DFT interpretive tools for describing the effect of microhydration on reactivity

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ABSTRACT

In atmospheric or interstellar environments, small (micro-)hydrated organic molecules can react. How does this hydration modify their reactivity? This aspect remains complex to describe, especially as numerous isomers close in energy can co-exist and be characterised by different reactivities. At the molecular level, this difference in reactivity is due to a change in electron density.

The formation of non-covalent complexes and their reactivity are partly governed by the intrinsic properties of the isolated partners: geometry, location and nature of electrophilic and nucleophilic sites, sites available for proton or electron transfer.... These intrinsic properties can be mapped using interpretative tools, such as conceptual DFT, topological analysis of the electron density (QTAIM), [1] electron localisation function (ELF), [1] and analysis of the molecular electrostatic potential (MESP). [2] Inter-molecular interactions, particularly with a polar molecule such as water, can affect a molecule's electron density and the availability of reactive sites, and therefore its reactivity. A precise description of this effect is fundamental to a better description of reaction mechanisms in hydrated environments such as atmospheric chemistry or astrochemistry. Using the interpretative tools of theoretical chemistry, and in particular the QTAIM and ELF approaches, we will show how a small number of water molecules modify the electron density, the availability of electron pairs and therefore the reactivity of acetic acid and methylamine, to form methylacetamide.

Using the interpretative tools of theoretical chemistry, and in particular the QTAIM and ELF approaches, we will show how a restricted number of water molecules modifies the electron density, the availability of electron pairs and therefore the reactivity of acetic acid and methylamine, to form methylacetamide. Analysis of the strength of the reaction will also be used to characterise changes in the reaction pathways, in terms of the regions of the reactants, the transition state and the products.

References

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