THEORETICAL AND EXPERIMENTAL ROTATIONAL SPECTROSCOPIC STUDIES OF SUBSTITUTED BENZOIC ACID HETERODIMERS

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The complex tunnelling dynamics of double proton transfers in carboxylic acid dimers has been the focus of many theoretical and experimental studies.[1,2] Here we combine spectroscopic and computational approaches to model and understand how functional groups in substituted benzoic acid (BA) heterodimers can influence these dynamics. Dimers of BA with its 4-chloro-, 4-nitro-, and 4-amino-analogues were studied using a 2 to 6 GHz chirped-pulse Fourier transform microwave spectrometer, which is based on the design by Pates et al.,[3] to obtain experimental tunneling line splittings. Jacobi field instanton theory (JFI)[4,5] was used to compute tunneling splittings in the ground vibrational state. The use of the JFI method, which necessitates fewer number of potential energy and gradient calculations compared to other methods, enabled us to use ab initio on-the-fly potentials and compute the splitting in full dimensionality, in spite of the large system sizes. Furthermore, final expressions for the tunneling splittings provided a way to examine the influence of substituents on both the potential energy barrier height and shape, and on the vibrational modes, which can either promote or inhibit tunnelling.

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