This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

The $D^+ + H_2$ Reaction: Differential and Integral Cross Sections at Low Energy and Rate Constants at Low Temperature

Journal:	<i>The Journal of Physical Chemistry</i>
Manuscript ID:	jp-2014-01446y.R2
Manuscript Type:	Special Issue Article
Date Submitted by the Author:	n/a
Complete List of Authors:	González-Lezana, Tomás; CSIC, FAMA-Instituto de Física Fundamental Scribano, Yohann; Laboratoire Univers et Particules de Montpellier , Honvault, Pascal; Université de Franche-Comté, Equipe DREAM, Institut Utinam; Univ. Bourgogne,

SCHOLARONE™
Manuscripts

The $D^+ + H_2$ reaction at low temperatures and energies
214x129mm (96 x 96 DPI)

The $D^+ + H_2$ Reaction: Differential and Integral Cross Sections at Low Energy and Rate Constants at Low Temperature

Tomás González-Lezana*

Instituto de Física Fundamental (CSIC), Serrano 123, 28006 Madrid, Spain

Yohann Scribano

Lab. Univers et Particules de Montpellier, Univ. de Montpellier II,

LUPM - UMR CNRS 5299, 34095 Montpellier Cedex, France

Pascal Honvault

Lab. Interdisciplinaire Carnot de Bourgogne,

UMR CNRS 6303, Univ. Bourgogne, 21078 Dijon Cedex,

France, and UFR Sciences et Techniques,

Univ. de Franche-Comté, 25030 Besançon cedex, France

(Dated: May 6, 2014; submitted to Journal of Physical Chemistry A)

Abstract

The $D^+ + H_2$ reaction is investigated by means of a time independent quantum mechanical (TIQM) and a statistical quantum mechanical (SQM) methods. Differential cross sections and product rotational distributions obtained with these two theoretical approaches for collision energies between 1 meV and 0.1 eV are compared to analyze the dynamics of the process. The agreement observed between the TIQM differential cross sections and the SQM predictions as the energy increases revealed the role played by the complex-forming mechanism. The importance of a good description of the asymptotic regions is also investigated by calculating rate constants for the title reaction at low temperature.

KEYWORDS: H_3^+ , Reactive Scattering, Low Temperature

* Corresponding author; Email: t.gonzalez.lezana@csic.es

I. INTRODUCTION

Due to its abundance in the early stage of universe, H_2 is one of the most important molecules. Indeed, it plays an important role in the cooling of the primordial gas at temperatures of about few hundred Kelvin¹ and can influence the fragmentation of the proto-clouds which lead to the first stellar structures just after the recombination era. However in some cases, its deuterated species HD can be more efficient^{2,3} as a coolant agent decreasing the temperature of the gas down below 100 K due to the smaller spacing of the rotational levels in comparison with hydrogen molecules. This effect is increased even more thanks to the non-zero permanent electric dipole moment of HD even if the cosmological fractional abundance of HD/ H_2 is small⁴

There are two principal routes¹ to produce HD involving a deuteron exchange with H_2 . The first is $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$, experimentally investigated in several works at a wide range of temperature and in general in good agreement with theoretical predictions^{5,6} The second is the $\text{D}^+ + \text{H}_2 \rightarrow \text{HD} + \text{H}^+$ reaction and represents the primary source of HD in diffuse interstellar clouds (and also in ionized halos⁷) but there are not too many either experimental or theoretical data over the low temperature range of astrophysical interest. It is then important to predict an accurate rate constant to be used in chemical networks. Moreover the comparison with the constant Langevin value of $2.1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ or other simple models can provide useful information regarding the dynamics of the process.

As a result of its astrophysical importance, several potential energy surfaces (PES) have been computed⁸⁻¹³ to probe the dynamics of reactive processes involving H_3^+ and/or its isotopologues. The reaction $\text{D}^+ + \text{H}_2 \rightarrow \text{HD} + \text{H}^+$ was indeed studied by quantum and classical methods mainly on the adiabatic ground state PES at collisional energies, E_c , generally below 1.6 eV, where an electronic curve crossing leads to the competition among reactive charge transfer, non-reactive charge transfer and reactive non-charge transfer channels. For higher energy regimes non-adiabatic effects play then a role as manifested in the studies for the title reaction by quantum wave packet method^{14,15} and by classical method like the trajectory surface hopping approach^{16,17}.

A variety of theoretical methods¹⁸ were employed to obtain rate coefficients in terms of the collisional energy, $k(E_c)$, which were compared with ion beam measurements performed on the system^{19,20}. The temperature rate constant of this reaction was also studied between

10 K – 400 K by McCarroll using a statistical mixing model²¹ and between 30 K – 130 K by Gerlich using a dynamically biased statistical theory²² From an experimental point of view, integral cross sections (ICS) and energy distributions were reported by Hollidays *et al.*²³ whereas Gerlich *et al.*¹⁹ have measured the rate constant for the $D^+ + (\text{normal})H_2$ for medium temperature (180 K – 350 K) and the energy dependent rate constant down to 1 meV. It should also be mentioned that an older measurement of the temperature rate coefficient was done by Feshenfeld *et al.*²⁴ which gives a value of $1.0 (-0.25; +0.5) \times 10^{-9} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ nearly constant over the temperature range 80 K – 278 K in good agreement with the more recent value of Gerlich estimated at $1.6 \times 10^{-9} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.

In previous works we have performed time independent quantum mechanical (TIQM) and statistical quantum mechanical (SQM) calculations for the $D^+ + H_2 \rightarrow HD + H^+$ reaction to obtain accurate rate constants for astrophysical applications at temperatures below 100 K^{25,26}. The PES employed on these studies is the surface by Velilla *et al.*¹² which includes an analytical expression for the long range electrostatic interactions. The reaction pathway is affected by the existence of a deep well (~ 4.3 eV) and a barrierless entrance channel. This deep potential well can support many narrow resonances as it was shown²⁵ in the reaction probability for $J = 0$. Despite the fact that the ICS is highly oscillatory we have found that the SQM gives the right behavior in average²⁶. For the temperature rate coefficient $k(T)$, SQM results slightly overestimate the TIQM values although both methods yield very close rates in the low temperature range (10 K – 100 K) investigated. This good agreement seems to confirm that the reaction takes place through a long-lived intermediate complex which gives a statistical behavior for this ion-molecule reaction at a wide range of collisional energy. In fact previous applications of the SQM approach to isotopic variants of the title reaction support this idea^{27–32}.

