Cite this: DOI: 10.1039/xxxxxxxxxx

Unexpected dynamical effects change the lambda-doublet propensity in the tunneling region for the $O(^3P)+H_2$ reaction.

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Received Date

Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

One of the most relevant features of the $O(^3P)+H_2$ reaction is that it occurs on two different potential energy surfaces (PESs) of symmetries A' and A'' that correlate reactants and products. The saddle points, which correspond to a collinear arrangement, are the same for both PESs, whilst the barrier height rises more abruptly on the $^3A'$ than on the $^3A''$ PES. Accordingly, the reactivity on the $^3A''$ PES should be always higher than on the $^3A'$ PES. In this work, we present accurate quantum-scattering calculations showing that this is not always the case for rotationless reactants, where dynamical factors near the reaction threshold cause the $^3A'$ to dominate at energies around the barrier. Further calculation of cross sections and Λ -doublet populations, has allowed us to establish how the reaction mechanism changes from the deep tunneling regime to hyperthermal energies.

1 Introduction

Since its formulation in the 1930s, transition state theory (TST) has become one of the most successful and appealing theories in chemistry.^{1–3} One of its main contributions has been to rationalize the chemical reactivity in terms of the height and width of the barrier, and the zero-point energies (ZPEs) of reactants and transition state. Indeed, it has been always assumed that a higher (smaller) barrier correlates with a decrease (increase) of the reactive flux. When it comes to reaction dynamics, these concepts are complemented by the Polanyi Rules^{4,5} and their extensions to deal with polyatomic reactions like the sudden vector projection model⁶ that predict how mode selectivity modifies the amount of reactive flux across the barrier.

These intuitive ideas can be used for reactions that proceed via multiple potential energy surfaces (PESs) as, for example, in triatomic systems where two PESs of symmetries A' and A'' correlate with reactants and products. When the products are diatomic radicals, like OH or NO in their ground electronic state, $^2\Pi$, rotational levels split into spin-orbit states and each of them into two nearly degenerate Λ -doublet levels, $\Pi(A')$ and $\Pi(A'')$. In spite of the tiny energy difference between them, a clear propensity to-

wards one of the two Λ -doublet components has been found in many chemical processes.^{7–12}

One of the prototypical reactions involving two PESs correlating with reagents and products is $O(^3P)+H_2 \rightarrow OH(^2\Pi)+H$, which has received a great deal of attention due to its relevance in astrochemistry^{13–16} and in the hydrogen combustion.^{17,18} Due to the large electronic barrier, the experimental study of its reaction dynamics by crossed molecular beams required an atomic beam in which the $O(^3P)$ atoms are accelerated to hyperthermal energies.^{11,12,19,20} In a series of experiments, Minton and coworkers have determined the excitation function, that is, the collision energy dependence of the integral cross section (ICS),¹⁹ differential cross section (DCSs),²⁰ and rotational energy distributions.^{11,12,20} The results were in very good agreement with quantum dynamics calculations on the two $^3A'$ and $^3A''$ adiabatic PESs, showing that the Born-Oppenheimer approximation is accurate enough to account for most of the experimental findings^{19,21–25}, in contrast with the reaction of $O(^3P)$ with H_2^+ in which the Renner-Teller effect was shown to be relevant.²⁶ Similarly, with regard to the intersystem crossing, it has been demonstrated that, if occurs, it does so with small probability and at energies well above the reaction threshold. This was attributed to the small values of the spin-orbit couplings, and to the location of the singlet-triplet crossing, which occurs at the top of the barrier.^{20,27,28}

More recently, the $O(^3P)+D_2$ reaction has been subject of detailed experiments that, among other things, have measured the population ratio of the Λ -doublet levels of the nascent OD radical

