Tunneling Splittings of the Enolic Acetylacetone

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Proton transfer reactions play a central role in many chemical and biological processes, ranging from enzymatic catalysis and hydrogen-bond rearrangements to proton transport in condensed phases. The study of such tunneling processes provides valuable insight into the quantum nature of molecular dynamics in hydrogen-bonded systems. Acetylacetone represents a well-known example of an intramolecular proton transfer system. In its enol form, the molecule contains a strong intramolecular hydrogen bond that forms a six-membered quasi-ring structure. Within this configuration, the proton can be located on either of the two oxygen atoms, leading to two equivalent minima on the potential energy surface (Figure 1). In the case of acetylacetone, the tunneling process is not governed solely by the motion of the proton along the hydrogen bond. Instead, it involves a multidimensional large-amplitude motion of the molecular framework. It has been shown that the proton transfer is strongly coupled to several additional motions, including deformation of the six-membered quasi-ring and torsional motions of the methyl groups attached to the carbon skeleton. These coupled motions significantly influence the tunneling dynamics of the system [1]. Tunneling splittings are calculated using the modified WKB (Wentzel–Kramers–Brillouin), a semiclassical method based on instanton theory [2]. The method starts with finding the minimum action path, along which the semiclassical wavefunction is constructed and inserted into the Herring formula, yielding tunneling matrix elements. Finally, splittings are obtained by diagonalizing the tunneling matrix.

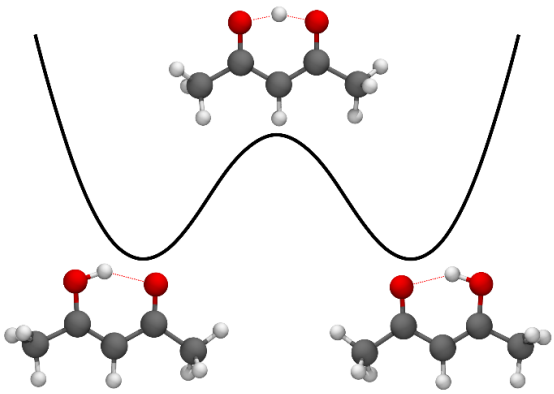

Figure 1. The proton transfer in the enolic form of acetylacetone

References:

[1] Y.–C. Chou, *J. Mol. Spectrosc.* **263** (2010) 34–43.

[2] M. Eraković, M. T. Cvitaš, *J. Chem. Phys.* **153** (2020) 134106.