The ground state water molecule and the reactions O (^1D)+H_2/D_2/HD and H + OD that occur in this system

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Due to their importance in atmospheric and combustion chemistry, the reactions of $O(^1D)$ with H_2 and its isotopic variants HD and D_2 have been subject of several theoretical[1,2] and experimental[2,3] studies. At low energies these reactions proceeds on the $\tilde{X}\,^1A'$ H_2O ground state adiabatic surface by an insertion mechanism. For energies above 2 kcal mol^{-1} (or temperatures above 500 K) these reactions can also proceed through the first excited adiabatic surface $1\,^1A''$. It should also be taken into account the contribution from the $^1\Pi$ state due to non-adiabatic electrostatic coupling at collinear geometries.[4] It has been found a good agreement between theory and experiment for the H_2 or D_2 reactions (for example, see Refs.[1] and references therein), but for the O (^1D) + DH reaction, there is a general agreement in all dynamical features except for the OD/OH product ratio.

The isotopic exchange reaction OH + D → OD + H is one of the few neutral processes of importance in astrophysics, where it is one of the deuterium fraction reaction with the major contribution for the OD formation in the interstellar molecular clouds. The reaction is also theoretically interesting as a radical-radical reaction proceeding through a transient collision complex. So far only two experimental kinetic studies were reported[5,6] and, to our knowledge, only one theoretical kinetic result has been published for this reaction.[7]

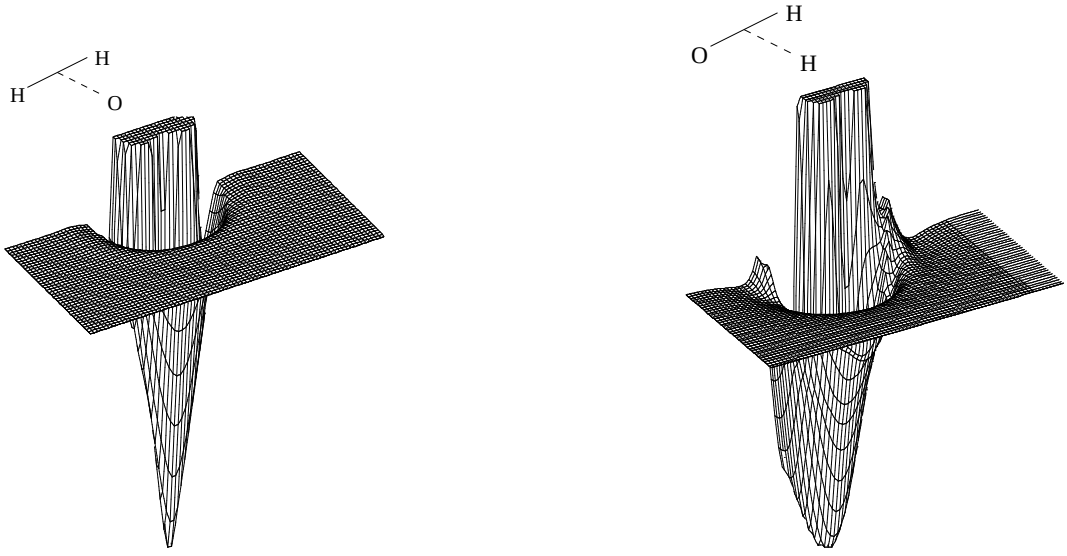

Figure 1: Perspective view of H_2O $(X\,^1A')$ for a O atom moving around an H_2 and for an H atom moving around an OH.

We have published a double-valued potential energy surface for the ground adiabatic state of the water molecule $(X\,^1A')$ sate[8] that uses a carefully description of the long-range forces[9] between all the dissociation fragments. The anisotropy of those interactions should play an important role in the mechanism of complex formation. This PES also presents a small barrier (< 0.1 kcal mol^{-1}) favouring a perpendicular approach of the O atom. The

double-value form of this potential allow us to describe the different crosses between the diabatic surfaces, in particular those occurring in the product channels. These features have shown to be of importance to the study of the exchange reaction D+OH → H+OD.[10] Fitted to high quality *ab initio* data this $^1A'$ BR PES also accurately reproduces the saddle point for H_2O isomerization that plays an important role on the dynamics of the highly excited H_2O^* intermediate complex.

The computed thermal rate constants using the BR PES are in excellent agreement with the best experimental data.

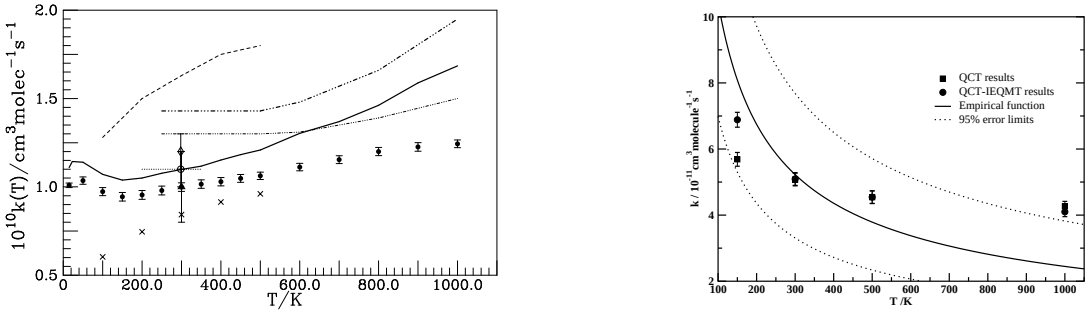

Figure 2: Comparison of the theoretical and experimental rate constants for the $O(^1D)$+H_2 reaction, • and —— obtained in this work with corrections; experimental data: ♢, Talukdar;[11] △, DeMore;[12] ⊙ and · · · · ·, Atkinson;[13] and H + OD reaction, where • and ■ represent our results and the lines represent an empirical function.[6]

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