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for different rovibrational levels using laser-induced fluorescence detection.^{11,12} The interest of the latter experiments relies on the assumption that the Λ -doublet propensity contains valuable information about the relative importance of the PESs involved in the reaction and the respective reaction mechanisms.²⁹ The measurements, carried out at hyperthermal energies, show that regardless of the collision energy and final vibrational state, the $\Pi(A')$ Λ -doublet state is preferentially populated with respect to $\Pi(A'')$, where the labelling of the states refers to the location of the singly occupied orbital on the rotation plane of the diatom, $\Pi(A')$, or perpendicular to it, $\Pi(A'')$. At first glance, under the simpler assumption that reaction on the $^3A'$ ($^3A''$) PES would populate the $\Pi(A')$ ($\Pi(A'')$) state, this is somewhat surprisingly since the $^3A''$ is more reactive than the $^3A'$ PES.²⁵ Using a new theoretical treatment,^{24,30} we could reproduce the experimental results, showing that the preference towards $\Pi(A')$ is due to a mechanism on the $^3A''$ PES, for which the three-atom and the OD rotational planes are orthogonal, that entails a change in the direction of the O doubly occupied orbital.²⁴ However, it is not clear if the same mechanism will hold at low enough energies, where tunneling is important and the steric hindrances imposed by the different topography of the two PESs might be very relevant.

In this work, we carry out a comparative study of the reactivity on the two competing PESs for the $O(^3P)+H_2$ using accurate quantum mechanics (QM) scattering methods and quasiclassical trajectories (QCT). All dynamical calculations have been carried out using the recent refined set of $^3A'$ and $^3A''$ PESs by Zanchet *et al.* that accurately reproduces the degeneracy of the saddle point at collinear geometries,²⁵ and are specially suitable for this kind of studies. The paper is laid out as following: the methodology is succinctly presented in section 2, whilst the results and discussion are shown in section 3. Section 4 contains the summary of this work and the most relevant results.

2 Method

2.1 QM Scattering Calculations

Time independent QM scattering calculations were carried out using the ABC code³¹ on the two adiabatic PESs, described in Ref. 25. Calculations were carried out at 64 total energies between 0.30 and 2.00 eV including all partial waves to convergence. The propagation was carried out in 300 log-derivative steps up to a hyperradius of 20 a_0 (for $E_{\text{tot}} < 0.75$ eV) and 15 a_0 for the rest of energies. The calculations include all helicity projections, Ω , up to 25.

2.2 Quasiclassical Trajectories

Batches of 2×10^5 – 5×10^5 trajectories were run for the $O(^3P) + H_2(v=0, j=0, 2)$ reaction at 14 collision energies (between 0.5 eV–1.75 eV) on each of the two $^3A'$ and $^3A''$ PESs. The calculations were carried out following the procedure described in Refs. 32–33. The maximum value of the impact parameter was found to change with the energy up to a maximum value of 1.65 Å. The initial atom-diatom distance was set to 10 Å. An integration step of 0.1 fs was used, which guarantees a total energy conservation better than one part in 5×10^5 . The rovibrational energies of the

OH diatom were calculated by semiclassical quantisation of the action using the diatomic potential (which is the same on the two PESs), with their values fitted to Dunham expansions. The real v' and j' values were rounded to its nearest integer value. The procedure to assign the Λ -doublet state is detailed in subsection 2.4.

2.3 Transmission coefficients

The transmission coefficients through the respective 1D vibrationally adiabatic barriers were calculated solving the time independent 1-D Schrödinger equation using a Numerov algorithm. For each energy, the 1-D wavefunction is propagated from the products to the reactants asymptote, and matched with plane waves in both asymptotic channels (where the potential is constant). The transmission coefficients are thus extracted based on the different amplitudes of the plane waves associated to reactants and products. The procedure was tested using an Eckart barrier for which the transmission coefficients are analytical, showing an excellent agreement (within three significant figures).

