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Influence of the Reactants Rotational Excitation on the H + D₂($v=0, j$) Reactivity

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Abstract

We have analyzed the influence of the rotational excitation on the H+D₂($v=0, j$) reaction through quantum mechanical (QM) and quasiclassical trajectories (QCT) calculations at a wide range of total energies. The agreement between both types of calculations is excellent. We have found that the rotational excitation largely increases the reactivity at large values of the total energy. Such increase cannot be attributed to a stereodynamical effect but to the existence of recrossing trajectories that become reactive as the target molecule gets rotationally excited. At low total energies, however, recrossing is not significant and the reactivity evolution is dominated by changes in the collision energy; the reactivity decreases with the collision energy as it shrinks the acceptance cone. When state-to-state results are considered, rotational excitation leads to cold product's rovibrational distributions, so that most of the energy is released as recoil energy.

1 Introduction

The distinct effects of translational, rotational and vibrational energy on chemical reactivity for elementary A + BC processes with an energy barrier have attracted the interest of a wide scientific community at least since the pioneering studies of Polanyi and co-workers.^{1,2} These studies, which were mostly based on the results of classical trajectory calculations, provided general criteria on the relationship between dynamical observations and the properties of the potential energy surfaces (PESs) governing chemical reactions. The effects of translation and vibration were largely understood by considering the location of the barrier on the PES.³ Translational energy was found to be more efficient for promoting reactions with an early barrier, whereas vibrational energy was found to be preferable for reactions with a late barrier, where “early” and “late” refer to the reactants’ and products’ valleys of the PES respectively. This simple rule has of course limitations,⁴ but it has proven quite general and most useful for the prediction and interpretation of results in reaction dynamics.

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The influence of rotational energy on reactivity turned out to be more complex (see 5 and references therein). In general no simple predictions can be made about the influence of rotational excitation from a first sight inspection of the PES. The first trajectory calculations, carried out by Porter, Karplus and Sharma 6 for the $\text{H}+\text{H}_2(j)$ reaction, led to an increase in the reaction threshold, and thus to an inhibition of reactivity, upon rotational excitation of H_2 . The result was interpreted as a decrease in the “orienting effect” of the PES, an effect that would drive the triatomic system toward a favorable configuration to surpass the saddle point. For energies slightly above the energetic barrier, the range of viable angular configurations is restricted to a narrow “cone of acceptance” around the collinear orientation. Later work 7–10 on the $\text{H}+\text{H}_2$ and $\text{D}+\text{H}_2$ reaction showed that for a given collision energy in the post threshold region, the reaction cross section falls initially with growing j , but at a given point rises again for higher values of j . This dual behavior has been conventionally described 5 in terms of an “orientation effect” (negative) for the first j values, and an “energy effect” (positive) for the higher j values. With the higher energy of these rotational states reactive encounters are not restricted to quasi-collinear configurations and the orienting effect of the PES loses its relevance. However, the actual mechanism behind the “energy effect” is not clearly defined.

The negative influence of rotation in the vicinity of the reaction threshold should be more pronounced for quick rotation and slow translation. Consequently, for any system and, to a larger extent, for the H_3 one, the disorienting effects of rotation should be isotope specific and would be expected to decrease along the sequence $\text{D}+\text{H}_2$, $\text{H}+\text{H}_2$ and $\text{H}+\text{D}_2$. This is precisely what is found in detailed quasi-classical trajectory (QCT) calculations. 9–12 The calculations show that rotational excitation inhibits the reactivity for $\text{D}+\text{H}_2$ and to a lesser extent for $\text{H}+\text{H}_2$, but is always beneficial for $\text{H}+\text{D}_2$. These results were confirmed by a series of QM calculations on several PESs. 13–16

It was also found that rotational excitation strongly affects the reactivity for other direct reactions for which the transition state is bent and/or the cone of acceptance is broader than that of the H_3 system, as in the $\text{F}+\text{H}_2$ and $\text{F}+\text{HCl}$ cases. 17–20 QCT calculations 21 for the $\text{Cl}+\text{H}_2$ reaction on a strongly collinearly constrained PES 22 showed a very negative effect of rotation excitation on the reactivity. However, subsequent calculations on a more recent *ab initio* PES with a broader cone of acceptance and a van der Waals well in the entrance channel displayed just the opposite effect, with rotation promoting the reaction even at the same total energy. 23

