Effects of the rotational excitation of D_2 and of the potential energy surface on the $H^+ + D_2 \rightarrow HD + D^+$ reaction

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The $H^+ + D_2 \rightarrow HD + D^+$ reaction has been theoretically investigated by means of an exact quantum mechanical approach, a quasiclassical trajectory method, and two statistical methods based in the propagation of either wave functions or trajectories. The study addresses the possible changes on the overall dynamics of the title reaction when the D_2 diatom is rotationally excited to its $v=0$, $j=1$ state. In addition, the reactivity for the ground rotational state on two different potential energy surfaces (PESs), namely, the surface by Aguado *et al.* [J. Chem. Phys. **112**, 1240 (2000)] and the PES by Kamisaka *et al.* [J. Chem. Phys. **116**, 654 (2002)], is examined. Reaction probabilities and cross sections at 0.524 and 0.1 eV collision energies are calculated. The major differences with respect to the reaction initiated with D_2 in its ground rovibrational state are observed for the lowest collision energy $E_c=0.1$ eV. Differential cross sections have been found to depend to some extent on the PES employed. In addition, at $E_c=0.1$ eV further discrepancies in the total and rotational cross sections are noticeable. © 2009 American Institute of Physics. [DOI: 10.1063/1.3183538]

I. INTRODUCTION

In the last few years, the dynamics of the $H^+ + H_2$ reaction and its corresponding isotopic variants has been largely investigated. Recent experimental studies by means of the Rydberg H-atom translational spectroscopy technique¹ have enabled the analysis of translational energy distributions, time-of-flight (TOF) spectra, differential cross sections (DCSs), and relative rotational populations for the $H^+(n) + D_2$ reaction,^{2–5} where $H^+(n)$ corresponds to a highly excited Rydberg H atom. Due to this high excitation, $H(n \sim 35)$, the Rydberg excited H atom behaves in practice as an ion, H^+ , during the collision with D_2 . Motivated for this experimental work, comparisons with theoretical results obtained in exact quantum mechanical (EQM) (that is, fully converged close coupling) and quasiclassical trajectory (QCT) calculations were soon reported.^{3,5–7} QCT angular distributions were found to be more symmetric about the sideways scattering direction ($\theta \sim 90^\circ$) than the corresponding experimental result at a collision energy of $E_c=0.524$ eV.³ Hayes and Skodje⁶ showed that at least part of the apparent slight asymmetry of the measured DCS could be attributed to an attenuation of the TOF signal as a function of the scattering angle due to the finite lifetime of the Rydberg state. The predictions of a statistical quantum method^{8,9} (SQM) were in good

agreement⁷ with the total and vibrationally resolved experimental angular cross sections reported by Song *et al.*,³ although the limited angular range covered in the experiment ($20^\circ \leq \theta \leq 130^\circ$) precluded to extract any conclusion regarding the pronounced peaks of the statistical result at the forward ($\theta \sim 0^\circ$) and backward ($\theta \sim 180^\circ$) scattering directions. The comparison was then completed with the distributions obtained with a time-independent (TI) EQM method, a quantum wave packet (WP) approach, and a QCT calculation.⁵ Monte Carlo simulations of the experimental kinetic energy spectra at different laboratory (LAB) angles Θ_{LAB} were calculated using sets of the DCSs obtained with the TI EQM, WP, QCT, and SQM approaches. The corresponding theoretical spectra were found to provide an overall good description of the experimental result, especially at sideways scattering ($\Theta_{LAB}=52^\circ$), although a complete quantitative agreement between the measured and the simulated spectra was jeopardized by the presence of a significant contribution from inelastic processes in the experimental findings.

These comparisons between different theoretical approaches reveal two interesting features. The QCT method seriously underestimates the probability as compared to the EQM calculation. Thus, reaction probabilities obtained with the trajectory method at specific values of the collision energy for the $H^+ + H_2$ (Ref. 10) and $H^+ + D_2$ (Ref. 5) reactions clearly diverged from the EQM results as the total angular momentum J increases. Authors of Ref. 5 found a significant number of trajectories which, despite to reach the potential well region, return to the reagents as J increases beyond a

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purely statistical prediction. In a separate work, Bonnet¹¹ proposed an adiabaticity correction to the Gaussian weighted trajectory method employed in the QCT calculation, leading to a better agreement with EQM probabilities.

The other issue as regard the comparison with the EQM results concerns the apparent validity of statistical techniques to describe the dynamics of the H_3^+ atom-diatom collisions. The participation of a complex-forming mechanism in the course of this kind of reactions, especially in the low energy regime, has been proposed in previous investigations.^{12–16} Such a reaction pathway is clearly supported by the existence of a deep potential well (~ 4.3 eV) and the absence of any barrier at the entrance channel. Besides earlier statistical estimates of cumulative reaction probabilities for $J=0$,^{17,18} SQM predictions have been found to reproduce fairly well probabilities, rotational integral cross sections (ICSs), and DCSs.^{5,10} The trajectory-based version of this method, the statistical QCT (SQCT) approach, which properly takes into account the triatomic parity conservation^{19,20} and the reagent and product zero point energies, has been recently applied to study the $\text{H}^+ + \text{H}_2$ and $\text{H}^+ + \text{D}_2$ reactions.^{21,22} The results obtained with the SQCT method were in perfect agreement with those calculated with the coupled-channel version of the SQM approach.²² In both cases, the DCSs exhibit pronounced peaks at extreme forward and backward scattering directions similar to those observed in the EQM angular distributions.