2.4 Calculation of Λ -doublet cross sections

Assuming that the reaction takes place adiabatically on both PESs, the relation between the reaction cross sections on each PES and the respective cross section $\sigma_R[\Pi(A')]$ and $\sigma_R[\Pi(A'')]$ is given by^{24,30}

$$\sigma_R[\Pi(A')] = W_{A'} \sigma_R(A') + (1 - W_{A''}) \sigma_R(A'') \quad (1)$$

$$\sigma_R[\Pi(A'')] = (1 - W_{A'}) \sigma_R(A') + W_{A''} \sigma_R(A''), \quad (2)$$

where $\sigma_R(A')$ and $\sigma_R(A'')$ are the cross sections on the $^3A'$ and $^3A''$, respectively, and $W_{A'}$, $W_{A''}$ are weight factors connecting the cross sections on the two PESs and the populations of the $\Pi(A')$ and $\Pi(A'')$ Λ -doublet states. It has been shown that the weights $W_{A'}$, and $W_{A''}$ (in short $W_{A'/A''}$) are related to the cosine of the angle between the normal vectors that define the three-atom plane and that of the OH molecule, which is no other than the OH rotational angular momentum.²⁴ It was further shown that the weights can be calculated from the distribution of helicities, Ω' , the projection of j' on the products recoil direction, k' , using the expression:

$$W_{A'/A''} = 1 - \left[\frac{\langle \Omega'^2 \rangle_{A'/A''}}{j'(j'+1)} \right]^{1/2} \quad (3)$$

rendering $W_{A'}$ or $W_{A''}$ when $\langle \Omega'^2 \rangle$ is calculated on $^3A'$ or on $^3A''$ PES, respectively.

The average value of $|\Omega'|^2$ is closely related to the $k=2, q=0$ (k and q are the rank and the spherical component of the polarization moments) product rotational alignment moment along k' , $a_0^{(2)}$,²⁴

$$W_{A'/A''} \approx 1 - \left[\frac{2[a_0^{(2)}]_{A'/A''} + 1}{3} \right]^{1/2} \quad (4)$$

Regarding the $a_0^{(2)}$ moments that appear in Eq. 3, it is worth emphasizing that:

Fig. 1 Minimum energy Path (MEP) (solid lines), and vibrationally adiabatic potentials (dashed lines) for the $\text{O}(^3\text{P}) + \text{H}_2 \rightarrow \text{OH}(^2\Pi) + \text{H}$ reaction at different Jacobi angles ($\gamma = 0^\circ, 20^\circ, 30^\circ$, and 40°) calculated on the $^3A'$ (red) and $^3A''$ (blue) PESs. The reaction coordinate is defined as the difference between the HH and the OH distances, so very negative and positive values correspond to the reactant and product channel, respectively. The zero potential corresponds to the minimum of the reactant asymptote (minimum of the H_2 potential).

- They correspond to the $\mathbf{k} - \mathbf{k}' - \mathbf{j}'$ correlation³⁴ that describes the direction of the rotational angular momentum of the nascent OH molecule. They are different from those corresponding to the $\mathbf{k} - \mathbf{j} - \mathbf{k}'$ vector correlation, used in Refs. 35–37 to describe the extent of control that could be achieved by the polarisation of the initial rotational angular momentum.
- The reference frame in which they are calculated is defined with z along $\mathbf{k}'$. This reference frame is rotated by the scattering angle with respect to the frame in which z is along $\mathbf{k}$.³⁸

If $\mathbf{k}'$ and $\mathbf{j}'$ are preferably aligned perpendicularly to each other (negative $a_0^{(2)}$), $|\Omega'| \approx 0$ and $W_{A'/A''} \approx 1$. This limit corresponds to A' (A'') correlating with $\Pi(A')$ ($\Pi(A'')$) Λ -doublet states. When $\mathbf{k}'$ and $\mathbf{j}'$ are parallel (positive $a_0^{(2)}$), $|\Omega'| \approx j'$, $W_{A'/A''} \approx 0$. Hence, an appreciable amount of the reactive flux ending on the A' (A'') PES would correspond to the $\Pi(A'')$ ($\Pi(A')$) Λ -doublet state.

Note that the weight factors have to be calculated for each final rovibrational state. The weight factors averaged over different final states, $\langle W_{A'/A''} \rangle$, are given by:

$$\langle W_{A'/A''} \rangle = \frac{\sum_{v',j'} W_{A'/A''}(v',j') \sigma_R(A'/A'')(v',j')}{\sum_{v',j'} \sigma_R(A'/A'')(v',j')} \quad (5)$$

where the state-to-state $W_{A'/A''}$ are weighted using their respective state-to-state cross sections.