Models of varying complexity were developed by various groups in an attempt to unveil the key features of the influence of rotation on reactivity. 24–30 These models were based on the solution of the equations of motion with some dimensionality reducing approximation and, although they differ in the details of their formulation, they all share the central idea that dynamical reorientation caused by the anisotropy of the potential is responsible for most of the observed effects of rotational excitation on reactivity. In a recent work, Jiang et al. 31 have advanced a sudden vector projection (SVP) model, that highlights the importance of the coupling between the rotational mode and the reaction coordinate at the transition state. This model can account for the high positive effect of rotation in reactions with bent transition

states like $F+H_2$ and $F+HCl$ as compared with the much smaller and often negative effect of rotation for the characteristically collinear $H+H_2$ reaction.

Whereas the negative orientation effects of rotational excitation have been intensively discussed, less attention has been paid to the dynamics of the positive effect of rotation on reactivity. In the present work we analyze this effect using the $H+D_2(v=0, j)$ reaction. As mentioned above, rotational excitation enhances the reactivity of this isotopic variant. Our investigation, based on the combination of accurate QM and QCT calculations, shows that the positive effect of rotational excitation on reactivity is not merely an “energy effect” but has also specific dynamical features associated with rotation.

The paper is organized as follows. Section 2 presents the main features of the QM and QCT scattering calculations that serve as starting point for the analysis of the influence of the rotational excitation on the target reaction unfolded in Section 3. Finally, the content of the work are summarized in Section 4.

2 Scattering calculations

We will briefly describe the scattering calculations that form the basis of the discussion unfolded in Section 3. QM (Section 2.1) and QCT (Section 2.2) calculations have been carried out. In both cases, we used the BKMP2 PES by Boothroyd et al. 32 as PES.

2.1 Quantum mechanical calculations

All the QM results presented throughout the manuscript were obtained from time-independent scattering calculations performed with the hyperspherical coordinate method by Skouteris *et al.* 33 For all the total energies considered (see below), this methodology rendered the scattering matrix^{34,35} in the helicity representation. Such matrix contains all the available information about the reaction and its elements are represented as $S_{v'j'\Omega',vj\Omega}^{EJ}$, where the superscripts specify the values of some of the conserved quantities; E is the total energy and J is the total angular momentum. Regarding the subscripts, primed and unprimed quantities label the products and reactants asymptotic states, respectively. In particular, v and v' hold for the vibrational levels, j and j' for the rotational levels and Ω and Ω' are the helicity quantum numbers that represent the projection of the reagents or products rotational angular momentum onto the approaching, $\mathbf{k}$, or recoiling, $\mathbf{k}'$, relative velocities, respectively.

The scattering matrix was obtained for a grid of total energies from 0.5 eV up to 2.35 eV and the convergence of the calculations was assured through a suitable choice of the parameters. The cutoff energy for truncation of the basis was 3.15 eV so that the rovibrational basis set included all the states below that energy and characterized by an absolute value of the helicity quantum number $|\Omega_{\max}| = 24$, which ensures the convergence of the total integral cross section for the $H+D_2(v=0, j)$ reaction regardless of the value of j . The coupled equations were propagated up to a maximum hyperradius of $\rho_{\max} = 24 a_0$ in 250 sectors. Finally, the maximum value of the total angular momentum, $J_{\max}$, was 47.

The QM product's translational energy distribution for the $H+D_2(v=0, j)$ reaction, $P(E_{\text{rec}})$, was calculated by using an expansion in Gaussian functions each of them centered at the

recoil (translational) energy of each HD rovibrational state, $E_{\text{rec}}^{(v',j')}$, and weighted proportionally to the corresponding state-to-state integral cross section, $\sigma_{v',j'}$. The $P(E_{\text{rec}})$ is given by

$$P(E_{\text{rec}}) = \frac{1}{\sigma_{\text{R}}} \sum_{v'} \sum_{j'} \sigma_{v',j'} G(E_{\text{rec}} - E_{\text{rec}}^{(v',j')}) \quad (1)$$

where $G(E_{\text{rec}} - E_{\text{rec}}^{(v',j')})$ is a normalized Gaussian function

$$G(E_{\text{rec}} - E_{\text{rec}}^{(v',j')}) = N \exp \left[-\frac{(E_{\text{rec}} - E_{\text{rec}}^{(v',j')})^2}{2s^2} \right] \quad (2)$$

where N is a normalization constant and s^2 the variance. The width of the distribution was chosen such that would be that of experiments of medium resolution (FWHM=0.2 eV).

