Theoretical study of proton tunneling in the excited state of tropolone

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Ab initio CIS/6-311++G(d,p) calculations concerning geometry and vibrational frequencies have been carried in the Å state of tropolone. The grids of potential energy surfaces (PES) along the coordinates of high frequency-tunneling vibration and the low-frequency coupled vibration have been calculated. Two-dimensional model potentials, formed from symmetric mode coupling potential and squeezed double well potential, have been fitted to the calculated PES and frequencies, and used to analyze proton dynamics. The tunneling splittings for different vibrationally excited states have been calculated and compared with the available experimental data. The model PES, based on the CIS/6-311++G(d,p) calculations, gives good estimation of the tunneling energy splitting in the vibrationally ground and excited states of tropolone, and explain monotonic decrease in tunneling splittings with the excitation of low-frequency out-of-plane modes and increase of the tunneling splitting with the excitation of low-frequency planar modes.