In a similar way as our study on the ortho-para $H^+ + H_2$ reaction³¹, in this work we focus on the low energy regime, using as well the PES from Ref. ¹² in an attempt to track possible changes on the dynamics of the process when E_c varies. For low values of E_c , it is important to ensure a sufficiently large asymptotic region for a proper description of the long range interactions^{26,33}. Otherwise rate coefficients in terms of the energy may manifest a spurious deviation²⁵ from the quasi constant dependence observed when $E_c \rightarrow 0$ in previously reported measurements¹⁹. Without this correct long propagative scheme, the

computed (TIQM and SQM) rate constants exhibit a too much pronounced decrease as T diminishes giving a incorrect value at the low temperature regime. This constant behaviour with the temperature for $k(T)$ is similar to the one predicted by the Langevin model for ion-molecule reactions with no entrance barrier. In the present study, with TIQM results converged down to $E_c \sim 10^{-3}$ eV and accurate rate constants beyond ~ 10 K, we discuss about the issue of the calculation of $k(T)$ at the low temperature regime.

Another feature investigated in this paper deals with the possible effect of the initial rotational excitation of the reactants, $H_2(v=0, j>0)$. A similar discussion was reported in the dynamical study done for the reaction $H^+ + D_2 \rightarrow HD + D^+$ ²⁹ Differential cross sections (DCS) calculated when the reaction was initiated with $D_2(v=0, j=1)$ were found to exhibit some differences with respect to the process with D_2 in its ground rovibrational state at the lowest collision energy there investigated $E_c = 0.1$ eV. We therefore expect to see some kind of sensitivity on the rotational excitation of the reactants at the energy regime of interest in this work. Reaction probabilities, product distributions and DCS are calculated with the TIQM and SQM methods in order to address this issue and to confirm (or not) the possible description of this reaction at low temperature by means of statistical techniques.

The structure of the paper is as follows: In Section II details on the theoretical methods and on the actual calculation are given; results are presented on Section III and discussed on Section IV. Finally conclusions are listed in Section V.

II. THEORETICAL METHODS

A. Time independent quantum mechanical method

We have performed three-dimensional quantum-mechanical calculations using a time-independent method based on body-frame hyperspherical democratic coordinates. This approach, originally developed by J. M. Launay^{34–36} and presented in detail in Ref.³⁷, has already been used for the calculation of rate coefficients for the title reaction^{25,26}. It has also previously proved successful in describing the quantum dynamics of other complex-forming reactions, such as $H + O_2 \rightarrow OH + O$ ³⁸ and ultracold alkali-dialkali collisions³⁹.

In short, we employ principal axis democratic hyperspherical coordinates to represent the nuclear wavefunction. We determine surface states which are eigenfunctions of a fixed-

hyperradius reference hamiltonian without Coriolis coupling (CC). These states are labelled by Ω , the projection of the total angular momentum J on the axis of least inertia. The partial wavefunction for given parity, permutation symmetry and total angular momentum quantum numbers is then expanded on a set of surface states. Both rotational terms and CC are included at this stage as shown for instance on Ref.³⁴ with second order differential equations to obtain the hyperradial functions to expand the total wavefunction which include matrix elements connecting states with $\Delta\Omega = 0, \pm 1$ and ± 2 . Close-coupling equations are solved with a logarithmic derivative propagation method⁴⁰. The range of variation of the hyperradius is divided into 395 equal sectors between 0.5 and 40 a_0 . Basis transformations are performed at the boundary between sectors and at large hyperradius, the numerically integrated wavefunction is matched onto a set of regular and irregular asymptotic functions expressed in the laboratory frame. The K , S and T -matrices are then extracted and state-to-state reaction probabilities are obtained from standard equations.

In this work, 200 hyperspherical states for $J = 0$ have been considered and we have included all allowed Ω components up to 25 in the close-coupling expansion states, yielding a total of 1938 hyperspherical states. We have to do this in order to obtain accurate ICS and DCS because symmetric top configurations, where the CC is large, are energetically accessible. A maximum hyperradius of 40 a_0 has been employed to ensure convergence for ICS and DCS even at 1 meV which is the lowest collision energies considered in the present study. It is worthwhile to recall that a time-independent formalism is the most appropriate choice for the low energy scattering. Given the already tested bad performance of Coriolis decoupling schemes for the present reaction and isotopical variants^{14,27,41,42}, no approximations have been employed here.

State-to-state ICS needed for the product rotational distributions are generated for each partial wave J , from the T matrix using the standard formula,

$$\sigma_{vj \rightarrow v'j'} = \frac{\pi}{\tilde{k}_{vj}^2} \sum_{J=0}^{\infty} (2J+1) \sum_{l=|J-j|}^{J+j} \sum_{l'=|J-j'|}^{J+j'} |T_{v'j'l',vj l}^J|^2, \quad (1)$$

with $\tilde{k}_{vj}^2 = (2j+1)2\mu E_c/\hbar^2$, where μ is the reduced mass.

In this paper, we also present the first accurate DCS for the $D^+ + H_2$ reaction in the [0.001 eV, 0.1 eV] collision energy range. The state-to-state magnetically averaged DCS is given by

$$\sigma_{v'j',vj}(\theta, E) = \frac{1}{4\tilde{k}_{vj}^2} \sum_{\Omega, \Omega'} \left| \sum_J (2J+1) d_{\Omega', \Omega}^J(\pi-\theta) T_{v'j'\Omega', vj\Omega}^J \right|^2, \quad (2)$$

where $d_{\Omega', \Omega}^J$ is a Wigner reduced rotation matrix element and θ is the scattering angle in the center-of-mass (CM) coordinate system. $\theta = 0^\circ$ is defined as the direction of the CM velocity vector of initial D^+ atoms and corresponds to backward scattering for the H^+ products and forward scattering for the HD products.

Initial state selected rate coefficients have also been calculated by means of the following expression:

$$k_{vj}(T) = \frac{1}{k_B T} \left(\frac{8}{\pi \mu k_B T} \right)^{1/2} \int_0^\infty \sigma_{vj}(E_c) e^{-E_c/k_B T} E_c dE_c, \quad (3)$$

where T and k_B are the temperature and the Boltzmann constant, respectively. ICSs of Eq. (3) are evaluated at collision energies between $E_c \sim 10^{-4}$ eV and 0.1 eV, with steps of 10^{-5} eV, 5×10^{-5} eV and 5×10^{-4} eV for the $[10^{-4} \text{ eV}, 10^{-3} \text{ eV}]$, $[10^{-3} \text{ eV}, 10^{-2} \text{ eV}]$ and $[10^{-2} \text{ eV}, 10^{-1} \text{ eV}]$ ranges respectively. Less dense energy grids and integrations with and without an interpolation scheme (a fourth-grade Lagrange approach) for the ICSs were employed until final values of the $k_{vj}(T)$ rates converged at less than 1 % were obtained.

B. Statistical quantum mechanical method

The SQM approach has been explained in detail before in previous works^{43–45}. Designed for complex-forming processes, the state-to-state reaction probability is approximated as the product between the individual probability of the complex to be formed from the initial state ($p_{vj\Omega}$) and the fraction of complexes fragmentating into the final state $v'j'\Omega'$, as follows:

$$|S_{v'j'\Omega', vj\Omega}^J(E)|^2 \simeq \frac{p_{v'j'\Omega'}^J(E) p_{vj\Omega}^J(E)}{\sum_{v''j''\Omega''} p_{v''j''\Omega''}^J(E)}, \quad (4)$$

where J stands for the total angular momentum. The sum in the denominator runs for all energetically accessible states at both the reactants and product arrangements ($v''j''\Omega''$).