2.2 Quasiclassical trajectories

QCT calculations have been carried out for the H + D₂ reaction and four different reactants rovibrational states ($v=0, j=0, 6, 12$, and 18) by running batches of 15 million trajectories in the 0.4 eV - 2.3 eV total energy range following the procedure described in Refs. 36,37 The integration step size in the trajectories was chosen to be 0.04 fs, which guarantees a total energy conservation better than one part in 10⁵. The trajectories were started and finished at an atom-diatom R distance of 10 Å. The rovibrational energies of the D₂ and HD molecules were calculated through semiclassical quantization of the action using the diatomic potentials given by the asymptotic limits of the PES. The resulting rovibrational energies were then fitted to a Dunham expansion containing 20 terms (fourth power in $(v + 1/2)$ and third power in $j(j + 1)$). The values of the quasiclassical rovibrational coincide with the exact QM ones within four/five significant figures.

Additionally, $5 \cdot 10^6$ trajectories were run at $E_{\text{tot}}=2.16$ eV for the each of the aforementioned D₂ rotational states (being their respective collision energies: 1.97 eV for $j=0$, 1.82 eV for $j=6$, 1.42 eV for $j=12$, and 0.844 eV for $j=18$). The assignment of the HD rotational product quantum number, j' , was done by equating the square of the classical product rotational momentum to $j'(j' + 1)\hbar$. With the real value so obtained, the vibrational quantum number v' is found by equating the internal energy of the outgoing molecule to the rovibrational Dunham expansion. Both v' and j' were rounded to their nearest integers. The values of the total reaction cross sections and opacity functions so obtained were very similar to those calculated using a Gaussian binning procedure, with small differences in the threshold regions.

As it will be shown below, we also investigated the role played by the recrossing mechanism in the reaction. In classical mechanics terms, recrossing takes place whenever a given trajectory crosses the transition state (TS) more than once. The most common type of

recrossing trajectories are those that cross twice, forward and backward, the same TS, and end being non-reactive. Henceforth, we will refer to them as *recrossing trajectories*. Of course, it is possible to have an even number of TS crossings with the trajectory being a reactive one, in such a way that the mechanism implies circling around the conical intersection and successively crossing two different TSs: $\text{H}-\text{D}_\text{B}\text{D}_\text{C} \rightarrow \text{HD}_\text{B}-\text{D}_\text{C} \rightarrow \text{HD}_\text{C}-\text{D}_\text{B}$. It is also conceivable that a trajectory crosses the same TS three times ending as a reactive trajectory. However, at the energies studied in this work, in the most favorable case, only a small number (< 1 in 10^4) of trajectories go around the conical intersections (two crossings through two different TS), and even less experience three or more crossing over the same TS. The possibility of various crossings was discussed in previous works.^{38–40} For the $\text{H} + \text{D}_2$ reaction, we can consider that recrossing occurs when one of the R_{HD} distances is smaller than the R_{DD} distance and the trajectory is finally nonreactive.

We have calculated opacity functions (probability as a function of the orbital angular momentum or impact parameter) for the total number of trajectories that cross the TS, $P_{\text{cr}}(\ell)$, for reactive trajectories (that cross once the TS without return), $P_{\text{R}}(\ell)$, and for non-reactive recrossing trajectories (that cross twice the same TS), $P_{\text{rc}}(\ell)$. As indicated above, at the energies of the present work, $P_{\text{cr}}(\ell) = P_{\text{R}}(\ell) + P_{\text{rc}}(\ell)$. In all cases, the respective opacity functions are calculated as an expansion in Legendre polynomial moments as in previous works.^{36,37}