The study of highly excited rotational spectra of the H_3^+ has motivated that numerous groups have focused their efforts in the development of global analytical representations of the potential energy surface (PES) for this system. Some of the most recent examples can be found in Refs. 18 and 23–26. In our previous investigations on the reactive processes associated with the H_3^+ system and its isotopic variants,^{5,7,10} we have used the global adiabatic PES by Aguado *et al.* (hereafter ARTSP PES).²⁴ Those studies have been limited to values of the energy far below the electronic curve crossing which occurs at around 1.8 eV above the $\text{H}^+ + \text{H}_2$ asymptotic region. Beyond that crossing, the ion-atom collision may lead, besides the reactive non-charge-transfer (RNCT) channel considered here, to a two other different product channels depending on whether there is only a charge-transfer process (the nonreactive charge-transfer channel) or the reaction is accompanied by a transfer of the charge from the reactant ion to the product diatom (the reactive charge-transfer channel).^{17,18,27–37} Previous studies concerning the RNCT channel on the title reaction⁵ suggest that at least some fine details of the process may be influenced by the PES employed in the theoretical calculations. Thus, the precise description of the large number of resonances existing in the reaction probabilities or the extremely oscillating shape of the opacity functions in terms of J could possibly depend on the topology of the surface. In order to investigate this issue, in this work, we have also used the ground electronic state surface by Kamisaka *et al.* (hereafter KBNN PES),¹⁸ based on the diatomics-in-molecules method, which used *ab initio* data from Ref. 38.

In the crossed molecular beam studies on the $\text{H}^+ + \text{D}_2$ reaction, *ortho*- D_2 was cooled in the supersonic expansion

yielding a population of at least 97.5% in its rovibrational ground state ($v=0, j=0$).⁴ The theoretical calculations performed to reproduce the experimental findings were restricted therefore to this initial state for the D_2 molecule.⁵ However, up to our knowledge, no calculations have been previously published on the role of vibrational or rotational excitation of the reagents on the overall dynamics of the title reaction. WP investigations of the $\text{H}^+ + \text{D}_2$ (Ref. 31) and $\text{D}^+ + \text{H}_2$ (Ref. 30) reactions restricted to a zero total angular momentum and covered an energy regime, $E_c > 1.7$ eV, further above the energies considered here.

In this work, we address the possible effects of the rotational excitation of the D_2 molecule in the $v=0, j=1$ initial state. The endothermicity of the reaction initiated with this rotational excitation in the D_2 reagent is slightly lower than for the $v=0, j=0$ state, thus yielding a reduction on the corresponding threshold for reaction. Whether or not this might lead to noticeable differences between the dynamics of both collisions is yet to be analyzed. This investigation has been performed with the same PES than in Ref. 24; namely, the ARTSP surface.

Reaction probabilities and product cross sections at the two collision energies of 0.1 and 0.524 eV have been calculated by means of a TI EQM approach, the QCT method, and two statistical models, the above mentioned SQM and SQCT approaches. The theoretical bases of these methods are explained in Sec. II; results are shown in Sec. III and discussed in Sec. IV. Finally conclusions are presented in Sec. V.

II. THEORY

A. Exact quantum method

Accurate quantum mechanical (QM) scattering calculations have been performed by using a TI method based on body-frame democratic hyperspherical coordinates. This method was presented in detail in Ref. 39 and has already been used for our previous study on $\text{H}^+ + \text{D}_2$ (Ref. 5) and for its isotopic variant $\text{H}^+ + \text{H}_2$.¹⁰ This method has also previously proved successful in describing the quantum dynamics of atom-diatom insertion reactions, such as $\text{N}(^2D) + \text{H}_2 \rightarrow \text{NH} + \text{H}$,⁴⁰ ultracold alkali-dialkali collisions,⁴¹ and more recently OH+atom reactions.⁴² Thus, a brief summary will suffice here. At each hyper-radius, the scattering wave function is expanded on a set of hyperspherical adiabatic states of a reference Hamiltonian $H = T + V$ which incorporates the kinetic energy T arising from deformation at fixed hyper-radius and the potential energy V . The expansion coefficients are the solution of a set of coupled second-order differential equations which are solved using the Johnson–Manolopoulos log-derivative propagator.⁴³ For a total angular momentum $J=0$, 211 states dissociate at large hyperradius into the D_2 (28,26,24,22,20,16,14,10,6) rovibrational set (this notation indicates the largest rotational level j for each vibrational manifold $v=0, 1, \dots, 8$) and the HD (23,21,19,16,14,11,8) rovibrational set. Propagation goes from 0.26 Å up to the asymptotic matching distance at 8.46 Å, where the S matrix is extracted. When computing $J > 0$ partial waves, we have considered the components from 0 to 28 in the close-

coupling expansion, to obtain accurate ICSs and DCSs. Thus, the number of coupled equations increases from 211 for $J=0$ to 2211 for $J \leq 28$.