In this version of the method, the capture probabilities are solution of coupled-channel equations which are solved in the time independent domain by means of a log derivative procedure taking into account 350 sectors. The corresponding propagation is performed between the so-called capture radius, R_c , defining the region in which the complex is formed, and the asymptotic distance, $R_{\max}$. Values employed in the present calculation for these two

distances are 3 a_0 and 70 a_0 respectively. All reactant and product states below a total energy of 1.2 eV have been included in the calculation.

DCSs are calculated via the random phase approximation where interference terms between different values of the total angular momentum J are neglected and square modulus terms of the scattering matrix are employed as follows:

$$\sigma_{v'j',vj}(\theta, E) \simeq \frac{1}{8\tilde{k}_{vj}^2} \sum_{J\Omega'\Omega} (2J+1)^2 |S_{v'j'\Omega',vj\Omega}^J(E)|^2 \times [d_{\Omega'\Omega}^J(\pi-\theta)^2 + d_{\Omega'\Omega}^J(\theta)^2]. \quad (5)$$

The angular cross sections calculated as Eq. (5) exhibit by construction a forward-backward symmetry around the sideways scattering direction $\theta \sim 90^\circ$. In principle, the deviation or not from this symmetrical behaviour of the TIQM results (see Eq. (2)), in combination with the analysis of other quantities such as reaction probabilities and cross sections enable us to analyze up to which extent the complex-forming mechanism plays a relevant role in the overall dynamics of the process.

III. RESULTS

A. Reaction probabilities

The lowest energy range here investigated in detail comprises values of E_c within the 10^{-3} – 10^{-1} eV region. The reaction probabilities as a function of the total angular momentum J , $P(J)$, at $E_c = 1$ meV for the $D^+ + H_2(v=0, j=0)$ process are shown in Fig. 1.

The TIQM values extend up to a maximum value $J_{\max} = 10$ and exhibit a somehow erratic behaviour with a prominent peak around $J = 5-6$. The statistical probabilities also have the same $J_{\max}$ but display a plateau of ~ 0.85 for almost the whole range of values of the total angular momentum up to the cutoff value. The accord between both set of results is not extremely good.

The situation becomes quite different however when the collision energy is increased. Thus when a similar comparison is established for $E_c = 5$ meV, as shown in Fig. 2, the SQM reaction probabilities are found to constitute a fairly good reproduction of the trend

followed by the TIQM result. Despite the oscillations as the value of J increases, a commonly observed feature for the title reaction and isotopic variants^{28,29,48}, the statistical probabilities, close to ~ 0.85 for a wide range, $J = 2 - 11$, provides the average value of the TIQM results.

B. Cross Sections

The rotational distributions for the $D^+ + H_2(v = 0, j = 0) \rightarrow HD(v' = 0, j') + H^+$ reaction at the energies above considered in Section III A, $E_c = 1$ meV and 5 meV have been calculated with the two theoretical approaches described in Section II. The comparison between the TIQM and SQM results can be seen in Table I. For both energies the highest populated HD rotational state is $j' = 2$, for which a surprisingly good agreement is observed between the two sets of results. The differences found for the reaction probabilities (see Fig. 1) are then justified by the distinct population of the $j' = 0$ and 1 states which the statistical predictions seem to overestimate.

As revealed by Fig. 2, a much closer accord is expected between the cross sections obtained by means of the two methods at $E_c = 5$ meV. In fact, results shown in Table I for that energy manifest that both TIQM and SQM distributions are quite similar.

A detailed insight about the dynamics of the reaction can be extracted by analysis of the DCSs. In this work we have calculated the corresponding angular cross sections at $E_c = 1$ meV with the TIQM approach. The results for both the total and state-to-state process, $D^+ + H_2(v = 0, j = 0) \rightarrow HD(v' = 0, j') + H^+$ are presented in Figs. 3 and 4 respectively. At this energy, the DCS for the process exhibits an asymmetrical profile in which the scattering through the forward directions $\theta \sim 0^\circ$ (~ 900 a₀² sr⁻¹) is about twice the value observed at the backward scattering direction $\theta \sim 180^\circ$ (~ 450 a₀² sr⁻¹). The SQM result, also included for comparison in Fig. 3, is not capable to reproduce this asymmetry with a value of ~ 700 a₀² sr⁻¹ for both forward and backward peaks.

According to the DCSs for the state-to-state processes (see Fig. 4) the prominent peak at the forward scattering direction has its origin in the production of rotationally excited $HD(v' = 0, j' > 0)$. In addition, $D^+ + H_2(v = 0, j = 0) \rightarrow HD(v' = 0, j' = 1) + H^+$ displays a profile with a negligible value at strictly $\theta \approx 180^\circ$. The angular distribution for the formation of rotationless $HD(v' = 0, j' = 0)$ is almost completely symmetrical around the sideways direction $\theta \sim 90^\circ$ although in this case the SQM result does not quite reproduce

the TIQM DCS, which remains clearly below.

The TIQM total DCSs at $E_c = 5$ meV, shown in Fig. 5, still displays an almost 2:1 forward-backward ratio, as the precedent case of $E_c = 1$ meV. The statistical distribution however peaks at these two directions with a value (~ 500 a₀² sr⁻¹) which is close to the average of the TIQM peaks at $\theta \sim 0^\circ$ and $\theta \sim 90^\circ$.

Interestingly the comparison of the state-to-state distributions, shown in Fig. 6, reveals quite the opposite situation observed for $E_c = 1$ meV, with the largest asymmetry found for the $D^+ + H_2(v = 0, j = 0) \rightarrow HD(v' = 0, j' = 0) + H^+$ case. As the rotational excitation of the formed HD increases the accord between the TIQM and SQM DCSs becomes better.

Besides the above discussed analysis of the title reaction at energies within the meV region, in this work we have also investigated the process at the 10⁻¹ eV range. In particular, rotational cross sections have been calculated between $E_c = 0.01$ eV and 0.1 eV. Fig. 7 shows cross sections for the $D^+ + H_2(v = 0, j = 0) \rightarrow HD(v' = 0, j') + H^+$ reaction calculated by means of the TIQM and SQM approaches for some energies within that range: 0.02 eV, 0.04 eV, 0.07 eV and 0.08 eV. Both methods yield distributions in an overall good agreement, thus suggesting a possible complex-forming nature of the reaction at this energy range.

