Tunneling reaction rate constants on a surface:
a case study of $H + H_2O_2 \rightarrow H_2O + OH$

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In the dense and cold regions of the Interstellar Medium (ISM), water is known to be formed on the surface of dust grains via sequential hydrogenation of O, O_2, or O_3. The full water surface reaction network consists of ~ 15 reactions and depending on density, temperature and H, H_2, O abundance of the interstellar region, different reaction pathways towards the formation of water are important [1]. In the most dense regions, the absolute amount of oxygen becomes sufficiently high for the following reaction pathway to contribute significantly to the formation of H_2O and OH:
$O\ (+O) \rightarrow O_2\ (+H) \rightarrow HO_2\ (+H) \rightarrow H_2O_2\ (+H) \rightarrow H_2O + OH$.
The final step in this reaction route has been reported to have a large activation barrier. It has been studied experimentally on the surface at low temperatures and a kinetic isotope effect was found [2]. This indicates the importance of tunneling yielding it efficient even at 15 K.
Furthermore, the detections and non-detections of H_2O_2 in a diverse sample of sources in different environments gave rise to the conclusion that the production of peroxide is very sensitive to temperature. The production of peroxide was taken into account by rescaling the reaction rate according to experimental data [3, 4]. Quantitatively rescaling rates is, however, not trivial for reactions that are deeply embedded in a reaction network.
Therefore, we present a theoretical study of the reaction $H + H_2O_2 \rightarrow H_2O + OH$ within the framework of studying tunneled reactions on a surface. Calculations are performed using a DFT functional benchmarked to CCSD(T)-F12 single-point energies. Rate constants are calculated with instanton theory. We present activation barriers and rate constants for three different cases: the gas-phase reaction, the gas-phase reaction with several spectator H_2O molecules (small clusters) and we show how to extend these to studying the reaction on a crystalline water surface using a QM/MM method.

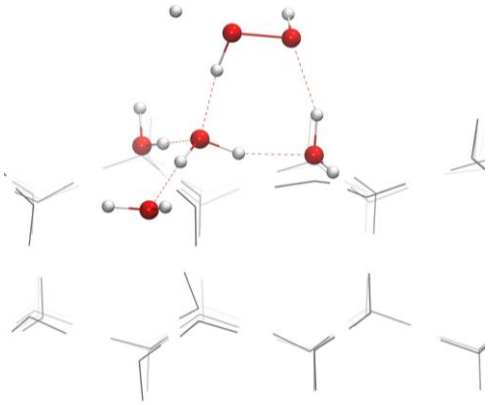

Figure 1: Example of a transition state structure on a water surface, the colored atoms are part of the QM region, whereas the gray lines represent water molecules described on an MM level.

References

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