tunneling — Electronic structure, potential energy surfaces — Spectroscopy as an analytical tool — Structure determination — Comparing theory and experiment — Vibrational structure/frequencies — Small molecules — Infrared/Raman — Theory and Computation

Mini-Symposia Requested: None — None

Competing for Rao Prize? No

Competing for Miller Prize? No