However the DCS for the $D^+ + H_2(v = 0, j = 0) \rightarrow HD + H^+$ reaction at $E_c = 10^{-2}$ eV (see Fig. 8) exhibits a pronounced asymmetry with a prominent peak through the forward scattering direction, with a slightly larger than 2:1 ratio with respect to the peak at the backward direction. The interesting thing is that the corresponding DCS when the process starts with rotationally excited $H_2(v = 0, j = 1)$ (see bottom panel of Fig. 8) agrees quite well with the results obtained on statistical grounds. A similar dependence on the initial rotational state of D_2 was observed for the $H^+ + D_2 \rightarrow HD + D^+$ reaction⁴⁸. For that isotopic process the same kind of TIQM calculations found a noticeably better agreement with statistical DCSs at $E_c = 0.1$ eV but specially at $E_c = 0.524$ eV.

Also at $E_c = 10^{-1}$ eV we have analysed possible differences between the $D^+ + H_2(v = 0, j = 0)$ and $D^+ + H_2(v = 0, j = 1)$ cases. The comparison of the rotational distributions obtained with the TIQM method shown in Fig. 9 does not manifest remarkable differences. On the other hand, both situations, $j = 0$ and $j = 1$, at this energy seem to be well reproduced by the SQM predictions.

The values of the total ICS of $D^+ + H_2(v = 0, j)$ for both $j = 0$ and $j = 1$ are shown in Table II at $E_c = 10^{-2}$ eV and 10⁻¹ eV. The comparison between the TIQM and SQM results

show that with the only exception of the $D^+ + H_2(v = 0, j = 0) \rightarrow HD + H^+$ at $E_c = 10^{-2}$ eV, the statistical cross sections are always slightly larger than the TIQM values. The best agreement between both set of results is found for the reaction initiated from the rotationally excited $H_2(v = 0, j = 1)$ and in particular, differences are only of about $\sim 7 \text{ a}_0^2$ at $E_c = 10^{-1}$ eV.

According to the TIQM calculation, at $E_c = 10^{-1}$ eV, the processes initiated from $HD(v = 0, j = 0)$ and $HD(v = 0, j = 1)$ lead to DCSs with some features in common as shown in Fig. 10. Maxima of both distributions are at the forward-backward directions, and without exhibiting a strict symmetry around the sideways direction, values at $\theta \sim 0^\circ$ and $\theta \sim 180^\circ$ do not differ too much, ranging between $\sim 100 \text{ a}_0^2 \text{ sr}^{-1}$ and $\sim 150 \text{ a}_0^2 \text{ sr}^{-1}$. The SQM results, also shown in Fig. 10, which constitute a fairly good reproduction of the distributions for almost the entire angular range, remain slightly above the forward and backward peaks for the $HD(v = 0, j = 0)$ case but agree fairly well with the TIQM DCS for $HD(v = 0, j = 1)$.

C. Rate constants

As explained in the Introduction the present study is completed with a detailed analysis of the rate constant for the low temperature regime. The dependence with T of the rates $k(T)$ for the title reaction has been already examined in previous studies²⁵ however the asymptotical distance employed in the corresponding TIQM calculation was found to be not large enough^{26,33} With a proper radial propagation the new converged values of $k(T)$ for the $D^+ + H_2(v = 0, j = 0) \rightarrow HD + H^+$, already shown in a table before³³ are those shown in Fig. 11.

The new TIQM $k(T)$ results are larger than those reported in Honvault and Scribano²⁵ with differences of $\sim 58\%$ at $T = 10 \text{ K}$ and $\sim 9\%$ at $T = 100 \text{ K}$. Moreover the dependence with T is noticeably smaller now, with a much less pronounced decrease as T diminishes. The remarkably good agreement with the experimental results, specially at the larger temperatures here considered, can be understood as an indication of both the accuracy of PES from Ref. ¹² and the present dynamical calculations. The statistical predictions, also included for comparison in Fig. 11, seem almost constant along the temperature range under consideration in the present study, with only some small deviation at $T \sim 15 \text{ K}$. SQM rates however slightly overestimate the TIQM results.

The values of the parameters of the corresponding fits of both the TIQM and SQM rate constants to Kooij-Arrhenius analytical expressions are given in Table III. The deviation from the actual values of $k(T)$ does not exceed 0.5 % in any of the two calculations at any value of the temperature, thus suggesting its validity for the temperature range under study in this work.

The $k(T)$ results obtained by means of the TIQM ABC code⁴⁹ on an earlier PES¹⁰ at $T = 100$ K¹⁸ and the analytical formula proposed by Gerlich *et al.*²² for $30 \text{ K} \leq T \leq 130$ K based on statistical considerations are also included in Fig. 11. The comparison reveals that the present TIQM and SQM results remain larger at the entire temperature range investigated. It is worth mentioning that those calculations^{18,22} were performed considering Boltzmann averaged normal- H_2 whereas the here obtained rate constants only come from H_2 at its ground para-hydrogen state. Given the similarities between the rate coefficients $k(E_c)$ for the $j = 0$ and $j = 1$ cases²⁵ and the low population of the rotationally excited H_2 below 100 K the comparison established in Fig. 11 suffices for the scope of this study.

In addition estimates of the rate constant derived from the corresponding measurements of $k(E)$ ¹⁹ and from the Langevin value ($2.1 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) have also been added to Fig. 11. Whereas the latter is clearly above all the other values of $k(T)$ shown in the comparison, the estimated rates agrees well with the present TIQM at the larger temperature range. This accord is somehow an expected result given the comparison between the corresponding rate coefficients previously reported³³

IV. DISCUSSION

A widely discussed issue regarding the H_3^+ reaction and the corresponding isotopic variants deals with the possible change of the dynamics of the reactive process as the energy changes⁴⁵. Pioneering works on the system concluded that the reaction evolves from a short-lived collision complex below $E_c \sim 3 \text{ eV}$ pathway to a direct mechanism for larger energies ($E_c > 4.5 \text{ eV}$)^{17,50–52}. Those values of the collision energy are clearly out of the scope of the present study and correspond to a region in which dynamics is affected by the competition between different reaction channels depending on whether or not the charge is transferred. Much closer to the low energy range under consideration here are previous investigations on the system focussed on the conditions of experimental work performed for the $\text{H}^+ + \text{D}_2$

reaction^{53–55}. DCSs and product distributions were obtained by means of Rydberg H-atom time-of-flight spectroscopy at $E_c = 0.524$ eV. Theoretical calculations were there performed at such collision energy^{27,29,42,55} and eventually compared with the situation at $E_c = 0.1$ eV^{29,48}. Although the highly oscillating nature of the reaction, both for probabilities and cross sections (integral and differential) precludes to conclude anything in definitive terms, some slight improvement in the comparison between statistical and TIQM results at 0.1 eV collision energy with respect to $E_c = 0.524$ eV and reported deviations from a statistical description at larger energies^{56,57} would lead to support this idea of a dominant complex-forming mechanism as the energy decreases for the H_3^+ system. However results for the $H^+ + H_2$ reaction down to the μ eV regime³¹ indicated that the dynamics of the process is also far for being reproduced on statistical grounds.

