Quasiclassical trajectory study of the dynamics of the $O + D_2^+ \rightarrow OD^+ + D$ gas phase reaction.

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I. System and potential energy surface (PES)

The O + H_2^+ system is of interest in Astrochemistry and leads to the OH^+ + H (proton transfer on the ground PES, $^2A''$) and OH + H^+ (hydrogen atom transfer on the first excited PES, $^2A'$), reactions (1) and (2), respectively (Figure 1). Both PESs are barrierless and exhibit a deep minimum ($H_2O^+(X^2B_1)$ and $H_2O^+(1^2\Pi_u)$, respectively) in the MEP connecting reactants and products.

(1) $O(^3P) + H_2^+(X^2\Sigma_g^+) \rightarrow OH^+(X^3\Sigma^-) + H$ $\quad \Delta_r H^0_{0K}$ = -2.49 eV

(2) $O(^3P) + H_2^+(X^2\Sigma_g^+) \rightarrow OH(X^2\Pi) + H^+$ $\quad \Delta_r H^0_{0K}$ = -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:

$^2A''$ the MEP occurs for Cs≈C2v symmetry and the O atom shows a tendency to insert into the H_2^+ bond, forming a deep well with an isosceles triangle configuration and a $(H\text{-}O\text{-}H)^+$ angle of about 110º for the absolute minimum.

$^2A'$ similar shape as the ground PES but with collinear geometry for the minimum.

Up to date, there are no available experimental studies for $O(^3P) + H_2^+$ 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) $O(^3P) + D_2^+(X^2\Sigma_g^+) \rightarrow OD^+(X^3\Sigma^-) + D$

