Quasiclassical trajectory study of the dynamics of the
O + D₂ → OD + D gas phase reaction.

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1. System and potential energy surface (PES)

The O + H₂ system is of interest in Astrochemistry and leads to the OH+ + H (proton transfer on the ground PES, 2'A''), OH+ and OH+ (hydrogen atom transfer on the first excited PES, 2'A''), reactions (1) and (2), respectively (Figure 1). Both PESs are barrierless and exhibit a deep minimum (H₂O(+X') and H₂O(12T'), respectively) in the MEP connecting reactants and products.

(1) O(2P) + H₂ (X'Σg⁻) → OH(2Σg⁻) + H
(2) O(2P) + H₂ (X'Σg⁻) → OH(XΣg⁻) + H⁺

ΔH(2P) = -2.49 eV
ΔH(2P) = -1.69 eV

Both analytical PESs are based on MRCI/aug-cc-pVQZ ab initio points fitted to Aguado-Paniagua many body expressions. [1] Among their characteristics:

- the MEP occurs for Cσ=Cπ2 symmetry and the O atom shows a tendency to insert into the H₂⁺ bond, forming a deep well with an isoosceles triangle configuration and a (H-O-H)* angle of about 110° for the absolute minimum.
- similar shape as the ground PES but with collinear geometry for the minimum.

Up to date, there are no available experimental studies for O(2P) + H₂⁺ system. A merged-beam experimental study [2] for the deuterated proton transfer reaction is the only possibility to compare with the experiments, at least for our ground analytical PES.

(3) O(2P) + D₂(X'Σg⁻) → OD(XΣg⁻) + D

2A''

2A'

II. Results

In the experimental setup the D₂⁺ beam was produced by electron impact on D₂ at high energy (2025 eV) producing an approximately Frank-Condon distribution of D₂⁺ vibrational states with an average vibrational excitation energy of 0.9 eV.

According to this, quasiclassical trajectories (QCT) were run simulating the D₂⁺(v=0-15) distribution to get integral cross sections (ICSs), differential cross sections (DCSs) and final relative kinetic energy distributions, P(E'), for reaction (3), at the experimental values of E_exp (0.002, 0.96, 1.94, 5.10 and 10.1 eV).

In general, there is a reasonably good agreement between the experimental and QCT results, thus reinforcing the validity of the ground PES and the theoretical approach used here.

References