In this sense the present analysis is not conclusive either. Despite the agreement between the SQM and TIQM cross sections is certainly fairly good in general, some deviations are observed, for example, for opacity functions, $P(J)$, and DCSs at the lowest energy here investigated ($E_c = 1$ meV). Further work should be done in order to clarify whether or not this constitutes an indication of a possible limit of the validity of statistical techniques, and therefore, the absence of a complex-forming mechanism when the energy is sufficiently decreased. Departures from a symmetrical forward-backward profile for angular distributions can also be found in situations of existing resonances as shown, for instance, for $F + H_2$ ⁴⁶ and $F + HD$ ⁴⁷. For these reactions however, these resonance features do not lead to a complex-forming dynamics suitable to be described on statistical grounds, with a specificity established by the state-to-state processes connecting certain initial and final states. The angular distributions are in those cases result of interferences either among J -components of metastable states or between specific long lived resonances localized in different partial waves. Previous studies on the title reaction and isotopic variants on the contrary have revealed that the situation seems to respond to the formation of relatively stable intermediate complexes which yield dynamical features in close agreement for some energy regimes with statistical predictions.

Results reported here suggest a better agreement between statistical and TIQM results when the reaction involves some rotational excitation in the H_2 reactant. Thus for example, as shown in Section III, TIQM DCSs at $E_c = 10^{-2}$ eV and 10^{-1} eV are found in a better accord with SQM predictions, when we consider the $D^+ + H_2(v = 0, j = 1)$ case (see Figs. 8

and 10). Given the marked dependence of fine details of the dynamics of the H_3^+ system on the PES employed for the calculations, it is difficult to establish conclusive similarities with some of the findings of the study on the $\text{H}^+ + \text{D}_2$ reaction by González-Lezana *et al.*⁴⁸. None of the two surfaces employed in that work (the one by Aguado *et al.*¹⁰ and that by Kamisaka *et al.*⁹) correspond to the PES we have used here. However a noticeable improvement in the TIQM versus SQM comparison was observed for the DCS at $E_c = 0.524$ eV when the reaction starts from rotationally excited $\text{D}_2(v = 0, j = 1)$ ^{29,48}.

The TIQM calculation with a larger radial propagation yields rate constants with a behaviour which is much closer to be independent with T than in our previous works^{25,26}. This is a confirmation of the importance of the long range potential part in the dynamics at such low temperature regime. For even lower temperatures and for the ultra-cold regime (Wigner regime), not reached in the present study, it should be necessary to use a more efficient propagator scheme and possibly to introduce additional modifications. Recent applications of a refined version of the present TIQM method can be seen for instance in Lara *et al.*⁵⁸ for the $\text{S}(^1D) + \text{H}_2$ reaction. In that work the theoretical formalism includes the electrostatic interaction between the permanent quadrupole moments of the colliding species, forcing the introduction of anisotropy in the outer regions. Analogously in Ref.⁵⁹ an accurate propagation scheme for ultra-cold collisions was implemented to investigate the $\text{He} + \text{H}_2^+ \rightarrow \text{HeH}^+ + \text{H}$ reaction.

One of the reasons of the constant behaviour at low T of those $k(T)$ (see Fig. 11) estimated from measured rate coefficients is the extrapolation down to 10^{-6} eV of the results reported by Gerlich¹⁹ (originally for collision energies beyond $E_c \sim 10^{-3}$ eV). Whether or not actual measurements at such low energy regime would in fact lead to this trend for the rate constants is still a subject to confirm. In principle we could attribute the slight deviation of the present theoretical results from a constant value with respect to the temperature as limitations on the SQM and TIQM calculations here performed. ICSs have been calculated in our study beyond $E_c \sim 10^{-4}$ eV, so in order to examine the dependence of the rate constants as the temperature decreases to $T \sim 10$ K, we have carried out a similar extrapolation under the assumption of a linear behaviour in a double log scale representation of the cross sections down to the μeV region. According with results from our previous tests on the title reaction (see Fig. 9 in González-Lezana *et al.*²⁶), deviations from such behaviour were found to correspond to deficiencies in the correct value of the asymptotic radial distance in the

SQM calculation. With cross sections obtained with this extrapolation procedure, we have calculated estimates of the TIQM and SQM $k(T)$, as shown in Fig. 11 (in dashed-dotted line). The actual values of the rate constants have been found not to change if the ICSs are extrapolated to even lower values of the collision energy ($E_c \sim 10^{-8}$ eV). Deviations of the actual rate constants from these asymptotically estimated values (which are not strictly constant either) are only noticeable at $T \sim 20$ K and 40 K for the SQM and TIQM results respectively. More precisely, the relative differences between the rate coefficients estimated from the TIQM cross sections extrapolated down to $E_c = 10^{-6}$ eV and the rate coefficients calculated from the computed TIQM cross sections (down to 10^{-4} eV) are at 10 K, 20 K and 50 K, respectively, $\sim 10\%$, 4% and 1% .

V. CONCLUSIONS

A time independent quantum mechanical (TIQM) method has been employed to calculate reaction probabilities in terms of the total angular momentum, rotational cross sections and differential cross sections at values of the collisional energy, E_c which range from the meV regime up to 0.1 eV for the $D^+ + H_2$ reaction. Predictions by means of a statistical quantum mechanical (SQM) method have been obtained and compared with the TIQM results to establish the possible complex-forming nature of the dynamics at such low energy regime. Some differences have been observed at the lowest energy under consideration $E_c = 1$ meV, but the agreement between both methods is fairly good in general.

Initial excitation of the $H_2(v = 0, j = 1)$ reactant seems to reduce some slight features of the DCS, such as certain forward-backward anisotropy, thus leading to a better performance of the SQM approach to reproduce the TIQM angular distributions.

Rate constants have been calculated with a properly large asymptotic range in the TIQM calculation, and an almost independent behaviour with the temperature has been found. Details of the calculation at the low temperature range have been discussed.

We hope that the theoretical results reported in this paper will encourage future experiments at the state-to-state level for this system at low energy and temperature.

VI. ACKNOWLEDGMENTS

P.H. and Y. S. acknowledge support from the Programme National de Physique et Chimie du Milieu Interstellaire (INSU/CNRS). TIQM calculations were performed using HPC resources from DSI-CCUB (Université de Bourgogne). This work has been supported by MICINN Grant No. FIS2011-29596-C02-01. It is a pleasure to dedicate this contribution to Prof. Franco A. Gianturco

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

TABLE I: Rotational integral cross sections, in a_0^2 , for the $\text{D}^+ + \text{H}_2(v = 0, j = 0) \rightarrow \text{HD}(v' = 0, j') + \text{H}^+$ reaction at $E_c = 1$ meV and 5 meV, calculated by means of the TIQM and SQM methods.

	$E_c = 1$ meV		$E_c = 5$ meV	
	TIQM	SQM	TIQM	SQM
0	181.86	266.63	168.23	125.14
1	335.59	527.46	210.75	249.10
2	685.54	689.75	269.12	295.08

TABLE II: Integral cross sections, in a_0^2 , for the $\text{D}^+ + \text{H}_2(v = 0, j) \rightarrow \text{HD} + \text{H}^+$ reaction at $E_c = 10^{-1}$ eV and 10^{-2} eV, calculated with the TIQM and SQM methods.