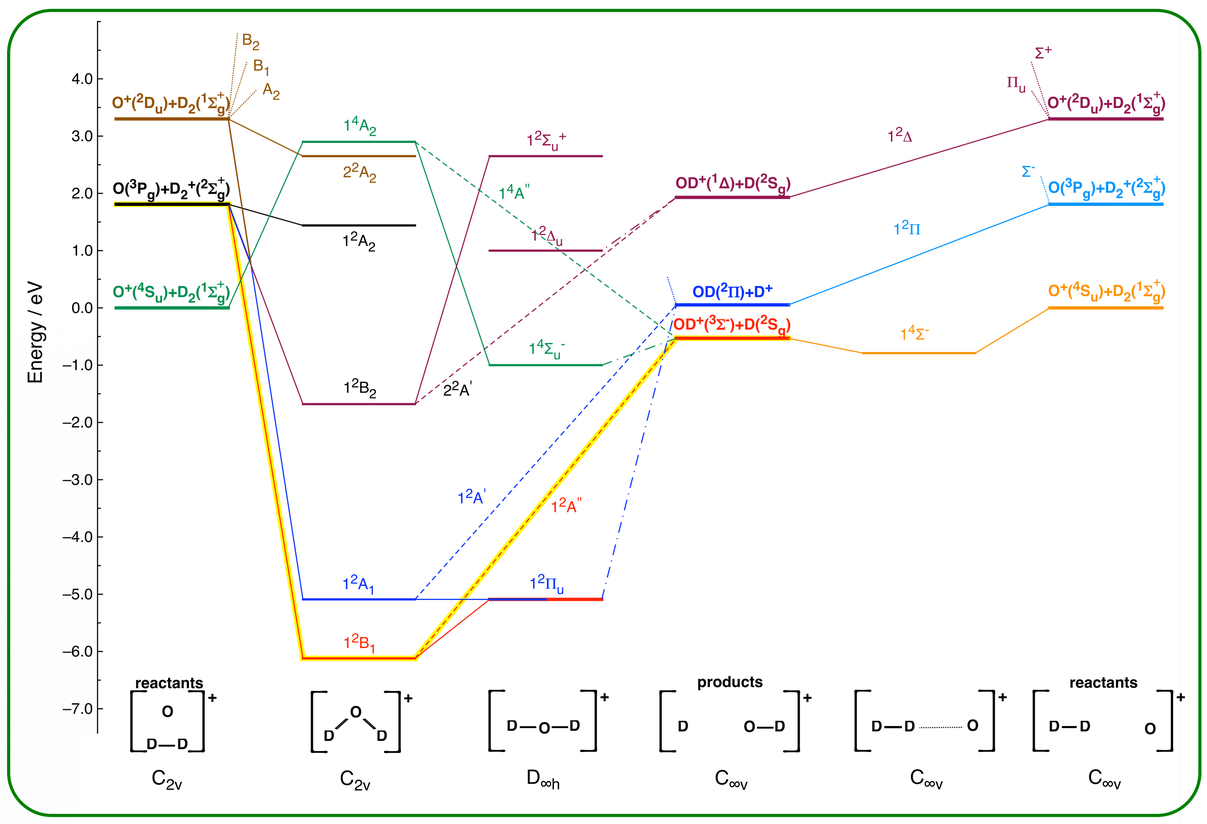

Figure 1.▲
Electronic correlation diagram [1]. The ground PES used for studying Reaction (3) is highlighted in yellow colour.

The system exhibits nonadiabatic coupling of the $^2A''$ and $^2A'$ PESs for collinear geometries (Renner-Teller effect). Our previous nonadiabatic quantum dynamics study [3] pointed out the small effect of including RT couplings in the dynamics. According to this, we have studied the dynamics of reaction (3) through the ground PES (see also ref. [4] for a QCT dynamics study on reactions (1) and (2)).

II. Results

In the experimental setup the D_2^+ beam was produced by electron impact on D_2 at high energy (2025 eV) producing an approximately Frank-Condon distribution of D_2^+ vibrational states with an average vibrational excitation energy of 0.9 eV.

According to this, quasiclassical trajectories (QCT) were run simulating the D_2^+(v=0-15) distribution to get integral cross sections (ICSs), differential cross sections (DCSs) and final relative kinetic energy distributions, $P(E_T')$, for reaction (3), at the experimental values of E_{col} (0.002, 0.96, 1.94, 5.10 and 10.1 eV).

ICS

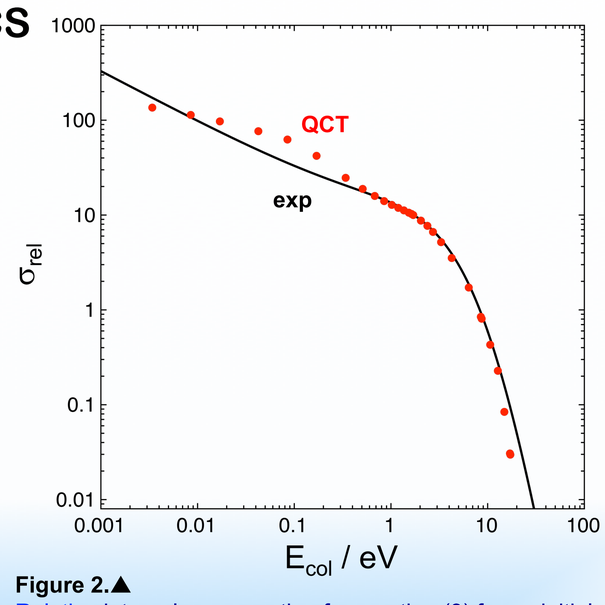

Figure 2.▲
Relative integral cross section for reaction (3) for an initial D_2^+ vibrational distribution (v=0-15). Experimental data from Ref. [2].