3 Results and Discussion

Figure 1 depicts the minimum energy path (MEP) and the corresponding vibrationally adiabatic potential for different Jacobi

Fig. 2 Height of the electronic barrier as a function of the $\text{O}-\widehat{\text{H}}-\text{H}$ angle (bending potential) on the $^3A'$ (red dash-dot line) and $^3A''$ (blue continuous line). As can be seen, the potential is steeper on the former than on the latter, and hence the cone of acceptance at a given energy is broader on the $^3A''$ PES. The black horizontal dotted line represents the collinear barrier, $\text{O}-\widehat{\text{H}}-\text{H}=180^\circ$, which is the same for both PESs. The red dash line and blue dash line indicate the saddle point zero point energies on the $^3A'$ and $^3A''$, respectively, including the symmetric stretch and the degenerate bending mode.

angles, γ , (the angle between $\mathbf{r}_{\text{HH}}$ internuclear axis and the vector from the O atom to the center-of-mass of the H_2 molecule, $\mathbf{R}_{\text{O}-\text{H}_2}$). The saddle point occurs at $\gamma=0^\circ$ ($\text{O}-\widehat{\text{H}}-\text{H}$ collinear configuration) and $\Delta E^\ddagger = 0.597$ eV. For the collinear configuration

Fig. 3 Panels (a) and (b): QM Excitation functions for the $\text{O}(^3\text{P}) + \text{H}_2$ ($v=0, j=0,2$) reaction on the $^3\text{A}'$ (red) and $^3\text{A}''$ (blue) PESs. The insets in these panels represent the excitation functions at low energies in logarithmic scale. Solid and open circles in panels (a) and (b) are for QM and QCT results, respectively. Panels (c) and (d): Ratio between the QM cross sections on the $^3\text{A}'$ and $^3\text{A}''$ as a function of the energy. QCT ratios are shown as dashed olive lines, and the ratio between the tunneling transmission factors for the vibrationally adiabatic potentials at $\gamma=0^\circ$ is shown in pink. The vertical line in panel (c) indicates the actual QCT threshold (no reaction is found below this value). Results for $j=0$ are shown in the left panels whilst those for $j=2$ are shown in the right panels.

both PESs are degenerate along the MEP, except for the presence of a very shallow van der Waals well observed in the entrance channel, which is slightly deeper on the $^3\text{A}''$.²⁵ For non-collinear approaches, the degeneracy breaks down and the $^3\text{A}'$ PES becomes more repulsive than the $^3\text{A}''$. Accordingly, the bending potential is steeper for the $^3\text{A}'$ PES leading to a broader cone of acceptance on the $^3\text{A}''$, as shown in Fig. 2, where the barrier height is represented as a function of the $\text{O}-\text{H}-\text{H}$ bending angle.

The vibrationally adiabatic potentials are also represented in Fig. 1. Although for $\gamma=0^\circ$ the symmetric stretch frequency is identical on both PESs, the higher quantum for the degenerate bending motion of the TS causes the effective barrier, including the ZPE, to be higher on the $^3\text{A}'$ PES even at $\gamma=0^\circ$. From these observations, higher reactive cross sections on the $^3\text{A}''$ PES are always expected.²⁵

The top panels of Fig. 3 display the QM and QCT excitation functions, $\sigma_{\text{R}}(E_{\text{coll}})$, for H_2 in $v=0$ and $j=0$ and $j=2$ on the two adiabatic PESs. The excitation functions calculated with both approaches are very similar on each of the two PESs, and show the typical behavior of direct reactions on repulsive PESs: a monotonically rising $\sigma_{\text{R}}(E_{\text{coll}})$ with collision energy. Due to the existence of tunneling across the barrier, a clear-cut reaction threshold cannot be defined (other than the small endothermicity of the reaction) as can be appreciated in the insets of Fig. 3. The actual threshold for QCT calculations is $E_{\text{coll}} \approx 0.425$ eV on both PESs. Interestingly, this energy corresponds to the height of adiabatic barrier considering only the symmetric stretch. Therefore, it seems that

classical calculations preserve the symmetric stretch ZPE along the reaction coordinate but not the bending ZPE, which is seemingly used to overcome the barrier. A similar effect was observed for the $\text{H}+\text{H}_2$ reaction and its isotopic variants.^{39,40}