E_c	$j = 0$		$j = 1$	
	TIQM	SQM	TIQM	SQM
10^{-2} eV	551.74	482.25	379.58	417.05
10^{-1} eV	130.27	149.57	141.82	148.64

TABLE III: Parameters for the fits of the TIQM and SQM rate constants to Kooij/Arrhenius expressions $k(T) = \alpha(T/300)^\beta \exp(-\gamma/T)$. α is given in $10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ units and γ in K.

TIQM	1.7663	0.04577	1.0704
SQM	1.9049	0.02003	0.12536

FIG. 1: Reaction probability as a function of the total angular momentum J at a collision energy of 1 meV for the $D^+ + H_2(v = 0, j = 0) \rightarrow HD + H^+$ reaction. TIQM (solid squares) and SQM (empty circles) are compared.

FIG. 2: Same as Fig. 1 at $E_c = 5 \text{ meV}$.

FIG. 3: Differential cross sections for the $D^+ + H_2(v=0, j=0) \rightarrow HD + H^+$ reaction at $E_c = 1$ meV measured in $a_0^2 \text{ sr}^{-1}$. TIQM results are in solid black line and SQM cross sections are in dashed red line.

FIG. 4: Comparison between the TIQM (black solid lines) and SQM (red dashed lines) DCSs for the $\text{D}^+ + \text{H}_2(v = 0, j = 0) \rightarrow \text{HD}(v' = 0, j') + \text{H}^+$ reactions at $E_c = 1 \text{ meV}$.

FIG. 5: Same as Fig. 3 at $E_c = 5 \text{ meV}$.

FIG. 6: Same as Fig. 4 at $E_c = 5 \text{ meV}$.

FIG. 7: Rotational cross sections for the $D^+ + H_2(v=0, j=0) \rightarrow HD(v'=0, j') + H^+$ reaction for $E_c = 0.02$ eV, 0.04 eV, 0.07 eV and 0.08 eV. TIQM results (black squares) are compared with SQM values (empty circles).

FIG. 8: DCSs, in $a_0^2 \text{ sr}^{-1}$, for the $D^+ + H_2(v=0, j) \rightarrow HD + H^+$ reaction for $E_c = 0.01 \text{ eV}$. TIQM (black solid line) and SQM cross sections (red dashed line) for $j=0$ (top panel) and $j=1$ (bottom panel).

FIG. 9: Rotational cross sections, in a_0^2 , for the $D^+ + H(v=0, j) \rightarrow HD + H^+$ reaction for $E_c = 0.01$ eV. TIQM (black squares and solid line) and SQM cross sections (empty circles and dashed line) for $j = 0$ (top panel) and $j = 1$ (bottom panel).

FIG. 10: Same as Fig. 8 for $E_c = 10^{-1}$ eV.

FIG. 11: Temperature dependence of the rate constants for the $\text{D}^+ + \text{H}_2(v=0, j=0) \rightarrow \text{HD} + \text{H}^+$ reaction. Present TIQM results (blue lines) and SQM predictions (red lines) are compared with the Langevin value (dashed black line), estimates from measurements of $k(E_c)$ ¹⁹ (dotted black line) and the statistical results of Gerlich *et al.*²² (solid black line). Estimates from TIQM and SQM cross sections extrapolated down to $E_c = 10^{-6}$ eV have been also included (dotted-dashed line). The value at $T = 100$ K (black square) corresponds to the result of the TIQM calculation of Jambrina *et al.*¹⁸ using a different PES. See text for details.

-
- [1] Galli, D.; Palla, F. The Dawn of Chemistry *Ann. Rev. Astron. Astrophys.* **2013**, *51*, 163–206.
- [2] Glover, S. C.; Savin, D. W. Is H_3^+ Cooling Ever Important in Primordial Gas? *Mon. Not. R. Astron. Soc.* **2009**, *393*, 911.
- [3] Glover, S. C. O.; Abel, T. Uncertainties in H_2 and HD Chemistry and Cooling and Their Role in Early Structure Formation *Mon. Not. R. Astron. Soc.* **2008**, *388*, 1627–1651.
- [4] Puy, D.; Signore, M. Cooling Balance and Thermal Instability of a Collapsing Molecular Protocloud *New Astron.* **1998**, *3*, 247–257.
- [5] Mielke, S. L.; Lynch, G. C.; Truhlar, D. G.; Schwenke, D. W. Ab Initio Chemical Kinetics: Converged Quantal Reaction Rate Constants For the $\text{D} + \text{H}_2$ System *J. Phys. Chem.* **1994**, *98*, 8000–8008.
- [6] Charutz, D. M.; Last, I.; Baer, M. The Toeplitz Approach to Treating Three-Dimensional Reactive Exchange Processes: Quantum Mechanical Cross Sections and Rate Constants for the $\text{D} + \text{H}_2$ and $\text{H} + \text{D}_2$ Reactions *J. Chem. Phys.* **1997**, *106*, 7654–7661.
- [7] McGreer, I. D.; Bryan, G. L. The Impact of HD Cooling on the Formation of the First Stars *Astrophys. J.* **2008**, *685*, 8.
- [8] Prosimi, R.; Polyansky, O. L.; Tennyson, J. A Global Potential Energy Surface for the H_3^+ Molecule *Chem. Phys. Lett.* **1997**, *273*, 107–114.
- [9] Kamisaka, H.; Bian, W.; Nobusada, K.; Nakamura, H. Accurate Quantum Dynamics of Electronically Nonadiabatic Chemical Reactions in the DH_2^+ System *J. Chem. Phys.* **2002**, *116*, 654–665.
- [10] Aguado, A.; Roncero, O.; Tablero, C.; Sanz, C.; Paniagua, M. Global Potential Energy Surfaces for the H_3^+ System. Analytical Representation of the Adiabatic Ground-state $1^1A'$ Potential *J. Chem. Phys.* **2000**, *112*, 1240–1254.
- [11] Sanz, C.; Roncero, O.; Tablero, C.; Aguado, A.; Paniagua, M. The Lowest Triplet State $^3A'$ of H_3^+ : Global Potential Energy Surface and Vibrational Calculations *J. Chem. Phys.* **2001**, *114*, 2182–2191.
- [12] Velilla, L.; Lepetit, B.; Aguado, A.; Beswick, J. A.; Paniagua, M. The H_3^+ Rovibrational Spectrum Revisited With a Global Electronic Potential Energy Surface *J. Chem. Phys.* **2008**, *129*, 084307.