B. Statistical methods

Statistical calculations have been performed in the present study by means of the SQM^{8,9} and SQCT^{21,22} approaches. These methods are based on the assumption of the occurrence of a complex-forming mechanism during the course of the reaction. In both cases, the state-to-state reaction probability is calculated as the product of the capture probability for the complex to be formed from the initial rovibrational state of the reactant channel and the fraction of complexes which decay via the final state of the products. The calculation of DCSs is performed by invoking the random phase approximation which neglects the interference terms between different values of the total angular momentum J .⁹ As extensively discussed before, the DCSs so obtained are symmetric about the sideways scattering direction. The only significant difference between both models is that wave functions are propagated in the case of the QM version of the method, solving the corresponding coupled equations, while in the SQCT approach, classical equations of motion are solved up to the capture point.

The SQM has been successfully applied to study atom-diatom reactions in which the formation of long-lived intermediate complexes are expected to play an important role. A review of previous applications can be found in Ref. 44. In turn, the SQCT approach has been found to produce results in an almost perfect agreement with the predictions of its QM counterpart for both the title reaction^{21,22} and collisions between an electronically excited atom of C, N, O, or S with molecular hydrogen.⁴⁵

Calculation details regarding the values of the capture radii which define the region where the intermediate complex is supposed to exist and of the potential energy at the point in which the trajectory is captured have been given in our previous study of different isotopic variants of the H₃⁺ system.²²

C. QCT method

The QCT calculation is similar to that performed on our previous works on the title reaction. Batches of 3×10^5 trajectories at the two collision energies of 0.1 and 0.524 eV on both PESs for D₂($v=0$, $j=0,1$) were run following the procedures described in detail elsewhere.⁵

The integration step size in the trajectories was chosen to be 3×10^{-17} s. This guarantees a total energy conservation better than one part in 10^4 and conservation of total angular momentum better than one part in 10^6 . The trajectories were started at a distance between the incoming atom and the center of mass of the diatomic of 12 Å, given the long-range interaction in the entrance channel of the potential surface. The maximum impact parameter $b_{\max}$ has been 5 Å at $E_c = 0.1$ eV and 3.7 Å at 0.524 eV.

As in previous works,^{46,47} we have used a Gaussian-weighted binning (GWB) procedure, in which a Gaussian function centered at the quantal action and with a given

width has been used to weight the trajectories following the criteria that the closer the vibrational action of a given trajectory to the nearest integer, the larger the weighting coefficient for that trajectory. In particular, in the present work we have used a full width at half maximum for the Gaussian functions of 0.1.

Using the GWB procedure, DCSs were calculated at the two collision energies for every rovibrational state of the HD product molecule by the method of moments expansion in Legendre polynomials. The Smirnov–Kolmogorov test was used to decide when to truncate the series. The calculation of reaction probabilities has been performed by the method of moment expansion in Legendre polynomials and employing the GWB procedure commented on above to assign final vibrational states.

Reaction probabilities for the D₂($v=0$, $j=1$) case were determined following the procedure described in Ref. 48.

III. RESULTS

We start our study by considering the collisions of the H⁺ ion with the D₂ molecule on its first rotationally excited state ($v=0$, $j=1$). These calculations have been performed on the ARTSP surface by Aguado *et al.*²⁴ The other PES considered here, the KBNN surface by Kamisaka *et al.*,¹⁸ is employed in the study of the H⁺+D₂($v=0$, $j=0$) reaction. The most prominent dynamical features on this study will be then compared at the end of the section with findings of our previous study on the title reaction⁵ on the ARTSP surface.

A. Dynamics of the reaction with D₂($v=0$, $j=1$)

We have employed the EQM method discussed in Sec. II A to calculate the opacity function $P(J)$ or reaction probability in terms of the total angular momentum J of the H⁺+D₂($v=0$, $j=1$) reaction at the collision energy $E_c = 0.524$ eV. This is the average collision energy of the experiments reported in Refs. 2–4. The corresponding comparison between the EQM results and those obtained with the SQM, SQCT, and QCT approaches are shown in Fig. 1.

The EQM $P(J)$ function displays a slow increase with the total angular momentum beyond $J \approx 15$, reaching a maximum at $J \approx 43$ –44 after some noticeable oscillations. The maximum occurs just before the reaction probability ends almost abruptly at the maximum value of J , $J_{\max} \approx 50$, and is less pronounced than the feature observed for the reaction initiated with the D₂ diatom in its rotationless state. Apart from this, the overall shape of the $P(J)$ function is quite similar to the results for D₂($v=0$, $j=0$).⁵ The predictions obtained by means of the SQCT and SQM approaches agree extremely well and, despite some overestimation, manage to give a reasonable average description of the EQM reaction probability. In turn, the QCT result reproduces the exact probability better than any of the statistical methods up to $J \approx 18$ –19, but remains clearly below for the higher values of the total angular momentum.

A similar comparison for the case of the rotationally resolved ICS of the H⁺+D₂($v=0$, $j=1$) → HD($v'=0$, j')+D⁺ reaction at the same collision energy $E_c = 0.524$ eV is shown in Fig. 2.