To discern the different reactivity on both PESs, especially in the deep tunneling regime, it is appropriate to inspect the ratio of cross sections, $\sigma_{\text{R}}(\text{A}')/\sigma_{\text{R}}(\text{A}'')$, as a function of E_{coll} , as shown in the lower panels of Figure 3. We can distinguish three different regions for the reaction with H_2 ($v=0, j=0$) shown in Figure 3(c). A first one, at $E_{\text{coll}} < 0.5$ eV, below the collinear vibrationally adiabatic barrier, where the reaction proceeds exclusively via tunneling and $^3\text{A}''$ PES dominates, although $\sigma_{\text{R}}(\text{A}')/\sigma_{\text{R}}(\text{A}'')$ increases steadily from a value of 0.5 at $E_{\text{coll}}=0.2$ eV, until the cross section on both PES becomes the same. A second region, at $0.5 \text{ eV} < E_{\text{coll}} < 0.7$ eV, around the barrier height, where, surprisingly, the reaction on the $^3\text{A}'$ PES prevails over that on the $^3\text{A}''$ PES, reaching a maximum of ≈ 1.15 at $E_{\text{coll}} = 0.6$ eV. A third region, for $E_{\text{coll}} > 0.7$ eV, well above the vibrational adiabatic barriers (0.534 eV and 0.494 eV for the $^3\text{A}'$ and $^3\text{A}''$ PESs, respectively), where the $^3\text{A}''$ PES is again more reactive, due to its broader cone of acceptance, as can be inferred from the respective evolution of the barrier height with the attacking angle (Figure 1 and 2). The latter effect is essentially classical in origin, and indeed the QCT and QM cross section ratio are the same for $E_{\text{coll}} > 1.1$ eV, with a constant value of 0.75.

We have also calculated the ratio of the 1D transmission coefficients across the collinear vibrationally adiabatic barrier, depicted as a pink solid line in Figure 3(c). The result predicts a faster rise

Fig. 4 R - γ contour plot of the $^3A'$ and $^3A''$ PESs for a fixed r_{HH} that corresponds to the collinear transition state. Superimposed to the contour-plots, we show a given trajectory at $E_{\text{coll}}=0.6$ eV run on the $^3A'$ (panel a) and $^3A''$ (panel b) PESs. The initial conditions are identical for the two represented trajectories (initial $\gamma \sim 150^\circ$).

in the ratio of the transmission coefficients with E_{coll} than that found in the QM results. Although there are obvious differences with regard to the actual scattering calculations, the 1D tunneling model indicates that the behaviour of the $\sigma_{\text{r}}(A')/\sigma_{\text{r}}(A'')$ at low energies can be mainly attributed to tunneling through the adiabatic collinear barrier. However, the 1D model predicts that the quotient of the transmission coefficients becomes one as soon as the collinear barrier on both PESs are attained, failing to describe the intermediate region in which the reactivity on the $^3A'$ takes over that on the $^3A''$. Clearly, some effect other than tunneling has to contribute to the observed behavior.

The results of the QCT $\sigma_{\text{r}}(A')/\sigma_{\text{r}}(A'')$ for $j=0$ are shown in Fig. 3(c) as a dashed line. Although at collision energies above 1.1 eV QCT and QM $\sigma_{\text{r}}(A')/\sigma_{\text{r}}(A'')$ ratios are in an excellent agreement, they diverge below $E_{\text{coll}} < 1.1$ eV, where the cross-section ratio predicted by the QCT method soars quickly with decreasing energy until $E_{\text{coll}}=0.45$ eV where its value is somewhat above 2. Detailed inspection of reactive trajectories in this energy region shows that, on the $^3A'$ PES, non-collinear trajectories may be re-oriented towards collinearity after hitting the strongly repulsive walls. As a consequence, those trajectories can reach the transition state in a nearly collinear geometry and are reactive. On the $^3A''$ PES this reorienting effect is considerably smaller due to its broader cone of acceptance. Indeed, trajectories with identical initial conditions that are reactive by the reorientation on the $^3A'$ PES, prior to the TS, are not reactive on the $^3A''$ PES.