- [13] Pavanello, M.; Tung, W.-C.; Leonarski, F.; Adamowicz, L. New More Accurate Calculations of the Ground State Potential Energy Surface of H_3^+ *J. Chem. Phys.* **2009**, *130*, 074105.
- [14] Chu, T.-S.; Han, K.-L. Nonadiabatic Time-Dependent Wave Packet Study of the $\text{D}^+ + \text{H}_2$ Reaction System *J. Phys. Chem. A* **2005**, *109*, 2050–2056.
- [15] Chu, T.-S.; Varandas, A. J. C.; Han, K.-L. Nonadiabatic Effects in $\text{D}^+ + \text{H}_2$ and $\text{H}^+ + \text{D}_2$ *Chem. Phys. Lett.* **2009**, *471*, 222–228.
- [16] Schlier, C.; Nowotny, U.; Teloy, E. Proton-Hydrogen Collisions: Trajectory Surface Hopping Calculations and New Measurements *Chem. Phys.* **1987**, *111*, 401.
- [17] Ichihara, A.; Shirai, T.; Yokoyama, K. A Study on IonMolecule Reactions in the H_3^+ System with the Trajectory-Surface-Hopping Model *J. Chem. Phys.* **1996**, *105*, 1857–1861.
- [18] Jambrina, P. G.; Alvarino, J. M.; Gerlich, D.; Hankel, M.; Herrero, V. J.; Sáez-Rábanos, V.; Aoiz, F. J. Dynamics of the $\text{D}^+ + \text{H}_2$ and $\text{H}^+ + \text{D}_2$ Reactions: A Detailed Comparison Between Theory and Experiment *Phys. Chem. Chem. Phys.* **2012**, *14*, 3346–3359.
- [19] Gerlich, D. Inhomogeneous RF Fields: A Versatile Tool for the Study of Processes with Slow Ions *Adv. Chem. Phys.* **1992**, *82*, 1–176.
- [20] Villinger, H.; Henchman, M. J.; Lindinger, W. Drift Tube Investigation of the Reactions $\text{H}^+ + \text{D}_2 \rightarrow \text{HD} + \text{D}^+$ and $\text{D}^+ + \text{H}_2 \rightarrow \text{HD} + \text{H}^+$ in the Relative Energy Range 0.04–0.3 e V *J. Chem. Phys.* **1982**, *76*, 1590–1591.
- [21] McCarroll, R. Formation of HD in Reactive Collisions of D^+ Ions with H_2 at Low Temperatures *Phys. Scr.* **2011**, *84*, 028106.
- [22] Gerlich, D.; Schlemmer, S. Deuterium Fractionation in Gas-Phase Reactions Measured in the Laboratory *Planet. Space Sci.* **2002**, *50*, 1287–1297.
- [23] Holliday, M. G.; Muckerman, J. T.; Friedman, L. Isotopic Studies of the Proton–Hydrogen Molecule Reaction *J. Chem. Phys.* **1971**, *54*, 1058–1072.
- [24] Fehsenfeld, F. C.; Dunkin, D. B.; Ferguson, E. E.; Albritton, D. L. Measurement of the Rate Constant for the Reaction $\text{D}^+ + \text{H}_2 \rightarrow \text{HD} + \text{H}^+$ *Astrophys. J* **1973**, *183*, L25.
- [25] Honvault, P.; Scribano, Y. State-to-State Quantum Mechanical Calculations of Rate Coefficients for the $\text{D}^+ + \text{H}_2 \rightarrow \text{HD} + \text{H}^+$ Reaction at Low Temperature *J. Phys. Chem. A* **2013**, *117*, 9778.
- [26] González-Lezana, T.; Honvault, P.; Scribano, Y. Dynamics of the $\text{D}^+ + \text{H}_2 \rightarrow \text{HD} + \text{H}^+$ reaction at the low energy regime by means of a statistical quantum method *J. Chem. Phys.*

- 2013**, *139*, 054301.
- [27] González-Lezana, T.; Aguado, A.; Paniagua, M.; Roncero, O. Quantum Approaches for the Insertion Dynamics of the $\text{H}^+ + \text{D}_2$ and $\text{D}^+ + \text{H}_2$ Reactive Collisions *J. Chem. Phys.* **2005**, *123*, 194309.
- [28] González-Lezana, T.; Roncero, O.; Honvault, P.; Launay, J.-M.; Bulut, N.; Aoiz, F. J.; Bañares, L. A Detailed Quantum Mechanical and Quasiclassical Trajectory Study on the Dynamics of the $\text{H}^+ + \text{H}_2 \rightarrow \text{H}_2 + \text{H}^+$ Exchange Reaction *J. Chem. Phys.* **2006**, *125*, 094314.
- [29] Carmona-Novillo, E.; González-Lezana, T.; Roncero, O.; Honvault, P.; Launay, J.-M.; Bulut, N.; Aoiz, F. J.; Bañares, L.; Trottier, A.; Wrede, E. On the Dynamics of the $\text{H}^+ + \text{D}_2(v = 0, j = 0) \rightarrow \text{HD} + \text{D}^+$ reaction: A Comparison Between Theory and Experiment *J. Chem. Phys.* **2008**, *128*, 014304.
- [30] Honvault, P.; Jorfi, M.; González-Lezana, T.; Faure, A.; Pagani, L. Ortho-Para H_2 Conversion by Proton Exchange at Low Temperature: An Accurate Quantum Mechanical Study *Phys. Rev. Lett.* **2011**, *107*, 023201.
- [31] Honvault, P.; Jorfi, M.; González-Lezana, T.; Faure, A.; Pagani, L. Quantum Mechanical Study of the Proton Exchange in the Ortho-Para H_2 Conversion Reaction at Low Temperature *Phys. Chem. Chem. Phys.* **2011**, *13*, 19089–19100.
- [32] Honvault, P.; Jorfi, M.; González-Lezana, T.; Faure, A.; Pagani, L. Erratum: Ortho-Para H_2 Conversion by Proton Exchange at Low Temperature: An Accurate Quantum Mechanical Study [Phys. Rev. Lett. 107, 023201 (2011)] *Phys. Rev. Lett.* **2012**, *108*, 109903.
- [33] Honvault, P.; Scribano, Y. Correction to "State-to-State Quantum Mechanical Calculations of Rate Coefficients for the $\text{D}^+ + \text{H}_2 \rightarrow \text{HD} + \text{H}^+$ Reaction at Low Temperature" *J. Phys. Chem. A* **2013**, *117*, 13205–13205.
- [34] Launay, J.; Dourneuf, M. L. Hyperspherical Close-coupling Calculation of the Integral Cross Sections for the Reaction $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ *Chem. Phys. Lett.* **1989**, *163*, 178 – 188.
- [35] Launay, J.; Dourneuf, M. L. Quantum-Mechanical Calculation of Integral Cross Sections for the Reaction $\text{F} + \text{H}_2(v = 0, j = 0) \rightarrow \text{FH}(v', j') + \text{H}$ *Chem. Phys. Lett.* **1990**, *169*, 473 – 481.
- [36] Launay, J. Computation of Cross Sections for the $\text{F} + \text{H}_2(v = 0, j = 0) \rightarrow \text{FH}(v', j') + \text{H}$ Reaction by the Hyperspherical Method *Theor. Chim. Acta* **1991**, *79*, 183–190.
- [37] Honvault, P.; Launay, J. M. Quantum Dynamics of Insertion Reactions In Lagana, A and