DCS

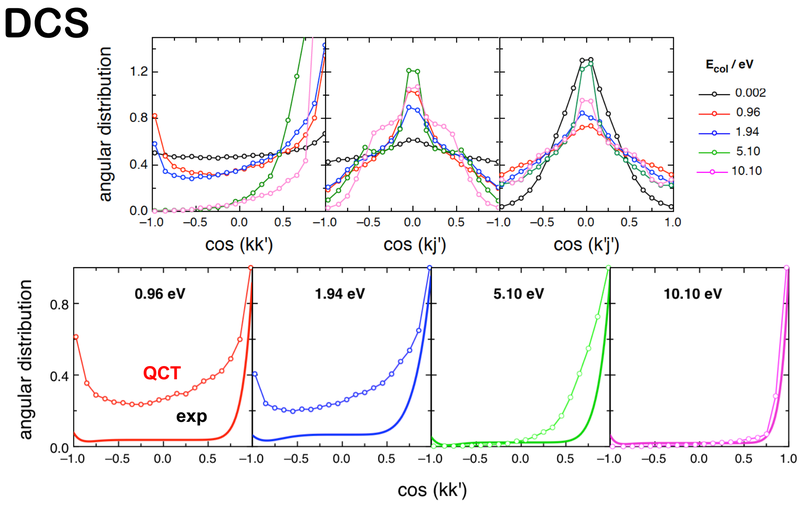

Figure 3.▲
Top: Differential cross sections: kk' (left), kj' (middle) and k'j' (right) for reaction (3) at representative experimental E_{col} values.
Bottom: Comparison between the QCT and experimental [2] DCS kk' values.

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.

Product distributions

Vibrational

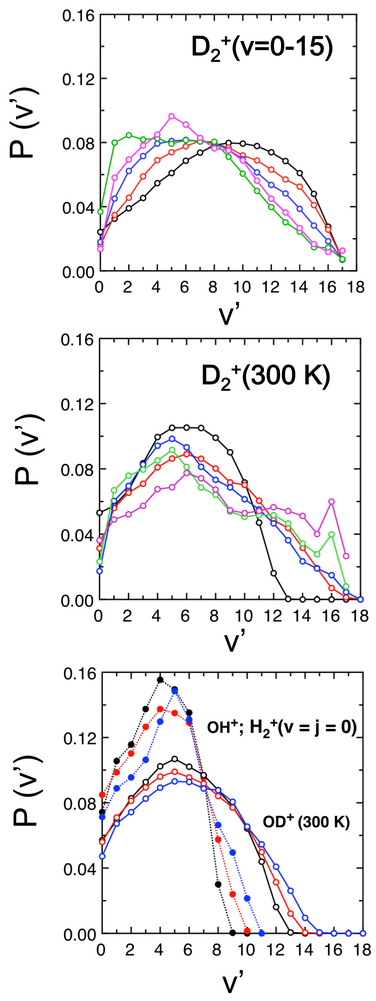

Figure 4.▲
Product vibrational distributions (OD^+):
Top: for D_2^+ initial distribution (v=0-15).
Middle: for D_2^+ at 300 K.
Bottom: comparison between products formed in reaction (1) and (3) at state-selected and thermal initial conditions.

Relative kinetic Energy

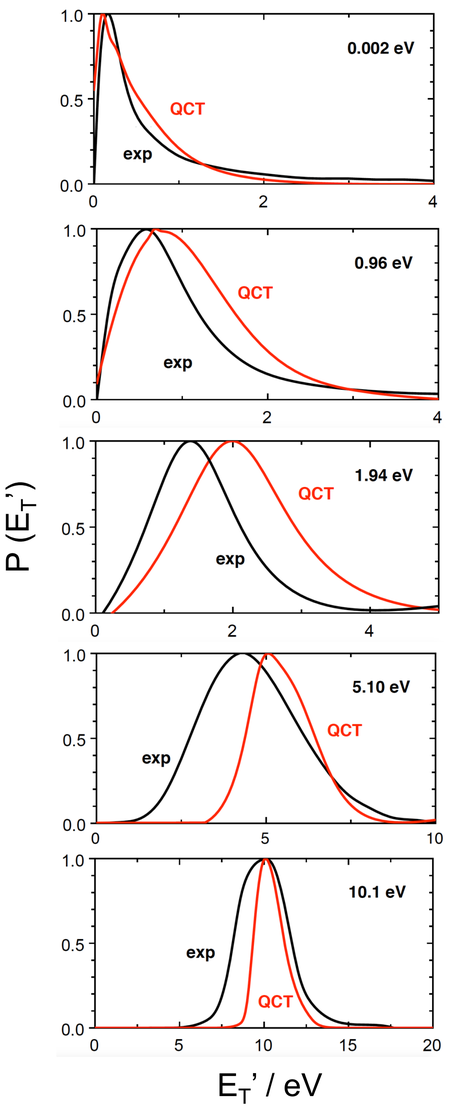

Figure 5.▲
QCT and experimental [2] products relative kinetic energy at representative experimental E_{col} values.

Aknowlegments

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References

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