To illustrate this effect, Fig. 4 depicts two representative trajectories at $E_{\text{coll}}=0.6$ eV superimposed to the respective R - γ contour plots of the $^3A'$ and $^3A''$ PESs for a fixed r_{HH} that corresponds to the collinear transition state. The trajectory ran on the $^3A'$ PES (panel a) hits at $\gamma=150^\circ$ the strongly repulsive wall centered at

90° , and is deflected towards collinearity ($\gamma=180^\circ$) where lies the saddle point at $R \approx 1.6$ Å. As a result, the trajectory turns to be reactive. However, when the trajectory, with identical initial conditions, is run on the $^3A''$ PES (panel b), it is driven towards 120° where it hits the repulsive wall, which is less protruding and more confined than on the $^3A'$ PES, and is back-deflected as non-reactive. This effect is only observed at energies close to the threshold, where the barrier can only be surmounted at collinear geometries. At higher energies, the effect of broadening the $^3A''$ PES cone of acceptance dominates, and the $^3A''$ PES turns to be more reactive.

The explanation of the observed QM behavior now emerges clear. At collision energies below the adiabatic barrier two effects come into play and compete with each other. Tunneling favors reaction on the $^3A''$ PES, whose adiabatic barrier is smaller. On the other side, the stronger repulsive character of $^3A'$ causes some reorientation and paradoxically promotes reaction on this PES. Below $E_{\text{coll}}=0.5$ eV, tunneling through the adiabatic barrier dominates and hence the reaction on the $^3A''$ PES. But as the collision energy increases, still below the barrier, the reorienting effect takes over favoring the reaction on the $^3A'$, and $\sigma_{\text{r}}(A')/\sigma_{\text{r}}(A'')$ becomes somewhat greater than one. For QCT calculations, as there is not tunneling, the reorienting effect does not have any counterpart and accordingly higher $\sigma_{\text{r}}(A')/\sigma_{\text{r}}(A'')$ are found. Finally, well above the adiabatic barrier, the broader cone of acceptance and the lower bending ZPE favors reaction on $^3A''$.

The results obtained for the reaction with $\text{H}_2(j=2)$ underpin this argument. Initial rotation suppresses the reorienting effect to a large extent and, accordingly, $\sigma_{\text{r}}(A')/\sigma_{\text{r}}(A'')$ is never above one (Figure 2(d)). Below the adiabatic barrier, tunneling dominates favoring reaction on the $^3A''$ PES. Above the barrier, $E_{\text{coll}} > 0.7$ eV,

Fig. 5 Top panels: QM excitation functions (summed over all rovibrational states) for the $\text{O}(^3\text{P}) + \text{H}_2$ ($v=0, j=0,2$) reaction resolved on the two Λ -doublet manifolds. Bottom panels: Λ -doublet ratio as a function of collision energy. Results for $j=0$ are shown in the left panels, whilst those for $j=2$ are shown in the right panels.

the broader cone of acceptance on the $^3A''$ PES determines the larger reactivity on this PES and QM and QCT predict the same cross-section ratio.

Unlike $\sigma_{\text{r}}(A')/\sigma_{\text{r}}(A'')$, which cannot be measured, the Λ -doublet population ratio can be experimentally determined.^{11,12} Hence, to predict the effect of the different $^3A'$ and $^3A''$ PESs reactivities on the Λ -doublet ratio, we have calculated $\sigma_{\text{r}}[\Pi(A')]$ and $\sigma_{\text{r}}[\Pi(A'')]$ by applying the model developed in Ref. 24 and summarized in Section 2.4.

