

THEORETICAL AND EXPERIMENTAL ROTATIONAL SPECTROSCOPIC STUDIES OF SUBSTITUTED BENZOIC ACID HETERODIMERS

MOHAMAD H. AL-JABIRI, *Department of Chemistry, University of Alberta, Edmonton, AB, Canada*; MIHAEL ERAKOVIĆ, *Department of Physical Chemistry, Ruder Boskovic, Zagreb, Croatia*; ARAN INSAUSTI, *Departamento de Química Física, Universidad del País Vasco (UPV-EHU), Bilbao, Spain*; MARKO CVITAŠ, *Department of Physical Chemistry, Ruder Boskovic, Zagreb, Croatia*; WOLFGANG JÄGER, *Department of Chemistry, University of Alberta, Edmonton, AB, Canada*.

The complex tunnelling dynamics of double proton transfer 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 heterodimers can influence these dynamics. Dimers of benzoic acid 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 a smaller 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.

(1) Evangelisti, L.; Écija, P.; Cocinero, E. J.; Castaño, F.; Lesarri, A.; Caminati, W.; Meyer, R. J. *Phys. Chem. Lett.* 2012, 3 (24), 3770–3775. (2) Tautermann, C. S.; Voegelé, A. F.; Liedl, K. R. *J. Chem. Phys.* 2004, 120 (2), 631–637. (3) Pérez, C.; Lobsiger, S.; Seifert, N. A.; Zaleski, D. P.; Temelso, B.; Shields, G. C.; Kisiel, Z.; Pate, B. H. *Chem. Phys. Lett.* 2013, 571, 1–15. (4) Eraković, M.; Vaillant, C. L.; Cvitaš, M. *T. J. Chem. Phys.* 2020, 152 (8), 084111. (5) Mil'nikov, G. V.; Nakamura, H. *J. Chem. Phys.* 2001, 115 (15), 6881–6897.