FIG. 1. Reaction probability in terms of the total angular momentum J for the $\text{H}^+ + \text{D}_2(v=0, j=1)$ reaction at $E_c=0.524$ eV calculated on the ARTSP PES (Ref. 24) by means of the EQM (circles), SQM (red squares), SQCT (green triangles), and QCT (in blue line) approaches.

The EQM rotational distribution shares several features in common with the corresponding cross section obtained for the reaction with $\text{D}_2(v=0, j=0)$. In both cases, the population of the rotational states of the $\text{HD}(v'=0, j')$ products increases with j' , reaching a maximum value at $j' \sim 6$. Then it decreases rapidly with an almost negligible population at $j'=10$. Moreover, although the actual population of the different j' states differ in both cases, the value of the cross section summed over all the rotational states for $\text{HD}(v'=0)$ seems to depend weakly on the initial state of the D_2 diatom: $18.35 \text{ \AA}^2$ for $j=0$ and $17.71 \text{ \AA}^2$ for $j=1$.

There are no noticeable differences between the SQCT and SQM distributions, which, however, turn out to be slightly larger than the EQM values. As a result, the ICS for the formation of $\text{HD}(v'=0)$ at $E_c=0.524$ eV according to

FIG. 2. Rotational cross sections, in $\text{\AA}^2$, for the $\text{H}^+ + \text{D}_2(v=0, j=1) \rightarrow \text{HD}(v'=0, j') + \text{D}^+$ reaction at $E_c=0.524$ eV, calculated with the ARTSP PES (Ref. 24). EQM results are shown with circles, SQM with red squares, SQCT with green triangles, and QCT with blue triangles.

FIG. 3. DCSs, in $\text{\AA}^2 \text{sr}^{-1}$, for the $\text{H}^+ + \text{D}_2(v=0, j=1)$ reaction calculated at $E_c=0.524$ eV on the ARTSP PES with the EQM (black solid line), SQM (red dashed-dotted line), SQCT (green dashed line), and QCT (blue dotted line) approaches. In the inset, an amplified view of the backward scattering direction. The SQM and SQCT results are barely distinguishable.

the statistical approaches ($\sim 20 \text{ \AA}^2$) exceeds the exact result. QCT cross sections are markedly smaller than the QM distribution, similarly as to what has been observed in the reaction initiated with $\text{D}_2(v=0, j=0)$.

One of the observables theoretically calculated to compare with recent experimental findings is the DCS at the average collision energy of 0.524 eV. Although, given the conditions of the experiment, the angular distributions for the reaction initiated with the ground rovibrational state of D_2 would suffice; in the present study, we have employed the theoretical methods described in Sec. II to calculate the DCS for the $\text{H}^+ + \text{D}_2(v=0, j=1)$ reaction. The results are shown in Fig. 3.

Whereas the predictions from the two statistical techniques are in a good agreement with the TI distribution, especially at the forward and backward directions, the QCT result clearly underestimates the magnitude of the DCSs over the whole angular range with respect to the corresponding EQM results. The same feature was also observed for the case of the $\text{H}^+ + \text{D}_2(v=0, j=0)$ reaction at the same energy $E_c=0.524$ eV.⁵ Results reported in Ref. 5 showed a similar SQM versus EQM accord at the sideways region, but the statistical predictions for the cross section at both the forward and backward scattering directions were clearly larger than the values obtained with the EQM calculation. Despite the EQM distribution does not significantly change (apart from a more pronounced overall oscillating shape) with the initial rotational state j of D_2 , a larger effect is observed in the statistical results. In particular, more pronounced peaks at the forward and backward scattering directions are found for $\text{D}_2(v=0, j=0)$. The origin of these differences can be traced back to the larger effect introduced by the triatomic parity conservation for the $j=0$ case, as discussed in Ref. 22.

A similar analysis has been performed at a lower collision energy, $E_c=0.1$ eV. The comparison of the reaction probabilities at such energy in terms of the total angular mo-

FIG. 4. Same as Fig. 1 at 0.1 eV collision energy.

mentum obtained with the different methods described in Sec. II is shown in Fig. 4. The EQM $P(J)$ seems to exhibit more moderate oscillations than the probability for the $\text{H}^+ + \text{D}_2(v=0, j=0)$ case as J increases. Moreover, at wide ranges of the total angular momentum (in particular, $0 \leq J \leq 6$ and $18 \leq J \leq 23$) the probability for $\text{H}^+ + \text{D}_2(v=0, j=1)$ is clearly larger. The statistical results give a fair average description of the exact result. In turn, the QCT probability remains at noticeably lower values than the EQM result. Although the differences are certainly not large at low total angular momentum, $J \leq 10$, with increasing J , it becomes evident that the result obtained with the trajectory approach underestimates the QM probability. In this sense the discrepancies between the EQM and QCT probabilities are more pronounced than in the previously investigated case with the rotationless D₂ reactant.⁵

In Table I, we report the values of the rotationally resolved ICS at the 0.1 eV collision energy. The EQM cross sections and the statistical predictions obtained with the SQM and SQCT approaches are in a fairly good agreement. The total cross section for the $\text{H}^+ + \text{D}_2(v=0, j=1) \rightarrow \text{HD}(v'=0) + \text{D}^+$ reaction ($v'=0$ being the only open channel at this energy), according to the EQM result, 27.4 Å², is larger than the value for the corresponding collision with D₂($v=0, j=0$), 23.6 Å².⁵

The DCS at $E_c=0.1$ eV calculated by means of the EQM, the QCT, and the two statistical methods are compared in Fig. 5. One of the most remarkable things regarding the EQM angular distribution is the noticeable reduction in

TABLE I. Rotationally resolved cross sections, in Å², for the $\text{H}^+ + \text{D}_2(v=0, j=1) \rightarrow \text{HD}(v'=0, j') + \text{D}^+$ reaction at $E_c=0.1$ eV calculated by means of the EQM, SQM, and SQCT approaches on the ARTSP PES. The total ICS summed on all the rotational states is also included.