The excitation functions summed over all final rovibrational states for the two Λ -doublet manifolds are shown in Fig. 5 for initial $j=0, 2$. The $\sigma_{\text{r}}[\Pi(A')]/\sigma_{\text{r}}[\Pi(A'')]$ ratio is shown in the respective lower panels. The contrast with the results shown in Figure 2 is evident. Above $E_{\text{coll}}=0.4$ eV for $j=0$ and 0.7 eV for $j=2$, the predicted population of the $\Pi(A')$ levels overtakes that of the $\Pi(A'')$ levels in spite of the smaller cross sections for the reaction on the $^3A'$ PES. The ‘inversion’ of the $\sigma_{\text{r}}[\Pi(A')]/\sigma_{\text{r}}[\Pi(A'')]$ with respect to $\sigma_{\text{r}}(A')/\sigma_{\text{r}}(A'')$ at E_{coll} well above the barrier was also observed for the $\text{O}(^3\text{P}) + \text{D}_2$ reaction^{11,24}. However, so far, no experiments or predictions have been carried out at energies where tunneling is the major or exclusive contribution to the overall reactivity.

To understand why this ‘inversion’ appears starting a given collision energy, the central panel of Figure 6 shows the evolution of $W_{A'}$ and $W_{A''}$ with E_{coll} , averaged over all rotational states for initial $v=0, j=0$ and final $v'=0$. As can be seen, $W_{A'}$ is consistently larger than $W_{A''}$, and the difference between them gradually increases with energy. This result implies that products on the

$^3A''$ PES would tend to appear as $\Pi(A')$, and explains the results shown in Figure 5. A similar effect is found for $j=2$, at energies above 0.6 eV (results not shown), although for energies below the barrier $W_{A'}$ and $W_{A''}$ have a similar magnitude. A detailed analysis showed that whilst the prevailing reaction mechanism on the $^3A'$ PES preserves the three-atom plane - and hence $A' \rightarrow \Pi(A')$ preferentially - there is an additional mechanism on the $^3A''$ PES whereby the H atom abstraction takes place at a bent configuration inducing the OH to rotate on a plane perpendicular to the scattering frame. This mechanism, essentially classical in nature, show up clearly at energies well above the classical reaction threshold. The present study gives the opportunity of probing the reaction mechanism at energies where tunneling is the major or exclusive contribution to the overall reactivity.

An insightful clue on the reaction mechanism is given by the cross section resolved in j' and Ω' , $\sigma_{\text{r}}(j', \Omega')$, which contains the necessary information to determine the correspondence between reaction yield on each PESs and the respective Λ -doublet populations as shown in Eqs. 3 and 4. The joint distributions on the $^3A'$ and $^3A''$ PESs are represented as gradational maps, in the top and bottom panels, respectively, at collision energies corresponding to the three regions referred to in Figure 3(c). At $E_{\text{coll}}=0.20$ eV, and 0.6 eV, the joint $\sigma_{\text{r}}(j', \Omega')$ shows a clear preference for low j' and Ω' on both PESs. However, even at the lowest energy, the Ω' distributions are broader on the $^3A''$ PES, drawing part of the OH product on the $^3A''$ PES to the $\Pi(A')$ state. A much more significant, qualitative, difference can be observed in the the Ω' distributions at energies well above the barrier. Whilst on the $^3A'$

Fig. 6 Middle panel: Weight factors for initial $j=0$ that determine the cross sections in the lambda doublet states $\Pi(A')$ and $\Pi(A'')$ from the results on the $^3A'$ and $^3A''$ PESs according to eq (1). The upper and bottom panels depict the joint distributions of j' and Ω' calculated on the $^3A'$ and $^3A''$ PESs, respectively, at $E_{\text{coll}}=0.2, 0.6$ and 1.23 eV and initial $j=0$

PES the tendency towards $\Omega' \approx 0$ is preserved, on the $^3A''$ PES, in addition to a wider range of Ω' values, another mechanism takes place (already found for the $\text{O}+\text{D}_2$ reaction), in which the highest possible Ω' for a given j' are preferred.

