Modelling reactivity at the interstellar ice interface: exploring HCN isomerization for the identification of accurate methods.

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Unveiling the role of interstellar ices in the process of prebiotic molecules formation is a challenge from both the experimental and theoretical points of view. On the one side, the difficulties in setting up an experiment mimicking the extreme conditions of the interstellar medium (ISM) and the obvious hustles in collecting samples reduce the amount of information available. On the other, the heterogeneous composition and the morphology of the icy grains make the modelling of such structures a challenging task.[1-2] Building up a strategy based on the interplay between experimental and theoretical chemistry can give more insights about the chemistry in such extreme conditions. Regarding the modelling, accurate methods for the simulation of the chemistry at the ice interface are required to both drive experiments and assist in their analysis. Moreover, accurate data are mandatory for the interpretation of the observed spectroscopic fingerprints. Although such accurate methods are available, they become quickly unaffordable when heterogeneous processes on extended surfaces are involved. Walking on this path, we undertook a study to define the quantum chemical methods with the best accuracy/computational cost trade-off for such studies. Despite the amount of benchmark works, to the best of our knowledge, the performance methods rooted in density functionals theory (DFT) methods in the field of astrochemistry hasn't been thoroughly assessed yet. For the purpose, we investigated the isomerization of hydrogen cyanide to hydrogen isocyanide on icy grain surfaces as a paradigmatic test case.[3-4] We compared accurate post Hartree-Fock results[5] with respect to common DFT methods for a small model system (HCN-$(H_2O)_2$). Next, the reliability of our procedure was checked by scaling up the size of the cluster up to 192 water molecules to reproduce the environmental effect of the icy grain surface. Our results indicate that four water molecules are directly involved in a proton relay mechanism. The cooperative effect of the superficial water molecules reduces the activation energy with respect to the direct proton transfer occurring in the isolated molecule. Finally, reaction rates obtained from transition state theory (TST) applied to the computed thermochemical data suggest that the isomerization of HNC to HCN on icy surface could occur quite easily at low temperatures overcoming the energy barrier by tunnelling.

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