3 Results and discussion

The starting point for the discussion of the influence of rotational excitation on the $\text{H} + \text{D}_2(v=0, j)$ reactions is the excitation function, that is, the dependence of the reactive cross section on collision energy, $\sigma_{\text{R}}(E_{\text{coll}})$. Specifically, Figure 1 depicts the QM excitation functions as a function of the collision energy for various D_2 rotational states. In all cases, translational excitation promotes the reactivity for a given j in the E_{coll} range shown in the figure. This result is well known although it has seldom been calculated for such high rotational states. More importantly, rotational excitation for a given collision energy promotes the reactivity considerably, and the effect is more marked for small collision energies. As an instance, at $E_{\text{coll}}=0.5$ eV the value of $\sigma_{\text{R}}(E_{\text{coll}})$ is a factor 6.5 larger for $j=18$ than for $j=0$; at 1 eV this factor is about 3. Accordingly, the effective threshold - a value of the excitation function of, say, the order of $0.05 \text{ \AA}^2$ - becomes smaller as j increases.

Given the considerable enhancement of the reactivity with rotational excitation, the obvious question is about the origin of this effect. As a first step in answering this question, it is pertinent to investigate the reliability of the QCT calculations as the analysis of trajectories is more intuitive and easier to interpret than time-independent QM results.^{41–43} Figure 2 shows a comparison between the QM and QCT excitation functions at selected values of j . For all the initial D_2 rotational states considered in the figure, the agreement between the excitation functions calculated with both methodologies is excellent. As expected, the only discrepancies appear in the threshold region. This good agreement suggests that the role played by rotation in this reaction can be understood in classical terms and lends credence to a classical interpretation of its origin.

It is also convenient to consider the explicit expression for the integral cross section in terms of reaction probabilities: 44

$$\sigma_R = \frac{\pi}{k^2} S = \frac{\pi}{k^2} \sum_{\ell} (2\ell+1) P_R(\ell) \quad (3)$$

where $P_R(\ell)$ is the opacity function, that is, the reaction probability as a function of the orbital angular momentum, where ℓ represents the respective quantum number,

$$k^2 = \frac{2\mu}{\hbar^2} E_{\text{col}}, \quad (4)$$

and μ is the reduced mass of the atom-diatom system. The values of the $P_R(\ell)$ functions can be computed from the values of the scattering matrix. 45 According to Eq. (3), any change in reactivity could be attributable to the prefactor π/k^2 , which gets larger as the collision energy decreases, to a net dynamical effect embedded in the summation of $(2\ell+1)P_R(\ell)$ or to a combination of both effects.

Looking again at Figs. 1 and 2, the large enhancement of σ_R with growing j may not be too surprising inasmuch as the total energy grows quickly with the initial j value. The same effect on the total energy lies behind the increase associated to the collision energy. However, it remains open the question of which of the two possible ways to promote the reactivity is more effective: that consisting of increasing the collision energy or that due to the rotational excitation of the reactants. To assess the comparative effect of the two kinds of excitation it is necessary to analyze the values of the reaction cross section as a function of j at a fixed value of the total energy. Such comparison is presented in Figure 3, where the QM total reaction cross section is plotted against j for three values of the total energy.

The top panel of Figure 3 corresponds to $E_{\text{tot}}=0.70$ eV. For this value of the total energy, increasing j reduces the available E_{coll} to a point where the cone of acceptance decreases appreciably; only very collinear configurations can access the transition state. Under these circumstances, the net effect of rotational excitation is to diminish the reactivity. In the middle panel, the evolution of σ_R with j is displayed for a total energy of 1.20 eV. Here an increase in j from 0 to 8 hardly changes the value of σ_R . A detailed analysis shows that this is due to a compensation of the growth of the inverse translational factor, proportional to $1/k^2$, with the reduction of the summation term, S (see Eq. (3)). For values of $j > 8$ ($E_{\text{coll}} < 0.85$ eV) the cross-section decreases as the available collision energy begins again to be too low.