A cursory glance at panels (c) and (d) of Fig. 5, where the energy dependence of $\sigma_{\text{r}}[\Pi(A')]/\sigma_{\text{r}}[\Pi(A'')]$ is depicted, may suggest that the behaviour for $j=0$ and $j=2$ is more alike than the ratio of the cross sections on both PESs. However, there are very important differences between the $j=0$ and $j=2$ Λ -doublet population ratios below and near the barrier that reveal the underlying mechanism. As can be seen, for $j=0$, $\sigma_{\text{r}}[\Pi(A')]/\sigma_{\text{r}}[\Pi(A'')] < 1$ only at $E_{\text{coll}} < 0.3$ eV, whilst for $j=2$ this ratio is less than 1 even at $E_{\text{coll}} \lesssim 0.8$ eV; that is, not only at the tunneling regime but well above the barrier. The different behaviour can be traced back to the reorientation mechanism described above. For $j=0$ there are two effects that contribute to foster the population of $\Pi(A')$ manifold over that of $\Pi(A'')$. On the one hand, the change of the rotation planes in the course of the reaction that causes $W_{A''} < W_{A'}$, as shown in Fig. 6. On the other hand, below and near the vibrational adiabatic barrier the reorientation mechanism increases the reactive yield on the $^3A'$ PES, as discussed when Fig. 3 was presented. For $j=2$ the situation is rather different. Due to rotation, the reorientation effect that promotes the reaction on the $^3A'$ PES is completely disrupted, and in this respect the behaviour on both PESs is the same. In addition, at low collision energies rotation causes that $W_{A''} \approx W_{A'}$. As a consequence, the switch to $\sigma_{\text{r}}[\Pi(A')]/\sigma_{\text{r}}[\Pi(A'')] > 1$ only takes place at a collision energy as high as 0.8 eV, when clearly $W_{A''} < W_{A'}$. Therefore, the Λ -doublet

population ratio at low energies contains a clear signature of reorientation mechanism for rotationless reagents, corroborated by the results for $j=2$.

4 Conclusions

In summary, our calculations show that, as expected from their respective shapes, the $^3A''$ PES is in general more reactive than the $^3A'$ PES. However, at energies below or close to the vibrationally adiabatic barrier for H_2 in $j=0$, the reactive flux is larger on the latter PES, due to a reorienting effect that promotes collinear approaches at the transition state, and that is crucially more important on the $^3A'$ PES. At higher collision energy or with initial rotation ($j \geq 1$) the reorientation effect becomes negligible, and reaction on the $^3A''$ PES prevails.

The Λ -doublet population ratio, calculated over the whole collision energy range, shows a general preference for the $\Pi(A')$ reflecting the various mechanisms taking place at different collision energies. In particular, the reorientation effect that promotes the reaction on the $^3A'$ PES for $j=0$ at low E_{coll} is evinced by the significant differences of $\sigma_{\text{r}}[\Pi(A')]/\sigma_{\text{r}}[\Pi(A'')]$ for $j=0$ and $j=2$. In the deep tunneling region, the preference for $\mathbf{j}' \perp \mathbf{k}'$ alignment occurs on both PESs, and consequently the $A' \rightarrow \Pi(A'')$ transfer nearly compensates that of $A'' \rightarrow \Pi(A')$. At energies above the barrier, the range of Ω' becomes even wider intensifying the transfer from $A'' \rightarrow \Pi(A')$. The variation of the stereodynamics with collision energy is essentially dictated by the topography of the $^3A''$ PES which has a wider cone of acceptance than that of the $^3A'$ PES, and allows for a wider range of $\mathbf{j}'\text{-}\mathbf{k}'$ orientations. Of course,

the information about the reaction mechanism in the tunneling regime cannot be obtained with classical trajectories.

Acknowledgment

The authors thank Prof. Enrique Verdasco for his help with the calculations. Funding by the Spanish Ministry of Science and Innovation (grants MINECO/FEDER-CTQ2015-65033-P, and PGC2018-096444-B-I00 and FIS2016-77726-C3-1-P) is also acknowledged. P.G.J. and A. Z. acknowledge funding by Fundación Salamanca City of Culture and Knowledge (programme for attracting scientific talent to Salamanca).

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