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Description of multiple pathways on rearrangement the H atom on methylchlorocarbene

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Abstract: The purpose of this paper is to demonstrate the Sub-Arrhenius behavior in the H atom intramolecular rearrangement in the methylchlorocarbene molecule, accounting the temperature dependence of quantum effects. Previous similar works pointed a deep curvature upwards, characteristic of the Sub-Arrhenius behavior [1,2]. The series of hypotheses has been conditioned to this behavior, are specially competitive paths, reaction in the excited state, tunneling and variable transition state, however, these studies were inconclusive [3,4]. We believe that the neglect of certain arguments has boosted the discrepancy among previous theoretical papers and the experimental behavior. To solve this botleneck, we have performed a set of semi-classical and quantum simulations. Applying Car−Parrinello molecular dynamics (CPMD), coupled with a quantum treatment using Path Integral molecular dynamics (PIMD) [5,6]. This allowed us to identify five distinct reaction pathways, including the conventional rearrangement. It was evaluated the formation of intermediates and products using electronic structures methods at several level of calculation.

Key-words: branching ratios, deep tunneling, Feynman integrals, small mass.

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