	EQM	SQM	SQCT
$j'=0$	4.3	4.8	4.8
$j'=1$	11.7	12.2	12.5
$j'=2$	11.2	11.8	11.9
Total	27.2	28.8	29.2

FIG. 5. DCS on the ARTSP PES at 0.1 eV collision energy. Colors and lines are as in Fig. 3. The inset amplifies the forward scattering direction.

the cross section in both the forward and backward directions in comparison with the previously reported situation observed for the $\text{H}^+ + \text{D}_2(v=0, j=0)$ reaction.⁵ The degree of asymmetry about $\theta=90^\circ$ is, however, not too large with a quotient between the forward and the backward peaks of about 1.3, somehow similar to the case of the collision of H⁺ with D₂ in its rovibrational ground state (1.5). The agreement of the statistical predictions with the EQM angular cross section is noticeable. The DCS obtained with the trajectory calculation, on the contrary, remains clearly too low in comparison with the QM result.

B. Comparison between two PESs for D₂($v=0, j=0$)

As mentioned in Sec. I, in order to complete the present study on the $\text{H}^+ + \text{D}_2$ reaction, we have used a different PES, the KBNN surface¹⁸ for the reaction initiated with the D₂ diatom in its ground rovibrational state. The comparison with some of the findings of our previous work presented in Ref. 5 will enable the investigation of the possible effects that different surfaces might introduce.

In particular, the reaction probability in terms of the total angular momentum for the $\text{H}^+ + \text{D}_2(v=0, j=0)$ reaction has been calculated on the KBNN surface at $E_c=0.524$ eV by means of the EQM approach. The comparison with the corresponding opacity function calculated on the ARTSP PES (Ref. 5) is included in Fig. 6.

The EQM results for both surfaces exhibit a strongly oscillating behavior as J increases with no significant overall differences between the two corresponding $P(J)$ probabilities. The results obtained with the KBNN PES (Ref. 18) remain below the probability found on the ARTSP surface for the high values of J , $40 \leq J \leq 43$ before the final fall off at $J_{\text{max}}=47$. Moreover, no maximum at $J=44$ is observed, as in the calculation performed on the latter PES.

The statistical results included in Fig. 6 correspond to the SQM probabilities on both surfaces. Given the almost perfect agreement found with its SQCT version, we limit ourselves hereafter to present the SQM results. As expected,

FIG. 6. Comparison between the reaction probabilities for the $\text{H}^+ + \text{D}_2(v=0, j=0) \rightarrow \text{HD} + \text{D}^+$ reaction obtained at $E_c=0.524$ eV, in terms of J , with the EQM approach on the KBNN PES (Ref. 18) (empty black squares) and on the ARTSP PES (Ref. 24) (full red squares) adapted from Ref. 5. SQM results for the KBNN PES (solid blue circles) and for the ARTSP PES (empty green circles) are included for comparison.

the statistical predictions hardly change with the use of different PESs and provide, in both cases, a reasonably good description of the EQM $P(J)$ function at $E_c=0.524$ eV.

The corresponding comparison for the rotational ICSs, shown in Fig. 7, deserves similar comments. No further differences are observed between the distributions obtained in calculations with the two PESs. In addition, the SQM results are found to slightly overestimate the EQM cross sections only for some particular $\text{HD}(v'=0, j')$ final states, $j'=3-5$, providing nevertheless a fairly acceptable reproduction of the EQM result.

The sum over all the available final j' rotational states of the $\text{HD}(v'=0)$ manifold is $18.27 \text{ \AA}^2$ for the cross section obtained on the KBNN surface and $18.35 \text{ \AA}^2$ for the ARTSP

FIG. 7. Rotationally resolved cross sections, in $\text{\AA}^2$, for the $\text{H}^+ + \text{D}_2(v=0, j=0) \rightarrow \text{HD}(v'=0, j') + \text{D}^+$ reaction at $E_c=0.524$ eV obtained with the EQM and SQM approaches on the KBNN and ARTSP PESs (from Ref. 5). Lines and colors are as in Fig. 6.

FIG. 8. DCS, in $\text{\AA}^2 \text{sr}^{-1}$, for the $\text{H}^+ + \text{D}_2(v=0, j=0) \rightarrow \text{HD} + \text{D}^+$ reaction at $E_c=0.524$ eV obtained with the EQM approach on the KBNN (red solid line) and on the ARTSP (black dotted line) PESs. The SQM result on the former surface is included in blue dashed line. The inset corresponds to a detailed zoom of the backward scattering direction.

