Electric field at the microscopic level: from water dissociation to Miller-like experiments

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In the last decade, thanks to Berry-phase theory and its implementation in DFT schemes, it is possible to study the effect of finite homogenous electric fields in ab initio molecular dynamics simulations [1]. Here we present a study of bulk liquid water under intense electric fields [2]. We observe that the hydrogen-bond length and the molecular orientation are significantly modified at low-to-moderate field intensities. Fields beyond a threshold of about 0.35 V/Å are able to dissociate molecules and sustain an ionic current via a series of correlated proton jumps, in good agreement with experimental values [3]. Upon applying even more intense fields ($\sim$ 1.0 V/Å), a 15%-20% fraction of molecules are instantaneously dissociated and the resulting ionic flow yields a conductance of about 7.8 Ω^{-1} cm^{-1}. We then undertake the first ab initio computer simulations of the celebrated Miller experiment, that we perform in the condensed phase [4] Our study shows that glycine spontaneously forms from mixtures of simple molecules once an electric field is switched on. Moreover, combining the electric field approach with a metadynamics-based analysis of chemical reactions[5], we identify formic acid and formamide as key intermediate products of the early steps of the Miller reactions, and the crucible of formation of complex biological molecules.

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