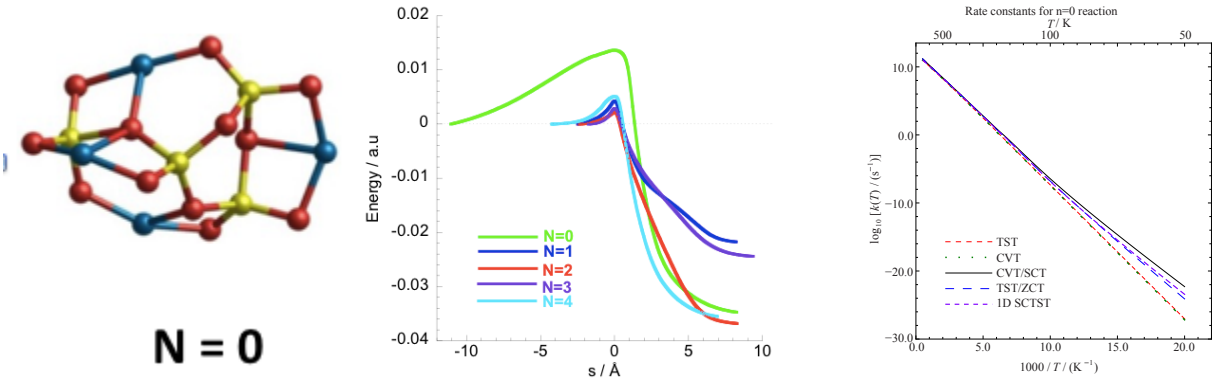
Understanding H_2 Formation on hydroxylated nanopyroxene clusters : *Ab initio* Study of the Reaction Energetics and Kinetics

Boutheïna Kerkeni[a], Marie-Christine Bacchus-Montabonnel[b], Xiao Shan[c], Stefan T Bromley[d]

[a] *Département de Physique, Laboratoire de Physique de la Matière Condensée (LPMC) Faculté des Sciences de Tunis. Université de Tunis El Manar. Campus Universitaire 2092, Tunisia.* [b] *Université de Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, Villeurbanne cedex 69622, France.* [c]*Physical and Theoretical Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom.* [d] *Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona 08010, Spain.*
boutheina.kerkeni@fst.utm.tn

The rate constants of H_2 formation on five models of silicate nanoclusters [1] with varying degrees of hydroxylation $(Mg_4Si_4O_{12})(H_2O)_N$ were computed for a wide temperature range [50-2000K]. We tested the efficiency of nine combinations of density functional methods and basis sets in reproducing accurate reaction energies and barrier heights, and computed the minimum energy H + H → H_2 reaction paths on each nanocluster. The convergence of the energetic data shows a preference for the largest basis set tested in combination with the hybrid-meta GGA functional M05-2X. The computation of the rate constants employed three semi-classical approaches that take into account tunneling and non-classical reflection effects by means of the canonical variational transition state theory with small curvature tunneling (CVT/SCT) corrections when possible [2], ZCT and the 1D Small Curvature Transition State Theory (SCTST) methods [3], which provided comparable results. Our investigations show that the H_2 process formation following the Langmuir-Hinshelwood (LH) mechanism is more efficient on the hydroxylated (N = 1 - 4) nanoclusters than on the bare (N = 0) one due to the barrier height being higher than for the hydroxylated nanoclusters. Overall, we conclude that all the considered nanoclusters are very efficient catalyzing grains for H_2 formation in the physical conditions of the Interstellar Medium (ISM) with pyroxene nanosilicates having moderate to high hydroxylation being more efficient than bare nanograins.

Figure 1: Logarithmic plot of the calculated reaction rate constants for the N=0 reaction.



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