PES, thus revealing a similar reactivity on the two surfaces at this particular energy. The corresponding SQM values, 20.36 and $20.23 \text{ \AA}^2$, for the KBNN and ARTSP surfaces, respectively, indicate the above mentioned overestimation of some of j' levels. For the other vibrational product channel, $\text{HD}(v'=1)$, differences between the ICS calculated with both PESs are also small: The EQM method predicts an ICS of $0.11 \text{ \AA}^2$ on the KBNN surface, whereas, the use of the ARTSP PES leads to a value of $0.19 \text{ \AA}^2$. The ICS for the production of HD in its first excited vibrational state obtained with the SQM approach on the KBNN surface is $0.15 \text{ \AA}^2$, while for the ARTSP PES is $0.22 \text{ \AA}^2$.

The analysis of the DCSs at $E_c=0.524$ eV, however, indicates some interesting differences for each surface. The corresponding comparison is shown in Fig. 8 and reveals that despite both angular distributions are certainly similar over the majority of the angular directions, the results for the scattering at $\theta \approx 0^\circ$ are significantly different. Whereas the DCS on the ARTSP PES at the forward direction is about $12.5 \text{ \AA}^2 \text{sr}^{-1}$, the result on the KBNN surface is more than twice this value, $\sim 26 \text{ \AA}^2 \text{sr}^{-1}$, which are indeed very close to the statistical prediction for both forward and backward peaks in the KBNN PES ($24.4 \text{ \AA}^2 \text{sr}^{-1}$). The statistical calculation on the ARTSP surface yields an almost identical DCS, and therefore has not been included in Fig. 8.

The agreement with the SQM angular distribution also extends to the overall shape of the EQM DCS, almost symmetric around the sideways direction. On the ARTSP PES, differences between the EQM and SQM distributions obtained are found, on the contrary, to be larger.⁵

A further investigation of the possible differences introduced by the use of distinct PESs can be performed at the state-to-state level by inspection of the DCSs for $\text{H}^+ + \text{D}_2(v=0, j=0) \rightarrow \text{HD}(v'=0, j') + \text{D}^+$ reactions. In particular, the comparison between the angular cross sections for

FIG. 9. Comparison between the state-to-state DCSs, measured in $\text{\AA}^2 \text{sr}^{-1}$, for the $\text{H}^+ + \text{D}_2(v=0, j=0) \rightarrow \text{HD}(v'=0, j'=1, 3, 5, 7) + \text{D}^+$ reaction obtained with the EQM approach on the KBNN surface (in red solid line), the EQM on the ARTSP surface (in black dotted line), and the SQM approach also on the KBNN PES (in blue dashed line).

some final rotational states $j'=1, 3, 5$, and 7 for both the KBNN and ARTSP PESs obtained by means of the EQM method is shown in Fig. 9.

The formation of HD seems to be accompanied, according to the calculations performed on the KBNN surface, with a more marked preference either for the scattering along the forward direction (see the $j'=1$ and 3 cases) or for the backward direction (as for $j'=5$ and 7). The corresponding DCSs for the ARTSP surface are more symmetric and only the cases $j'=5$ and $j'=7$ show a pronounced peak at the backward or forward direction, respectively. These differences with respect to the state-to-state DCSs obtained with the ARTSP surface also explain the larger values of the total angular cross sections for the forward and backward peaks (see Fig. 8) calculated with the KBNN PES. Although the angular distributions obtained with the SQM on the latter surface provide a good average description over most scattering angles the statistical predictions are certainly not too precise at either the forward or backward directions in some cases. Thus, significant deviations from the EQM cross sections at, at least, one of the above mentioned scattering directions, are observed for all the HD rotational states except for $j'=3$ (and $j'=4$ not shown here). These differences observed at the state-to-state level seem to suggest some dynamical mechanisms unsuitable of a statistical description, which, however, do not preclude a better overall agreement between the EQM and SQM total DCS.

Besides the theoretical study of the dynamics of the title reaction at $E_c=0.524$ eV, the energy of the existing experimental work on this system,²⁻⁴ our previous study also considered a lower energy, 0.1 eV collision energy. It is at this such low energy regime where one would expect to find more evident effects on the various observables if the differences between the two surfaces employed here were not sub-

stantially large. Calculations on the KBNN PES at 0.1 eV are therefore aimed to detect specific peculiarities with respect to the ARTSP surface which are not manifested in the results obtained at 0.524 eV. In particular, the $P(J)$ reaction probabilities on both surfaces are shown in Fig. 10.

The EQM reaction probabilities obtained in the two PESs considered in this work display a good overall agreement. Existing maxima and minima in the oscillatory trend observed for the $P(J)$ function seem to match fairly well for specific ranges of J , as, for example, $0 \leq J \leq 5$ and $13 \leq J \leq 20$. However, a quite remarkable discrepancy between both sets of probabilities is found for the highest values of the total angular momentum $J \geq 26$. The statistical predictions are also affected, at this collision energy of 0.1 eV, by

FIG. 10. Same as Fig. 6 for $E_c=0.1$ eV.

