Nuclear Quantum Effects on the Proton/Deuteron Transmission through Hexagonal Boron Nitride and Graphene Monolayers

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Abstract: Atomically thin hexagonal boron nitride and graphene can be exploited as possible platforms for the development of novel technologies related to energy storage, gas separation and membrane. Recent experiments suggest that h-BN and graphene monolayers are highly permeable to thermal protons under ambient conditions. We have examined energetics and mechanism of proton tunneling through h-BN and graphene within a molecular model of H_2O - $H(D)^+$- material - H_2O to mimic the experimental conditions. The potential energy surfaces along the transmission direction are obtained using correlated electronic structure methods. Exact quantum mechanical scattering approach is employed to assess the nuclear quantum effects such as tunneling factors and kinetic isotope effect (KIE). We found that nuclear quantum effects influence the thermal reaction rate constants (KIE of 3-4 for hexagonal boron nitride and 20-30 for graphene) and lowers the activation energy by 0.2 and 0.4 eV for two monolayers, respectively. The lowering effect is reduced by approximately a factor of 3 for the deuteron. As future work, a more descriptive model of the proton transmission with an extended aqueous environment and dynamics studies with flexible membranes employing on-the-fly quantum- trajectory-electronic structure approach will be pursued.