- Lendvay, G., Ed., *Theory of Chemical Reaction Dynamics*, Vol. 145, pages 187–215, 2004.
- [38] Honvault, P.; Lin, S. Y.; Xie, D.; Guo, H. Differential and Integral Cross Sections for the $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ Combustion Reaction *J. Phys. Chem. A* **2007**, *111*, 5349–5352.
- [39] Quémener, G.; Launay, J.-M.; Honvault, P. Ultracold Collisions Atoms and Li_2 Diatoms in High Vibrational States *Phys. Rev. A* **2007**, *75*, 050701.
- [40] Manolopoulos, D. E. An Improved Log Derivative Method for Inelastic Scattering *J. Chem. Phys.* **1986**, *85*, 6425–6429.
- [41] Markovic, N.; Billing, G. D. Wavepacket Calculations on Ion-Molecule Reactions: The Coplanar Approximation *Chem. Phys. Lett.* **1996**, *248*, 420–426.
- [42] Aoiz, F. J.; González-Lezana, T.; Sáez Rábanos, V. Stringent Test of the Statistical Quasiclassical Trajectory Model for the $\text{H} + \text{H}_3^+$ Exchange Reaction: A Comparison with Rigorous Statistical Quantum Mechanical Results *J. Chem. Phys.* **2007**, *127*, 174109.
- [43] Rackham, E. J.; Huarte-Larrañaga, F.; Manolopoulos, D. E. Coupled-Channel Statistical Theory of the $\text{N}(^2D) + \text{H}_2$ and $\text{O}(^1D) + \text{H}_2$ Insertion Reactions *Chem. Phys. Lett.* **2001**, *343*, 356–364.
- [44] Rackham, E. J.; González-Lezana, T.; Manolopoulos, D. E. A Rigorous Test of the Statistical Model for Atom–Diatom Insertion Reactions *J. Chem. Phys.* **2003**, *119*, 12895.
- [45] González-Lezana, T. Statistical Quantum Studies on Insertion Atom–Diatom Reactions *Int. Rev. Phys. Chem.* **2007**, *26*, 29.
- [46] Sokolovski, D.; De Fazio, D.; Cavalli, S.; Aquilanti, V. On the Origin of the Forward Peak and Backward Oscillations in the $\text{F} + \text{H}_2(v = 0) \rightarrow \text{HF}(v' = 2) + \text{H}$ Reaction *Phys. Chem. Chem. Phys.* **2007**, *9*, 5664.
- [47] De Fazio, D.; Aquilanti, V.; Cavalli, S.; Aguilar, A.; Lucas, J. M. Exact State-to-state Quantum Dynamics of the $\text{F} + \text{HD} \rightarrow \text{HF}(v' = 2) + \text{D}$ Reaction on Model Potential Energy Surfaces *J. Chem. Phys.* **2008**, *129*, 064303.
- [48] González-Lezana, T.; Honvault, P.; Jambrina, P. G.; Aoiz, F. J.; Launay, J. M. Effects of the Rotational Excitation of D_2 and of the Potential Energy Surface on the $\text{H}^+ + \text{D}_2 \rightarrow \text{HD} + \text{D}^+$ Reaction *J. Chem. Phys.* **2009**, *131*.
- [49] Skouteris, D.; Castillo, J.; Manolopoulos, D. ABC: A Quantum Reactive Scattering Program *Comp. Phys. Comm.* **2000**, *133*, 128.
- [50] Csizmadia, I. G.; Polanyi, J. C.; Roach, A. C.; Wong, W. H. Distribution of Reaction Products

- (Theory). VII. $D^+ + H_2 \rightarrow DH + H^+$ Using an Ab Initio Potential-Energy Surface *Can. J. Chem.* **1969**, *47*, 4097–4099.
- [51] Krenos, J. R.; Preston, R. K.; Wolfgang, R.; Tully, J. C. Molecular Beam and Trajectory Studies of Reactions of H^+ with H_2 *J. Chem. Phys.* **1974**, *60*, 1634–1659.
- [52] Gerlich, D.; Nowotny, U.; Schlier, C.; Teloy, E. Complex Formation in Proton– D_2 Collisions *Chem. Phys.* **1980**, *47*, 245 – 255.
- [53] Wrede, E.; Schnieder, L.; Seekamp-Schnieder, K.; Niederjohann, B.; Welge, K. H. Reactive Scattering of Rydberg Atoms: $H^+ + D_2 \rightarrow HD + D^+$ *Phys. Chem. Chem. Phys.* **2005**, *7*, 1577–1582.
- [54] Dai, D.; Wang, C. C.; Wu, G.; Harich, S. A.; Song, H.; Hayes, M.; Skodje, R. T.; Wang, X.; Gerlich, D.; Yang, X. State-to-State Dynamics of High- n Rydberg H-Atom Scattering with D_2 *Phys. Rev. Lett.* **2005**, *95*, 013201.
- [55] Song, H.; Dai, D.; Wu, G.; Wang, C. C.; Harich, S. A.; Hayes, M. Y.; Wang, X.; Gerlich, D.; Yang, X.; Skodje, R. T. Chemical Reaction Dynamics of Rydberg Atoms with Neutral Molecules: A comparison of Molecular-Beam and Classical Trajectory Results for the $H(n) + D_2 \rightarrow HD + D(n)$ Reaction *J. Chem. Phys.* **2005**, *123*, 074314.
- [56] Jambrina, P. G.; Alvarino, J. M.; Aoiz, F. J.; Herrero, V. J.; Sáez-Rábanos, V. Reaction Dynamics of the $D^+ + H_2$ System. A Comparison of Theoretical Approaches *Phys. Chem. Chem. Phys.* **2010**, *12*, 12591.
- [57] Jambrina, P. G.; Aoiz, F. J.; Bulut, N.; Smith, S. C.; Balint-Kurti, G. G.; Hankel, M. The Dynamics of the $H^+ + D_2$ Reaction: A Comparison of Quantum Mechanical Wavepacket, Quasi-classical and Statistical-quasi-classical results *Phys. Chem. Chem. Phys.* **2010**, *12*, 1102–1115.
- [58] Lara, M.; Dayou, F.; Launay, J. M. Reaching the Cold Regime: $S(^1D) + H_2$ and the Role of Long-Range Interactions in Open Shell Reactive Collisions *Phys. Chem. Chem. Phys.* **2011**, *13*, 8359–8370.
- [59] De Fazio, D.; de Castro-Vitores, M.; Aguado, A.; Aquilanti, V.; Cavalli, S. The $He + H_2^+ \rightarrow HeH^+ + H$ Reaction: Ab initio Studies of the Potential Energy Surface, Benchmark Time-Independent Quantum Dynamics in an Extended Energy Range and Comparison with Experiments *J. Chem. Phys.* **2012**, *137*, 244306.