TABLE II. ICS, in $\text{\AA}^2$, for the $\text{H}^+ + \text{D}_2(v=0, j=0) \rightarrow \text{HD}(v'=0, j') + \text{D}^+$ reaction at 0.1 eV collision energy calculated, employing the surface by KBNN (Ref. 18) and the PES by ARTSP (Ref. 24) by means of the EQM, SQM, and SQCT approaches.

	EQM		SQM	
	KBNN PES	ARTSP PES	KBNN PES	ARTSP PES
$j'=0$	8.53	6.24	8.95	8.57
$j'=1$	8.19	10.61	10.11	11.91
$j'=2$	4.15	6.74	5.65	8.77
Total	20.87	23.59	24.71	29.25

this different behavior depending on the PES employed in the calculation. Thus, the SQM probabilities reproduce the distinct reactivity for $J \geq 26$ found with the EQM approach on each surface.

The values of the ICS for the rotational states j' of the vibrationless state $\text{HD}(v'=0)$ obtained on both PESs with the EQM and SQM approaches are presented in Table II. The EQM calculations on the two surfaces yield rotational distributions with noticeable discrepancies for all the j' states. Similar deviations are found between the statistical predictions on each PES. The SQM total ICSs, shown in Table II, are slightly larger than the EQM results on both the KBNN and ARTSP surfaces. Since the statistical model only samples the exit and entrance valleys, the observed discrepancies between the results on both PESs are indicative of some differences in these regions outside the well. This point will be examined in more detail in Sec. IV.

Finally, the DCS at $E_c=0.1$ eV is reported in Fig. 11. The EQM calculation on the KBNN surface yields an angular distribution with a more marked preference for the forward scattering direction than the result obtained on the ARTSP surface, also shown in the figure. The statistical DCS on the KBNN PES turns out to be smaller in both the forward and backward peaks. A similar comparison on the surface by Aguado *et al.*, however, reveals that the SQM provides a better description of the EQM result.

FIG. 11. Same as Fig. 8 for $E_c=0.1$ eV. SQM result on the ARTSP PES (in dash-dotted green line) has been taken from Ref. 5.

IV. DISCUSSION

The goal of this paper is twofold. On the one hand we intend to investigate the effect on the overall dynamics of the $\text{H}^+ + \text{D}_2 \rightarrow \text{HD} + \text{D}^+$ reaction when the D_2 diatom is rotationally excited to its $v=0, j=1$ state. On the other hand, and due to the apparent sensitivity of the reactivity with small changes in the collision energy, we have undertaken a comparison of the results obtained employing two of the available global PESs for the system: The KBNN surface from Ref. 18 and the ARTSP PES.²⁴

The calculation of reaction probabilities and product cross sections at the 0.524 eV collision energy by means of the EQM approach reveals that no significant differences are found when D_2 is promoted to its first excited rotational state with respect to the $\text{H}^+ + \text{D}_2(v=0, j=0)$ process. Consequently, a possible contribution from $\text{D}_2(v=0, j=1)$ is expected to be hardly detectable in a given experiment. As already mentioned in Sec. III, the situation for the lowest collision energy investigated here, $E_c=0.1$ eV, is somehow different with an angular distribution exhibiting larger cross sections at the forward and backward peaks when the reaction is initiated with $\text{D}_2(v=0, j=0)$. The same feature is also found for the SQM results for both energies. Cross sections for the formation of HD in its ground vibrational state $\text{HD}(v'=0)$ seem to be independent on the specific initial rotational state of D_2 at $E_c=0.524$ eV. At $E_c=0.1$ eV, however, a difference between the $j=0$ and $j=1$ cases of about 3 $\text{\AA}^2$ (in favor of $j=1$) and 2 $\text{\AA}^2$ (in favor of $j=0$) is found for the EQM and SQM results, respectively.

In this sense, the present results bare some resemblance with the findings of similar investigations on reactions with a significant participation of complex-forming mechanisms in the overall dynamics. More prominent peaks at both the forward and backward scattering directions were obtained with the SQM approach for the $\text{C}(^1D) + \text{D}_2(v=0, j=0)$ collision than in the case of $\text{C}(^1D) + \text{D}_2(v=0, j=1)$ (Refs. 45 and 49) and, for the $\text{S}(^1D) + \text{H}_2$ (Ref. 47) or $\text{N}(^2D) + \text{H}_2$ reactions,^{50,51} the DCSs display a slightly more pronounced peak at $\theta \sim 0^\circ$ when the reaction was initiated from the rotational ground state of the diatom. Product rovibrational cross sections at fixed values of the energy were found not to depend significantly on the specific value of the initial rotational state j for this sort of reactions.^{47,49,51,52} A similar investigation by means of QCT and SQM methods on the $\text{N}(^2D) + \text{H}_2$ collision concluded that the major dependence on the initial rotation state j is found for the $\text{N}(^2D) + \text{HD}(v=0, j=0-3) \rightarrow \text{NH} + \text{D}$ processes.⁵³

For the observables here examined, the statistical models have proven to describe fairly well the atom-diatom collisions associated with the H_3^+ system, at least for $E_c \leq 0.524$ eV. Beyond that energy, recent studies reveal, however, discrepancies between reaction probabilities obtained with the SQCT method and those calculated by means of EQM approaches, specially for large values of the total angular momentum.^{54,55} According to the present results for $\text{H}^+ + \text{D}_2$, the validity of such approaches still remains for the case of reactions initiated with the D_2 diatom in its first rotational excited state. In fact, in view of the comparison

established between the EQM and statistical DCSs at both 0.524 and 0.1 eV collision energies, the agreement between both methods is even better than for the H⁺+D₂($v=0$, $j=0$) case.