At higher total energies, such as $E_{\text{tot}}=2.16$ eV, which is the value corresponding to some of the more recent works on the title reaction, 41,42,46 (lower panel of Figure 3) rotational excitation is clearly more efficient than translation in promoting reactivity. Only for values of $j > 18$, corresponding to $E_{\text{coll}} < 0.84$ eV, the collision energy becomes small enough such that the cone of acceptance is significantly reduced, and the reactivity begins plummeting. It is remarkable that for $j=16$ and $E_{\text{coll}}=1.05$ eV, the cross section is about a factor of 2 bigger

than for $j=0$ and $E_{\text{coll}}=1.97$ eV. From the present results, it becomes evident that, for high enough values of the total energy, such that E_{coll} is clearly above the barrier, depositing the energy in rotation is more efficient than in translation.

To further investigate the role of rotation at high total energies, Figure 4 shows the QM and QCT $P_R(j)$ functions for the reaction with $D_2(v=0)$ in $j=0, 6, 12$ and 18 at $E_{\text{tot}}=2.16$ eV. The reaction probability values have been multiplied by $(2j+1)$ so as to reflect the contribution of each partial wave to the cross section. The value of the QM S in Eq. (3) is also shown in each panel. The most significant change experienced by the probability functions for values of j going from 0 up to 12 is an increase in its magnitude as the reactants get rotationally excited without any significant change in ℓ_{max} , in such a way that the value of S grows monotonically up to $j=12$. Beyond that j value, the maximum value of ℓ retreats and the contribution of the remaining partial waves becomes smaller, causing S to decrease; at $j=18$, for instance, S is smaller than at $j=0$. Moreover, the agreement between QM and QCT calculations is excellent, in particular at the highest j values here examined.

Therefore, the evolution of the cross section displayed in the bottom panel of Figure 3 is not only due to the prefactor in Eq. (3) but also to the contribution of the reaction probabilities. This picture is valid until $j=12$; beyond this value, the collision energy becomes small enough so that the effective barrier begins to take its toll by reducing the number of partial waves and decreasing the reaction probability for those that still contribute to the process. This effect is illustrated in the right-bottom panel of Figure 4 for $j=18$. For higher j values, the increase experienced by the prefactor π/k^2 cannot further compensate for the rapid decrease in S leading to a decrease in the σ_R .

While it is easy to understand that at a given (low) total energy the increase of rotational excitation (and hence a decrease in translational energy) reduces the reactivity, due to the progressive narrowing of the cone of acceptance, it is not straightforward to explain how rotational excitation causes an increase in S at sufficiently high energies (such as $E_{\text{tot}}=2.16$ eV). Thus, our aim will be now to determine the dynamical origin of the net increase in the reaction probability described in the former paragraph. One could wonder, in the first place, if an stereodynamical effect is behind such finding. To ascertain whether or not this is the case, examining the helicity quantum number Ω dependence of the reaction probability is in order. In Figure 5 the QM reaction probabilities $P_R(J, |\Omega|)$ are plotted for the $H+D_2(v=0, j=6, 12 \text{ and } 18) \rightarrow HD(v'=all, j'=all)+D$ collisions at $E_{\text{tot}}=2.16$ eV. Such probabilities were calculated as follows: 33,47

$$P_R(J, |\Omega|) = \frac{1}{2 \min(J, j) + 1} \sum_{v' j'} \sum_{\Omega'} \left(|S_{v' j' \Omega', v j \Omega}^J(E)|^2 + |S_{v' j' \Omega', v j -\Omega}^J(E)|^2 \right) \quad (5)$$

and are presented for selected values of the absolute value of the helicity quantum number $|\Omega|$. Leaving aside the fact that collisions characterized by a certain value of $|\Omega|$ can only occur with values of $J \geq |\Omega|$, for every j state considered in the figure the $P_R(J, |\Omega|)$ curves are almost identical regardless of $|\Omega|$: the reaction probability corresponding to a certain value of $|\Omega|$ depends exclusively on the number of J values compatible with it and no stereodynamical

