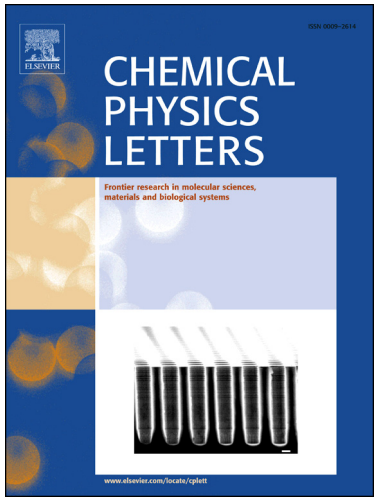

On the tunneling splitting in a cyclic water trimer

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On the tunneling splitting in a cyclic water trimer

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Abstract

We propose an alternative explanation of the "bifurcation" splittings observed for the water trimer in the VRT experiments of Saykally's group [Chem. Rev. 103 (2003) 2533]. In our interpretation, the splittings originate from the quantum delocalization of hydrogen bonded protons in the mean field potential between two oxygen neighbors. The pattern and the order of our calculated splittings is in the range of experimentally observed values. Consequently, quantum delocalization of protons should be considered seriously as the origin of experimentally observed fine splittings. The presented model can be extended to a water pentamer and, hopefully, advance our understanding of liquid water.

Keywords: Cyclic water clusters, water trimer, hydrogen tunneling

1. Introduction

Despite continuous efforts, liquid water still eludes a full theoretical description. Studies of small water clusters provide insight into the interactions of water building blocks, "Untangling the mysteries of the liquid, one molecule at a time", as expressed by Keutsch and Saykally [1].

The water trimer has been the most studied cyclic water cluster to date. An excellent, comprehensive review of the experimental and theoretical work on the trimer, through 2003, was presented by Keutsch *et al.* [2]. More recently, Han *et al.* completed the characterization of the 2.94 THz band of $(D_2O)_3$, obtained in their vibration-rotation-tunneling (VRT) experiment [3]. IR absorption of the O-H bond stretch in a supersonic expansion beam was studied recently by Moudens *et al.* [4], while Otto *et al.* identified trimer bands in the Raman spectra obtained in the slit-jet expansion of an atomic carrier gas [5]. The vibrational spectra in solid matrices were characterized in a wide energy range [6, 7, 8]. The dissociation energy of a water trimer was determined experimentally by Ch'ng *et al.* [9]. All of these experiments provide valuable results that should help to explain the quite elusive properties of water. In this paper we provide an alternative interpretation of the small tunneling splitting, commonly known as the "bifurcation" splitting, observed in the VRT spectra of the water trimer [2]. We believe that our model will further the explanation of the trimer

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