The use of different PESs to investigate the dynamics of the title reaction has revealed some interesting features. The existence of a rich structure of resonance peaks in the EQM reaction probabilities as a function of the energy⁵ is indicative of an extreme sensitivity on the precise value of the energy chosen for a detailed analysis. Analogously, the shape of the probabilities in terms of the total angular momentum is characterized by a highly oscillating behavior. Besides the expected mismatch between the peaks in the profile of the $P(J)$ probabilities at the two collision energies investigated here, the most remarkable differences between the results obtained on the KBNN and ARTSP PESs at $E_c=0.524$ eV are perhaps observed in the DCSs. In particular, the DCSs calculated by means of the EQM approach (shown in Fig. 8) display noticeable differences in the predicted values at the forward and backward peaks. This is though not surprising, since small differences in the topology of the PESs employed in the theoretical calculations may introduce modifications in the fine details of both reaction probabilities and cross sections in EQM calculations. As mentioned in Sec. III, the DCSs for some H⁺+D₂($v=0$, $j=0$) → HD($v'=0$, j') + D⁺ transitions exhibit more pronounced forward or backward peaks when the PES by Kamisaka *et al.* is employed. Unfortunately, the comparison of the EQM DCSs on both surfaces with those derived from previous experimental works does not allow any definitive conclusions regarding the goodness of either surface due to the inherent limited resolution at those extreme scattering angles and the experimental collision energy spread.

Another possible comparison with experimental results in order to test the performance of different PESs is the simulation of kinetic energy spectra.⁵ However, the corresponding calculation on the ARTSP PES performed in Ref. 5 at $E_c=0.524$ eV indicated that the observed discrepancies between theory and experiment could be attributed to the presence of an appreciable contribution from inelastic processes rather than to possible inaccuracies of the ARTSP surface. Therefore it is questionable that the use of a different PES, such as the KBNN one employed here, might lead to remarkable improvements in the quality of the simulated spectra.

However, it is at $E_c=0.1$ eV where significant differences between the results obtained on the two surfaces are appreciated. The EQM total cross sections are about 3–4 Å² larger on the ARTSP PES than on the KBNN surface. As commented on above, the differences are also noticeable in the $P(J)$ functions and DCSs (see Figs. 10 and 11, respectively). It is interesting to notice that, specially for the opacity functions, similar discrepancies also appear in the statistical calculations. This suggests the existence of slight differences on the PESs located in the entrance/exit channel outside the well. Figure 12 shows that this is indeed the case. In this figure, the comparison between contour plots of the KBNN [Fig. 12(a)] and the ARTSP surfaces [Fig. 12(b)] as a function of the Jacobi coordinates R and γ at the D₂ equilib-

FIG. 12. Contour plots of the KBNN (a) and ARTSP PESs (b) as a function of the Jacobi coordinates R and γ at the D₂ equilibrium distance. Energies are in eV referred to the asymptotic reactant valley.

rium distance is represented. The topologies of both surfaces are very similar. In fact, the potential well region looks almost identical in both surfaces. However, two small barriers in the KBNN PES at the collinear configuration and $R \sim 4.5$ Å constitute a remarkable distinct feature. The height of the barriers does not exceed the 0.02 eV, certainly a small magnitude, but apparently, sufficient to manifest on such a low energy as $E_c=0.1$ eV. The origin of these features is not clear, but likely, they could be due to a possible artifact in the fit of the corresponding *ab initio* points.

V. CONCLUSIONS

This work addresses the possible influence that either the rotation of the D₂ diatom or the use of different PESs might have on the overall dynamics of the H⁺+D₂ → HD+D⁺. Reaction probabilities in terms of the total angular momentum and product cross sections have been calculated at 0.524 and 0.1 eV collision energies by means of an accurate full converged close-coupling QM method, a QCT approach, and two statistical models: A statistical QM approach and its corresponding QCT version.

The analysis of the present findings for the H⁺+D₂($v=0$, $j=1$) reaction in comparison with the corresponding results for the process with the D₂ diatom in its ground rotational state reveals some differences, specially at

the lowest collisional energy $E_c=0.1$ eV. The comparison of the calculations obtained using the PES by Kamisaka *et al.* and the surface developed by Aguado *et al.* for the $H^+ + D_2(v=0, j=0)$ indicates that subtle effects are mainly due to the distinct topology of the two surfaces outside the potential well region.

DCSs are found to be the most sensitive quantities to both the initial rotation state of the D_2 reactant and the specific description of the potential energy employed in the calculation. In particular, values of the angular cross sections at both the forward and backward scattering directions significantly depend on the two aspects investigated in the present work.

For the two collision energies investigated here, statistical techniques provide a fairly good description of the reaction probabilities and cross sections obtained here with the exact method in all cases, thus giving support to a complex-forming reaction mechanism for the $H^+ + D_2$ collision at low energy. As in previous studies, at low energies the trajectory calculations underestimate the QM results.

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