preference or bias towards any $|\Omega|$ value exists. The interpretation of these results will be facilitated if we keep in mind that large (small) values of $|\Omega|$ correspond to side-on (head-on) collisions where the internuclear axis lies perpendicular (parallel) to the k direction. Accordingly, the $P_I(J, |\Omega|)$ functions suggest that neither head-on, side-on or intermediate collisions are preferred so that the spatial distribution of the D_2 internuclear axis representing the directional preferences of the reaction should be isotropic. As a matter of fact, this can be rigorously confirmed because such distributions can be exactly calculated from the scattering matrix elements for the initial states here considered. The resulting figures, termed “internuclear axis portraits” and included in Figure 5, display the anticipated spherical shape for $j=6$ and 12 and an almost spherical one for $j=18$, where a small alignment of the internuclear axis along the k ($z=k$) direction exists. Overall, Figure 5 proves that the total integral cross section is mainly insensitive to the initial arrangement of the internuclear axis before the collision and that no directional effect lies behind the increase experienced by the reactivity, and in particular S , as the reactants get rotationally excited. At this point, we decided to resort to QCT results in order to search for alternative explanations for the increase observed in the reaction probability.

It is well known that recrossing plays an important role at high enough energies contributing to a considerable decrease of the reactivity. As discussed in Section 2.2, recrossing takes place when a trajectory crosses the same transition state an even number of times, in such a way that it ends up being inelastic. Recrossing can be easily quantified through QCT calculations, whose reliability for the present study has been already established in Figures 2 and 4. It seems pertinent to elucidate how rotational excitation influences the recrossing at a given total energy. In order to perform such quantification, we have calculated the functions $P_R(\ell)$ and $P_{cr}(\ell)$ representing the reaction probability and the probability of crossing the transition state, respectively, as a function of the ℓ quantum number. Please notice that the value of the second function is given by the sum of the probability of reaction, $P_R(\ell)$, plus the probability of having recrossing, $P_{rc}(\ell)$. These functions for $j=0, 6$ and 12 at $E_{tot}=2.16$ eV are presented in Figure 6, where the hatched red area corresponds to $P_R(\ell)$, while the blue one represents $P_{cr}(\ell)$. The shape and magnitude of the curves show unequivocally that the reduction of the recrossing with increasing j at a given E_{tot} causes the reaction probability to grow. Indeed, as can be seen in Figure 6, for medium and, especially, large values of j , the vast majority of the trajectories that cross the TS do not turn back but end up giving rise to products.

The values of the $P_{cr}(\ell)$ function for $j=0, 6, 12$ and 18 at $E_{tot}=2.16$ eV are compared in Figure 7. Although the reaction probability for $j=0$ is smaller than for $j=6$ (see Figure 6), the probability of crossing the barrier is essentially the same. It is interesting to point out that, although the $P_{cr}(\ell)$ function for $j=12$ experiences a significant decrease at the largest ℓ values, at small and medium values of ℓ the crossing probability is the same than for $j=0$, and 6. This picture changes for $j=18$ when the collision energy is so low that the effect of the effective barrier becomes significant, causing the $P_{cr}(\ell)$ function to shrink.

The analysis of trajectories allows one to visualize the cone of acceptance for the different initial rotational states. Figure 8 represents a sort of differential cross section as a function of the $\widehat{HDD}$ bending angle, α , calculated when the trajectory first crosses the TS. Notice that

what is represented is the “in plane” cone of acceptance, and that $\alpha = 180^\circ$ corresponds to a linear configuration. As can be seen, the smallest accessible bending angle (*i. e.*, the largest cone of acceptance) increases with increasing rotational energy (decreasing E_{coll}), but it does abruptly when the collision energy becomes too small. As it could be expected from the above considerations and is clearly displayed in the inset, for high j values, the reactivity shows a maximum for collinear approaches ($\alpha \sim 180^\circ$). For $j=0$, that is not longer true since collinear approaches are more prone to experience recrossing.

The overall picture that emerges is therefore as follows. Increasing collision energy promotes the reactivity as it broadens the cone of acceptance allowing more bent transition state configurations. However, for low j values at sufficiently high collision energies, recrossing becomes important enough to counteract this effect. In turn, we have shown that, under these circumstances, rotational excitation enhances the reactivity by impairing recrossing. Since at a fixed total energy, rotational excitation comes at expenses of the collision energy, the two effects counteract each other. At low (fixed) total energies the recrossing probability is small and the broadening of the cone of acceptance prevails. In contrast, at high (and fixed) total energies, the recrossing probability increases significantly and, thus, rotational excitation, which inhibits recrossing, dominates.

So far, we have concentrated on results summed over final states. Figure 9 presents the QM rotational distributions for the $\text{H}+\text{D}_2(v=0, j)$ reaction at $E_{\text{tot}}=2.16$ eV and for $j=0, 6, 12$ and 18 . Each panel refers to a different vibrational state of the products (v'). The distributions corresponding to rotationless reactants are characterized by a single maximum and possess values that decrease monotonically with v' . The interest of the figure, however, lies on the changes experienced by these distributions as j gets larger: the increase in reactivity associated to the rotational excitation of the reactants correlates with distributions which become increasingly colder, in particular for $v' > 0$, and whose cross section values are larger/smaller for small/large values of v' , to the extent that for $j=18$ three quarters of the reactivity is concentrated in $v'=0$ while hardly any products are formed in $v'=3$ and $v'=4$ (see Table 1 for the v' resolved values of the integral cross sections). These results show that rotational excitation causes colder rovibrational distributions. This effect has a similar origin than that causing the decrease of recrossing. As the rotational energy increases the chances to hit the repulsive wall after the barrier diminish rapidly. This causes, on the one hand, that recrossing becomes less likely; on the other hand, the emergence in the exit channel is more straightforward and product vibrational excitation less probable.

To further illustrate this effect, Figure 10 shows the QM product's recoil energy distributions at $E_{\text{tot}}=2.16$ eV and $j=0, 6, 12$ and 18 . These distributions were calculated by characterizing each state-to-state process through a Gaussian function centered in the corresponding value of the recoil energy (see Sec. 2.1). As a summary to the data presented in Figure 9, it is clearly shown that the amount of energy released as kinetic energy increases drastically with rotational excitation, while the probability for those collisions where the products are formed in highly excited internal states, either vibrational or rotational, approaches zero.

4 Conclusions

Motivated by the continuous flow of new results concerning the dynamics and mechanism of the $\text{H}+\text{D}_2$ reaction, we have presented an analysis of the influence of rotational excitation of the reactants on the dynamics. Our discussion has been based on QM and QCT calculations and serves to complement former studies, mainly concentrated on collisions where only the lowest rotational levels of the target molecule are populated, and to widen our understanding of the process.

We have proved that increasing the total energy by rotationally exciting the reactants is more effective when it comes to raising the reactivity than increasing the collision energy, with the proviso that the last one should be large enough as to guarantee a sufficiently large cone of acceptance. The increase in reactivity cannot be only attributed to a decrease in the prefactor that appears in the expression on the integral cross section but corresponds as well with a genuine increment of the total reaction probability. Such increment does not stem from any stereodynamical effect, as the total cross section is almost insensitive to the preparation of the reactants for all values of j .

The agreement between QM and QCT results is very good, the more so as the initial rotational state of the reactants increases. Based on this good accordance, we used QCT calculations to quantify the non-reactive recrossing as a function of j and found that the aforementioned increase in reaction probability with growing j can be explained via a decrease of the recrossing.

Finally, the explicit consideration of the internal state of the products served to prove that the rotational energy of the reactants ends up mainly as recoil energy and that the transfer to vibrational or rotational excitation of the products is increasingly inefficient as j increases.

The present study is restricted to the $\text{H}+\text{D}_2$ reaction for which the beneficial role of rotation has been found to be linked to a decrease of non-reactive recrossing. However, the conclusions are likely to be extendable to other reactions. Similar behavior can be expected for other isotopic variants of the H_3 system, such as $\text{D}+\text{H}_2$ and $\text{H}+\text{H}_2$, for which rotation favors reactivity but only at sufficiently high collision energies. For other prototypical reactions for which rotation also favors the reactivity, such as $\text{F}+\text{H}_2$, it would be interesting to examine if recrossing plays any role. For those reactions the PES is not so collinearly dominated and the cone of acceptance is broader than for the $\text{H}+\text{H}_2$ reaction. Reactions collinearly dominated with late transition states, such as $\text{Br}+\text{H}_2$, cannot be expected to give rise to substantial recrossing and rotation is likely to hamper the reactivity irrespective the collision energy.

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Figure 1.

Reactive cross section as a function of the collision energy (excitation function) for the $\text{H} + \text{D}_2(v=0, j)$ collisions and different rotational excitations of the reactants. All the cross sections are total (summed over final states) and quantum mechanical.

Figure 2. QM (black-dotted lines) and QCT (red dashed lines) excitation functions for the $\text{H} + \text{D}_2(v=0, j=0, 6, 12 \text{ and } 18)$ reactions.

Figure 3.

Total QM reactive cross section for the $\text{H}+\text{D}_2(\nu=0, j)$ collisions as a function of the rotational excitation of the reactants (j) and three total energies: $E_{\text{tot}}=0.70$ eV (top panel), $E_{\text{tot}}=1.20$ eV (middle panel), and $E_{\text{tot}}=2.16$ eV (bottom panel). The value of the collision energy is also indicated.

Figure 4.

Total QM (black-dotted lines) and QCT (red dotted lines) probability functions $P_R(\ell)$ for the $\text{H}+\text{D}_2(v=0, j=0, 6, 12 \text{ and } 18)$ reactions at $E_{\text{tot}}=2.16$ eV. The values of the probability functions have been multiplied by $(2\ell+1)$ so as to reflect the contribution of each partial wave to the integral cross section. S indicates the value of $\sum_{\ell} (2\ell+1)P_r(\ell)$ for each of the initial states considered in the figure.

Figure 5.

Total QM $P_R(J, |\Omega|)$ probability functions for the $\text{H} + \text{D}_2(\nu=0, j=6, 12 \text{ and } 18)$ reactions at $E_{\text{tot}}=2.16 \text{ eV}$. The internuclear axis portraits reflecting the preferred molecular arrangement for each initial state of the reactants are also included.

Figure 6.

Total QCT $P_{\text{R}}(l)$, $P_{\text{rc}}(l)$, and $P_{\text{cr}}(l)$ (see the text) opacity functions for the $\text{H} + \text{D}_2$ ($v=0$, $j=0$, 6 and 12) reactions at $E_{\text{tot}}=2.16 \text{ eV}$. Recrossing amounts to 28% for $j=0$, 21% for $j=6$ and 7.2% for $j=12$ of those trajectories that cross the transition state.

Figure 7. Total QCT $P_{\text{cr}}(l)$ (see the text) probability functions for the $\text{H}+\text{D}_2$ ($v=0$, $j=0, 6, 12$ and 18) reactions at $E_{\text{Tot}}=2.16$ eV.

Figure 8.

QCT differential cross section as a function of the $\widehat{\text{HDD}}$ bending angle, α , calculated when the trajectory first crosses the TS. Results are shown for $j=0$ (solid black line), $j=6$ (red dashed-dot line), and $j=12$ (dashed blue line) at the total energy $E_{\text{tot}}=1.20$ eV. The normalized (to one in the maximum) distributions are shown as an inset. This inset clearly shows that for high j the differential cross sections shows a maximum for collinear approaches, while for $j=0$ it prefers more sideways encounters (due to recrossing).

Figure 9.

QM rotational distributions for the HD product vibrational states, $v'=0-4$, resulting from the $\text{H}+\text{D}_2(v=0, j)$ reaction with $j=0$ (black open squares), $j=6$ (blue open circles), $j=12$ (green solid squares) and $j=18$ (red solid circles), at the total energy $E_{\text{tot}}=2.16$ eV.

Figure 10. QM product's translational energy distributions of the products for the $\text{H}+\text{D}_2(\nu=0, j=0, 6, 12$ and $18)$ reactions at $E_{\text{tot}}=2.16$ eV.

Table 1

QM integral cross section (in $\text{\AA}^2$) resolved in v' for the $\text{H}+\text{D}_2(v=0, j) \rightarrow \text{HD}(v', j') + \text{D}$ reaction at $E_{\text{tot}}=2.16$ eV and the same reactants rotational states considered in Figure 9.

v'/j	$v'=0$	$v'=1$	$v'=2$	$v'=3$	$v'=4$	all v'
$j=0$	0.584	0.371	0.182	0.0676	0.0070	1.212
$j=6$	0.771	0.425	0.195	0.0734	0.0094	1.474
$j=12$	1.389	0.465	0.165	0.0568	0.0104	2.086
$j=18$	1.812	0.523	0.095	0.0156	0.0016	2.447